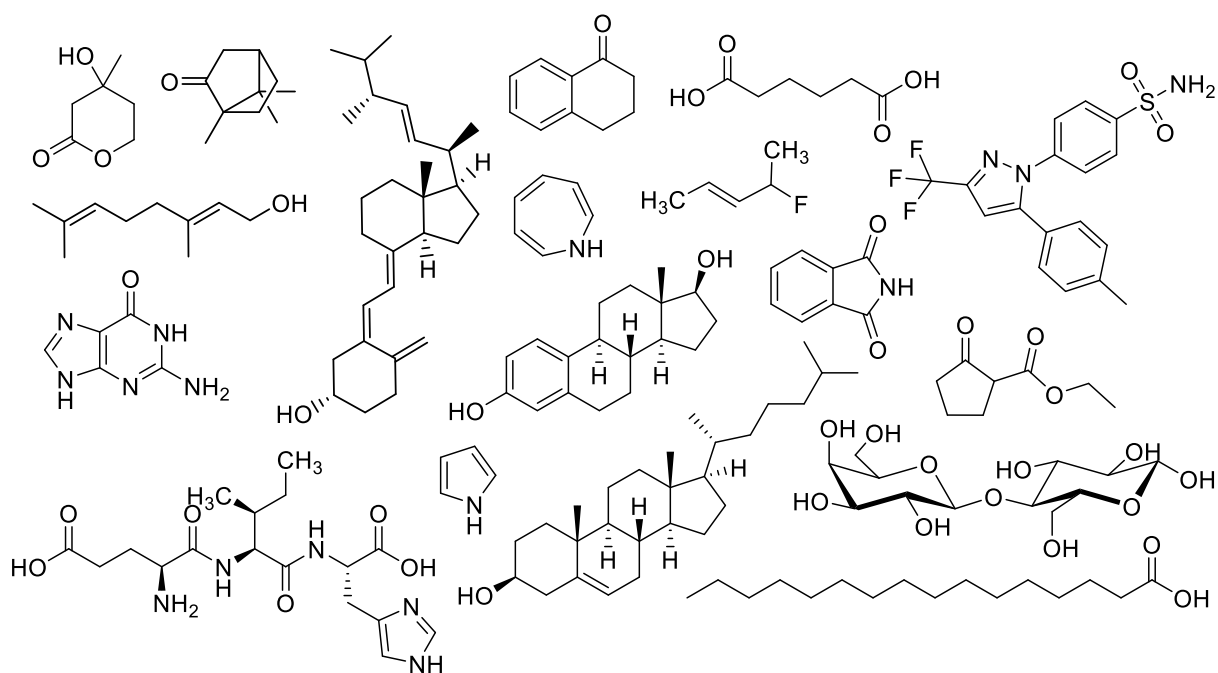


**SEMMELWEIS UNIVERSITY**  
**FACULTY OF PHARMACEUTICAL SCIENCES**  
**DEPARTMENT OF ORGANIC CHEMISTRY**

**Organic chemistry test questions**



**Budapest**

**2023**

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## Foreword

The 5th of March 2020 became a memorable Thursday morning: the first cases of coronavirus identified in our country were announced the night before. I was supposed to give an English Organic chemistry lecture to our second-year students but I haven't known yet how the recent occurrences will affect our daily lives. Following the arrival of the SARS-CoV-2 coronavirus outbreak in Hungary in spring 2020, the higher education had to switch from face-to-face to online distance learning within a short time. ZOOM, Moodle or Kaltura suddenly became an integral part of our everyday vocabulary. Although in hindsight this has had several positive benefits, such as speeding up the use of online tools or e-learning platforms, many challenges had to be addressed quickly. These resulted in methods retained also after the epidemic, but also in some perhaps less successful solutions. For example, viewing a video content or live streaming organic chemistry laboratory experiments during the months of the curfew could not recreate the experience of a hands-on organic chemistry synthesis. Initially, we used online organic chemistry tests for mid-term and end-of-year examinations during the epidemic. In the case of organic chemistry test questions, it has proved to be a difficult problem what do we actually measure, to what extent the students are able to go beyond recognition to problem solving or even to reproduce certain structures and transformations. Despite the various innovative tools, the most effective way to acquire a solid organic chemistry knowledge, even at the beginning of the 21st century, seems to be practicing to draw compounds, equations and reaction mechanisms, as well as solving organic chemistry problems. Despite our mixed experience for using them for assessment, the test problems prepared during the epidemic can be a useful aid for independent learning or revising what has been learned. It is with this in mind that we have collected and publish in this volume the exercises with their solutions, sometimes with explanations, primarily for our pharmacy students.

dr. Petra Dunkel



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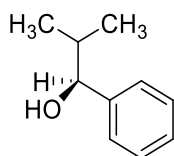
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# 1. Nomenclature of organic compounds

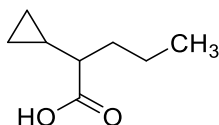
## Naming organic compounds

1. Assign the following compound its IUPAC name!



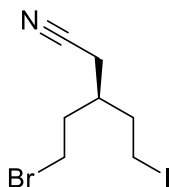
- A/ (R)-1-phenyl-isobutyl alcohol
- B/ (S)-1-phenyl-isobutil alcohol
- C/ (R)-1-phenyl-2-methylpropan-1-ol
- D/ (S)-1-phenyl-2-methylpropan-1-ol
- E/ (R)- $\alpha$ -isopropylbenzyl alcohol
- F/ (S)- $\alpha$ -isopropylbenzyl alcohol

2. Assign the following compound its IUPAC name!



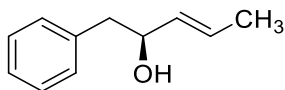
- A/ butylcyclopropan-1-carboxylic acid
- B/ cyclopropylbutan-1-carboxylic acid
- C/ 2-cyclopropylpentanoic acid
- D/ 2-cyclopropyl-2-propylacetic acid

3. Assign the following compound its IUPAC name!



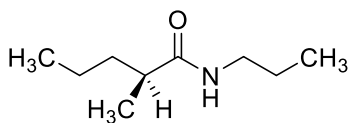
- A/ (R)-3-(2-bromoethyl)-5-iodopentanenitrile
- B/ (S)-5-bromo-3-(2-iodoethyl)pentanenitrile
- C/ (R)-5-bromo-3-(2-iodoethyl)pentanenitrile
- D/ (S)-3-(2-bromoethyl)-5-iodo-pentanenitrile

4. Choose the correct name for the compound below:



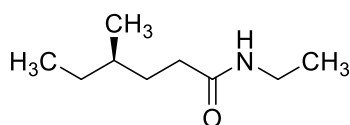
- A/ (2S,3E)-1-phenyl-3-penten-2-ol
- B/ (2R,3E)-1-phenyl-3-penten-2-ol
- C/ (4R,2E)-6-phenyl-2-penten-4-ol
- D/ (4S,2E)-6-phenyl-2-penten-4-ol

5. Choose the correct name for the compound below:



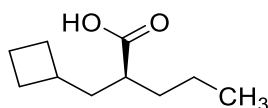
- A/ (R)-2-methyl-N-propyl-pentanamide
- B/ (S)-2-methyl-N-propyl-pentanamide
- C/ (R)-3-methyl-N-propyl-hexanamide
- D/ (S)-3-methyl-N-propyl-hexanamide

6. Choose the correct name for the compound below:



- A/ (4*R*)-*N*-ethyl-4-methylhexanamide  
 B/ (4*S*)-*N*-ethyl-4-methylhexanamide  
 C/ (3*S*)-*N*-ethyl-3-methylhexanamide  
 D/ (3*R*)-*N*-ethyl-3-methylhexanamide

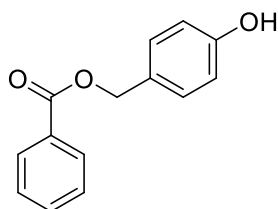
7. Assign the following compound its IUPAC name!



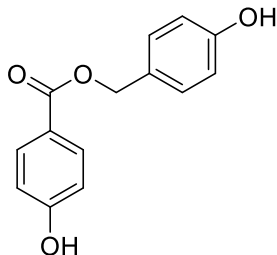
- A/ (2*S*)-cyclobutylpentan-2-carboxylic acid  
 B/ (2*R*)-pentylcyclobutan-2-carboxylic acid  
 C/ (2*R*)-2-(cyclobutylmethyl)-2-propylacetic acid  
 D/ (2*R*)-cyclobutylpentan-2-carboxylic acid  
 E/ (2*S*)-2-(cyclobutylmethyl)pentanoic acid

8. Assign the IUPAC names to the following compounds!

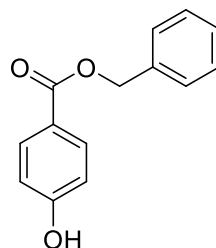
A



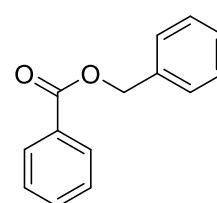
B



C



D



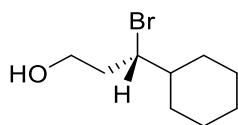
1 – benzyl benzoate

2 – benzyl 4-hydroxybenzoate

3 – 4-hydroxybenzyl benzoate

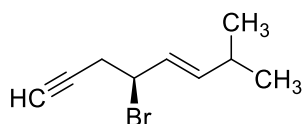
4 – 4-hydroxybenzyl 4-hydroxybenzoate

9. Assign the following compound its IUPAC name!



- A/ (3*S*)-3-bromo-3-cyclohexylpropan-1-ol  
 B/ (1*R*)-1-bromo-3-hydroxyprop-1-yl-cyclohexane  
 C/ (3*R*)-3-bromo-3-cyclohexylpropan-1-ol  
 D/ (1*S*)-1-bromo-3-hydroxyprop-1-yl-cyclohexane

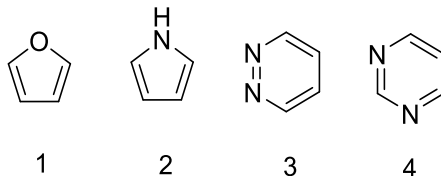
10. Assign the following compound its IUPAC name!



- A/ (4*S*,5*E*)-4-bromo-7,7-dimethylhept-5-en-1-yn-1-ol  
 B/ (4*S*,2*E*)-4-bromo-1,1-dimethylhept-2-en-6-in  
 C/ (4*S*,5*E*)-4-bromo-7-methyloct-5-en-1-yn-1-ol  
 D/ (5*S*, 3*E*)-5-bromo-2-methyloct-3-en-7-yn-1-ol

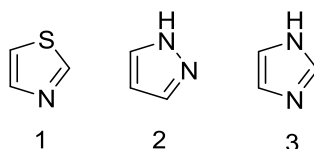
## Nomenclature of heterocyclic compounds

11. Which row corresponds to the trivial names of the following compounds?



- A - 1. pyran, 2. pyrrole, 3. pyrazine, 4. pyrimidine  
B - 1. furan, 2. thiophene, 3. pyridazine, 4. piperazine  
C - 1. furan, 2. pyrrole, 3. pyridazine, 4. pyrimidine  
D - 1. pyran, 2. pyrrole, 3. pyridazine, 4. pyrimidine  
E - 1. furan, 2. thiophene, 3. pyrazine, 4. pyridazine

12. Which row corresponds to the trivial names of the following compounds?



- A - 1. pyrazine, 2. imidazole, 3. oxazole  
B - 1. thiazole, 2. pyrazole, 3. imidazole  
C - 1. thiazole, 2. pyrrole, 3. pyridazine

13. Pair the structures with their corresponding names!

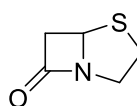
A



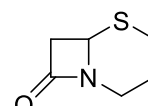
B



C



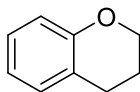
D



E



F



G

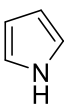








H



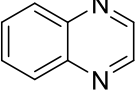


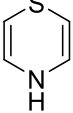
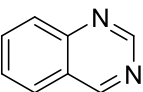



- 1 – pyrrolidine                  2 – izoxazole                  3 – chromane  
4 – azidine                  5 – penam

**14. Pair the structures with their corresponding names!**

A		B		C		D	
E		F		G			



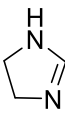

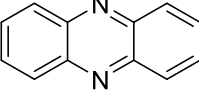


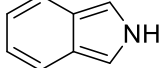
1 – 1*H*-azirine                      2 – 2*H*-thiete                      3 – [1,3]-thiazole                      4 – 2*H*-pyrrole

**15. Pair the structures with their corresponding names!**

A		B		C		D	
E		F		G		H	

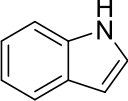
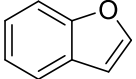
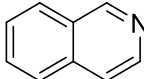
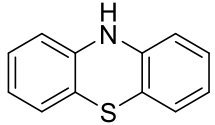
1 – thiirene                      2 – 2-azetine                      3 – 4*H*-pyran  
4 – 2*H*-1,4-thiazine                      5- quinoxaline

**16. Pair the structures with their corresponding names!**

A		B		C		D	
E		F		G		H	

1 – thietane                      2 – azetid-2-one                      3 – 2-imidazoline  
4 – isoindole                      5 – 1,3-dioxolane

**17. Choose the names of the following structures!**

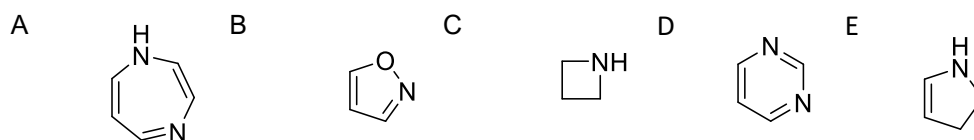
A		B		C		D	
---	---	---	---	---	---	---	---

1 - benzo[*b*]furan                      2 – 3*H*-indole                      3 - 10*H*-phenoxazine                      4 - quinoline  
5 - isoquinoline                      6 – 1*H*-indole                      7 - benzo[*b*]thiophene                      8 - 10*H*-phenothiazine



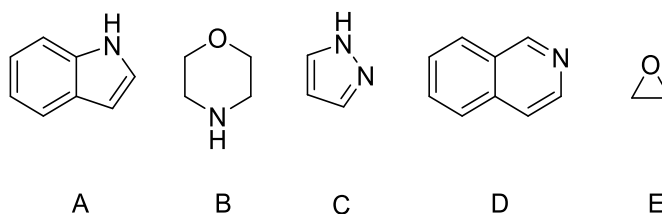


**18. Pair the structures with their corresponding names!**



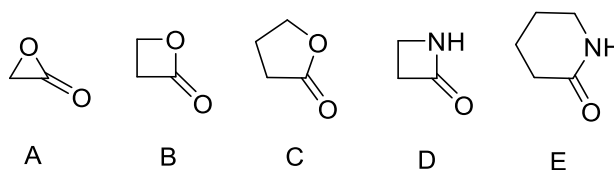
- 1 – pyrimidine      2 - 3-pyrroline      3 – pyridazine      4 - 1*H*-1,4-diazepine  
 5 – azetidine      6 - izoxazole      7 - 1*H*-1,3-diazepine      8 - 2,3-dihydro-1*H*-pyrrole

**19. Give the names of the following compounds:**



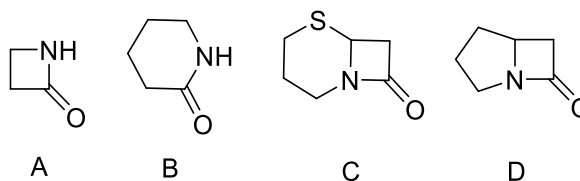
- 1 – isoquinoline      2 – oxiran      3 – phthalazine      4 – pyrazole  
 5 – pyrazine      6 – oxazole      7 - 1*H*-indol      8 - morpholine

**20. Match the following structures with their corresponding names:**



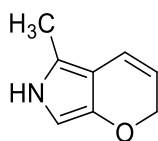
- 1 -  $\beta$ -lactame      2 -  $\delta$ -lactame      3 –  $\alpha$ -lactone  
 4 -  $\gamma$ -lactone      5 -  $\beta$ -lactone      6 -  $\gamma$ -lactame

**21. Pair the structures with their names!**



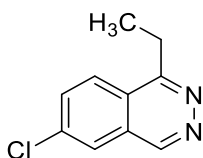
- 1 – cepham scaffold      2 – carbapenam scaffold      3 -  $\beta$ -lactame      4 -  $\delta$ -lactame

22. Give the correct IUPAC name for the structure!



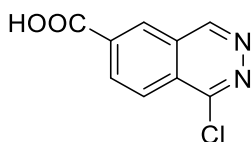
- A/ 2-methyl-1,5-dihydropyrano[2,3-c]pyrrole
- B/ 2-methyl-1*H*-pyrano[2,3-c]pyrrole
- C/ 5-methyl-2*H*,6*H*-pyrano[2,3-c]pyrrole
- D/ 4-methyl-3,7-dihydropyrano[2,3-c]pyrrole

23. Choose the correct IUPAC name for the compound below!



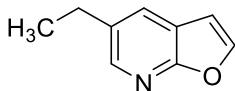
- A/ 6-chloro-1-ethylphthalazine
- B/ 3-chloro-6-ethylphthalazine
- C/ 6-chloro-1-ethylquinazoline
- D/ 3-chloro-6-ethylquinazoline

24. Give the correct IUPAC name for the structure!



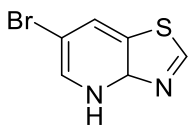
- A/ 1-chlorophthalazine-6-carboxylic acid
- B/ 4-chlorophthalazine-6-carboxylic acid
- C/ 4-chloroquinazoline-7-carboxylic acid
- D/ 4-chloroquinazoline-6-carboxylic acid

25. Give the correct IUPAC name for the structure!



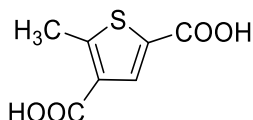
- A/ 5-ethylpyrido[2,3-*b*]furan
- B/ 5-ethylfuro[2,3-*b*]pyridine
- C/ 3-ethylfuro[2,3-*b*]pyridine
- D/ 3-ethylpyrido[2,3-*b*]furan

26. Give the correct IUPAC name for the structure



- A/ 3-bromo-3*aH*,4*H*-[1,3]thiazolo[2,3-*b*]pyridine
- B/ 3-bromo-3*aH*,4*H*-[1,3]thiazolo[4,5-*b*]pyridine
- C/ 6-bromo-3*aH*,4*H*-[1,3]thiazolo[4,5-*b*]pyridine
- D/ 6-bromo-3*aH*,4*H*-[1,3]thiazolo[2,3-*b*]pyridine

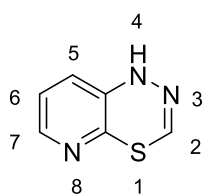
27. What is the correct IUPAC name for the following compound?



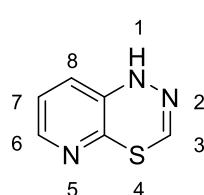
- A/ 1,3-thiazole-3,6-dicarboxylic acid
- B/ 1,2-oxazole-2,4-dicarbaldehyde
- C/ 5-methylthiophene-2,4-dicarboxylic acid
- D/ 1-methylthiophene-2,4-dicarboxylic acid

28. Choose the structure below that is correctly numbered!

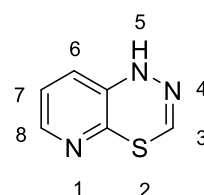
A



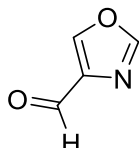
B



C



29. Choose the correct IUPAC name for the structure below!



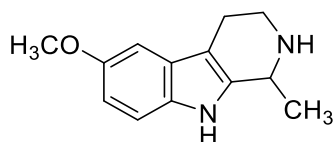
A/ 1,3-thiazole-4-carbaldehyde

B/ 1,2-oxazole-5-carbaldehyde

C/ 1,4-thiazole-3-carbaldehyde

D/ 1,3-oxazole-4-carbaldehyde

30. Choose the correct name of the compound below ( $\beta$ -carboline structure):



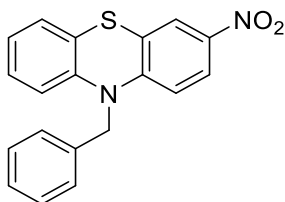
A/ 6-methoxy-1-methyl-1,2,3,4-tetrahydro-9H-pyrido[5,4-b](1H)-indole

B/ 6-methoxy-1-methyl-1H,2H,3H,4H,9H-pyrido[3,4-b]indole

C/ 4-methoxy-9-methyl-6,7,8,9-tetrahydro-1H-pyrido[3,4-b](1H)-indole

D/ 8-methoxy-4-methyl-1,2,3,4-tetrahydro-5H-pyrido[3,4-b](1H)-indole

31. Choose the correct name of the compound below (phenothiazine derivative):



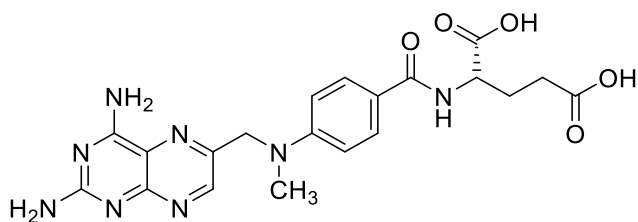
A/ N-benzyl-3-nitro-dibenzo[b,e][1,4]-thiazine

B/ N-benzyl-7-nitro-dibenzo[b,e][1,4]-thiazine

C/ N-benzyl-2-nitro-dibenzo[b,e][1,4]-thiazine

D/ N-benzyl-8-nitro-dibenzo[b,e][1,4]-thiazine

32. Which structural elements are present in the following molecule?



A/ purine scaffold

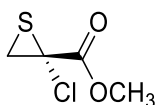
B/ glutamic acid

C/ quinoline ring

D/ pyridazine ring

E/ pteridine scaffold

33. Choose the correct name for the structure below:



A/ methyl (2S)-2-chlorothiirane-2-carboxylate

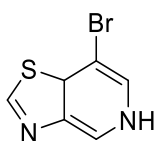
B/ methyl (2R)-2-chlorothiirane-2-carboxylate

C/ methyl (2S)-2-chloro-2,3-dihydrothiirene-2-carboxylate

D/ 2S-2-chlorothiirane-2-carboxylic acid methyl ester

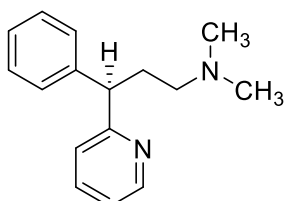
E/ methyl (1R)-1-chloro-2,3-dihydrothiirene-1-carboxylate

34. Choose the correct name for the structure below:



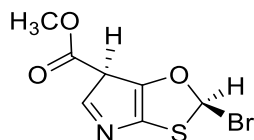
- A/ 7-bromo-5H,7aH-dihydro[1,3]thiazolo[4,5-c]pyridine
- B/ 7-bromo-5H,7aH-[1,3]thiazolo[4,5-c]pyridine
- C/ 4-bromo-3a,6-dihydro[1,3]thiazolo[4,5-c]pyridine
- D/ 4-bromo-3aH,6H[1,3]thiazolo[4,5-c]pyridine

35. Choose the correct name for the structure below!



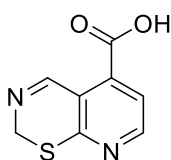
- A/ (3S)-N,N-dimethyl-3-phenyl-3-(pyridin-3-yl)propan-1-amine
- B/ (3R)-N,N-dimethyl-3-phenyl-3-(pyridin-2-yl)butan-1-amine
- C/ (3R)-N,N-dimethyl-3-phenyl-3-(pyridin-2-yl)propan-1-amine
- D/ (3S)-N,N-dimethyl-3-phenyl-3-(pyridin-3-yl)butan-1-amine

36. Choose the correct name for the structure below!



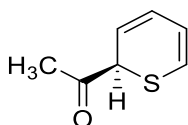
- A/ methyl (2R,6R)-2-bromo-2H,6H-[1,3]oxathiolopyrrole-4-carboxylate
- B/ methyl (2R,6R)-2-bromo-2,6-dihydro[1,3]oxathiolopyrrole-6-carboxylate
- C/ methyl (2R,6R)-2-bromo-6H-[1,3]oxathiolopyrrole-6-carboxylate
- D/ methyl (2R,6R)-2-bromo-2H,6H-[1,3]oxathiolopyrrole-6-carboxylate

37. Choose the correct name for the structure below!



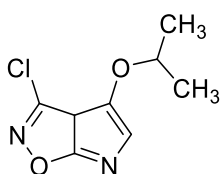
- A/ 2H-pyrido[3,2-e][1,3]thiazine-5-carboxylic acid
- B/ 3H-pyrido[3,2-e][1,3]thiazine-8-carboxylic acid
- C/ 6H-pyrido[3,2-e][1,3]thiazine-1-carboxylic acid
- D/ 7H-pyrido[3,2-e][1,3]thiazine-4-carboxylic acid

38. Choose the correct name for the structure below!



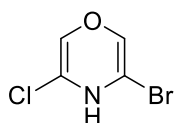
- A/ 1-[(2R)-2H-thiopyran-2-yl]ethan-1-one
- B/ 1-[(2S)-2H-thiopyran-2-yl]ethan-1-one
- C/ 2S-2-acetyl-(2H-thiopyran)
- D/ 2R-2-acetyl-(2H-thiopyran)

39. Choose the correct name for the structure below!



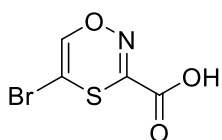
- A/ 3-chloro-4-(propan-2-yloxy)-3aH-pyrrolo[3,2-d][1,2]oxazole
- B/ 4-chloro-3-(propan-2-yloxy)-3aH-pyrrolo[3,2-d][1,2]oxazole
- C/ 1-chloro-6-(propan-2-yloxy)-6aH-pyrrolo[3,2-d][1,2]oxazole
- D/ 3-chloro-5-(propan-2-yloxy)-4aH-pyrrolo[3,2-d][1,2]oxazole

40. Choose the correct name of the compound below:



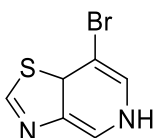
- A/ 2-bromo-6-chloro-1*H*-(1,4)-oxazine
- B/ 5-bromo-3-chloro-4*H*-(1,4)-oxazine
- C/ 3-bromo-5-chloro-4*H*-(1,4)-oxazine
- D/ 6-bromo-2-chloro-1*H*-(1,4)-oxazine

41. Choose the correct name of the compound below:



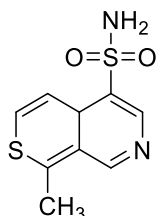
- A/ 5-bromo-1,4,2-oxathiazine-3-carboxylic acid
- B/ 6-bromo-4,1,3-oxathiazine-2-carboxylic acid
- C/ 4-bromo-2,5,1-oxathiazine-6-carboxylic acid
- D/ 4-bromo-6,3,1-oxathiazine-2-carboxylic acid

42. Choose the correct name of the compound below:



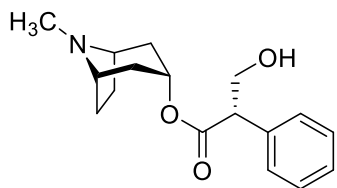
- A/ 7-bromo-5,7*a*-dihydro[1,3]thiazolo[4,5-*c*]pyridine
- B/ 7-bromo-5*H*,7*aH*-[1,3]thiazolo[4,5-*c*]pyridine
- C/ 4-bromo-3*a*,6-dihydro[1,3]thiazolo[4,5-*c*]pyridine
- D/ 4-bromo-3*aH*,6*H*-[1,3]thiazolo[4,5-*c*]pyridine

43. Choose the correct name of the compound below:



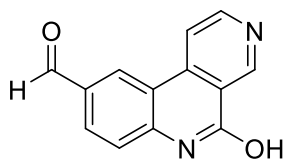
- A/ 8-methyl-4*aH*-thiopyrano[3,4-*c*]pyridine-4-sulfonamide
- B/ 1-methyl-4*aH*-thiopyrano[4,3-*d*]pyridine-5-sulfonamide
- C/ 1-methyl-4*aH*-thiopyrano[3,4-*c*]pyridine-5-sulfonamide
- D/ 5-methyl-8*aH*-thiopyrano[3,4-*c*]pyridine-1-sulfonamide

44. Choose the correct name of the compound below ((-)-hyosciamine):



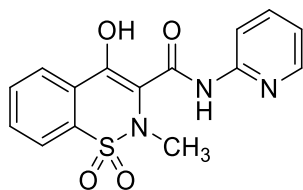
- A/ 1-methyl-1-azabicyclo[3.2.1]octan-4-yl (2*S*)-3-hydroxy-2-phenylpropanoate
- B/ 1-methyl-1-azabicyclo[3.2.1]octan-4-yl (2*R*)-3-hydroxy-2-phenylpropanoate
- C/ 8-methyl-8-azabicyclo[3.2.1]octan-3-yl (2*S*)-3-hydroxy-2-phenylpropanoate
- D/ 8-methyl-8-azabicyclo[3.2.1]octan-3-yl (2*R*)-3-hydroxy-2-phenylpropanoate

45. Choose the correct name of the compound below:



- A/ 5-hydroxybenzo[*c*]2,7-naphthyridine-9-carbaldehyde
- B/ 10-hydroxypyrido[3,4-*c*]quinoline-6-carbaldehyde
- C/ 2-hydroxypyrido[3,4-*c*]quinoline-8-carbaldehyde
- D/ 5-hydroxypyrido[3,4-*c*]quinoline-9-carbaldehyde

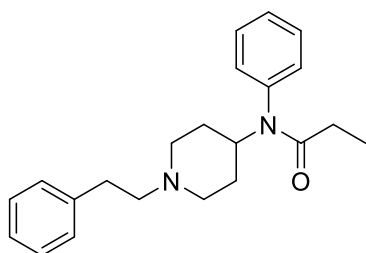
46. Which heterocyclic scaffold does the following drug molecule contain?



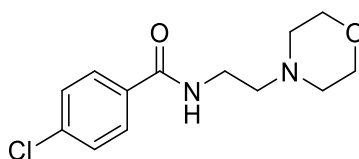
- A/ phenothiazine
- B/ 1,3-benzothiazepine
- C/ [1,2]-benzothiazine
- D/ benzothiazole
- E/ 1,3-benzothirane
- F/ 1,2-benzothiazepine

47. Assign the name of the respective heterocyclic scaffold to the following compounds!

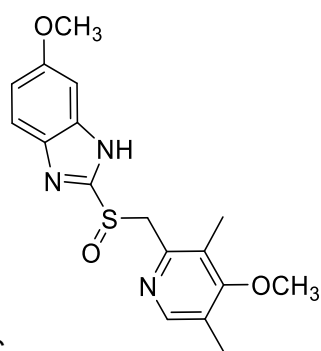
A



B



C



1 – piperazine

2 – morpholine

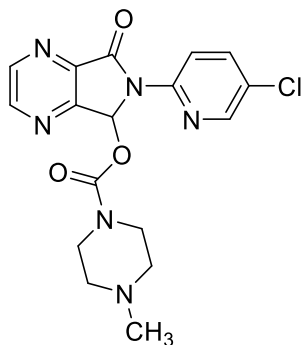
3 – pyridazine

4 – piperidine

5 – pyridine

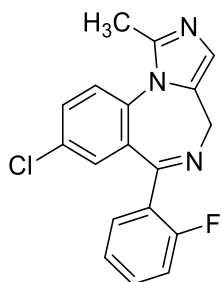
6 – 1,4-oxazepine

48. Which of the following structural elements are found in the molecule below?



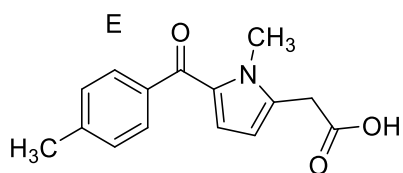
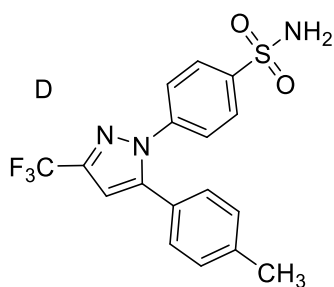
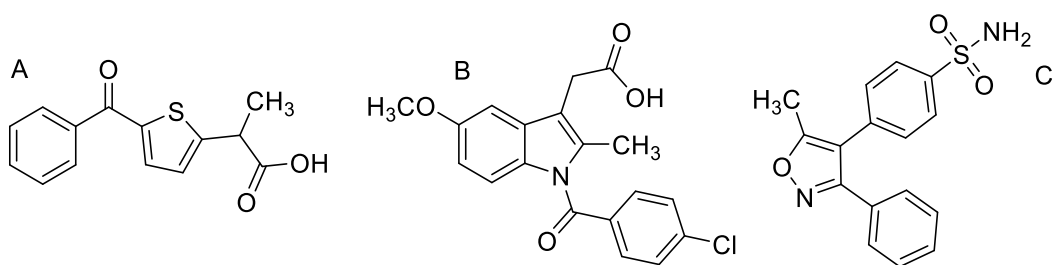
- A/ pyrazine
- B/ piperazine
- C/ pyridine
- D/ imidazole
- E/ isoquinoline
- F/ morpholine

49. Which heterocyclic ring is found in the compound below?



- A/ isoindole
- B/ quinolizine
- C/ imidazole
- D/ isoquinoline
- E/ pyrazole

50. Assign to the following compounds the heterocyclic ring present in their structure!



1 – pyridine

2 – pyrazole

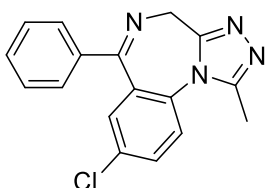
3 - isoxazole

4 – indole

5 – thiophene

6 – pyrrole

51. Which heterocyclic ring is present in the compound below?



A/ 1,2,4-triazole

B/ 1,2,3-triazole

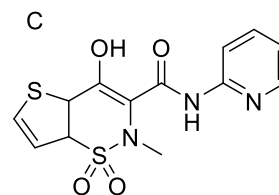
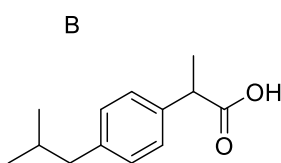
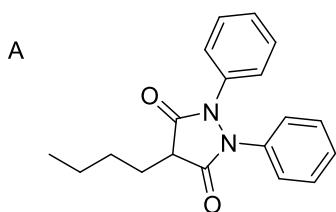
C/ 1,4-benzodiazepine

D/ 1,5-benzodiazepine

E/ 1,2,4-pyrazole

F/ 1,2,3-pyrazole

52. Pair the structures with the name of the corresponding compound family!



1 – arylpropionic acid derivative

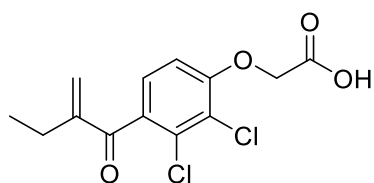
2 – anthranilic acid derivative

3 – arylacetic acid derivative

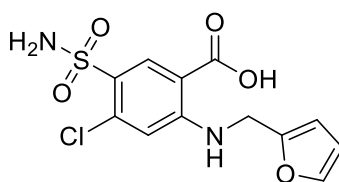
4 - 3,5-pyrazolidinedione derivative

5 - 2H-benzo[1,2]thiazine derivative

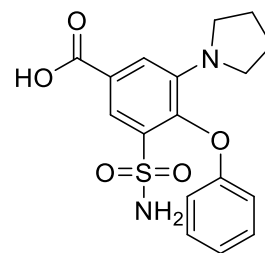
**53. Assign the chemical names of compounds to the corresponding structure!**



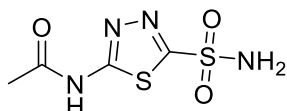
1



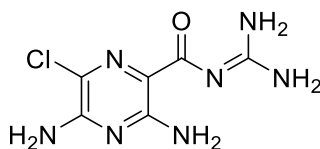
2



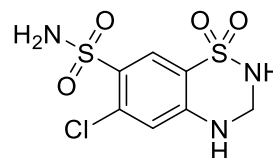
3



4



5



6

- 1) 6-chloro-1,1-dioxo-3,4-dihydro-2H-1,2,4-benzothiadiazine-7-sulfonamide
- 2) *N*-(5-sulfamoyl-1,3,4-thiadiazol-2-yl)acetamide
- 3) 3,5-diamino-6-chloro-*N*-(diaminomethylidene)pyrazine-2-carboxamide
- 4) 2-[2,3-dichloro-4-(2-methylidenebutanoyl)phenoxy]acetic acid
- 5) 4-chloro-2-[[furan-2-yl)methyl]amino]-5-sulfamoylbenzoic acid

**54. Select the correct phrase. The purine is:**

- A/ imidazo[4,5-*d*]pyrimidine
- B/ imidazo[4,5-*c*]pyrimidine
- C/ imidazo[4,5-*b*]pyrimidine
- D/ imidazo[4,5-*a*]pyrimidine

**55. Select the correct phrase. The isoquinoline is:**

- A/ benzo[*c*]pyridine
- B/ benzo[*b*]pyridine
- C/ benzo[*d*]pyridine
- D/ benzo[*a*]pyridine



# 1. Nomenclature of organic compounds

## Solutions

### 1. D - (S)-1-phenyl-2-methylpropan-1-ol

If the compound contains both a chain and a ring, the parent compound is the unit that: i) contains (the most) functional groups, ii) contains (the most) side chains and/or cyclic groups (here: the compound named as a substituted propan-1-ol). The configuration of the stereogenic centre is assigned according to the Cahn-Ingold-Prelog convention: i) ranking of ligands, ii) read the circumference of the atoms/groups ranked in the first three places (S - counterclockwise, R - clockwise) from the side opposite the atom/group ranked to the last place. Here: 1 - OH, 2 - phenyl, 3 - alkyl group, 4 - hydrogen.

### 2. C - 2-cyclopropylpentanoic acid

If the compound contains both a chain and a ring, the parent compound is the unit that: i) contains (the most) functional groups, ii) contains (the most) side chains and/or cyclic groups (here: the compound named as a substituted pentanoic acid). Upon numbering, the functional group is given the smallest possible number (in which case the carbon atom of the suffix is counted in the main chain).

### 3. C - (R)-5-bromo-3-(2-iodoethyl)pentanenitrile

For choosing the parent chain: i) the parent chain contains (the most) functional groups (here: the nitrile), ii) the parent chain contains the prefix first mentioned in the alphabet (bromo/iodoethyl vs. bromoethyl/iodo). The configuration of the stereogenic centre is assigned according to the Cahn-Ingold-Prelog convention: i) ranking of ligands, ii) read the circumference of the atoms/groups ranked in the first three places (S - counterclockwise, R - clockwise) from the side opposite the atom/group ranked to the last place. Here: 1 - iodoethyl, 2 - bromoethyl, 3 - cyanomethyl, 4 - hydrogen. For selecting the parent chain the ranking by alphabetical order is considered, whereas for assigning the configuration the atomic number of the atoms in a given sphere!

### 4. A - (2S,3E)-1-phenyl-3-penten-2-ol

If the compound contains both a chain and a ring, the parent compound is the unit that contains (the most) functional groups. Upon numbering, the lowest possible position number is assigned to the functional group (here: the alcohol). The configuration of the stereogenic centre is assigned according to the Cahn-Ingold-Prelog convention: i) ranking of ligands, ii) read the circumference of the atoms/groups ranked in the first three places (S - counterclockwise, R - clockwise) from the side opposite the atom/group ranked to the last place. Here: 1 - OH, 2 -  $\text{-CH=CH-CH}_3$ , 3 -  $\text{-CH}_2\text{Ph}$ , 4 - H. The Z and E isomerism give the relationship of the higher ranking substituents on the same pillar atoms to the molecular plane.

### 5. B - (S)-2-methyl-N-propyl-pentanamide

The names of the primary carboxylic acid amides are formed from the name of the corresponding acid by using the suffix -amide instead of the suffix -acid. The substituted primary amides with the general formula  $\text{R-CO-NHR'}$  are named as derivatives substituted on the nitrogen with an R' group. Upon numbering, the functional group is given the lowest possible position number. The configuration of the stereogenic centre is assigned according to the Cahn-Ingold-Prelog convention: i) ranking of ligands, ii) read the circumference of the atoms/groups ranked in the first three places (S - counterclockwise, R - clockwise) from the side opposite the atom/group ranked to the last place. Here: 1 - amide, 2 - propyl, 3 - methyl, 4 - hydrogen.

### 6. A - (4R)-N-ethyl-4-methylhexanamide



The names of the primary carboxylic acid amides are formed from the name of the corresponding acid by using the suffix -amide instead of the suffix -acid. The substituted primary amides with the general formula R-CO-NHR' are named as derivatives substituted on the nitrogen with an R' group. Upon numbering, the functional group is given the lowest possible position number. The configuration of the stereogenic centre is assigned according to the Cahn-Ingold-Prelog convention: i) ranking of ligands, ii) read the circumference of the atoms/groups ranked in the first three places (S - counterclockwise, R - clockwise) from the side opposite the atom/group ranked to the last place. Here: 1 - amide, 2 - ethyl, 3 - methyl, 4 - hydrogen.

7. E - (2S)-2-(cyclobutylmethyl)pentanoic acid

Ha a vegyület láncot és gyűrűt is tartalmaz, az az egység az alapvegyület: i) amely a (legtöbb) főcsoportot tartalmazza, ii) amely a (legtöbb) oldalláncot és / vagy ciklusos csoportot tartalmazza (itt: szubsztituált pentánsavként történik az elnevezés). Számozásnál a főcsoport a lehető legkisebb helyzettszámot kapja (ebben az esetben az utótag szénatomja beleszámít a főláncba). A sztereogén centrum konfigurációját a Cahn-Ingold-Prelog konvenció szerint adjuk meg: i) ligandumok rangsorolása, ii) sorrendben utolsó atommal/atomcsoporttal ellenkező oldalról leolvassuk az első három helyre rangsorolt atomok/csoportok körüljárását (S - óramutató járásával ellentétes, R - óramutató járasa szerinti). Itt: 1 - COOH, 2 - ciklobutilmetil, 3 - propil, 4 - hidrogén.

8. 1 - D, 2 - C, 3 - A, 4 - B

In the name of esters, if the ester functional group has the highest priority, the alkyl/aryl group of the alcohol/phenol component is listed first, followed by the acid residue of the carboxylic acid component.

9. A

10. C

11. C

12. B

13. 1 - H, 2 - A, 3 - F, 4 - B, 5 - C

14. 1 - F, 2 - G, 3 - E, 4 - B

15. 1 - C, 2 - B, 3 - G, 4 - H, 5 - A

16. 1 - B, 2 - G, 3 - C, 4 - H, 5 - F

17. A - 6, B - 1, C - 5, D - 8

18. A - 4, B - 6, C - 5, D - 1, E - 2

19. A - 7, B - 8, C - 4, D - 1, E - 2

20. A - 3, B - 5, C - 4, D - 1, E - 2

21. A - 3, B - 4, C - 1, D - 2

22. C - 5-methyl-2H,6H-pyrano[2,3-c]pyrrole

In the case of the compound in the question: i) the rings are separated and their ranking is determined, here: the ring containing the nitrogen atom has the higher rank (N>O>S), ii) the parent ring is lettered (a, b, c...) - the edges between the heteroatoms (O>S>N if there are more heteroatoms in the separated monocycle), then the edge of the annelation is given the lower letter, iii) the other ring is numbered (1, 2, 3...) - the heteroatoms (O>S>N, if there are more heteroatoms in the separated monocycle), then the annelation atoms get the lower number, iv) determine the prefixes (including the hydro prefixes), v) number the condensed ring system, in case of a position number match, the higher ranking heteroatom in the Hantzsch-Widman ranking (O>S>N) gets a lower number.



23. A - 6-chloro-1-ethylphthalazine

*Phthalazine contains nitrogen atoms at the 1,2 position, quinazoline at the 1,3 position. Upon numbering, first the heteroatoms are given the lowest position numbers, followed by the prefixes, always starting from the appropriate atom next to the annellation.*

24. A - 1-chlorophthalazine-6-carboxylic acid

*Phthalazine contains nitrogen atoms at the 1,2 position, quinazoline at the 1,3 position. Upon numbering, first the heteroatoms are given the lowest position numbers, followed by the prefixes, always starting from the appropriate atom next to the annellation.*

25. B - 5-ethylfuro[2,3-b]pyridine

*In the case of the compound in the question: i) the rings are separated and their ranking is determined, here: the ring containing the nitrogen atom has the higher rank (N>O>S), ii) the parent ring is lettered (a, b, c...) - the edges between the heteroatoms (O>S>N if there are more heteroatoms in the separated monocycle), then the edge of the annellation is given the lower letter, iii) the other ring is numbered (1, 2, 3... ) - the heteroatoms (O>S>N, if there are more heteroatoms in the separated monocycle), then the annellation atoms get the lower number, iv) determine the prefixes (including the hydro prefixes), v) number the condensed ring system, in case of a position number match, the higher ranking heteroatom in the Hantzsch-Widman ranking (O>S>N) gets a lower number.*

26. C - 6-bromo-3aH,4H-[1,3]thiazolo[4,5-b]pyridine

*In the case of the compound in the question: i) the rings are separated and their ranking is determined, here: the ring containing the nitrogen atom has the higher rank (N>O>S), ii) the parent ring is lettered (a, b, c...) - the edges between the heteroatoms (O>S>N if there are more heteroatoms in the separated monocycle), then the edge of the annellation is given the lower letter, iii) the other ring is numbered (1, 2, 3... ) - the heteroatoms (O>S>N, if there are more heteroatoms in the separated monocycle), then the annellation atoms get the lower number, iv) determine the prefixes (including the hydro prefixes), v) number the condensed ring system, so that the heteroatoms get the lowest possible numbers.*

27. C - 5-methylthiophene-2,4-dicarboxylic acid

*In a monocycle containing one heteroatom, we number starting from the heteroatom, so that the highest ranking functional group in the name is counted as the main group given as the suffix.*

28. B

*In a condensed bicycle, we number in such a way that, starting from the appropriate atom next to the annellation, the heteroatoms - regardless of their ranking - have the smallest possible position numbers. In the case of matching position numbers, the atoms with higher ranking according to the Hantzsch-Widman ranking (O>S>N) receive the lower position numbers.*

29. D - 1,3-oxazole-4-carbaldehyde

*The thiazole ring contains one nitrogen and one sulphur atom, the oxazole ring one nitrogen and one oxygen atom. In a monocycle with several heteroatoms, starting from the highest ranking heteroatom in the Hantzsch-Widman order (O>S>N), the numbering is done so that the heteroatoms have the lowest possible position numbers. The highest ranked functional group will be the suffix in the name (if it can be named as a suffix), and will be the main group.*

30. B - 6-methoxy-1-methyl-1H,2H,3H,4H,9H-pyrido[3,4-b]indole

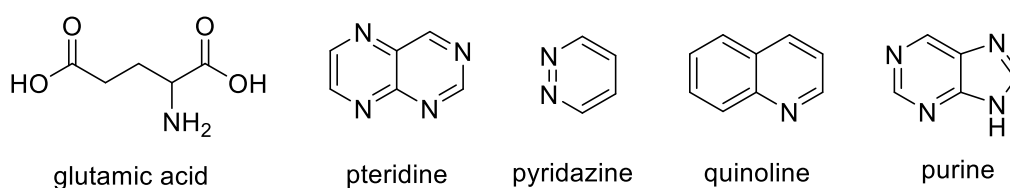


The higher ranking ring system (parent ring) contains most of the rings (here: the indole). For naming the compound: i) the rings are separated and their ranking is determined, ii) the parent ring is lettered (a, b, c...) - the edges between the heteroatoms (O>S>N), then the edge of the annelation is given the lower letter, iii) the other ring is numbered (1, 2, 3... ) - the heteroatoms (O>S>N, if there are more heteroatoms in the separated monocycle), then the anellation atoms get the lower number, iv) determine the prefixes, v) number the condensed ring system, so that the heteroatoms get the lowest possible numbers.

### 31. A - N-benzyl-3-nitro-dibenzo[b,e][1,4]-thiazine

In condensed heterocyclic systems: i) the heteroatoms are assigned the lowest numbers, ii) in the case of position number matching the higher ranking heteroatom is assigned a lower number, iii) all prefixes are assigned the lowest possible number.

### 32. B, E



### 33. B - methyl (2R)-2-chlorothiirane-2-carboxylate

In the substitution name of esters the name of the alkyl group of the alcohol is followed by the acid residue of the carboxylic acid component. Upon numbering, the lowest possible number is given to i) the heteroatom, ii) the functional group. The configuration of the stereogenic centre is assigned according to the Cahn-Ingold-Prelog convention: i) ranking of ligands, ii) read the circumference of the atoms/groups ranked in the first three places (S - counterclockwise, R - clockwise) from the side opposite the atom/group ranked to the last place. Here: 1 - chloro, 2 - sulphur, 3 - CH<sub>2</sub>S, 4 - COOCH<sub>3</sub>.

### 34. B - 7-bromo-5H,7aH-[1,3]thiazolo[4,5-c]pyridine

The higher ranking ring contains the monocycle with the highest number of members (here: the pyridine, since both rings contain nitrogen atoms). For assigning the name: i) the rings are separated and their ranking is determined, ii) the parent ring is lettered (a, b, c...) - the edges between the heteroatoms (O>S>N), then the edge of the annelation is given the lower letter, iii) the other ring is numbered (1, 2, 3... ) - the heteroatoms (O>S>N), then the anellation atoms get the lower number, iv) determine the prefixes, v) number the condensed ring system, so that the heteroatoms get the lowest possible numbers. The name indicates the position of the excess hydrogens in the heterocycle.

### 35. C - (3R)-N,N-dimethyl-3-phenyl-3-(pyridin-2-yl)propan-1-amine

If the compound contains both a chain and a ring, the parent compound is the unit that contains (the most) functional groups. Upon numbering, the functional groups is given the lowest possible locant. The configuration of the stereogenic centre is assigned according to the Cahn-Ingold-Prelog convention: i) ranking of ligands, ii) read the circumference of the atoms/groups ranked in the first three places (S - counterclockwise, R - clockwise) from the side opposite the atom/group ranked to the last place. Here: 1 - pyridine, 2 - phenyl, 3 - aminoalkyl group, 4 - hydrogen.

### 36. C - methyl (2R,6R)-2-bromo-6H-[1,3]oxathiol[4,5-b]pyrrole-6-carboxylate

In the substitution name of esters the name of the alkyl group of the alcohol is followed by the acid residue of the carboxylic acid component. The higher ranked cycle is the heterocyclic unit that contains a nitrogen atom (here: the pyrrole). For assigning the name: i) the rings are separated and their ranking is determined, ii) the

parent ring is lettered (a, b, c...) - the edges between the heteroatoms (O>S>N), then the edge of the annelation is given the lower letter, iii) the other ring is numbered (1, 2, 3...) - the heteroatoms (O>S>N), then the anellation atoms get the lower number, iv) determine the prefixes, v) number the condensed ring system, so that the heteroatoms get the lowest possible numbers. The configuration of the stereogenic centre is assigned according to the Cahn-Ingold-Prelog convention: i) ranking of ligands, ii) read the circumference of the atoms/groups ranked in the first three places (S - counterclockwise, R - clockwise) from the side opposite the atom/group ranked to the last place.

37. A - 2H-pyrido[3,2-e][1,3]thiazine-5-carboxylic acid

The higher ranked ring contains the most heteroatoms (here: the thiazine). For assigning the name: i) the rings are separated and their ranking is determined, ii) the parent ring is lettered (a, b, c...) - the edges between the heteroatoms (O>S>N), then the edge of the annelation is given the lower letter, iii) the other ring is numbered (1, 2, 3...) - the heteroatoms (O>S>N), then the anellation atoms get the lower number, iv) determine the prefixes, v) number the condensed ring system, so that the heteroatoms get the lowest possible numbers. The position of the excess hydrogen in the heterocycle (one of the types of indicated hydrogen) is given before the parent name.

38. A/ 1-[(2R)-2H-thiopyran-2-yl]ethan-1-one

For selecting the parent chain: the parent chain contains the most functional groups (here: the compound is named as an ethan-1-one). In the name we indicate the position of the excess hydrogens in the heterocycle. The configuration of the stereogenic centre is assigned according to the Cahn-Ingold-Prelog convention: i) ranking of ligands, ii) read the circumference of the atoms/groups ranked in the first three places (S - counterclockwise, R - clockwise) from the side opposite the atom/group ranked to the last place. Here: 1 - sulphur, 2 - acetyl, 3 - -CH=CH-, 4 - hydrogen.

39. A - 3-chloro-4-(propan-2-yloxy)-3aH-pyrrolo[3,2-d][1,2]oxazole

The higher ranked ring (both ring contains nitrogen atoms) contains the most heteroatoms (here: the oxazole). For assigning the name: i) the rings are separated and their ranking is determined, ii) the parent ring is lettered (a, b, c...) - the edges between the heteroatoms (O>S>N), then the edge of the annelation is given the lower letter, iii) the other ring is numbered (1, 2, 3...) - the heteroatoms (O>S>N), then the anellation atoms get the lower number, iv) determine the prefixes, v) number the condensed ring system, so that the heteroatoms get the lowest possible numbers.

40. C

41. A

42. A

43. C

44. C

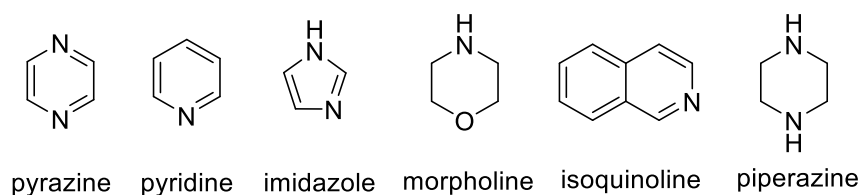
45. A

46. C - [1,2]-benzothiazine

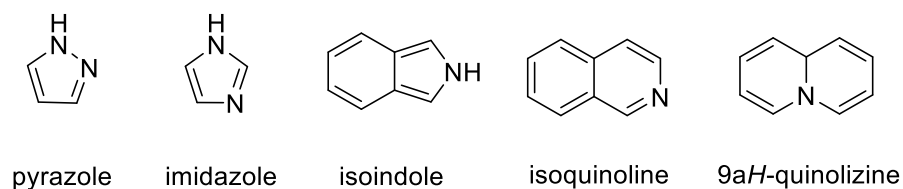
47. A - 4, B - 2, 5 - C



48. A, B, C



49. C



50. A – 5, B – 4, C – 3, D – 2, E – 6

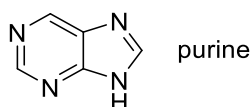
51. A, C

*Pyrazole is a five-membered ring containing two nitrogen atoms. Benzodiazepine is a seven-membered heteromonocycle containing two nitrogen atoms, triazole is a five-membered heteromonocycle containing three nitrogen atoms.*

52. A – 4, B – 1, C – 5

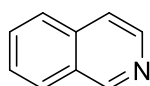
53. 1 – F, 2 – D, 3 – E, 4 – A, 5 – B

54. A - imidazo[4,5-d]pyrimidine



*For assigning the name: i) the rings are separated and their ranking is determined (here: the higher ranked ring contains the monocycle with the highest number of members, as both rings contain only nitrogen heteroatoms in the same number), ii) the parent ring is lettered (a, b, c...) - the edges between the heteroatoms (O>S>N), then the edge of the annelation is given the lower letter, iii) the other ring is numbered (1, 2, 3...) - the heteroatoms (O>S>N), then the anellation atoms get the lower number.*

55. A



*The heterocycle is ranked higher than the carbocycle. For assigning the name: i) the rings are separated and their ranking is determined, ii) the parent ring is lettered (a, b, c...) - the edges between the heteroatoms (O>S>N), then the edge of the annelation is given the lower letter, iii) the other ring is numbered (1, 2, 3...) - the heteroatoms (O>S>N), then the anellation atoms get the lower number.*

## 2. Structure and properties of organic compounds

### *Acidity-basicity*

1. Put the following compounds in ascending order of acidity (tested in aqueous solution).

- |                          |                      |                          |
|--------------------------|----------------------|--------------------------|
| 1. <i>p</i> -bromophenol | 2. phenol            | 3. <i>p</i> -nitrophenol |
| 4. cyclohexanol          | 5. 3,5-diethylphenol |                          |
- A - 4 < 5 < 2 < 1 < 3      B - 3 < 1 < 2 < 5 < 4  
C - 5 < 4 < 2 < 3 < 1      D - 1 < 2 < 3 < 4 < 5

2. The  $pK_a$  of acetylsalicylic acid is approx. 3.0. Choose the correct statement from the following!

- A/ at pH = 3, aspirin and its conjugate base are present in a ratio of about 50-50%  
B/ at pH = 3, aspirin is predominantly present in neutral form  
C/ at pH = 7.4, aspirin is predominantly present in the conjugate base form  
D/ at pH = 7.4, aspirin and its conjugate base are present in a ratio of about 50-50%

3. Give the correct acidity order of the following compounds: phenol, 2-methylphenol, 4-nitrophenol!

- A/ 4-nitrophenol < phenol < 2-methylphenol  
B/ 4-nitrophenol < 2-methylphenol < phenol  
C/ phenol < 2-methylphenol < 4-nitrophenol  
D/ 2-methylphenol < phenol < 4-nitrophenol

4. Put the following compounds in ascending order of acidity (tested in aqueous solution).

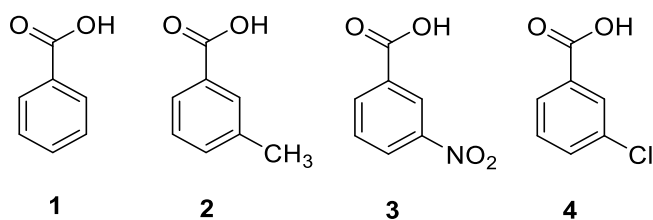
- |                                  |                                  |
|----------------------------------|----------------------------------|
| 1. acrylic acid                  | 2. <i>o</i> -hydroxybenzoic acid |
| 3. <i>p</i> -hydroxybenzoic acid | 4. carbonic acid                 |
- A/ 2 < 1 < 3 < 4      B/ 4 < 3 < 1 < 2  
C/ 4 < 1 < 3 < 2      D/ 4 < 3 < 2 < 1

5. Put the following nitrogen-containing compounds in ascending order of basicity (tested in aqueous solution).

- |                  |                   |
|------------------|-------------------|
| 1. methylamine   | 2. ammonia        |
| 3. dimethylamine | 4. trimethylamine |
- A/ 3 < 1 < 4 < 2      B/ 2 < 4 < 1 < 3  
C/ 1 < 2 < 3 < 4      D/ 2 < 1 < 4 < 3



6. Which of the following compounds is the most acidic and which is the least acidic?



7. Rank the following compounds in descending order of acidity.

- |                    |                    |
|--------------------|--------------------|
| 1. propionic acid  | 2. propanol        |
| 3. phenol          | 4. propyne         |
| A/ $4 > 3 > 2 > 1$ | B/ $1 > 2 > 3 > 4$ |
| C/ $1 > 3 > 4 > 2$ | D/ $1 > 3 > 2 > 4$ |

8. Put the following compounds in ascending order of acidity (tested in aqueous solution).

- |                    |                    |
|--------------------|--------------------|
| 1. $C_6H_5-OH$     | 2. $CH_3CH_2-OH$   |
| 3. $C_6H_5-SH$     | 4. $CH_3CH_2-SH$   |
| A/ $2 < 1 < 4 < 3$ | B/ $3 < 4 < 1 < 2$ |
| C/ $1 < 2 < 3 < 4$ | D/ $2 < 4 < 1 < 3$ |

9. Put the following compounds in ascending order of acidity (tested in aqueous solution).

- |                          |                        |
|--------------------------|------------------------|
| 1. 1 <i>H</i> -imidazole | 2. 1 <i>H</i> -pyrrole |
| 3. indoline              | 4. piperidine          |
| A/ $1 < 2 < 3 < 4$       | B/ $4 < 3 < 2 < 1$     |
| C/ $1 < 3 < 2 < 4$       | D/ $4 < 3 < 1 < 2$     |

10. Rank the following diazines in descending order of basicity.

- |                |                |                |
|----------------|----------------|----------------|
| 1. 1,2-diazine | 2. 1,3-diazine | 3. 1,4-diazine |
| A/ $1 > 2 > 3$ | B/ $3 > 2 > 1$ |                |
| C/ $1 > 3 > 2$ | D/ $2 > 1 > 3$ |                |

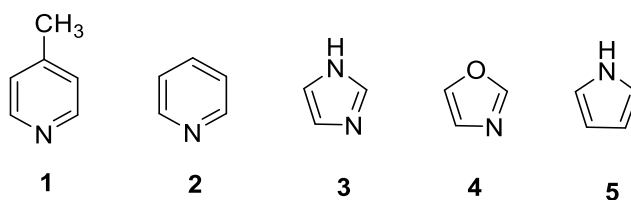
11. Put the following compounds in ascending order of acidity (tested in aqueous solution).

- |                          |                               |
|--------------------------|-------------------------------|
| 1. <i>p</i> -nitrophenol | 2. phenol                     |
| 3. cyclohexanol          | 4. cyclohexanecarboxylic acid |
| A/ $4 < 1 < 2 < 3$       | B/ $4 < 3 < 2 < 1$            |
| C/ $3 < 1 < 2 < 4$       | D/ $3 < 2 < 1 < 4$            |





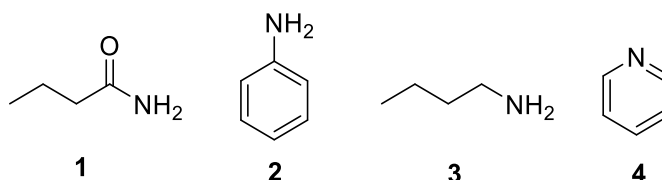
12. Which of the following compounds is the most basic and which is the least basic?



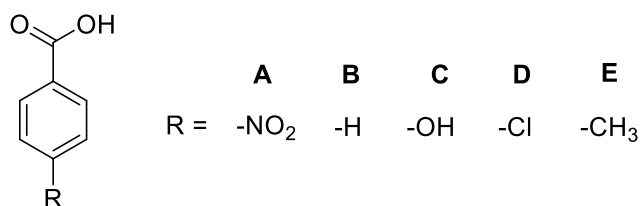
13. Select the amphoteric compounds from the following:

- A/ sulphanilamide                      B/ benzenesulfonic acid  
 C/ anthranilic acid                      D/ 4-methylsulfanylbenzene

14. Which of the following compounds is the most basic and which is the least basic?



15. Give the acidity order of the following compounds (in descending order, starting with the most acidic).

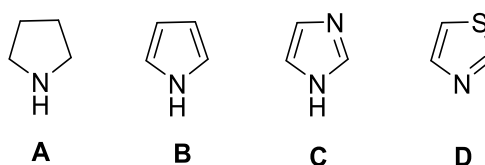


- A/ A > B > C > D > E                      B/ C > E > B > D > A                      C/ D > A > B > E > C  
 D/ A > D > E > B > C                      E/ A > D > B > E > C

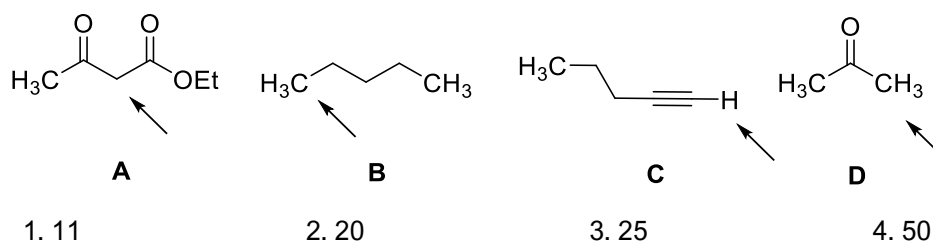
16. Rank the following compounds in order of increasing base strength (tested in aqueous hydrochloric acid solution).

1. pyrazine                      2. pyrimidine                      3. pyridazine  
 4. pyrazole                      5. imidazole
- A/ 5 < 4 < 3 < 2 < 1                      B/ 1 < 2 < 3 < 4 < 5                      C/ 1 < 3 < 5 < 2 < 4  
 D/ 2 < 4 < 1 < 3 < 5                      E/ 4 < 1 < 2 < 3 < 5

17. Which of the following compounds is THE LEAST basic?



**18. Match the structures with the corresponding pK<sub>a</sub> values!**



**19. Rank the following compounds in order of increasing basicity (tested in aqueous solution).**

- |                  |                        |
|------------------|------------------------|
| 1. pyrrolidine   | 2. pyridine            |
| 3. pyridazine    | 4. 1 <i>H</i> -pyrrole |
| A/ 4 > 3 > 2 > 1 | B/ 1 > 2 > 3 > 4       |
| C/ 3 > 4 > 1 > 2 | D/ 2 > 3 > 4 > 1       |

**20. Which of the following statements are true?**

- A/ The proximity of an electronwithdrawing group to the acidic hydrogen dissociating group increases the acidity of organic compounds.
- B/ The proximity of an electrondonating group to the group taking the acidic hydrogen increases the basicity of organic compounds.
- C/ The role of steric effects is negligible for organic acid-base properties.
- D/ The electronic effect of the substituent on the benzene ring exerts its influence mainly in the *ortho* and *para* positions relative to the substituent.

**21. Classify the following functional groups in terms of acid-base property!**

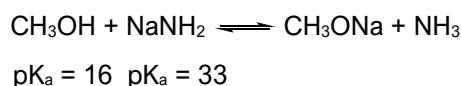
- |                       |              |                       |
|-----------------------|--------------|-----------------------|
| 1) acidic             | 2) basic     | 3) neutral            |
| A) -SO <sub>3</sub> H | B) -COOH     | C) Ar-NH <sub>2</sub> |
| D) -COOR              | E) -CH=CH-OH | F)                    |
| G) Ar-SH              | H) R-O-R'    | I) R <sub>2</sub> NH  |
| J)                    | I) R-CN      |                       |

**22. Match the concepts and definitions:**

- |  |                                   |
|--|-----------------------------------|
| A/ acid according to the Brønsted-Lowry theory | 1 - acid: H <sup>+</sup> donor    |
| B/ base according to the Brønsted-Lowry theory | 2 - acid: electron pair acceptor  |
| C/ acid according to the Lewis theory          | 3 - base: H <sup>+</sup> acceptor |
| D/ base according to the Lewis theory          | 4 - base: electron pair donor     |



23. Based on the  $pK_a$  values, is the equilibrium of the following reaction shifted to the right or to the left?



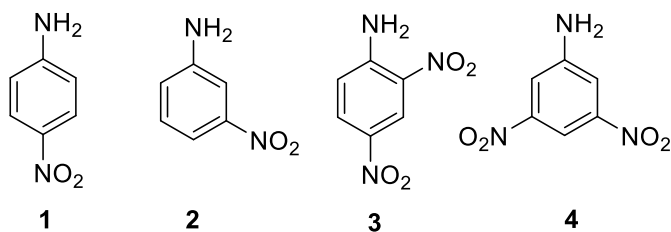
A/ to the right, because the  $\text{CH}_3\text{OH}$  is the stronger acid

B/ to the left, because the  $\text{CH}_3\text{OH}$  is the stronger acid

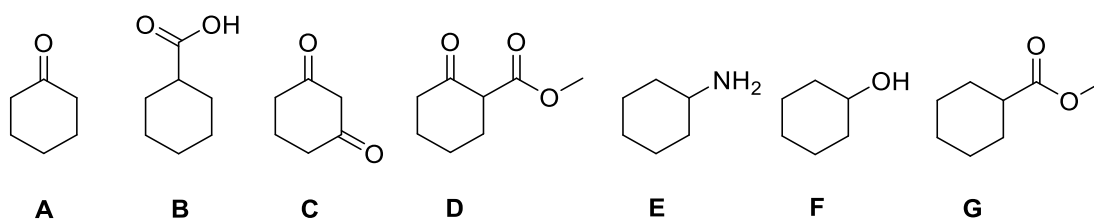
C/ to the right, because the  $\text{CH}_3\text{OH}$  is the stronger base

D/ to the left, because the  $\text{CH}_3\text{OH}$  is the stronger base

24. Which of the following aniline derivatives is the most basic and which is the least basic?



25. Arrange the following compounds in ascending order of acidity (in aqueous solution):



### ***Nucleophilicity-electrophilicity***

26. Arrange the following amines in ascending order of nucleophilicity, tested in  $S_NAc$  reactions!

1 - 4-methylaniline

2 - 4-nitroaniline

3 - aniline

4 - cyclohexyl amine

A/  $4 < 1 < 3 < 2$

B/  $1 < 2 < 3 < 4$

C/  $2 < 3 < 1 < 4$

D/  $3 < 2 < 1 < 4$

27. Choose the correct statement!

A/ Hydroxide ion and bromide ion are electrophilic reagents.

B/ Water is both an electrophilic and a nucleophilic reagent.

C/ Cyanide ion and alkoxide ion are nucleophilic reagents.

D/ Ammonia is an electrophilic reagent.



**28. Choose the correct statement!**

- A/ Cyanide ion and bromide ion are nucleophilic reagents.  
B/ Hydroxide ion and alkoxide ion are electrophilic reagents.  
C/ Ammonia is an electrophilic reagent because it has a lone electron pair.  
D/ Carbene is a nucleophilic reagent because it has an empty p orbital.

**Thermodynamic stability, reactivity**

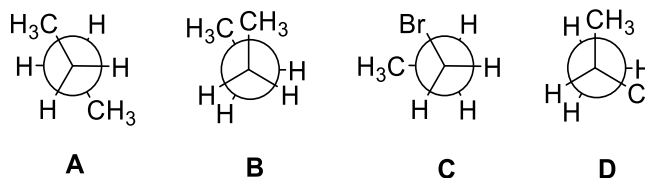
**29. Rank the following alkenes in order of increasing thermodynamic stability:**

- 1 - pent-1-ene                      2 - *E*-pent-2-ene  
3 - *Z*-pent-2-ene                  4 - *n*-pentane  
A/ 4 < 2 < 3 < 1                  B/ 1 < 3 < 2 < 4  
C/ 1 < 2 < 3 < 4                  D/ 3 < 1 < 2 < 4

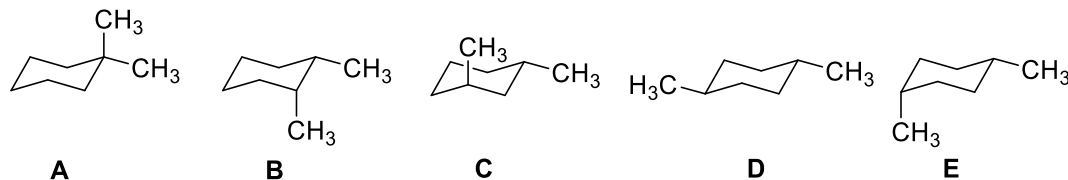
**30. Rank the following compounds in order of increasing thermodynamic stability:**

1. benzene                              2. allene  
3. isobutane                            4. *n*-butane  
A/ 2 < 4 < 3 < 1                  B/ 1 < 3 < 4 < 3  
C/ 4 < 3 < 2 < 1                  D/ 4 < 2 < 3 < 1

**31. Which of the following conformers is the least stable?**



**32. Which of the following isomers is thermodynamically the most stable?**



**33. Choose the correct statements from the following:**

- A/ combining an even and an odd number of atomic orbitals always forms a non-bonding molecular orbital  
B/ the number of molecular orbitals formed is always the same as the number of atomic orbitals combined  
C/ when an odd number of p-orbitals are combined, non-bonding molecular orbitals are also formed  
D/ the number of nodal planes is also a characteristic of the orbital energy



**34. What does the following depend on in terms of the energy level of molecular orbitals?**

1 - chemical reactivity

2 - thermodynamic stability

A/ only on the energy level of the highest unoccupied molecular orbital

B/ only on the energy level of the lowest occupied molecular orbital

C/ on the energy level of all the occupied molecular orbitals

D/ on the energy level of the HOMO-LUMO orbitals

**35. Choose the correct statement!**

A/ The molecularity of complex reactions is not always defined by the rate-determining step.

B/ Molecularity and reaction order are not the same in unimolecular reactions.

C/ By molecularity we mean the number of particles undergoing a change in bonds in a given elementary chemical reaction.

D/ The kinetic order of a reaction is the difference in the power exponents of the concentrations in the rate equation.

**36. Choose the correct statement!**

A/ A reaction molecularity is always the same as the kinetic order of the reaction.

B/ The molecularity of complex reactions is defined by the molecules involved in the rate-determining step.

C/ In the activated complex of bimolecular reactions two molecules (A and B, or A and A) are involved, therefore the kinetics of the elementary step is second order.

D/ Kinetic order, in a given elementary chemical reaction, is the number of particles undergoing bond change.

**37. Choose the correct statement!**

A/ The conditions for thermodynamic control are: shorter reaction times and lower temperatures.

B/ In the case of thermodynamic control, the end products are formed in the proportion corresponding to their activation free enthalpy, i.e. in the proportion corresponding to their rate of formation.

C/ In the case of thermodynamic control, the end products are formed in the proportion corresponding to their free enthalpy of formation, i.e. in the proportion corresponding to their thermodynamic stability.

D/ The conditions for kinetic control are: longer reaction time and higher temperature.

**38. Choose the correct statement!**

A/ If optimal conditions are provided to obtain the more stable product, the reaction proceeds under kinetic control.

B/ If optimal conditions are provided for the formation of the product forming faster, the reaction proceeds under thermodynamic control.

C/ In irreversible reactions, kinetic control always prevails.

D/ In reversible reactions, kinetic control always prevails.



**39. Choose the correct statement!**

- A/ According to the reactivity-selectivity rule, the less selective a reagent is, the less reactive it is.
- B/ According to the reactivity-selectivity rule, the more reactive a reagent is, the more selective it is.
- C/ The reactivity-selectivity rule applies to all types of reactions.
- D/ According to the reactivity-selectivity rule, the more selective a reagent is, the less reactive it is.

**40. For the interactions below, assign their classification.**

- A/ van der Waals interaction
- B/ Pitzer strain
- C/ Baeyer strain
- 1 - torsional strain
- 2 - angular strain
- 3 - steric (repulsive) interaction of atoms



## 2. Structure and properties of organic compounds

### *Solutions*

1. A

*The electron-withdrawing or electron-donating substituents attached to the aromatic ring affect the acidity of phenols in different ways. A substituent with negative inductive and negative mesomer/negative hyperconjugation effects promotes both increased proton dissociation and also stabilises the anion formed. Groups with positive inductive and positive mesomer/positive hyperconjugation effect have the opposite impact on acidity. Phenols are stronger acids than alcohols due to the resonance stabilisation of the conjugated base, and the mesomeric effect reduces the electronegativity of the oxygen atom not yet deprotonated, which results in the O-H bond being polarised even more towards the phenolic oxygen atom, promoting the electrofuge dissociation of the proton.*

2. A, C

3. D

*The electron-withdrawing or electron-donating substituents attached to the aromatic ring affect the acidity of aromatic carboxylic acids in different ways. A substituent with negative inductive and negative mesomer/negative hyperconjugation effects promotes both increased proton dissociation and stabilisation of the anion formed. Groups with positive inductive and positive mesomer/positive hyperconjugation effects have the opposite influence on acidity.*

4. B

*Carbonic acid is a weak acid ( $pK_a$  6.37). Carboxylic acids usually have a  $pK_a$  between 4 and 5 (acrylic acid:  $pK_a$  4.25), are weak acids compared to inorganic acids, but have several orders of magnitude higher acidity compared to e.g. alcohols. Intramolecular hydrogen bonding promotes deprotonation of the carboxyl group and stabilises the carboxylate group, thus increasing the acidity, which explains the higher acidity of 2-hydroxybenzoic acid ( $pK_a$  2.98) compared to 4-hydroxybenzoic acid ( $pK_a$  4.48).*

5. B

*The basicity of amines depends on the number of carbon atoms bonded directly to the nitrogen atom, subject to the medium (e.g. in aqueous solution or gas phase). In aqueous solution, the dipole-dipole interaction and hydrogen bonding are also involved. In aqueous solution, alkyl groups promote charge dispersion through electron donation and thus stabilise the ammonium ion, but also make solvation more difficult, which is a destabilising factor. Therefore in aqueous solution, secondary amines are the strongest bases.*

6. the most acidic – 3, the least acidic – 2

*The electron-withdrawing or electron-donating substituents attached to the aromatic ring affect the acidity of aromatic carboxylic acids in different ways. A substituent with negative inductive and negative mesomer/negative hyperconjugation effects promotes both increased proton dissociation and stabilisation of the anion formed. Groups with positive inductive and positive mesomer/positive hyperconjugation effects have the opposite influence on acidity.*

7. D

*Carboxylic acids usually have a  $pK_a$  between 4-5, phenols between 8-11 depending on the substituents, alcohols between 15-18 and alkynes between 25-35.*

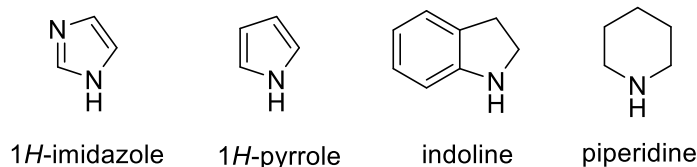


## 8. D

Phenols are stronger acids than alcohols, both because of the easier dissociation of the proton due to the positive mesomeric effect of the oxygen atom and because of the resonance stabilisation of the conjugated base. Phenols have a  $pK_a$  of 8-11 depending on the substituents, alcohols 15-18. The sulphur atom is larger and more easily polarised than oxygen, so the S-H bond is weaker than the O-H bond, and thiols are therefore stronger acids than the corresponding alcohols (thiols  $pK_a \sim 12$ , aryl thiols  $pK_a$  6-8).

## 9. B

In the aromatic nitrogen heterocycles below, the N-H bond is acidic because the non-bonding electron pair of the nitrogen atom in the N-H bond is also involved in the formation of the aromatic sextet, which makes the proton more easily dissociate, and the amide anion formed is resonance stabilised. The introduction of a second nitrogen atom into the aromatic ring increases the N-H acidity. Cycloaliphatic secondary amines (piperidine) are much less acidic due to the lack of the above properties. In indoline, however, the anion formed during deprotonation is partially resonance stabilised by the aromatic ring (not to the extent of pyrrole or imidazole), so the N-H bond of indoline is relatively more acidic than the N-H bond of piperidine.



## 10. A

The basicity of six-member heterocycles with two nitrogen heteroatoms depends on the position of the two nitrogen atoms relative to each other. The non-bonding electron pairs of the nitrogen atoms at 1,2-position are significantly repelled by each other due to the space proximity. Protonation of one nitrogen atom reduces this effect, which is energetically advantageous. This effect decreases as the distance between the two nitrogen atoms increases, so that the basicity order of the diazines decreases in the order 1,2 > 1,3 > 1,4.

## 11. D

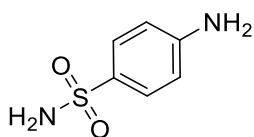
Carboxylic acids usually have a  $pK_a$  of 4-5, phenols 8-11, depending on the substituents, and alcohols 15-18. The electron-withdrawing or electron-donating substituents attached to the aromatic ring affect the acidity of phenols in different ways. A substituent with negative inductive and negative mesomer/negative hyperconjugation effects promotes both increased proton dissociation and also stabilises the anion formed. Groups with positive inductive and positive mesomer/positive hyperconjugation effect have the opposite impact on acidity.

## 12. the strongest base – 3, the weakest base - 5

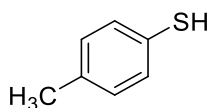
In compounds containing two nitrogen heteroatoms at 1,3-position, the resonance formed via the second heteroatom increases the electron density at the nitrogen atom, and thus its basicity. However, the negative inductive effect of the second heteroatom tends to decrease the basicity. The resulting effect is an increase in basicity compared to single heteroatom systems. In pyrrole, the non-bonding electron pair of nitrogen contributes to the  $6\pi$ -electron aromatic system, so that this nitrogen is not basic in character.



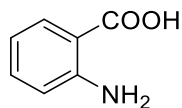
13. A, C



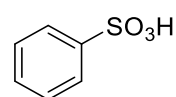
sulfanilamide



4-methylsulfanybenzene



anthranilic acid



benzenesulfonic acid

14. the most basic - 3, the least basic - 1

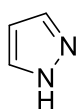
Aromatic amines are weaker bases than their aliphatic analogues. The non-bonding electron pair of the nitrogen atom interacts with the  $p_z$ -orbitals of the ring carbon atoms, making it more difficult to protonate (+M effect). Amines containing multiple carbon-nitrogen bonds (e.g. pyridine) are also less basic than the corresponding aliphatic amines (higher s-ratio in the hybrid state of the nitrogen atom, which makes the electrons more strongly attracted to the nucleus). The nitrogen of acid amides is only very weakly basic due to the negative inductive and negative mesomeric effect of the carbonyl group (these are acidic nitrogen atoms).

15. E

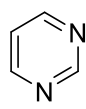
The electron-withdrawing or electron-donating substituents attached to the aromatic ring affect the acidity of aromatic carboxylic acids in different ways. A substituent with negative inductive and negative mesomer/negative hyperconjugation effects promotes both increased proton dissociation and stabilisation of the anion formed. Groups with positive inductive and positive mesomer/positive hyperconjugation effects have the opposite influence on acidity. In phenol, it is not only the acidity of the carboxyl group that is important, but also that of the OH group. Phenolate is a very strong electron-donating group.

16. B

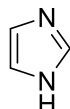
For five-membered heterocycles with two nitrogen heteroatoms either in 1,2 or 1,3 position, the resonance formed with the involvement of the other heteroatom (nitrogen containing N-H bond) increases the electron density at the newly introduced nitrogen atom, thus increasing the basicity. The negative inductive effect of the second heteroatom, in turn, decreases the electron density on the nitrogen, thus decreasing the basicity. The resulting effect is an increase in basicity compared to compounds with one heteroatom. Since the -I effect decreases with distance, this effect is stronger at the 1,2-position, making the 1,2-isomers weaker bases (i.e. imidazole is a stronger base than pyrazole).



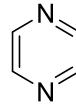
pyrazole



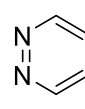
pyrimidine



imidazole



pyrazine



pyridazine

17. B

In compounds containing two nitrogen heteroatoms at 1,3-position, the resonance formed via the second heteroatom increases the electron density at the nitrogen atom, and thus its basicity. However, the negative inductive effect of the second heteroatom tends to decrease the basicity. The resulting effect is an increase in basicity compared to single heteroatom systems. In pyrrole, the non-bonding electron pair of nitrogen contributes to the  $6\pi$ -electron aromatic system, so that this nitrogen is not basic in character.

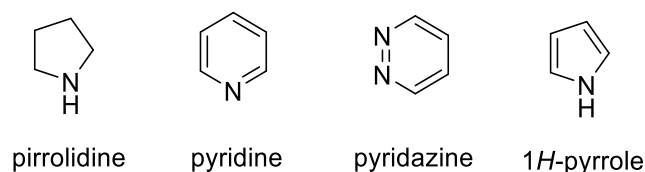
18. A - 1, B - 4, C - 3, D - 2



The conjugate base of an acid is a stronger base, the higher the s-ratio of the hybrid orbitals hosting the electron pair (hence the acidic strength of alkynes is higher than that of the corresponding alkanes). In  $\beta$ -oxoesters, the electron-withdrawing property of the oxo group and the carboxyl group significantly increases the acidity of the methylene group between them.

19. B

Amines containing nitrogen atoms with multiple bonds (e.g. pyridine, pyrrole, imidazole) have a lower basicity than the corresponding aliphatic amines (higher s-fraction in the hybrid state of the nitrogen atom). In pyrrole, the non-bonding electron pair of nitrogen contributes to the  $6\pi$ -electron aromatic system, so this nitrogen is not basic. The basicity of six-membered nitrogen heterocycles containing two heteroatoms depends on the position of the two nitrogen atoms relative to each other. The non-bonding electron pairs of nitrogen atoms in the 1,2-position repel each other significantly due to the proximity of the two nitrogen atoms. Protonation of one nitrogen atom reduces this effect, which is energetically advantageous. This effect decreases as the distance between the two nitrogen atoms increases, so that the basicity order of the diazines decreases in the order 1,2 > 1,3 > 1,4.



20. A, B, D

21. 1 – A, B, E, G, J; 2 – C, I; 3 – D, F, H, I

22. A – 1, B – 3, C – 2, D – 4

23. A

24. the strongest base: 2; the weakest base: 3

25. B > C > D > F > A > G > E

26. C

Nucleophilicity describes how quickly a nucleophilic reagent can displace the leaving group from an appropriate substrate. For identical nucleophilic atoms, the more basic the nucleophile, the more reactive it is. Arylamines are weaker bases than alkylamines. Electron donating groups on the aromatic ring slightly increase the basicity, while electron withdrawing groups decrease it.

27. C

Electrophilic reagents: cationic reagent or electron-deficient molecule/atom that receives both members of the bonding electron pair from the carbon atom when forming a C-X bond

Nucleophilic reagents: an anionic reagent or a molecule/atom with a lone pair of electrons which provides both members of the bonding electron pair when forming a C-X bond

28. A

29. B

Olefins have a higher energy content than alkanes with the same number of carbon atoms. The substitution of the vinylic carbons of the double bond with electron-donating substituents (alkyl groups) increases the thermodynamic stability of olefins. Among the geometric isomers, the E isomer is more stable (the bulkier substituents are further apart).



30. A

*Cumulated dienes (e.g. allene) are characterised by a high degree of instability, due to mutual repulsion resulting from the spatial proximity of the two isolated electron pairs. Olefins have a higher energy content than alkanes of the same carbon number. Aromatic hydrocarbons are highly stable. Branched-chain alkanes are thermodynamically more stable than straight-chain alkanes of the same carbon number due to the higher number of homo(sigma)conjugations.*

31. B

*For open-chain alkanes, the highest energy conformers are the eclipsed ones. In the case of the synperiplanar isomer of butane, the steric strain between the eclipsed methyl groups also represents an energy barrier.*

32. D

*For substituted cyclohexanes, the axial (perpendicular to the plane of the three non-adjacent atoms of the cyclohexane ring) position of the bulkier (non-hydrogen) groups is unfavourable.*

33. B, C, D

34. 1 – D, 2 – C

35. C

*The molecularity of a reaction is defined by the number of molecules (or atoms) that change valence (chemical valence) in the rate-determining transition state of the reaction, reacting as a collision complex to produce either the reaction product or the starting compound leading to it. Molecularity is defined for elementary reactions only.*

*The (gross) kinetic order of the reactions is equal to the sum of the exponents of the equilibrium concentration terms of the reactants in the equilibrium. For elementary reactions, the molecularity and kinetic orders are the same. If a reaction is composed of several elementary reactions, the reaction order can be a fraction, as occurs especially in chain reactions.*

36. B

37. C

*Kinetic control: the product composition is determined by the rates of formation. In this case, the reaction is considered irreversible under the given conditions.*

*Thermodynamic control: the product composition is determined by the relative thermodynamic stability of the products under the reaction conditions. In this case, chemical equilibrium can be achieved in the reaction.*

38. C

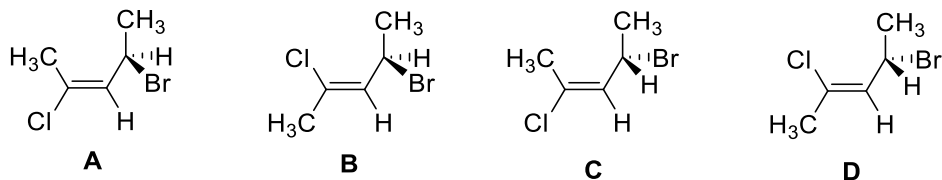
39. D

40. A – 3, B – 1, C - 2



### 3. Stereochemistry

1. What is the stereochemical relationship between the following compounds?

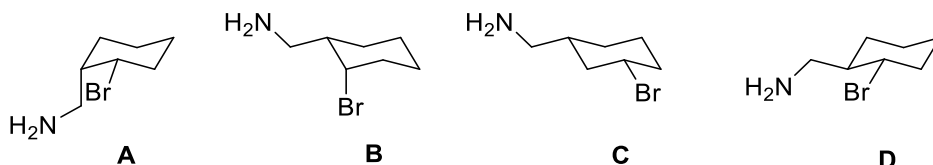


A:B                      A:C                      A:D                      B:C                      B:D                      C:D  
 1. configurational enantiomers                      2. configurational diastereomers

2. Which of the following statements are true?

- A/ Structural isomers differ from each other in atomic connectivity.
- B/ Stereoisomers do not necessarily have to have the same atomic connectivity.
- C/ Enantiomeric structures are mirror image pairs that cannot be overlapped by shifting or rotating the whole molecule.
- D/ Diastereomers are always chiral.
- E/ Conformers can be converted into each other either by rotation or by pseudorotation.
- F/ Most of the time, no bond breaking is required to convert configurational isomers into each other.

3. Identify the isomeric relationship (constitutional, conformational, configurational) between the following molecules.

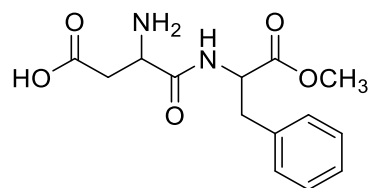


A:B                      A:C                      A:D                      B:C                      B:D                      C:D  
 1. conformational                      2. constitutional                      3. configurational

4. One of the following  $C_7H_{14}$  compounds does not have *E-Z* isomerism. Which one is it?

- A/ hept-2-ene                      B/ hept-3-ene                      C/ 2-methylhex-2-ene
- D/ 3-methylhex-2-ene                      E/ 3-methylhex-3-ene

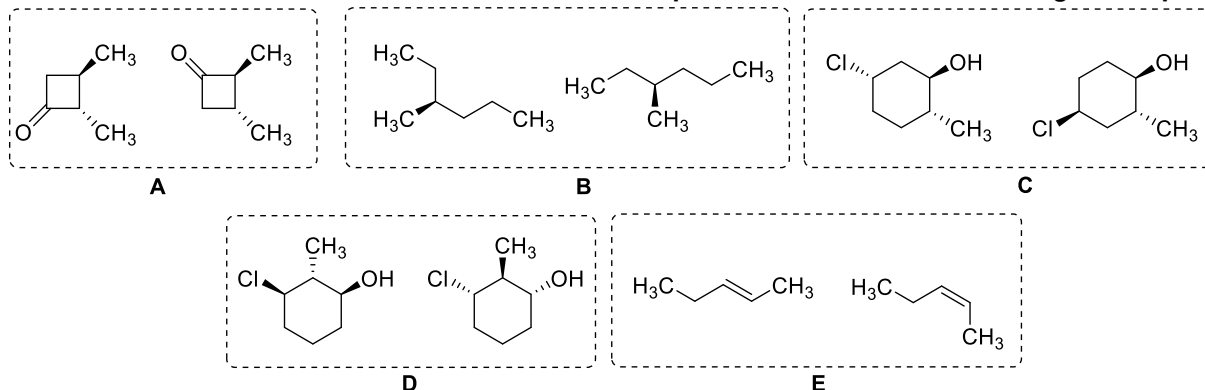
5. How many stereogenic centres are in aspartame?



**6. Choose the correct statement!**

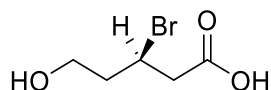
- A/ The determination of the relative configuration is derived from *D* (+) lactic acid.  
 B/ The determination of the relative configuration is derived from *D* (+) glyceraldehyde.  
 C/ The determination of the relative configuration is derived from *L* (-) lactic acid.  
 D/ The determination of the relative configuration is derived from *L* (-) glyceraldehyde.

**7. What is the stereochemical relationship between the following compounds?**



1. constitutional isomers  
 2. configurational enantiomers  
 3. configurational diastereomers  
 4. identical compounds

**8. The oxidation of (*R*)-3-bromo-5-hydroxypentanoic acid shown below yields the corresponding 3-bromopentanedicarboxylic acid product, which is:**

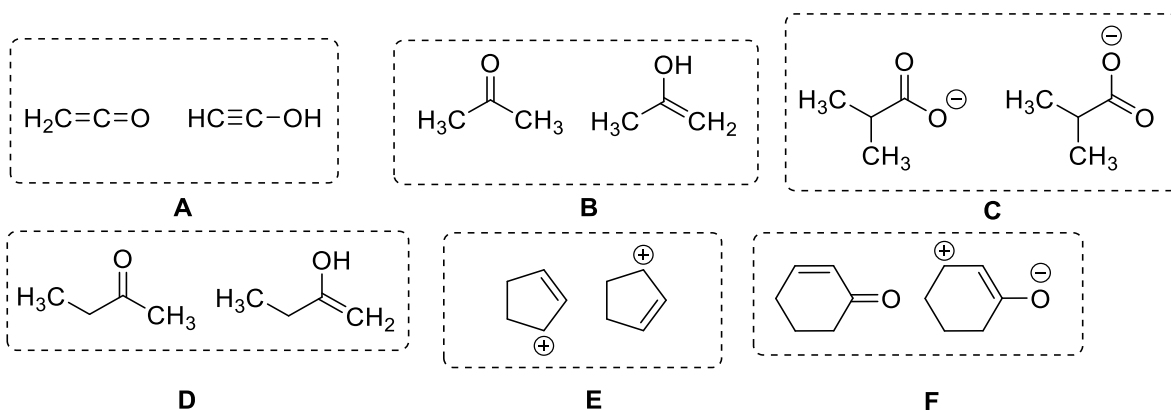


- A/ a mixture of two diastereoisomers in different proportions  
 B/ a racemic mixture  
 C/ a pure enantiomer  
 D/ a meso compound  
 E/ an achiral compound

**9. Match the following concepts with the correct statements.**

- A/ they differ only in their electron distribution and consequently in their charge distribution  
 B/ they differ in atomic connectivity  
 C/ they are not real structures  
 D/ they usually differ in the position of a double bond and a mobile hydrogen
- 1 – resonance structures  
 2 - tautomers

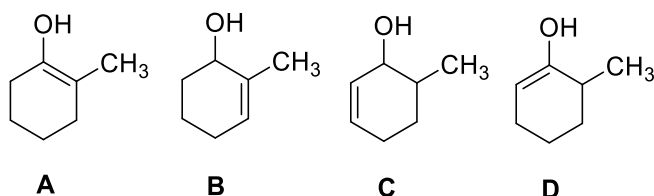
10. Which of the following pairs are resonance or tautomeric structures?



1 – resonance structures

2 – tautomeric structures

11. Select the tautomers of 2-methylcyclohexanone!



12. Which statement is NOT correct?

A/ Resonance structures differ in the position of the electrons.

B/ Resonance structures are different Lewis structures.

C/ Resonance structures can differ in the position of a double bond and a charge.

D/ Tautomers have different structures and connectivity.

E/ Tautomers differ in the position of a double bond and a mobile hydrogen.

13. Select the correct statement!

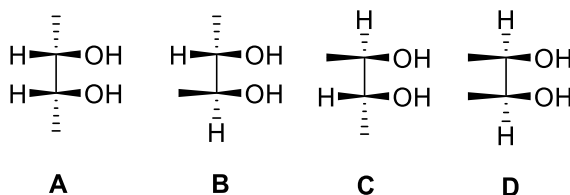
A/ If several products are formed in a reaction, the selectivity is full (100 %), otherwise partial.

B/ A specific reaction is necessarily selective and vice versa.

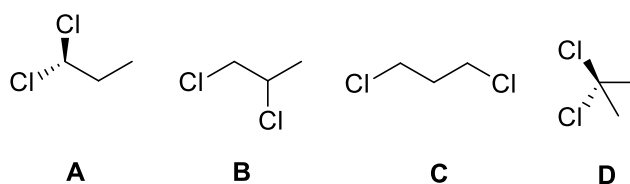
C/ Selectivity refers to the distribution of products formed from several starting materials in a reaction.

D/ Specificity refers to the distribution of products in the reaction from different isomeric starting materials.

14. Which of the following are meso structures?



15. Which of the following structures is chiral?



16. Which of the following are types of tautomerism?

- |                |             |                    |
|----------------|-------------|--------------------|
| A/ Z-E         | B/ R-S      | C/ lactame-lactime |
| D/ ring-chainc | E/ enol-oxo | F/ cis-trans       |

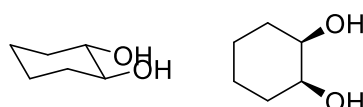
17. Rank the following groups according to the Cahn-Ingold-Prelog convention!

- |                                       |                      |        |
|---------------------------------------|----------------------|--------|
| A/ cyclopenthyl                       | B/ -OCH <sub>3</sub> | C/ -OH |
| D/ -CH(CH <sub>3</sub> ) <sub>2</sub> | E/ -COOH             |        |

18. In which property do enantiomers differ from each other?

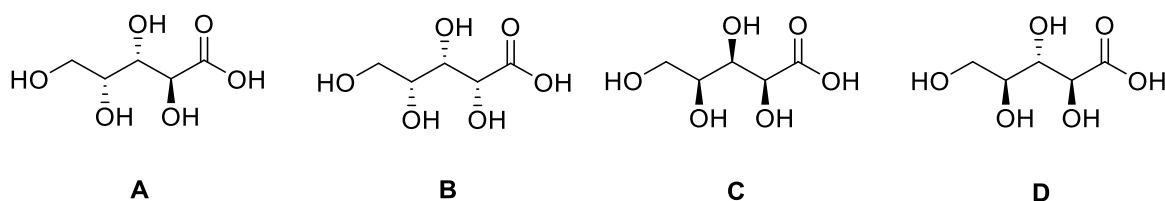
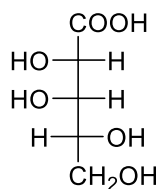
- A/ melting point
- B/ UV absorption
- C/ molecular weight
- D/ atomic connectivity
- E/ optical rotation

19. What is the stereochemical relationship between the following compounds?



- |                                  |                                |
|----------------------------------|--------------------------------|
| 1. constitutional isomers        | 2. configurational enantiomers |
| 3. configurational diastereomers | 4. identical compounds         |

20. Choose the perspective formula for the Fischer projection below!



### 3. Stereochemistry Solutions

1. A:B – 2, A:C – 1, A:D – 2, B:C – 2, B:D – 1, C:D – 2

*Enantiomers: non-overlapping mirror image pairs; geometric characteristics: same internuclear distance, groups in different order (configuration)*

*Diastereomers: stereoisomers that are not in an enantiomeric relationship; geometric characteristics: identical connectivity, different internuclear distance*

*Configurational isomers (when the carbon atom is the stereogenic centre): cannot be converted into each other without breaking and reforming a covalent bond*

2. A, C, E

*Configurational isomers (if the stereogenic centre is a carbon atom): cannot be converted into each other without breaking and reforming a covalent bond*

*Stereoisomers: same molecular formula, same constitution, but different 3D structure*

3. A:B – 1, A:C – 2, A:D – 3, B:C – 2, B:D – 3, C:D – 2

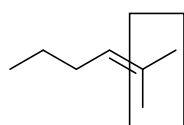
*Constitutional isomers: compounds with the same molecular formula but different structures – the atoms are connected in different order*

*Conformational isomers: can be converted into each other by rotation (or pseudorotation) around single bond(s)*

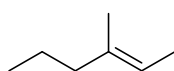
*Configurational isomers (when the carbon atom is the stereogenic centre): cannot be converted into each other without breaking and reforming a covalent bond*

4. C

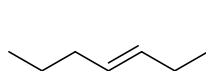
same substituents



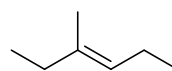
2-methylhex-2-ene



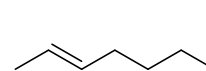
3-methylhex-2-ene



hept-3-ene

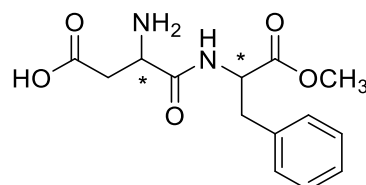


3-methylhex-3-ene



hept-2-ene

5. 2



6. B

7. A - 4, B - 4, C - 1, D - 2, E - 3





8. E

*The product no longer contains a stereogenic centre.*

9. A – 1, B – 2, C – 1, D - 2

10. A – 2, B – 2, C – 1, D – 2, E – 1, F - 1

11. A, D

12. D

13. D

14. A, D

*Meso-isomer: a stereoisomer containing chiral carbon atoms, but the molecule has a mirror plane and is therefore optically inactive,*

15. B

*Chiral: a molecule that cannot be overlapped with its mirror image. In the simplest chiral compound, the molecule has a carbon atom to which four different achiral ligands are attached (chirality centre/stereogenic centre).*

16. C, D, E

*Tautomerism: a special form of constitutional isomerism in which the isomers (tautomers) differ in the position of a double bond and a hydrogen and require low activation energy to form into each other.*

17. 1 – B, 2 – C, 3 – E, 4 – A, 5 – D

*We first rank the atoms directly connected to the chirality centre, and if identical, examine the further connected atoms (until we find a difference). Ranking of substituents according to the Cahn-Ingold-Prelog convention: a) element with higher atomic number ranks higher, b) element with higher mass number ranks higher, c) of geometric isomer substituents, the Z isomer ranks higher than the E isomer, d) of optical isomer substituents, the R configuration substituent ranks higher than the S configuration substituent. The coordination number of the ligands is complemented to four, the atoms in the multiple bonds are multiplied to form single bonds.*

18. E

19. 3

20. A



## 4. Alkanes, alkenes, alkynes

1. Which formula is typical for cycloparaffins?

- A/  $C_nH_{2n+2}$                       B/  $C_nH_{2n}$   
C/  $C_nH_{2n-2}$                       D/  $C_nH_{2n-6}$

2. Which formula is typical for alkanes?

- A/  $C_nH_{2n+2}$                       B/  $C_nH_{2n}$   
C/  $C_nH_{2n-2}$                       D/  $C_nH_{2n-6}$

3. Which of the following compounds can be used to prepare *n*-butane by Clemmensen reduction?

- A/ butan-2-one                      B/ pentanal  
C/ pentan-2-one                      D/ butan-2,3-dione

4. Choose the correct statement!

- A/ Alkenes are prepared from alcohols by thermal decomposition.  
B/ Alkenes are prepared from alkanes by partial hydrogenation.  
C/ Alkenes are prepared from alkyl halides by hydrogen halide elimination.  
D/ Alkenes are prepared from alkynes by dehydration.

5. Choose the correct statement!

- A/ Addition of water to acetylene results in the formation of a secondary alcohol.  
B/ Addition of water to acetylene results in the formation of a vinyl alcohol.  
C/ Addition of water to acetylene results in the formation of formaldehyde.  
D/ Addition of water to acetylene results in the formation of acetic acid.

6. Choose the correct statement!

- A/ The Markovnikov rule does not apply to the electrophilic hydrogen-halide addition characteristic of alkenes.  
B/ The first step of the electrophilic hydrogen-halide addition characteristic of alkenes is a heterolytic dissociation.  
C/ The Markovnikov hydrogen-halide addition is nucleophilic.  
D/ The electrophilic hydrogen-halide addition characteristic of alkenes is not regioselective.



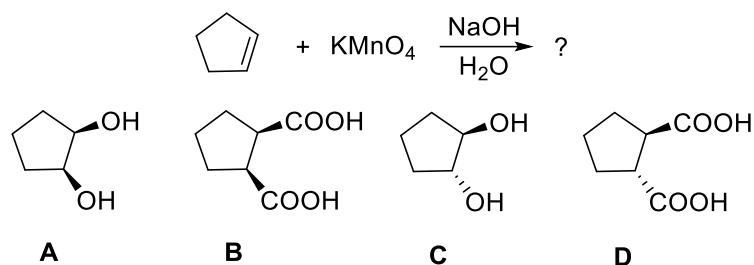
### 7. Choose the correct statement!

- A/ *Cis*-1,2-dibromocyclohexane is formed from cyclohexene with elemental bromine.
- B/ The electrophilic addition characteristic of alkenes, usually results in a *syn* and not an *anti* product.
- C/ *Trans*-1,2-dibromocyclohexane is formed from cyclohexene with elemental bromine.
- D/ *Anti*-addition leads to a *cis* product, while *syn*-addition leads to a *trans* product in the electrophilic additions characteristic of alkenes.

### 8. What is the main product of the following reactions?

- A/ but-1-ene + HBr  $\rightarrow$
  - B/ but-1-ene + HBr/H<sub>2</sub>O<sub>2</sub>  $\rightarrow$
  - C/ but-1-ene + H<sub>2</sub>O/acid  $\rightarrow$
  - D/ but-1-ene + BH<sub>3</sub>, then H<sub>2</sub>O<sub>2</sub>/base  $\rightarrow$
1. *n*-butyl bromide
  2. *sec*-butyl bromide
  3. *n*-butyl alcohol
  4. *sec*-butyl alcohol

### 9. What is the main product of the following reaction?



### 10. Choose the correct statement!

- A/ Alkenes are prepared from alkynes by thermal decomposition.
- B/ Alkenes are prepared from alkanes by partial hydrogenation.
- C/ Alkenes are prepared from alkyl halides by dehydrogenation.
- D/ Alkenes are prepared from alkanes by dehydrogenation.

### 11. Choose the correct statement!

- A/ By dimerization acetylene is converted to vinyl acetylene.
- B/ By dimerization acetylene is converted to buta-1,2-diene.
- C/ By trimerization acetylene is converted to cyclohexane.
- D/ By trimerization acetylene is converted to naphthalene.

### 12. Choose the correct statement!

- A/ When alkenes are prepared from alkynes by hydrogenation, *trans* olefins are obtained.
- B/ When alkenes are prepared from alkynes with lithium in the presence of ethylamine, *cis*-olefin is obtained.
- C/ When alkenes are prepared from alkynes with lithium in the presence of ethylamine, *cis* and *trans* olefins are obtained.
- D/ When alkenes are prepared from alkynes by hydrogenation, *cis* olefins are obtained.

**13. Give the missing reagents for the following reactions!**

A/ cyclohexene + ?  $\rightarrow$  *cis*-cyclohexane-1,2-diol

B/ *cis*-cyclohexane-1,2-diol + ?  $\rightarrow$  1,2-dibromocyclohexane

C/ cyclohexene + ?  $\rightarrow$  1,2-epoxycyclohexane

D/ 1,2-epoxycyclohexane + ?  $\rightarrow$  *trans*-cyclohexane-1,2-diol

E/ cyclohexene + ?  $\rightarrow$  *trans*-1,2-dibromocyclohexane

F/ *trans*-1,2-dibromocyclohexane + ?  $\rightarrow$  cyclohexane-1,2-diol

1. NaOH

2. KMnO<sub>4</sub>

3. perbenzoic acid

4. Br<sub>2</sub>

5. HBr

**14. Choose the correct statement!**

A/ Hydrogen-halide addition with a radical mechanism characteristic of alkenes is not regioselective.

B/ Cyclohexene is converted to *cis*-cyclohexane-1,2-diol by peroxycarboxylic acid.

C/ Cyclohexene is converted to *trans*-cyclohexane-1,2-diol by potassium permanganate.

D/ The Markovnikov orientation does not apply to the hydrogen-halide addition with a radical mechanism characteristic of (asymmetric) alkenes.

**15. Which of the following statements are correct for the allyl anion?**

A/ it contains two carbon atoms

B/ it contains three carbon atoms

C/ it contains four carbon atoms

D/ it has 2 delocalised  $\pi$ -electrons

E/ it has 3 delocalised  $\pi$ -electrons

F/ it has 4 delocalised  $\pi$ -electrons

G/ it usually occurs as a reaction intermediate

**16. Which of the following statements are correct for the allyl radical?**

A/ it contains two carbon atoms

B/ it contains three carbon atoms

C/ it contains four carbon atoms

D/ it has 2 delocalised  $\pi$ -electrons

E/ it has 3 delocalised  $\pi$ -electrons

F/ it has 4 delocalised  $\pi$ -electrons

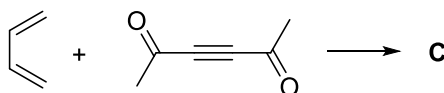
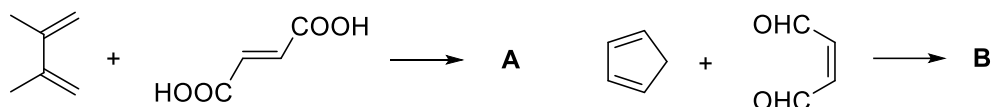
G/ it usually occurs as a reaction intermediate



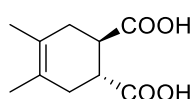
**17. Which of the following statements are correct for the allyl cation?**

- A/ it contains two carbon atoms
- B/ it contains three carbon atoms
- C/ it contains four carbon atoms
- D/ it has 2 delocalised  $\pi$ -electrons
- E/ it has 3 delocalised  $\pi$ -electrons
- F/ it has 4 delocalised  $\pi$ -electrons
- G/ it usually occurs as a reaction intermediate

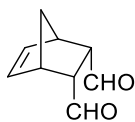
**18. What are the main products of the following reactions?**



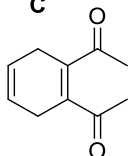
1. A



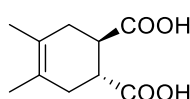
B



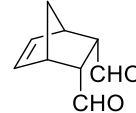
C



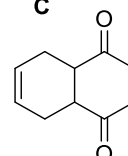
2. A



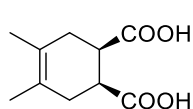
B



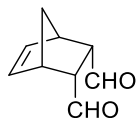
C



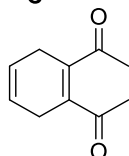
3. A



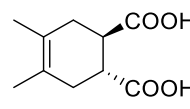
B



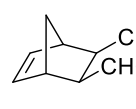
C



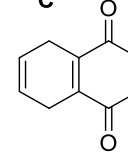
4. A



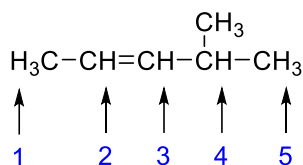
B



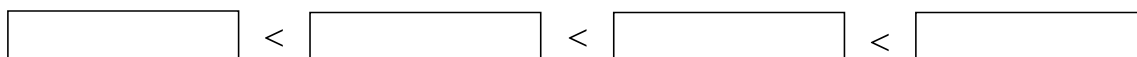
C



**19. Which of the indicated hydrogens reacts the fastest in a radical bromination reaction at moderate temperature?**



**20. Arrange the following structures in order of increasing radical stability:**



A – *tert*-butyl radical

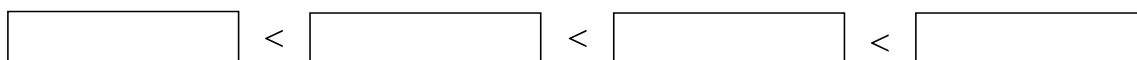
B – methyl radical

C – *sec*-propyl radical

D – primary butyl radical



21. Arrange the following structures in order of increasing radical stability::



A – diphenylmethyl radical

B – methyl radical

C – sec-butyl radical

D – benzyl radical

22. When you prepare tetrahydrophthalic anhydride from butadiene using a Diels-Alder reaction, what are the characteristics of the reaction? (more than one correct answer is possible)

A/ it can be regioselective

B/ it can be conducted by ultraviolet light

C/ it is regiospecific

D/ the anellation hydrogen atoms are characterised by a *cis* relative configuration

E/ it can be conducted by refluxing in toluene

23. Choose the conditions for isoconjugation from the statements below!

A/ equal number of conjugating atoms (electron orbitals)

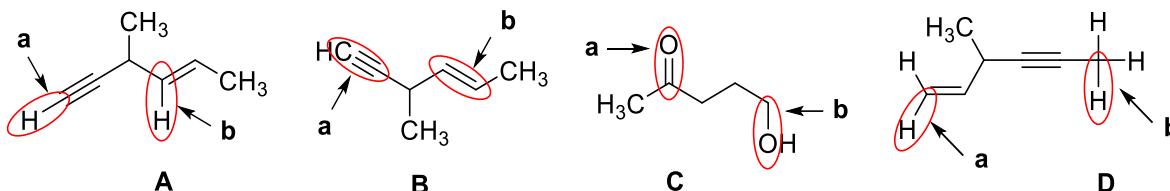
B/ only sp hybrid state atoms can participate in it

C/ the same type of connection of conjugating atoms (electron orbitals)

D/ only sp<sup>2</sup> hybrid state atoms can participate in it

E/ isoconjugated compounds have the same number of electrons in the conjugating orbitals

24. Indicate in pairs which bond length is longer!



1 – a > b

2 – a = b

3 – b > a

25. From which pair(s) of compounds can 2-methylpent-2-ene be prepared by Wittig reaction?

A/ acetone + triphenylpropylphosphonium bromide

B/ ethyl bromide + isobutene

C/ propionaldehyde + triphenylisopropylphosphonium bromide

D/ methyl bromide + pent-2-ene

## 4. Alkanes, alkenes, alkynes

### *Solutions*

1. B

*For each carbon atom in the ring, there are two hydrogen atoms.*

2. A

*In the case of open chain hydrocarbons, there are two hydrogens for each interchain carbon atom, and two additional hydrogens for each of the two carbon atoms at the chain ends.*

3. A, D

*Four-carbon n-butane can only be formed from four-carbon oxo compounds by Clemmensen reduction. In the reduction, the number of carbon atoms does not change.*

4. C

*Alkenes can be prepared from alkynes with water addition (and not dehydration). Alkenes can be prepared from alcohols with dehydration, by heating under acidic conditions. The hydrogenation is a reduction process, whereas the preparation of alkenes from alkanes is an oxidation.*

5. B

*Upon water addition to acetylene, a hydroxyl group is added to one pillar atom, while a hydrogen is added to the other pillar atom, resulting in vinyl alcohol. Vinyl alcohol is not a viable compound, it instantly tautomerizes into acetaldehyde.*

6. B

*The electrophilic hydrogen halide addition characteristic of alkenes proceeds regioselectively, according to the Markovnikov rule. The result of the heterolytic dissociation of the hydrogen halide is the formation of a proton, which reacts as an electrophile with the  $\pi$ -electrons of the alkene in the first step.*

7. C

*The elemental halogen addition characteristic of alkenes is an electrophilic addition that takes place by anti addition, resulting in a trans product. This is also true for cyclohexene.*

8. A – 2, B – 1, C – 4, D - 3

*Water addition (in an acidic medium) and HBr addition proceed according to Markovnikov's rule. The HBr addition in a peroxide medium proceeds by a radical mechanism (Kharas reaction), during which the product halogenated at the chain-end is obtained due to the thermodynamic stability of the radical intermediate more substituted with alkyl groups (higher-order radical). The hydroboration followed by the subsequent oxidation step also formally results in an anti-Markovnikov product. The proton, the bromine radical (albeit a radical-donating reagent) and the boron atom are electrophilic. In the case of hydroboration, the hydrogen atom does not come from a proton, but from a hydride anion, in contrast to the addition of hydrogen bromide. However, the electron theoretical background is the same for both reactions.*



9. A

*Under the given conditions, only cis diols are formed. Considering the reaction mechanism, the two oxygen atoms of the permanganate approach the double bond from the same side, and then form a bond with the two pillar atoms.*

10. D

*Hydrogenation is a reduction step, so alkenes cannot be produced from alkanes in this way, but with hydrogen removal (dehydrogenation) they can be prepared. Alkenes can be prepared from alkyl halides by dehydrohalogenation.*

11. A

*Benzene can be prepared from acetylene by trimerization, while vinyl acetylene can be prepared by dimerization. In the latter case, the metal- $\sigma$  complex formed during the metal catalytic cycle forms a dimer with the metal- $\pi$  complex, forming vinyl acetate.*

12. D

*In the Lindlar reaction, the cis olefin can be prepared with hydrogenation. The reaction with lithium presumably proceeds by a radical mechanism, during which a trans-vinyl anion is formed in the presence of ethylamine. From the trans-vinyl anion only trans olefin is obtained.*

13. A – 2, B – 5, C – 3, D – 1, E – 4, F – 1

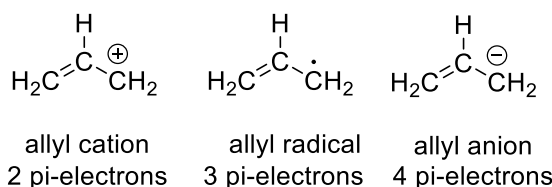
*In the reaction of 1,2-epoxycyclohexane with NaOH, the hydroxide anion, as a nucleophile, attacks one of the carbon atoms of the ring (with an  $S_N2$  mechanism, inversion occurs), thus forming a trans diol. Cyclohexene reacts with elemental bromine ( $Br_2$ ) in anti-addition, resulting in a trans product. When cyclohexene is reacted with  $KMnO_4$ , only cis diols are formed. Considering the reaction mechanism, the two oxygen atoms of the permanganate approach the double bond from the same side, and then form a bond with the two pillar atoms. Cyclohexene forms an epoxide derivative with peracids.*

14. D

*The hydrogen-halide addition with a radical mechanism characteristic of alkenes regioselectively yields the anti-Markovnikov product. From cyclohexene with peroxy-carboxylic acid trans diol can be prepared through an epoxide ring, while with  $KMnO_4$  a cis diol.*

15. B, F, G

*The allyl anion is a three centers system with four delocalized  $\pi$ -electrons, and a linear  $\pi$ -orbital system. It usually occurs as a reaction intermediate. It can be depicted with two  $\pi$ -resonance structures.*



16. B, E, G

*The allyl radical is a three centers system with three delocalized  $\pi$ -electrons, and a linear  $\pi$ -orbital system. It usually occurs as a reaction intermediate. It can be depicted with two  $\pi$ -resonance structures.*





17. B, D, F

The allyl cation is a three centers system with two delocalized  $\pi$ -electrons, and a linear  $\pi$ -orbital system. It usually occurs as a reaction intermediate. It can be depicted with two  $\pi$ -resonance structures.

18. 1

19. 4

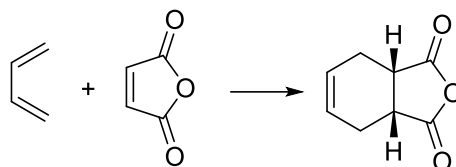
20. B < D < C < A

The relative stability of carbocations gradually increases with order (tertiary > secondary > primary).

21. B < C < D < A

The relative stability of carbocations gradually increases with order (tertiary > secondary > primary).

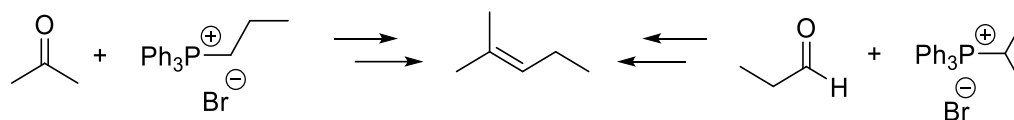
22. C, D, E



23. A, C, E

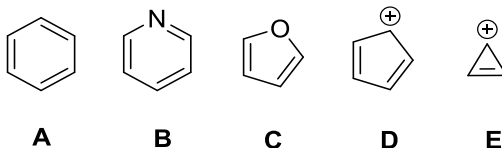
24. A - 3, B - 3, C - 3, D - 3

25. A, C

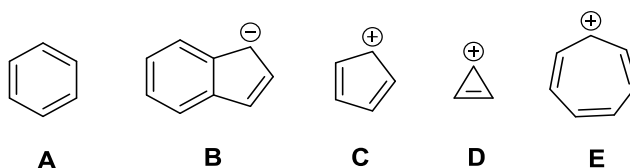


## 5. Aromatic compounds

1. All of the compounds below are aromatic, EXCEPT:



2. All of the compounds below are aromatic, EXCEPT:



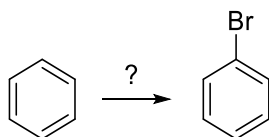
3. Choose the correct statement!

- A/ Naphthalene is a condensed ring aromatic hydrocarbon.
- B/ Naphthalene is a condensed ring, non-aromatic hydrocarbon.
- C/ Anthracene is a non-condensed ring aromatic hydrocarbon.
- D/ Phenanthrene is a condensed ring, non-aromatic hydrocarbon.

4. The indene could be deprotonated with the following base:

- A/ sodium amide
- B/ sodium methoxide
- C/ butyl lithium
- D/ sodium hydrogencarbonate
- E/ sodium hydroxide

5. Under which reaction conditions is the product below formed?

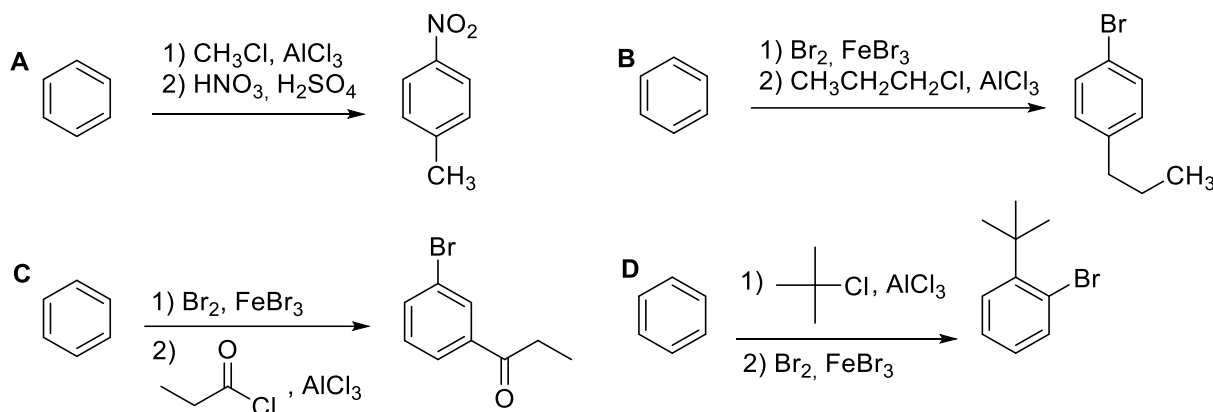


- A/  $\text{Cu}_2\text{Br}_2/\text{HBr}$
- B/  $\text{HBr}, \text{H}_2\text{O}_2$
- C/  $\text{Br}_2, \text{FeBr}_3$
- D/  $\text{Br}_2, \text{CCl}_4$
- E/  $\text{KBr}$

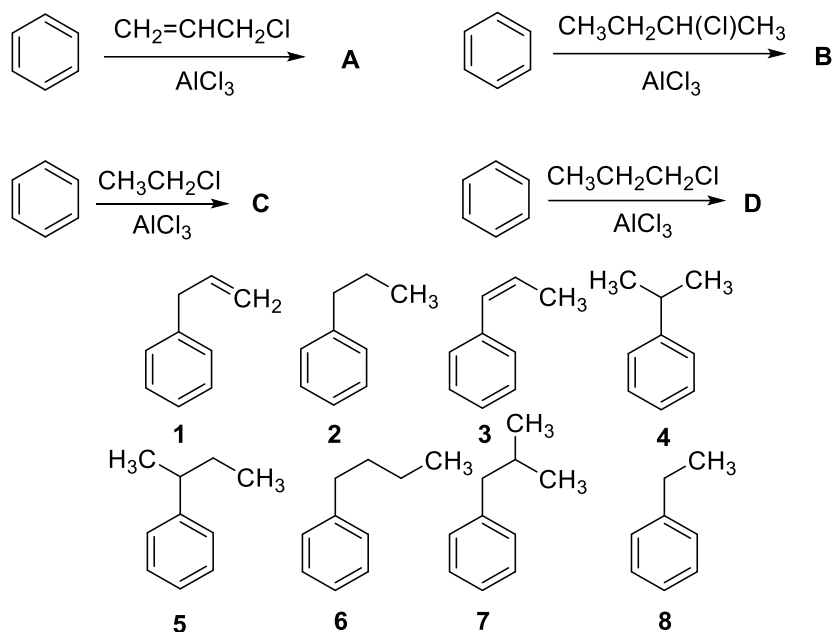
**6. Choose the correct statement!**

- A/ In the nitration of benzene with nitric acid, 1,2-dinitrobenzene is formed.  
 B/ In the nitration of benzene with nitric acid, 1,3-dinitrobenzene is formed.  
 C/ In the nitration of benzene with nitric acid, nitrobenzene is formed.  
 D/ In the nitration of benzene with nitric acid, 1,4-dinitrobenzene is formed.

**7. Only one of the following reaction conditions provides the indicated product as the main product.**



**8. What are the main products of the Friedel-Crafts alkylation reactions below?**



**9. Choose the correct order of relative reactivity of the compounds in  $S_EAr$  reactions (increasing reactivity from left to right).**

- A/ nitrobenzene < benzaldehyde < benzyl bromide < *o*-xylene < aniline  
 B/ aniline < *o*-xylene < benzyl bromide < benzaldehyde < nitrobenzene  
 C/ nitrobenzene < *o*-xylene < benzyl bromide < benzaldehyde < aniline  
 D/ benzyl bromide < *o*-xylene < aniline < nitrobenzene < benzaldehyde

**10. Choose the correct statements from the list below regarding the Friedel-Crafts acylation reaction of naphthalene:**

A/ no catalyst is needed

B/ a Lewis acid catalyst is required

C/ the reagent is acetic acid

D/ the reagent can also be acetic anhydride

E/ two regioisomers are formed: in carbon disulfide solvent, under the experimental conditions of kinetic control, the 1-acetyl product is the main product

F/ two regioisomers are formed: the 1-acetyl and 2-acetyl products are formed in comparable amounts

G/ multiple acylation takes place in positions 1 and 4

**11. Choose the correct order of relative reactivity of the following compounds in  $S_EAr$  transformations in descending order (i.e. proceeding from the most reactive to the least reactive).**

A: benzene

B: bromobenzene

C: phenol

D: nitrobenzene

E: toluene

1.  $A > B > C > D > E$

2.  $D > B > A > E > C$

3.  $C > E > A > B > D$

4.  $E > A > D > C > B$

**12. Choose the correct order of relative reactivity of the following compounds in  $S_EAr$  transformations: in descending order (i.e. proceeding from the most reactive to the least reactive).**

A: benzene

B: nitrobenzene

C: *p*-cresol

D: *p*-xylene

E: toluene

1.  $A > B > C > D > E$

2.  $B > A > E > D > C$

3.  $C > E > D > B > A$

4.  $C > D > E > A > B$

**13. Choose the correct order of relative reactivity of the following compounds in  $S_EAr$  transformations: in descending order (i.e. proceeding from the most reactive to the least reactive).**

A: benzene

B: bromobenzene

C: *m*-dibromobenzene

D: *m*-xylene

E: toluene

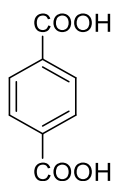
1.  $A > B > C > D > E$

2.  $C > B > A > E > D$

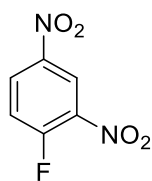
3.  $D > E > A > B > C$

4.  $D > B > E > A > C$

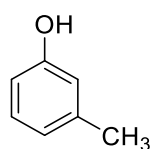
**14. In the following compounds, is the benzene ring activated or deactivated ( $S_EAr$  reaction)?**



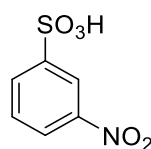
**A**



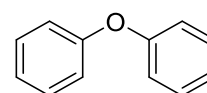
**B**



**C**



**D**



**E**

1. deactivated

2. activated

15. Which of the following groups has an activating effect in the  $S_EAr$  reaction?

A/  $-NO_2$

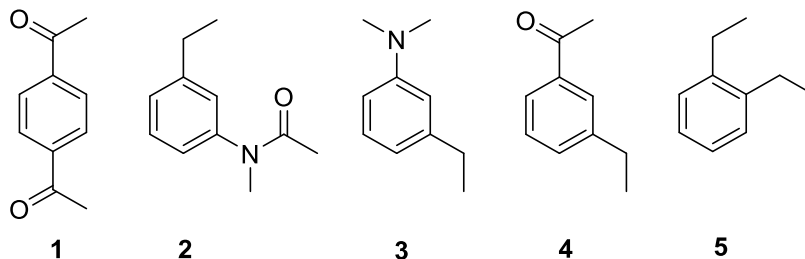
B/  $-CF_3$

C/  $-COOH$

D/  $-OCH_3$

E/  $-Br$

16. Which of the following compounds is the most reactive and the least reactive in the electrophilic substitution reaction with  $Br_2$ ,  $FeBr_3$ ?



17. For acetanilide, bromination compared to benzene:

A/ proceeds more easily

B/ is more regioselective

C/ proceeds at the same rate

D/ is more difficult to occur

18. Which of the following is NOT a *meta*-directing group?

A/  $-NHCOR$

B/  $-CONH_2$

C/  $-COOH$

D/  $-CN$

E/  $-NH_3^+$

19. Which of the following statements about  $S_EAr$  reactions is FALSE?

A/ The cyano group is a strongly deactivating, *meta* directing group.

B/ The acyl group has a medium deactivating effect, and it is a *meta* directing group.

C/ The ethoxy group is a moderately deactivating, *meta* directing group.

D/ Iodine is a moderately deactivating, *ortho/para* directing group.

E/ The hydroxyl group is a strongly activating, *ortho/para* directing group.

20. Which of the following is NOT an *ortho,para*-directing group?

A/  $-OCOR$

B/  $-NHCOR$

C/  $-Cl$

D/  $-CH_2Cl$

E/  $-SO_2NH_2$

21. Which of the following is NOT a *meta*-directing group?

A/  $-NHR$

B/  $-NO_2$

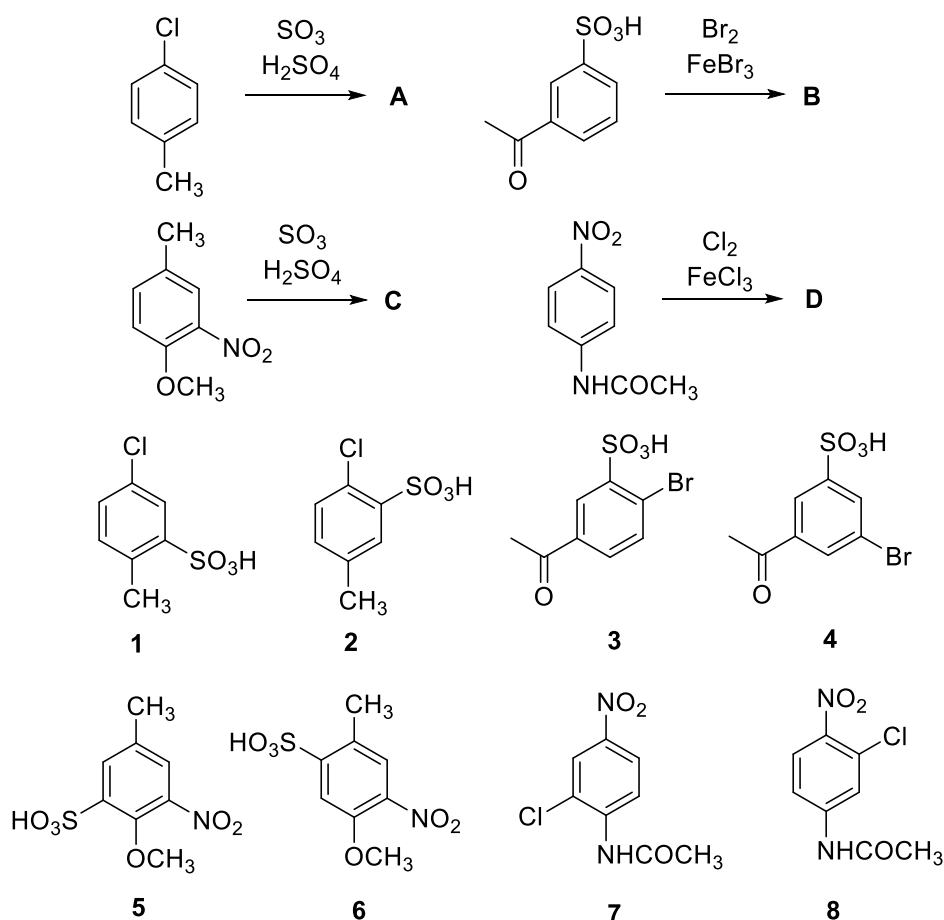
C/  $-CONH_2$

D/  $-COOH$

E/  $-CHO$



22. Choose the main product of the reactions below.



23. Which of the following statements are correct?

A/ In the case of  $S_EAr$  reaction under kinetic control, the condition for *ortho* and *para* direction is the +M or +H effect of the substituent on the ring.

B/ In the case of  $S_EAr$  reaction under kinetic control, the condition for *ortho* and *para* direction is the -I effect of the substituent on the ring.

C/ In the case of  $S_EAr$  reaction under kinetic control, the condition for *meta* direction is the -M or -H effect of the substituent on the ring.

D/ In the case of  $S_EAr$  reaction under kinetic control, the condition for *meta* direction is the +I effect of the substituent on the ring.

E/  $S_NAr$  reactions are facilitated by electron withdrawing groups on the aromatic ring.

F/ In the case of  $S_EAr$  and  $S_NAr$  reactions, the activating and deactivating effect is a function of the resultant electronic effect of all the substituents on the ring.

24. Give the relative order of reactivity of the following compounds in  $S_NAr$  reactions:

1: 1-chloro-2,4-dinitrobenzene

2: 1-chloro-2,4,6-trinitrobenzene

3: chlorobenzene

4: *p*-chloronitrobenzene

A/ B > A > D > C

B/ D > C > A > B

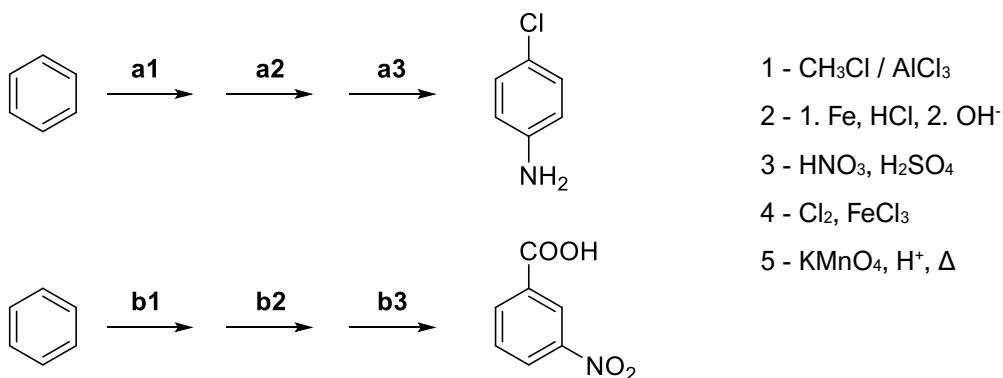
C/ A > B > C > D

D/ D > C > A > B

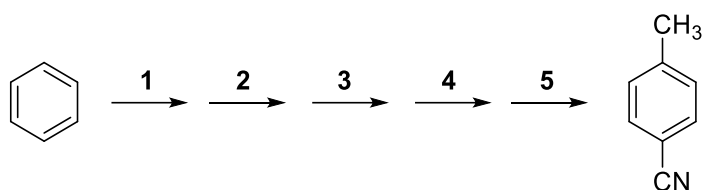




30. Give the correct order of the reaction steps (the same condition can be used several times)!



31. Give the correct order of the reaction steps!



A/ 1.  $\text{Fe}, \text{HCl}$ , 2.  $\text{OH}^-$

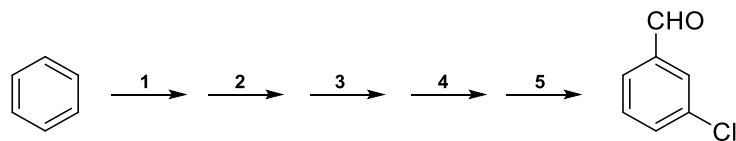
B/  $\text{HNO}_3, \text{H}_2\text{SO}_4$

C/  $\text{NaNO}_2, \text{HCl}$

D/  $\text{Cu}_2(\text{CN})_2$

E/  $\text{CH}_3\text{Cl} / \text{AlCl}_3$

32. Give the correct order of the reaction steps!



A/ PCC

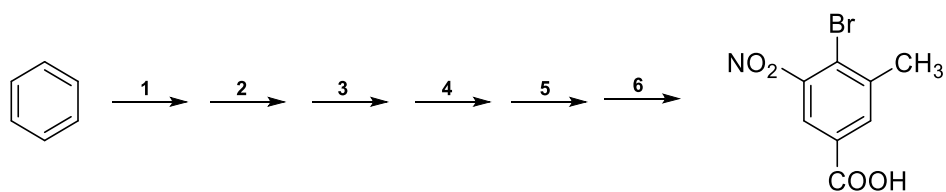
B/  $\text{CH}_3\text{Cl}, \text{AlCl}_3$

C/ NBS

D/  $\text{Cl}_2, \text{FeCl}_3$

E/  $\text{OH}^-$

33. Give the correct order of the reaction steps!



A/  $\text{H}_3\text{O}^+$

B/  $(\text{CH}_3)_2\text{CHCl}, \text{AlCl}_3$

C/  $\text{HNO}_3, \text{H}_2\text{SO}_4$

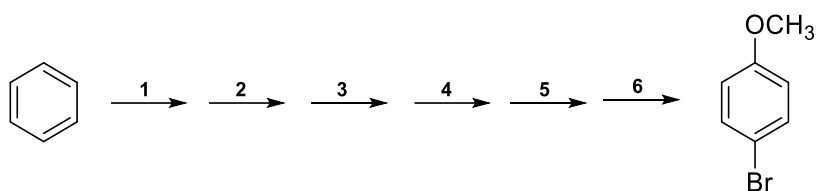
D/  $\text{KMnO}_4, \text{NaOH}, \Delta$

E/  $\text{Br}_2, \text{AlBr}_3$

F/  $\text{Cl}_2, \text{AlCl}_3$



34. Give the correct order of the reaction steps!



A -  $\text{CH}_3\text{O}^-$ ,  $\Delta$

B/  $\text{Br}_2$ ,  $\text{FeBr}_3$

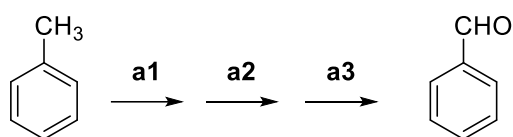
C/  $\text{Cu}_2\text{Br}_2$  /  $\text{HBr}$

D/  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$

E/ 1.  $\text{Fe}$ ,  $\text{HCl}$ ; 2.  $\text{OH}^-$

F/  $\text{NaNO}_2$ ,  $\text{HCl}$

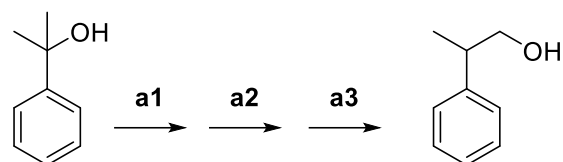
35. Give the correct order of the reaction steps!



A/  $\text{NaOH}$

B/  $\text{H}_2\text{O}_2$ ,  $\text{NaOH}$

C/  $\text{NBS}$ ,  $\Delta$

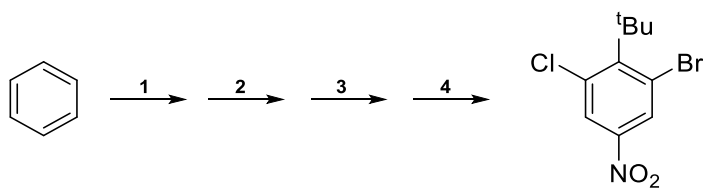


D/  $\text{BH}_3$  /  $\text{THF}$

E/  $\text{PCC}$

F/ *cc.*  $\text{H}_2\text{SO}_4$ ,  $\Delta$

36. Give the correct order of the reaction steps!



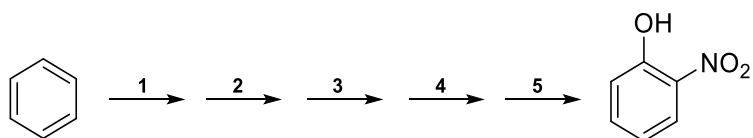
A/ 1:  $(\text{CH}_3)_3\text{CCl}$ ,  $\text{AlCl}_3$ ; 2:  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ; 3:  $\text{Br}_2$ ,  $\text{AlBr}_3$ ; 4:  $\text{Cl}_2$ ,  $\text{AlCl}_3$

B/ 1:  $\text{Br}_2$ ,  $\text{AlBr}_3$ ; 2:  $\text{Cl}_2$ ,  $\text{AlCl}_3$ ; 3:  $(\text{CH}_3)_3\text{CCl}$ ,  $\text{AlCl}_3$ ; 4:  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$

C/ 1:  $\text{Br}_2$ ,  $\text{AlBr}_3$ ; 2:  $\text{Cl}_2$ ,  $\text{AlCl}_3$ ; 3:  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ; 4:  $(\text{CH}_3)_3\text{CCl}$ ,  $\text{AlCl}_3$

D/ 1:  $(\text{CH}_3)_3\text{CCl}$ ,  $\text{AlCl}_3$ ; 2:  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ; 3:  $\text{NBS}$ ; 4:  $\text{Cl}_2$ ,  $\text{AlCl}_3$

37. Give the correct order of the reaction steps!



A/  $\text{Zn}(\text{Hg})$ ,  $\text{HCl}$

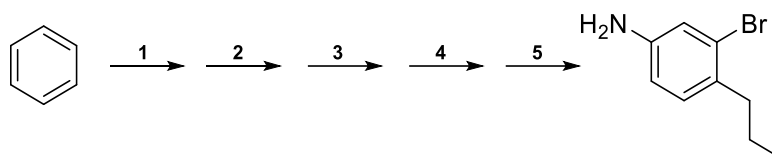
B/  $\text{CH}_3\text{CH}_2\text{COCl}$ ,  $\text{AlCl}_3$

C/  $\text{Br}_2$ ,  $\text{AlBr}_3$

D/  $\text{Zn}$ ,  $\text{HCl}$

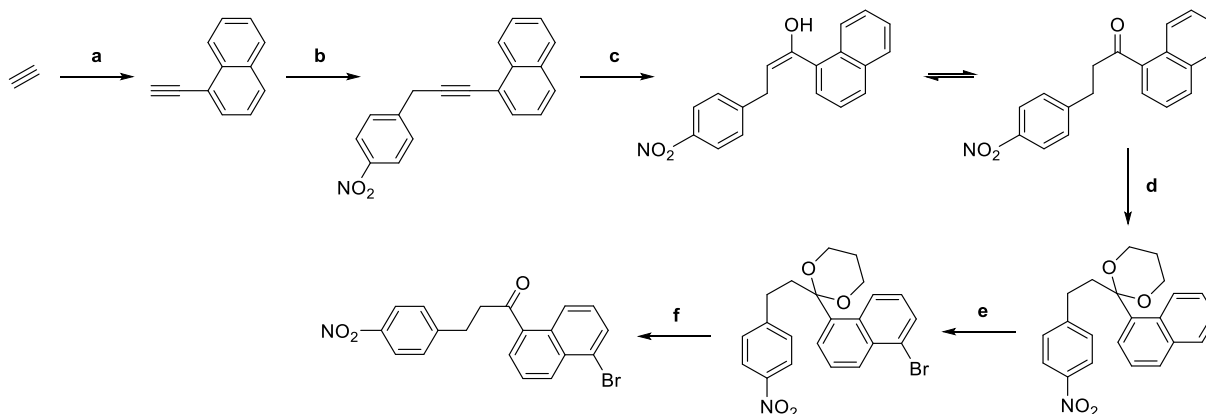
E/  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$

38. Give the correct order of the reaction steps!



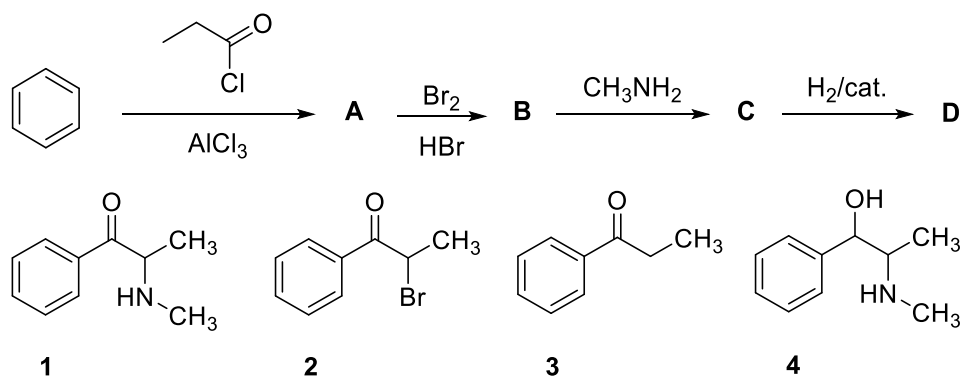
- A/ H<sub>2</sub>O                      B/ NaNO<sub>2</sub>, HCl  
 C/ HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>        D/ 1. Fe, HCl, 2. OH<sup>-</sup>

39. Give the reaction partners and reaction conditions for each step in the synthesis below!



- A/ Br<sub>2</sub>/FeBr<sub>3</sub>                      B/ HgSO<sub>4</sub> and H<sub>2</sub>O/H<sub>2</sub>SO<sub>4</sub>                      C/ propane-1,3-diol and H<sub>2</sub>O/H<sub>2</sub>SO<sub>4</sub>  
 D/ H<sub>2</sub>O/H<sub>2</sub>SO<sub>4</sub>                      E/ 1-bromonaphthalene, NaNH<sub>2</sub>/NH<sub>3</sub>                      F/ *p*-nitrobenzyl chloride and NaNH<sub>2</sub>/NH<sub>3</sub>  
 G/ NBS                                  H/ 2-bromonaphthalene, NaNH<sub>2</sub>/NH<sub>3</sub>                      I/ *p*-chloro-nitrobenzene, NaNH<sub>2</sub>/NH<sub>3</sub>  
 J/ cc. H<sub>2</sub>SO<sub>4</sub>                      K/ Sn/HCl and H<sub>2</sub>O/H<sub>2</sub>SO<sub>4</sub>                      L/ ethan-1,2-diol and H<sub>2</sub>O/H<sub>2</sub>SO<sub>4</sub>

40. Complete the synthesis pathway below with the missing structures!



## 5. Aromatic compounds

### Solutions

1. D

Conditions for the formation of an aromatic system (Hückel):

- the atomic framework forming the ring should be coplanar (or nearly coplanar)
- all atoms forming the ring should have  $p_z$ -atomic orbitals
- $4n+2$  ( $n=0$  or positive integer)  $p$ -electrons should take part in the delocalization

2. C

Conditions for the formation of an aromatic system (Hückel):

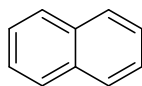
- the atomic framework forming the ring should be coplanar (or nearly coplanar)
- all atoms forming the ring should have  $p_z$ -atomic orbitals
- $4n+2$  ( $n=0$  or positive integer)  $p$ -electrons should take part in the delocalization

3. A

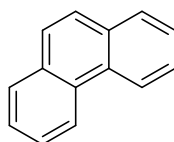
Conditions for the formation of an aromatic system (Hückel):

- the atomic framework forming the ring should be coplanar (or nearly coplanar)
- all atoms forming the ring should have  $p_z$ -atomic orbitals
- $4n+2$  ( $n=0$  or positive integer)  $p$ -electrons should take part in the delocalization

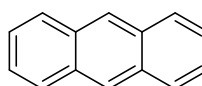
naphthalene



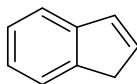
phenanthrene



anthracene



4. A, B, C



indene  
 $pK_a \sim 20$

5. C

The bromination of benzene requires a Lewis acid catalyst, which enables the formation of the reactive bromonium cation for the  $S_EAr$  reaction.

6. C



7. A

B: in the second step, an isopropyl derivative is formed in the para position (due to rearrangement)

C: the para product would be the main product

D: the tert-butyl group gives the para-substituted compound as the main product due to steric hindrance

8. A – 2, B – 8, C – 6, D - 4

The Friedel-Crafts alkylation of benzene with alkyl halogenides provides the appropriate alkyl substituted derivatives. In the reaction of benzene with 1-chloropropane, following the isomerization of the reagent, benzene reacts with in situ formed, thermodynamically more stable secondary carbocation. This results in a substitution with an isopropyl group.

9. A

Due to the net electronic effect of the amino, methyl, bromomethyl groups (the substituted benzene ring becomes more electron dense than the unsubstituted benzene due to the resulting electronic effects), the  $S_EAr$  reactions of these benzene derivatives have an increased rate. On the other hand, the nitro and formyl groups have the opposite effect. Due to the net electronic effect on the benzene ring (the substituted benzene ring becomes less electron dense than unsubstituted benzene due to the resulting electronic effects), the  $S_EAr$  reaction proceeds with a decreased rate in these cases.

10. B, D, E

The  $S_EAr$  acylation reaction of naphthalene requires a Lewis acid catalyst and a reactive carboxylic acid derivative. The formation of two regioisomers (1-acetyl and 2-acetyl products) is possible, but the reaction can be made selective by using a suitable solvent (the 1-acetyl product is the main product in carbon disulfide, whereas the 2-acetyl derivative in nitrobenzene).

11. 3

12. 4

*p*-Cresol is the most reactive due to the strong activating effect of the hydroxyl group (+M effect), and due to the activating effect of the methyl group (+H effect), followed by *p*-xylene due to the activating effect of its two methyl groups (+H effect). The activating methyl group of toluene makes the benzene ring more reactive compared to unsubstituted benzene. The reactivity of nitrobenzene is decreased due to the deactivating effect of the nitro group (-M effect).

13. 3

In the case of xylene and toluene, the methyl group has an activating effect (+H effect), while the halogens have a deactivating effect (-I>+M)

14. A – 1, B – 1, C – 2, D – 1, E - 1

Activating groups (+M effect): -OH, -CH<sub>3</sub>, -OPh.

Deactivating groups (-M): -SO<sub>3</sub>H, -NO<sub>2</sub>, -F, -COOH.



15. D

The methoxy group has an activating effect ( $-I$ + $M$  effect), as opposed to the other groups ( $-I$ ,  $-M$ , and  $-H$  effect).

16. most reactive: 3, least reactive: 1

17. A

18. A

19. C

*Not correct, because the ethoxy group is an o/p-directing group due to its +M effect.*

20. E

*The  $-SO_2NH_2$  is a meta directing, deactivating group, with  $-I$  and  $-M$  effect.*

21. A

*The  $-NHR$  has medium strong +M effect, It is an activating,, ortho/para-directing group.*

22. A – 1, B – 4, C – 5, D - 7

23. A, C, E, F

*B: not correct, because the condition is the +M or +H effect*

*D: not correct, because the condition is the  $-M$  or  $-H$  effect*

24. A

*The  $S_NAr$  reaction on a carboaromatic ring requires on the one hand a relatively good leaving group and on the other hand the presence of electron-withdrawing groups, mainly in the ortho and para positions. The more electron withdrawing groups on the ring, the more reactive the compound is towards nucleophilic reactants.*

25. A – 1, B – 2, C – 1, D – 2, E – 1, F - 2

*In the  $S_EAr$  reaction, the attacking agent is an electrophile, which reacts with the benzene ring to form a positively charged intermediate ( $\sigma$ -complex). The leaving atom (usually an  $H^+$ ) leaves behind its bonding electron pair in an electrofuge manner. Groups that increase the electron density of the aromatic ring relative to the benzene ring (electron donating groups) accelerate the  $S_EAr$  reaction.*

*In the  $S_NAr$  reaction, the attacking agent is a nucleophile, which reacts with the benzene ring to form a negatively charged intermediate ( $\sigma$ -complex). The leaving atom leaves the ring in a nucleofuge manner, together with its bonding electron pair. Groups that reduce the electron density of the benzene ring (electron-withdrawing groups) accelerate the  $S_NAr$  reaction.*

26. A – 3, B – 4, C – 2, D – 1

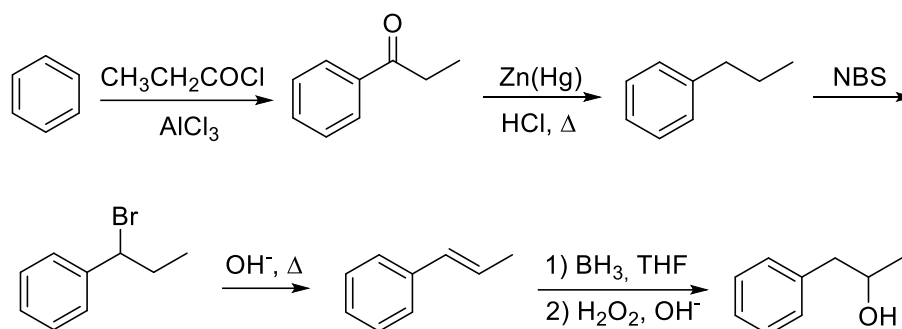


The aromatic diazonium salts are useful intermediates for the preparation of different substituted aromatic compounds. The reactions proceeding with nitrogen release in the presence of copper(I)-salts are the so-called Sandmeyer reactions.

27. B

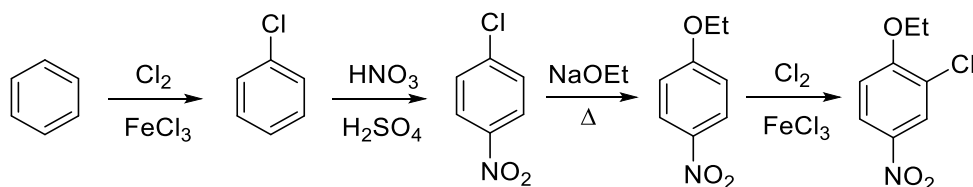
The reaction proceeds via an aryne mechanism, so that the bromine and the hydrogen in the ortho position relative to it leave the benzene ring during the reaction, resulting in a triple bond (aryne) intermediate from which ammonia cannot enter the ortho position.

28. 1 – C, 2 – B, 3 – A, 4 – D, 5 – E



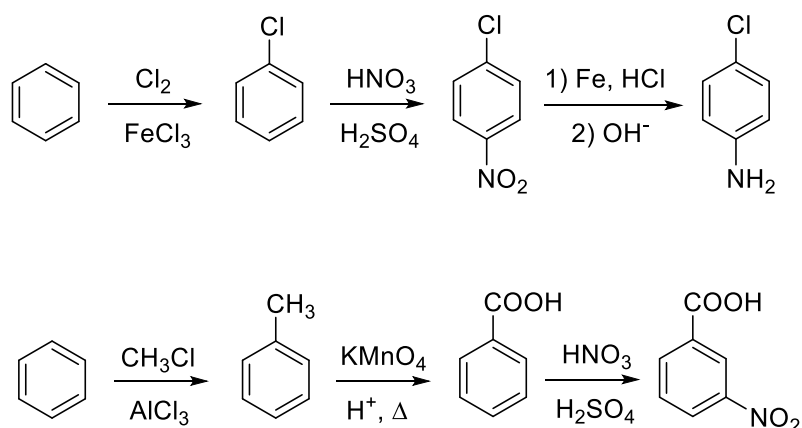
29. 1 – B, 2 – C, 3 – A, 4 – B

When choosing the sequence of reaction steps and the reaction conditions, the activating/deactivating and the controlling effect of each substituent is taken into account.  $\text{Cl}$ : *o/p*-directing, deactivating;  $\text{NO}_2$ : *m*-directing, deactivating. Aryl halides with *o/p*-nitro substituents can undergo aromatic nucleophilic substitution reactions. The  $\text{S}_{\text{E}}\text{Ar}$  reactions of polysubstituted benzene derivatives occur under the resulting controlling effect of the substituents.



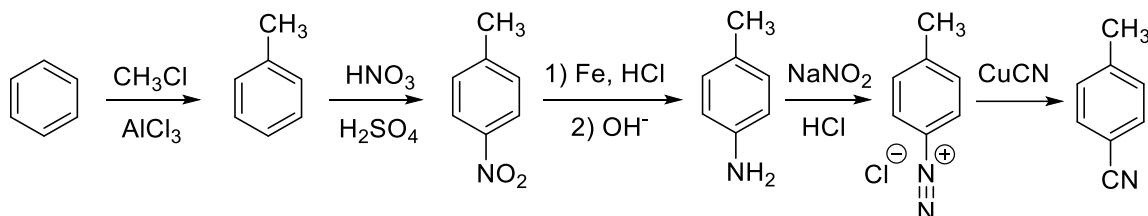
30. a1 – 4, a2 – 3, a3 – 2, b1 – 1, b2 – 5, b3 – 3

When choosing the sequence of reaction steps and the reaction conditions, the activating/deactivating and the controlling effect of each substituent is taken into account.  $\text{Cl}$ : *o/p*-directing, deactivating;  $\text{NO}_2$ : *m*-directing, deactivating;  $\text{CH}_3$ : *o/p*-directing, activating,  $\text{COOH}$ : *m*-directing, deactivating.

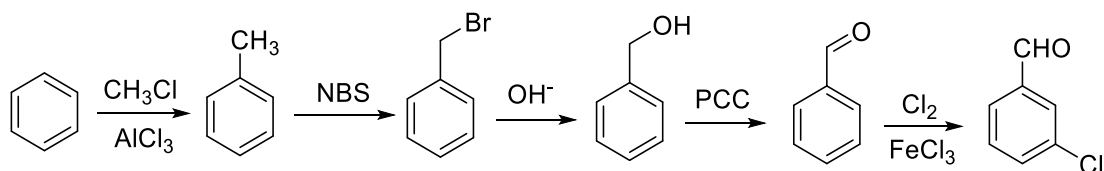


31. 1 – E, 2 – B, 3 – A, 4 – C, 5 - D

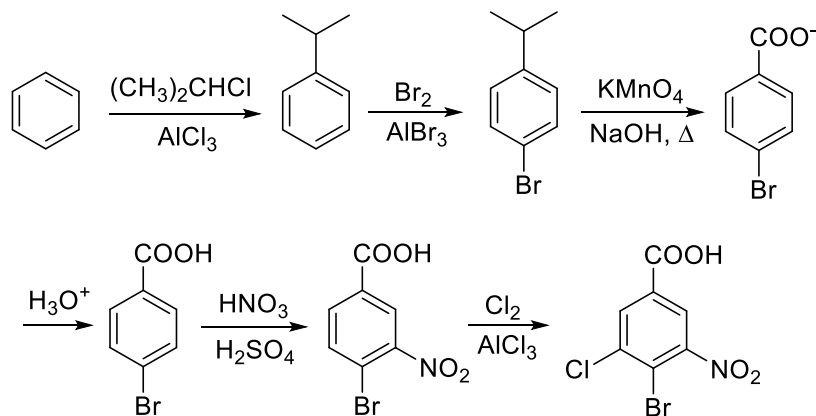
When choosing the sequence of reaction steps and the reaction conditions, the activating/deactivating and the controlling effect of each substituent is taken into account.  $\text{CH}_3$ : *o/p*-directing, activating;  $\text{NO}_2$ : *m*-directing, deactivating. The replacement of the diazonium group with nucleophiles can provide a solution for the preparation of many otherwise difficult-to-obtain compounds (see Sandmeyer reaction).



32. 1 – B, 2 – C, 3 – E, 4 – A, 5 - D

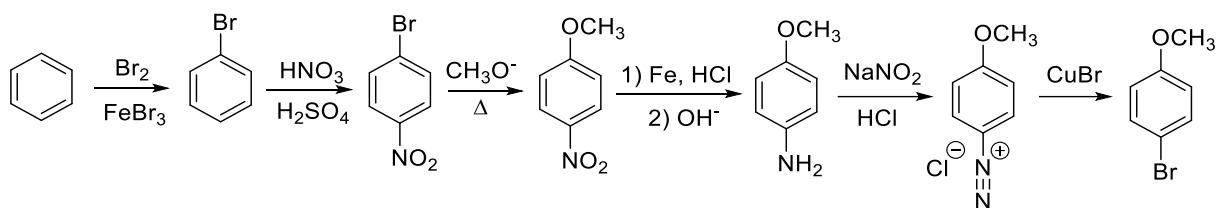


33. 1 – B, 2 – E, 3 – D, 4 – A, 5 – C, 6 - F

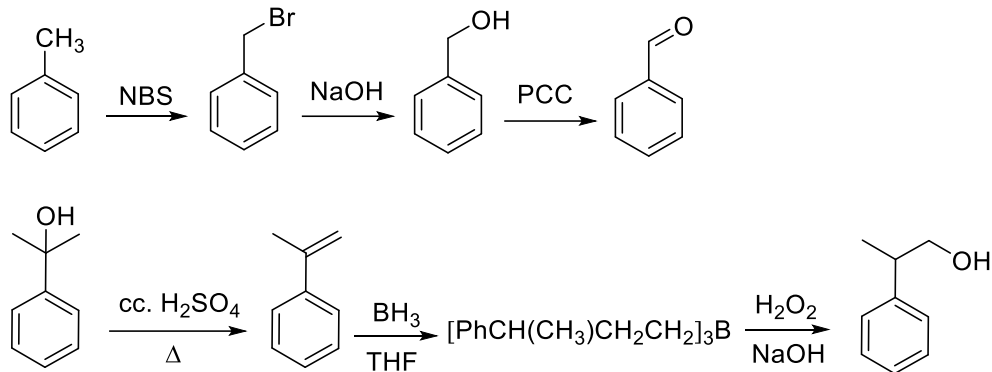


34. 1 – B, 2 – D, 3 – A, 4 – E, 5 – F, 6 - C



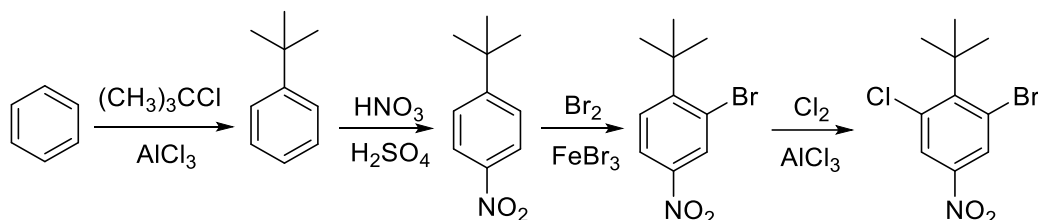


35. a1 – C, a2 – A, a3 – E, b1 – F, b2 – D, b3 – B



36. A

When choosing the sequence of reaction steps and the reaction conditions, the activating/deactivating and the controlling effect of each substituent is taken into account. Cl, Br: *o/p*-directing, deactivating; NO<sub>2</sub>: *m*-directing, deactivating; <sup>t</sup>Bu: *o/p*-directing, activating. The S<sub>E</sub>Ar reactions of polysubstituted benzene derivatives occur under the resulting controlling effect of the substituents.



37. 1 – B, 2 – A, 3 – E, 4 – C, 5 – D

38. 1 – C, 2 – D, 3 – B, 4 – A, 5 – C

39. a – E, b – F, c – B, d – C, e – A, f – D

40. A – 3, B – 2, C – 1, D – 4

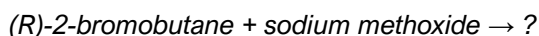


## 6. Halogenated compounds, alcohols, phenols, ethers

1. What is formed from chloroform during improper storage?

- A/ methyl chloroformiate      B/ phosgene      C/ cyanic acid  
D/ ure      E/ carbamoyl chloride

2. What is the main product of the following reaction?



- A/ but-2-ene      B/ but-1-ene  
C/ (R)-butan-2-ol      D/ (S)-2-bromobutane

3. What is the main product of the following reaction?



- A/ but-2-ene      B/ but-1-ene  
C/ (R)-butan-2-ol      D/ (S)-2-bromobutane

4. Pair which reagent can be used to prepare the following compounds as the MAJOR PRODUCT from *n*-propyl iodide in a substitution reaction!

1. *n*-propyl iodide + A  $\rightarrow$  butanenitrile      2. *n*-propyl iodide + B  $\rightarrow$  propyl isocyanide  
3. *n*-propyl iodide + C  $\rightarrow$  1-nitropropane      4. *n*-propyl iodide + D  $\rightarrow$  *n*-propyl nitrite  
A/ silver nitrite      B/ silver cyanide  
C/ potassium cyanide      D/ sodium nitrite

5. What are the appropriate conditions for preparing bromoform from heptane-2-one?

- A/ NaBr + sulfuric acid solution, room temperature  
B/ anhydrous bromine + sulfuric acid solution, heating  
C/ aqueous bromine + NaOH solution, room temperature  
D/ NBS + toluene, heating

6. Which of the following compounds give a positive iodoform reaction?

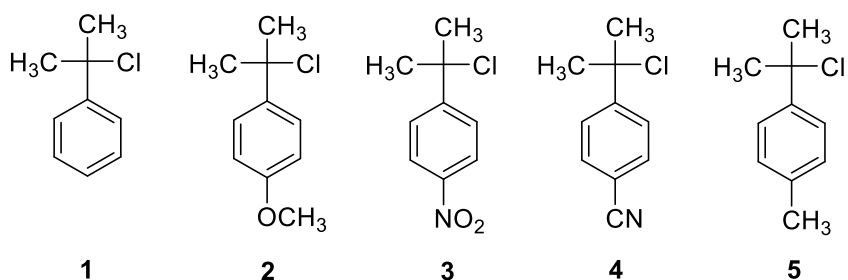
- A/ *para*-benzoquinone      B/ *sec*-butanol      C/ cyclohexanone  
D/ pentan-2,4-dione      E/ isopropyl alcohol

7. Choose the appropriate reagent for preparing 2,2-dichlorohexane from a ketone!

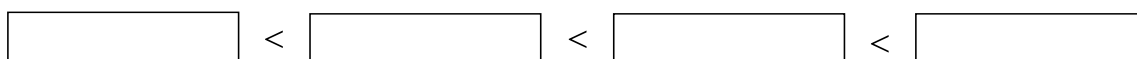
- A/ hexanal +  $\text{PCl}_3$   
B/ hexan-3-one +  $\text{PCl}_5$   
C/ hexan-2-one +  $\text{PCl}_5$   
D/ hexan-2-one +  $\text{PCl}_3$



8. In a S<sub>N</sub>1 reaction with H<sub>2</sub>O in acetone, which of the following compounds reacts the fastest?



9. Rank the following compounds in increasing order of reactivity with nucleophilic reagents.



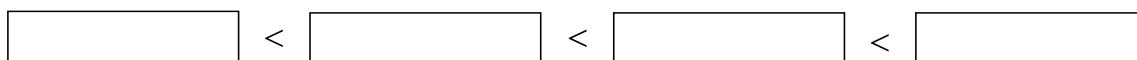
A/ benzyl bromide

B/ allyl bromide

C/ prop-1-enyl bromide

D/ cyclohexyl bromide

10. Rank the following compounds in increasing order of reactivity with nucleophilic reagents.



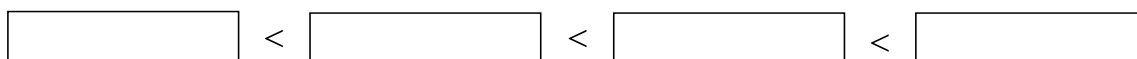
A/ benzyl chloride

B/ allyl chloride

C/ vinyl chloride

D/ ethyl chloride

11. Rank the following compounds in increasing order of reactivity with nucleophilic reagents



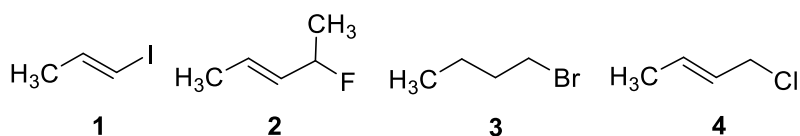
A/ benzyl bromide

B/ 1-bromo-3-phenylpropane

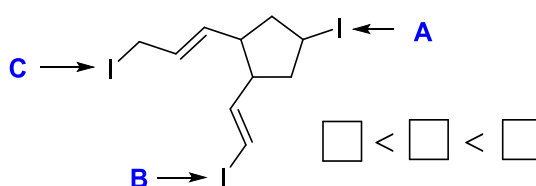
C/ propionyl bromide

D/ bromobenzene

12. Which of the following compounds is the most and the least reactive towards NaCN?



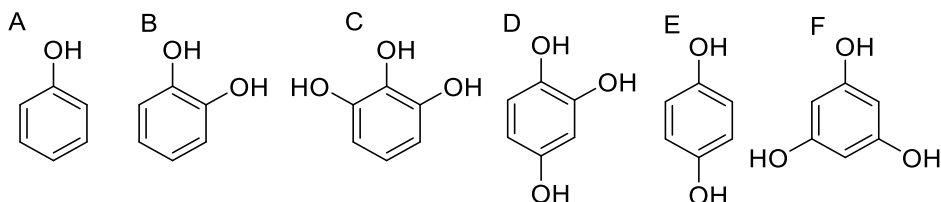
13. Give the increasing order of reactivity of the halogen atoms of the following compound towards nucleophilic reagents.



**14. Choose the correct statement!**

- A/ Resorcinol is benzene-1,4-diol.
- B/ Salicylic acid is 3-hydroxybenzoic acid.
- C/ Resorcinol is benzene-1,3-diol.
- D/ Salicylic acid is 4-hydroxybenzoic acid.

**15. Match the following compounds with the corresponding trivial names listed.**



- 1 – hydroquinone
- 2 – hydroxyhydroquinone
- 3 - phenol
- 4 – pyrogallol
- 5 – phloroglucin
- 6 - pyrocatechine

**16. Choose the correct statements for alcohols and their corresponding thiols:**

- A/ the bigger size sulfur atom is more difficult to polarise than the oxygen
- B/ the S-H bond is stronger, than the O-H bond
- C/ the bigger size sulfur atom is easier to polarise than the oxygen
- D/ thiols are stronger acids, than the corresponding alcohols

**17. For preparing *cis* cyclopentane-1,2-diol from cyclopentene, which is the appropriate reagent?**

- A/ manganese dioxide
- B/ chromium trioxide
- C/ vanadium pentoxide
- D/ osmium tetroxide

**18. Assign the appropriate starting material (1-4) to the final products listed (A-D) in the case of a Grignard reaction.**

- 1 – formaldehyde
- 2 – oxirane
- 3 - acetaldehyde
- 4 – acetone
- A/ 2-phenylethan-1-ol
- B/ *n*-butanol
- C/ butan-2-ol
- D/ 2-methylbutan-2-ol

**19. Assign the appropriate concepts to the following processes!**

- 1. oxidation
- 2. reduction
- A/ electron release
- B/ electron uptake
- C/ oxygen release
- D/ oxygen uptake
- E/ hydrogen release
- F/ hydrogen uptake



20. Which of the following reagents is an oxidizing or a reducing agent?

- A/  $\text{LiN}(\text{i-Pr})_2$                       1 – reducing agent  
B/  $\text{H}_3\text{O}^+$                               2 – oxidizing agent  
C/  $\text{Ag}_2\text{O}$                                 3 – none  
D/  $\text{LiAlH}(\text{O}^t\text{Bu})_3$

21. What is the main product of the following reactions?

- A/ ethanol + sulfuric acid, high temperature  
B/ ethanol + sulfuric acid, mild heating  
C/ elimination reaction of *sec*-butanol

1. ethene                                  2. but-2-ene                                  3. diethyl ether

22. What is the main product of the following reactions?

- A/ elimination reaction of butan-1-ol  
B/ elimination reaction of butan-2-ol  
C/ butan-2-ol + thionyl chloride

1. *sec*-butyl chloride                      2. but-1-ene                                  3. but-2-ene

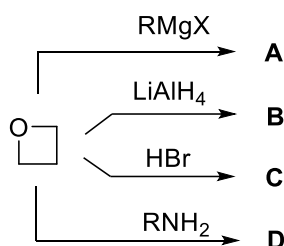
23. Choose which of the following is the appropriate reagent/solvent for preparing (*R*)-2-chlorobutane starting from (*R*)-butan-2-ol!

- A/ 10 % aqueous HCl                      B/ NaCl dissolved in DMSO  
C/ 36 % aqueous HCl                      D/  $\text{SOCl}_2$ , triethyl amine

24. For preparing 3,4,5-trimethylcyclopent-2-en-1-ol from an aliphatic starting material, which reaction pathway can be applied?

- A/ intramolecular Claisen condensation, then reduction of the product with hydride anion  
B/ intramolecular aldol condensation, then reduction of the product with hydride anion  
C/ intramolecular Wittig reaction, then reduction of the product with hydride anion  
D/ intramolecular Grignard reaction

25. Complete the following scheme with the structure of the missing products!



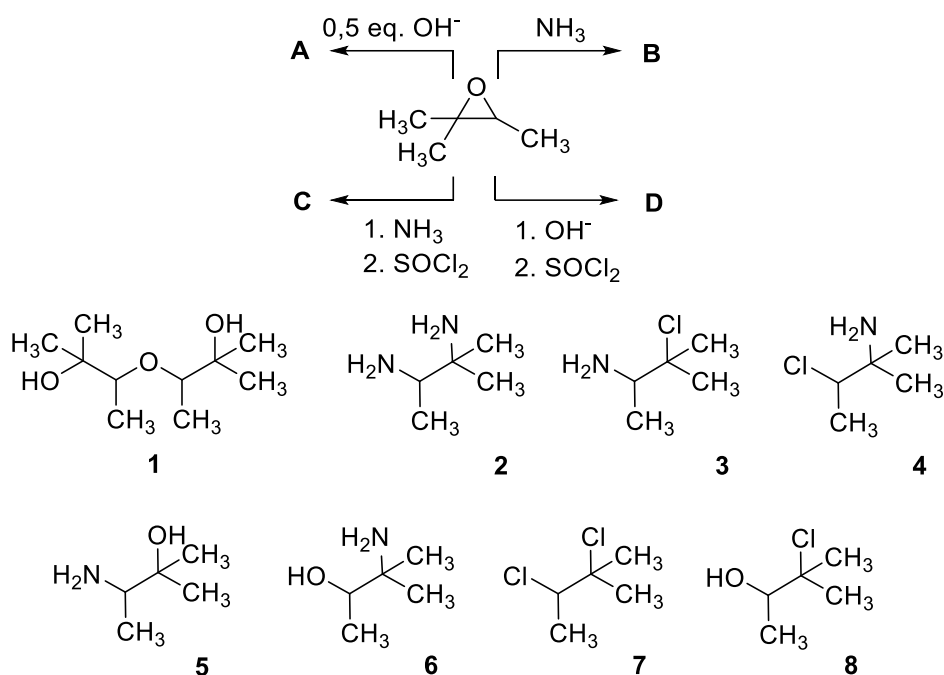
1.  $\text{R-CH}_2\text{CH}_2\text{CH}_2\text{OH}$                       2.  $\text{R-NH-CH}_2\text{CH}_2\text{CH}_2\text{OH}$                       3.  $\text{MgBr-CH}_2\text{CH}_2\text{CH}_2\text{OH}$   
4.  $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$                       5.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$                       6.  $\text{HO-CH}_2\text{CH}_2\text{CH}_2\text{OH}$   
7.  $\text{Br-CH}_2\text{CH}_2\text{CH}_2\text{-Br}$



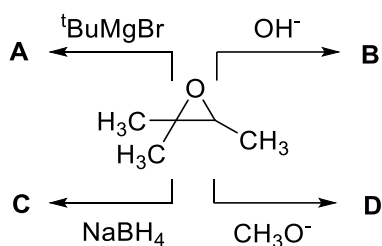
26. Under which conditions can 2-aminopropane-1-ol and 1-aminopropane-2-ol be prepared regioselectively from 2-methoxyirane by ring opening?

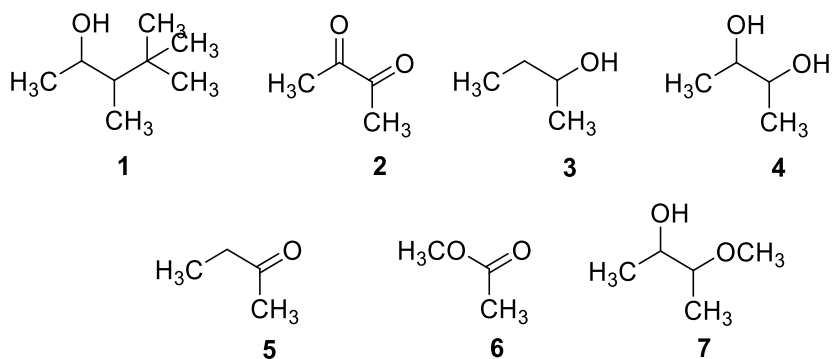
- A/ for both 2-aminopropane-1-ol and 1-aminopropane-2-ol the reaction is independent of the pH of the medium  
 B/ both 2-aminopropane-1-ol and 1-aminopropane-2-ol are obtained under neutral conditions  
 C/ 2-aminopropane-1-ol can be obtained under alkaline conditions, 1-aminopropane-2-ol under acidic conditions  
 D/ 2-aminopropane-1-ol can be obtained under acidic conditions, 1-aminopropane-2-ol under alkaline conditions

27. What is the main product of the following reactions?

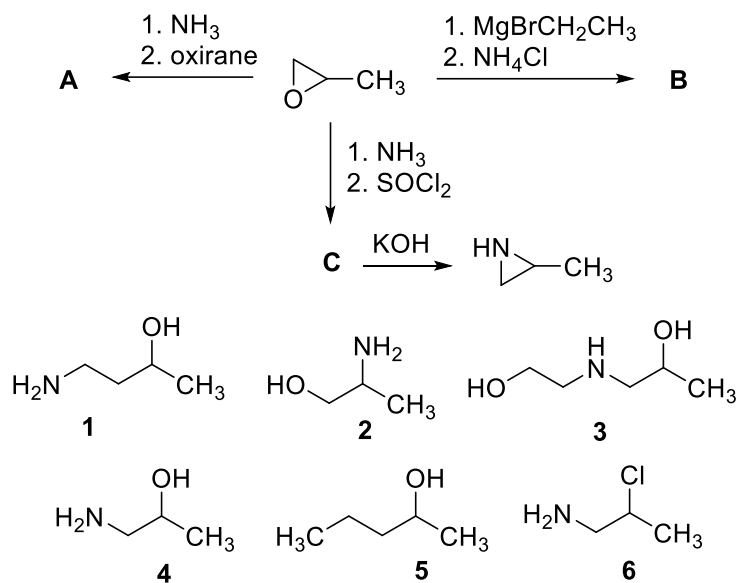


28. What is the main product of the following reactions?





29. What is the main product of the following reactions?



30. Rendelje hozzá az alábbi elemi lépésekhez az adott reakció lejátszódását segítő paramétert!

A/ nucleofuge dissociation B/ electrofuge dissociation

C/ radical association D/ radical dissociation

1 - apolar, or slightly polar group on the reaction centre

2 - electron-donating group on the reaction centre

3 - electron-withdrawing group on the reaction centre

31. Choose the correct statement!

A/ ethers can be cleaved with hydrogen iodide

B/ from cyclic ethers diols can be obtained

C/ linear ethers are not stable in the presence of bases

D/ from vinyl ethers aldehydes can be obtained



**32. Choose the correct statement!**

- A/ The  $S_N1$  reaction is always monomolecular and second order.
- B/ The  $S_N2$  reaction is bimolecular and second order.
- C/ The  $S_N2$  reaction could be monomolecular and first order.
- D/ The  $S_N1$  reaction could be bimolecular and first order.

**33. Choose the correct statement!**

- A/ The  $S_N2$  reaction is monomolecular, because the number of particles undergoing a bond change is 2.
- B/ The  $S_N1$  reaction is bimolecular, because the number of particles undergoing a bond change is 2.
- C/ The  $S_N2$  reaction is bimolecular, because the number of particles undergoing a bond change is 1.
- D/ The  $S_N1$  reaction is monomolecular, because the number of particles undergoing a bond change is 1.

**34. Assign the statements below to the reaction types!**

A/  $S_N1$  reaction

B/  $S_N2$  reaction

- 1 - occurs without the formation of intermediates
- 2 - occurs through intermediates
- 3 - it is a two-step reaction
- 4 - it is a one-step reaction
- 5 - dipolar aprotic solvents favour the reaction
- 6 - polar protic solvents favour the reaction
- 7 - a primary reaction centre (carbon atom) favours the reaction
- 8 - a tertiary reaction centre (carbon atom) favours the reaction

**35. Choose the correct statement!**

- A/ In monomolecular nucleophilic substitution an inversion and a retention is occurring.
- B/ In bimolecular nucleophilic substitution an inversion and/or a retention is occurring.
- C/ In bimolecular nucleophilic substitution a retention is occurring.
- D/ In monomolecular nucleophilic substitution an inversion and/or a retention is occurring.

**36. Assign the statements below to the reaction types!**

A/  $E_1$  reaction

B/  $E_2$  reaction

- 1 - it can be regioselective
- 2 - it cannot be regioselective
- 3 - a tertiary carbon atom, carrying the leaving group favours the process
- 4 - a tertiary carbon atom, carrying the leaving group is not favourable for the process



**37. What are the stereochemical characteristics of...**

A/ an E<sub>1</sub> reaction

B/ an E<sub>2</sub> reaction

1 – it is stereoselective                      2 – it is stereospecific

3 – overall it is not a concerted reaction

4 – it is a concerted reaction

**38. Choose the correct statement!**

A/ Regiospecificity: the starting materials are (configurational) stereoisomers.

B/ Stereospecificity: the starting materials are structural (constitutional) isomers.

C/ Regioszelektivitás: a termékek szerkezeti (konstitúciós) izomerek.

Regioselectivity: the products are structural (constitutional) isomers.

D/ Stereoselectivity: the products are (constitutional) stereoisomers.

**39. Choose the correct statement!**

A/ Bimolecular β-elimination is a complex reaction because it consists of two elementary steps.

B/ The β-elimination mechanism can be mono- or bimolecular (E<sub>1</sub> and E<sub>2</sub>).

C/ The intermediate of bimolecular β-elimination is the carbenium ion.

D/ The intermediate of monomolecular β-elimination is the carbenium anion.

**40. From which starting material can the following products be prepared by stereospecific E<sub>2</sub> elimination?**

A/ *E*-α-methylstilbene

B/ *Z*-α-methylstilbene

1 – (1*R*,2*S*)-1-bromo-1,2-diphenylpropane

2 – (1*S*,2*S*)-1-bromo-1,2-diphenylpropane

3 – (1*R*,2*R*)-1-bromo-1,2-diphenylpropane

4 – (1*S*,2*R*)-1-bromo-1,2-diphenylpropane

**41. For preparing methylenecyclohexane with E<sub>1</sub>cB reaction, which is the appropriate starting material?**

A/ *trans*-1-bromo-2-methylcyclohexane

B/ *N,N,N*-trimethyl-1-methylcyclohexan-1-ammonium hydroxide

C/ 1-bromo-1-methylcyclohexane

D/ *cis*-1-bromo-2-methylcyclohexane





**42. Choose the correct statement!**

- A/ The course of the E1 reaction is significantly influenced by the stereochemistry of the eliminating groups.
- B/ In reactions by the monomolecular E1 mechanism, usually the Zaitsev product is formed predominantly.
- C/ Of two regioisomeric alkenes, the Zaitsev product containing an olefin bond with multiple alkyl substituents is thermodynamically less stable than the less substituted Hofmann product.
- D/ Regioisomeric olefins cannot be formed in an elimination reaction.

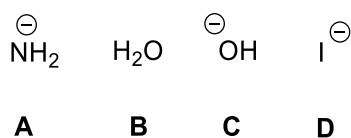
**43. Which is the main alkene product of the dehydrohalogenation (-HBr) reaction of *cis*-1-bromo-2-methylcyclohexane?**

- A/ methylenecyclohexane
- B/ 4-methylcyclohex-1-ene
- C/ 1-methylcyclohex-1-ene
- D/ 3-methylcyclohex-1-ene

**44. Choose the correct statement!**

- A/ The thermodynamically more favourable  $\beta$ -elimination is more frequent.
- B/ The preparative significance of  $\beta$ -elimination reactions is much smaller than that of  $\alpha$ -eliminations.
- C/ Elimination reactions could be either 1,2 ( $\alpha$ ) or 1,1 ( $\beta$ ) eliminations.
- D/ In  $\beta$ -elimination a carbene intermediate is formed.

**45. Arrange the following groups in ascending order according to their ability to act as a leaving group in elimination reactions.**

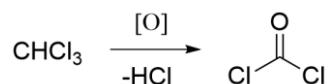


## 6. Halogenated compounds, alcohols, phenols, ethers

### Solutions

1. B

The reaction of chloroform with oxygen induced by light results in the formation of phosgene.



2. A

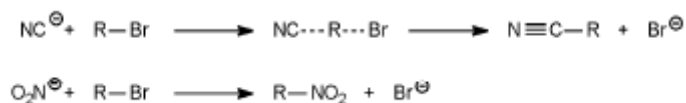
Sodium methoxide, as a smaller size base, is able to deprotonate the methylene group, resulting in the thermodynamically more stable Zaitsev product.

3. B

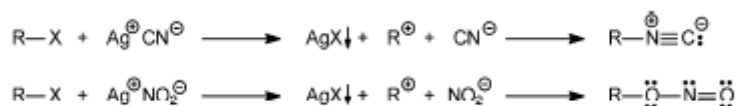
Sodium *tert*-butoxide is a bulkier base and thus, due to steric hindrance, deprotonates the methyl group more easily, resulting in the thermodynamically less stable Hofmann product.

4. 1 – C, 2 – B, 3 – D, 4 - A

Ambident nucleophilic agents (e.g. cyanide or the nitrite anion) that have more nucleophilic centers could lead to the formation of different products in alkylation reactions.



The  $S_N2$  mechanism reaction occurs with the more polarisable, lower electron density centre, the carbon atom or the nitrogen atom (potassium or sodium salts).

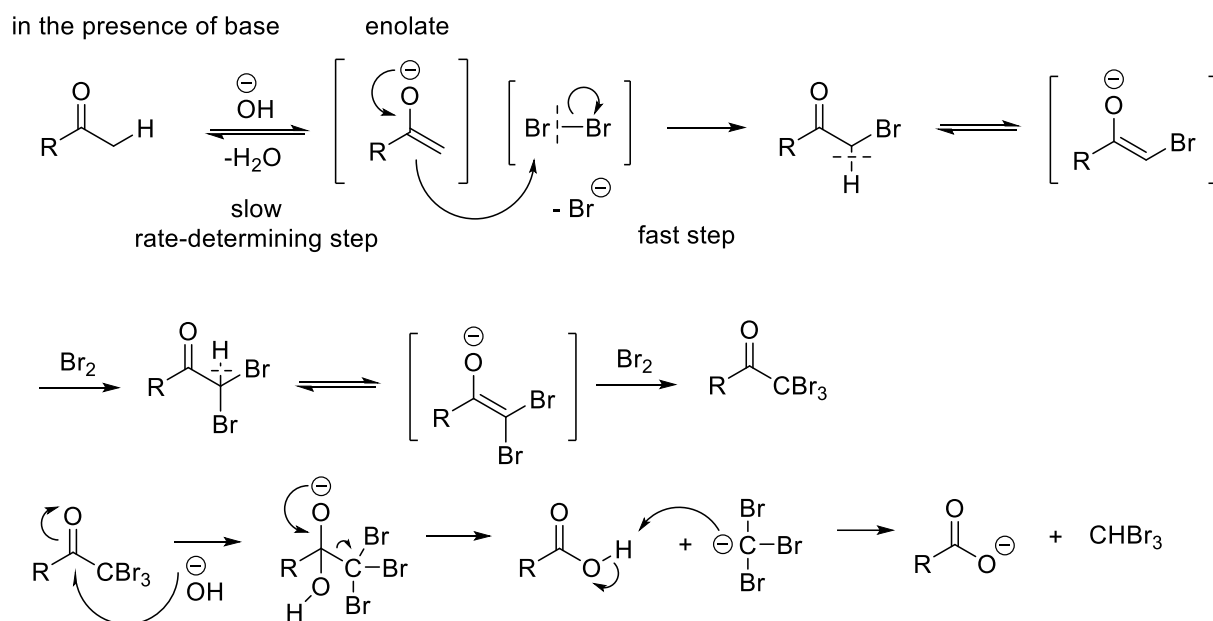


Alkylation by the  $S_N1$  mechanism, on the other hand, takes place at the nucleophilic centre with the higher electron density, the nitrogen atom or the oxygen atom (silver salts). The poorly soluble silver halide formed in the reaction promotes the formation of the carbenium ion.

5. C

Haloform reaction can be used to detect the presence of methyl ketone units. The reaction of methyl ketones in the presence of a base leads to the formation of the haloform ( $\text{CH}_3\text{X}$ ) in successive steps. On heating, the haloform formed is hydrolysed to formic acid in a nucleophilic substitution reaction. From this, under the action of base, bromoform and carboxylic acid salt are formed by nucleophilic substitution on the carbonyl group





6. B, D, E

The iodoform reaction requires that the starting compound is either a methyl ketone or an alcohol in which the alcoholic hydroxyl group is in position 2, because elementary iodine oxidizes this structural unit to methyl ketone in the first step, from which the iodoform can be cleaved subsequently.

7. C

8. 3

9.  $C < D < B < A$

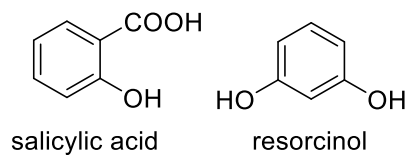
10.  $C < D < B < A$

11.  $D < B < A < C$

12. the most reactive: 4; the least reactive: 1

13.  $B < A < C$

14. C

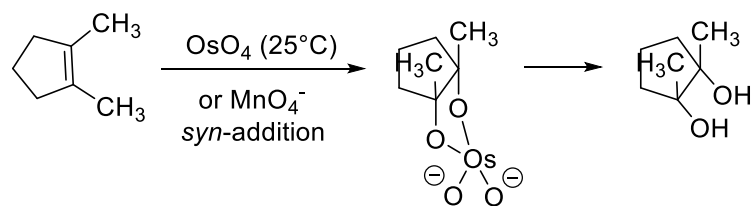


15. 1 - E, 2 - D, 3 - A, 4 - C, 5 - F, 6 - B

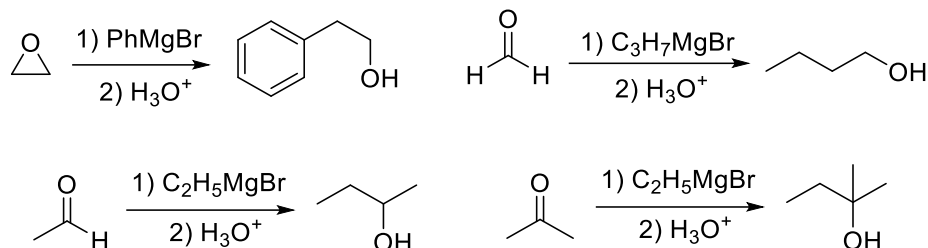
16. C, D

17. D





18. 1 – B, 2 – A, 3 – C, 4 – D



19. 1 – A, D, E; 2 – B, C, F

20. A – 3, B – 3, C – 2, D – 1

21. A – 1, B – 3, C – 2

Higher temperatures favour elimination reactions. The elimination reaction of *sec*-butanol with a smaller size base results in the thermodynamically more stable *but*-2-ene. With a bulkier base, *but*-1-ene is formed as the main product (due to steric hindrance). Alkenes with pillar atoms more highly substituted with alkyl groups are thermodynamically more stable due to C-H  $\sigma$  - C-C  $\pi$  conjugations.

22. A – 2, B – 3, C – 1

The elimination reaction of *sec*-butanol (*butan*-2-ol) with a smaller size base results in the thermodynamically more stable *but*-2-ene. With a bulkier base, *but*-1-ene is formed as the main product (due to steric hindrance). Alkenes with pillar atoms more highly substituted with alkyl groups are thermodynamically more stable due to C-H  $\sigma$  - C-C  $\pi$  conjugations.

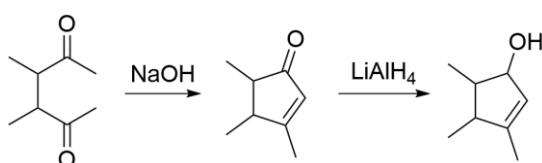
With thionyl chloride ( $\text{SOCl}_2$ ) a substitution reaction takes place due to the slight basicity of the chloride ion.

From *butan*-1-ol only *but*-1-ene can be formed by  $\beta$ -elimination, since there is only one hydrogen atom at the  $\beta$  position relative to the hydroxyl group in the molecule.

23. D

The reaction of alcohols with thionyl chloride involves configuration retention due to the  $\text{S}_{\text{Ni}}$  mechanism. In contrast to the  $\text{S}_{\text{N}}1$  mechanism, in the  $\text{S}_{\text{Ni}}$  reaction the carbocation is not completely dissociated, which would lead to racemization.

24. B



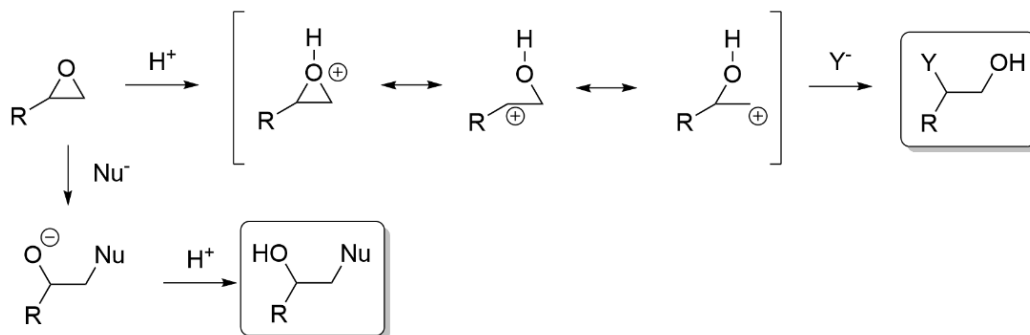
25. A – 1, B – 5, C – 7, D – 2



As a result of ring tension, the oxetane ring opens up relatively easily (due to the positive polarity created by the electron-withdrawing effect of the oxygen atom) by nucleophilic attack on the carbon atom directly attached to the oxygen,

26. D

The explanation of the regioselectivity is the different, pH-dependent mechanism of the two reactions. In acidic medium an  $S_N1$ -like mechanism (the higher order alkyl cation is more stable), whereas in basic medium an  $S_N2$  mechanism (due to steric reasons the nucleophile attacks at the lower order carbon atom) prevails

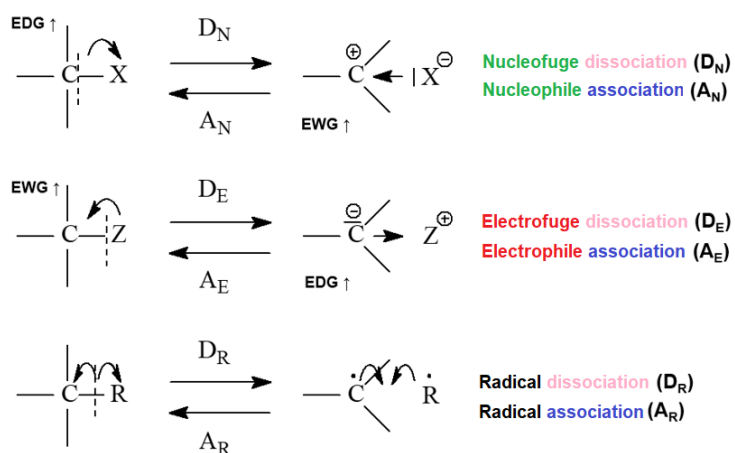


27. A - 1, B - 5, C - 3, D - 7

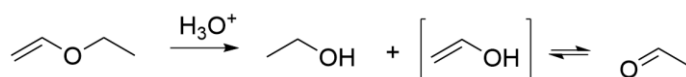
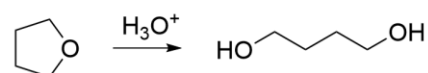
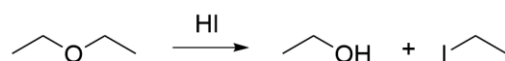
28. A - 1, B - 4, C - 3, D - 7

29. A - 3, B - 5, C - 6

30. A - 2, B - 3, C - 1, D - 1



31. A, B, D



32. B

33. D

34. A – 2, 3, 6, 8; B – 1, 4, 5, 7

35. A

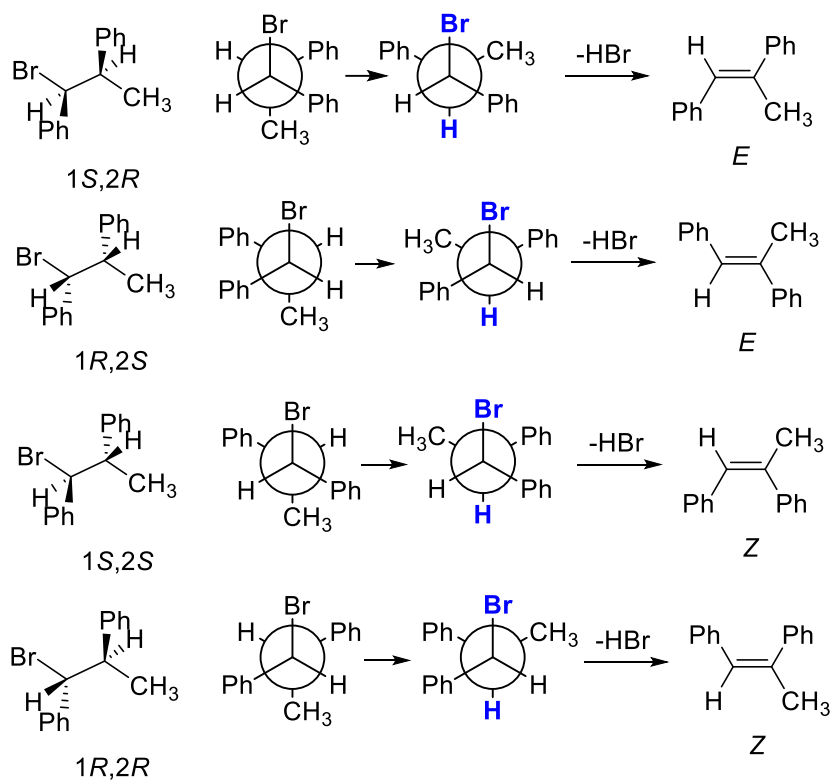
36. A – 1, 3; B – 2, 4

37. A – 1, 3; B – 2, 4

38. C

39. B

40. A – 1, 4; B – 2, 3



41. B

42. B

43. C

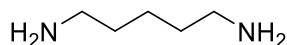
44. A

45. A < C < B < D



## 7. Nitrogen, sulfur and phosphorous compounds

1. Assign the name to the compound below (there could be several correct solutions).



- A/ pentane-1,5-diamine      B/ pentane-1,5-diyl-diamine  
C/ 1,5-diaminopentane      D/ cadaverine

2. Give the classification of the amines below!

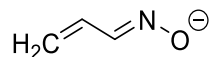
- A/ *N,N'*-dimethyl-ethylene-diamine      B/ methyl amine  
C/ propane-1,3-diamine      D/ diisopropyl amine  
E/ triethyl amine      F/ *N,N,N',N'*-tetramethyl-ethylene diamine

1. primary, with one amine function      2. secondary, with one amine function  
3. tertiary with one amine function      4. primary, with two amine functions  
5. secondary, with two amine functions      6. tertiary, with two amine functions

3. Select the catecholamines from the following compounds!

- A/ adrenaline      B/ tyrosine  
C/ dopamine      D/ 1-phenylethyl amine

4. How many electrons are involved in the following delocalised system?



- A/ 12      B/ 10      C/ 6      D/ 4

5. Arrange the following compounds in order of increasing boiling point at atmospheric pressure.

- A/ n-butane      B/ ammonia      C/ methane  
D/ water      E/ diethyl ether

6. Select the suitable starting compound(s) for the selective synthesis of the following products (so that no other alkylation degree compound is formed).

- A/ isopropyl amine      1. 1) acetone + methyl amine; 2) reduction  
B/ methyl-isopropyl amine      2. benzyl amine + formaldehyde + formic acid  
C/ *N,N*-dimethyl-benzyl amine      3. acetone + ammonia, then reduction



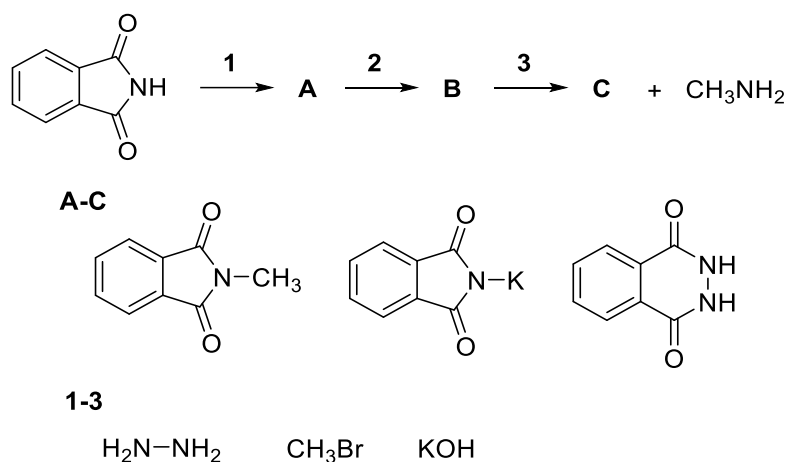
7. Which compound type(s) listed below can be used to prepare an aliphatic secondary amine in one step?

- A/ aliphatic carboxylic acid nitrile
- B/ *N*-alkyl aliphatic carboxylic acid nitrile
- C/ by the reaction of aliphatic aldehyde and aliphatic primary amine in a reducing medium
- D/ alkyl azide
- E/ *N,N*-dialkyl aliphatic carboxylic acid amide

8. Which of the following statements are true?

- A/ nitronic acid is the aci-form of aliphatic primary and secondary nitro compounds
- B/ nitrobenzene is a solid at room temperature
- C/ the anion formed by deprotonation of nitromethane is isoconjugated with the allyl anion
- D/ nitro compounds containing a hydrogen atom on their  $\alpha$ -carbon atom form nitroolefins with oxo compounds in several steps

9. Complete the following scheme with the missing reagents (1-3) and products (A-C).



10. Give the correct order of reaction steps!



11. Which type of transformation is the reaction of ketones and primary amines?

- A/ electrophilic substitution
- B/ electrophilic addition
- C/ nucleophilic substitution
- D/ condensation
- E/ radical elimination



**12. Which of the following statements are correct?**

- A/ a Schiff base and an enamine can be in a structural isomeric relationship
- B/ aliphatic and aromatic diazonium salts have approximately the same stability
- C/ secondary amines form nitrosamines with nitric acid
- D/ ephedrine is a catecholamine

**13. Assign the suitable reagent to the product for the S<sub>N</sub>Ar reaction of 2-naphthylthiazonium chloride.**

2-naphthylthiazonium chloride + **1** → 2-nitronaphthalene

2-naphthylthiazonium chloride + **2** → 2-naphthyl isocyanate

2-naphthylthiazonium chloride + **3** → naphthalene-2-thiol

2-naphthylthiazonium chloride + **4** → 2-naphthylthiazonium hydroxide

- A/ KNCO + Cu
- B/ KHS, then acid
- C/ NaNO<sub>2</sub> + CuO
- D/ NaOH

**14. Which of the following statements are correct?**

- A/ Phenols react in azocoupling reactions in weakly acidic media.
- B/ The azocoupling reaction is facilitated by electron donating groups on the aromatic amine or phenol.
- C/ Aromatic amines react in azocoupling reactions in weakly alkaline media.
- D/ Electron-withdrawing groups on the aromatic diazonium compound promote the azocoupling reaction.

**15. Which set of starting compounds is NOT suitable for the Mannich reaction?**

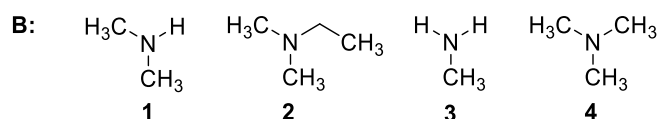
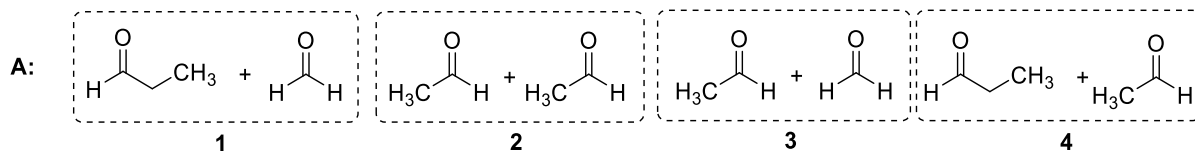
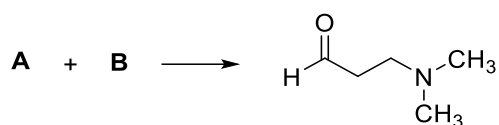
- A/ acetaldehyde, formaldehyde and dimethylamine
- B/ acetaldehyde, formaldehyde and triethylamine
- C/ acetaldehyde, formaldehyde and butylamine
- D/ benzophenone, formaldehyde, triethylamine
- E/ benzophenone, acetaldehyde, *N,N*-dimethyl-ethylamine

**16. What is the product of the reaction of acetaldehyde, formaldehyde and dimethylamine?**

- A/ 2-(dimethylamino)-propanal
- B/ 3-(dimethylamino)-propanal
- C/ 2-(dimethylamino)-butanal
- D/ 1-(dimethylamino)-butanal
- E/ the above set of starting compounds is not suitable for Mannich reaction



17. How would you prepare the following Mannich base??



18. Rank the following amines in ascending order of nucleophilicity, studied in  $S_NAc$  reactions.

A/ 3-ethylaniline

B/ 2-nitroaniline

C/ aniline

D/ pentyl amine

19. Match the following compounds with their corresponding chemical reactions!

A/ *N,N*-dimethylbenzenesulfonamide

B/ *N*-methylbenzenesulfonamide

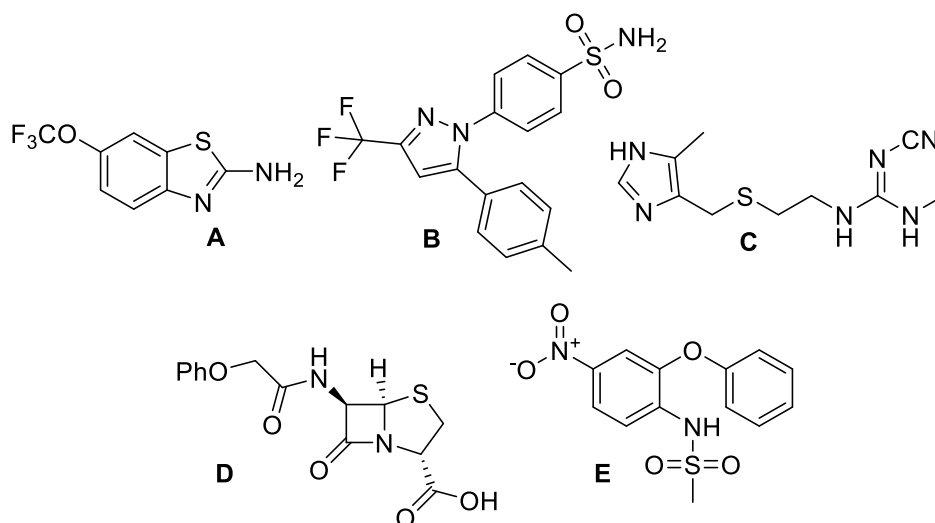
C/ *N,N,N*-trimethylbenzenesulfonamide

1 - forms a precipitate in alkaline medium which does not dissolve on acidification

2 - its pure solution in alkaline medium gives a precipitate on acidification

3 - gives a precipitate in alkaline medium which, when hydrolysed in alkaline solution, gives a clear solution

20. Which molecule contains a benzenesulfonic acid amide unit?



21. Rank the following compounds in order of increasing oxidation state relative to the sulphur atom:

<  <  <

A/ sulfoxide

B/ dialkyl sulfide

C/ sulfone

D/ alkanesulfonic acid

22. Rank the following compounds in order of increasing oxidation state relative to the phosphorous atom:

<  <  <

A – trialkyl phosphite

B – trialkyl phosphate

C – trialkyl phosphonate

D – trialkyl phosphine-oxide

23. Which statements are correct for phase transfer catalysis (PTC)?

A/ the ions in the reaction mixture are completely solvated in both phases

B/ the catalyst could be a quaternary phosphonium salt

C/ the reaction takes place on the surface of the organic and aqueous phases

D/ the catalyst could be a quaternary ammonium salt

24. Choose the correct statement!

A/ Since sulfonic acid is a weak acid, its conjugate base is a strong base. The sulfonate group is therefore a good leaving group.

B/ Sulfonyl chlorides can be used to activate OH groups. The resulting sulfonate ester may react with nucleophiles under mild conditions.

C/ The *para*-toluenesulfonate group is about two orders of magnitude weaker leaving group than the chloride ion.

D/ Alcohols can be converted to alkyl halides by thionyl chloride. The conversion is most rapid for tertiary alcohols, but may require harsher conditions for primary or secondary alcohols.

25. Rank the following compounds in ascending order of acidity, tested in aqueous solution.

A/ HCl

B/ phenol

C/ benzenesulfonic acid

D/ 4-chlorobenzoic acid



## 7. Nitrogen, sulfur and phosphorous compounds

### Solutions

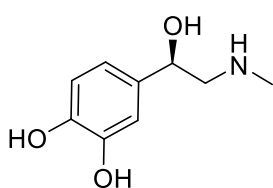
1. A, B, D

2. A – 5, B – 1, C – 6, D – 2, E – 4, F – 3

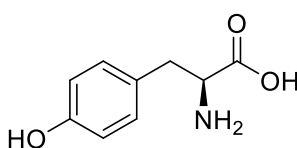
Order of amines: the number of bonds of the amine nitrogen with carbon atoms

3. A, C

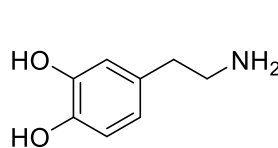
*Catecholamines: monoamine neurotransmitters derived from tyrosine. In their structure there is an amine side chain on the pyrocatechine ring.*



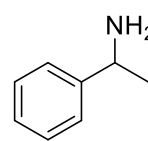
adrenaline



tyrosine



dopamine



1-phenylethyl amine

4. C

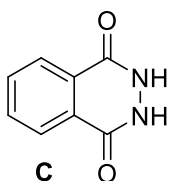
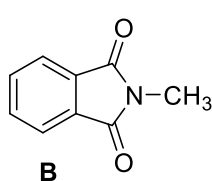
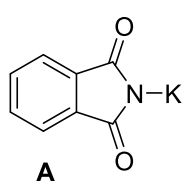
5. C < B < A < E < D

6. A – 3, B – 1, C – 2

7. B, C

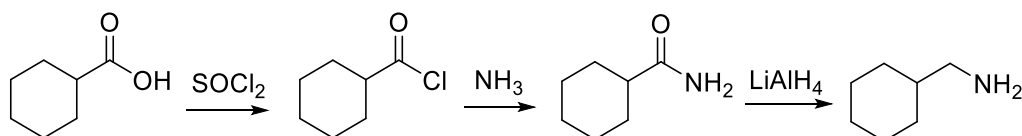
8. A, D

9. 1 – KOH, 2 – CH<sub>3</sub>Br, 3 – H<sub>2</sub>N-NH<sub>2</sub>



*Gabriel synthesis can be used to prepare primary amines starting from potassium salts of phthalimide and alkyl halides. The resulting N-alkylphthalimide can be converted to the primary amine end product by hydrazine.*

10. 1 – SOCl<sub>2</sub>, 2 – NH<sub>3</sub>, 3 – LiAlH<sub>4</sub>



11. D



First step: nucleophilic addition, second step: elimination of a water molecule.

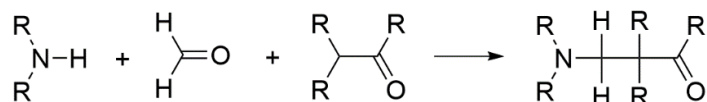
12. A, C

13. 1 – C, 2 – A, 3 – B, 4 - D

14. B, D

15. B, D, E

Tertiary amines do not enter into Mannich reaction.



16. B

17. A – 3, B – 1

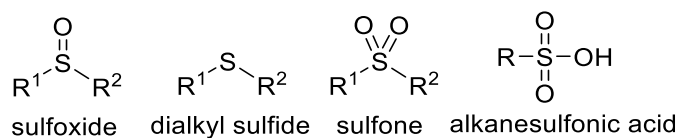
18. B < C < A < D

19. A – 1, B – 2, C - 3

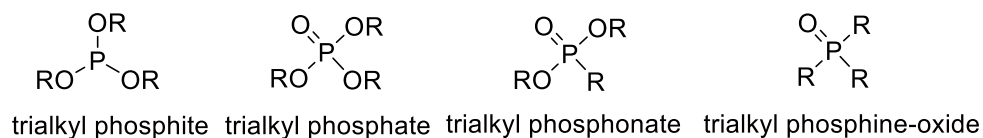
The so-called Hinsberg reaction can be used to determine the order of amines. The sulfonamide formed from primary amines by benzenesulfonic acid chloride dissolves in the alkaline reaction mixture, the secondary sulfonamide precipitates out as an oil or a solid, while tertiary amines do not form sulfonamide.

20. B

21. B < A < C < D



22. D < A < C < B



23. B, C, D

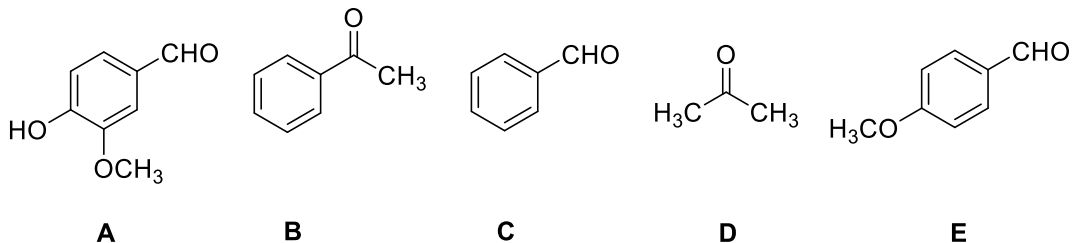
24. B

25. B < D < C < A



## 8. Oxo compounds

1. Pair the structures with their names!



1 – benzaldehyde

2 – acetophenone

3 – acetone

4 – vanilline

5 – anisaldehyde

2. What compound is formed by oxidation of aldehydes with Tollens reagent (alkaline solution of silver-ammonia complex)?

A/ alcohol

B/ carboxylic acid

C/ carboxylic acid amide

D/ ketone

E/ peroxyacid

3. From which of the compounds below can cyclohexane be prepared with reduction?

A/ cyclohexanone

B/ cyclopentanone

C/ hexanal

D/ cyclohexan-1,4-dione

4. With which reagents can cyclohexanol be prepared from cyclohexanone?

A/  $\text{H}_2\text{SO}_4$

B/  $\text{LiAlH}_4$

C/  $\text{KMnO}_4$

D/  $\text{NaBH}_4$

E/  $\text{H}_2\text{O}_2$

5. What compound is formed in the reaction of oxo compounds and hydroxylamine?

A/ hydrazone

B/ acetal

C/ semicarbazone

D/ oxime

E/ imine

6. What compound is formed in the reaction of oxo compounds and ammonia?

A/ hydrazone

B/ semicarbazone

C/ acetal

D/ oxime

E/ imine

7. What compound is formed in the reaction of oxo compounds and semicarbazide?

A/ imine

B/ oxime

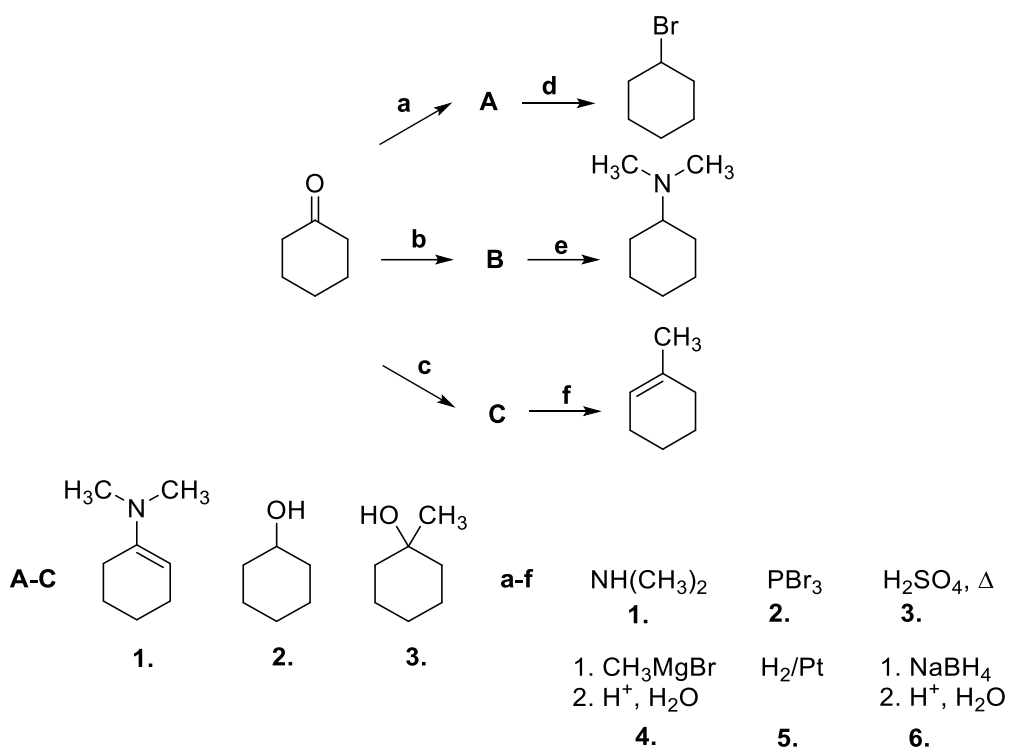
C/ acetal

D/ semicarbazone

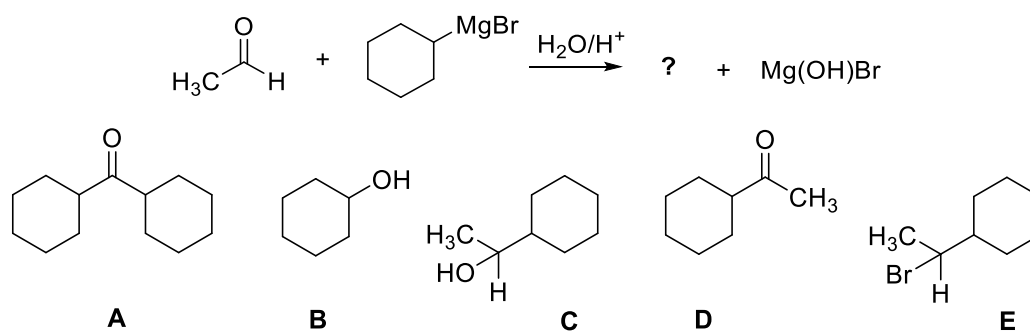
E/ hydrazone



8. Complete the scheme with the missing reagents (a-f) and intermediates (A-C)!



9. What is the main product of the following reaction?



10. What kind of reaction is the Grignard reaction of oxo compounds?

- A/ oxidative cationic acylation
- B/ oxidative anionic alkylation
- C/ reductive anionic acylation
- D/ reductive cationic alkylation
- E/ reductive anionic alkylation

11. Formaldehyde reacts with ethylmagnesium bromide. After acidification what is the product?

- A/ acetic acid
- B/ isopropyl alcohol
- C/ acetaldehyde
- D/ ethanol
- E/ propanol



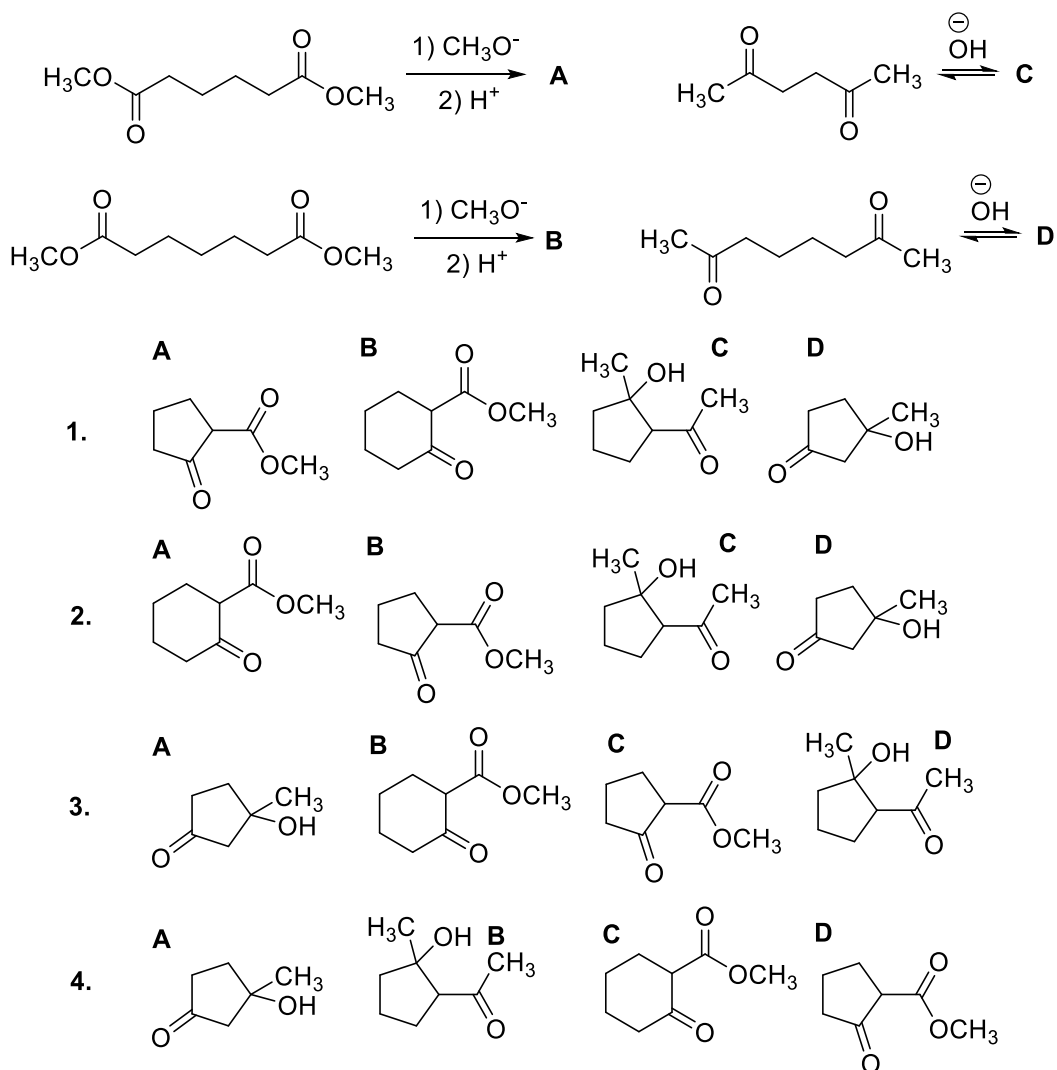
**12. What product is formed from ketones in Grignard reaction?**

- A/ tertiary alcohol
- B/ secondary alcohol
- C/ carboxylic acid
- D/ aldehyde
- E/ primary alcohol

**13. Starting from ethyl magnesium bromide, what will be the end product (1-3) of the reactions with the following substrates (A-C)?**

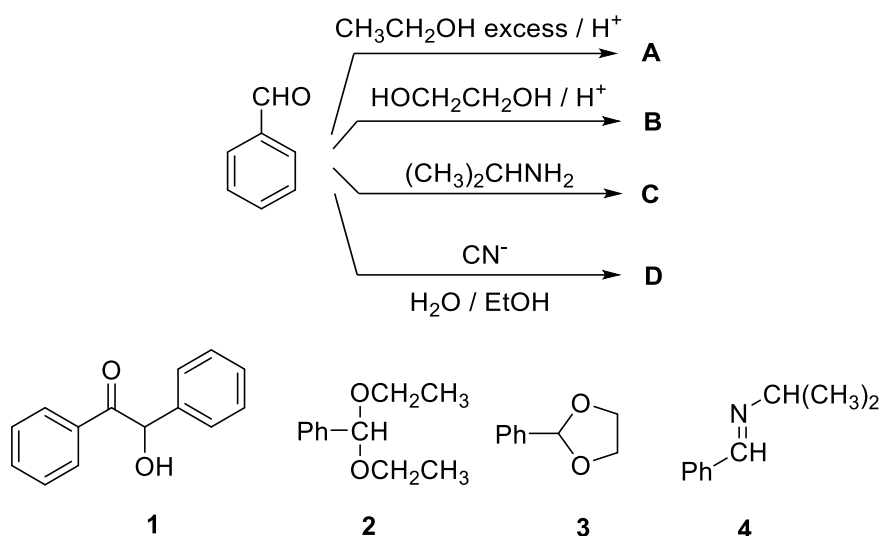
- |                          |                    |
|--------------------------|--------------------|
| A/ triethyl orthoformate | 1. propionic acid  |
| B/ dry carbon-dioxide    | 2. propionaldehyde |
| C/ ethyl-formate         | 3. pentan-3-ol     |

**14. Give the missing products!**

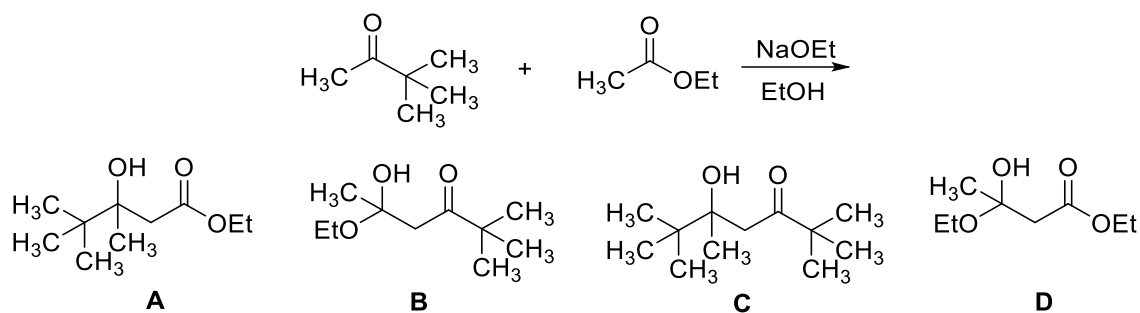




15. What is the product of the following reactions?



16. What will be the main product of the first step of the following reaction?



17. How Schiff bases can be prepared?

- A/ primary/secondary amine + formaldehyde + aldehyde/ketone
- B/ oxo compound + primary amine
- C/ oxo compound + HCN
- D/ two different oxo compounds with  $\alpha$ -CH atoms
- E/ oxo compound +  $\text{Br}_2$  in alkaline medium

18. Which statement about the Mannich reaction is false?

- A/ it requires formaldehyde
- B/ the ketone must react in the enol form
- C/ an iminium ion must be formed from formaldehyde and the primary or secondary amine
- D/ it is an aminoacylation reaction
- E/ it is a three-component reaction

**19. At which positions  $\alpha,\beta$ -unsaturated carbonyl compounds can be attacked by nucleophilic reagents in addition reactions?**

- A/ it reacts only on the  $\beta$  carbon atom
- B/ 1,3-addition (rarely)
- C/ 1,4-addition
- D/ they do not enter into addition reactions
- E/ 1,2-addition

**20. Which statement about the nucleophilic addition reactions of  $\alpha,\beta$ -unsaturated carbonyl compounds is false?**

- A/ with a stronger base a 1,2-addition is more probable
- B/ with a weaker base a 1,4-addition is more probable
- C/ with a sterically hindered carbonyl group a 1,4-addition is more probable
- D/ with primary amines a 1,2-addition is more probable
- E/  $\text{LiAlH}_4$  favours the 1,2-addition

**21. The aldol addition of two different carbonyl compounds can give how many different products (if the aldol reaction does not proceed further)?**

- A/ 2
- B/ 6
- C/ 8
- D/ 4

**22. Under what conditions can an aldol cross-condensation be sufficiently selective?**

- A/ asymmetric ketones are used as starting materials
- B/ one of the carbonyl compounds has no  $\alpha$ -hydrogen
- C/ aliphatic aldehydes are used as starting materials
- D/ in the case of an acid-catalysed reaction
- E/ using a mono-enolizable ketone as nucleophilic partner

**23. Which statements about the aldol condensation are correct?**

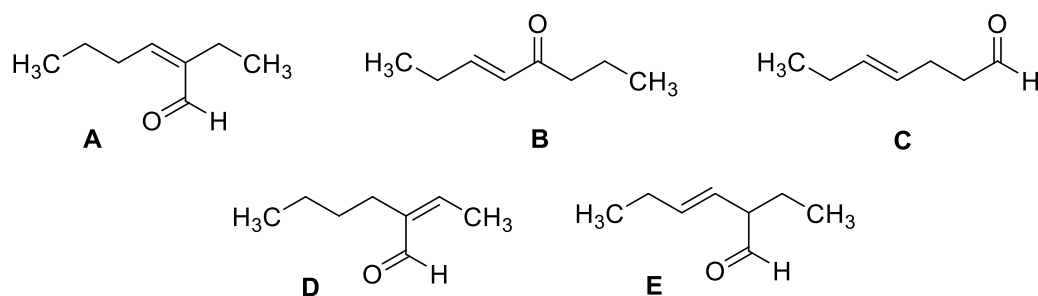
- A/ the reaction between two different oxo compounds is called a crossed aldol dimerization
- B/ the starting oxo compound should have a hydrogen on the  $\alpha$ -carbon
- C/ if the aldol product is dehydrated, an  $\alpha,\beta$ -unsaturated oxo compound is formed
- D/ the product is a  $\beta$ -hydroxyaldehyde or  $\beta$ -hydroxyketone
- E/ none of the above statements is correct

**24. Cyclohexanone reacts with hydroxylamine. What is the product?**

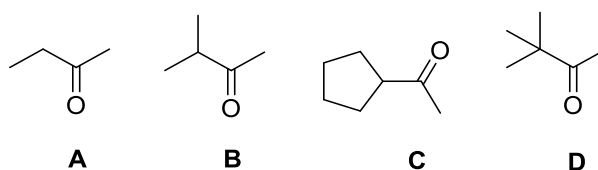
- A/ cyclohexyl amine
- B/ *N,N*-dimethyl-cyclohexyl amine
- C/ cyclohexanone oxime
- D/ cyclamic acid
- E/ cyclohexanol



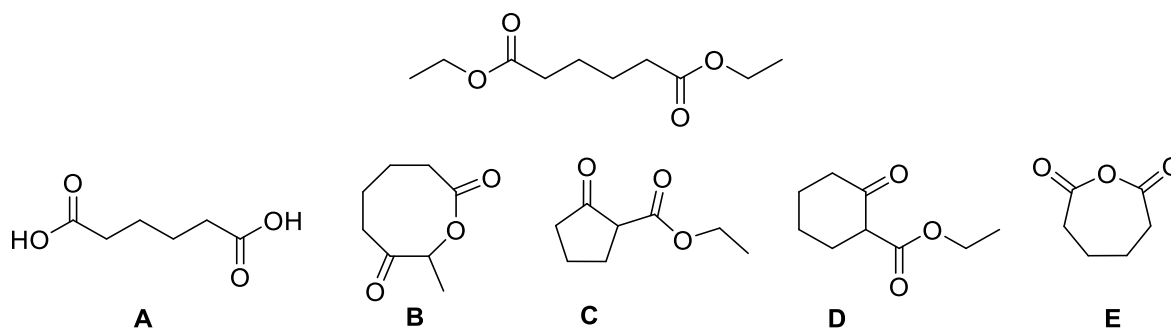
25. Which of the following is the main product of the aldol condensation of butanal?



26. Which of the following compounds CANNOT be prepared from ethyl acetoacetate without a subsequent alkylation step?



27. Which of the following products is obtained in the Dieckmann-condensation of diethyl hexandioate?



28. Which statements are correct about cyclic acetals?

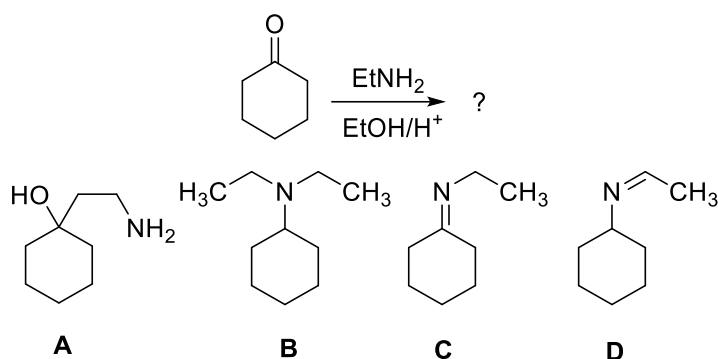
- A/ they can serve as the protecting groups of oxo compounds
- B/ they are formed in the reaction of oxo compounds and diols
- C/ they are formed in the reaction of oxo compounds and amino alcohols
- D/ one type of them can be prepared with ethylene glycol
- E/ they can be cleaved with acids

29. Acetone is halogenated in which position in an acid-catalysed reaction?

- A/ at the  $\beta$  carbon atom
- B/ it cannot be halogenated
- C/ at the  $\alpha$  carbon atom
- D/ at the carbonyl carbon atom
- E/ at the carbonyl oxygen atom



30. What is the main product of the following reaction?



31. Acetaldehyde reacts with an excess of ethanol. What is the product?

- A/ 1,1-dimethoxyethane      B/ 2,2-diethoxypropane      C/ 1,2-diethoxyethane  
D/ 1,1-diethoxymethane      E/ 1,1-diethoxyethane

32. Acetaldehyde reacts with ethylene glycol. What is the product?

- A/ 4-methyl-1,3-dioxane      B/ 2-methyl-1,3-dioxane      C/ 2-methyl-1,3-dioxolane  
D/ 4-methyl-1,3-dioxolane      E/ 1,1-diethoxyethane

33. What is formed when ketones are hydrated?

- A/ oximes  
B/ they decompose to water and carbon dioxide  
C/ geminal diols  
D/ hydrazones  
E/ cyclic acetals

34. What compound is formed when oxo compounds react with hydrazine?

- A/ semicarbazone      B/ acetal      C/ oxime  
D/ imine      E/ hydrazone

35. The preparation of 2,4-dimethylhexan-3-ol from 2-chloropropane by Grignard reaction gave too many by-products. What could be a correct alternative (non-Grignard) reaction sequence to avoid the formation of by-products?

- A/ first perform a Wittig reaction and then hydrate the double bond by an *anti*-Markovnikov reaction  
B/ first carry out an alkylation reaction of an aldehyde and then carry out its reduction  
C/ first synthesise hexan-3-ol and then carry out further alkylations at both  $\alpha$ -positions  
D/ first carry out an acylation reaction and then carry out the reduction of the ketone



**36. Which compound group does (*E,E*)-1,5-diphenylpenta-1,4-dien-3-one belong to?**

- A/ a symmetrical ketone                      B/ an  $\alpha,\beta$ -unsaturated ketone  
 C/ a diene derivative                        D/ an aldol product

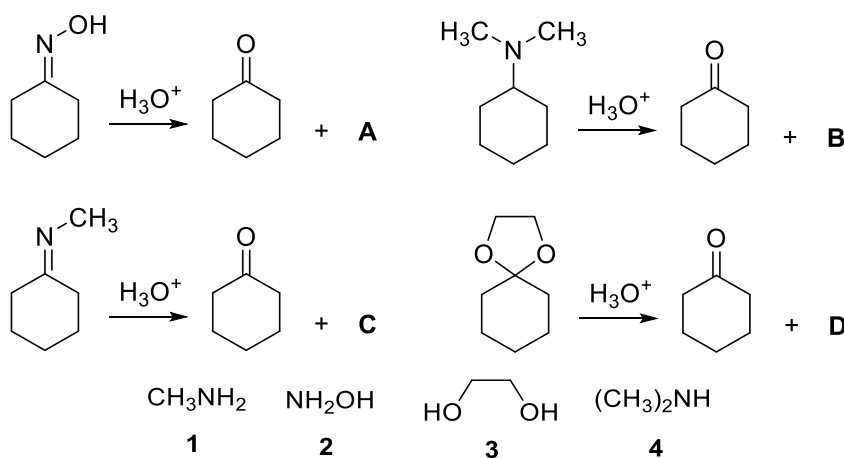
**37. Which of the following statements is NOT correct?**

- A/ cyclohexanone oxime can be prepared by reacting cyclohexanone with hydrazine  
 B/ the synthesis of cyclohexanone oxime consists of equilibrium processes  
 C/ in the synthesis of cyclohexanone oxime the hydroxylamine is the attacking nucleophile  
 D/ cyclohexanone oxime cannot be prepared by reacting cyclohexanone with primary alkyl amines

**38. Which of the following statements is NOT correct?**

- A/ no geometric isomerism is possible for oximes  
 B/ oximes can be converted to amines by catalytic hydrogenation  
 C/ cyclohexanone oxime can be converted back to cyclohexanone by acid hydrolysis  
 D/ by Beckmann rearrangement of cyclohexanone oxime  $\epsilon$ -caprolactam is formed  
 E/ the mechanism of oxime formation is analogous to that of imines

**39. What is the product of the following acid hydrolysis reactions?**



**40. From which of the following compounds can iodoform be cleaved?**

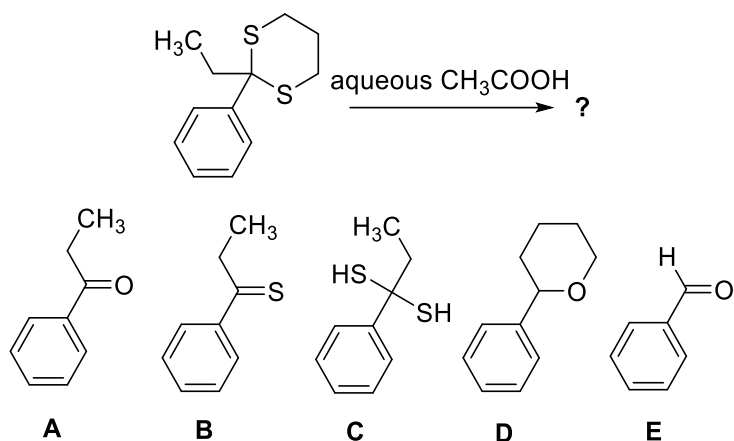
- A/ *tert*-butanol                                  B/ butan-2-ol                                  C/ butan-2,3-dione  
 D/ diisopropyl ketone                        E/ acetone

**41. Acetaldehyd dimerized into 3-hydroxybutanal. Which type of reaction did occur?**

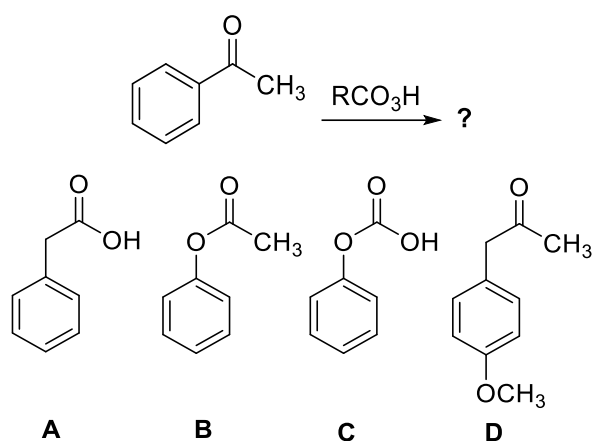
- A/ Fries-rearrangement                      B/ Mannich-reaction                      C/ Cannizzaro-reaction  
 D/ aldol dimerisation                        E/ haloform reaction



42. What is formed in the following reaction?



43. What is the main product of the following reaction?



44. What type of transformation is the reaction of ketones with  $\text{NaBH}_4$ ?

- A/ electrophilic substitution      B/ nucleophilic substitution      C/ electrophilic addition  
 D/ nucleophilic addition      E/ radical elimination

45. What is formed from benzaldehyde in a Cannizzaro-reaction?

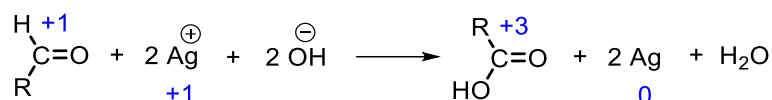
- A acetophenone  
 B/ benzyl amine and benzamide  
 C/ phenacetin  
 D/ benzyl alcohol and benzoic acid  
 E/ phenol



## 8. Oxo compounds Solutions

1. 1 - C, 2 - B, 3 - D, 4 - A, 5 - E

2. B



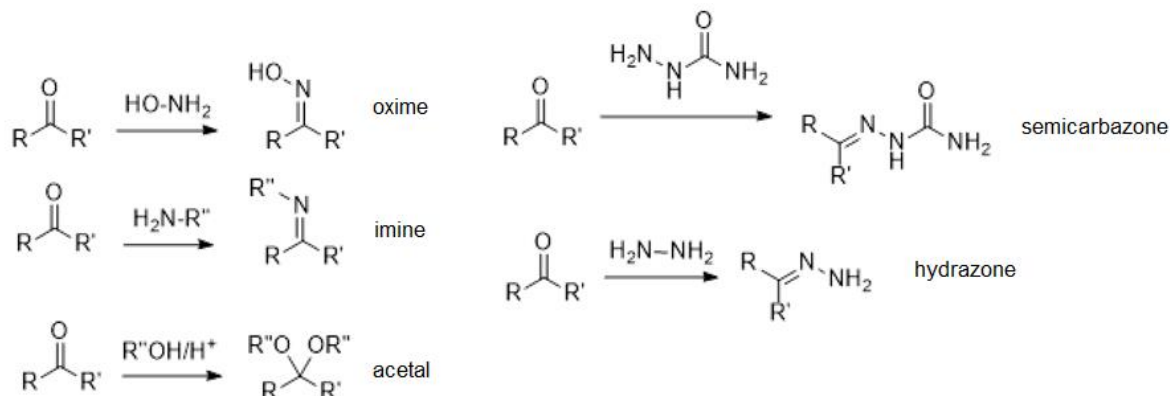
3. A, D

*In the Clemmensen reduction the number of carbon atoms does not change (i.e. a carbon number-retaining reaction), so the carbon framework should already contain the required number of carbon atoms in the correct bonding sequence.*

4. B, D

*In complex metal hydride reductions the number of carbon atoms does not change (i.e. carbon number-retaining reactions), so the carbon framework should already contain the required number of carbon atoms in the correct bonding order.*

5. D



6. E

7. D

8. A - 2, B - 1, C - 3, a - 6, b - 1, c - 4, d - 2, e - 5, f - 3

9. C

10. E

*Reductive: from an oxo compound (2<sup>nd</sup> oxidation state) an alcohol (1<sup>st</sup> oxidation state) is formed*

*Anionic: from the Grignard-reagent (due to polarity inversion - Umpolung) the alkyl group leaves in an anionic form*



Alkylation: the alkylation degree increases, the (secondary) carbon atom carrying the oxygen becomes tertiary (i.e. the number of carbon atoms directly attached to that carbon increases)

11. E

12. A

13. A - 2, B - 1, C - 3

14. A

15. A - 2, B - 3, C - 4, D - 1

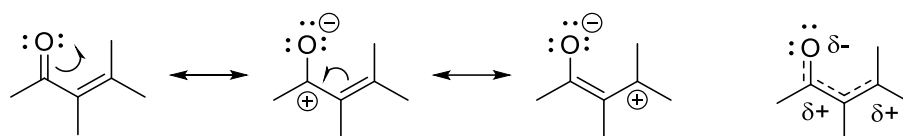
16. B

Of an ester and an oxo compound of analogous structure, the oxo compound is more enolized (stronger CH acid) than the ester, resulting in the oxo compound reacting with its negatively charged  $\alpha$ -carbon atom and the ester with its positively polarized carbonyl carbon atom.

17. B

18. D

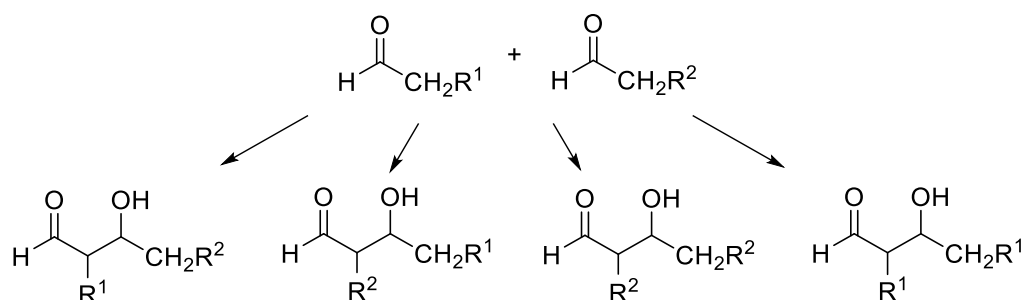
19. B, C, E



resonance structures of an  $\alpha,\beta$ -unsaturated carbonyl compound

20. D

21. D



22. B, E

23. A, B, C, D

24. C

25. A

26. D





27. C

28. A, B, D, E

29. C

30. C

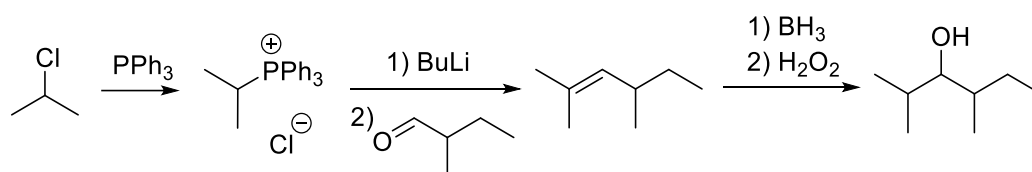
31. E

32. C

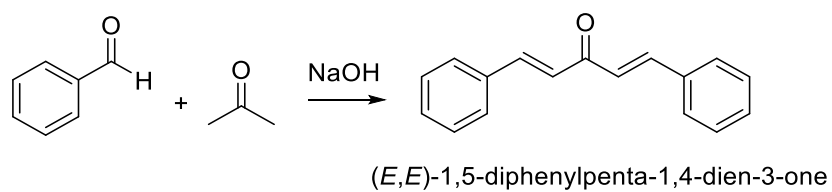
33. C

34. E

35. A



36. A, B, C



37. A

38. A

39. A - 2, B - 4, C - 1, D - 3

40. B, C, E

41. D

42. A

43. B

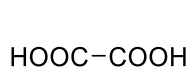
44. D

45. D



## 9. Carboxylic acids and their derivatives

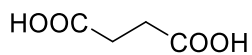
1. Match the name of the compound with the corresponding structure!



A

1 – phthalic acid

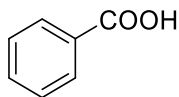
5 – benzoic acid



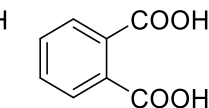
B

2 – maleic acid

6 – butyric acid



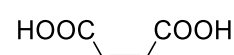
C



D

3 – oxalic acid

7 – fumaric acid

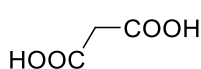


E

4 – succinic acid

8 – malonic acid

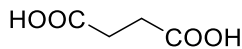
2. Match the name of the compound with the corresponding structure!



A

1 – butyric acid

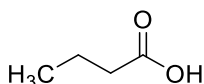
5 – fumaric acid



B

2 – benzoic acid

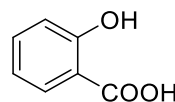
6 – oxalic acid



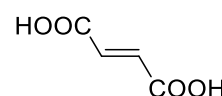
C

3 – malonic acid

7 – salicylic acid



D

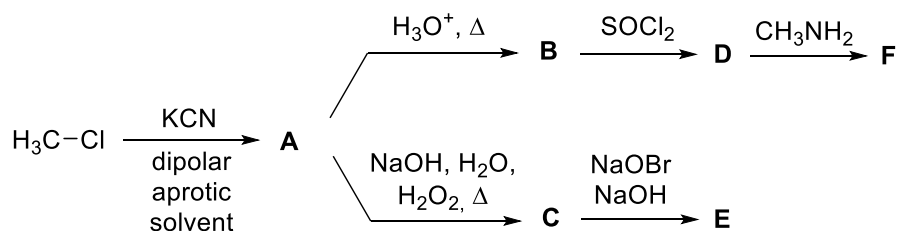


E

4 – succinic acid

8 – phthalic acid

3. Complete the following reaction scheme with the missing structures!



1.  $\text{CH}_3\text{COCl}$

2.  $\text{CH}_3\text{NH}_2$

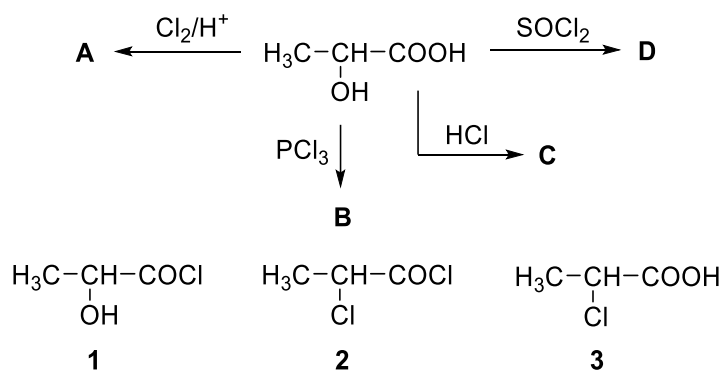
3.  $\text{H}_3\text{C}-\text{CO}-\text{NH}_2$

4.  $\text{H}_3\text{C}-\text{NH}-\text{CO}-\text{CH}_3$

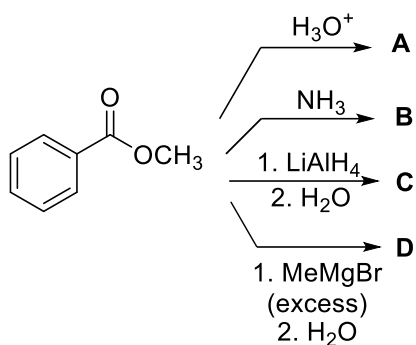
5.  $\text{CH}_3\text{CN}$

6.  $\text{CH}_3\text{COOH}$

4. Insert the following structures in the correct places! You can use a structure more than once.

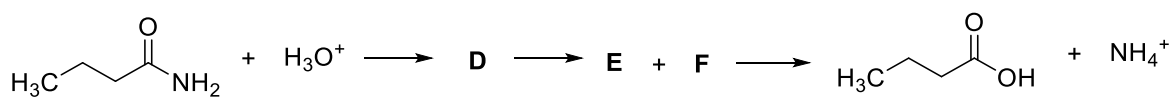
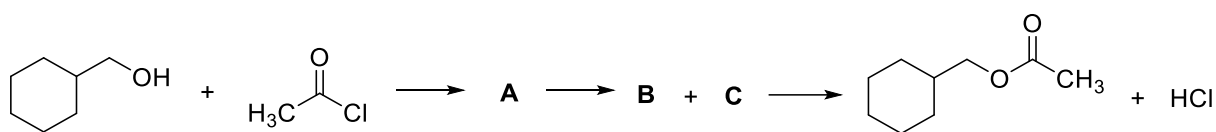


5. What is the major product of the following reactions?



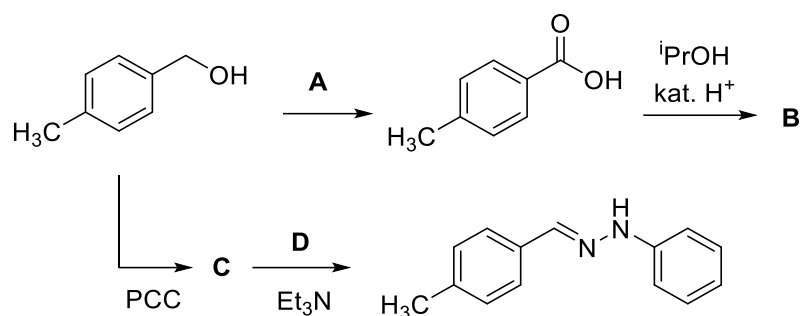
- A**   
 **B**   
 **C**   
 **D**
- A**   
 **B**   
 **C**   
 **D**
- A**   
 **B**   
 **C**   
 **D**
- A**   
 **B**   
 **C**   
 **D**

6. Complete the following reaction pathways with the missing structures!



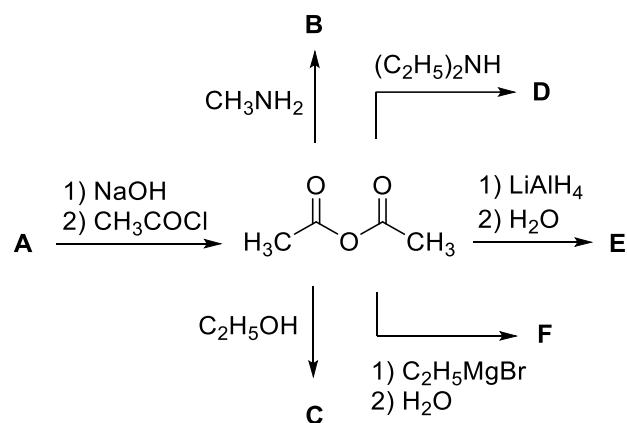
- $\text{NH}_3$
- 
- 
- $\text{Cl}^-$
- 
-

7. Complete the following scheme with the missing products/reagents!



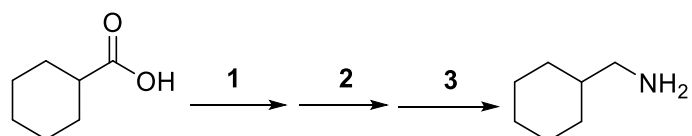
- |                                    |                           |                                 |
|------------------------------------|---------------------------|---------------------------------|
| 1. NaBH <sub>4</sub>               | 2. ethyl-4-methylbenzoate | 3. 4-hydroxybenzoic acid        |
| 4. KMnO <sub>4</sub>               | 5. phenylhydrazine        | 6. propan-2-yl-4-methylbenzoate |
| 7. Na <sub>2</sub> CO <sub>3</sub> | 8. 4-methylbenzaldehyde   | 9. aniline                      |
|                                    |                           | 10. guanidine                   |

8. Complete the scheme with the missing products!



- |    |    |    |
|----|----|----|
| 1. | 2. | 3. |
| 4. | 5. | 6. |

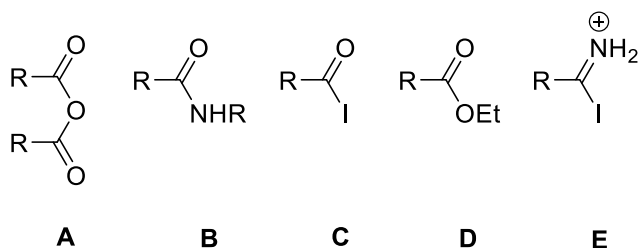
9. Give the correct sequence of reaction steps!



- |                       |                                    |                    |
|-----------------------|------------------------------------|--------------------|
| A/ LiAlH <sub>4</sub> | B/ SOCl <sub>2</sub>               | C/ NH <sub>3</sub> |
| D/ NaOH               | E/ CH <sub>3</sub> NH <sub>2</sub> | F/ PCC             |



10. Arrange the following carboxylic acid derivatives in ascending order of reactivity in acylation reaction (R: alkyl group):



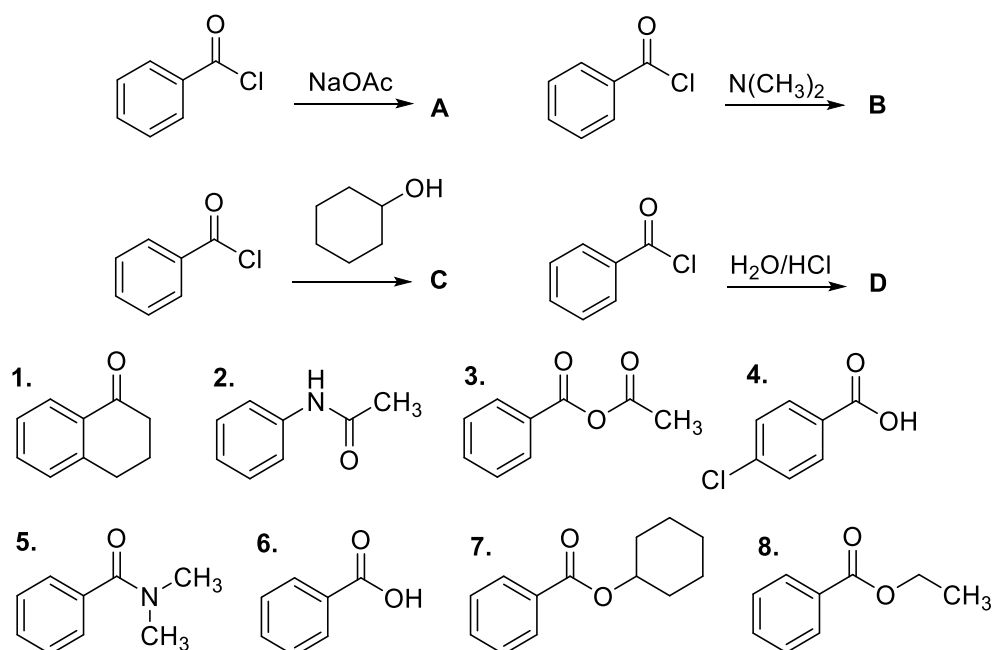
A/E < C < A < D < B

B/A < B < C < D < E

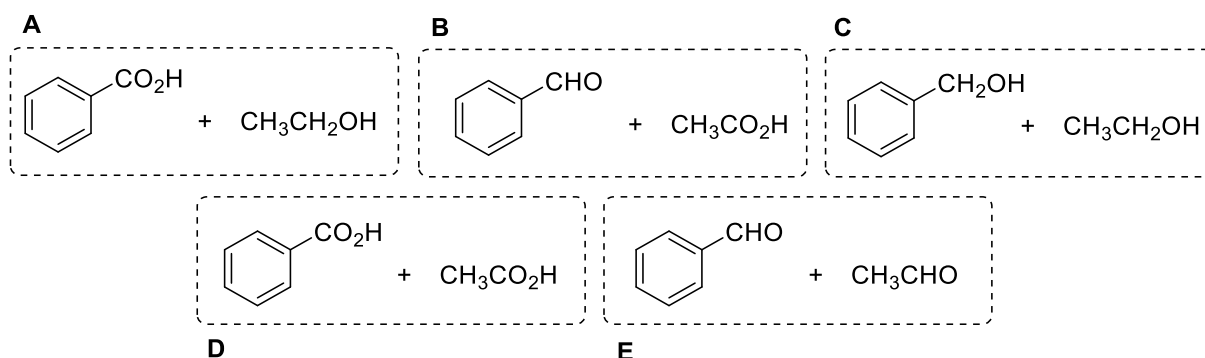
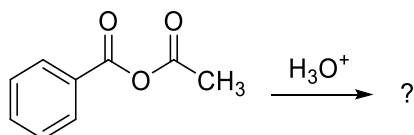
C/D < A < C < E < B

D/B < D < A < C < E

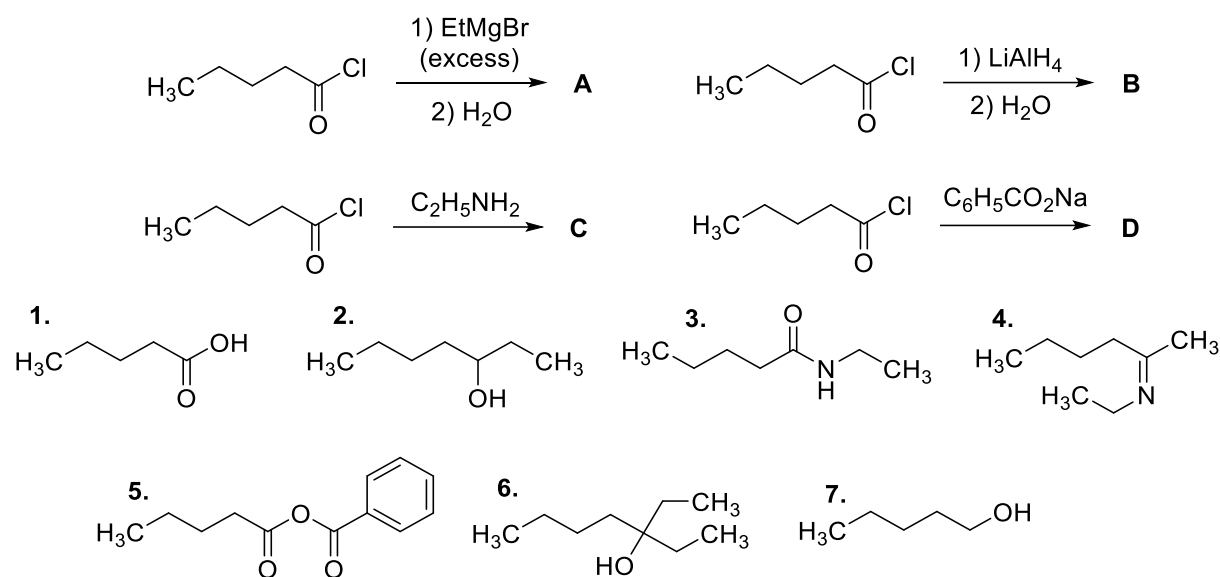
11. Complete the reaction equations with the formulas of the corresponding products!



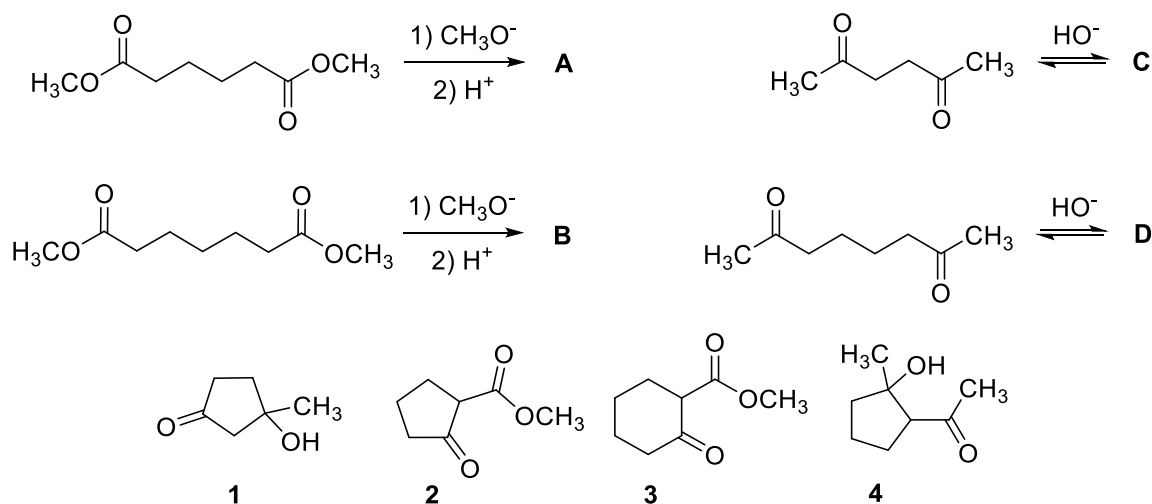
12. Which of the following molecules could be the products of the reaction below?



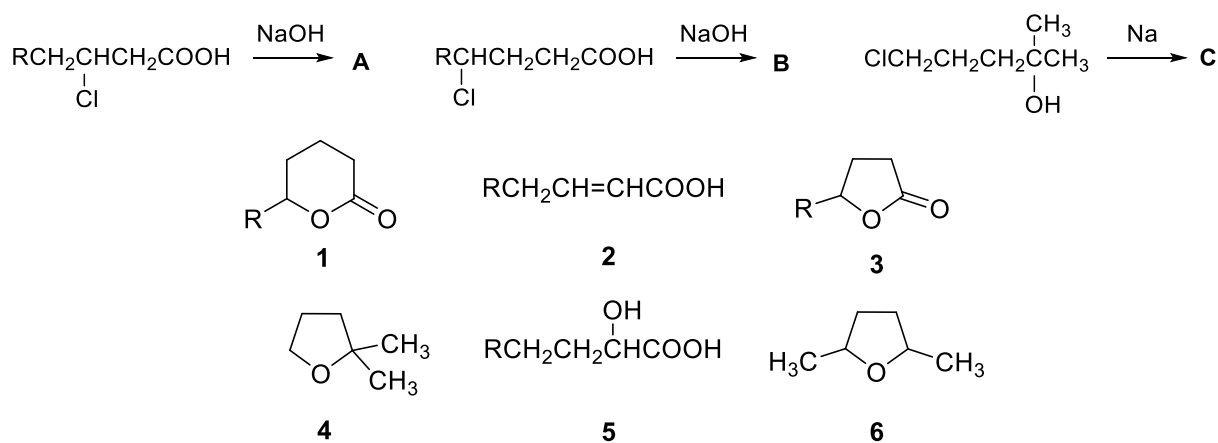
13. What are the main products of the following reactions?



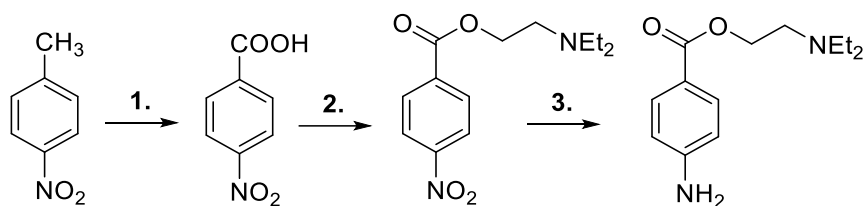
14. Complete the reaction equations with their major reaction products.



15. What is the product of the following reactions?



16. Which reagents can be used to perform the following synthesis?

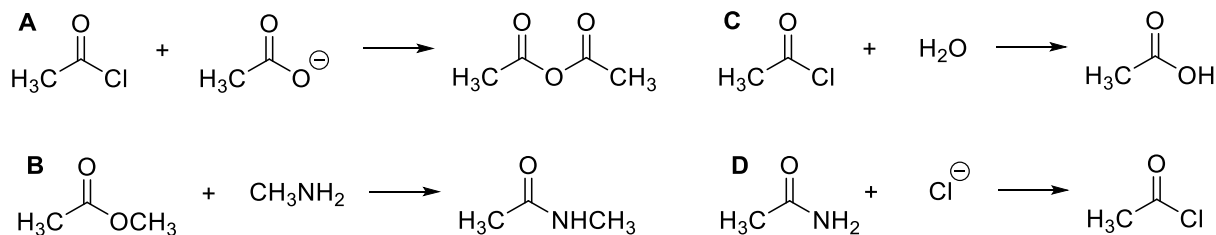


- A/ 1.  $\text{Na}_2\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4$   
 2.  $\text{SOCl}_2$ , then  $\text{HOCH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$   
 3. Sn, HCl, then NaOH
- B/ 1.  $\text{Na}_2\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4$   
 2.  $\text{SOCl}_2$ , then  $\text{HOCH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$   
 3.  $\text{H}_2\text{O}, \text{HCl}$
- C/ 1.  $\text{H}_2\text{O}, \text{HCl}$   
 2.  $\text{HOCH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$   
 3. Fe, HCl, then NaOH
- D/ 1.  $\text{Na}_2\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4$   
 2. diethyl amine,  $\text{H}_2\text{SO}_4$   
 3. Sn, HCl, then NaOH
- E/ 1.  $\text{LiAlH}_4$   
 2.  $\text{SOCl}_2$ , then  $\text{HOCH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$   
 3. Sn, HCl, then NaOH

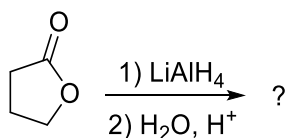
17. Which of the following statements is correct?

- A/ The aminoacetic acid is an open-chain, aliphatic, monoamino dicarboxylic acid.
- B/ The alanine is an open-chain, aromatic, monoamino monocarboxylic acid.
- C/ The 6-aminohexanoic acid is an open-chain, aliphatic, monoamino monocarboxylic acid.
- D/ The tyrosine is an open-chain, aliphatic, monoamino dicarboxylic acid.

18. Which of the following reactions DOES NOT proceed the way as indicated below?



19. What is the main product of the following reaction?



- A/  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$       B/  $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{COOH}$       C/  $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
- D/  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$       E/  $\text{HCOOCH}_2\text{CH}_2\text{CH}_2\text{COOH}$

**20. Which of the following compounds is NOT a dicarboxylic acid?**

- A/ tartaric acid                      B/ propionic acid                      C/ caprylic acid  
D/ citric acid                          E/ oxalic acid                          F/ malonic acid

**21. Choose the correct statements about oleic acid:**

- A/ it is a saturated fatty acid  
B/ it has Z-isomerism  
C/ it does not show geometric isomerism  
D/ it is an unsaturated fatty acid

**22. Which of the following compounds is NOT a dicarboxylic acid?**

- A/ adipic acid                          B/ malonic acid                          C/ caprylic acid  
D/ succinic acid                      E/ glutaric acid

**23. Potential applications of phthalimide are:**

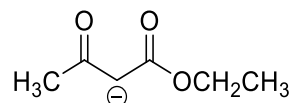
- A/ plastic production  
B/ anthranilic acid synthesis  
C/ indigo synthesis  
D/ fertilizer production

**24. Which type of reaction is the following transformation?**



- A/ esterification                      B/ hydrolysis                          C/ alkylation  
D/ acylation                          E/ reduction

**25. How many electrons are involved in the delocalised system below?**



- A/ 14 electrons                      B/ 7 electrons                          C/ 6 electrons  
D/ 5 electrons                          E/ 4 electrons

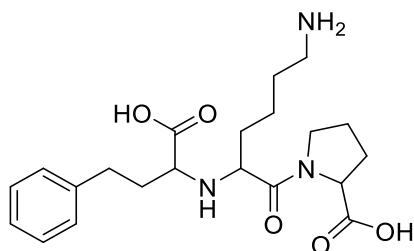
**26. Arrange the compounds given below in the correct order for the preparation of ethyl 3-hydroxypropionate by Reformatsky synthesis.**

- A/ ethyl 2-bromoacetate                      B/ ethyl acetate  
C/ ethyl 2-bromozincacetate + formaldehyde                      D/ ethyl 2-bromozincacetate





27. How many stereogenic centers (a) and protonable/deprotonable groups (b) are there in the following compound?



A/ a=1, b=2

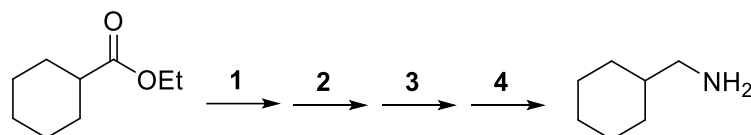
B/ a=3, b=4

C/ a=3, b=2

D/ a=2, b=3

E/ a=4, b=1

28. Give the correct order of the reaction steps!



A/  $\text{NH}_2\text{OH}$

B/  $\text{SOCl}_2$

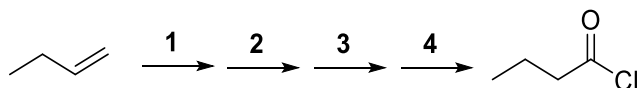
C/ i)  $\text{LiAlH}_4$ , ii)  $\text{H}_2\text{O}$

D/  $\text{H}_3\text{O}^+$

E/  $\text{NH}_3$

F/  $\text{Na}_2\text{Cr}_2\text{O}_7$

29. Give the correct order of the reaction steps!



A/  $\text{H}_2\text{O}_2$ ,  $\text{NaOH}$

B/  $\text{SOCl}_2$

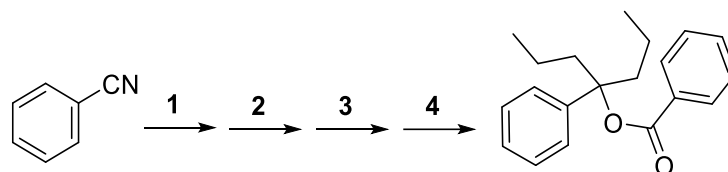
C/ i)  $\text{LiAlH}_4$ , ii)  $\text{H}_2\text{O}$

D/  $\text{BH}_3\cdot\text{THF}$

E/  $\text{H}_2\text{SO}_4$ ,  $\text{HgSO}_4$

F/  $\text{Na}_2\text{Cr}_2\text{O}_7$

30. Give the correct order of the reaction steps!



A/  $\text{CH}_3\text{CH}_2\text{CH}_2\text{MgBr}$

B/  $\text{SOCl}_2$

C/  $\text{PhCOCl}$

D/  $\text{H}_3\text{O}^+$

E/  $\text{H}_2\text{O}_2$ ,  $\text{NaOH}$

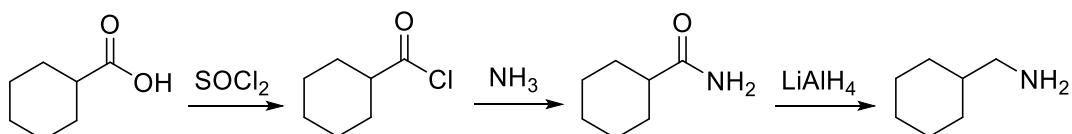
F/  $\text{Na}_2\text{Cr}_2\text{O}_7$

## 9. Carboxylic acids and their derivatives

### Solutions

1. A - 3, B - 4, C - 5, D - 1, E - 2
2. A - 3, B - 4, C - 1, D - 7, E - 5
3. A - 5, B - 6, C - 3, D - 1, E - 2, F - 4
4. A - 3, B - 1, C - 3, D - 2
5. A
6. A - 2, B/C - 5/4, D - 6, E/F - 1/3
7. A - 4, B - 6, C - 8, D - 5
8. A - 5, B - 2, C - 4, D - 1, E - 3, F - 6

9. 1 - B, 2 - C, 3 - A



10. D

*The greater the negative inductive effect and the smaller the positive mesomeric effect of the group (not the carbonyl or iminium) connected to the acyl carbon atom, the more reactive the given carboxylic acid derivative will be against nucleophilic reagents due to the partial positive charge of the acyl carbon atom. In the case of carboxylic acid salts, also the inductive effect is positive, not just the mesomeric effect. The iminium group - due to its positive charge - is a much stronger electron withdrawer than the neutral carbonyl group in the other derivatives (or as the imino group would be itself).*

11. A - 3, B - 5, C - 7, D - 6

12. D

*The hydrolysis of mixed carboxylic acid anhydrides results in two different carboxylic acids.*

13. A - 6, B - 7, C - 3, D - 5

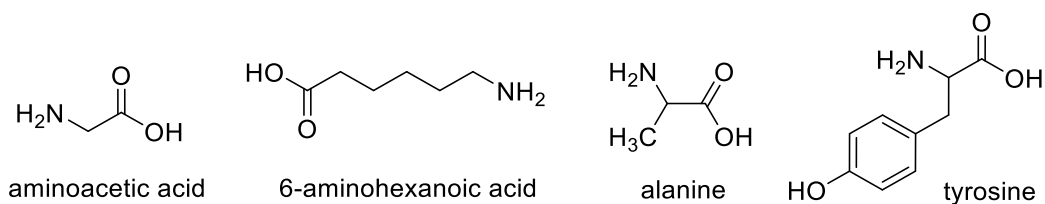
14. A - 2, B - 3, C - 1, D - 4

15. A - 2, B - 3, C - 4

16. A

17. C





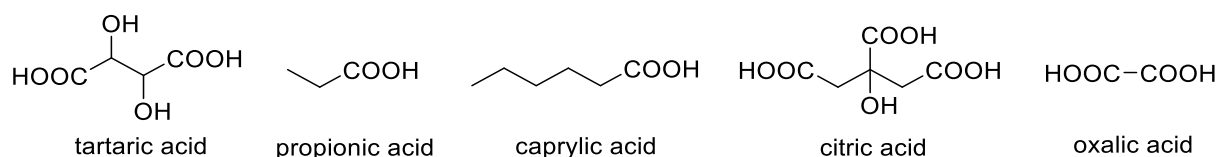
18. D

*By listing the carboxylic acid derivatives in descending order of reactivity, a given compound can be prepared from the previous, more reactive derivatives and converted into a less reactive derivative. The acid chloride is more reactive than the acid amide, so it cannot be formed from it (in a one step,  $S_NAc$  reaction).*

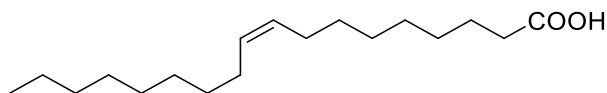
19. C

*Complex metal hydride reductions are carbon number retaining reactions, therefore the carbon framework should already contain the required number of carbon atoms, with the appropriate connection sequence. The carboxylic acid component of cyclic esters is also reduced to a hydroxyl group, which is why the diol with the appropriate number of carbon atoms is formed.*

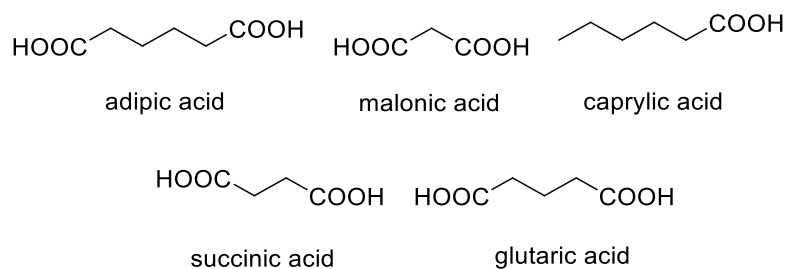
20. B, C, D



21. B, D



22. C



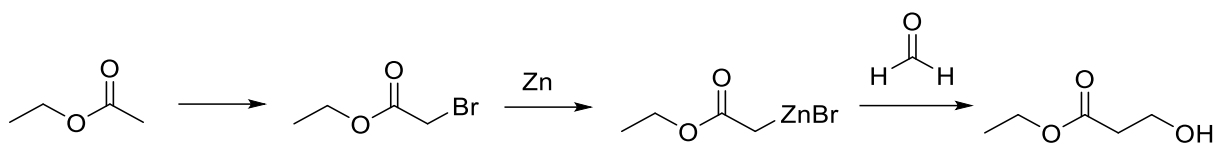
23. B, C

24. B

25. C

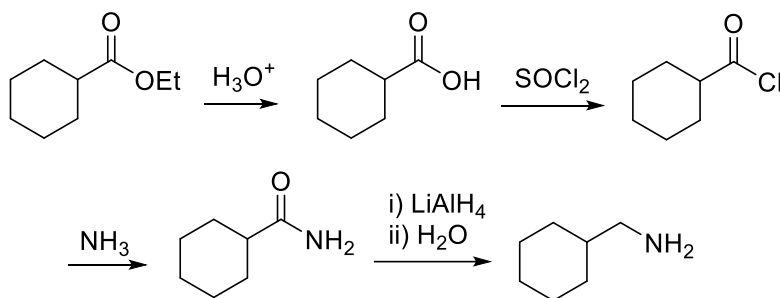
26. B → A → D → C



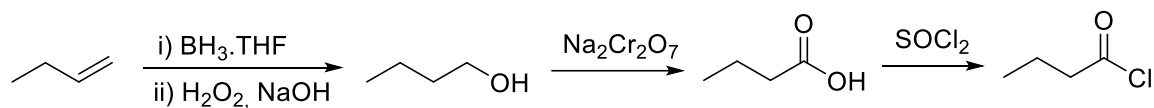


27. B

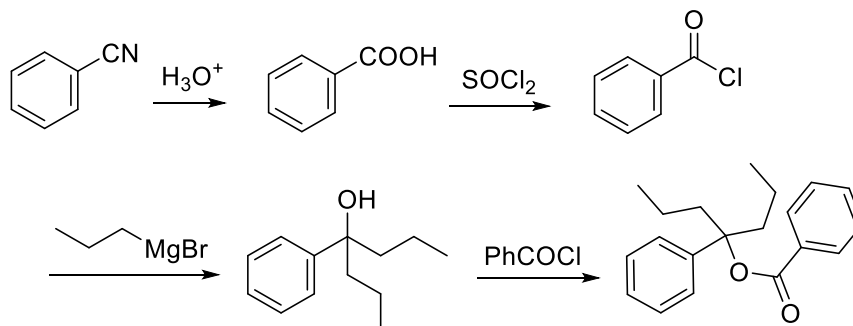
28. 1 - D, 2 - B, 3 - E, 4 - C



29. 1 - D, 2 - A, 3 - F, 4 - B



30. 1 - D, 2 - B, 3 - A, 4 - C



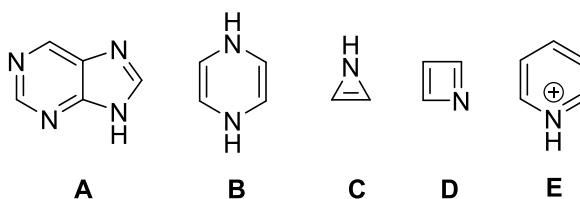
## 10. Heterocyclic compounds

### Properties

#### 1. Group the following molecules:

A/ thiazole	B/ indolizine	C/ 1,3,5-triazine
D/ azet	E/ azocine	F/ quinuclidine
1 – aromatic	2 – antiaromatic	3 – not aromatic

#### 2. Which of the following compounds is aromatic/antiaromatic/not aromatic?

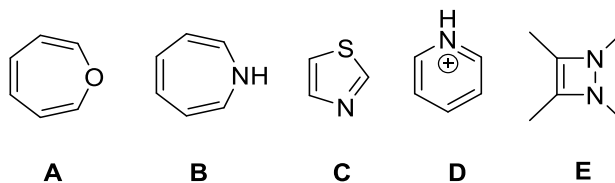


1 – aromatic

2 – antiaromatic

3 – not aromatic

#### 3. Which of the following compounds is aromatic/antiaromatic/not aromatic?

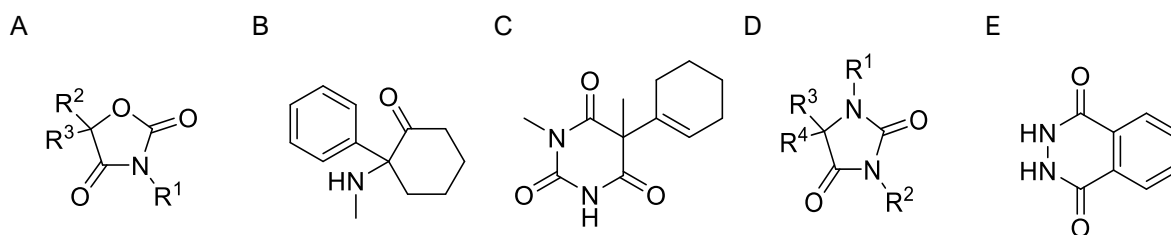


1 – aromatic

2 – antiaromatic

3 – not aromatic

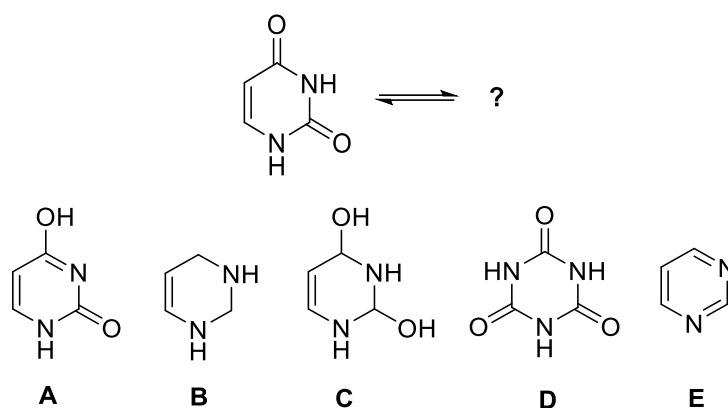
#### 4. Which of the following molecules is a barbituric acid derivative?



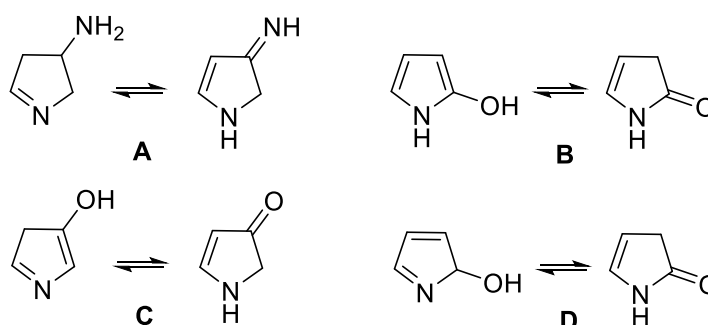
#### 5. Choose the correct statement!

- A/ The  $\pi$ -electron density of the carbon atoms of the ring is lower in thiophene than in benzene.  
 B/ The  $\pi$ -electron density of the carbon atoms of the ring is higher in pyridine than in benzene.  
 C/ The  $\pi$ -electron density of the carbon atoms of the ring in pyrrole is the same as in benzene.  
 D/ The  $\pi$ -electron density of the carbon atoms of the ring is higher in furan than in benzene.

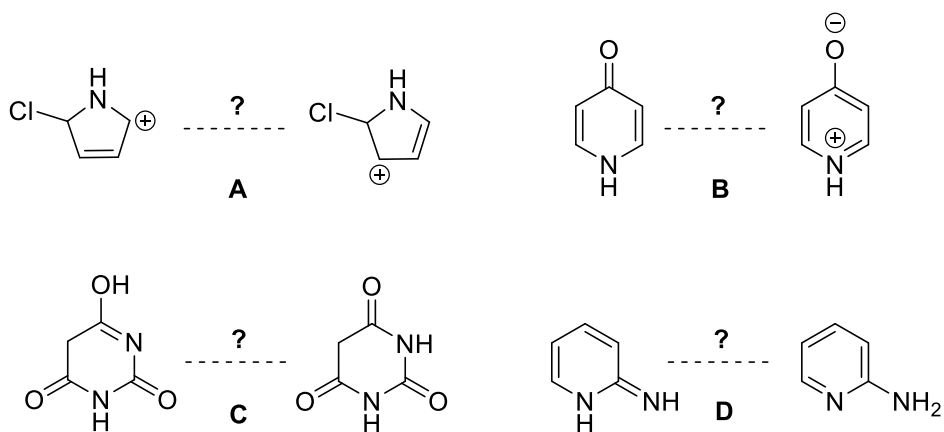
6. Choose which of the following is a tautomer of the molecule in the question.



7. Which of the following examples is NOT a pair of tautomers?



8. Choose the correct category for the following pairs of structures!

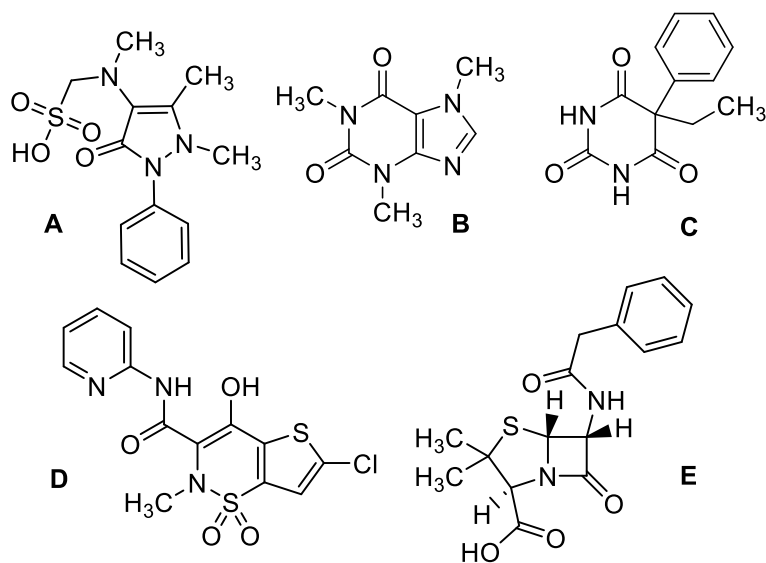


1 – resonance structures

2 – tautomers

3 – neither resonance, nor tautomer structures

**9. For which of the following drug molecules is lactam-lactim tautomerism possible?**



**10. Which of the following properties is usually a characteristic of  $\pi$ -electron-deficient and  $\pi$ -electron-excessive aromatic heterocyclic compounds?**

- A/ an excess of electrons compared to the heteroatom on the carbon atoms of the ring
  - B/ a lack of electrons compared to the heteroatom on the carbon atoms of the ring
  - C/ an excess of electrons compared to the carbon atoms of benzene on the carbon atoms of the ring
  - D/ a lack of electrons compared to the carbon atoms of benzene on the carbon atoms of the ring
  - E/ characterized mainly by aromatic electrophilic substitutions
  - F/ characterized mainly by aromatic nucleophilic substitutions
  - G/ sensitivity to acids
  - H/ can be prepared from 1,5-dioxo compounds
  - I/ can be prepared from 1,2 and 1,4 dioxo compounds
  - J/ with electrophilic reagents under kinetic control they react mainly in position 2
  - K/ with electrophilic reagents they react mainly in position 3
- 1 -  $\pi$ -electron deficient                  2 -  $\pi$ -electron excessive

**11. Choose the correct statement!**

- A/  $\pi$ -Electron deficient heteroaromatic compounds show reduced reactivity in both electrophilic and nucleophilic substitution.
- B/  $\pi$ -Electron deficient heteroaromatic compounds show increased reactivity in both electrophilic and nucleophilic substitution.
- C/  $\pi$ -Electron excessive heteroaromatic compounds show increased reactivity in electrophilic substitution and decreased reactivity in nucleophilic substitution.
- D/  $\pi$ -Electron excessive heteroaromatic compounds show reduced reactivity in electrophilic substitution and increased reactivity in nucleophilic substitution.

**12. Choose the correct statement!**

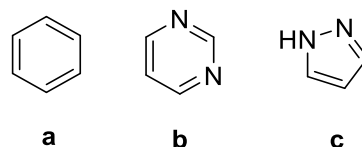
A/ Aromatic electrophilic substitution is the most common reaction of furan, pyrrole and thiophene.

B/ In the case of furan, thiophene and pyrrole, the aromatic electrophilic substitution reactions require a lower activation energy compared to benzene, and are therefore faster.

C/ Aromatic nucleophilic substitution reactions – as halogenation, sulfonation, alkylation, acylation and carboxylation - usually proceed with good yields.

D/ The aromatic electrophilic substitution on the carbon atom of the heteroaromatic ring takes place with nucleophilic reagents.

**13. Give the correct reactivity order of the following compounds in aromatic electrophilic substitution (in descending order from left to right).**



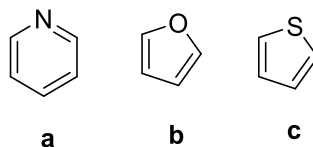
A/  $c > a > b$

B/  $c > b > a$

C/  $b > a > c$

D/  $a > b > c$

**14. Give the correct reactivity order of the following compounds in aromatic electrophilic substitution (in descending order from left to right).**



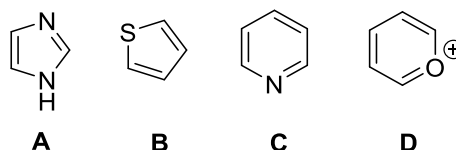
A/  $b > c > a$

B/  $c > b > a$

C/  $b > a > c$

D/  $a > b > c$

**15. Which of the following compounds is the most reactive in aromatic electrophilic substitution?**



**16. Arrange the following compounds in order of increasing  $S_EAr$  reactivity!**

A: indole

B: naphthalene

C: pyrazine

D: thiophene

A/  $A < B < C < D$

B/  $C < B < A < D$

C/  $D < A < B < C$

D/  $C < A < B < D$



**17. Arrange the following compounds in order of increasing S<sub>E</sub>Ar reactivity!**

A: benzene

B: furan

C: pyrimidine

D: thiophene

1. C > D > A > B

2. B > D > A > C

3. A > B > C > D

4. B > A > D > C

**18. Choose the correct statement!**

A/ Pyrrole is less reactive in S<sub>E</sub>Ar reactions than furan.

B/ Thiophene is more reactive in S<sub>E</sub>Ar reactions than benzene.

C/ Benzene is more reactive in S<sub>E</sub>Ar reactions than furan.

D/ Pyrrole is more reactive in S<sub>E</sub>Ar reactions than thiophene.

**19. Choose the correct statement!**

A/ Furan is a π-electron deficient heteroaromatic compound.

B/ Thiophene is a π-electron excessive non-heteroaromatic compound.

C/ Pyrrole is a π-electron deficient non-heteroaromatic compound.

D/ Pyridine is a π-electron deficient heteroaromatic compound.

**20. Choose the correct statement!**

A/ Aromatic electrophilic substitutions of furan, thiophene and pyrrole taking place under kinetic control, provide mainly β-(3)-substituted products.

B/ Aromatic electrophilic substitutions of furan, thiophene and pyrrole taking place under kinetic control, provide mainly α-(2)-substituted products.

C/ Aromatic electrophilic substitutions of furan, thiophene and pyrrole taking place under thermodynamic control, provide mainly α-(2)-substituted products.

D/ Aromatic electrophilic substitutions of furan, thiophene and pyrrole taking place under thermodynamic and kinetic control, provide mainly α-(2)-substituted products.

**21. Choose the correct statement!**

A/ The nitrogen in pyrrole is in sp<sup>2</sup> hybrid state, and the lone electron pair contributes to aromatic delocalization.

B/ The nitrogen in pyrrole is in sp<sup>2</sup> hybrid state, and the lone electron pair does not contribute to aromatic delocalization.

C/ The nitrogen in pyrrole is in sp<sup>3</sup> hybrid state, and the lone electron pair contributes to aromatic delocalization.

D/ The nitrogen in pyrrole is in sp<sup>3</sup> hybrid state, and the lone electron pair does not contribute to aromatic delocalization.



**22. Choose the correct statements. Pyrimidine is:**

- A/ a weak base
- B/ a strong base
- C/ is a stronger base than piperidine.
- D/ is a stronger base than pyrazine

**23. Choose the correct statement.**

- A/ Pyrrole is a strong acid and a weak base.
- B/ Pyrrole is a weak acid and a strong base.
- C/ Pyrrole is a strong acid and a strong base.
- D/ Pyrrole is a weak acid and a weak base.

**24. Choose the correct statement.**

- A/ Pyrrolidine is a monocyclic pyrrole derivative.
- B/ The S-pyrrolidine-2-carboxylic acid is the pseudoproline.
- C/ Pyrrolidone is not a monocyclic pyrrole derivative.
- D/ The 4-hydroxypyrrolidine-2-carboxylic acid is the 4-oxypoline.

**25. Which statements are correct about pyrrole?**

- A/ it is isoelectronic with the aromatic cyclopentadienyl anion
- B/ it can be prepared from 1,4-dicarbonyl derivatives by Paal-Knorr synthesis
- C/ in electrophilic aromatic substitution reactions, typically the product substituted in position 3 is the main product
- D/ compared to amines, pyrrole is more basic

**26. Which statement is FALSE about purine?**

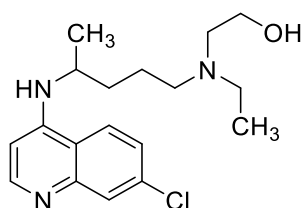
- A/ it shows tautomerism
- B/ It can be prepared from 4,5-diaminopyrimidine and glyoxal
- C/ it contains a pyrimidine ring
- D/ it contains an imidazole ring

**27. Which of the following statements is NOT correct?**

- A/ histamine contains an imidazole ring
- B/ imidazole is a 1,2-diazole
- C/ in imidazole, the electron pair of one nitrogen participates in the aromatic  $\pi$ -electron system, whereas the electron pair of the other nitrogen does not
- D/ imidazole is a stronger acid than pyrrole
- E/ imidazole is amphoteric

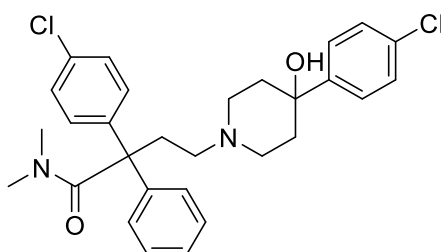


28. Which statement is correct about hydroxychloroquine?



- A/ its nitrogen atoms have similar basicity
- B/ it has an isoquinoline core
- C/ it has two stereogenic centers in its structure
- D/ it contains a  $\pi$ -electron excessive heteroaromatic ring
- E/ it contains both heteroaromatic and alkylamino nitrogen atoms

29. Which structural element does NOT contain the following compound?



- A – acide amide group
- B – chiral carbon atom
- C – piperidine ring
- D – piperazine ring
- E - tertiary alcoholic hydroxyl group

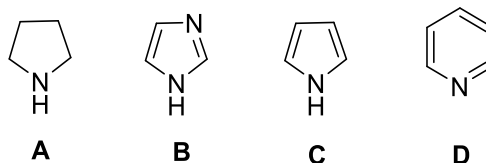
30. Arrange the following compounds in order of increasing basicity, tested in aqueous solution.

- |                        |                        |
|------------------------|------------------------|
| 1. pyrrolidine         | 2. 1 <i>H</i> -azepine |
| 3. 1 <i>H</i> -pyrrole | 4. indolizine          |
| A/ 4 < 3 < 2 < 1       | B/ 1 < 2 < 3 < 4       |
| C/ 4 < 2 < 3 < 1       | D/ 4 < 3 < 2 < 1       |

31. Arrange the six-membered two nitrogen atom-containing aromatic heterocyclic compounds in descending order of basicity, examined in aqueous solution.

- |               |               |             |
|---------------|---------------|-------------|
| 1. pyridazine | 2. pyrimidine | 3. pyrazine |
| A/ 3 > 2 > 1  | B/ 1 > 3 > 2  |             |
| C/ 2 > 1 > 3  | D/ 1 > 2 > 3  |             |

32. Which of the following compounds is the most basic?



**33. Arrange the following compounds in order of increasing basicity (examined in an aqueous hydrochloric acid solution).**

1. *N*-methylpyrazole                      2. 2-methylpyrimidine                      3. *N*-methylimidazole  
4. 2-methylpyrazine                      5. 3-methylpyridazine
- A/  $5 < 2 < 4 < 1 < 3$                       B/  $5 < 4 < 3 < 2 < 1$                       C/  $3 < 1 < 5 < 2 < 4$   
D/  $4 < 2 < 5 < 1 < 3$                       E/  $4 < 2 < 3 < 1 < 5$

### ***Preparation, reactions***

**34. How can thiophene derivatives be prepared from a 1,2-dioxo compound?**

- A/ by reaction with an ester derivative of thioether dicarboxylic acid  
B/ by reaction with  $\text{H}_2\text{N-NH}_2$   
C/ by reaction with  $\text{P}_2\text{S}_5$   
D/ by reaction with  $\text{H}_2\text{N-OH}$  in ethanol in the presence of NaOAc

**35. From which components can isoxazole be prepared?**

- A/ hydrazine + 3-chloro ketone    B/ propandial-monooxime  
C/ ethene + nitrilimine              D/ ethene + nitril-oxide

**36. Choose the correct statement!**

- A/ Furan derivatives can be prepared by Feist-Benary synthesis from  $\alpha$ -haloaldehydes and  $\beta$ -dicarbonyl compounds.  
B/ The Feist-Benary condensation reaction is catalyzed by acids.  
C/ The Feist-Benary ring synthesis is an intramolecular alkylation.  
D/ Furan derivatives can be prepared by Feist-Benary synthesis from  $\alpha$ -halogen ketones and  $\beta$ -dicarboxyl compounds.

**37. How can thiophene derivatives be prepared from a 1,4-dioxo compound?**

- A/ with  $\text{P}_2\text{S}_5$  reagent  
B/ with  $\text{H}_2\text{N-OH}$  reagent in the presence of NaOAc and ethanol  
C/ with  $\text{NH}_3$  reagent  
D/ with  $\text{H}_2\text{SO}_4$  reagent

**38. Match the reagents below with the corresponding name reactions.**

- A/  $\alpha$ -chloro ketone +  $\beta$ -oxoester                      1. Knorr synthesis  
B/  $\alpha$ -chloro ketone +  $\beta$ -oxoester + ammonia (or primary amine)                      2. Hantzsch synthesis  
C/  $\beta$ -oxoester (+  $\text{NaNO}_2$ ) +  $\alpha$ -aminoketone                      3. Feist-Benary synthesis  
D/ phenylhydrazine + oxo derivative                      4. Fischer indole synthesis



### 39. Choose the correct statement!

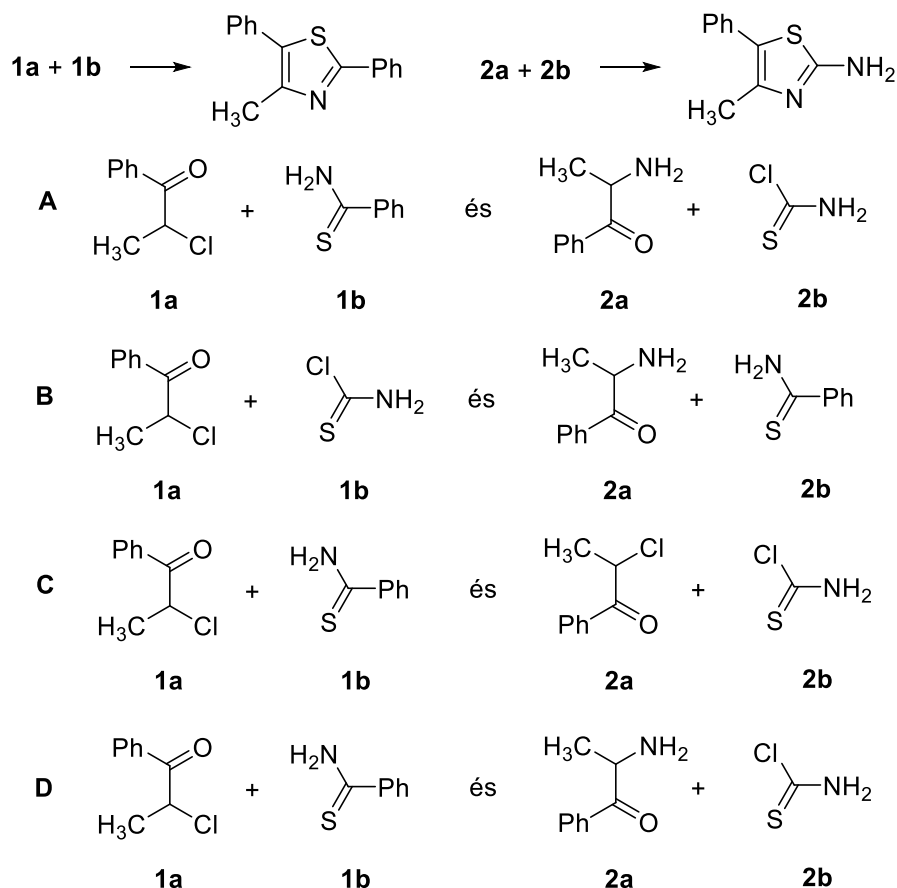
A/ Pyrrole and furan can be prepared by Hinsberg synthesis.

B/ Furan, pyrrole and thiophene can be prepared by the cyclocondensation reaction of 1,2-diketones and the appropriate 2,2'-acetic acid esters.

C/ Basic conditions are used during the Hinsberg synthesis.

D/ Furan, pyrrole and thiophene can be prepared by the cyclocondensation reaction of 1,4-diketones and the appropriate 2,2'-diacetic acid diesters.

### 40. Choose the correct starting compounds for preparing the following products.



### 41. Choose the correct statement!

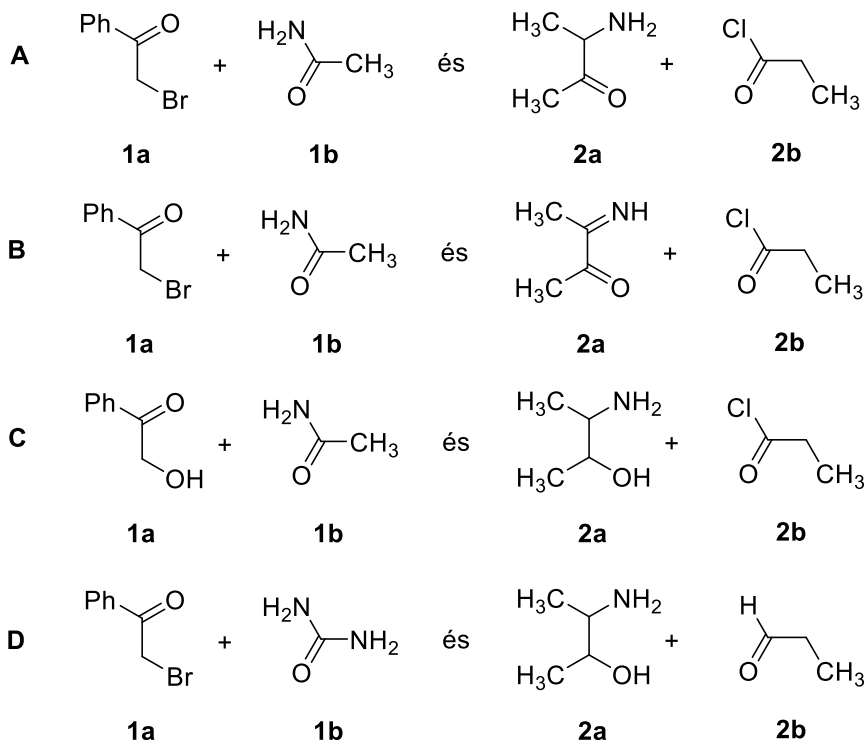
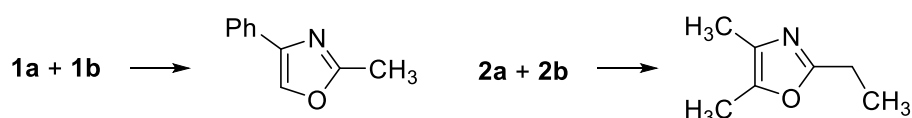
A/ When thiophene derivatives are prepared by Paal-Knorr synthesis, the starting material is heated with phosphorus pentoxide.

B/ When pyrrole derivatives are prepared by Paal-Knorr synthesis, the starting material is heated with phosphorus pentoxide.

C/ When thiophene derivatives are prepared by Paal-Knorr synthesis, the starting material is heated with phosphorus pentasulfide.

D/ When pyrrole derivatives are prepared by Paal-Knorr synthesis, the starting material is heated with phosphorus pentasulfide.

42. . Choose the correct starting compounds for preparing the following products.



43. Which statements are correct about the Knorr pyrrole synthesis?

- A/ the  $\alpha$ -nitroso ketone formed (or the tautomeric form of the  $\alpha$ -hydroxyimino ketone) is reduced in an acetic acid medium with zinc powder
- B/ as a side reaction, keto or ester groups can also be reduced during the reduction with zinc powder in an acetic acid medium
- C/ with appropriate reagents *N*-substituted pyrrole derivatives can also be prepared
- D/ the component containing the active methylene group is often a 1,3-diketone or a  $\beta$ -ketoester
- E/ the Knorr synthesis is the condensation of a  $\beta$ -amino ketone with a compound containing an active methylene group

44. From which starting compounds could we prepare diethyl (3,5-dimethylpyrrole-2,4-dicarboxylate)?

- A/ ethyl (2-amino-3-oxobutanoate) + ethyl acetoacetate
- B/ ethyl (2-amino-3-oxobutanoate) + acetylacetone
- C/ ethyl (2-methylamino-3-oxobutanoate) + methyl acetoacetate
- D/ ethyl (2-amino-3-oxopentanoate) + ethyl acetoacetate
- E/ ethyl (2-amino-3-oxopentanoate) + acetylacetone

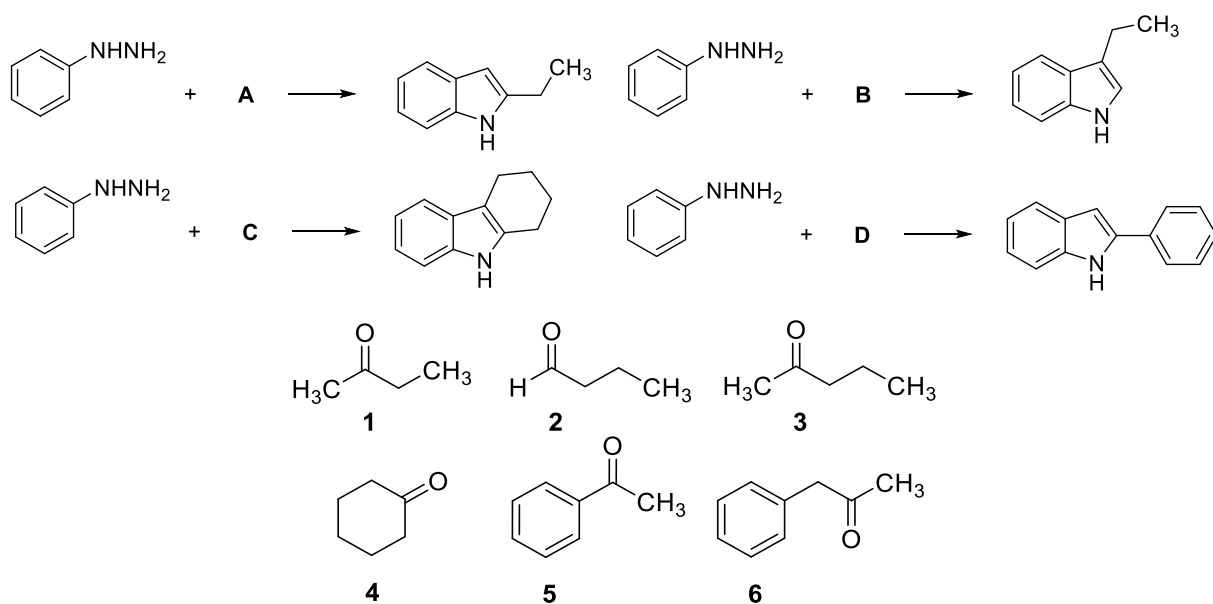
**45. How can pyrrole derivatives be prepared from 1,4-dioxo compounds?**

- A/ by reaction with  $\text{H}_2\text{N-NH}_2$
- B/ by reaction with  $\text{P}_2\text{S}_5$
- C/ by reaction with the ester derivative of azadicarboxylic acid
- D/ by reaction with  $\text{NH}_3$  or a primary amine

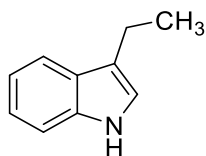
**46. Choose the correct statement!**

- A/ During the Hinsberg synthesis, we use acidic conditions.
- B/ The Hinsberg synthesis is a cyclocondensation reaction of 1,2-diketones and the appropriate 2,2'-diacetic acid diester derivatives.
- C/ Thiophene cannot be prepared by the Hinsberg synthesis.
- D/ The Hinsberg synthesis is a cyclocondensation reaction of 1,4-diketones and the appropriate 2,2'-diacetic acid diester derivatives.

**47. From which starting compounds could the following indole derivatives be prepared by Fischer synthesis?**

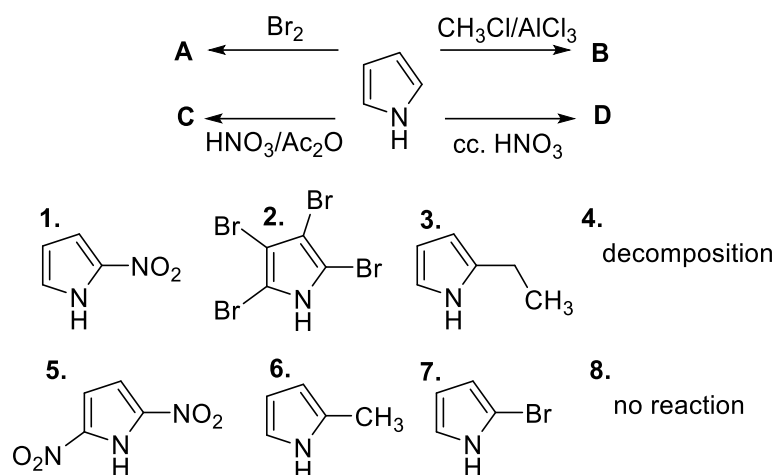


**48. Select the appropriate starting compounds for the Fischer indole synthesis of the structure below.**

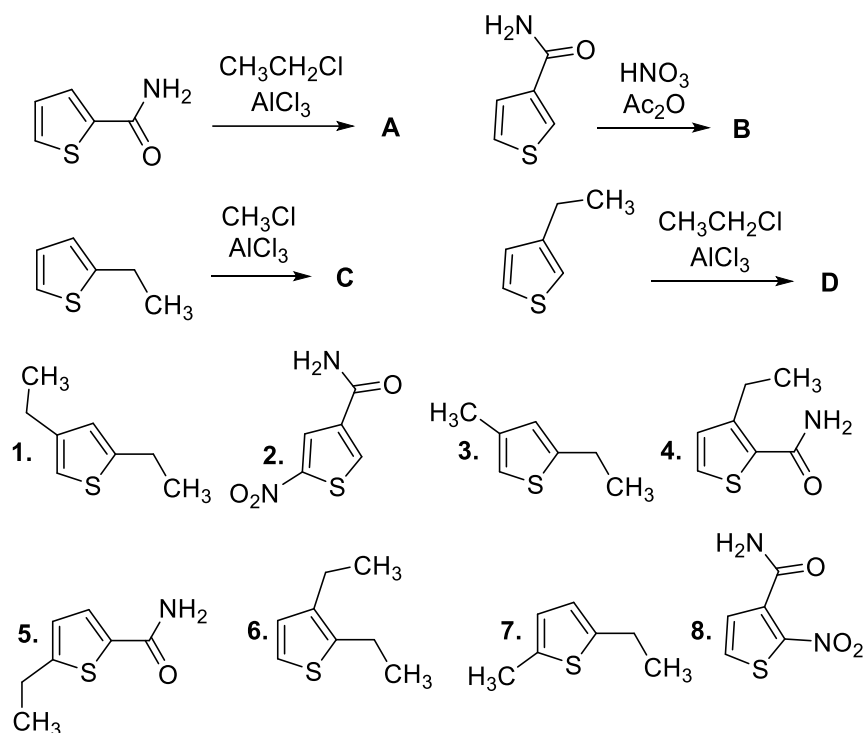


- A/ phenylhydrazine + butanone
- B/ phenylhydrazone + butanone
- C/ phenylhydrazine + butanal
- D/ phenylhydrazone + butanal

49. Give the main products of the following reactions.



50. Give the main products of the following reactions.

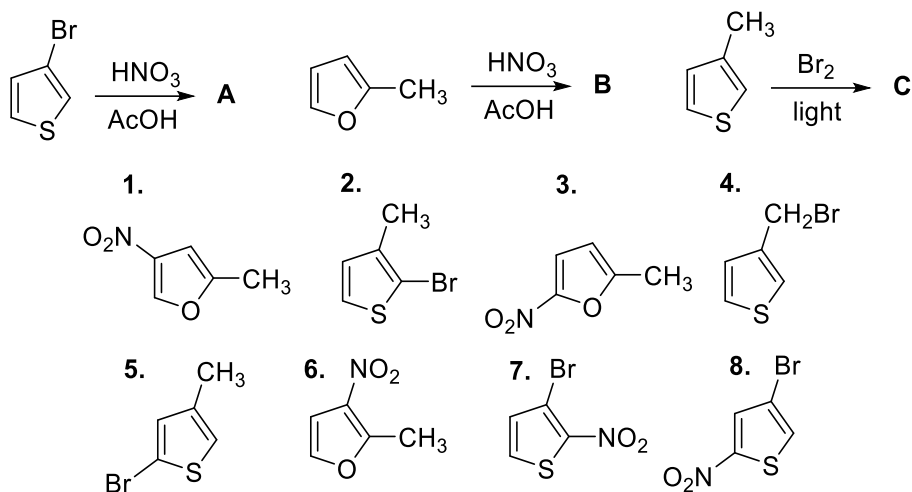


51. Choose the correct statement!

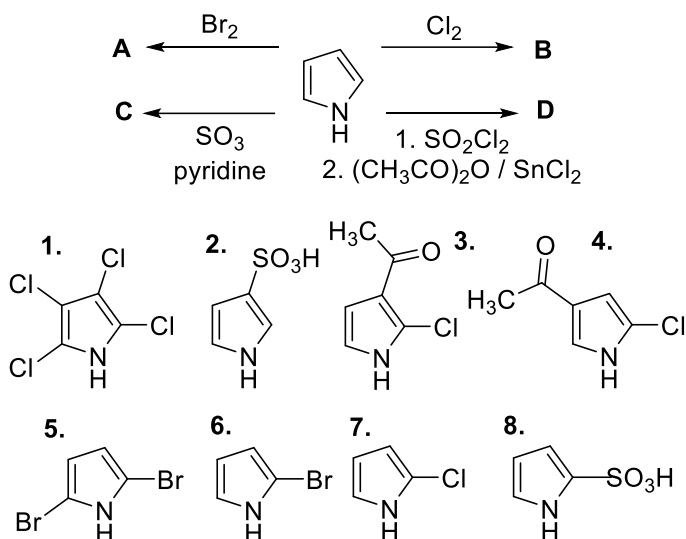
- A/ By reacting pyrrole with sulfur trioxide in the presence of pyridine, pyrrole-3-sulfonic acid is obtained.
- B/ Under milder conditions, using acetyl nitrate, dinitroindole is obtained from pyrrole.
- C/ With concentrated nitric acid nitroindole is obtained from pyrrole.
- D/ Concentrated nitric acid decomposes the aromatic ring of pyrrole.



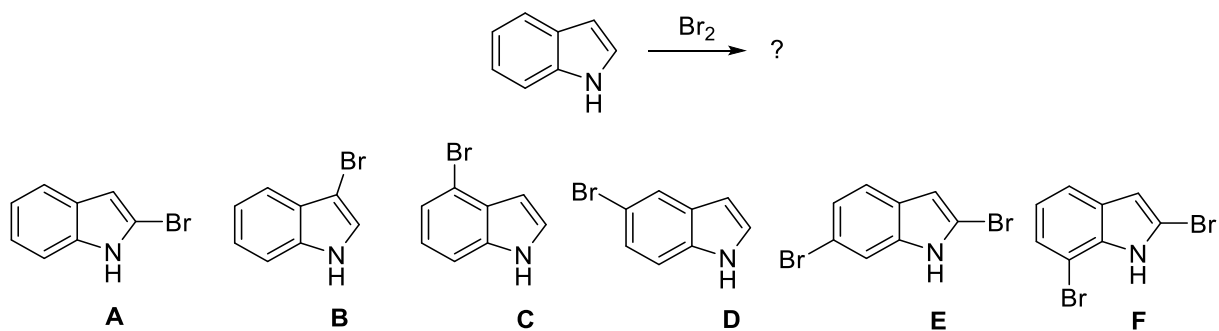
52. Give the main products of the following reactions.



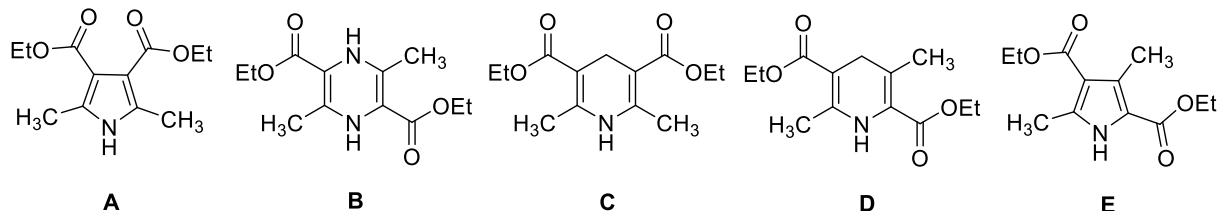
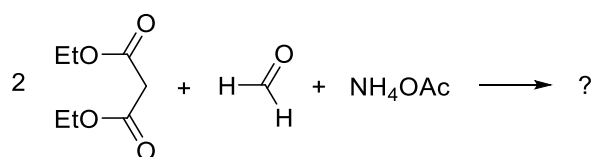
53. Complete the reaction scheme below with the appropriate products.



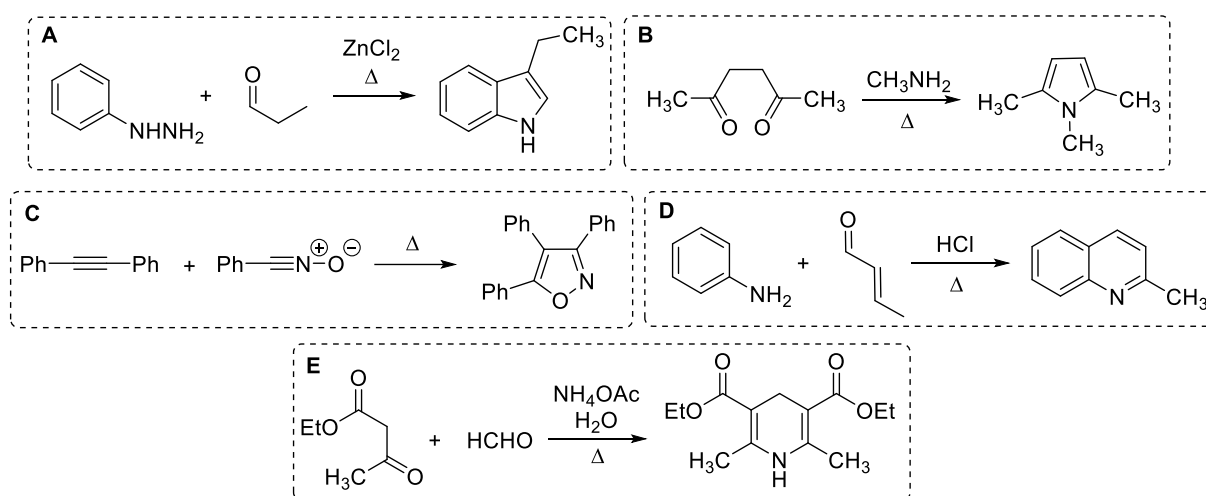
54. What is the main product of the following reaction?



55. What is the main product of the following reaction?



56. In which of the following reactions not the indicated product is formed?



57. Match the reagents below with the corresponding name reactions.

A/ 1,4-dicarbonyl derivative + strong mineral acid

1. Skrap quinoline synthesis

B/ anilin + glicerin + kénsav + oxidálószer

2. Perkin coumarin synthesis

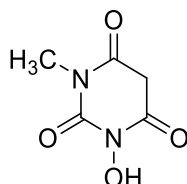
C/ szalicilaldehid + ecetsavanhidrid

3. Paal-Knorr furan synthesis

D/ arilhidrazin + karbonilvegyület

4. Fischer indole synthesis

58. Choose the appropriate starting compounds to prepare the structure below.



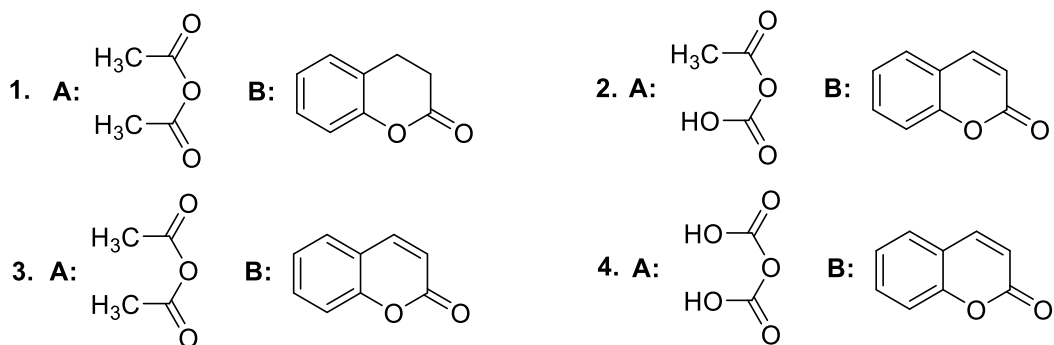
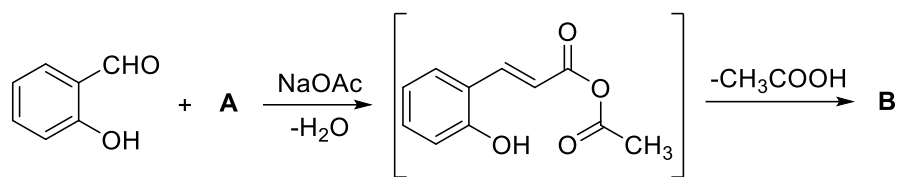
A/ diethyl malonate + urea

B/ *N*-hydroxy-*N'*-methylurea + acetaldehyde

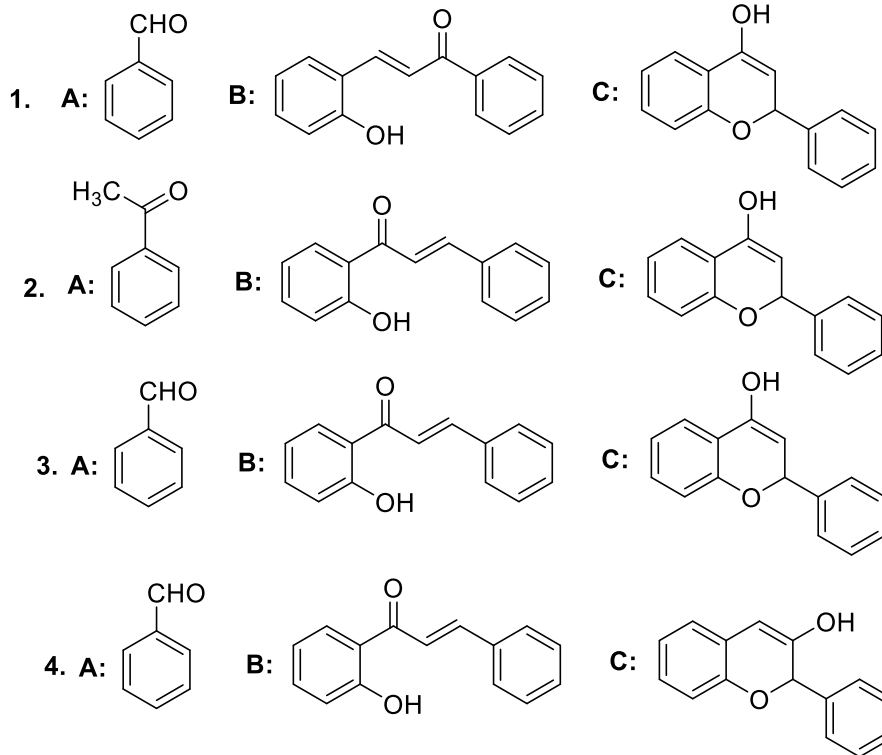
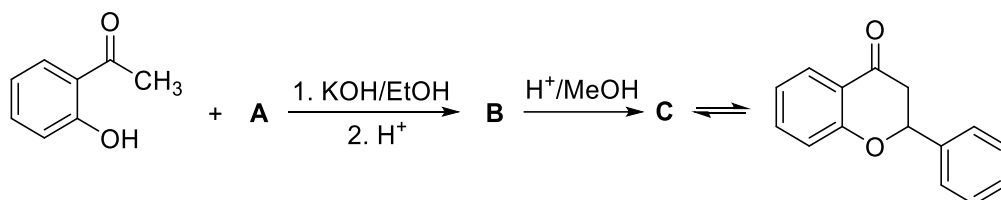
C/ diethyl malonate + phenylhydrazine

D/ diethyl malonate + *N,N'*-dimethylurea

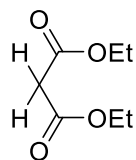
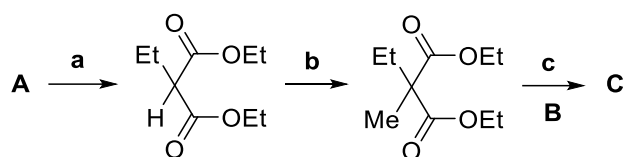
59. Give the missing products and the reagent in the reaction scheme below.



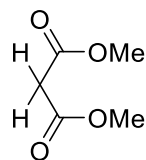
60. Give the missing products and the reagent in the reaction scheme below.



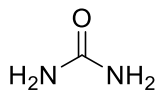
61. Complete the following reaction scheme with the appropriate reagents (a-c) and products (A-C)!



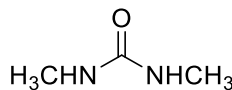
I



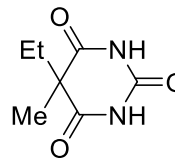
II



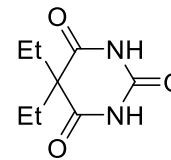
III



IV



V



VI

NaOEt

1.

NaOH

2.

1. NaOMe; 2. MeI

3.

1. NaOEt; 2. MeI

4.

1. NaOEt; 2. EtI

5.

1. NaOH; 2. EtI

6.

62. Choose the correct answers! During the Skraup synthesis of dihydroquinoline:

A/ the first step is a Michael addition

B/ in the first step a Schiff's base is formed

C/ the starting compounds are aniline and acrolein

D/ the starting compounds are aniline and glycerol

63. From which components can 1-methylisoquinoline be prepared?

A/ 2-phenylethylamine + acetyl chloride

B/ N-methylpyridine + 1,2-dibromobenzene

C/ acetic acid chloroimine + styrene

D/ aniline + acrolein

64. From which components can quinoline be prepared?

A/ 3-phenylpropylamine + acrylic acid

B/ aniline + akrolein

C/ 2-phenylethylamine + acetyl chloride

D/ pyridine + 1,2-dichlorobenzene

65. Choose the correct answers! When 1,2-phenylenediamine is reacted with...

A/ ...1,2-benzoquinone, a quinoxaline product is obtained

B/ ...glyoxal, a phenazine product is obtained

C/ ...glyoxal, a quinoxaline product is obtained

D/ ... 1,2-benzoquinone, a phenazine product is obtained

66. What is the major product of the Chichibabin reaction of pyridine?

A/ N-aminopyridine

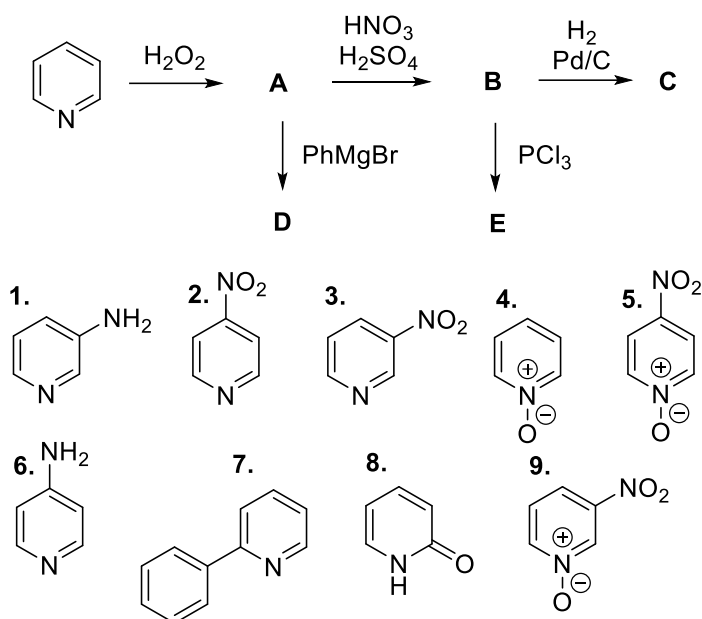
B/ pyridine-2-amine

C/ pyridine-3-amine

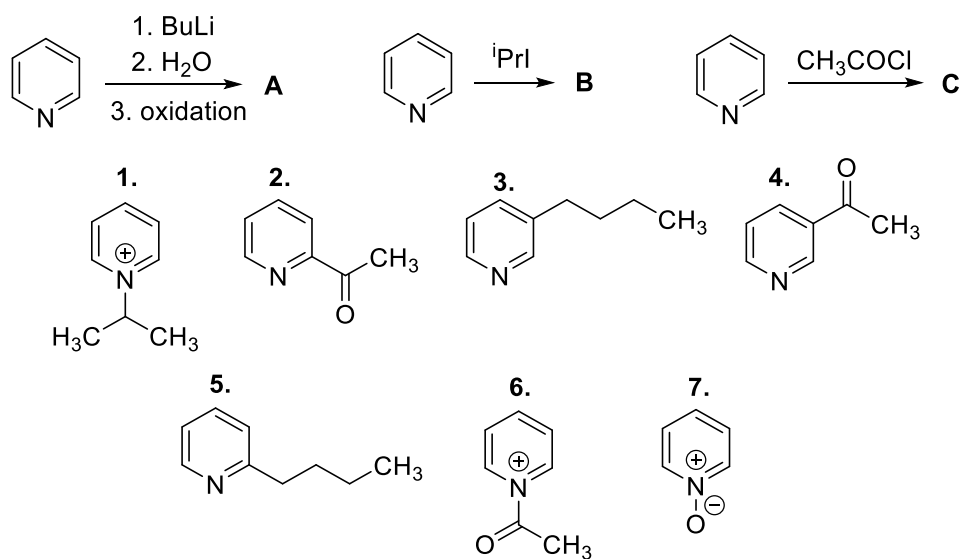
D/ pyridine-4-amine



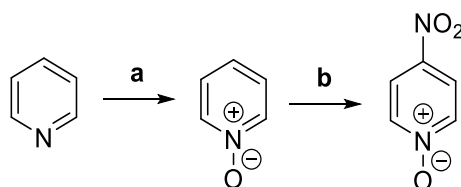
67. Complete the following scheme with the missing structures!



68. Give the major products of the following reactions!



69. Complete the following reaction scheme with the missing reagents!



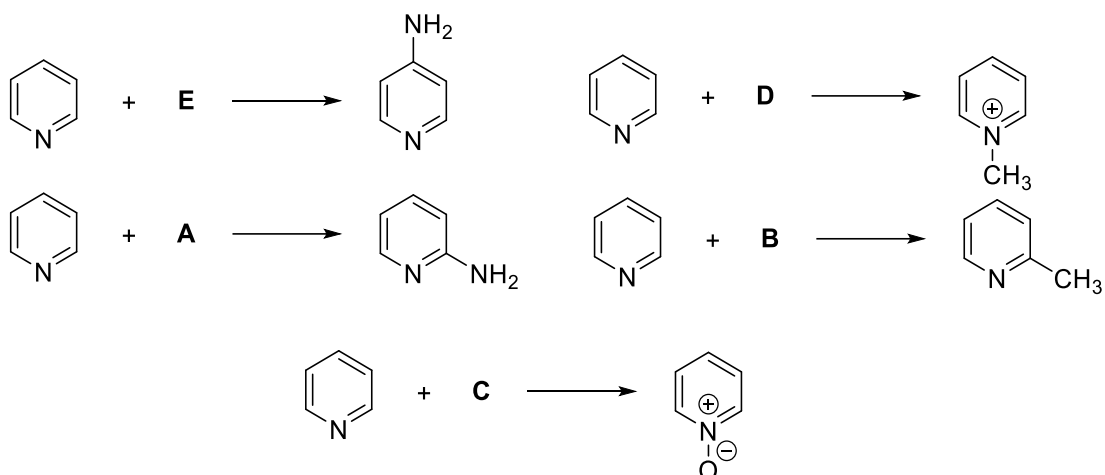
A/ a:  $\text{H}_2\text{O} / \text{HCl}$  and b:  $\text{NaNO}_2 / \text{HCl}$

B/ a:  $\text{H}_2\text{O}_2 / \text{AcOH}$  and b:  $\text{NaNO}_2 / \text{HCl}$

C/ a:  $\text{H}_2\text{O}_2 / \text{AcOH}$  and b:  $\text{HNO}_3 / \text{H}_2\text{SO}_4$

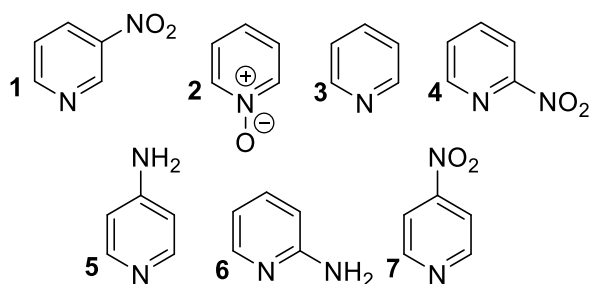
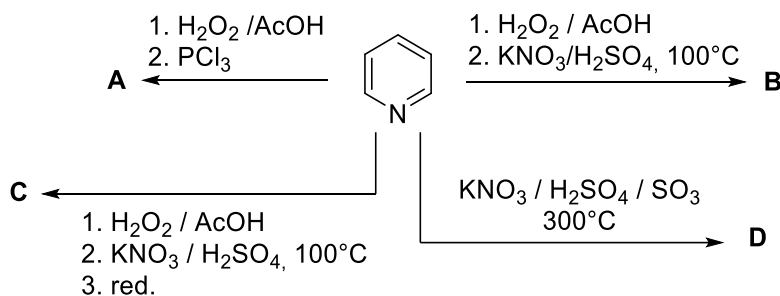
D/ a:  $\text{H}_2\text{O} / \text{HCl}$  and b:  $\text{HNO}_3 / \text{H}_2\text{SO}_4$

70. Complete the following reactions with the missing reagents!



- |   |   |  |                        |
|---|---|--|------------------------|
| 1. 1. H <sub>2</sub> O <sub>2</sub> , CH <sub>3</sub> COOH<br>2. HNO <sub>3</sub> /H <sub>2</sub> SO <sub>4</sub><br>3. Pd/H <sub>2</sub> | 2. 1. H <sub>2</sub> O <sub>2</sub> , CH <sub>3</sub> COOH<br>2. PCl <sub>3</sub> | 3. 1. H <sub>2</sub> O <sub>2</sub> , CH <sub>3</sub> COOH<br>2. HNO <sub>3</sub> /H <sub>2</sub> SO <sub>4</sub><br>3. PCl <sub>3</sub><br>4. Pd/H <sub>2</sub><br>7. CH <sub>3</sub> I | 4. NaNH <sub>2</sub>   |
| 5. H <sub>2</sub> O <sub>2</sub> , CH <sub>3</sub> COOH   | 6. 1. CH <sub>3</sub> Li<br>2. H <sub>2</sub> O, Δ<br>3. oxidation                |  | 8. NH <sub>4</sub> OAc |

71. Complete the following reaction scheme with the appropriate products!



72. Choose the correct answer: S<sub>E</sub>Ar or S<sub>N</sub>Ar or neither!

The reaction of pyridine with the following reagents:

A/ Cl<sub>2</sub> / FeCl<sub>3</sub>

B/ Pd / H<sub>2</sub>

C/ SO<sub>3</sub>

D/ CH<sub>3</sub>MgBr

E/ SO<sub>3</sub> / cc.H<sub>2</sub>SO<sub>4</sub>

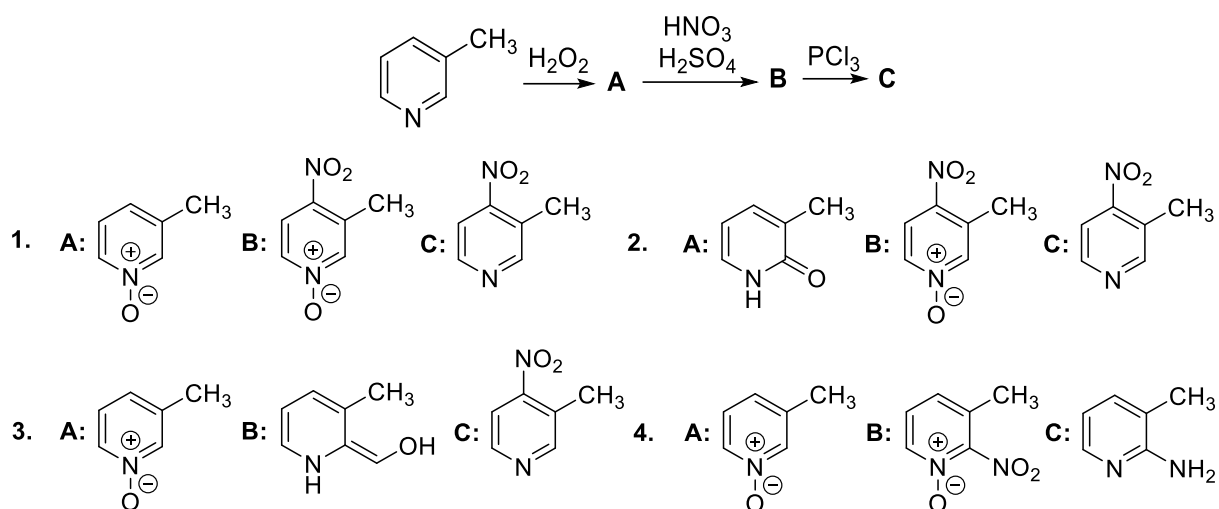
1. S<sub>E</sub>Ar

2. S<sub>N</sub>Ar

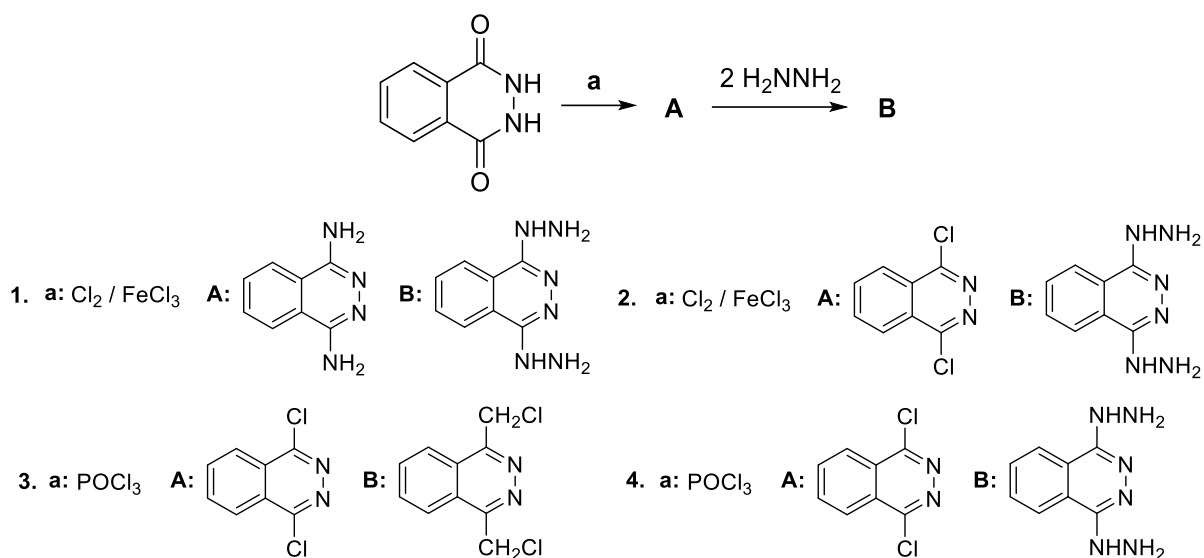
3. neither



**73. Give the missing structures!**



**74. Complete the following synthesis with the appropriate reagent (a) and products (A-B).**



**75.  $\text{S}_{\text{E}}\text{Ar}$  or  $\text{S}_{\text{N}}\text{Ar}$  or neither?**

A/ the nitration of pyridine-*N*-oxide

B/ the reaction of 2-methylthiophene with *N*-bromosuccinimide under light

C/ the reaction of quinoline with sodium amide

D/ the sulfonation of isoquinoline

E/ the reaction of pyrimidine with hydrogen gas

1 –  $\text{S}_{\text{E}}\text{Ar}$

2 –  $\text{S}_{\text{N}}\text{Ar}$

3 – neither

**76. What is the major product of the Chichibabin reaction of quinoline?**

A/ *N*-aminoquinoline

B/ quinoline-4-amine

C/ quinoline-2-amine

D/ quinoline-3-amine



**77. Mark the correct answer for sulfonation of isoquinoline:**

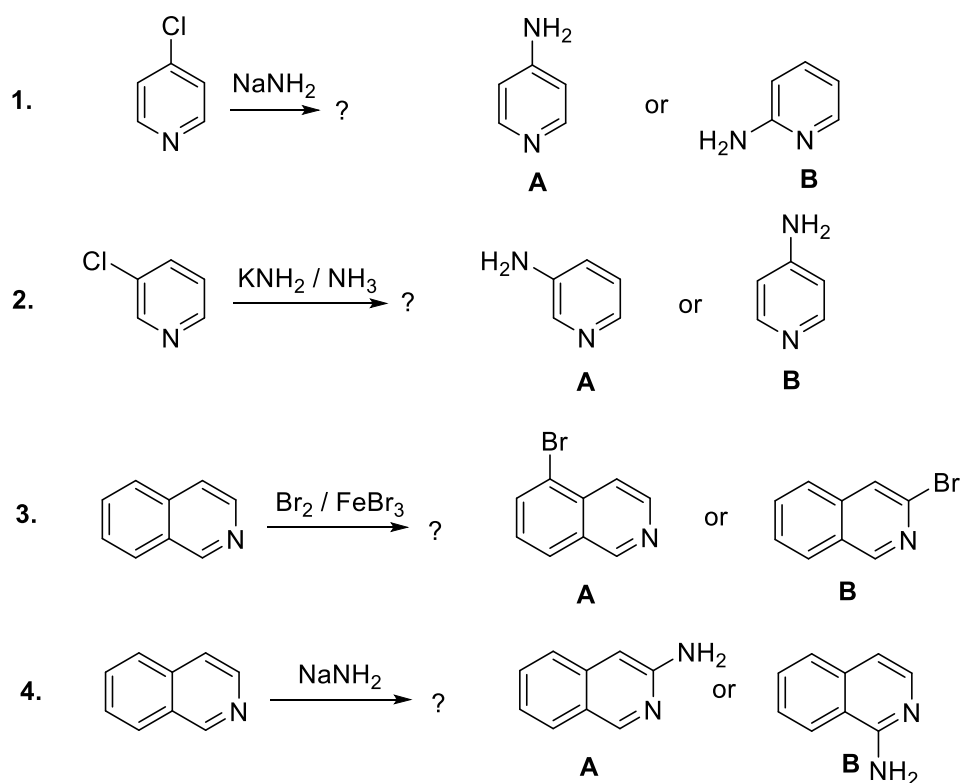
A/ the reaction takes place only in position 4

B/ the reaction takes place only in position 6

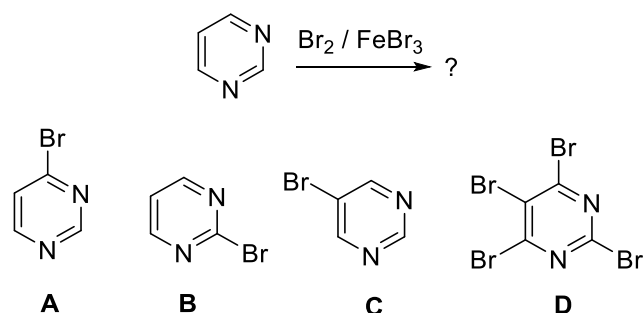
C/ the reaction takes place only in position 7

D/ there will be more of the product sulfonated in position 5 than the product sulfonated in position 8

**78. Give the major products of the following reactions!**



**79. Give the major product of the following reaction!**



**80. Which of the reactions carried out with the following reagents take place primarily on the HETERORING of quinoline?**

A/  $\text{NaNH}_2/\text{liquid NH}_3$

B/  $\text{Br}_2$

C/  $\text{CH}_3\text{I}$

D/  $\text{R-Li/THF}$





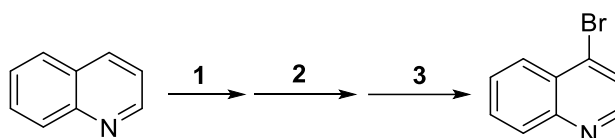
**81. Choose the correct statements! In the presence of  $\text{KMnO}_4$ , quinoline is:**

- A/ oxidized on the carbocycle under acidic conditions
- B/ oxidized on the carbocycle under basic conditions
- C/ oxidized on the heterocycle under acidic conditions
- D/ oxidized on the heterocycle under basic conditions

**82. What is the product of the sulfonation of quinoline under kinetic and thermodynamic control?**

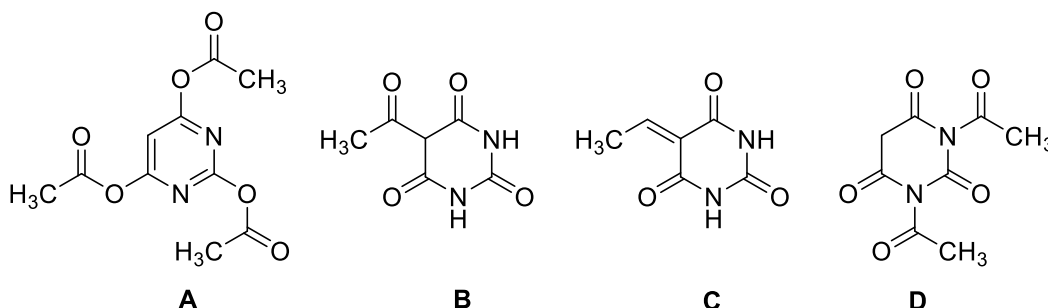
- A/ under kinetic control, it is sulfonated primarily in position 6
- B/ under thermodynamic control, it is sulfonated primarily in position 6
- C/ under thermodynamic control, it is sulfonated primarily in positions 5 and 8
- D under kinetic control, it is sulfonated primarily in positions 5 and 8

**83. What are the appropriate reagents and what is their correct order for the following synthesis?**

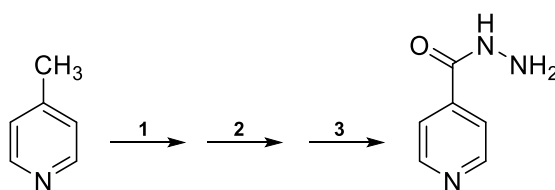


- |                                 |                     |                            |
|---------------------------------|---------------------|----------------------------|
| A – $\text{PCl}_3$              | B – $\text{KMnO}_4$ | C – $\text{NaNO}_2$        |
| D – $\text{Br}_2/\text{FeBr}_3$ | E – $\text{KBr}$    | F – $\text{H}_2\text{O}_2$ |

**84. Choose the product of the reaction of barbituric acid with acetaldehyde.**

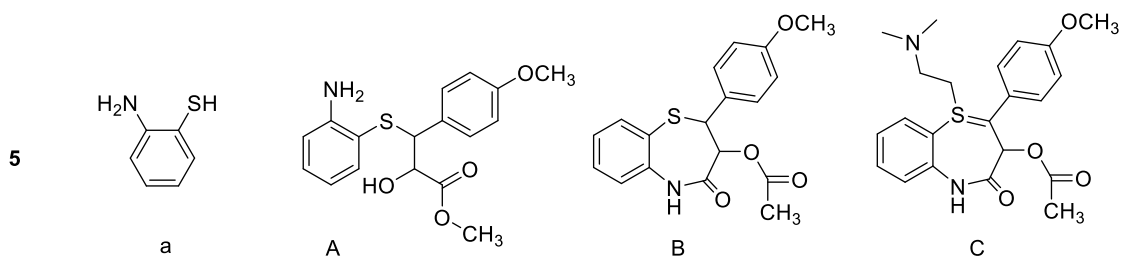
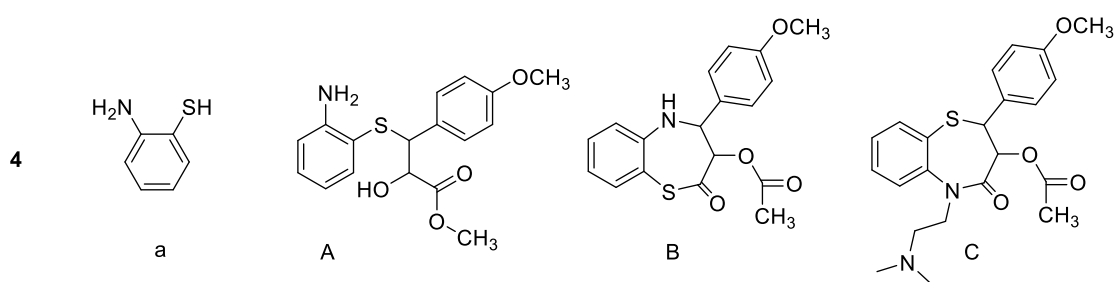
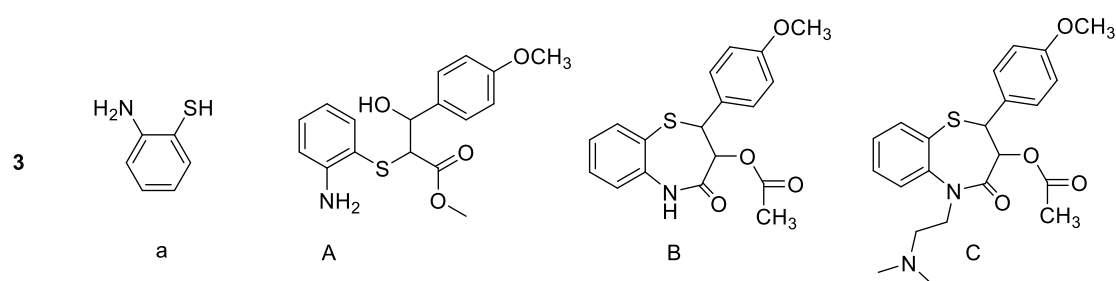
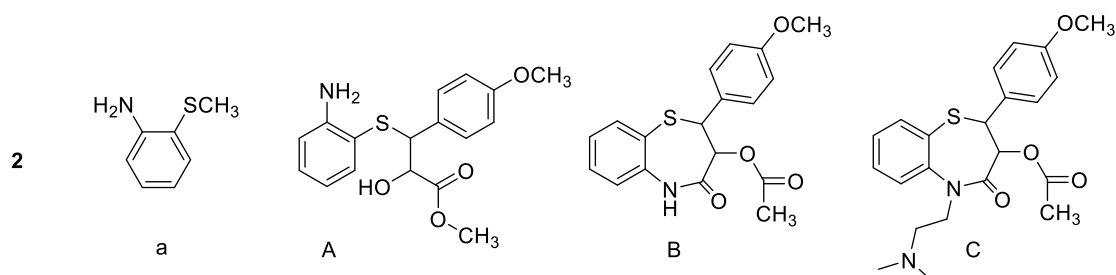
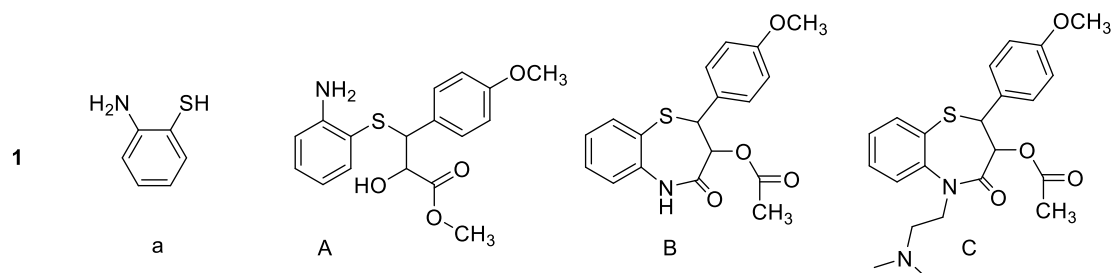
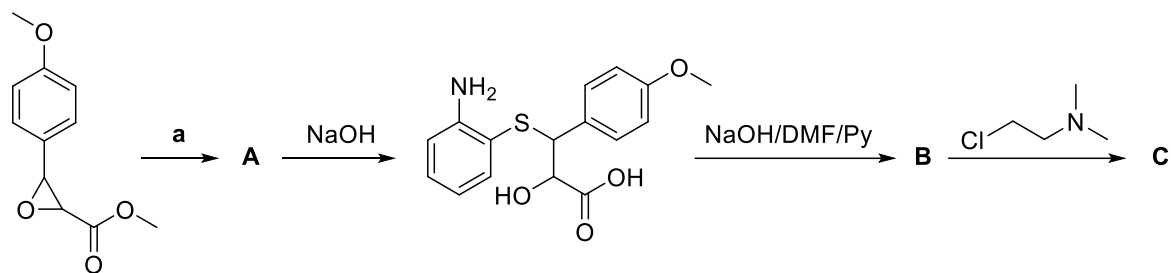


**85. What is the correct order of the reaction steps?**

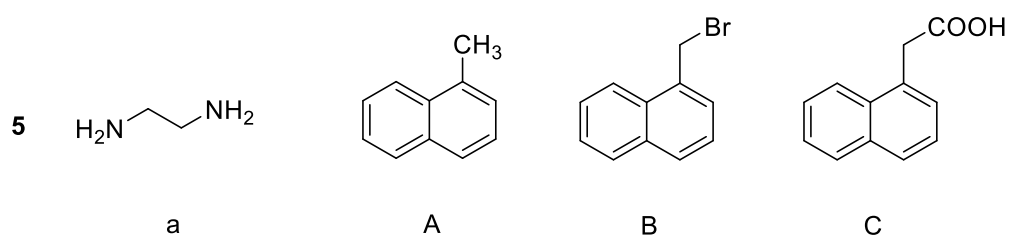
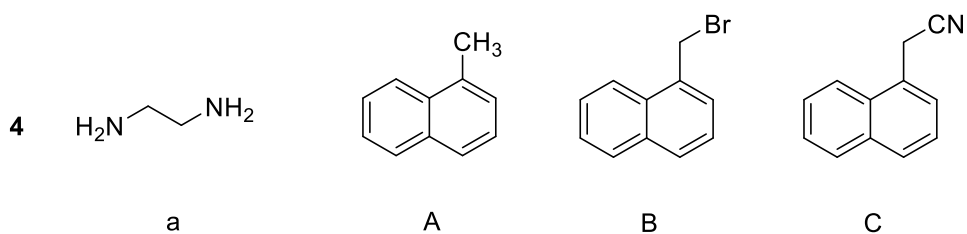
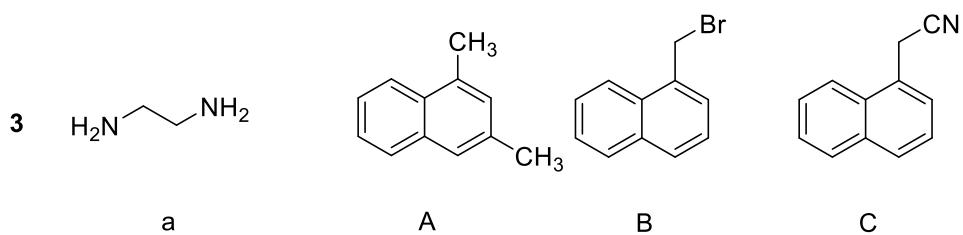
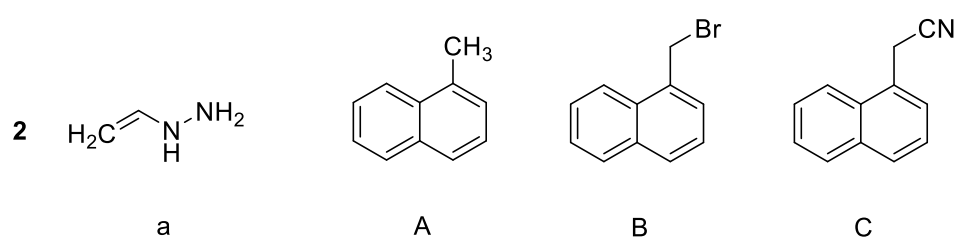
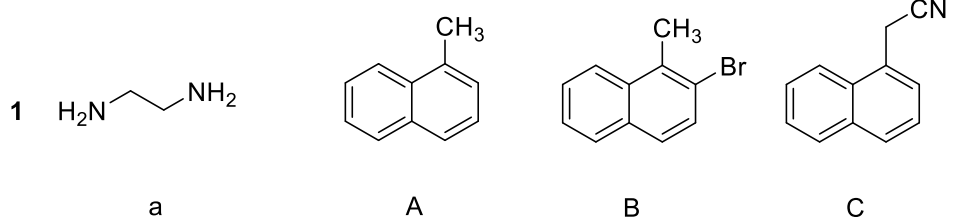
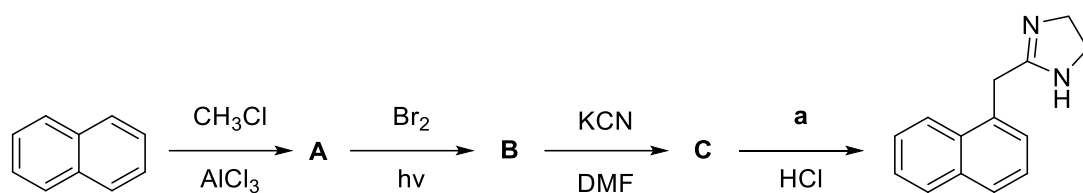


- |   |                             |                    |
|---|-----------------------------|--------------------|
| A/ $\text{CH}_3\text{CH}_2\text{OH} / \text{H}^+$ | B/ $\text{H}_2\text{NNH}_2$ | C/ $\text{KMnO}_4$ |
|---|-----------------------------|--------------------|

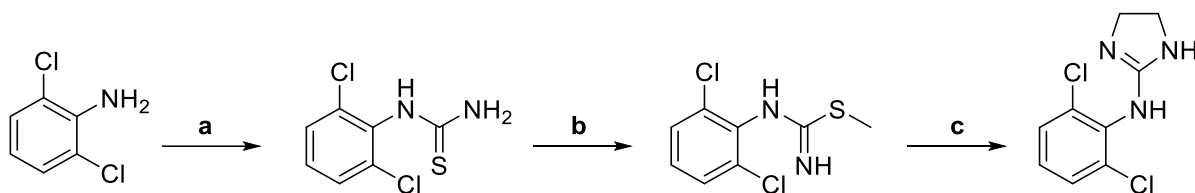
86. Complete the following synthetic pathway with the missing reagent (a) and products (A-C)!



87. Complete the following synthetic pathway with the missing reagent (a) and products (A-C)!



88. Give the missing reagents of the following synthesis!



A/  $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$

B/  $\text{K}_4\text{SCN}$

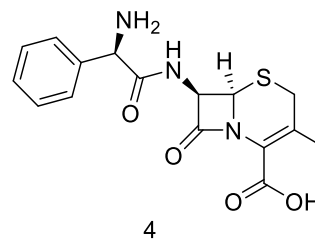
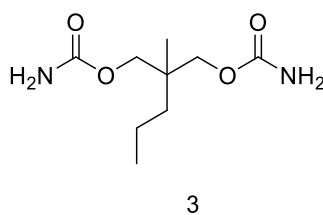
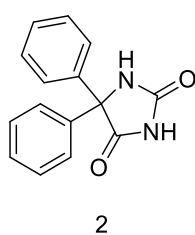
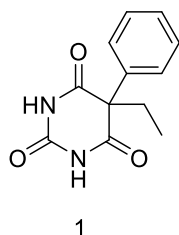
C/  $\text{CH}_3\text{I}$

D/  $\text{H}_2\text{N}-\text{CH}=\text{CH}-\text{NH}_2$

E/  $\text{NH}_4\text{SCN}$

F/  $\text{CH}_3\text{OH}$

89. Match the compounds with the structural elements they contain!



A/ carbamate derivative

B/ pyrimidine derivative

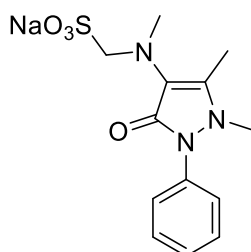
C/ hydantoin derivative

D/ guanidine derivative

E/ hydrazide derivative

F/  $\beta$ -lactame derivative

90. Which statement is false about the compound below?



A/ It contains a lactame moiety.

C/ It has a 3-pyrazolidinone core structure.

D/ It contains two basic nitrogens.

E/ It has a methyl(sulfomethyl)amino group in position 4.

## 10. Heterocyclic compounds

### Solutions

1. A – 1, B – 1, C – 1, D – 2, E – 3, F – 3

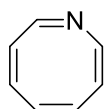
Conditions for the formation of an aromatic system (Hückel):

- the atomic framework (more precisely, the orbitals that build up the aromatic system) forming the ring should be coplanar (or nearly coplanar)

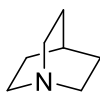
- all atoms forming the ring should have  $p_z$ -atomic orbitals

-  $4n+2$  ( $n=0$  or positive integer)  $p$ -electrons should take part in the delocalization

Indolizine is considered aromatic only because of the pyrrole ring and not because of the total number of  $\pi$ -electrons. Azocine derivatives move out from the plane and are therefore not aromatic, but a not aromatic system containing high-energy conjugated double bonds.



azocine



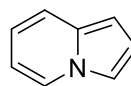
quinuclidine



azet



thiazole



indolizine



triazine

2. A – 1, B – 3, C – 3, D – 2, E – 1

3. A – 3, B – 3, C – 1, D – 1, E – 1

4. C

5. D

*Pyrrole, furan and thiophene belong to  $\pi$ -electron excessive aromatic heterocycles.*

*Pyridine is a the  $\pi$ -electron deficient aromatic heterocycle.*

6. A

7. D

8. A – 1, B – 1, C – 2, D – 2

9. C

10. A – 2, B – 1, C – 2, D – 1, E – 2, F – 1, G – 2, H – 1, I – 2, J – 2, K – 1

*A,G/ The five-membered heteroaromatic compounds containing one heteroatom belong to the  $\pi$ -electron-excessive aromatic heterocycles (pyrrole, thiophene, furan). Pyrrole and furan are sensitive to acids.*

*B/ The six-membered heteroaromatic compounds containing one heteroatom belong to the  $\pi$ -electron-deficient aromatic heterocycles (pyridine).*

*C,D/ In  $\pi$ -electron deficient heteroaromatic compounds, the non-bonding electron pair of the heteroatom is not involved in delocalisation, whereas in  $\pi$ -electron excessive heteroaromatic compounds the non-bonding electron pair of the heteroatom is also involved in delocalisation.*



*E,F/ The  $\pi$ -electron-deficient heteroaromatic compounds react relatively easily in  $S_NAr$  reactions. The reactivity of  $\pi$ -electron-excessive heteroaromatic compounds in electrophilic substitution reactions is enhanced compared to benzene.*

*H/ Six-membered heteroaromatic compounds containing one heteroatom can be prepared from 1,5-dioxo compounds.*

*I/ Five-membered heteroaromatic compounds containing one heteroatom can be prepared from 1,2- and 1,4-dioxo compounds.*

*J/ From five-membered heteroaromatic compounds containing one heteroatom with electrophilic reagents under kinetic control the 2-substituted product is formed (resonance-stabilized  $\sigma$ -complex).*

*K/ In electrophilic substitution reactions, from pyridine products substituted at position 3 are obtained.*

11. C

12. A, B

*A, B: correct, because all three compounds are  $\pi$ -electron-excessive systems and are therefore more reactive in  $S_EAr$  reactions compared to benzene.*

*C: false, as the enumerated reactions are  $S_EAr$  reactions*

*D: false, as the electrophilic reaction proceeds with electrophilic reagents*

13. A

*Pyrazole is a  $\pi$ -electron-excessive heteroaromatic compound, although the second heteroatom reduces the  $\pi$ -electron density of the ring. Its electrophilic substitution reactions require a lower activation energy than benzene and are therefore faster. Pyridine is a  $\pi$ -electron deficient heteroaromatic compound, and its reactivity in electrophilic substitutions is decreased compared to benzene. Pyrimidine shows lower reactivity than pyridine.*

14. A

*Furan and thiophene are  $\pi$ -electron-excessive heteroaromatic compounds. Their electrophilic substitution reactions require a lower activation energy than benzene and are therefore faster. Experimental data demonstrate the higher reactivity of furan in e.g. acetylation and formylation reactions. Pyridine is a  $\pi$ -electron deficient heteroaromatic compound with a lower reactivity in electrophilic substitutions compared to benzene.*

15. B

*Of the listed compounds thiophene is the most  $\pi$ -electron-excessive heteroaromatic system and therefore the most reactive in  $S_EAr$  reactions.*

16. B

*Thiophene is a  $\pi$ -electron-excessive heteroaromatic system, therefore it is more reactive than the benzofused systems in  $S_EAr$  reactions, while indole contains a pyrrole ring, which is a  $\pi$ -electron-excessive ring, therefore it is more reactive than naphthalene. Pyrazine is a  $\pi$ -electron deficient heteroaromatic system and thus shows decreased reactivity in  $S_EAr$  reactions.*

17. 2



Furan and thiophene are  $\pi$ -electron-excessive heteroaromatic systems and are therefore more reactive in  $S_EAr$  reactions than benzene and pyrimidine (the latter being a  $\pi$ -electron deficient heteroaromatic system).

18. B

Thiophene and furan are  $\pi$ -electron-excessive heteroaromatic compounds and are therefore more reactive in  $S_EAr$  reactions than benzene. The  $S_EAr$  reactivity order is: thiophene > pyrrole > furan.

19. D

20. B

21. A

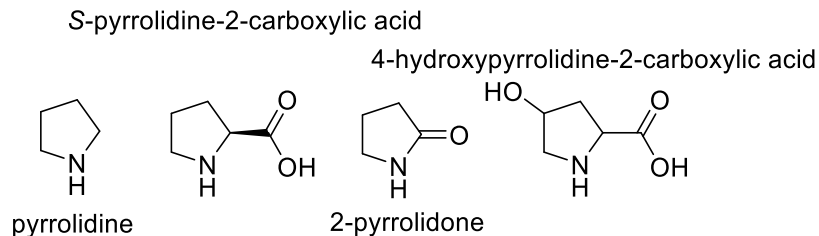
22. A, D

The basicity of diazines decreases in the  $1,2 > 1,3 > 1,4$  order. In piperidine, the nitrogen is in  $sp^3$  hybrid state, it is more basic than the  $sp^2$  or  $sp$  hybrid state nitrogens.

23. D

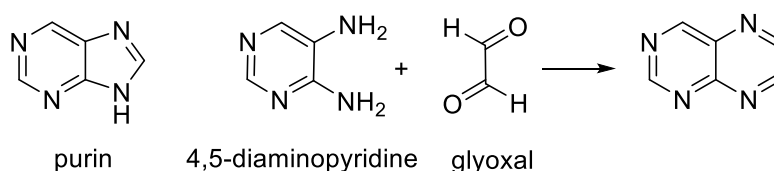
In pyrrole, the non-bonding electron pair of the nitrogen contributes to the  $6\pi$ -electron aromatic system, therefore the nitrogen does not have a basic character (the proton is bonded to carbon 3, in small degree). The nitrogen atom of pyrrole can be deprotonated by strong bases in anhydrous media.

24. A



25. A, B

26. B



27. B

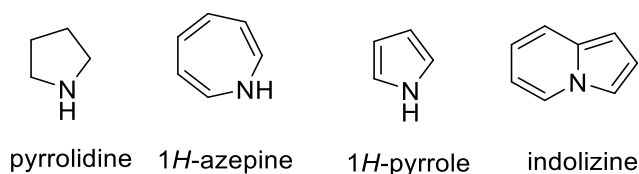
28. E

29. D

30. A



Amines containing multiple bonded nitrogen atoms (e.g. pyridine, pyrrole, imidazole) have lower basicity than the corresponding aliphatic amines (higher s-fraction in the hybrid state of the nitrogen atom). In pyrrole, the non-bonding electron pair of nitrogen contributes to the formation of the  $6\pi$ -electron aromatic system, therefore this nitrogen is not basic.



31. D

The basicity of six-membered heteroaromatic compounds containing two nitrogens depends on the position of the two nitrogen atoms relative to each other. The non-bonding electron pairs of nitrogen atoms at 1,2-position are significantly repelled by each other due to the space proximity. Protonation of a nitrogen atom reduces this effect, which is energetically advantageous. This effect decreases as the distance between the two nitrogen atoms increases, therefore the basicity order of diazines is: 1,2 > 1,3 > 1,4.

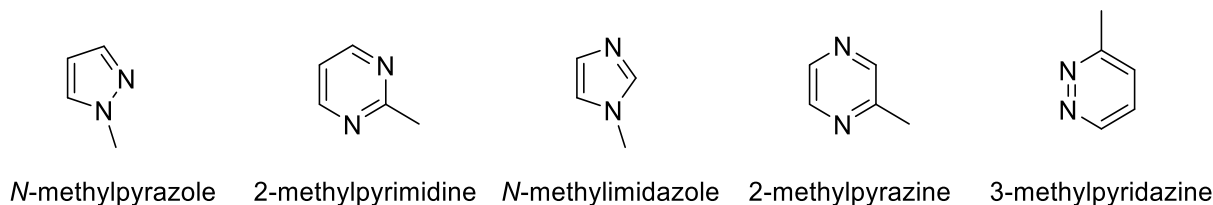
32. A

Amines containing multiple bonded nitrogen atoms (e.g. pyridine, pyrrole, imidazole) have lower basicity than the corresponding aliphatic amines (higher s-fraction in the hybrid state of the nitrogen atom). I

33. D

The basicity of six-membered heteroaromatic compounds containing two nitrogens depends on the position of the two nitrogen atoms relative to each other. The non-bonding electron pairs of nitrogen atoms at 1,2-position are significantly repelled by each other due to the space proximity. Protonation of a nitrogen atom reduces this effect, which is energetically advantageous. This effect decreases as the distance between the two nitrogen atoms increases, therefore the basicity order of diazines is: 1,2 > 1,3 > 1,4.

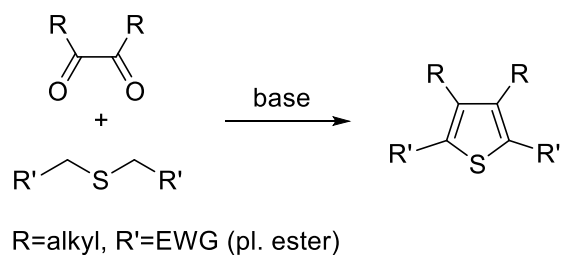
In five-membered heteroaromatic compounds with two nitrogens, both in the case of 1,2- and 1,3-position nitrogens, the resonance formed by the participation of the other heteroatom (the nitrogen with the N-H bond) increases the electron density at the newly introduced nitrogen atom, thus increasing the basicity. The negative inductive effect of the second heteroatom, in turn, decreases the electron density on the nitrogen, thus decreasing the basicity. The resulting effect is an increase in basicity compared to compounds with one heteroatom. As the -I effect decreases with distance, this effect is stronger at the 1,2-position, rendering the 1,2-isomers weaker bases (i.e. imidazole is a stronger base than pyrazole).



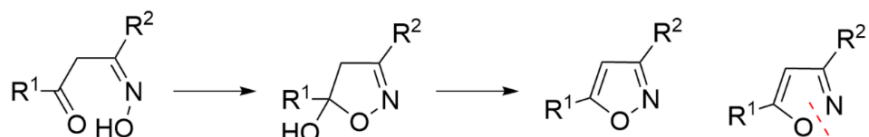
34. A

Furan, thiophene and pyrrole can be prepared by the cyclocondensation reaction of 1,2-diketones with the appropriate 2,2'-diacetic acid diesters [3+2]. In the case of thiophene, this is the so-called Hinsberg synthesis. In Hinsberg synthesis, the conversion can also be carried out in the presence of other electron-withdrawing groups than the ester group.





35. B



36. C

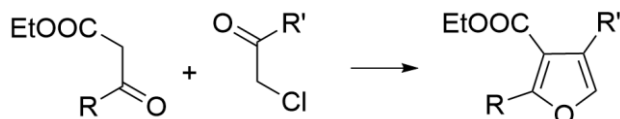
Substituted furan derivatives can be prepared from  $\alpha$ -haloketones and  $\beta$ -dicarbonyl compounds by Feist-Benary synthesis. The reaction can be catalysed by amines.

37. A

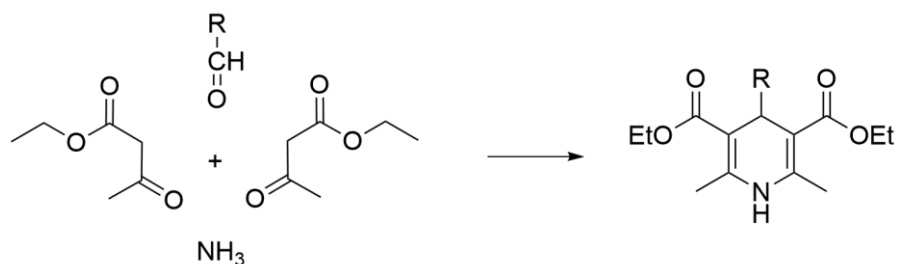
For the synthesis of thiophene from 1,4-dicarbonyl compounds, phosphorus pentasulphide can be used as a sulphur source.

38. A – 3, B – 2, C – 1, D – 4

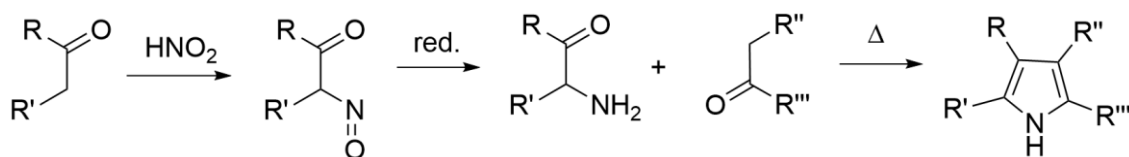
Feist-Benary synthesis



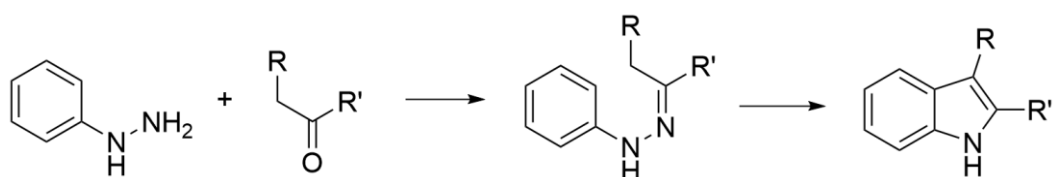
Hantzsch synthesis



Knorr synthesis

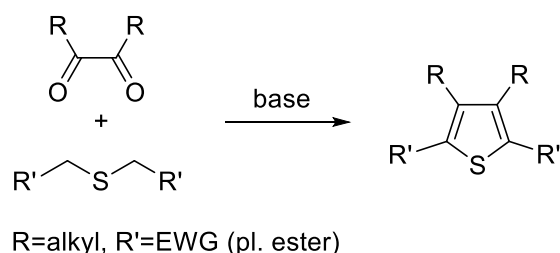


### Fischer indole synthesis



39. C

Furan, thiophene and pyrrole can be prepared by the cyclocondensation reaction of 1,2-diketones with the appropriate 2,2'-diacetic acid diesters [3+2]. In the case of thiophene, this is the so-called Hinsberg synthesis. In Hinsberg synthesis, the conversion can also be carried out in the presence of other electron-withdrawing groups than the ester group.



40. A

Upon the synthesis of heterocyclic compounds, the ring is often made up of several parts. Thiazole derivatives can be prepared from various carboxylic acid derivatives with 2-chloro ketones or 2-aminoketones ([3+2] cyclocondensations).

41. C

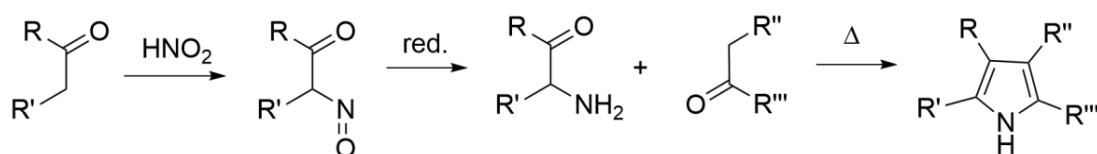
In the Paal-Knorr synthesis of thiophene derivatives, phosphorus pentasulphide can be the source of sulphur.

42. A

Upon the synthesis of heterocyclic compounds, the ring is often made up of several parts. Oxazole derivatives can be prepared from various carboxylic acid derivatives with 2-halo ketones or 2-aminoketones ([3+2] cyclocondensations).

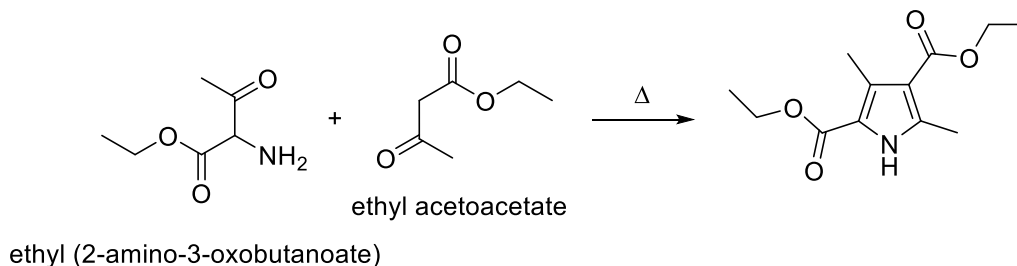
43. A, C, D

Knorr pyrrole synthesis is a condensation reaction of an  $\alpha$ -aminoketone or an  $\alpha$ -amino- $\beta$ -ketoester with a compound containing an active methylene group. The  $\alpha$ -aminoketone is often prepared in situ by nitrosation of the ketone and reduction of the resulting  $\alpha$ -nitrosoketone (which tautomerizes to the isonitroso form). A mixture of zinc powder and acetic acid is commonly used for the reduction, this reagent does not reduce ketones or esters. The compound containing the active methylene group is often a 1,3-diketone, a  $\beta$ -ketoester or a  $\beta$ -cyanoester. With secondary aminoketones N-substituted pyrrole derivatives can also be prepared.



44. A

Knorr pyrrole synthesis is a condensation reaction of an  $\alpha$ -aminoketone or an  $\alpha$ -amino- $\beta$ -ketoester with a compound containing an active methylene group. The  $\alpha$ -aminoketone is often prepared in situ by nitrosation of the ketone and reduction of the resulting  $\alpha$ -nitrosoketone (which tautomerizes to the isonitroso form). A mixture of zinc powder and acetic acid is commonly used for the reduction, this reagent does not reduce ketones or esters. The compound containing the active methylene group is often a 1,3-diketone, a  $\beta$ -ketoester or a  $\beta$ -cyanoester.



45. D

When pyrrole derivatives are prepared by Paal-Knorr synthesis, the starting material is heated with ammonia or a primary amine.

46. B

The Hinsberg synthesis is a cyclocondensation reaction of 1,2-diketones and the appropriate 2,2'-diacetic acid diester derivatives in the presence of sodium or potassium alkoxide.

47. A - 1, B - 2, C - 4, D - 5

48. C

49. A - 7, B - 6, C - 1, D - 4

A, B, C - In the case of kinetic control, with electrophilic reagents the 2-substituted product is formed from pyrrole (resonance-stabilized  $\sigma$ -complex). When carrying out the substitution reaction, it must be taken into account that pyrrole is sensitive to acids.

D - Pyrrole is sensitive to acids (a polymerization reaction takes place).

50. A - 5, B - 2, C - 7, D - 6

In the case of kinetic control, with electrophilic reagents the 2-substituted product is formed from thiophene (resonance-stabilized  $\sigma$ -complex). The entry of the second substituent is influenced by the substituents of the heteroring already present in the same way as in the case of benzene (activation, directing effects). In the question, the formation of the 2,5-disubstituted product is expected due to the effect of the heteroatom.

A - The formation of the 2,5-disubstituted product is expected due to the effect of the heteroatom

B - Due to the effect of the substituent and the heteroatom, the formation of the 2-nitro product is expected

C - The formation of the 2-methyl product is expected due to the effect of the substituent and the heteroatom.

D - Due to the effect of the substituent and the heteroatom, the formation of the 2,3-disubstituted product is expected.

51. D



Pyrrole is sensitive to acids. Under mild conditions, aromatic electrophilic substitution gives the 2-monosubstituted product.

52. A – 7, B – 3, C - 4

In the case of kinetic control, with electrophilic reagents the 2-substituted product is formed from thiophene (resonance-stabilized  $\sigma$ -complex). The entry of the second substituent is influenced by the substituents of the heteroring already present in the same way as in the case of benzene (activation, directing effects).

A - Due to the effect of the substituent and the heteroatom, the formation of the 2-nitro product is expected

B - The formation of the 2,5-disubstituted product is expected due to the effect of the heteroatom

C – Under the given conditions, a product brominated in the side chain can be prepared by a reaction with a radical mechanism.

53. A – 6, B – 7, C – 8, D - 4

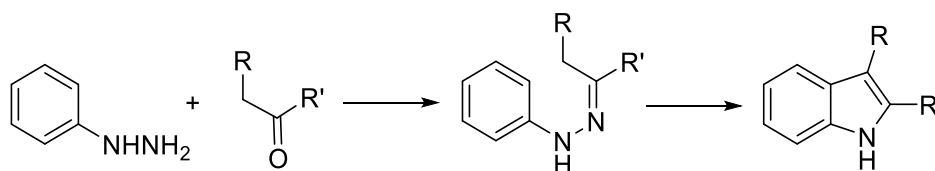
In the case of kinetic control, with electrophilic reagents the 2-substituted product is formed from pyrrole (resonance-stabilized  $\sigma$ -complex). The entry of the second substituent is influenced by the substituents of the heteroring already present in the same way as in the case of benzene (activation, directing effects).

54. B

55. C

In the Hantzsch synthesis, from two molecules of an identically disubstituted ketone/ $\beta$ -ketoester (e.g. ethyl acetoacetate) and one molecule of an aldehyde in an ammonia medium a 1,4-dihydropyridine derivative is obtained, which leads to a pyridine derivative upon oxidation.

56. A



57. A – 3, B – 1, C – 2, D - 4

58. D

59. 3

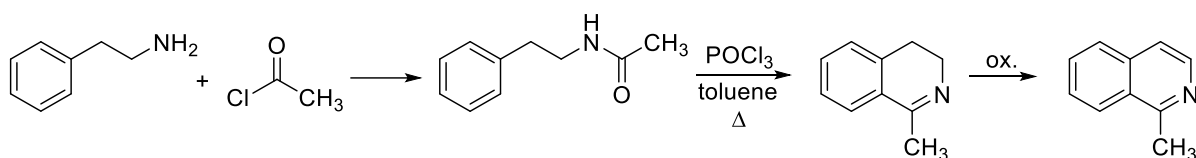
60. 3

61. A – I, B – III, C – V, a – 5, b – 4, c - 1

62. A, C

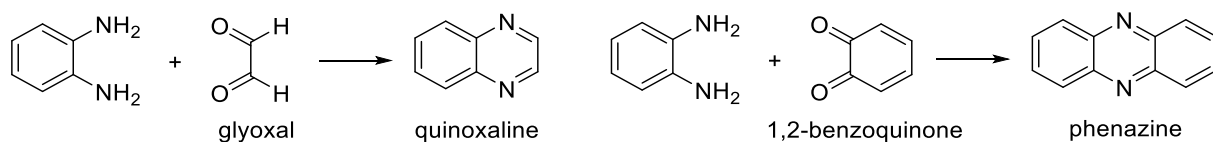
63. A

By the so-called Bischler-Napieralski reaction, 3,4-dihydroisoquinolines can be prepared from the  $\beta$ -ethylamide derivatives of electron-dense aryl compounds using  $\text{P}_2\text{O}_5$ ,  $\text{POCl}_3$  or  $\text{ZnCl}_2$  reagents. Oxidation of the product leads to the formation of the corresponding isoquinoline derivative.



64. B

65. C, D



66. B

The Chichibabin reaction is a  $S_NAr$  reaction proceeding via an addition-elimination mechanism, that is suitable for the introduction of an amino group (pyridine + sodium amide). The metal cation plays a coordinating role during the transformation, the product of which is 2-aminopyridine.

67. A – 4, B – 5, C – 6, D – 7, E – 2

Pyridine can be oxidized to N-oxide with peroxy acids or hydrogen peroxide. Pyridine N-oxide reacts more readily with electrophilic reagents than pyridine. The N-oxide group stabilizes the  $\sigma$ -complexes leading to products substituted in the 2- and 4-position. Upon nitration, substitution at the 2-position takes place to a lesser extent due to the steric hindrance between the oxide anion and the entering nitro group, and the repulsion between the negative charges of the groups.

Pyridine N-oxides can be reduced back to pyridine derivatives, e.g. using  $PCl_3$ . In the case of catalytic hydrogenation, the nitro group is also reduced, resulting in a pyridine-4-amine product. The reaction of pyridine-N-oxide with a Grignard reagent (under appropriate conditions) results in a product substituted at the 2-position. Often, in the synthetic field the purpose of N-oxide formation is to modify the  $S_EAr$  directing effect (compared to pyridine).

68. A – 5, B – 1, C – 6

A - 2-alkylpyridine derivatives can be prepared by the so-called Ziegler reaction, proceeding via an addition-elimination mechanism. The reaction of pyridine with alkyl lithium reagents gives a 2-position dihydro derivative, from which the corresponding 2-alkylpyridine product is formed upon heating. The metal cation plays a coordinating role during the transformation.

B - Pyridine can be N-alkylated with a cationic alkylating agent, in the reaction the corresponding N-alkylpyridinium salt is formed.

C - Acylating agents readily react with the nitrogen atom of pyridine. As a synthetic application, N-acylpyridinium derivatives are suitable for introducing an acyl group.

69. C

Pyridine N-oxide reacts more readily with electrophilic reagents than pyridine. The N-oxide group stabilizes the  $\sigma$ -complexes leading to products substituted in the 2- and 4-position. Upon nitration, the 2-position substitution takes place to a lesser extent due to the steric hindrance between the oxide anion and the entering nitro group, and the repulsion between the negative charges of the groups.

70. A – 4, B – 6, C – 5, D – 7, E - 1

*A – The Chichibabin reaction is a  $S_NAr$  reaction proceeding via an addition-elimination mechanism, that is suitable for the introduction of an amino group (pyridine + sodium amide). The metal cation plays a coordinating role during the transformation, the product of which is 2-aminopyridine.*

*B – 2-alkylpyridine derivatives can be prepared by the so-called Ziegler reaction, proceeding via an addition-elimination mechanism. The reaction of pyridine with alkyllithium reagents gives a 2-position dihydro derivative, from which the corresponding 2-alkylpyridine product is formed upon heating. The metal cation plays a coordinating role during the transformation*

*C - Pyridine can be oxidized to N-oxide with peroxy acids or hydrogen peroxide.*

*D – Pyridine can be N-alkylated with a cationic alkylating agent, in the reaction the corresponding N-alkylpyridinium salt is formed.*

*E – Pyridine can be oxidized to N-oxide with peroxy acids or hydrogen peroxide. Pyridine N-oxide reacts more readily with electrophilic reagents than pyridine. The N-oxide group stabilizes the  $\sigma$ -complexes leading to products substituted in the 2- and 4-position. Upon nitration, substitution at the 2-position takes place to a lesser extent due to the steric hindrance between the oxide anion and the entering nitro group, and the repulsion between the negative charges of the groups. Pyridine N-oxides can be reduced back to pyridine derivatives by various methods. In the case of catalytic hydrogenation, the nitro group is also reduced, resulting in a pyridin-4-amine product.*

71. A – 3, B - 7, C – 5, D – 1

*In electrophilic substitution reactions, products substituted in the 3-position are formed from pyridine. For nitration harsh conditions and high temperature are required. (Pyridine is a  $\pi$ -electron-deficient heteroaromatic compound, its reactivity in electrophilic substitutions is lower compared to benzene). Pyridine can be oxidized to N-oxide with peroxy acids or hydrogen peroxide. Pyridine N-oxides can be reduced back to pyridine derivatives, e.g. using  $PCl_3$ . Under appropriate conditions, the nitro group is also reduced, resulting in a pyridine-4-amine product. Pyridine N-oxide reacts more readily with electrophilic reagents than pyridine. The N-oxide group stabilizes the  $\sigma$ -complexes leading to products substituted in the 2- and 4-position. Upon nitration, substitution at the 2-position takes place to a lesser extent due to the steric hindrance between the oxide anion and the entering nitro group, and the repulsion between the negative charges of the groups. Often, in the synthetic field the purpose of N-oxide formation is to modify the  $S_EAr$  directing effect (compared to pyridine).*

72. A – 1, B – 3, C – 3, D – 2, E - 1

*Sulfonation of pyridine takes place in the presence of concentrated sulfuric acid, chlorination in the presence of a Lewis catalyst via an  $S_EAr$  reaction. Pyridine reacts with a Grignard reagent ( $CH_3MgBr$ ) as a nucleophilic reagent in an  $S_NAr$  reaction.*

73. 1

*Pyridine N-oxide reacts more readily with electrophilic reagents than pyridine. The N-oxide group stabilizes the  $\sigma$ -complexes leading to products substituted in the 2- and 4-position. Pyridine N-oxides can be reduced back to pyridine derivatives, e.g. using  $PCl_3$ . Often, in the synthetic field the purpose of N-oxide formation is to modify the  $S_EAr$  directing effect (compared to pyridine).*

74. 4

75. A – 1, B – 3, C – 2, D – 1, E - 3



Pyridine N-oxide reacts with electrophiles in an  $S_EAr$  reaction; the hydrogenation of pyrimidine takes place only in the presence of a catalyst, but not by an  $S_EAr$  mechanism. The reaction of 2-methylthiophene with N-bromosuccinimide (NBS) takes place by a radical mechanism in the presence of light.

76. C

77. D

78. 1 – A, 2 – A, 3 – B, 4 – B

On isoquinoline,  $S_EAr$  reactions ( $Br_2/FeBr_3$ ) take place mainly on the benzene ring (position 5 and/or 8), while  $S_NAr$  reactions ( $NaNH_2$ ) take place on the heteroaromatic ring (position 1). 3-Chloropyridine reacts with  $KNH_2/NH_3$  via an aryne mechanism, resulting in the product substituted in the 4-position as the main product. The reaction of 4-chloropyridine with  $NaNH_2$  takes place via an  $S_NAr$  reaction.

79. C

The least deactivated carbon atom of the pyrimidine is in meta position relative to both nitrogens.

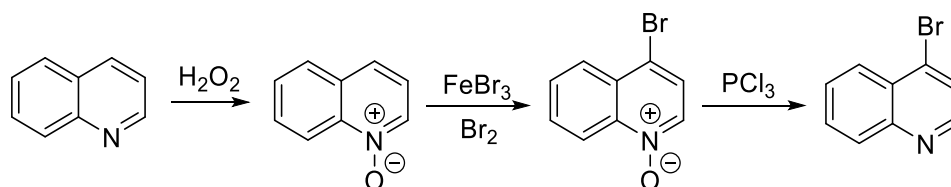
80. A, C, D

81. B, C

82. B, D

83. 1 – F, 2 – D, 3 – A

Pyridine N-oxide reacts more readily with electrophilic reagents than pyridine. The N-oxide group stabilizes the  $\sigma$ -complexes leading to products substituted in the 2- and 4-position due to its +I and +M effects. Pyridine N-oxides can be reduced back to pyridine derivatives, e.g. using  $PCl_3$ . Often, in the synthetic field the purpose of N-oxide formation is to modify the  $S_EAr$  directing effect (compared to pyridine).



84. C

85. 1 – C, 2 – A, 3 – B

86. 1

87. 4

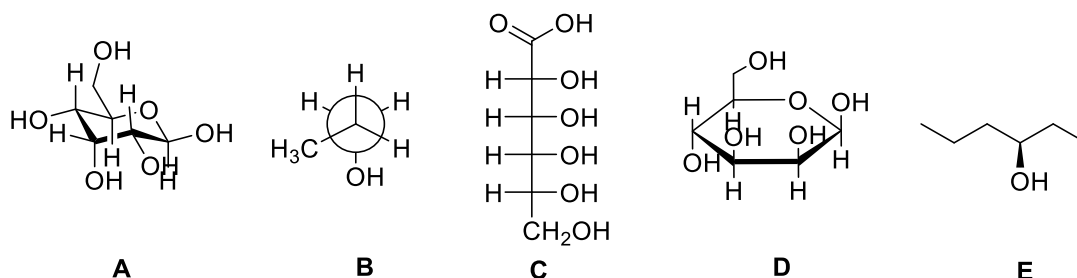
88. a – E, b – C, c – A

89. 1 – B, 2 – C, 3 – A, 4 – F

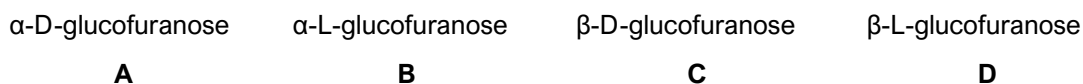
90. D

# 11. Carbohydrates

1. Which of the following is a Haworth projection?



2. Among those listed below, what is the stereochemical relationship between the following compounds?



A:B

A:C

A:D

B:C

B:D

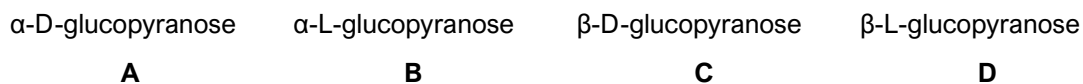
C:D

1 – configurational enantiomers

2 – configurational diastereomers

3 - anomers

3. Among those listed below, what is the stereochemical relationship between the following compounds?



A:B

A:C

A:D

B:C

B:D

C:D

1 – configurational enantiomers

2 – configurational diastereomers

3 - anomers

4. Which of the following is an aldo or a keto sugar?

A/ D-glucose

B/ D-fructose

C/ L-fructose

D/ L-glucose

1 - aldo-sugar

2 - keto-sugar

5. Choose the correct statement!

The position of the substituents in the chair conformer of  $\beta$ -D-Glcp is:

A/ all axial

B/ more axial and less equatorial

C/ more equatorial and less axial

D/ all equatorial





**6. Choose the correct statement!**

The position of the substituents in the chair conformer of  $\alpha$ -D-Glcp is:

- A/ all axial
- B/ more axial and less equatorial
- C/ more equatorial and less axial
- D/ all equatorial

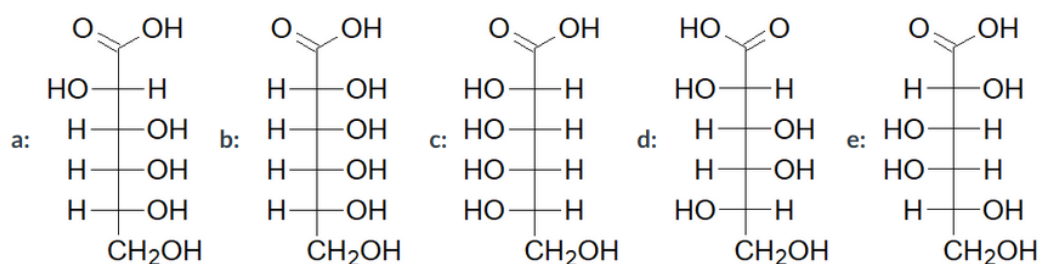
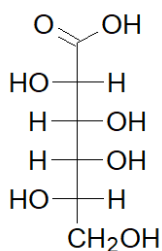
**7. Which of the following are enantiomers and which are epimers?**

- A/ D-glucose and L-glucose
  - B/ D-fructose and L-fructose
  - C/ D-glucose and D-mannose
  - D/ D-glucose and D-galactose
- 1 – enantiomer                      2 – epimer

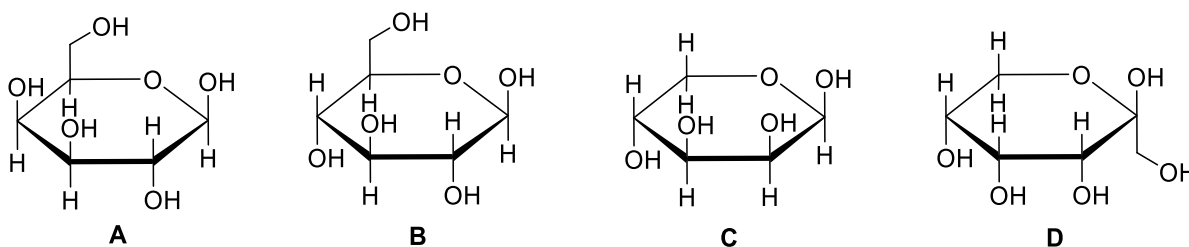
**8. Which of the following are epimers?**

- A/ D-glucose and L-glucose
- B/ D-fructose and L-fructose
- C/ D-glucose and D-mannose
- D/ D-glucose and L-fructose
- E/ D-fructose and L-galactose

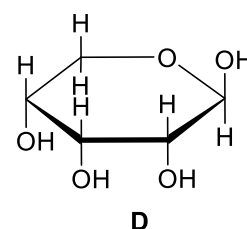
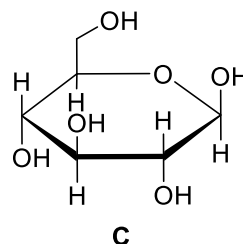
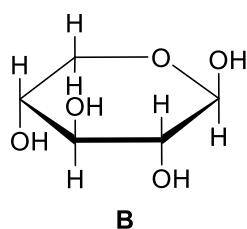
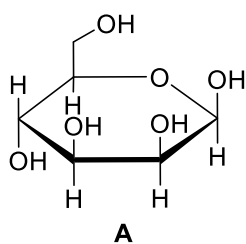
**9. Which of the following is the epimer of the molecule below?**



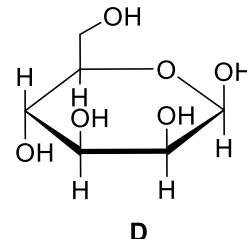
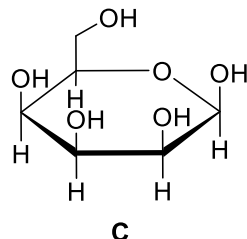
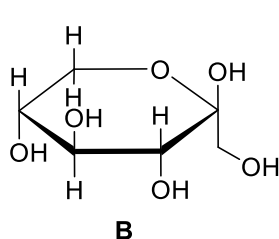
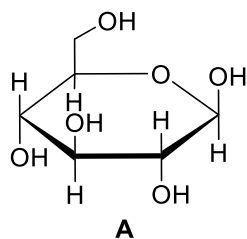
**10. Which of the following represents  $\beta$ -D-galactose?**



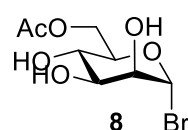
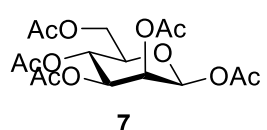
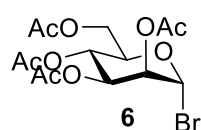
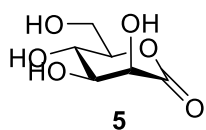
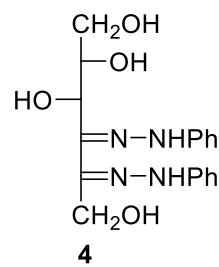
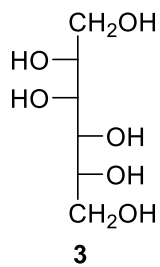
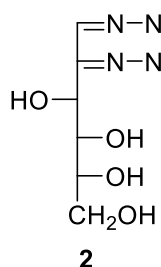
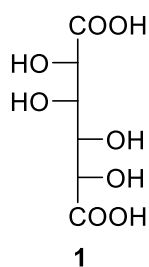
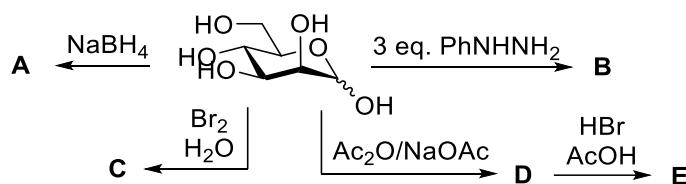
11. Which of the following represents  $\beta$ -D-mannose?



12. Which of the following represents  $\beta$ -D-glucose?



13. Complete the scheme below with the structure of the missing products!



14. Which of the following statements is correct?

A/ D-glucose and L-glucose can be distinguished by the Fehling reaction.

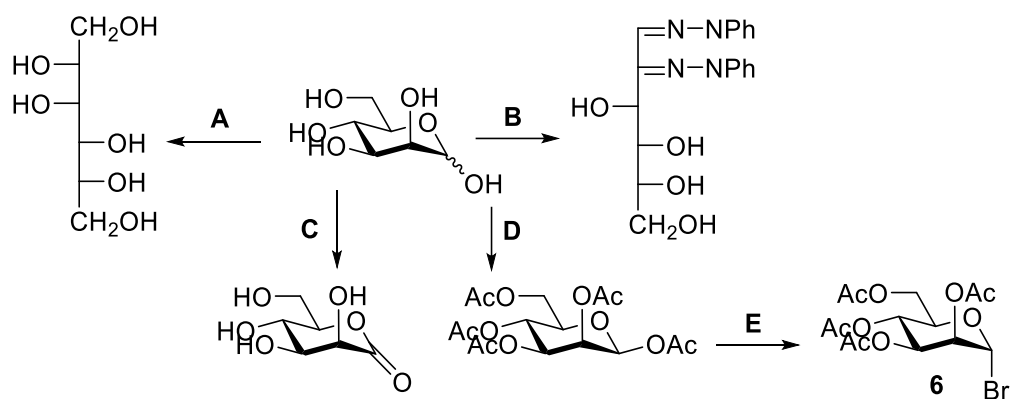
B/ Lactose is made up of fructose and glucose units.

C/ Disaccharides formed from two identical monosaccharides are reducing sugars.

D/ D-glucose contains 4 chirality centers.



**15. Complete the following scheme with the missing reagents!**



1 - NaF, H<sub>2</sub>O

2 - Br<sub>2</sub>, H<sub>2</sub>O

3 - HBr / AcOH

4 - 3 eq. PhNH<sub>2</sub>

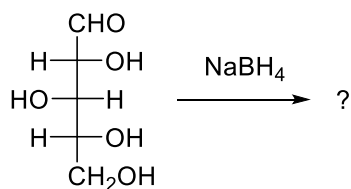
5 - NaBH<sub>4</sub>

6 - Na<sub>2</sub>CO<sub>3</sub>

7 - 3 eq. PhNHNH<sub>2</sub>

8 - Ac<sub>2</sub>O / NaOAc

**16. Which of the following could be the product(s) of the reduction below?**



A/ a mixture of two diastereomers in equal proportions

B/ purely one enantiomer

C/ a *meso* compound

D/ a racemic mixture

E/ a mixture of two diastereomers in different proportions

**17. Choose the correct statement about carbohydrates!**

The triphenylmethyl group can be used to selectively protect the following OH group(s):

A/ anomeric OH

B/ secondary OH

C/ all the OH groups

D/ primary OH

**18. Which of the following are monofunctional protecting groups?**

A/ acetyl

B/ isopropylidene

C/ mesyl

D/ tosyl

E/ benzylidene

**19. What does Fehling's reagent contain?**

A/ aqueous NH<sub>3</sub> solution

B/ aqueous NH<sub>3</sub> solution and AgNO<sub>3</sub>

C/ aqueous CuSO<sub>4</sub> and basic K,Na-tartrate

D/ aqueous NH<sub>3</sub> solution and basic K,Na-tartrate

**20. The reactivity of the hydroxyl groups of carbohydrates (ether formation) can be given as follows:**

1. anomer-OH                              2. primary-OH                              3. secondary-OH

A/ they are the same (1. = 2. = 3.)

B/ the reactivity decreases in this order (1. → 2. → 3.)

C/ the reactivity increases in this order (1. → 2. → 3.)

D/ none of them

**A szénhidrátok hidroxilcsoportjainak reaktivitása (éterképzés) az alábbiak szerint adható meg:**

1. anomer-OH                              2. primary-OH                              3. secondary-OH

A/ they are the same (1. = 2. = 3.)

B/ the reactivity decreases in this order (1. → 2. → 3.)

C/ the reactivity increases in this order (1. → 2. → 3.)

D/ none of them

**21. Which of the following is formed in the reaction of aldo-sugars with phenylhydrazine?**

A/ hydrazine

B/ phenylhydrazone

C/ osazone

D/ osone

E/ semicarbazone

**22. What is formed in the  $\text{HNO}_3/\text{H}_2\text{O}$  oxidation of D-glucose?**

A/ glycol

B/ gluconic acid

C/ glucaric acid

D/ glucuronic acid

**23. What is formed in the oxidation of D-glucose with  $\text{Br}_2/\text{H}_2\text{O}$ ?**

A/ gluconic acid

B/ glucaric acid

C/ glucuronic acid

D/ glycol

E/ glucuronide

**24. The reaction of D-glucose with  $\text{HNO}_3/\text{H}_2\text{O}$  is a(n):**

A/ oxidation

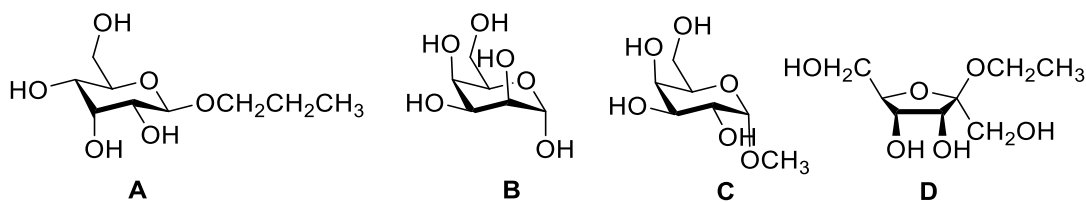
B/ reduction

C/ acylation

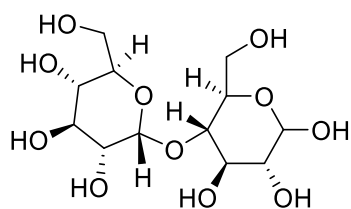
D/ substitution

E/ addition

**25. Which of the following compounds gives a positive Fehling reaction?**



26. Which statement is NOT correct about maltose?

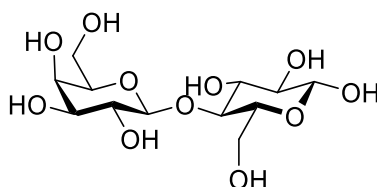


- A/ it is a 1→4 α-glycoside  
 B/ it consists of glucopyranose units  
 C/ it is a non-reducing disaccharide  
 D/ it shows mutarotation in solution  
 E/ it is optically active

27. Which of the following disaccharides contain a β-glycosidic bond?

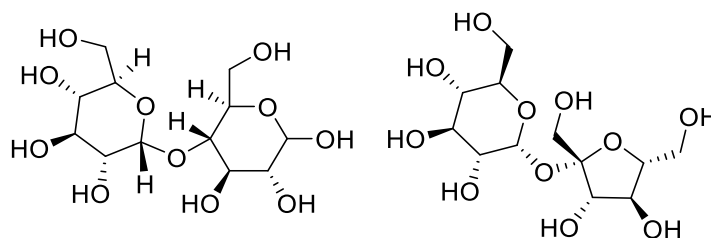
- A/ lactose  
 B/ cellobiose  
 C/ maltose  
 D/ amylose

28. Which statement is NOT correct about lactose?



- A/ it contains a 1,1'-α-glycosidic bond  
 B/ it is a reducing disaccharide  
 C/ it is optically active  
 D/ in acidic medium it can be hydrolyzed to monosaccharides  
 E/ it consists of glucose and galactose units

29. What is the isomeric relationship between maltose and saccharose?



- A/ geometric isomers  
 B/ diastereomers  
 C/ enantiomers  
 D/ there is no isomeric relationship between them  
 E/ structural isomers  
 F/ epimers

30. The following polysaccharides contain a β-glycosidic bond:

- A/ starch  
 B/ cellulose  
 C/ chitin  
 D/ amylose

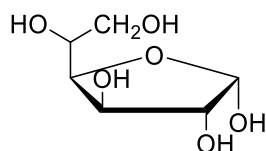


# 11. Carbohydrates

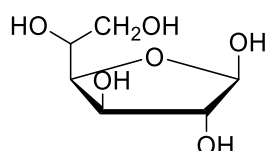
## Solutions

1. D

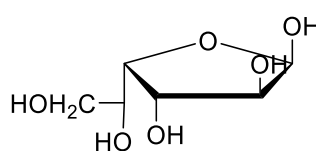
2. A:B – 1, A:C – 3, A:D – 2, B:C – 2, B:D – 3, C:D – 1



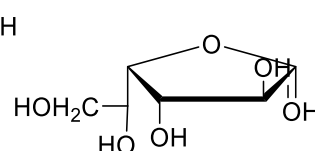
$\alpha$ -D-glucofuranose



$\beta$ -D-glucofuranose



$\alpha$ -L-glucofuranose



$\beta$ -L-glucofuranose

*Enantiomers: non-overlapping mirror image pairs*

*Diastereomers: stereoisomers that are not in an enantiomeric relationship*

*Configurational isomers (when the carbon atom is the stereogenic centre): cannot be converted into each other without breaking and reforming a covalent bond*

*Anomers: diastereomers that can be derived from the cyclic form of carbohydrates and differ in the configuration of the C(1) stereogenic center in the case of aldoses*

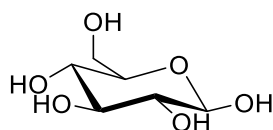
3. A:B – 1, A:C – 3, A:D – 2, B:C – 2, B:D – 3, C:D – 1

*Enantiomers (identical internuclear distance, different order of groups): non-overlapping mirror image pairs*

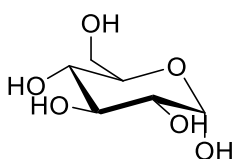
*Diastereomers (same connectivity, different internuclear distance): stereoisomers that are not in an enantiomeric relationship*

*Configurational isomers (when the carbon atom is the stereogenic centre): cannot be converted into each other without breaking and reforming a covalent bond*

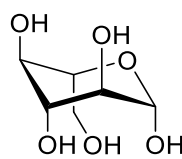
*Anomers: diastereomers – within this category epimers - that can be derived from the cyclic form of carbohydrates and differ in the configuration of the C(1) stereogenic center in the case of aldoses or the C(2) stereogenic center in the case of ketoses (i.e. in both cases the configuration of the hemiacetal carbon differs)*



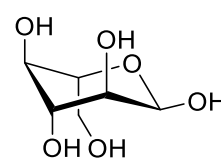
$\beta$ -D-glucopyranose



$\alpha$ -D-glucopyranose

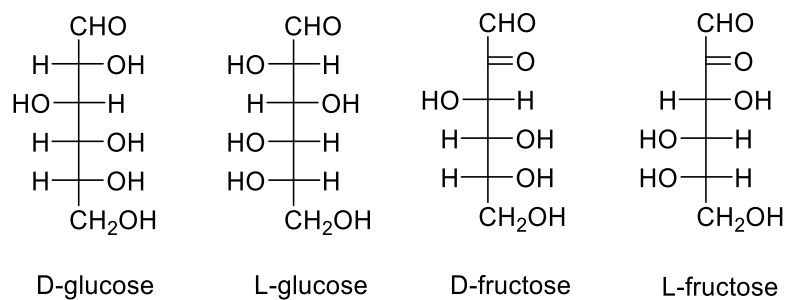


$\beta$ -L-glucopyranose

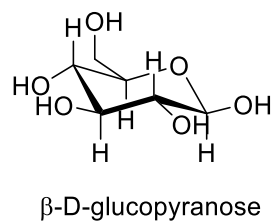


$\alpha$ -L-glucopyranose

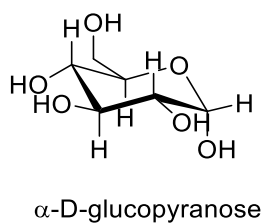
4. A – 1, B – 2, C – 2, D – 1



5. D



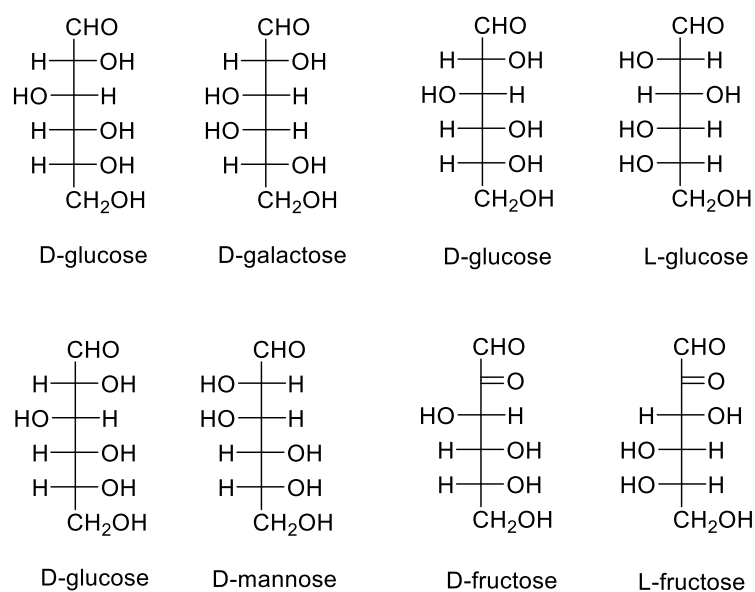
6. C



7. A – 1, B – 1, C – 2, D – 2

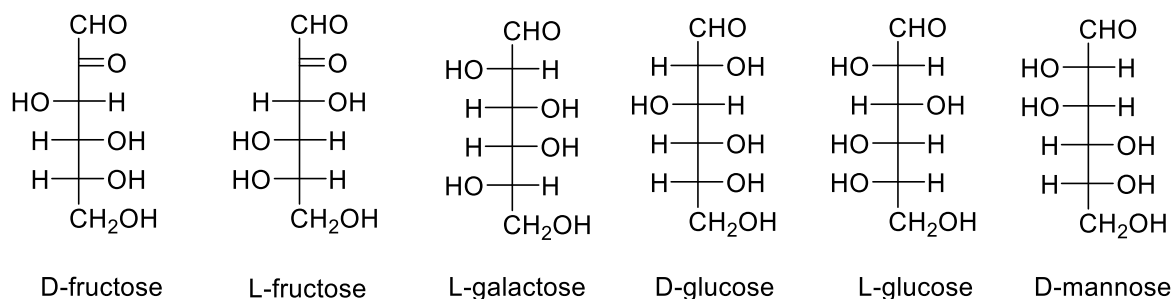
*Enantiomers: non-overlapping mirror image pairs*

*Epimers: diastereomers that differ only in the configuration of one stereogenic center*



8. C

*Epimers: diastereomers that differ only in the configuration of one stereogenic center*



9. A

*Epimers: diastereomers that differ only in the configuration of one stereogenic center*

10. A

11. A

12. A

13. A – 3, B – 2, C – 5, D – 7, E - 6

*Monosaccharides show the reactions of oxo and different hydroxyl groups. Aldoses can be reduced to sugar alcohols, alditols with  $\text{NaBH}_4$ . They can be converted into aldonic acids under mild oxidative conditions (e.g.  $\text{Br}_2/\text{H}_2\text{O}$ ,  $\text{pH}=5$ ), the primary product of the reaction being the  $\delta$ -lactone of the corresponding aldonic acid. With an excess of phenylhydrazine, so-called osazones are formed. Their formation involves hydrazone formation, oxidation and repeated hydrazone formation. Monosaccharides form esters with acid anhydrides, from D-glucose with acetic anhydride in the presence of sodium acetate penta-O-acetyl- $\beta$ -D-glucopyranose ( $\beta$ -D-glucopyranose pentaacetate) is formed. Sugar acetates can be converted into glucosyl halides, with hydrogen bromide, the  $\text{S}_{\text{N}}1$  transformation at the C1 carbon atom results in the  $\alpha$ -bromo derivative as the main product from both pentaacetate anomers.*

14. D

*D-glucose and L-glucose differ in their spatial structure, their functional groups are the same, so they cannot be distinguished from each other by Fehling's reaction. Lactones are cyclic esters, lactose does not contain such a structural unit. Reducing sugars are aldo sugars on the one hand and on the other hand they have a free glycosidic hydroxyl group.*

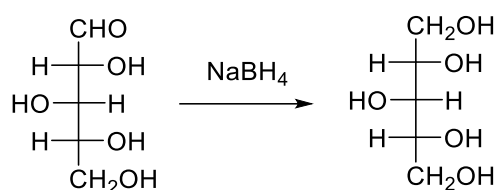
15. A – 5, B – 7, C – 2, D – 8, E - 3

*Monosaccharides show the reactions of oxo and different hydroxyl groups. Aldoses can be reduced to sugar alcohols, alditols with  $\text{NaBH}_4$ . They can be converted into aldonic acids under mild oxidative conditions (e.g.  $\text{Br}_2/\text{H}_2\text{O}$ ,  $\text{pH}=5$ ), the primary product of the reaction being the  $\delta$ -lactone of the corresponding aldonic acid. With an excess of phenylhydrazine, so-called osazones are formed. Their formation involves hydrazone formation, oxidation and repeated hydrazone formation. Monosaccharides form esters with acid anhydrides, from D-glucose with acetic anhydride in the presence of sodium acetate penta-O-acetyl- $\beta$ -D-glucopyranose ( $\beta$ -D-glucopyranose pentaacetate) is formed. Sugar acetates can be converted into glucosyl halides, with hydrogen bromide, the  $\text{S}_{\text{N}}1$  transformation at the C1 carbon atom results in the  $\alpha$ -bromo derivative as the main product from both pentaacetate anomers.*





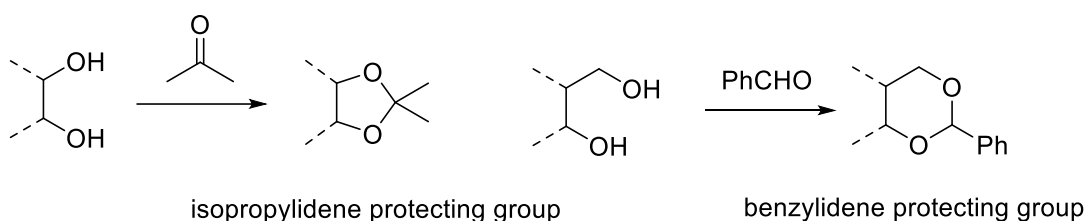
16. C



17. D

The primary hydroxyl group of sugars can be selectively etherified with the bulky triphenylmethyl (trityl) group. The protecting group can be subsequently easily cleaved with dilute acid or catalytic hydrogenation.

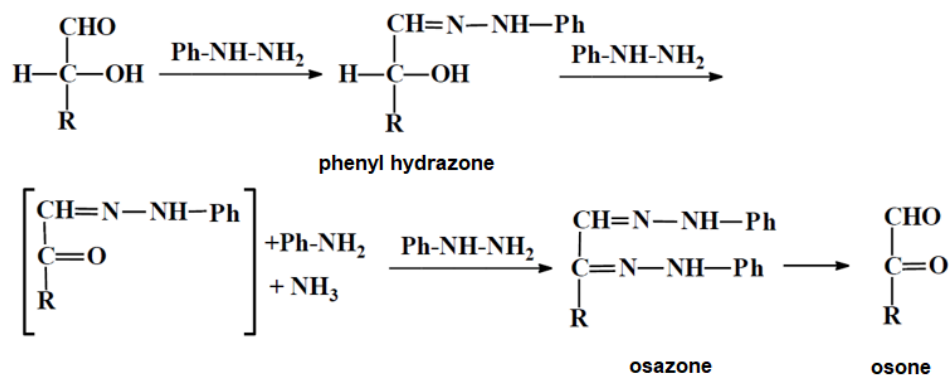
18. A, C, D



19. C

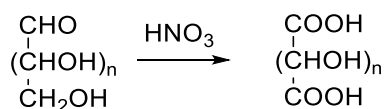
20. B

21. B, C, D



22. C

Upon the oxidation of aldoses under harsher conditions (e.g.  $\text{HNO}_3$ ), not only the aldehyde group is oxidized to carboxylic acid, but also the terminal hydroxymethyl group. In the oxidation aldaric acids can be obtained.

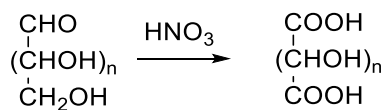


23. A



Monosaccharides can be converted into aldonic acids under mild oxidative conditions (e.g.  $Br_2/H_2O$ ,  $pH=5$ ), the primary product of the reaction being the  $\delta$ -lactone of the corresponding aldonic acid.

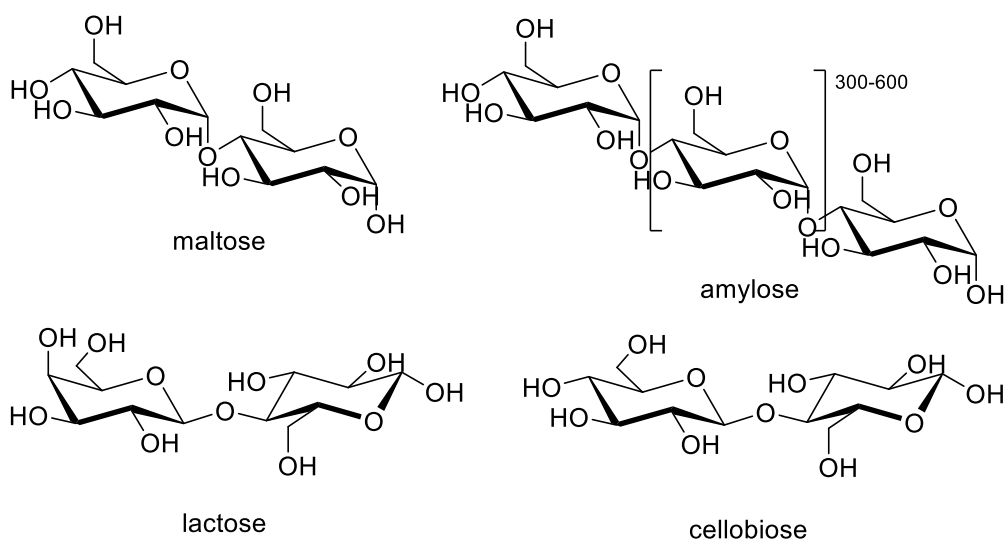
24. A



25. B

26. C

27. A, B



28. A

29. E

30. B, C

## 12. Amino acids, peptides, proteins

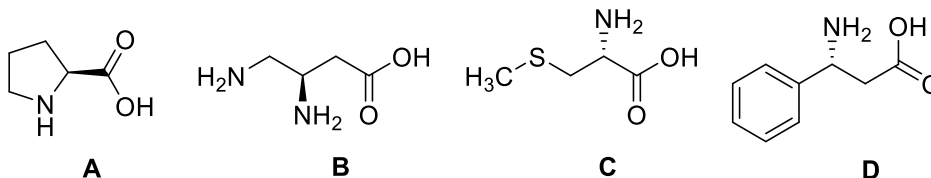
1. The absolute configuration of L-glyceraldehyde and natural amino acids is S. Select from the following the two exceptions to this:

- A/ glycine                                      B/ alanine                                      C/ cysteine  
D/ glutamine                                    E/ methionine

2. Which of the following amino acids contain two stereogenic centers?

- A/ isoleucine                                    B/ threonine                                    C/ serine  
D/ tyrosine                                      E/ tryptophan

3. In which amino acid is the stereogenic center in S configuration?



4. Choose the correct statement!

- A/ L-tryptophan has R configuration.                                      B/ L-cysteine has S configuration.  
C/ D-glutamic acid has R configuration.                                    D/ D-cysteine has R configuration.

5. Choose the correct statement!

- A/ L-phenylalanine has R absolute configuration.                                      B/ L-cysteine has S absolute configuration.  
C/ D-asparagine has R absolute configuration.                                    D/ D-cysteine has R absolute configuration.

6. Choose the correct statement!

- A/ Arginine is a basic amino acid.                                      B/ Alanine is a polar amino acid.  
C/ Leucine is an acidic amino acid.                                      D/ Tyrosine is a hydrophobic amino acid.

7. Choose the correct statement!

- A/ The isoelectric point of isoleucine is higher than that of arginine.  
B/ The isoelectric point of glycine is lower than that of aspartic acid.  
C/ The isoelectric point of asparagine is higher than that of tryptophan.  
D/ The isoelectric point of histidine is lower than that of lysine.



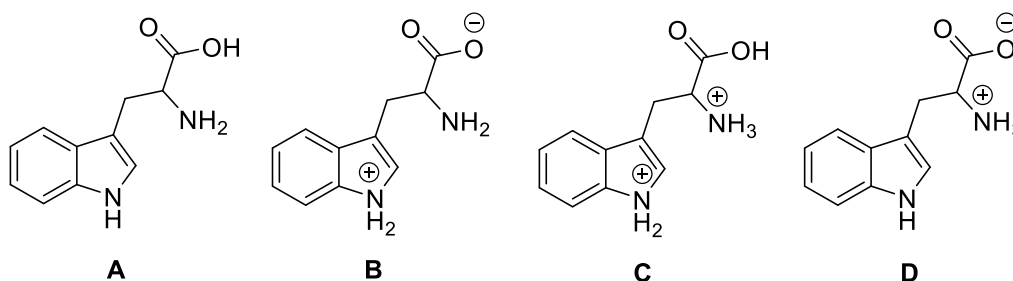
**8. Choose the correct statement from the following:**

- A/ The isoelectric point of leucine is higher than that of arginine.
- B/ The isoelectric point of glycine is higher than that of glutamic acid.
- C/ The isoelectric point of glutamine is higher than that of tryptophan.
- D/ The isoelectric point of histidine is lower than that of valine.

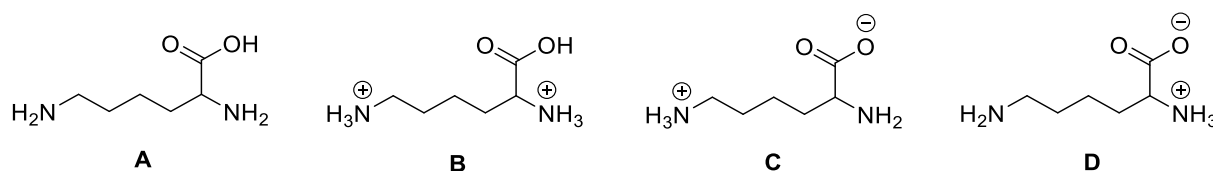
**9. Choose the correct statement about amino acids!**

- A/ In the zwitterionic form, the aminium cation is a strong acid.
- B/ In the zwitterionic form, the aminium cation is a strong base.
- C/ In the zwitterionic form, the aminium cation is a weak acid.
- D/ In the zwitterionic form, the aminium cation is a weak base.

**10. What is the predominant structure of tryptophan at pH = 7?**



**11. What is the predominant structure of lysine at pH = 7?**



**12. Choose the correct statement!**

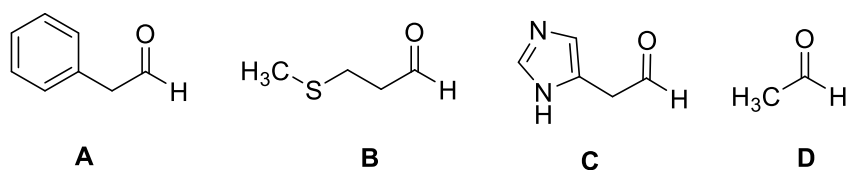
- A/ Glutamic acid can have a dianionic form in basic medium.
- B/ Lysine cannot have a dicationic form in acidic medium.
- C/ Glutamic acid cannot have a monoanionic form in basic medium.
- D/ Lysine can have a dianionic form in basic medium.

**13. Choose the correct statement about amino acids!**

- A/ The ninhydrin reaction gives a blue color if the amino group is not free.
- B/ The ninhydrin reaction gives a yellow color when the amino group is free.
- C/ The ninhydrin reaction gives a blue color when the amino group is free.
- D/ The scope of the application of the ninhydrin reaction is not limited to primary amino groups.



14. Which amino acids can be produced from the following aldehydes by Strecker synthesis?



1 - tryptophan

2 - methionine

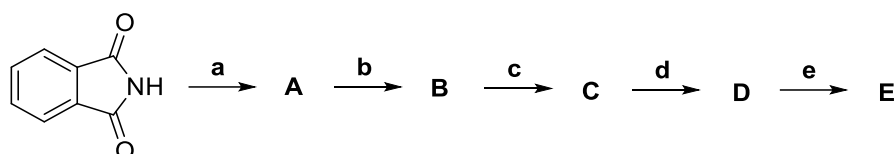
3 - cysteine

4 - phenylalanine

5 - histidine

6 - alanine

15. Phthalimide can be used to prepare amino acids. Give the reactants (a-e) and products (A-E) for each synthesis step.



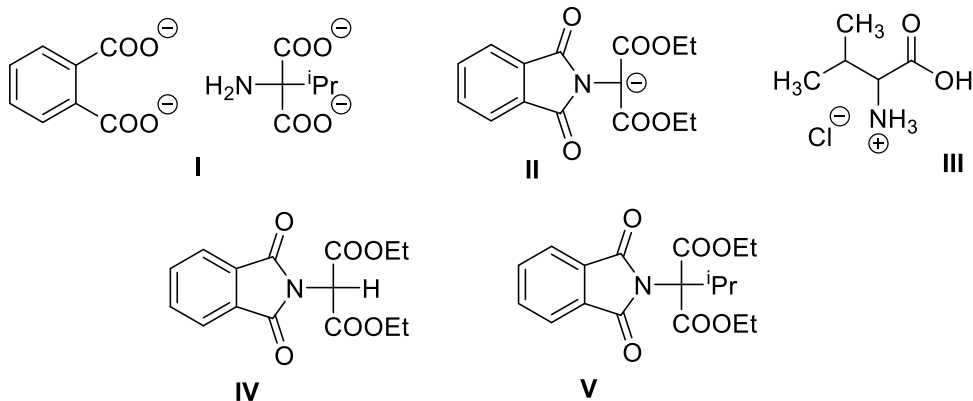
1 - *i*Pr-Br

2 -  $\text{BrCH}(\text{COOEt})_2$

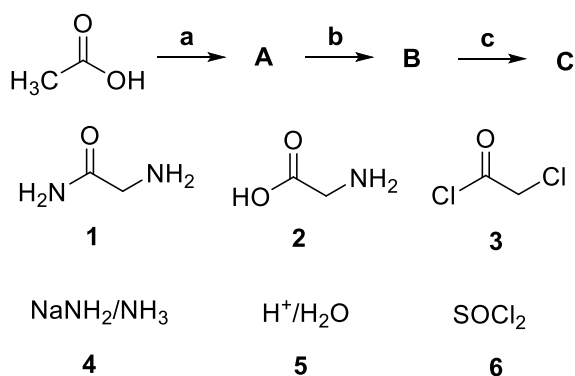
3 -  $\text{HCl} / \text{H}_2\text{O}$

4 -  $\text{NaOEt}$

5 -  $\text{NaOH}$



16. The following scheme shows the preparation of glycine from acetic acid. Give the missing reactants (a-c) and products (A-C)!



17. Which amino acids can be prepared starting from diethyl malonate with the following alkyl halides?

A/ methyl chloride

B/ 2-methyl-1-chloropropane

C/ isopropyl chloride

D/ 2-bromobutane

1 – isoleucine

2 – alanine

3 - valine

4 – cysteine

5 – tryptophan

6 - leucine

18. Choose the correct statement!

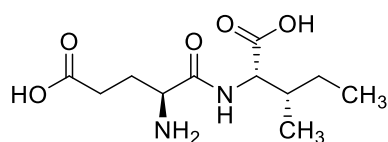
A/ Glycine can be prepared by Gabriel synthesis.

B/ Glutamic acid cannot be prepared by Gabriel synthesis.

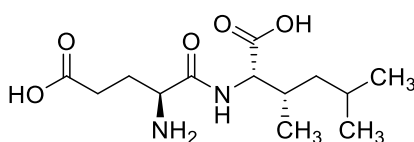
C/ Methionine can be prepared by azlactone synthesis.

D/ Phenylalanine cannot be prepared by azlacton synthesis.

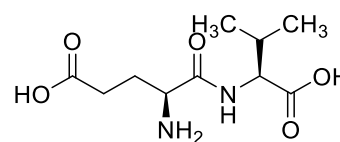
19. Which of the following formulas describes correctly the structure of the Glu-Ile dipeptide?



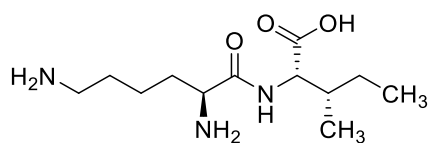
A



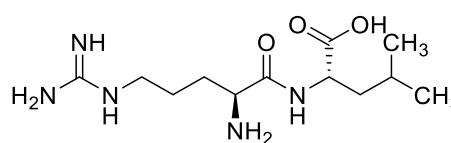
B



C

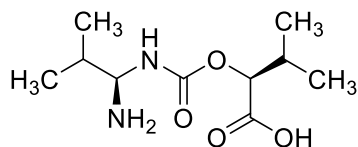


D

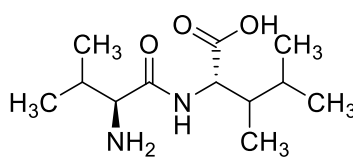


E

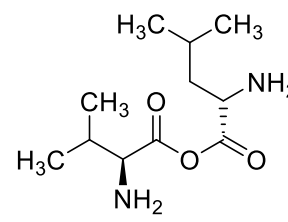
20. Which of the following formulas describes correctly the structure of the valyl-leucine dipeptide?



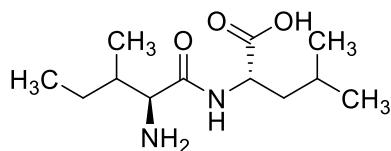
A



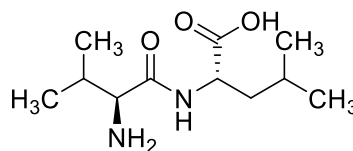
B



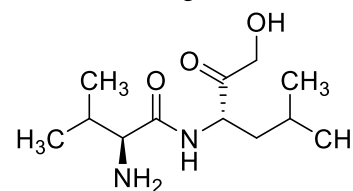
C



D

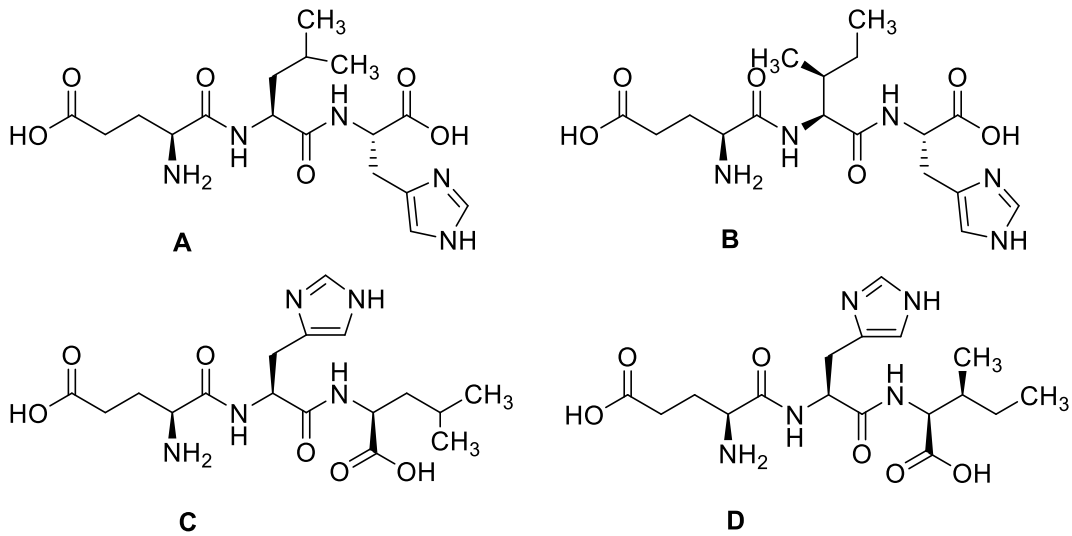


E



F

21. Which of the following formulas describes correctly the structure of the Glu-Leu-His tripeptide?

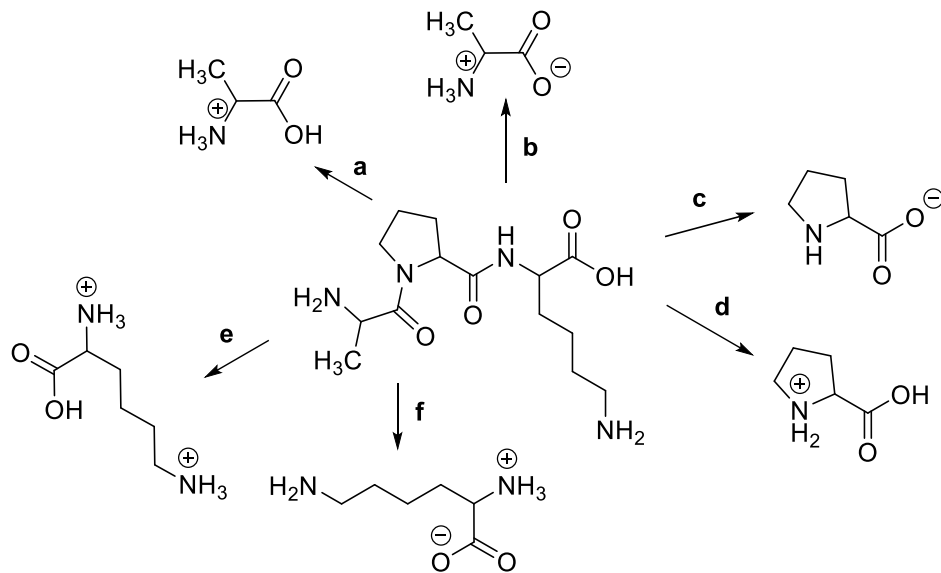


22. Which is the *N*-terminal amino acid in the peptide below?

*Phe-Ala-Gly-Arg*

- A/ Ala                      B/ Phe                      C/ Phe és Arg  
 D/ Arg                      E/ none of them

23. Which products are formed upon the acidic hydrolysis of the alanyl-prolyl-lysine tripeptide (pH=1)?



- A/ a, b and c                      B/ b, d and e  
 C/ a, d and e                      D/ b, c and f



**24. Choose the correct statement!**

- A/ Coupling Ala and Gly can result in 4 different di- and 8 tripeptides.
- B/ Coupling Ala and Gly can result in 2 different di- and 8 tripeptides.
- C/ Coupling Ala and Gly can result in 3 different di- and 8 tripeptides.
- D/ Coupling Ala and Gly can result in 4 different di- and 4 tripeptides.

**25. Choose the correct statement!**

- A/ The benzyloxycarbonyl protecting group is not an urethane type protecting group.
- B/ The Fmoc protecting group is an urethane type protecting group.
- C/ The Boc protecting group is not an urethane type protecting group.
- D/ Urethane-type protecting groups are only used in solution-phase peptide synthesis.
- E/ Urethane-type protecting groups are only used in solid-phase peptide synthesis.

**26. Choose the correct statement about the synthesis of peptides!**

- A/ If the yield per coupling step is 99%, then after 4 couplings the overall yield is 96%.
- B/ If the yield per coupling step is 93%, then after 5 couplings the overall yield is 85%.
- C/ If the yield per coupling step is 97%, then after 3 couplings the overall yield is 93%.
- D/ If the yield per coupling step is 95%, then after 6 couplings the overall yield is 70%.

**27. Choose the correct statement!**

- A/ In solution-phase peptide synthesis active ester couplings are always used.
- B/ In solid-phase peptide synthesis active ester couplings are always used.
- C/ In solution-phase peptide synthesis DCC can also be used.
- D/ In solid-phase peptide synthesis DCC is always used.

**28. How could you prepare the alanyl-valine (Ala-Val) dipeptide from the appropriate amino acids (protection or activation, coupling, then removal of the protective groups)? What is the correct order of the reactions and the reaction intermediates?**

(Z and X are protecting groups, Y is an activating group)

- A/  $Z\text{-NH-Ala-COOH} \rightarrow Z\text{-NH-Ala-COOY} \rightarrow \text{H}_2\text{N-Val-COOX} \rightarrow Z\text{-NH-Ala-COO-NH-Val-COOX} \rightarrow \text{H}_2\text{N-Ala-COO-NH-Val-COOH}$
- B/  $Z\text{-NH-Val-COOH} \rightarrow Z\text{-NH-Val-COOY} \rightarrow \text{H}_2\text{N-Ala-COOX} \rightarrow Z\text{-NH-Val-COO-NH-Ala-COOX} \rightarrow \text{H}_2\text{N-Ala-COO-NH-Val-COOH}$
- C/  $\text{NH-Ala-COOY} \rightarrow Z\text{-NH-Ala-COOY} \rightarrow \text{H}_2\text{N-Val-COOX} \rightarrow Z\text{-NH-Ala-COO-NH-Val-COOX} \rightarrow \text{H}_2\text{N-Ala-COO-NH-Val-COOH}$
- D/  $Z\text{-NH-Ala-COOH} \rightarrow Z\text{-NH-Ala-COOY} \rightarrow Z\text{-H}_2\text{N-Val-COOH} \rightarrow Z\text{-NH-Ala-COO-NH-Val-COOX} \rightarrow \text{H}_2\text{N-Ala-COO-NH-Val-COOH}$



**29. Choose the correct statement!**

- A/ The primary, secondary, tertiary and quaternary structure determine the chemical properties of the protein.
- B/ The primary and secondary structure determine the chemical properties of the protein.
- C/ The primary structure determines the chemical properties of the protein.
- D/ The secondary binding forces determine the chemical properties of the protein.

**30. Choose the correct statement!**

- A/ The secondary structure of a protein can only have alpha helix and beta sheet conformations.
- B/ The secondary structure of a protein can have disordered, alpha helix and beta sheet conformations.
- C/ The secondary structure of a protein can have either alpha helix or beta sheet or alpha helix + beta sheet conformations.
- D/ The secondary structure of a protein can have either only alpha helix or only beta sheet conformations.

**31. Choose the correct statement!**

- A/ Proteins are polypeptides consisting of hundreds (sometimes thousands) of amino acids.
- B/ The tertiary structure of proteins is typically fibrillar.
- C/ The quaternary structure of proteins describes the connectivity order of the amino acids that make up the protein.
- D/ The beta sheet is energetically more favorable than the alpha-helix conformation.

**32. Choose the correct statement!**

- A/ The molecular weight of proteins can also be determined by mass spectrometry.
- B/ The conformation of the peptides is determined by the DNA sequence.
- C/ X-ray diffraction only provides information on the secondary structure of proteins.
- D/ The composition of peptides can only be determined by NMR.

**33. Choose the correct statement!**

- A/ In the Edman degradation, phenylthiohydantoin is added to the first amino acid.
- B/ The Edman degradation starts from the *N*-terminal side.
- C/ In the Edman degradation, phenyl thiocyanate is added to the first amino acid.
- D/ The Edman degradation can also start from the *C*-terminal.

**34. Choose the correct statement!**

- A/ The solid-phase peptide synthesis (SPPS) is more expensive than the solution-phase.
- B/ SPPS uses fewer chemicals than the solution phase.
- C/ The overall yield of SPPS is less than 90%.
- D/ Solution-phase peptide synthesis can be automated.



**35. Choose the correct statement!**

A/ When two amino acids are coupled in solution phase, the carboxyl group of the first amino acid and the carboxyl group of the second amino acid must both be protected.

B/ When two amino acids are coupled in solution phase, the carboxyl group of the first amino acid and the amino group of the second amino acid must be protected.

C/ When two amino acids are coupled in solution phase, the amino group of the first amino acid and the amino group of the second amino acid must both be protected.

D/ When two amino acids are coupled in solution phase, the amino group of the first amino acid and the carboxyl group of the second amino acid must be protected.



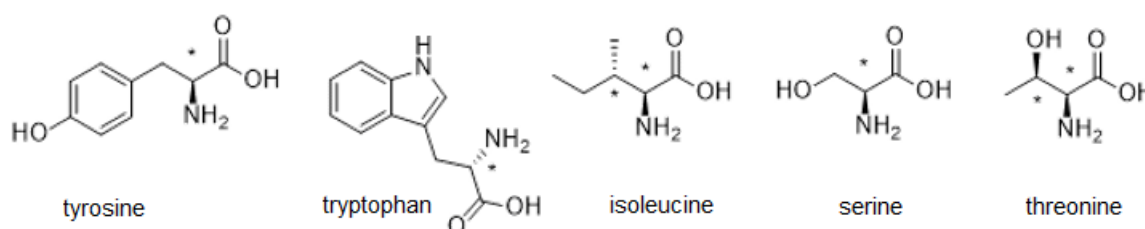
## 12. Amino acids, peptides, proteins

### Solutions

1. A, C

Glycine is an achiral amino acid. Due to the order of priority according to the Cahn-Ingold-Prelog convention, L-cysteine has an R absolute configuration, rather than S ( $\text{CH}_2\text{SH} > \text{COOH}$ ).

2. A, B



3. C

The configuration of the stereogenic centre is assigned according to the Cahn-Ingold-Prelog convention: i) ranking of ligands, ii) read the circumference of the atoms/groups ranked in the first three places (S - counterclockwise, R - clockwise) from the side opposite the atom/group ranked to the last place.

4. C

Most of the naturally occurring amino acids belong to the L series and have an S absolute configuration. Due to the order of priority according to the Cahn-Ingold-Prelog convention, L-cysteine has an R absolute configuration, rather than S ( $\text{CH}_2\text{SH} > \text{COOH}$ ).

5. C

Most of the naturally occurring amino acids belong to the L series and have an S absolute configuration. Due to the order of priority according to the Cahn-Ingold-Prelog convention, L-cysteine has an R absolute configuration, rather than S ( $\text{CH}_2\text{SH} > \text{COOH}$ ).

6. A

Amino acids containing a monobasic amino group and an acidic carboxyl group are considered neutral. One of the subgroups of neutral amino acids are amino acids containing an alkyl group (apolar) side chain (alanine, leucine). The side chain of tyrosine contains a phenolic hydroxyl group, while arginine contains a basic nitrogen atom.

7. D

The isoelectric point of amino acids can fall into the acidic, neutral or basic pH range, depending on the number and pK value of the acidic and basic groups in the molecule. If e.g. there are more acidic groups than basic ones, the isoelectric point falls in the acidic range, i.e.  $< 7$ . Lysine, arginine and histidine are basic amino acids, aspartic acid is an acidic one.

8. B



The isoelectric point of amino acids can fall into the acidic, neutral or basic pH range, depending on the number and  $pK$  value of the acidic and basic groups in the molecule. If e.g. there are more acidic groups than basic ones, the isoelectric point falls in the acidic range, i.e.  $< 7$ . Arginine and histidine are basic amino acids, glutamic acid is an acidic one.

9. C

10. D

The isoelectric point of amino acids can fall into the acidic, neutral or basic pH range, depending on the number and  $pK$  value of the acidic and basic groups in the molecule. In solution, the acidic group transfers its proton to the basic group and a zwitterionic form is formed.

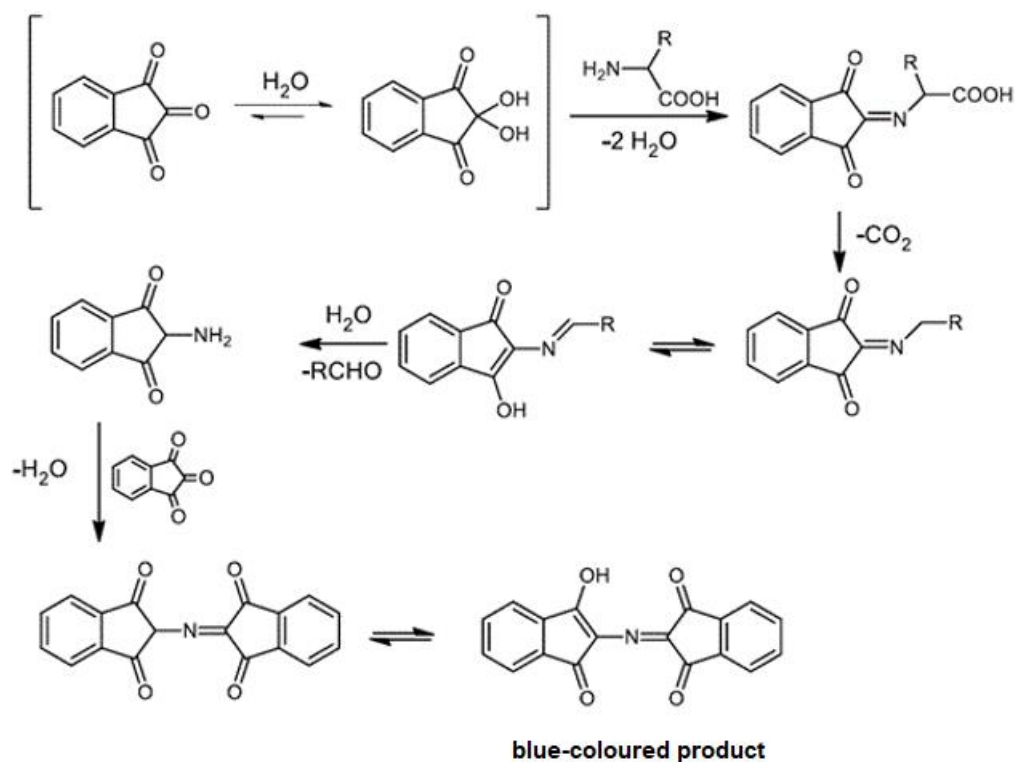
11. D

The isoelectric point of amino acids can fall into the acidic, neutral or basic pH range, depending on the number and  $pK$  value of the acidic and basic groups in the molecule. In solution, the acidic group transfers its proton to the basic group and a zwitterionic form is formed.

12. A

Lysine is a diamino monocarboxylic acid containing two basic amino groups, glutamic acid is a monoamino dicarboxylic acid.

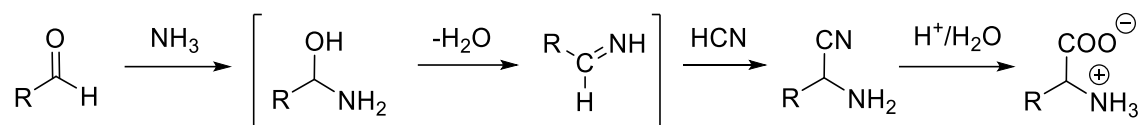
13. C



14. A – 4, B – 2, C – 5, D – 6



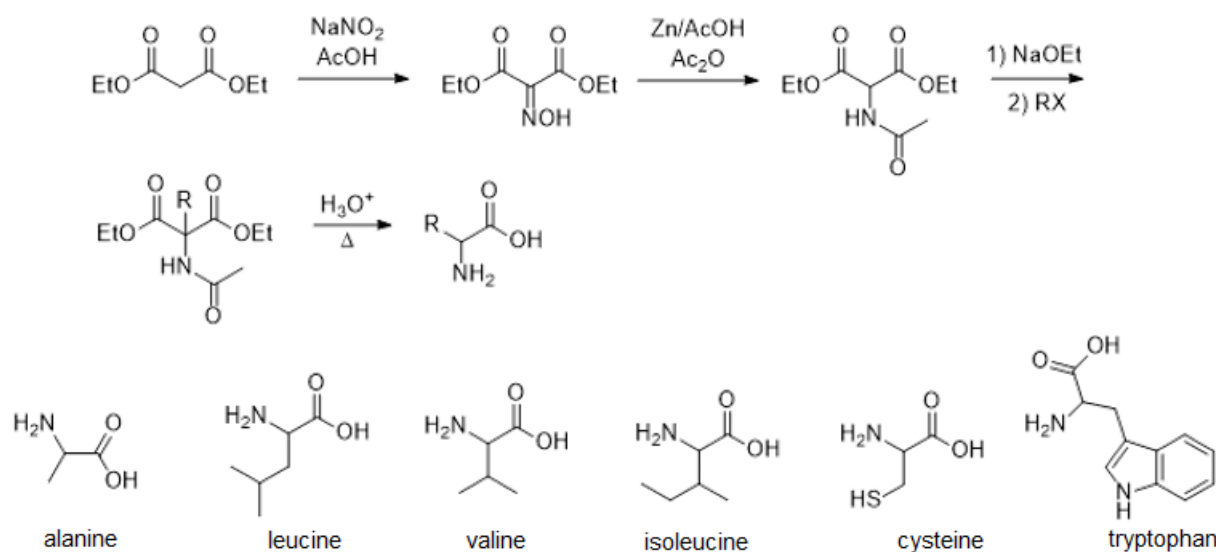
In the elimination of aldehydes accompanying the addition of ammonia, the resulting aldimine can be converted to  $\alpha$ -aminonitrile with HCN, from which an amino acid can be prepared by hydrolysis. The use of HCN can be avoided by using ammonium chloride and NaCN.



15. A – IV, B – II, C – V, D – I, E – III, a – 2, b – 4, c – 1, d – 5, e – 3

16. A – 3, B – 1, C – 2, a – 6, b – 4, c – 5

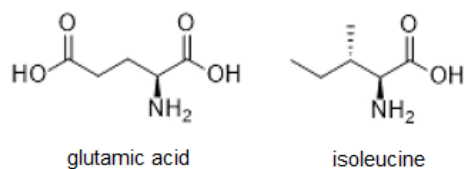
17. A – 2, B – 6, C – 3, D – 1



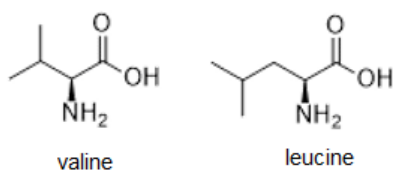
18. A

*N*-benzoylglycine (hippuric acid) forms a ring with acetic anhydride, and the resulting azlactone undergoes a condensation reaction with aldehydes containing an aromatic ring in the presence of sodium acetate. Amino acids can be prepared by the reaction of potassium phthalimide and  $\alpha$ -bromocarboxylic acid esters (Gabriel synthesis).

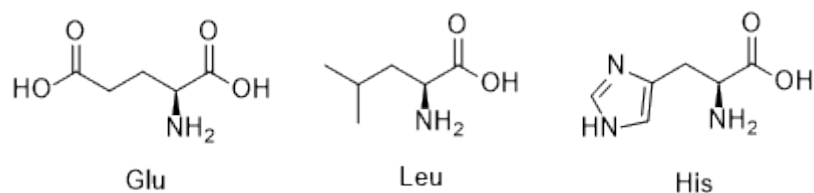
19. A



20. E



21. A



22. B

By convention the peptide chain is written with the N-terminal end on the left and the chain continues to the right (toward the C-terminal end).

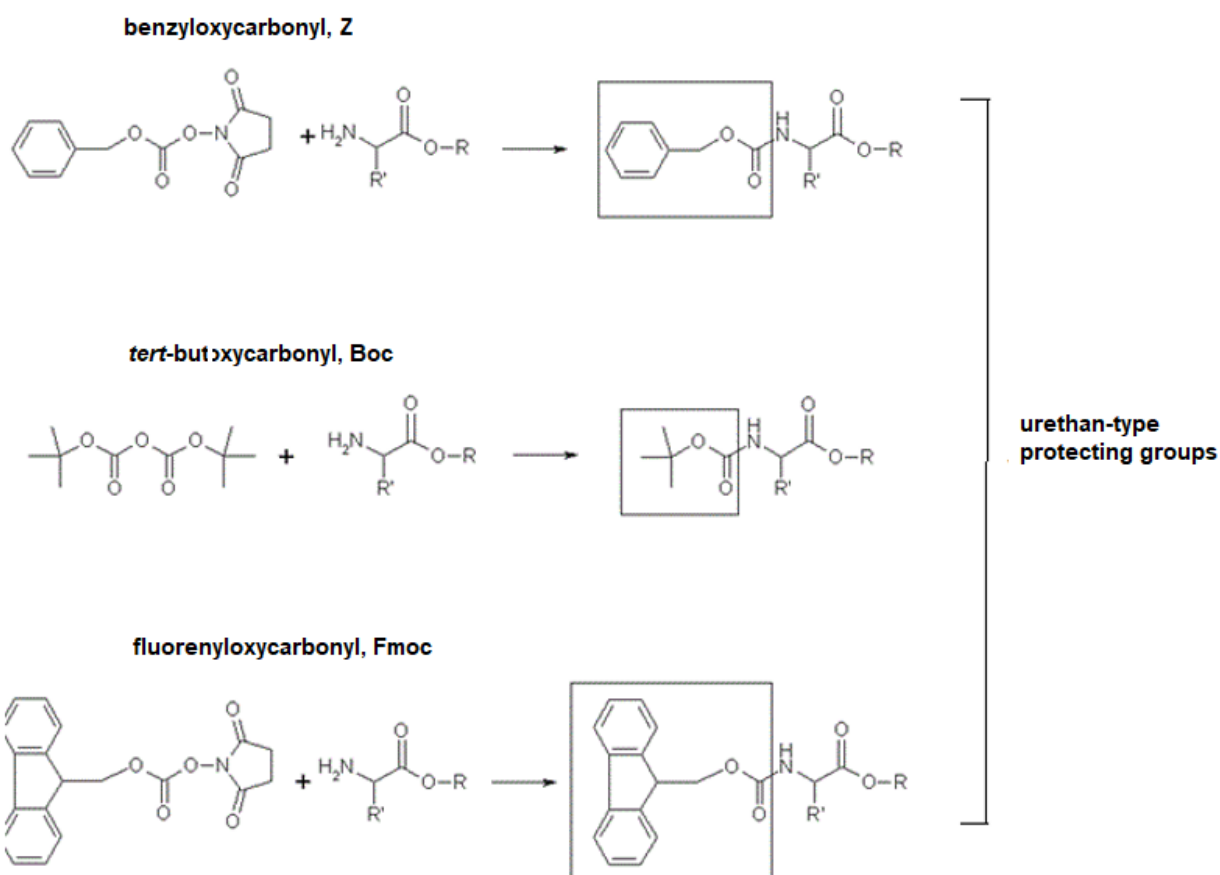
23. C

In a strongly acidic medium, the carboxyl group is neutral and the basic amino group is present in a protonated form.

24. A

When coupling amino acids to form peptides, the connectivity order is also an important factor.

25. B



26. A



$$0,93 \times 0,93 \times 0,93 \times 0,93 \times 0,93 = 0,70$$

$$0,99 \times 0,99 \times 0,99 \times 0,99 = 0,96$$

$$0,95 \times 0,95 \times 0,95 \times 0,95 \times 0,95 = 0,74$$

$$0,97 \times 0,97 \times 0,97 = 0,91$$

27. C

28. A

*In solution-phase peptide synthesis, the amino group of the N-terminal amino acid is coupled to a protecting group, then the carboxyl group is activated and the resulting protected and activated amino acid is reacted with an amino acid protected on the C-terminal carboxyl group. The procedure ends with the removal of the protecting groups.*

29. C

*The primary structure of proteins is the sequence of amino acids, the secondary structure is the local conformation of the peptide backbone of the protein due to hydrogen bonds.*

30. B

*The secondary structure of proteins is the local conformation of the peptide backbone of the protein due to hydrogen bonds.*

31. A

32. A

33. B

*In the Edman degradation, the protein or peptide is reacted with phenylisothiocyanate. From the resulting phenylthiourea derivative a phenylthiohydantoin substituted in the 5-position is cleaved off with aqueous hydrochloric acid. The N-terminal amino acid can be identified by determining the structure of the phenylthiohydantoin derivative.*

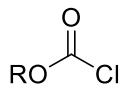
34. A

35. D

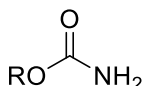


## 13. Carbonic acid derivatives

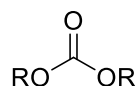
### 1. Pair the structures with the names!



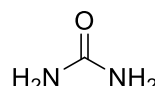
A



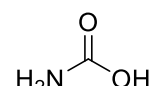
B



C



D



E

1 – alkyl chloroformate

2 – carbamic acid

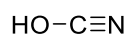
3 – dialkyl carbonate

4 – urea

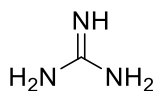
5 – alkyl carbamate

### 2. Pair the structures with the names!

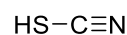
A



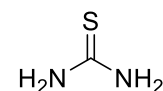
B



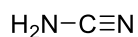
C



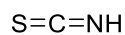
D



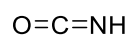
E



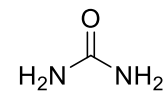
F



G



H



1 – cyanamide

2 – guanidine

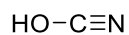
3 – isocyanic acid

4 – thiourea

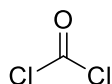
5 – thiocyanic acid

### 3. Pair the structures with the names!

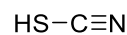
A



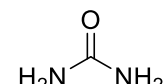
B



C



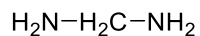
D



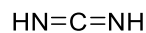
E



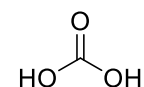
F



G



H



1 – carbonic acid

2 – phosgene

3 – carbodiimide

4 – urea

5 – cyanic acid

### 4. Which compound is imidocarbonic acid diamide?

A/ guanidine

B/ urea

C/ carbamide

D/ carbamic acid

E/ cyanic acid

### 5. Which carbonic acid derivatives can be derived from carbon dioxide?

A/ carbodiimide

B/ cyanic acid

C/ urea

D/ cyanamide

E/ thiourea





**6. Which of the following is NOT a tautomeric pair?**

- A/ thiocarbonic-S-acid – isothiocarbonic acid      B/ cyanamide – carbodiimide  
C/ urea – isokurea      D/ cyanic acid – isocyanic acid  
E/ carbonic acid – carbamic acid

**7. What is formed by heating ammonium cyanate?**

- A/ hydrazine      B/ semicarbazide      C/ guanidine  
D/ phosgene      E/ urea

**8. Which compound can be prepared from cyanamide with hydrogen sulfide?**

- A/ urea      B/ thiourea      C/ carbon disulfide  
D/ S-alkylisothiurea      E/ carbodiimide

**9. Semicarbazide is formed in the reaction of:**

- A/ urea      B/ acetyl chloride      C/ hydrazine  
D/ water      E/ ammonia

**10. What is formed in the reaction of cyanamide and ammonia?**

- A/ guanidine      B/ urea      C/ carbodiimide  
D/ cyanic acid      E/ semicarbazide

**11. What is formed in the reaction of urea and one equivalent acid halide (in the presence of a base)?**

- A/ diureide      B/ urea      C/ carbodiimide  
D/ monoureide      E/ semicarbazide

**12. What is formed in the reaction of potassium cyanate and alkyl bromides?**

- A/ dialkyl carbonate      B/ N-alkylurethane      C/ N,N'-dialkylurea  
D/ N-alkylurethane      E/ isocyanic acid esters

**13. Which statement is FALSE about urea?**

- A/ it is weakly basic  
B/ it decomposes into carbon dioxide and ammonia  
C/ it can be prepared by the reaction of phosgene and ammonia  
D/ reacts with hydrazine to form semicarbazide  
E/ reacts with acid amides to form mono-/diureides/



**14. Which statement is FALSE about guanidine?**

- A/ its protonated form is resonance-stabilized
- B/ it can be prepared from cyanamide with ammonia
- C/ it can be prepared by heating ammonium cyanate
- D/ it is an imidocarbonic acid diamide
- E/ it is one of the strongest organic bases

**15. Choose the correct answers for guanidine:**

- A/ guanidine is the imide acid analogue of urea
- B/ it is a strong organic acid
- C/ it contains two nitrogen and two carbon atoms
- D/ it is a strong organic base
- E/ it contains two nitrogen, one carbon and one oxygen atoms

**16. How phosgene can be prepared?**

- A/ by the photocatalytic oxidation of chloroform
- B/ by the reaction of carbon monoxide and chlorine gas
- C/ from carbon tetrachloride with fuming sulfuric acid
- D/ by the reaction of urea and glacial acetic acid
- E/ by mixing carbon disulfide with hydrochloric acid

**17. Which statement is FALSE about phosgene?**

- A/ it is a very toxic compound
- B/ if several nucleophiles (e.g. O, N, S) are present, it reacts with all of them
- C/ it is a very reactive compound even at low temperatures
- D/ it is liquid at room temperature (in its pure form)
- E/ it can also react with aromatic rings

**18. What product is formed when phosgene is reacted with 2 equivalents of diethylamine?**

- A/ carbamoyl chloride
- B/ *N,N'*-diethylurea
- C/ *N,N,N',N'*-tetraethylurea
- D/ *N,N'*-diethylguanidine
- E/ diethylcarbamoyl chloride

**19. In which case is the product not a mono- or diureid?**

- A/ in the reaction of urea and 1 equivalent of acetyl chloride
- B/ in the reaction of urea and 1 equivalent of propionyl chloride
- C/ in the reaction of urea and 2 equivalents of propionyl chloride
- D/ in the reaction of phosgene and 1 equivalent of propionyl chloride
- E/ in the reaction of phosgene and 2 equivalents of acetamide



20. What type of compound should be used to obtain *N*-alkylthiourethanes from alkyl isothiocyanates?

- A/ alcohol                                      B/ primary amine                                      C/ acid halide  
 D/ carboxylic acid                                      E/ acid amide

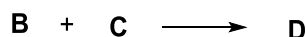
21. What is formed in the reaction of alkyl isothiocyanates and alcohols?

- A/ *N*-alkylthiourethanes                                      B/ alkylthiocyanates                                      C/ *N,N'*-dialkylthioureas  
 D/ *S*-alkylisothioureas                                      E/ *N,N'*-disubstituted carbodiimide

22. Which compounds would react to lead to *N,N'*-dicyclohexylthiourea?

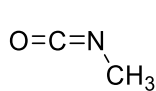
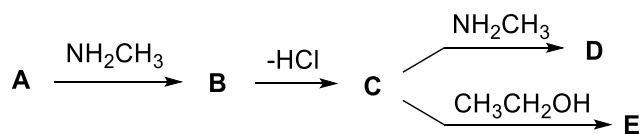
- A/ cyclohexyl isothiocyanate                                      B/ phosgene                                      C/ *N,N'*-dicyclohexylurea  
 D/ cyclohexanol                                      E/ cyclohexylamine

23. Complete the reaction scheme below with the missing compounds!

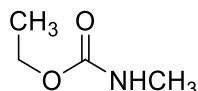


1.  $\text{H}_2\text{N}-\text{NH}_2$                                       2.  $\text{H}_2\text{O} / \text{H}^+$                                       3.  $\text{H}_2\text{N}-\text{CO}-\text{NH}-\text{NH}_2$                                       4.  $\text{H}_2\text{N}-\text{CO}-\text{NH}_2$

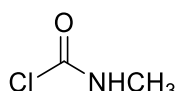
24. Complete the reaction scheme below with the missing compounds!



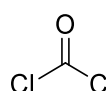
1



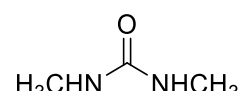
2



3

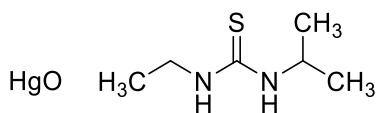
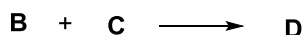
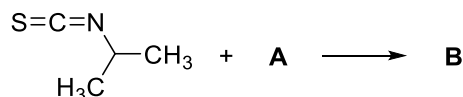


4



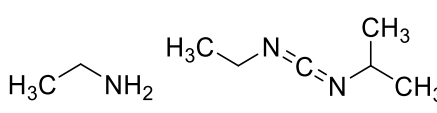
5

25. Complete the reaction scheme below with the missing compounds!



1

2

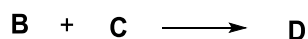


3

4



26. Complete the reaction scheme below with the missing compounds!



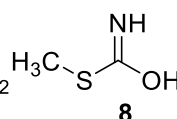
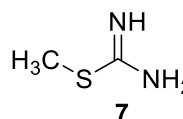
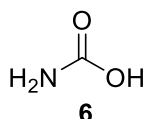
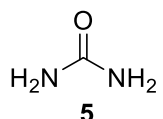
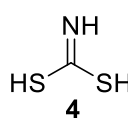
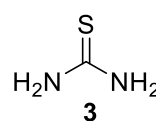
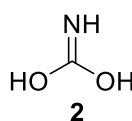
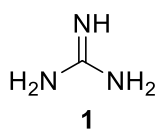
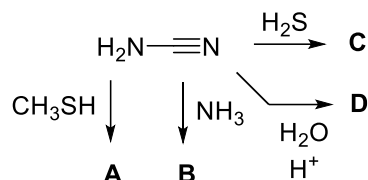
1.  $\text{ClCOCH}_3$

2.  $\text{H}_2\text{O} / \text{H}^+$

3.  $\text{H}_2\text{N-CO-NH-CO-CH}_3$

4.  $\text{H}_2\text{N-CO-NH}_2$

27. Complete the reaction scheme below with the missing compounds!



28. What type of reaction is the formation of *N,N'*-dialkyl ureas from phosgene?

A/ electrophilic addition

B/ nucleophilic addition

C/ nucleophilic substitution

D/ electrophilic substitution

E/ radical elimination

29. What type of reaction is the formation of dialkyl carbonates from phosgene?

A/ nucleophilic substitution

B/ nucleophilic addition

C/ electrophilic addition

D/ electrophilic substitution

E/ radical elimination

30. Which of the following is the strongest base?

A/ urea

B/ cyanamide

C/ guanidine

D/ thiourea

E/ phosgene



## 13. Carbonic acid derivatives

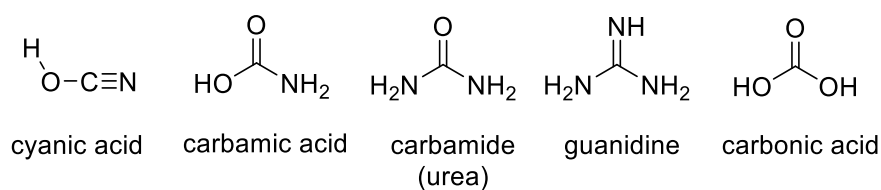
### Solutions

1. 1 - A, B - 5, C - 3, D - 4, E - 2

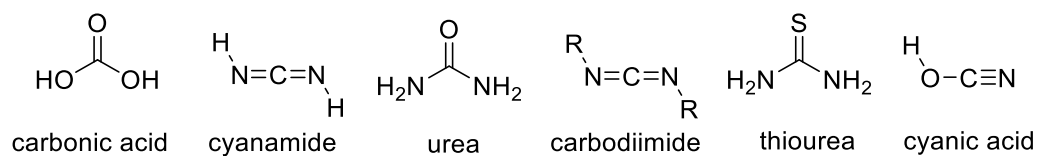
2. 1 - E, 2 - B, 3 - G, 4 - D

3. 1 - H, 2 - B, 3 - G, 4 - D, 5 - A

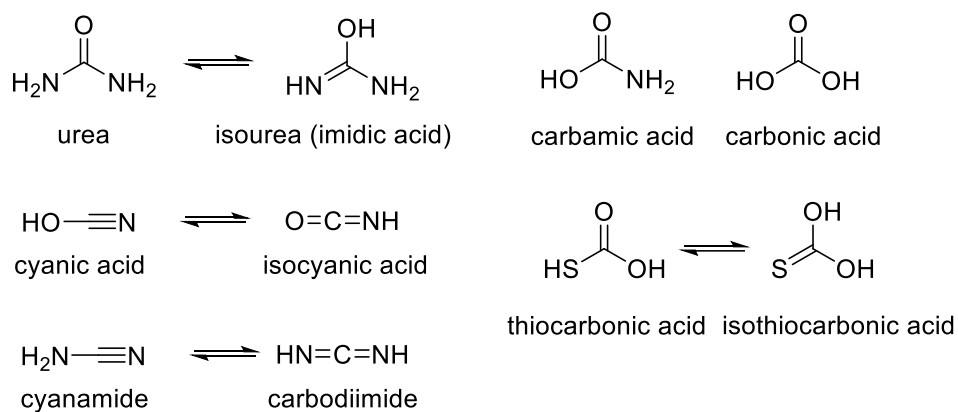
4. A



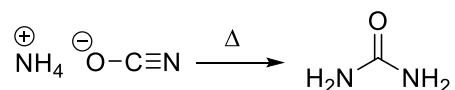
5. A, B, D



6. E

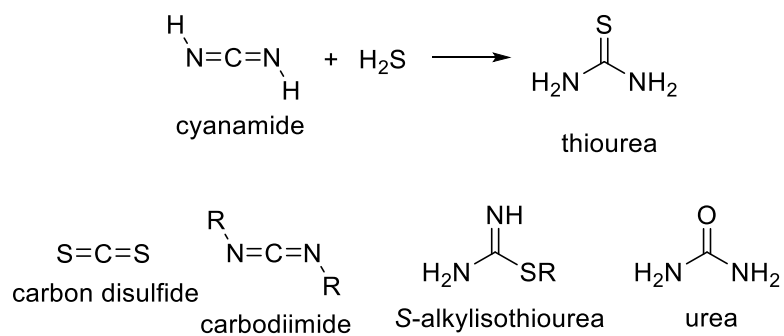


7. E

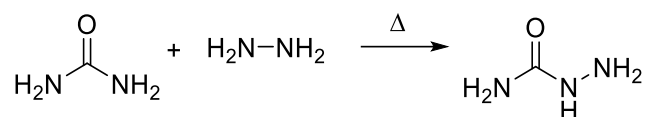


8. B

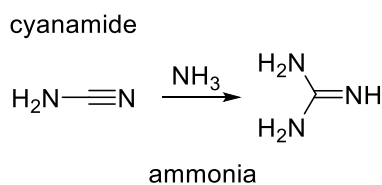




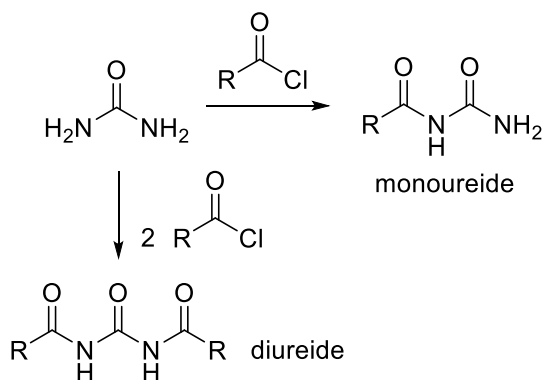
9. A, C



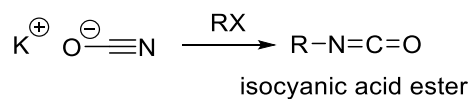
10. A



11. D



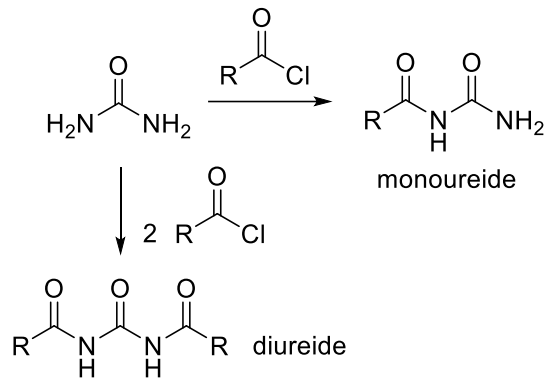
12. E



13. E

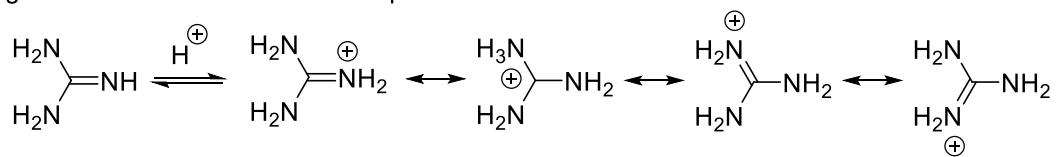
urea forms ureides with carboxylic acid halides



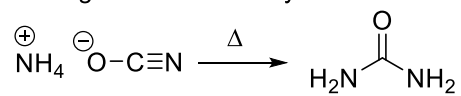


14. C

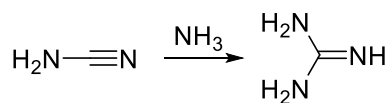
guanidine: resonance-stabilized protonated form



heating of ammonium cyanate

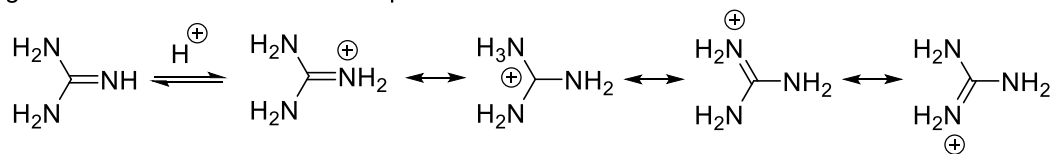


cyanamide + ammonia

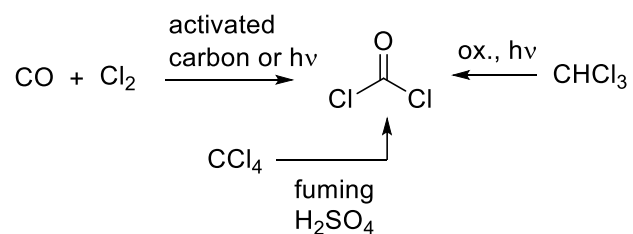


15. A, D

guanidine: resonance-stabilized protonated form



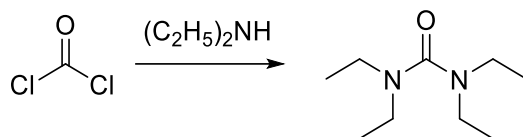
16. A, B, C



17. D

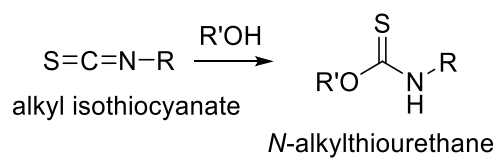
18. C





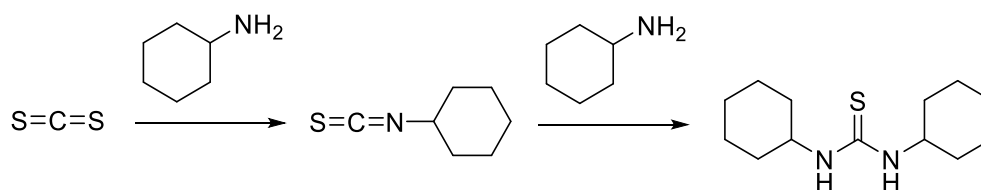
19. D

20. A



21. A

22. A, E



23. A - 2, B - 4, C - 1, D - 3

24. A - 4, B - 3, C - 1, D - 5, E - 2

25. A - 3, B - 2, C - 1, D - 4

26. A - 2, B - 4, C - 1, D - 3

27. A - 7, B - 1, C - 3, D - 5

28. C

29. A

30. C

*Guanidine is one of the strongest organic bases, its protonation results in a cross-conjugated, resonance-stabilized structure.*





## 14. Natural compounds

### 1. Group the following fatty acids according to their saturation!

A/ palmitic acid      B/ myristic acid      C/ oleic acid

D/ lauric acid      E/ linolenic acid

1 – saturated      2 - unsaturated

### 2. Indicate which of the following steroid compounds has an aromatic A-ring.

A/ cholesterol      B/ androsterone

C/ estradiol      D/ spironolactone

### 3. Indicate which steroid compound(s) has *cis-anti-trans-anti-trans* ring annulation:

A/ cholesterol      B/ glucocorticoids

C/ cholic acid      D/ estrane

### 4. Indicate which steroid compound has a *trans-anti-trans-anti-trans* ring annulation.

A/ cholesterol      B/ androsterone

C/ estrane      D/ spironolactone

### 5. Complete the following phrase to get a correct statement.

Estradiol is estrone's...

A/ ...reduced derivative    B/ ...oxidized derivative    C/ ...geometric isomer

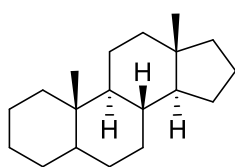
D/ ...diastereomer      E/ ...open chain form      F/ ...lactim form

### 6. Indicate which steroid compound is the building block of other steroids in plants:

A/ cholesterol      B/ squalene

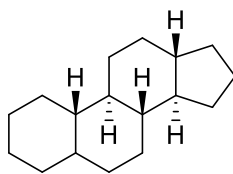
C/ vitamin D<sub>2</sub>      D/ lanosterol

### 7. Match the names of the steroid skeletons below with their formulas!



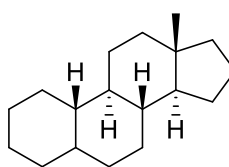
**A**

1 – gonane



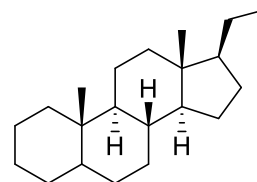
**B**

2 – estran



**C**

3 – pregnane



**D**

4 - androstane

**8. Which of the following compounds is a diterpenoid?**

- A/ squalene                                      B/ vitamin A  
C/ secologanin                                    D/ nerol

**9. Which of the following compounds is a monoterpenoid (there could be more correct answers)?**

- A/ mevalolacton                                    B/ camphor  
C/ geraniol                                         D/ vitamin D<sub>2</sub>

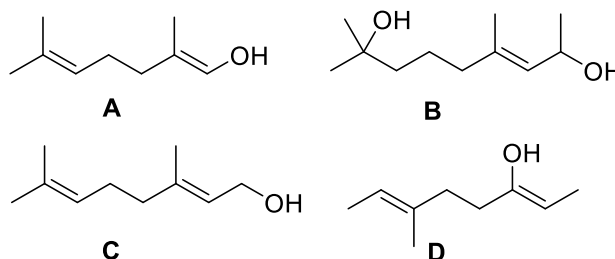
**10. Which of the following compounds is a sesquiterpenoid?**

- A/ linalool                                         B/ squalene  
C/ menthol                                         D/ guajazulen

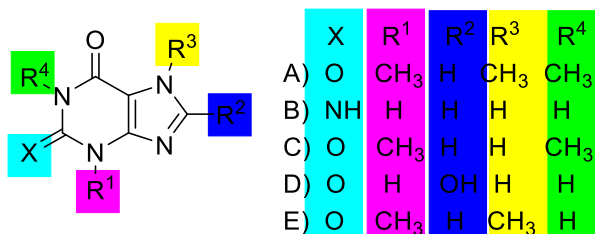
**11. Match the descriptions with the name.**

- A/ C<sub>10</sub> terpenoids containing two isoprene units  
B/ C<sub>15</sub> terpenoids containing three isoprene units  
C/ C<sub>20</sub> terpenoids containing four isoprene units  
D/ C<sub>25</sub> terpenoids containing five isoprene units
- 1 – sesterterpene                                      2 - diterpene  
3 – monoterpene                                      4 – sesquiterpene

**12. Which of the following compounds is a terpene?**



**13. Choose the substituents for the following compounds!**



1 – caffeine, 2 – theobromine, 3 - theophylline

**14. Which of the following statements about caffeine is FALSE?**

- A/ it is produced by Traube synthesis
- B/ it contains a basic nitrogen
- C/ it contains a purine scaffold
- D/ it can be written in two tautomeric forms
- E/ it is a methylxanthine derivative
- F/ it is not an isomer of theobromine

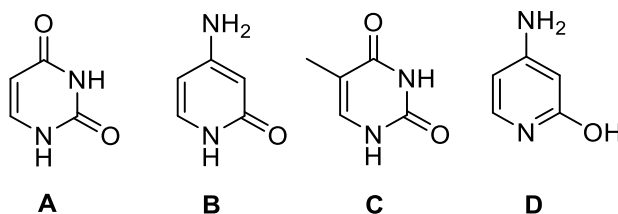
**15. Choose the correct statements:**

- A/ guanine corresponds to 2-aminopurine-6-one
- B/ xanthine corresponds to purine-2,6-dione
- C/ xanthine corresponds to 2-aminopurin-6-one
- D/ guanine corresponds to purine-2,6-dione

**16. Mark the correct answers for the Traube synthesis of guanine:**

- A/ its starting compound is 2,5,6-triaminopyrimidin-4-ol
- B/ the reagent used is formic acid
- C/ there is no need to apply heating
- D/ a substitution takes place

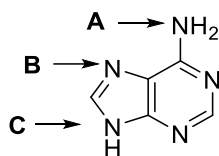
**17. Choose the tautomers of cytosine!**



**18. Choose the correct answers:**

- A/ RNA contains uracil and cytosine
- B/ DNA contains uracil and cytosine
- C/ DNA contains cytosine and thymine
- D/ RNA contains cytosine and thymine

19. Under acidic conditions, which nitrogen of adenine will be protonated?



20. How could true alkaloids be characterized compared to protoalkaloids?

- A/ true alkaloids are strong bases
- B/ true alkaloids are strongly toxic
- C/ true alkaloids are built up from biogenic amines and terpene components
- D/ true alkaloids are typically cyclic, sterically hindered tertiary amines with a rigid structure

21. What is the main characteristic of protoalkaloids regarding the position of the nitrogen atom?

- A/ in protoalkaloids, the nitrogens always form cations
- B/ in protoalkaloids, there are only secondary nitrogens
- C/ in protoalkaloids, the nitrogen atoms are located outside the ring
- D/ in protoalkaloids there are exclusively primary nitrogens

22. Which of the following statements are correct about  $\beta$ -lactams?

- A/ they contain a four-membered ring
- B/ part of the penam scaffold is a six-membered ring
- C/ they are cyclic acid amides
- D/ they have a strained structure
- E/ the  $\beta$ -lactam ring of penicillins is sensitive to acids and stable in alkaline media

23. Which of the following statements are correct about  $\beta$ -lactams?

- A/ they are contained in the structure of cephalosporin antibiotics
- B/ they contain also a carbonyl group
- C/ they contain a four-membered ring
- D/ they are resistant to acidic and basic conditions, and to enzymatic hydrolysis
- E/ they are cyclic acid amides

24. Which of the following functional groups are present in the structure of epinephrine?

- A/ phenolic hydroxyl group
- B/ primary aliphatic amine
- C/ tertiary alcohol
- D/ secondary aliphatic amine
- E/ tertiary aliphatic amine
- F/ primary alcohol

25. Which of the following functional groups are present in the structure of atropine?

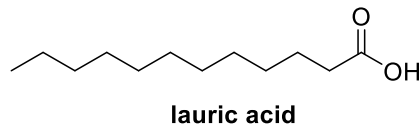
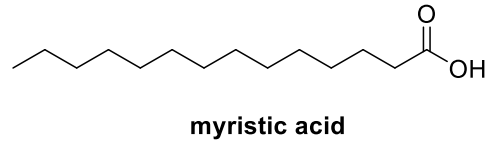
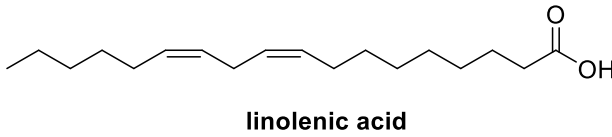
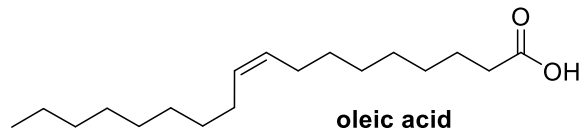
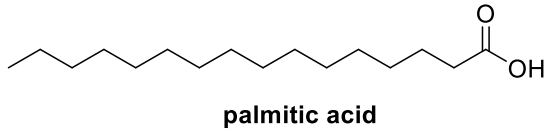
- A/ phenolic hydroxyl group
- B/ secondary aliphatic amine
- C/ tertiary aliphatic amine
- D/ primary alcohol
- E/ tertiary alcohol



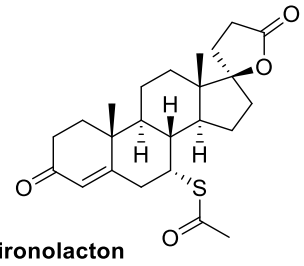
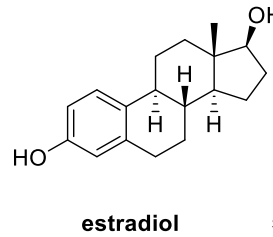
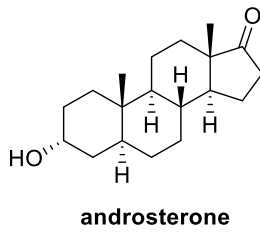
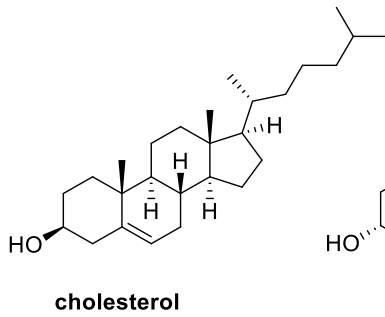
## 14. Natural products

### Solutions

1. A - 1, B - 1, C - 2, D - 1, E - 2

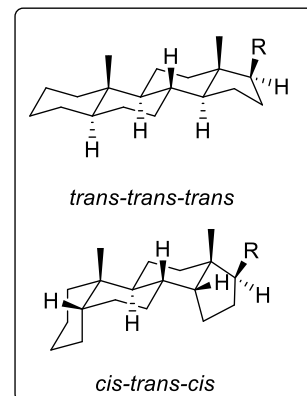
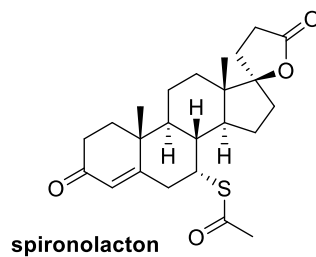
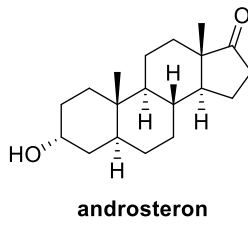
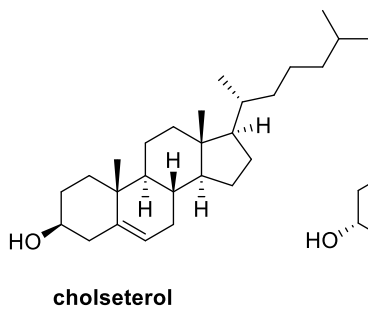


2. C

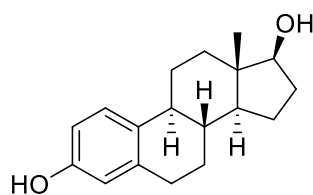


3. C

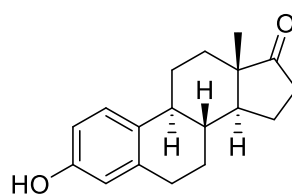
4. B



5. A



**estradiol**

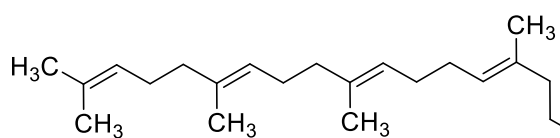


**estron**

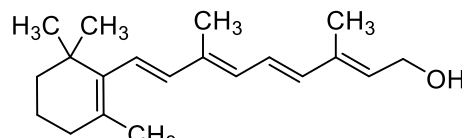
6. D

7. A - 4, B - 1, C - 2, D - 3

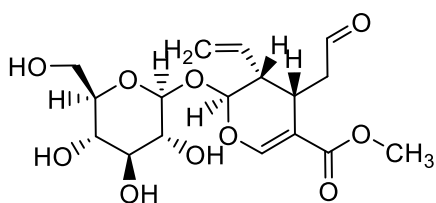
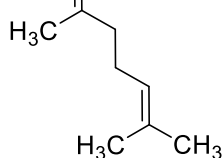
8. B



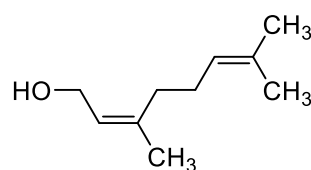
**squalene**



**vitamin A**

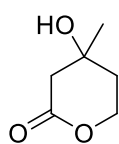


**secologanin**

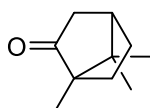


**nerol**

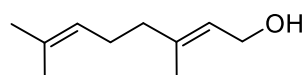
9. B, C



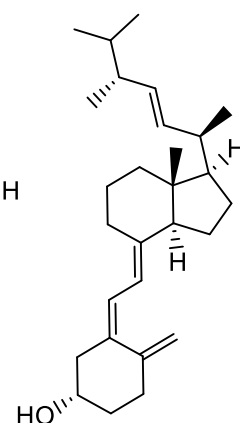
**mevalolacton**



**camphor**



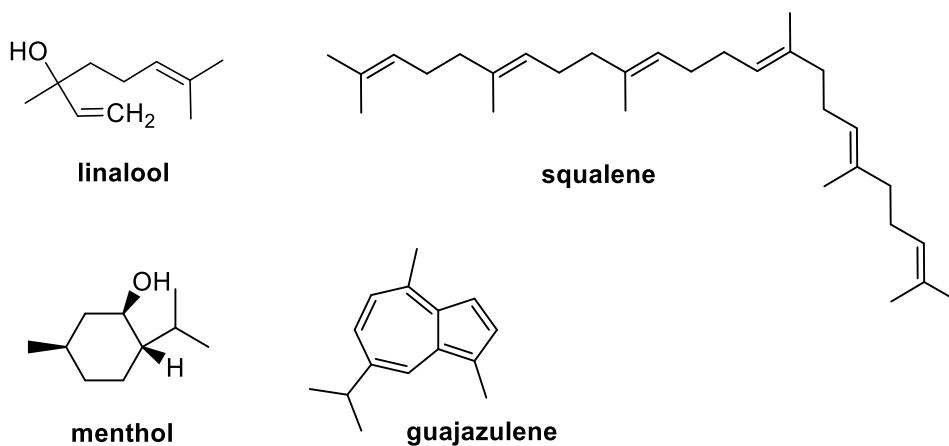
**geraniol**



**vitamin D<sub>2</sub>**



10. D



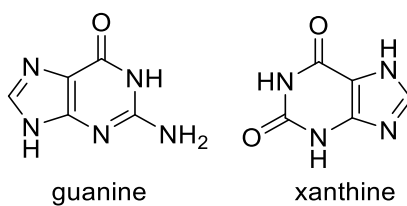
11. A - 3, B - 2, C - 1, D - 4

12. C

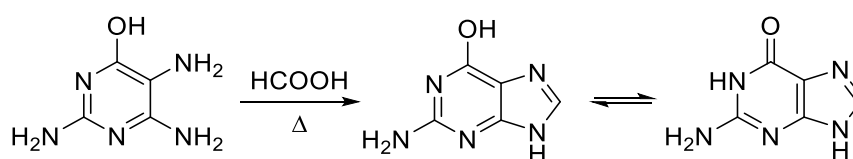
13. 1 - A, 2 - E, 3 - C

14. D

15. A, B



16. A, B



17. B, D

18. A, C

19. B

20. D

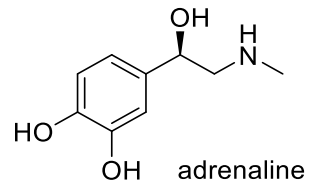
21. C

22. A, C, D

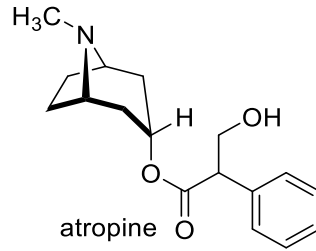
23. A, B, C, E

24. A, D





25. C, D





## Literature

Általános gyógyszerészeti ismeretek – ed.: Takácsné Novák Krisztina, Dévay Attila, Szabóné Révész Piroska, Szökő Éva, Medicina Kiadó Zrt., Budapest, 2011

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