Working on Questions

All questions are very closely related to the chapter´s contents so that the text answers most of them in words, by means of structural formulas or reaction equations. Chapter references are provided in these cases. More detailed solutions are given in the following when answers require analogous conclusions or the reader´s own reflections.

(1.1) What is an atomic orbital?
Chapter **1.2**

(1.2) How do p orbitals differ from s orbitals?
Chapter **1.2**

(1.3) How do p orbitals differ among themselves?
Chapter **1.2**

(1.4) Write the orbital occupancy for the atoms in the first two rows of the periodic table.
Chapter **1.4**, Table 1.1

(1.5) Is the tetravalency of carbon in accordance with the electronic configuration of carbon in Table 1.1?
The electronic configuration $1s^2\ 2s^2\ 2p^2$ of the carbon atom does not explain its tetravalence because only two singly occupied p orbitals (e.g. p_x and p_y) would be available for overlapping (see also Chapter **3.1**).

(2.1) What is a covalent bond?
Chapter **2.1**

(2.2) How is a molecular orbital (MO) generated?
Chapter **2.2**

(2.3) How can the covalent bond of the hydrogen molecule be explained?
Chapter **2.2**

(2.4) Calculate the particularly high electron density between covalently bonded atomic nuclei in terms of the MO model.
Chapter **2.2**, Table 1.1

(2.5) Which options of overlapping exist for p orbitals? Which types of bonding are the result?
Chapter **2.3**, Fig. 2.3

(3.1) Describe and draw the geometry of the methane molecule.
Chapter **3.1**

(3.2) The electronic configuration of the carbon atom does not explain the shape of the methane molecule. Why?
Chapter **3.1**

(3.3) What is hybridization of atomic orbitals? Hybrid orbitals offer better chances for overlapping. Why?
Chapter **3.2**

(3.4) What is the model explanation of the tetrahedral shape of the methane molecule and the genesis of its CH bonds?
Chapter **3.3**, Fig. 3.4

(4.1) What are the molecular shapes of ***(a)*** ethane, ***(b)*** ethene, and ***(c)*** ethyne?
Chapter **4.1**, Fig. 4.1: answering ***(a)***; Chapter **4.2**, Fig. 4.3, answering ***(b)***; Chapter **4.3**, Fig. 4.5: answering ***(c)***

(4.2) Explain the genesis of a CC single, a CC double and a CC triple bond in terms of the MO model.
Chapter **4.1**, Fig. 4.2, Chapter **4.2**, Fig. 4.4, Chapter **4.3**, Fig. 4.6

(4.3) Draw the areas around a CC double bond where the π electrons are most likely to be found.
Chapter **4.2**, Fig. 4.4

(4.4) Explain why CC multiple bonds are shorter than a CC single bond.
Chapter **4.3**, last section

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(5.1) What is a homologous series of compounds?
Chapter **5.1**

(5.2) What natural sources of alkanes exist and how are alkanes produced industrially?
Chapter **5.2.1**

(5.3) What reactions permit the preparation of specific alkanes?
Chapters **5.2.3**, **5.2.4** (symmetric alkanes R–R), Chapter **5.2.2** (depending on availability of alkenes)

(5.4) Alkanes are still an important source of energy. Why? Write the complete equation for an appropriate reaction.
Chapter **5.3**

(6.1) What are structural (skeletal) isomers?
Chapter **6.1**

(6.2) Which structural isomers exist for ***(a)*** butane, ***(b)*** pentane, and ***(c)*** hexane?
Chapters **6.1**, **6.2**

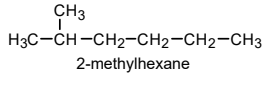
(6.3) Which properties are individual (specific) for structural isomers?
Chapter **6.2**

(6.4) Which one of these properties is the basis of a method for the separation and purification of structural isomers?
Chapter **6.2**, Table 5.2

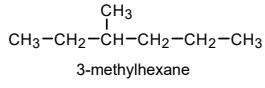
(6.5) Draw the structures of the skeletal isomers of heptane with ***(a)*** one methyl group and ***(b)*** two methyl groups in the side chain.

(a) Two singly and ***(b)*** four doubly methyl branched skeletal isomers of heptane C_7H_{16} exist.

(a)

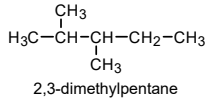


2-methylhexane

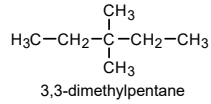


3-methylhexane

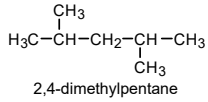
(b)



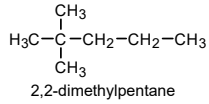
2,3-dimethylpentane



3,3-dimethylpentane

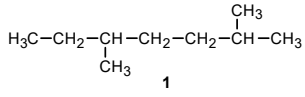


2,4-dimethylpentane

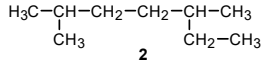


2,2-dimethylpentane

(6.6) Which of the following compounds (**1**-**6**) are structural isomers? Which ones are identical?



1



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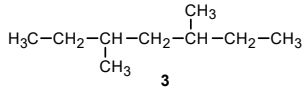

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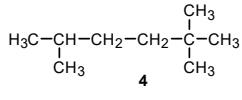

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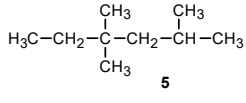

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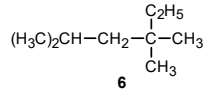
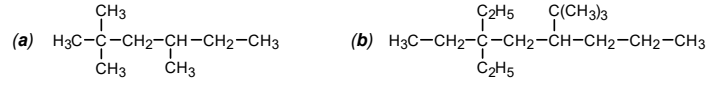


6

1 and **2** as well as **5** und **6** are identical; **3** displays two and **4** three methyl branchings.

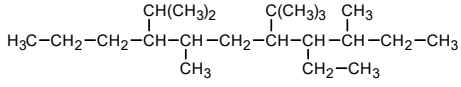
(7.1) What are the IUPAC names of all singly and doubly methyl branched isomers of heptane C_7H_{16}? #
IUPAC names are assigned to the structural formulas in answer ***(6.5)***.

(7.2) Draw the structural formulas of *(**a**)* 2,2,4-trimethylhexane, and *(**b**)* 5-*t*-butyl-3,3-diethyloctane.
Structural formulas of 2,2,4-trimethylhexane ***(a)*** and 5-*t*-butyl-3,3-diethyloctane ***(b)*** are the following:



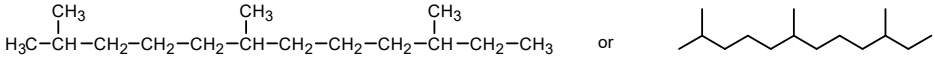
(7.3) Give the IUPAC names of the alkanes with structures drawn in question ***6.6***.
1 = ***2***: 2,5-dimethylheptane; ***3***: 3,5-dimethylheptane; ***4***: 2,2,5-trimethylhexane; ***5*** = ***6***: 2,4,4-trimethylhexane are the IUPAC names.

(7.4) What is the correct IUPAC name of the following alkane?



5-*t*-Butyl-4-ethyl-8-isopropyl-3,7-dimethylundecane (not 7-*t*-butyl-8-ethyl-4-isopropyl-5,9-dimethylundecane) is the correct IUPAC name.

(7.5) What is the structural formula of 2,6,10-trimethyldodecane which occurs in slate oil?
The *skeletal formula* of 2,6,10-trimethyldodecane (the sesquiterpene parent hydrocarbon, Chapter **76.1**) provides a more compact presentation.

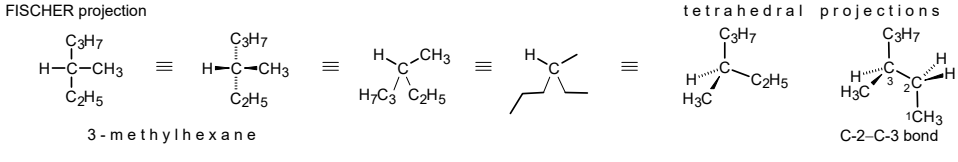


(8.1) Draw the skeletal formulas for cyclopropane, cyclopentane, cycloheptane, and cyclooctane.
Chapter **20.1**, cycloalkane formulas

(8.2) Draw the condensed and skeletal structural formula of 2,6,10-trimethyldodecane.
answer ***(7.5)***

(8.3) Draw the condensed and skeletal structural formula of 3-methylhexane and number the longest carbon chain.
answer ***(6.5a)***

(8.4) Draw one of the tetrahedral projections of the CH carbon (C-3) in 3-methylhexane.
Chapter **8.4.1**: The three-dimensional picture of tetrahedral bonds originating from a carbon facilitates the drawing of FISCHER- and tetrahedral projections as in the case of 3-methylhexane.



(8.5) Write the reaction equation for 1-bromobutane with sodium hydroxide by means of LEWIS formulas. What is the origin of the CO bond in the product 1-butanol?
Chapter **8.3**

(8.6) Draw NEWMAN projections of the central CC bond of hexane with staggered ethyl groups.
Chapter **8.4.2**: C_2H_5 replaces CH_3 in the NEWMAN projection of butane; the other two conformers with staggered substituents arise from rotation of the tetrahedron behind by 120°.

(9.1) Why do alkanes form conformers? Explain the terms conformation and conformer.
Chapter **9.1**

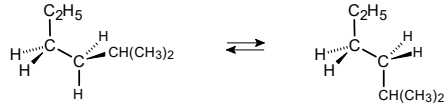
(9.2) How do conformers differ from structural isomers?
Chapter **9.2**, last section

(9.3) Draw NEWMAN projections of the C-2–C-3 bond of butane for all conformers with staggered methyl groups.
Fig. 9.1: CH_3 replaces staggered alkyl residues R (three conformers).

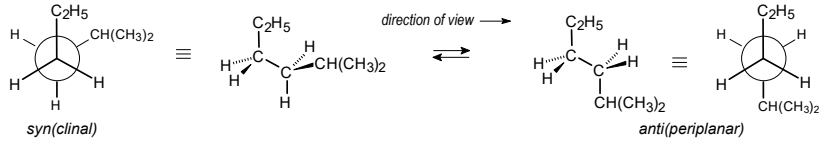
(9.4) Draw NEWMAN projections of the C-1–C-2 bond of ***(a)*** 1-bromopropane and ***(b)*** 1,2-dibromoethane for all conformers with staggered groups.
Fig. 9.1: ***(a)*** CH_3 and Br replace staggered alkyl residues R (three conformers);
(***b***) Br replaces staggered alkyl residues R (three conformers).

(9.5) Draw the energy diagram of rotation about the central CC bond of butane and use NEWMAN projections to present all conformers.
Chapter **9.2**, Fig. 9.1: CH_3 replaces alkyl residues R.

(9.6) Draw NEWMAN projections of the following conformers of 2-methylhexane and specify the spatial arrangements of the alkyl groups.



Chapter **9.2**: NEWMAN projections clearly show when alkyl groups are *syn*(*clinal*, dihedral angle 60°) or *anti*(*periplanar*, dihedral angle 180°).



(9.7) What are steric interactions? Which conformers particularly suffer from these interactions?
Chapter **9.2**: Eclipsed groups strongly repel each other and destabilize a conformer. This steric interaction is much weaker for staggered groups.

(10.1) Give appropriate examples for a homolysis and a heterolysis of a σ bond.
Chapter **10.1**

(10.2) What are radicals, carbenium ions, carbanions, and carbenes? How are these species formed?
Chapters **10.1**, **10.2**, **10.3**

(10.3) Draw the molecular orbital models of the methyl radical and the methyl cation. How do they differ?
Chapter **10.1**, Fig. 10.1

(10.4) Define the terms electrophile and nucleophile and classify carbenium ions, carbanions, and carbenes as such.
Chapters **10.2**, **10.3**

(10.5) Suggest a molecular orbital model for the low-energy carbene with unpaired electrons.
The bond angle (136°) is not too far apart from the interorbital angle of sp^2 hydrid orbitals (120°). Thus, it may be assumed that the biradical carbon atom of hot carbene overlaps with two sp^2 hybrid orbitals in order to form two CH bonds. The remaining sp^2 hybrid orbital and the unhybridized *p* orbital are singly occupied.

(11.1) Which kind of reactions are additions and eliminations? Formulate typical equations.
Chapters **11.1**, **11.2**

(11.2) Explain the term β-elimination.
β Elimination involves separation of H and X from adjacent C atoms; in an α elimination H and X separate from the same carbon atom (occuring infrequently, *e.g.* Chapter **42.6.1**).

(11.3) Which kind of reactions are oxidations and reductions? Formulate typical equations.
Chapters **11.3**, **11.4**

(11.4) Which kind of substitution reactions exist? Formulate typical equations.
Chapter **11.5**

(11.5) What kind of rearrangements do you know? Formulate typical equations.
Chapter **11.6**

(12.1) What is the transition state of a reaction?
Chapter **12.1**, Fig. 12.1

(12.2) Explain the terms activation energy and heat of reaction.
Chapter **12.1**, Fig. 12.1

(12.3) What are the effects of an exothermic and an endothermic reaction?
Chapter **12.1**

(12.4) What are the characteristics of a kinetically and a thermodynamically controlled reaction? Draw an energy diagram for explanation.
Chapter **12.3**, Fig. 12.2

(12.5) Characterize the action of a catalyst.
Chapter **12.2**

(13.1) Formulate all equations to describe the mechanism of the radical halogenation of alkanes.
Chapter **13.1**

(13.2) Which kind of substituents can be introduced into alkanes by radical substitutions?
Chapters **13.1**, **13.4**: Radical halogenation, sulfochlorination and nitration permit substitution of hydrogen atoms in alkyl groups (alkanes), introducing halogens, sulfonic acid and nitro groups.

(13.3) The 2-butyl radical is more stable than the 1-butyl radical. Why?
Chapter **13.2**, Fig. 13.1

(13.4) Define the term regioselectivity. How are regioselectivity and reactivity related to each other in the photo-halogenation of alkanes?
Chapter **13.3**

(13.5) What product is expected from the bromination of butane? Explain, write equations and give the product's name.
Chapters **13.2**, **13.3**: Replace propane by butane in Chapter **13.3**; 2-bromobutane is the major product because a 2-butyl radical is more stable, longer living, thus having more time to react than the less stabilized 1-butyl radical.

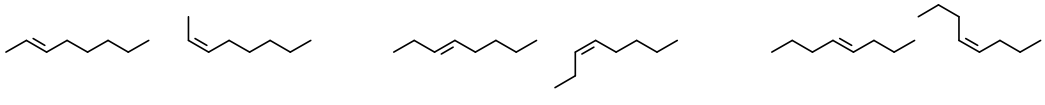
(14.1) Which unbranched structural isomers exist for the molecular formula C_8H_{16}? Give their IUPAC names.
Chapter **14.1**: 1-Octene, 2-octene (*cis*- and *trans*-), 3-octene (*cis*- and *trans*-) 4-octene, (*cis*- and *trans*) are unbranched isomeric alkenes with the molecular formula C_8H_{16}. Answer ***(14.5)*** provides the skeletal formulas of the cofigurational isomers.

(14.2) There is no free rotation about the π bond of alkenes. Look at Fig. 4.4 and provide an explanation.
Chapter **14.2**

(14.3) What are configurational isomers? How do they differ? How are they specified? Why do they differ from conformers?
Chapter **14.2**

(14.4) Which of the alkenes ***(a)*** propene, ***(b)*** 1-bromopropene, ***(c)*** 1-butene, ***(d)*** 2-butene, and ***(e)*** 3-hexene exist as configurational isomers? Draw condensed structural and skeletal formulas (Chapters **8.1**, **8.2**) of all compounds.
Only ***(b)***, ***(d)*** and ***(e)*** exist as *cis*- and *trans*- isomers (*Z*- and *E*- isomers).

(14.5) Draw condensed structural and skeletal formulas of all configurational isomers of the non-terminal octenes C_8H_{16} and name them.
The *skeletal formulas* of 2-octene (*trans*- and *cis*-), 3-octene (*trans*- and *cis*-), 4-octene (*trans*- and *cis*-) provide a compact sketch of the molecular geometry.



(15.1) What mechanisms exist for the dehydrohalogenation of alkyl halides? Formulate appropriate equations.
Chapter **15.1.1**

(15.2) What is the mechanism for the acid-catalyzed dehydration of an alcohol? Write an appropriate equation.
Chapter **15.1.2**

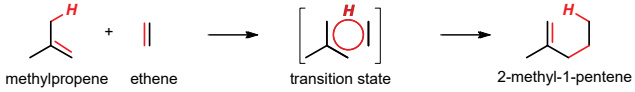
(15.3) Dehydrobromination of 2-bromobutane predominantly yields 2-butene. Why?
Chapter **15.1.1** in analogy to 2-bromopentane, set CH_3 instead of C_2H_5

(15.4) 2,3-Dimethyl-2-butanol dehydrates to give 2,3-dimethyl-2-butene and not to 2,3-dimethyl-1-butene. Why?
Chapter **15.1.2**

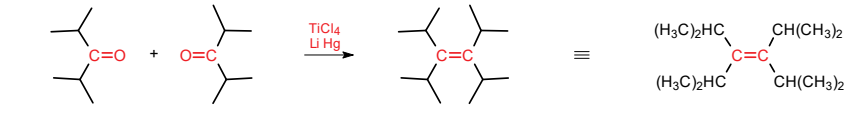
(15.5) Formulate the general conversion of a carbonyl compound into an alkene.
Chapter **15.2.4**

(15.6) 1-Butene reacts with *N*-bromosuccinimide. What product do you expect? Formulate the reaction.
Chapter **15.3.1**

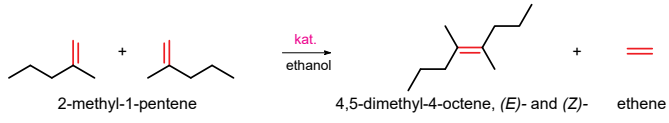
(15.7) Methylpropene and ethene are heated under pressure. What product is likely to be formed?
Chapter **15.3.3**: The ene reaction of methylpropene with ethene is expected to produce 2-methyl-1-pentene.



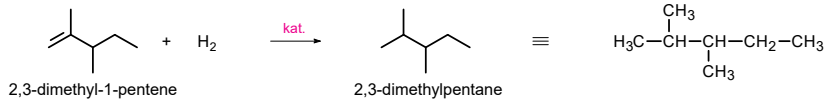
(15.8) Design a synthesis of *(**a**)* 3,4-diisopropyl-2,5-dimethyl-3-hexene and *(**b**) cis-* and *trans*-4,5-dimethyl-4-octene.
Chapter **15.2.3**, answering *(**a**)*: McMURRY reaction of diisopropylketone produces 3,4-diisopropyl-2,5-dimethyl-3-hexene (tetraisopropylethene).



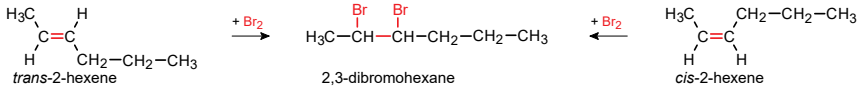
Chapter **15.3.4**, answering *(**b**)*: Metathesis of 2-methyl-1-pentene produces 4,5-dimethyl-4-octene and ethene.



(16.1) Suggest the preparation of *(**a**)* 2,3-dimethylpentane and *(**b**)* 2,3-dibromohexane from appropriate alkenes.
Chapter **16.1**, answering *(**a**)*: 2,3-Dimethylpentane is obtained by catalytic hydrogenation of 2,3-dimethyl-1-pentene (or regioisomers with the same carbon skeleton but CC double bonds in other positions).



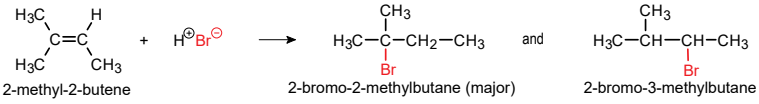
Chapter **16.2**, answering *(**b**)*: 2,3-Dibromohexane arises from the addition of bromine to 2-hexene (*cis*- or *trans*-).



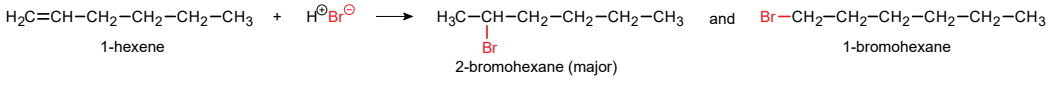
(16.2) What is an electrophilic addition? Write mechanisms for the bromination and hydrobromination of alkenes.
Chapters **16.2**, **16.3**

(16.3) What products are obtained by hydrobromination of *(**a**)* 2-methyl-2-butene and *(**b**)* 1-hexene?

Chapter **16.3**: In accordance with MARKOVNIKOV´s rule, *(**a**)* 2-bromo-2-methylbutane

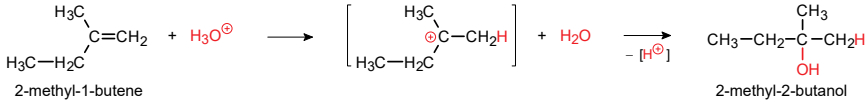


and *(**b**)* 2-bromohexane are expected to arise as major products from hydrobromination.

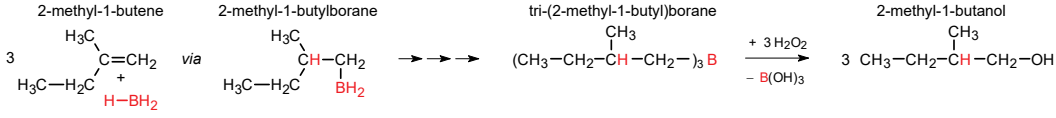


(16.4) What products arise from *(**a**)* hydration and *(**b**)* hydroboration of 2-methyl-1-butene?

Chapter **16.4**, answering *(**a**)*: 2-Methyl-1-butene is expected to undergo acid catalyzed hydration to 2-methyl-2-butanol, involving the more stable tertiary carbenium ion according to MARKOVNIKOV´s rule.



Chapters **16.6**, **33.3.4**, answering *(**b**)*: Hydroboration is expected to produce tri-(2-methylbutyl)borane which undergoes oxidation to 2-methyl-1-butanol and boric acid with hydrogen peroxide, H_2O_2.



(16.5) Which methods can be used to prepare 1,2-diols from alkenes? Formulate general reaction equations.

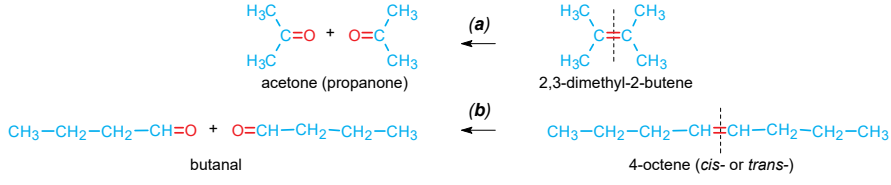
Chapter **16.7**

(16.6) Stereospecificity of hydrogenation, bromination and dihydroxylation for non-cyclic alkenes is not detectable. Why?

Chapters **16.1**, **16.2**, **16.7**

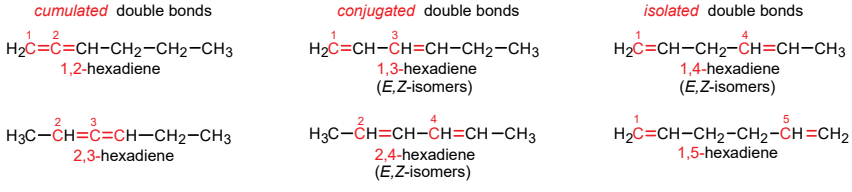
(16.7) Which alkenes give only *(**a**)* propanone and *(**b**)* butanal upon ozonolysis followed by hydrolysis?

Chapter **16.8**: Carbonyl compounds propanone *(**a**)* and butanal *(**b**)* permit reconstruction of the original alkenes 2,3-dimethyl-2-butene and 4-octene (*cis*- or *trans*-), respectively.



(17.1) Which structural isomeric hexadienes exist and how are these classified? Write the formulas.

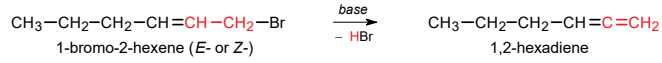
Chapter **17.1**: 1,2- and 2,3-hexadiene have cumulated, 1,3- and 2,4-hexadiene have conjugated, 1,4- and 1,5-hexadiene have isolated double bonds. 1,3-, 2,4- and 1,4-hexadiene exist as *E*- and *Z*-isomers.



(17.2) What are the appropriate formulas of 1,3-butadiene? What is the meaning of the term resonance in this context?
Chapter **17.2.2**

(17.3) There are several methods to prepare 1,3-butadiene. Formulate the equations for these reactions.
Chapters **17.3.1**, **17.3.2**, **17.3.3**

(17.4) Suggest a resonable synthesis of 1,2-hexadiene.
Chapter **17.3.4**: Dehydrobromination of 1-bromo-2-hexene is expected to produce 1,2-hexadiene. Dehydrobromination of 3-bromo-1-hexene would yield the conjugated diene, 1,3-hexadiene.



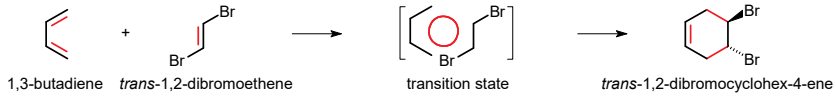
Memorizing Chapter **15.3.1**, 1-bromo-2-hexene can be prepared by bromination of 2-hexene with *N*-bromosuccinimide.

(18.1) What products are obtained by bromination and hydrobromination of 1,3-butadiene?
Chapter **18.1**

(18.2) How can the selectivity of hydrobromination of 1,3-butadiene be controlled?
Chapter **18.1**

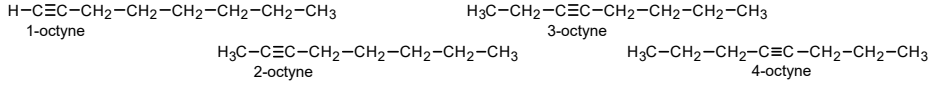
(18.3) Write the equation for a [4+2]-cycloaddition. What is the preparative significance of this reaction?
Chapter **18.2.1**

(18.4) What product is expected from the reaction of 1,3-butadiene and *trans*-1,2-dibromoethene? Write the equation.
Chapter **18.2.1**: [4+2]-Cycloaddition (DIELS-ALDER reaction) of 1,3-butadiene and *trans*-1,2-dibromoethene is expected to stereospecifically produce *trans*-1,2-dibromo-4-cyclohexene (1,2-dibromocyclohex-4-ene).

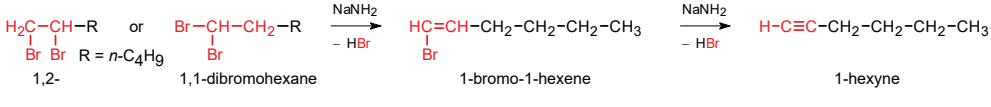


(19.1) *cis-trans*-Isomers do not exist for alkynes. Why?
Chapter **19.1**

(19.2) What structurally isomeric alkynes exist for the molecular formula C_8H_{14}? Name them.
Chapter **19.1**: 1-, 2-, 3- and 4-octyne are skeletally isomeric alkynes with molecular formula C_8H_{14}.

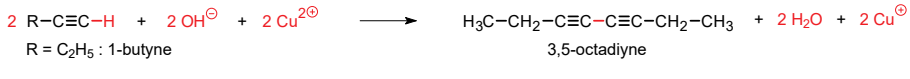


(19.3) Which dihaloalkanes are starting materials for the preparation of 1-hexyne? Formulate the equations for this.
Chapter **19.2.3**: 1,1- or 1,2-dibromohexane are expected to undergo dehydrobromination, yielding 1-hexyne.

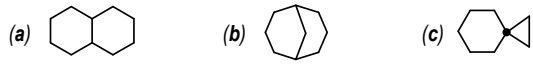


(19.4) How can the *(E)*- and *(Z)*-isomer of 2-hexene be prepared? Formulate the equations.
Chapter **19.3.1**: Starting from 2-hexyne (R = CH_3 and *n*-C_3H_7 in the reaction equations), catalytic hydrogenation affords *cis*-2-hexene while reduction with sodium in liquid ammonia is expected to yield the *trans*-isomer.

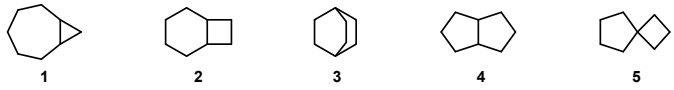
(19.5) Terminal alkynes are CH acids. Why? Suggest a reasonable synthesis of 3,5-octadiyne from a terminal alkyne.
Chapter **19.3.6**: 3,5-Octadiyne is feasible by oxidative (GLASER-) coupling of 1-butyne (R = C_2H_5).



(20.1) Draw the skeletal formulas of *(**a**)* bicyclo[4.4.0]decane, *(**b**)* bicyclo[3.3.1]nonane, and *(**c**)* spiro[5.2]octane.
Chapter **20.1**: Fused cycloalkanes are usually portrayed by means of skeletal formulas (Chapter **8.2**).



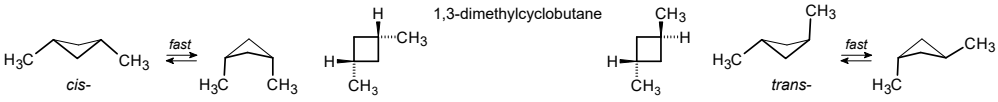
(20.2) Name the bicycles (**1**-**5**). Which kind of isomers are these cyclic hydrocarbons?



The fused cycloalkanes are named as **1**: bicyclo[5.1.0]octane; **2**: bicyclo[4.2.0]octane; **3**: bicyclo[2.2.2]octane; **4**: bicyclo[3.3.0]octane; **5**: spiro[4.3]octane. These are skeletal isomers with molecular formula C_8H_{14}.

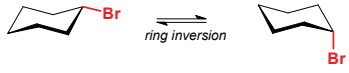
(20.3) Draw the conformers of *(**a**)* cyclopentane, *(**b**)* cyclohexane, and *(**c**)* cyclohexene, and describe their shapes.
Chapter **20.2.3**, concerning *(**a**)*; Chapter **20.2.4**, concerning *(**b**)*; Chapter **20.3.3**, concerning *(**c**)*

(20.4) What isomers exist for *(**a**)* dimethylcyclopropane, *(**b**)* 1,3-dimethylcyclobutane, *(**c**)* 1,2-, 1,3-, and 1,4-dimethylcyclohexane, and *(**d**)* bicyclo[4.4.0]decane? Draw skeletal formulas of the isomers and specify them.
Chapter **20.3.1**, answering *(**a**)*; Chapter **20.3.1**, Table 20.1, answering *(**c**)*; Chapter **20.3.2**, answering *(**d**)*;
*(**b**) cis-* and *trans*-isomers exist in the case of 1,3-dimethylcyclobutane; those can be portrayed as conformers or as projection formulas.

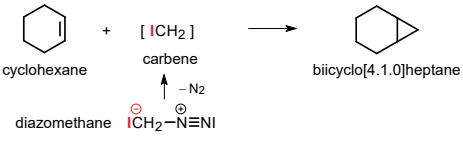


(20.5) Cyclohexane undergoes ring inversion at room temperature. Which conformers are involved? What happens to the axial and equatorial substituents?
Chapter **20.2.4**

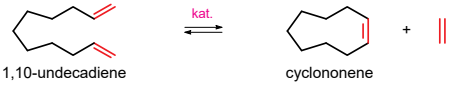
(20.6) Bromocyclohexane with *equatorial* Br and bromocyclohexane with *axial* Br cannot be separated by distillation. Why?
Chapter **20.2.4**: At room temperature, the kinetic energy of the molecules overcompensates the energy barrier of ring inversion, meaning that separation (*e.g.* by distillation) is not possible.



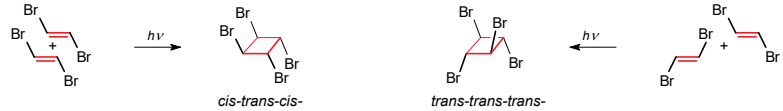
(21.1) Formulate equations to suggest the preparations of *(**a**)* bicyclo[4.1.0]heptane, *(**b**)* cyclopentene, and *(**c**)* cyclononene.
Chapter **21.1**, answering *(**a**)*: Bicyclo[4.1.0]heptane arises from [2+1]-cycloaddition of diazomethane (carbene precursor) to cyclohexene.



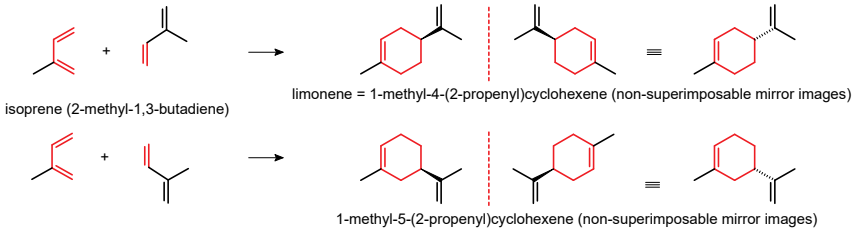
Chapter **21.3**, answering *(**b**)*
Chapter **21.6**, answering *(**c**)*: Ring-closing metathesis of 1,10-undecadiene is expected to produce cyclononene.



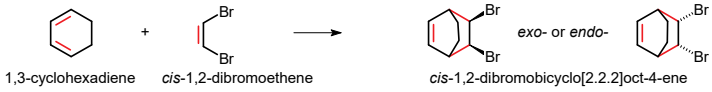
(21.2) *Trans*-1,2-dibromoethene is irradiated with UV light. What product is expected?
Chapter **21.2**: [2+2]-Photocycloaddition of *trans*-1,2-dibromoethene is expected to produce *cis-trans-cis*- and *trans-trans-trans*-1,2,3,4-tetrabromocyclobutane according to the orientations of the reactimg alkenes.



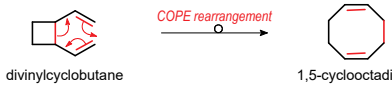
(21.3) A structural isomer of limonene could be a minor byproduct of the dimerization of isoprene. Which one?
Chapter **21.4**: [4+2]-Cycloaddition of isoprene permits two orientations of the starting dienes, producing the natural product limonene or the *regioisomeric* 1-methyl-5-(2-propenyl)cyclohexene.



(21.4) *cis*-1,2-Dibromoethene reacts with 1,3-cyclohexadiene. What product is expected? Write the equation.
Chapter **21.4**: [4+2]-Cycloaddition (DIELS-ALDER reaction, Chapter **18.2.1**) of 1,3-cyclohexadiene and *cis*-1,2-dibromoethene is expected to produce stereospecifically *cis*-1,2-dibromobicyclo[2.2.2]oct-4-ene. The dienophile is able to approach with bromine atoms outside (*exo*) as shown or with bromine atoms inside (*endo*), so that an *exo*- and/or an *endo*-stereoisomer may arise.



(21.5) Write an equation to suggest a synthesis of 1,5-cyclooctadiene. What kind of reaction occurs?
Chapter **21.5**, analogous reaction: A COPE sigmatropic rearrangement of 1,2-divinylcyclobutane (instead of divinylcycopropane) is the key step to the target compound 1,5-cyclooctadiene.

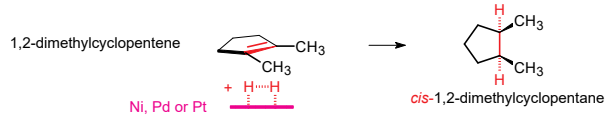


(22.1) Hydrobromination of methylcyclopropane yields 2-bromobutane as the major product. Write the mechanism and explain the regioselectivity. Look at Chapter **16.3**.
Chapters **22.1**, **16.3**

(22.2) Bromine reacts with ***(a)*** cyclopropane, ***(b)*** cyclohexane, and ***(c)*** cyclohexene: What products are obtained?
Chapters **22.1**, **22.2**, **22.3.1**

(22.3) Write the mechanism for the photochlorination of cyclohexane to give chlorocyclohexane. Look at Chapter **13.1**.
Chapter **13.1**: A *cyclohexyl* radical is the reactive intermediate in the chain reaction instead of the *methyl* radical.

(22.4) Suggest a one-step reaction to prepare pure *cis*-1,2-dimethylcyclopentane.
Chapter **22.3.2**: Catalytic hydrogenation of 1,2-dimethylcyclopentene (pre-determining the *cis*-configuration) produces *cis*-1,2-dimethylcyclopentane.



(22.5) Write equations to suggest the preparations of *cis*- and *trans*-1,2-cyclopentanediol.
Chapter **22.3.3**, analogous reactions: *Cyclopentene* instead of cyclohexene reacts to *cis*- and *trans*-1,2-cyclopentanediol, respectively.

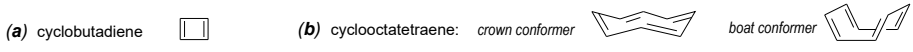
(23.1) Which facts indicate that benzene is more than just a 1,3,5-cyclohexatriene?
Chapter **23.1.1**, **23.1.2**

(23.2) Explain the term resonance energy and its physical (thermodynamic) origin.
Chapters **23.1.2**, **23.1.3**

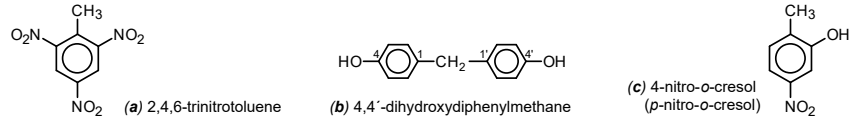
(23.3) Draw all formulas describing the benzene molecule and explain the term delocalized π bonding.
Chapter **23.1.3**, Fig. 23.2

(23.4) Which properties characterize an aromatic compound?
Chapter **23.3**

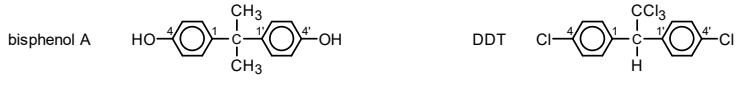
(23.5) Draw the skeletal formulas of ***(a)*** cyclobutadiene C_4H_4 and ***(b)*** cyclooctatetraene C_8H_8. Are these compounds aromatic?
Chapter **23.3**: The number of π electrons, 4 for cyclobutadiene ***(a)*** and 8 for cyclooctatetraene ***(b)***, does not follow the HÜCKEL rule ($4N+2$) meaning that both cycles are not aromatic. Moreover, bond distances in cyclobutadiene are different, and cyclooctatetraene is not a planar molecule, existing as a crown and a boat conformer.



(24.1) Draw the structural formulas of ***(a)*** 2,4,6-trinitrotoluene, ***(b)*** 4,4´-dihydroxydiphenylmethane, and ***(c)*** 4-nitro-*o*-cresol.
Chapters **24.1**, **24.2**: Formulas ***a***-***c*** are correct.

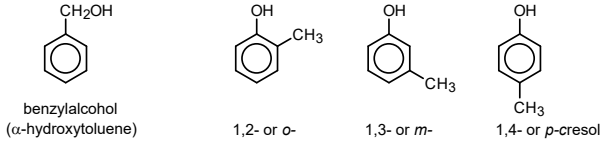


(24.2) What are other names for the industrial chemical known as bisphenol A and the contact insecticide known as DDT?



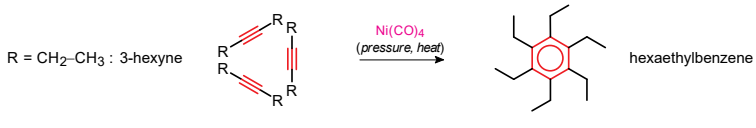
Chapters **24.1**, **24.2**: Bisphenol A is 2,2-bis(4-hydroxyphenyl)propane; DDT (from **D**ichloro**d**iphenyl**t**richlorethane) is 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane.

(24.3) Which structurally isomeric aromatic compounds with an OH group and the molecular formula C_7H_8O exist?
Chapters **24.1**, **24.2**: Benzylalcohol (α-hydroxytoluene), *o*-, *m*- and *p*-cresol are skeletal isomers with molecular formula C_7H_8O and hydroxy groups.



(24.4) What kind of chemicals are produced by the so-called platforming processes?
Chapter **24.3.1**

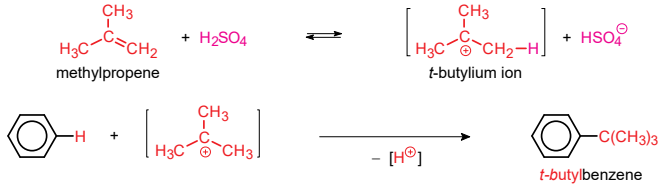
(24.5) Suggest a synthesis of hexaethylbenzene from an alkyne. Formulate the equation.
Chapter **24.3.2**, analogous reaction: Catalytic cyclotrimerization of 3-hexyne will produce hexaethylbenzene.



(25.1) Formulate a detailed reaction mechanism for the electrophilic substitution of benzene by an electrophile $E^{\oplus}$.
Chapter **25.1**

(25.2) Write this mechanism for ***(a)*** a bromination to give bromobenzene and ***(b)*** an alkylation to give isopropylbenzene.
Chapter **25.2**, answering ***(a)***: Electrophilic bromination of benzene with bromine (Br_2 instead of Cl_2) in the presence of a LEWIS acid ($FeBr_3$ instead of $AlCl_3$) produces bromobenzene.
Chapter **25.3**, answering ***(b)***

(25.3) Starting with benzene, how would you prepare ***(a)*** *t*-butylbenzene, ***(b)*** nitrobenzene, and ***(c)*** acetophenone?
(a) Chapter **25.3**: In analogy to the synthesis of isopropylbenzene, *t*-butylbenzene can be prepared by electrophilic alkylation of benzene with methylpropene (isobutylene), the precursor of the intermediate electrophilic *t*-butyl cation (*t*-butylium ion), and sulfuric acid as catalyst.



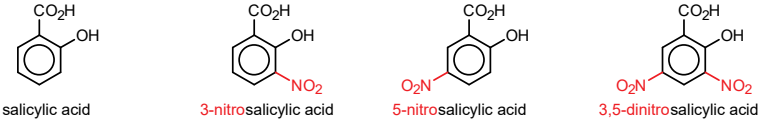
Chapter **25.5**, answering ***(b)***
Chapter **25.4**, answering (**c**)

(25.4) Sulfur trioxide is electrophilic at the sulfur atom. Why? Write the mechanism of the electrophilic sulfonation of benzene.
Chapter **25.6**

(26.1) Explain the *(+)-M* and *(–)-M* effect. In which manner do they influence the reactivity of substituted benzenes?
Chapters **26.1**, **26.2**

(26.2) Phenol reacts with ***(a)*** nitric acid and sulfuric acid and ***(b)*** fuming nitric acid. Which products are formed?
Chapter **26.2**, answering ***(a)***
(b): The *(+M)* effect of the OH group activates the *o*-, *o´*- and *p*-position for electrophilic substitution. Thus, fuming nitric acid nitrates phenol to yield 2,4,6-trinitrophenol (picric acid, Chapter **52.4.3**).

(26.3) Salicyclic acid (*o*-hydroxybenzoic acid) is nitrated. Which products are expected?
Chapter **26.2**: The OH group directs the electrophile to the *o*-, *o´*- und *p*- positions, the deactivating carboxy group, however, permits the electrophile to enter *m*-positions. To conclude, electrophilic nitration of salicylic acid is expected to produce 3-nitro-, 5-nitro- and 3,5-dinitrosalicylic acid.

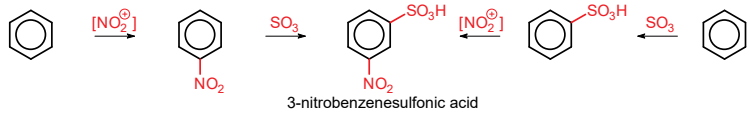


(26.4) Which alkene is an appropriate precursor of an intermediate electrophile to prepare 2,4,6-tri-*t*-butylphenol?
Chapter **25.3** and answer ***25.3***: Methylpropene (isobutylene) is protonated *in situ* to the *t*-butylium ion as electrophile. Thus, 2,4,6-tri-*t*-butylphenol is produced by bubbling isobutylene into a solution of phenol.

(26.5) Which products arise from the nitration of ***(a)*** bromobenzene and ***(b)*** nitrobenzene?
Chapter **26.2**: ***(a)*** Bromobenzene can be nitrated to 2-nitro-, 4-nitro-, 2,4-dinitro- and 2,4,6-trinitrobromobenzene due to the *(+M)* effect of Br; ***(b)*** nitration of nitrobenzene is expected to produce 1,3-dinitro- and 1,3,5-trinitrobenzene due to the *(–M)* effect of deactivating NO_2.

(26.6) Which reactions are suitable for the preparation of 3-nitrobenzenesulfonic acid from benzene?
Chapter **26.2**: 3-Nitrobenzenesulfonic acid arises either from nitration of benzene to nitrobenzene with nitric acid/sulfuric acid and subsequent sulfonation with sulfur trioxide or from sulfonation of benzene and subsequent

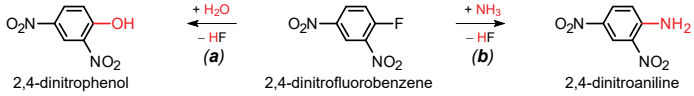
nitration. Both substituents deactivate due to their *(–M)* effects, permitting second substitution in *m*-positions.



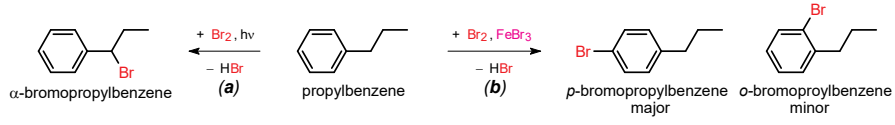
(26.7) Alkyl groups at benzene direct electrophiles to the *o*- and *p*-positions. How would you prepare 2,4,6-trinitrotoluene?
Chapter **26.2**: Nitration of toluene with fuming nitric acid produces the explosive 2,4,6-trinitrotoluene (TNT).

(27.1) In aryl halides, carbon–halogen bonds are shorter than in alkyl halides. Look at Chapters **3.2**, **26.1**, and **27.1** and explain why.
It is assumed that the carbon atom attached to halogen in aryl halides provides sp^2 hybrid orbitals for overlapping and these are more compact than sp^3 hybrid orbitals. In the same context, the carbon–halogen bond is a partial double bond because of the *(+M)* effect of the halogen atom as shown by the resonance formulas in Chapter **26.1**, replacing NH_2 in aniline by halogen with three non-bonding electron pairs.

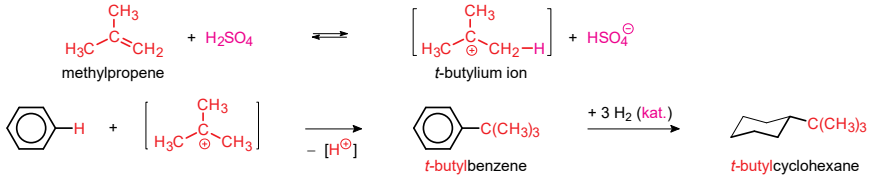
(27.2) 1-Fluoro-2,4-dinitrobenzene (2,4-dinitrofluorobenzene) reacts with *(**a**)* water and *(**b**)* ammonia. What products are formed? Draw resonance formulas to explain the influence of the nitro groups on the reactive intermediate.
Chapter **27.1**: In analogy to the nucleophilic substitution of the chloride anion in *o*-nitrochlorobenzene by hydroxide, nucleophilic substitution of the fluoride anion in 2,4-dinitrofluorobenzene by water *(**a**)* as a nucleophile produces 2,4-nitrophenol and by ammonia *(**b**)* as a nucleophile produces 2,4-dinitroaniline.



(27.3) Propylbenzene reacts with bromine in the presence of UV radiation *(**a**)* or ferric chloride in the cold *(**b**)*. Outline the mechanisms and explain the regioselectivity of both reactions.
Chapter **27.2**: Propylbenzene reacts with bromine *(**a**)* under UV light to give α-bromopropylbenzene (major product, radical substitution) and *(**b**)* in the presence of ferric bromide to produce predominantly *p*-bromopropylbenzene (electrophilic substitution).

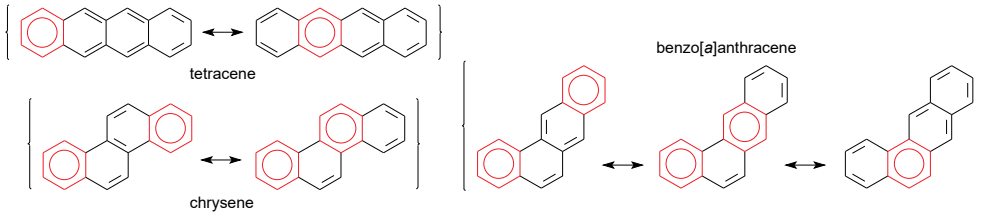


(27.4) Formulate equations to suggest the preparation of *t*-butylcyclohexane from benzene and methylpropene.
t-Butylbenzene is prepared from benzene and methylpropene (isobutylene, *answer **25.3***). Catalytic hydrogenation of *t*-butylbenzene produces *t*-butylcyclohexane (Chapter **27.3**).



(27.5) Write equations to describe the reactions of *(**a**)* benzene with sodium in liquid ammonia and a proton donor, and *(**b**)* of toluene with chromium trioxide (CrO_3).
Chapter **27.3**

(28.1) Draw the formulas of tetracene and its isomers containing benzenoid rings with autonomous π electron sextets.
Two non-equivalent resonance formulas can be written for linearly fused tetracene, each having one autonomous π electron sextet. Angularly fused chrysene and benzo[*a*]anthracene are hybrids of two resonance formulas, each one containing two benzenoid rings with autonomous π electron sextets. One additional resonance formula with one benzenoid autonomous π electron sextet can be written for benzo[*a*]anthracene.



(28.2) What products are obtained when naphthalene is reacted with electrophiles under mild conditions? Give reasons and examples.
Chapter **28.3**

(28.3) What is the driving force behind the DIELS-ALDER reaction of anthracene with maleic anhydride?
Chapter **28.5**: The generation of an additional benzenoid ring is the driving force for the DIELS-ALDER reaction of anthracene and maleic acid anhydride.

(28.4) Anthracene and phenanthrene react with ***(a)*** bromine, ***(b)*** oxidizing reagents, and ***(c)*** reducing reagents. Write equations for these reactions.
Chapter **28.5**: 9,10-Positions are reactive centers so that the second benzenoid ring is generated or preserved.

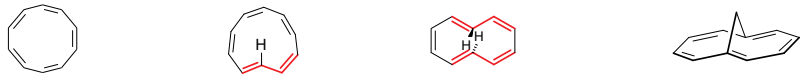
(28.5) Polycyclic arenes are known to be carcinogenic. Which reactions produce the carcinogens? Formulate these reactions.
Chapter **28.6**

(29.1) Which types of non-benzenoid aromatic compounds do you know? Draw formulas.
Chapter **29.1**, first section, Table 29.1

(29.2) Write equations describing the preparations of ***(a)*** potassium cyclopentadienide and ***(b)*** cycloheptatrienium bromide.
Chapter **29.1.2**, answering ***(a)***; Chapter **29.1.3**, answering ***(b)***

(29.3) What are π-electron-excessive and π-electron-deficient aromatics? Give examples and draw formulas.
Chapter **29.1.3**, last section

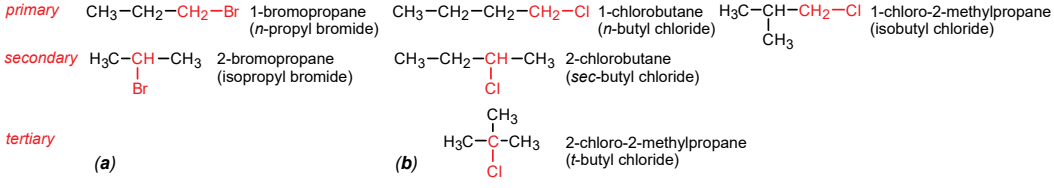
(29.4) ***(a)*** [10]Annulene does not exist. Why? ***(b)*** Write equations describing the preparations of [14]- and [18]annulene.
(a) [10]-Annulene could not be synthesized. Three configurational isomers can be formulated. The all-*cis*-configuration would have an internal bond angle of 144° which is much larger than the interorbital angle of sp^2 hybrid orbitals (120°). This large angle strain would destabilize the all-*cis*- as well as the mono-*trans*-isomer, although the latter has partly relaxed. No angle strain would destabilize the bis-*trans*-isomer but strong repulsion of the inner hydrogen atoms would prevent coplanarity of the ring as required for aromaticity.
Only bridged derivatives such as 1,6-methano[10]annulene have been prepared.



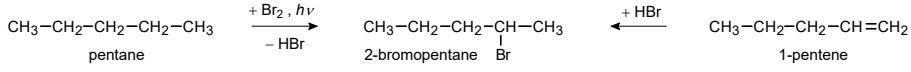
all-*cis*- mono-*trans*- bis-*trans*10]-annulene 1,6-methano[10]-annulene

Chapter **29.2**, answering ***(b)***

(30.1) Draw all structural isomers of ***(a)*** C_3H_7Br and ***(b)*** C_4H_9Cl, and classify them as primary, secondary, or tertiary.
Chapter **30.1**, Tables 30.1 and 7.2 exemplify formulation, nomenclature and classification of alkyl halides ***(a)*** and ***(b)***.



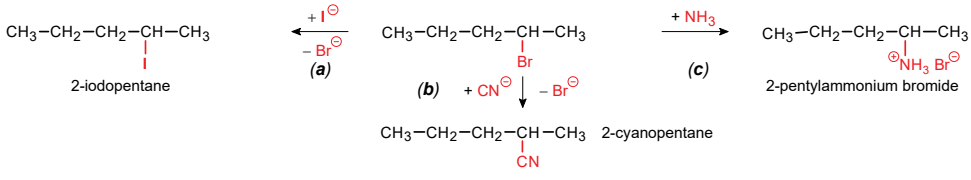
(30.2) 2-Bromopentane can be prepared by substitution and addition. Write the equations for these reactions.
Chapters **30.2.1**, **30.2.2**: 2-Bromopentane can be prepared by bromination of pentane (radical substitution) or by hydrobromination of 1-pentene (electrophilic addition). Radical substitution will also produce the regioisomers 3-bromopentane and 1-bromopentane (minor) while hydrobromination is expected to be more regioselective, predominantly producing 2-bromopentane (MARKOVNIKOV´s rule, Chapters **16.3**, **30.2.1**).



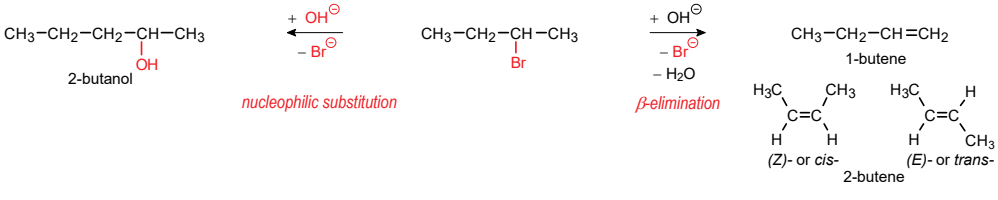
(30.3) What kind of compounds are the so-called ozonekillers? Write equations for the ozone-killing reactions.
Chapter **30.2.4**

(30.4) Explain the term inductive effect and describe its influence on the reactivity of alkyl halides.
Chapter **30.3**

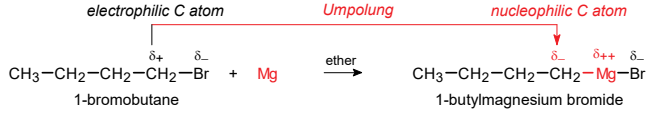
(30.5) 2-Bromopentane reacts with ***(a)*** potassium iodide, ***(b)*** potassium cyanide, and ***(c)*** ammonia. Write the equations.
Chapter **30.4.1**: 2-Bromopentane undergoes nucleophilic substitution to ***(a)*** 2-iodopentane (FINKELSTEIN reaction), ***(b)*** 2-cyanopentane (2-pentylcyanide, 2-pentylnitrile) and ***(c)*** 2-pentylammonium bromide.



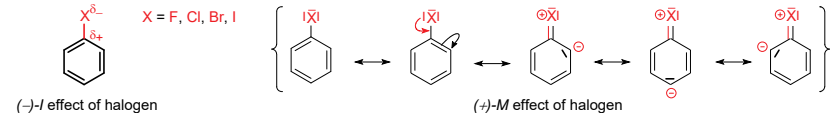
(30.6) 2-Bromobutane reacts with potassium hydroxide. Which products can be formed?
Chapters **30.4.1** and **30.4.2**: In keeping with the HSAB principle, β elimination (dehydrobromination) to 1- and 2-butene (*cis*- and *trans*-) is expected to compete with nucleophilic substitution to 2-butanol.



(30.7) Formulate the reaction of 1-bromobutane with magnesium in ether including the change of polarity of C-1.
Chapter **30.4.3**: Magnesium metalates 1-bromobutane, producing 1-butylmagnesium bromide. Metalation reverses the polarity of the electrophilic α carbon atom (δ_+) of 1-brombutane to a nucleophilic center (δ_-).



(30.8) Can the *(–)-I* effect of a halogen influence the regioselectivity of the electrophilic substitution of halobenzenes?
The inductive effect, the *(–)-I* effect, of halogens induces a partial positive charge at the carbon atom attached to halogen in halobenzenes; this influence significantly decreases with distance. The longer-ranging *(+)-M* effect of halogen atoms is the predominating influence [*(+)-M* > *(–)-I*], enhancing electron density at *o*, *o´* and *p* positions, directing second substitution to these positions as outlined in Chapter **26.2**.



(31.1) Draw equations to outline the mechanisms and rates of nucleophilic substitution.
Chapters **31.1** and **31.2**

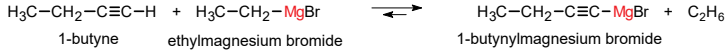
(31.2) Formulate the reactions of *(**a**) t*-butyl bromide with iodide *(S_N1)*, and *(**b**)* 1-bromobutane with hydroxide *(S_N2)*.
Chapter **31.2**, answering *(**a**)*; Chapter **31.1**, answering *(**b**)*: general mechanisms

(31.3) Which mechanism is probable for the reaction of α-bromoethylbenzene with sodium hydroxide?
Chapter **31.1**: *S_N1* is also reasonable. The intermediate benzylic carbenium ion is resonance stabilized as formulated for the phenylethyl radical in Chapter **27.2**; replace the unpaired electron by the positive charge, a singly occupied p orbital by a vacant p orbital α to the phenyl ring.

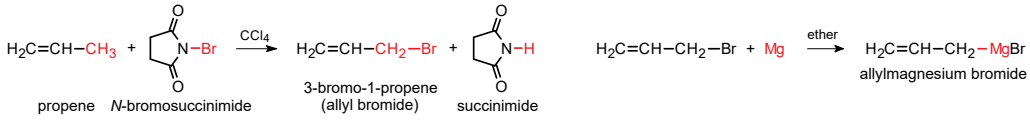
(31.4) What happens in the so-called WALDEN inversion? Why does this not play a role in substitutions with an *S_N1* mechanism?
Chapter **31.1**, last section

(32.1) Which reactions open access to organometallic compounds? Formulate general equations.
Chapter **32.2**

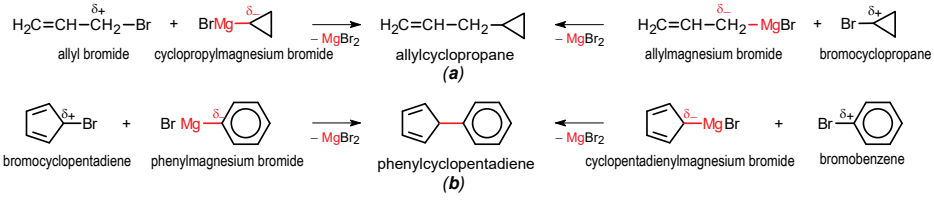
(32.2) Suggest reactions to prepare *(**a**)* butyllithium, *(**b**)* phenyllithium, and *(**c**)* butynylmagnesium bromide.
Chapter **32.2.1**, answering *(**a**)* and *(**b**)*; Chapter **32.2.4**, answering *(**c**)*: 1-Butynylmagnesium bromide is prepared by hydrogen-metal exchange, reacting 1-butyne and ethylmagnesium bromide.



(32.3) Formulate all reactions necessary to prepare allylmagnesium bromide from propene. Look at Chapter **15.3.1**.
Chapters **32.2.1**, **15.3.1**: Allyl bromide (3-bromo-1-propene), obtained by WOHL-ZIEGLER bromination of propene with *N*-bromosuccinimide, is metalated with magnesium to produce allylmagnesium bromide.

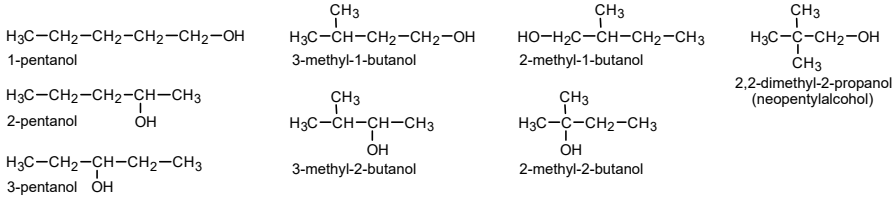


(32.4) Suggest syntheses of *(**a**)* allylcyclopropane and *(**b**)* phenylcyclopentadiene.
Chapter **32.3**: Two pathways are possible for both target compounds. Allylcyclopropane *(**a**)* is expected to arise from reacting allyl bromide with cyclopropylmagnesium bromide or bromocyclopropane with allylmagnesium bromide. Phenylcyclopentadiene can be prepared from 1-bromocyclopentadiene and phenylmagnesium bromide or from bromobenzene and cyclopentadienylmagnesium bromide (Chapter **32.2.4**).

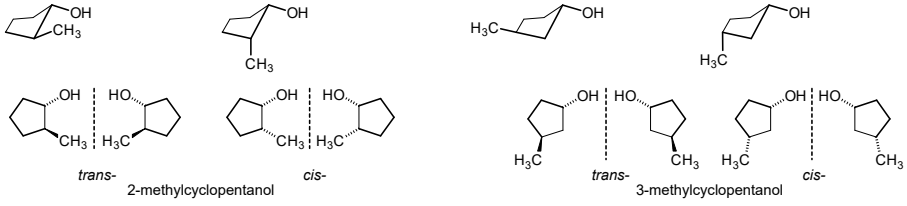


(33.1) 1-Butanol has a higher boiling point (74 g/mol, 118 °C) at normal pressure than pentane (72 g/mol, 36 °C). Why?
Chapter **33.2**

(33.2) Draw the formulas of all structurally isomeric alcohols (7) with the molecular formula $C_5H_{12}O$ and classify them as primary, secondary, or tertiary.
Eight structurally isomeric alcohols (primary: 4, secondary: 3, tertiary:1) with the molecular formula $C_5H_{12}O$ exist:

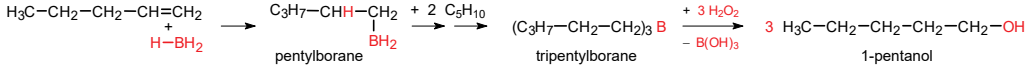


(33.3) Draw formulas of all structurally and configurationally isomeric methylcyclopentanols and name them.
Structurally isomeric 2- and 3-methylcyclopentanol exist as configurational isomers (*cis*- and *trans*-). One of the envelope conformers (Chapter **20.2.3**) is portrayed. Additionally, each *cis*- and *trans*-isomer exists as a pair of non-superimposible mirror images (enantiomers: Chapter **44**; *cis*-*trans*-pairs are diastereomers: Chapter **46**).

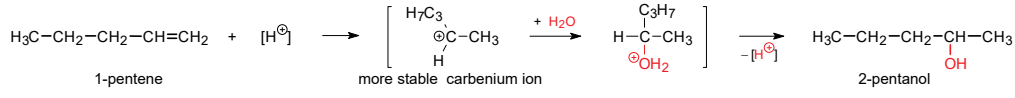


(33.4) Write equations describing the preparations of *(**a**)* *t*-butyl alcohol, *(**b**)* 2-methyl-1-propanol, and *(**c**)* allyl alcohol.
*(**a**)* Chapter **33.3.3**, answering *(**a**)*; Chapter **33.3.4**, answering *(**b**)*; Chapter **33.3.6**, answering *(**c**)*

(33.5) Suggest syntheses of *(**a**)* 1-pentanol (*n*-pentyl alcohol) and *(**b**)* 2-pentanol from 1-pentene.
Chapters **33.3.3, 33.3.4**, analogous reactions
*(**a**)* Hydroboration of 1-pentene and subsequent oxidation is expected to produce 1-pentanol.

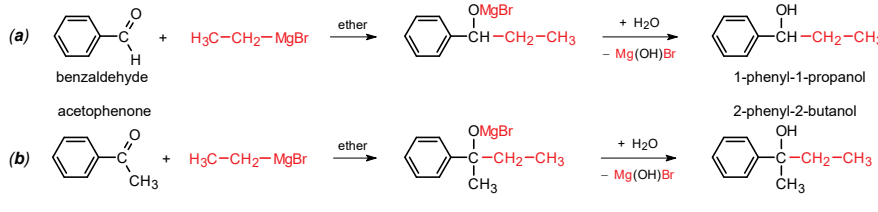


*(**b**)* Acid-catalyzed hydration of 1-pentene regioselectively produces 2-pentanol (MARKOVNIKOV´s rule).

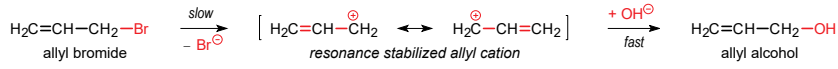


(33.6) Write equations describing the preparations of *(**a**)* primary and *(**b**)* secondary alcohols by reduction.
Chapter **33.3.5**: *(**a**)* Aldehydes are reduced to primary, *(**b**)* ketones are reduced to secondary alcohols.

(33.7) Which alcohols are obtained by reacting ethylmagnesium bromide with *(**a**)* benzaldehyde and *(**b**)* acetophenone? Write equations.
Chapter **33.3.7**: analogous reactions: Ethylmagnesium bromide reacts with *(**a**)* benzaldehyde to give 1-phenyl-1-propanol (secondary) and *(**b**)* with acetophenone to give 2-phenyl-2-butanol (tertiary alcohol).



(33.8) Nucleophilic hydroxylation of allyl bromide follows a S_N1 mechanism. Why? Look at Chapter **31.2**.
A S_N1 mechanism for the nucleophilic hydroxylation of allyl bromide to allyl alcohol is reasonable because the rate-determining step involves dissociation of the bromide anion, leaving an intermediate resonance-stabilized allyl cation.



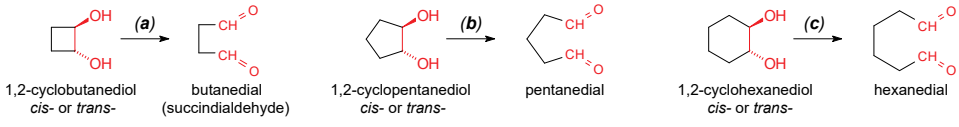
(34.1) Six isomeric cyclohexanediols exist (structural and configurational). Draw all of them; look at Table 20.1 for reference.
Chapter **20.3**: Replace R by OH in Table 20.1

(34.2) Formulate a synthesis of ***(a)*** *trans*- and ***(b)*** *cis*-1,2-cyclopentanediol from cyclopentene.
Chapter **34.1.1**, analogous reaction: Cyclopentene reacts instead of cyclohexene with ***(a)*** peroxycarboxylic acid *via* epoxide to produce *trans*-1,2-cyclopentanediol and with ***(b)*** osmiumtetroxide or permanganate to produce *cis*-1,2-cyclopentanediol.

(34.3) Write equations to describe a synthesis of glycerol from propene.
Chapter **34.1.2**

(34.4) What product is formed by reacting magnesium with acetone (propanone)? Write the equation.
Chapter **34.1.3**

(34.5) Formulate the cleavage of an α,β-diol with lead tetraacetate. Which products (formulas) do you expect from the oxidative cleavage of ***(a)*** 1,2-cyclobutanediol, ***(b)*** 1,2-cyclopentanediol, and ***(c)*** 1,2-cyclohexanediol?
Chapter **34.2**, analogous reactions: oxidative cleavage of 1,2-cycloalkanediols produces dialdehydes such as butanedial (succindialdehyde, Table 47.1) from ***(a)*** 1,2-cyclobutanediol, pentanedial from ***(b)*** 1,2-cyclopentanediol and hexanedial from ***(c)*** 1,2-cyclohexanediol.



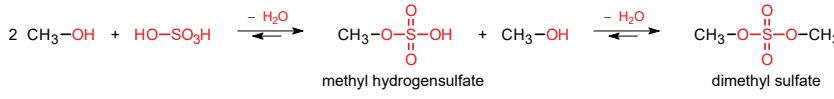
(35.1) Hydrogen chloride dissolves in cold ethanol. Which reaction takes place? What happens upon heating this mixture? Look at Chapter **15.1.2**.
Chapter **35.1**: Ethyloxonium chloride is formed. It is stable in the absence of water and undergoes dehydration upon heating to produce gaseous ethene which escapes (Chapter **15.1.2**).

(35.2) Anhydrous ethanol reacts with sodium metal. Write the reaction equation. What happens upon addition of water?
Chapter **35.1**

(35.3) Formulate the oxidation of ***(a)*** a primary alcohol (e.g. 1-pentanol) and ***(b)*** a secondary alcohol (e.g. 3-pentanol).
Chapter **35.2**: 1-Pentanol ***(a)*** undergoes oxidation to pentanoic acid (valeric acid) *via* pentanal (set R = C_4H_9 in the reaction equation); oxidation of 3-pentanol ***(b)*** yields 3-pentanone (set R = C_2H_5 in the reaction equation).

(35.4) Formulate the catalytic oxidation of a primary alcohol with copper metal as catalyst.
Chapter **35.2**

(35.5) Pure methanol is reacted with ***(a)*** acetic acid and ***(b)*** fuming sulfuric acid. What products are obtained?
Chapter **35.4**, analogous reactions: Methanol (R = CH_3) reacts with ***(a)*** anhydrous glacial acetic acid (R' = CH_3) to produce acetic acid methyl ester (methyl acetate), with ***(b)*** fuming sulfuric acid ($H_2S_2O_7 = H_2SO_4 \cdot SO_3$) to give dimethyl sulfate (diester) *via* methyl hydrogensulfate (monoester).

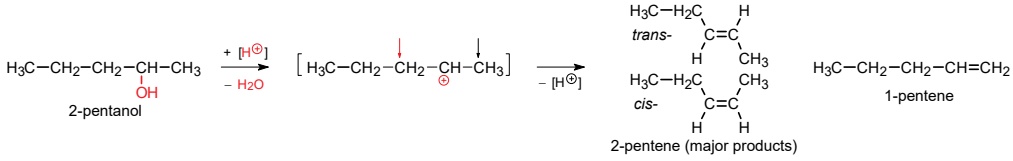


(35.6) The name nitroglycerin (nitroglycerol) is misleading. Draw the formula in order to explain this.
Chapter **35.4**, last section

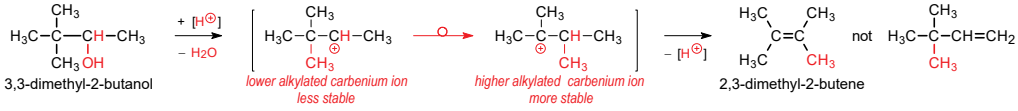
(36.1) Write the mechanism of alcohol dehydration.
Chapter **36.1**

(36.2) Which one of the alcohols ***(a)*** *t*-butyl alcohol or ***(b)*** 1-butanol undergoes dehydration more readily? Why?
Chapter **36.1**

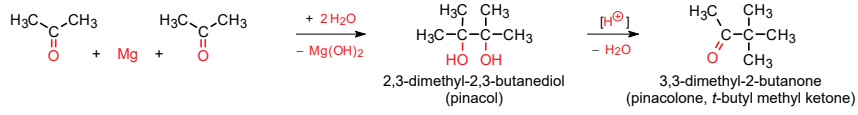
(36.3) Three products are expected from the dehydration of 2-pentanol. Which one will be a minor product?
Chapter **36.1**, analogous reaction: In keeping with SAYTZEFF´s rule, 2-pentanol is expected to undergo dehydration to yield *cis*- and *trans*-2-pentene (major) and 1-pentene (minor).



(36.4) What product is obtained by the acid-catalyzed dehydration of 3,3-dimethyl-2-butanol? Formulate the mechanism.
Chapter **36.1**, analogous reaction: WAGNER-MEERWEIN rearrangement, involving anionotropic 1,2-methyl shift of the primarily formed carbenium ion to the higher alkylated and more stable carbenium ion, produces 2,3-dimethyl-1-butene and not 3,3-dimethyl-1-butene.

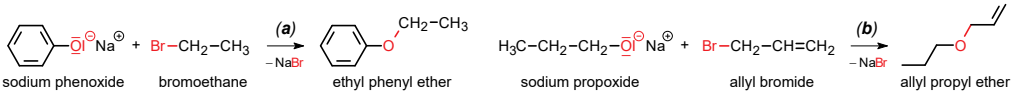


(36.5) Suggest a method to prepare *t*-butyl methyl ketone from acetone? Which reactions are needed?
Chapters **36.2**, **34.1.3**, basic reaction: Bimolecular reduction of acetone (propanone) with magnesium yields 2,3-dimethyl-2,3-butandiol (pinacol), which undergoes pinacol rearrangement to the target *t*-butyl methyl ketone.



(37.1) Formulate the synthesis of diethyl ether from ethanol. Which reaction, producing ethene, competes?
Chapter **37.3.1**: Monomolecular dehydration of ethanol yielding gaseous ethene competes with the bimolecular dehydration to diethyl ether.

(37.2) Write equations to suggest the preparation of ***(a)*** ethyl phenyl ether and ***(b)*** allyl propyl ether.
Chapter **37.3.2**, analogous reactions: WILLIAMSON synthesis permits preparation of ethyl phenyl ether ***(a)*** from sodium phenoxide (from phenol, Chapter **52.2**) as the nucleophile and bromoethane (S_N2); the bromide in bromobenzene cannot be readily substituted by nucleophiles (Chapter **27.1**). Allyl propyl ether ***(b)*** arises from reaction of sodium popanolate (sodium propoxide) and allyl bromide (S_N1), alternatively from sodium allyl alcoholate (from allyl alcohol) and 1-brompropane.



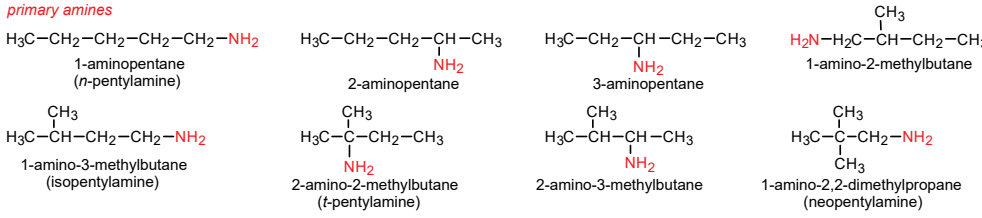
(37.3) Ethers should be stored protected from light and air. If not, which reaction may take place?
Chapter **37.4.2**

(37.4) What products are expected from the cleavage of ***(a)*** diisopropyl ether and ***(b)*** diallyl ether with hydrogen iodide?
Chapter **37.4.3** (mechanisms): Cleavage of diisopropyl ether ***(a)***, R = $CH(CH_3)_2$, with hydrogen iodide HI is expected to produce 2-iodopropane and 2-propanol (S_N2). Cleavage of diallyl ether ***(b)***, R = CH_2–CH=CH_2, with hydrogen iodide HI is expected to yield allyl iodide and allyl alcohol (probably S_N1 involving resonance-stabilized allyl cation).

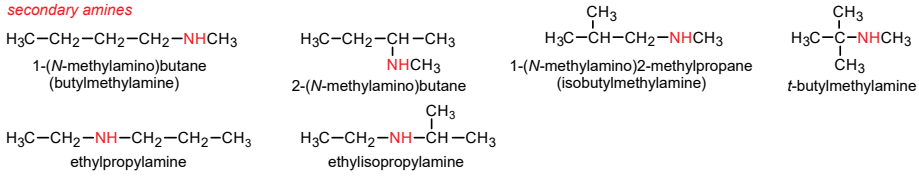
(38.1) Draw the structural formulas of all isomeric amines with the molecular formula $C_5H_{13}N$ and classify them.

Chapter **38.1**: Eight primary, six secondary and three tertiary amines with the molecular formula $C_5H_{13}N$ exist.

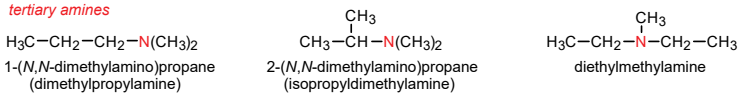
primary amines



secondary amines



tertiary amines



(38.2) Explain the geometry of the trimethylamine molecule. Where is the non-bonding electron pair?

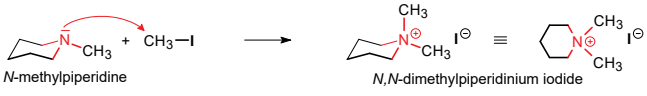
Chapter **38.2**, Fig. 38.1

(38.3) Alkylation of ammonia is not a clean method to prepare amines. Why?

Chapter **38.3.1**

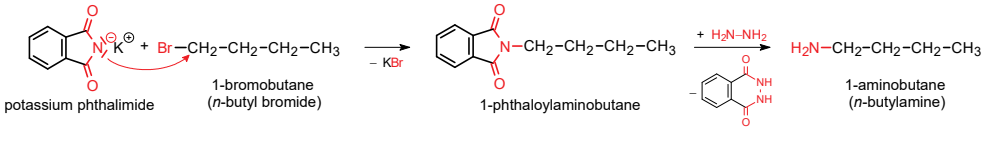
(38.4) *N*-Methylpiperidine (Chapter **38.1**) reacts with iodomethane. Formulate the reaction. What product is obtained?

Chapter **38.3.1**, analogous reaction: *N*-Methylpiperidine as nucleophile substitutes iodide in methyl iodide (S_N2). A tetraalkylammonium salt, *N*,*N*-dimethylpiperidinium iodide crystallizes.



(38.5) Suggest a method to prepare pure *n*-butylamine.

Chapter **38.3.2**, analogous reaction:. GABRIEL synthesis permits the preparation of *n*-butyl amine by reacting potassium phthalimide as the nucleophile with 1-bromobutane *via* 1-phthaloylaminobutane.



(38.6) How would you prepare benzylamine (α-aminotoluene) from ***(a)*** benzonitrile and ***(b)*** benzyl bromide?

Chapters **38.3.2**, **38.3.3**, analogous reactions: Benzylamine can be prepared from ***(a)*** benzonitrile by catalytic hydrogenation (phenyl instead of *o*-toluyl) or by GABRIEL synthesis ***(b)*** from benzyl bromide and potassium phthalimide (answer ***38.5***, benzyl bromide = α-hydroxytoluene instead of *n*-butyl bromide).

(39.1) Aniline is a much weaker base than cyclohexylamine and other alkylamines. Why?

Chapter **39.1**

(39.2) Formulate the mechanism of diazotization of primary amines. Explain the stability of arenediazonium ions.

Chapter **39.2**

(39.3) Which simple test tube reaction can distinguish between ***(a)*** cyclohexylamine and ***(b)*** aniline?

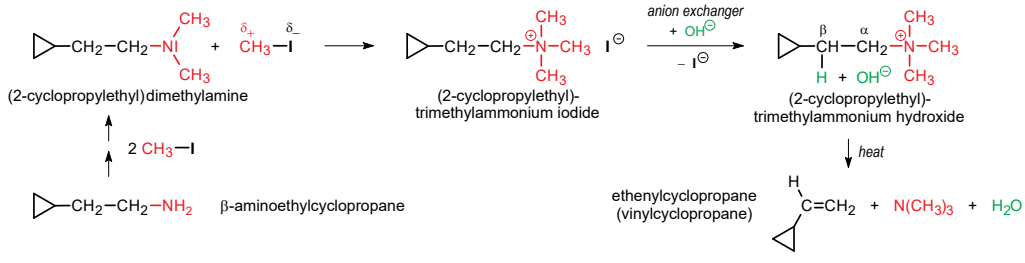
Chapter **39.2**: ***(a)*** Cyclohexylamine gives a positive VAN SLYKE reaction (evolution of gaseous N_2). ***(b)*** Aniline undergoes diazotization producing a stable diazonium salt (no evolution of nitrogen at room temperature).

(39.4) What products are expected from nitrosation of *(**a**) N*-methylaniline and *(**b**) N,N*-dimethylaniline with nitrite and acid?

Chapter **39.3**: *(**a**) N*-Methylaniline undergoes nitrosation to yield *N*-nitroso-*N*-methylaniline as formulated for dimethylaniline; *(**b**) N,N*-dimethylaniline is electrophilically nitrosated producing *p*-nitroso-*N,N*-dimethylaniline.

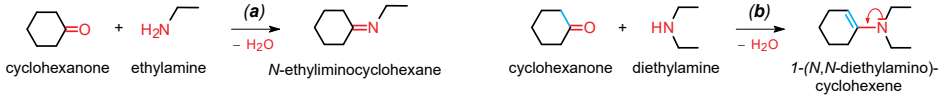
(39.5) Starting from β-aminoethylcyclopropane, formulate equations for all steps to synthesize vinylcyclopropane.

Chapter **39.4**, **39.5**: Exhaustive methylation of β-aminoethylcyclopropane with iodomethane produces (2-cyclopropylethyl)trimethylammonium iodide. Anion exchange converts iodide to hydroxide which undergoes HOFMANN elimination to produce vinylcyclopropane.



(39.6) What products are expected from the reactions of cyclohexanone with *(**a**)* ethylamine and *(**b**)* diethylamine?

Chapters **39.6**, **39.7**, analogous reactions: Cyclohexanone reacts *(**a**)* with ethylamine, yielding the imine *N*-ethyliminocyclohexane, *(**b**)* with diethylamine, affording the enamine 1-(*N,N*-diethylamino)cyclohexene.

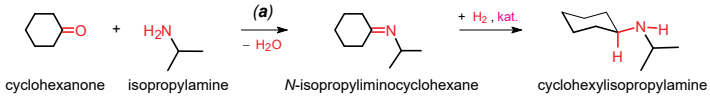


(39.7) Draw resonance formulas of an enamine to explain the nucleophilicity of the carbon β to the nitrogen.

Chapter **39.7**

(39.8) Using the concept of reductive amination of carbonyl compounds, draw equations to outline the syntheses of *(**a**) N*-isopropylcyclohexylamine and *(**b**) N,N*-diethylcyclohexylamine.

Chapter **39.8**, analogous reactions: Reductive amination of cyclohexanone with isopropylamine (2-aminopropane) is expected to produce *(**a**) N*-isopropylcyclohexylamine *via* the imine. A synthesis of *N,N*-diethylcyclohexylamine *(**b**)* is formulated in the last reaction equation of the chapter.



(40.1) Outline the mechanism of azo coupling of an arenediazonium chloride with a donor-substituted benzene.

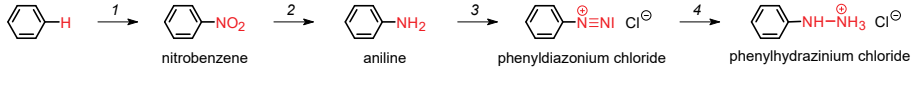
Chapter **40.1**

(40.2) Outline a synthesis of methyl orange and explain the function of this compound as a pH indicator.

Chapter **40.1**

(40.3) Which steps are necessary to synthesize phenylhydrazine from benzene as starting material? Write equations.

Chapter **40.1**: Electrophilic nitration of benzene produces nitrobenzene (*1*, Chapter **25.5**) which is reduced to aniline (*2*, Chapter **38.3.3**). Diazotization affords phenyldiazonium chloride (*3*, Chapter **39.2**) which is reduced with sodium sulfite to produce phenylhydrazinium chloride (*4*, Chapter **40.1**). Liquid phenylhydrazine is obtained upon addition of sodium hydroxide and extraction of phenylhydrazine.



(40.4) Formulate all equations to describe the preparation of azobisisobutyronitrile (AIBN) from acetone.

Chapter **40.2**

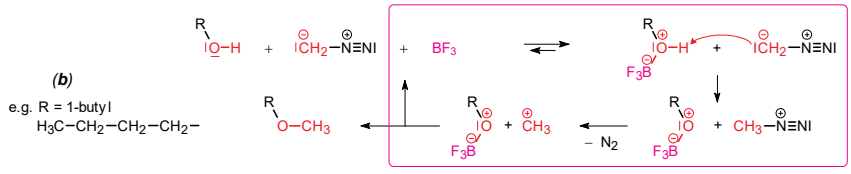
(40.5) What happens upon heating AIBN?

Chapter **40.2**

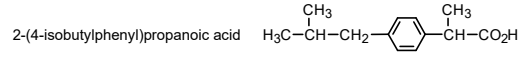
(40.6) Write an equation to outline a preparation of diazomethane.
Chapter **40.3**

(40.7) Which resonance formulas describe the bonding state of diazomethane and which one of these explains the thermolysis to generate carbene?
Chapter **40.3**

(40.8) Formulate the reaction of diazomethane with *(**a**)* phenol, *(**b**)* 1-butanol, and *(**c**)* benzene.
Chapter **40.3**: *(**a**)* Diazomethane methylates phenol to methyl phenyl ether (anisol) as formulated.
*(**b**)* Alcohols such as 1-butanol are not acidic enough. Their methylation by diazomethane is achieved in the presence of a LEWIS acid as catalyst. In the catalytic cycle (Chapter **12.2**), dissociation of the proton from the alcohol is facilitated (lower activation barrier, Figure 12.1) in the intermediate alkyloxonium borontrifluoride.



(41.1) Draw the structural formula of the analgesic and antipyretic 2-(4-isobutylphenyl)propanoic acid (ibuprofen).
Chapters **80.3.3** and **81.5** deal with the synthesis and structural features of 2-(4-isobutylphenyl)propanoic acid:



(41.2) Explain why the CO single bond of a carboxylic acid is shorter than the same bond in an alcohol.
Chapter **41.2**

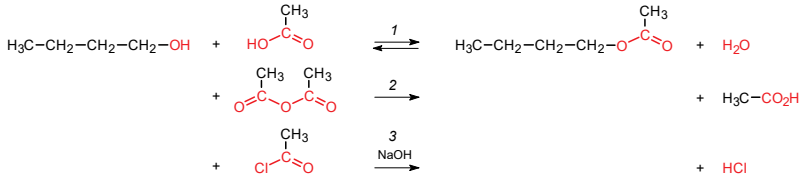
(41.3) Formulate equations to describe three general methods to prepare carboxylic acids without starting from CO_2.
Chapter **41.4.1**, **41.4.3** and **41.4.4**

(41.4) Write equations to suggest the preparation of carboxylic acids starting from CO_2.
Chapter **41.4.2**

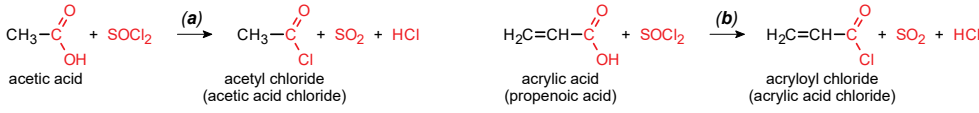
(41.5) Calculate the pH value of a 1 N carboxylic acid with $K_a \approx 10^{-5}$ using the acidity constant formula.
Chapter **41.5**: The logarithmic form of the equilibrium constant K_a correlates the pK_a of a carboxylic acid with the pH and the acid concentration $c(RCO_2H)$ in aqueous solution:
$pK_a = 2\ pH - \lg c(RCO_2H)$.
The pH turns out to be
$pH = 1/2\ (pKa + \lg c(RCO_2H)$.
Given $K_a = 10^{-5}$, meaning $pK_a = 5$, and $\lg c(RCO_2H) = 0$ for a 1 N aqueous carboxylic acid solution, the pH is
$pH = 1/2\ (5 + 0) = 2.5$.

(41.6) Arrange *(**a**)* acetic and chloroacetic acid, and *(**b**)* benzoic, *p*-hydroxybenzoic, and *p*-nitrobenzoic acid in order of increasing acidity and explain your reasoning.
Chapter **41.5**: *(**a**)* chloroacetic acid > acetic acid; *(**b**)* *p*-nitrobenzoic acid > benzoic acid > *p*-hydroxybenzoic acid

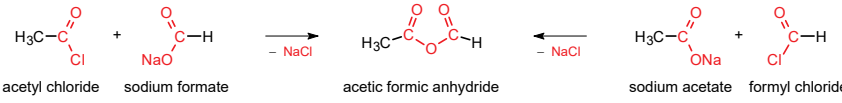
(42.1) *(**a**)* Write the mechanism of the acid-catalyzed esterification; *(**b**)* suggest three options to prepare *n*-butyl acetate.
Chapter **42.1**, answering *(**a**)*
*(**b**)* *n*-Butyl acetate (acetic acid *n*-butyl ester) can be prepared from *n*-butyl alcohol (1-butanol) *1.* by esterification with acetic acid, *2.* by acetylation with acetic anhydride (acetic acid anhydride), and *3.* by acetylation with acetyl chloride (acetic acid chloride).



(42.2) Outline the preparation of *(**a**)* acetyl chloride and *(**b**)* acryloyl chloride by using thionyl chloride as a reagent.
Chapter **42.2**, analogous reactions: *(**a**)* acetyl chloride and *(**b**)* acryloyl chloride are prepared with thionyl chloride. Gaseous byproducts (SO_2 and HCl) leave the almost pure acid halides as residues.

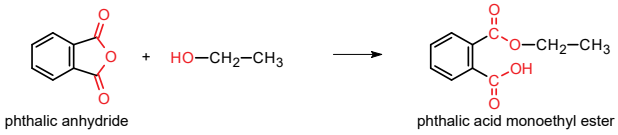


(42.3) Formulate the preparation of the mixed anhydride of formic and acetic acid (two options).
Chapter **42.3**, analogous reactions: Mixed acid anhydride of formic and acetic acid (acetic formic acid anhydride) can be prepared from acetyl chloride and sodium formate or from formyl chloride and sodium acetate.



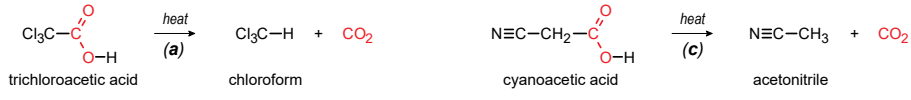
(42.4) What products are formed by heating *(**a**)* maleic acid, *(**b**)* phthalic acid, and *(**c**)* diammonium succinate?
Chapters **42.3**, **42.4**

(42.5) Formulate the reaction of phthalic anhydride with one equivalent of ethanol. What product is obtained?
Phthalic anhydride reacts with one equivalent of ethanol to produce pure phthalic acid monoethyl ester.

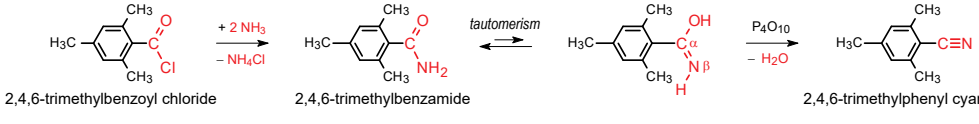


(42.6) Outline the steps of a test tube color reaction to identify a carboxylic acid.
Chapter **42.5**: Hydroxamic acid test tube reaction with ferric salt identifies carboxylic acids.

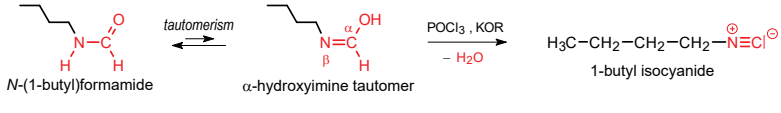
(42.7) What are the decarboxylation products of *(**a**)* trichloroacetic, *(**b**)* malonic, and *(**c**)* cyanoacetic acid? Formulate.
Chapter **42.6.3**, analogous reactions: *(**a**)* trichloroacetic acid undergoes thermal decarboxylation to chloroform, *(**b**)* malonic acid to acetic acid as formulated, and *(**c**)* cyanoacetic acid to acetonitrile (methylcyanide).



(42.8) Formulate the preparation of *(**a**)* 2,4,6-trimethylphenyl cyanide and *(**b**)* *n*-butyl isocyanide with suitable reagents.
Chapter **42.6.4**, analogous reactions: *(**a**)* 2,4,6-Trimethylphenyl cyanide (mesityl cyanide) is expected to arise from the dehydration of 2,4,6-trimethylbenzoic acid amide (β eliminination of H_2O).

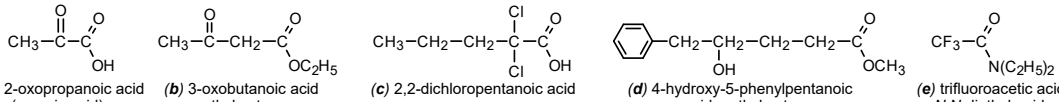


*(**b**)* *n*-Butyl isocyanide is expected to arise from the dehydration of *N*-(1-butyl)formamide (α elimination of H_2O).



(43.1) Draw the structural formulas of *(**a**)* 2-oxopropanoic acid, *(**b**)* 3-oxobutanoic acid ethyl ester, *(**c**)* 2,2-dichloropentanoic acid, *(**d**)* 4-hydroxy-5-phenylpentanoic acid methyl ester, and *(**e**)* trifluoroacetic acid *N,N*-diethylamide.

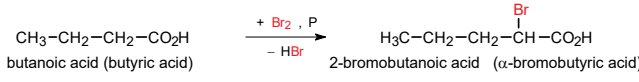
Chapter **43.1**: Structural formulas of substituted carboxylic acids are ***(a-e)***.



*(**a**)* 2-oxopropanoic acid (pyruvic acid) | *(**b**)* 3-oxobutanoic acid ethyl ester | *(**c**)* 2,2-dichloropentanoic acid | *(**d**)* 4-hydroxy-5-phenylpentanoic acid methyl ester | *(**e**)* trifluoroacetic acid *N,N*-diethylamide

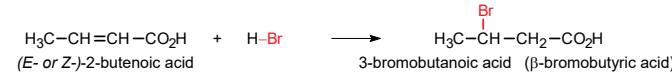
(43.2) Formulate equations to suggest the preparations of pure *(**a**)* 2-bromobutanoic acid and *(**b**)* 3-bromobutanoic acid.

Chapter **43.2.1**, analogous reactions: ***(a)*** 2-Bromobutanoic acid can be obtained by bromination of butanoic acid (butyric acid) with bromine in presence of phosphorous tribromide (HELL-VOLHARD-ZELINSKY reaction).



butanoic acid (butyric acid) → 2-bromobutanoic acid (α-bromobutyric acid)

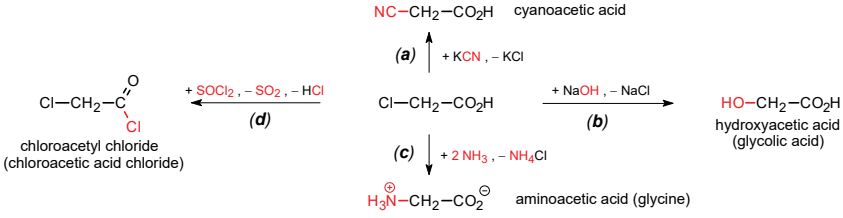
(b) Electrophilic hydrobromination of *E*- or *Z*-2-butenoic acid is expected to produce 3-bromobutanoic acid.



(E- or Z-)-2-butenoic acid → 3-bromobutanoic acid (β-bromobutyric acid)

(43.3) What products are obtained by reacting chloroacetic acid with *(**a**)* potassium cyanide, *(**b**)* sodium hydroxide, *(**c**)* ammonia, and *(**d**)* thionyl chloride. Write the equations.

Chapter **43.2.2**, analogous reactions: Chloroacetic acid reacts with ***(a)*** potassium cyanide to yield cyanoacetic acid, ***(b)*** sodium hydroxide to give hydroxyacetic acid (glycolic acid), ***(c)*** ammonia to afford aminoacetic acid (glycine, Chapter **68.1**) and ***(d)*** thionyl chloride to produce chloroacetic acid chloride (chloroacetyl chloride).



chloroacetyl chloride (chloroacetic acid chloride) ⟵ *(**d**)* chloroacetic acid ⟶ *(**b**)* hydroxyacetic acid (glycolic acid); *(**a**)* ⟶ cyanoacetic acid; *(**c**)* ⟶ aminoacetic acid (glycine)

(43.4) Ethyl bromoacetate reacts with zinc dust in toluene. What product is formed when benzaldehyde is added to the mixture? Formulate the appropriate equations.

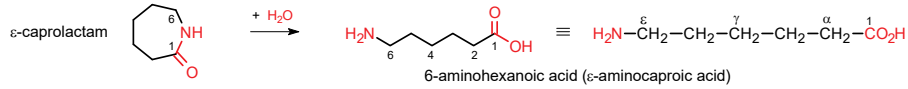
Chapter **43.3.1**: last reaction equation, REFORMATSKY reaction of bromoacetic acid ethyl ester (ethyl bromoacetate) with benzaldehyde

(43.5) What are *(**a**)* lactides, *(**b**)* lactones, and *(**c**)* lactams? Give examples.

Chapter **43.3.2**: ***(a)*** Lactides are bislactones of α-hydroxycarboxylic acids; ***(b)*** lactones are cyclic esters of β-, γ, and δ-hydroxycarboxylic acids; ***(c)*** lactams are cyclic amides of β-, γ, δ-, and ε-aminocarboxylic acids.

(43.6) Which lactam gives ε-aminocaproic acid (6-aminohexanoic acid) upon acidic hydrolysis?

Chapter **43.3.2**: Hydrolysis of ε-caprolactam produces ε-aminocaproic acid (6-aminohexanoic acid).



ε-caprolactam → 6-aminohexanoic acid (ε-aminocaproic acid)

(44.1) What is a stereogenic center? Define the term chirality. How do enantiomers of a specific compound differ?

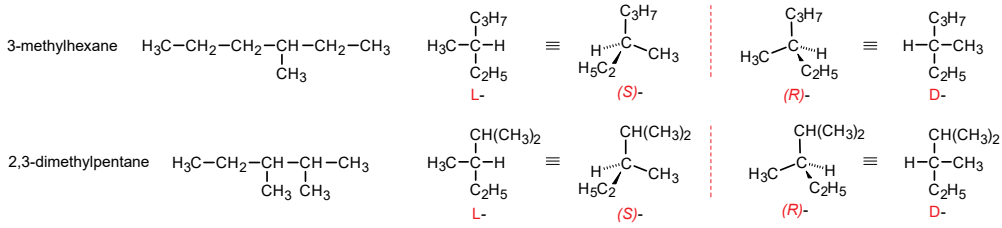
Chapter **44.1**

(44.2) Draw the enantiomers of 2-(4-isobutylphenyl)propanoic acid and assign the absolute configurations.

Chapter **81.5** answers this, including more information

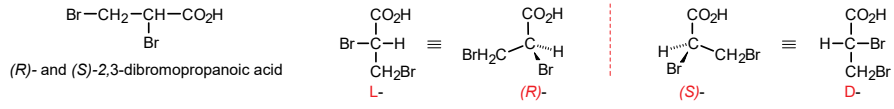
(44.3) Which structural isomers of heptane C_7H_{16} exist as enantiomers? Draw, name, and specify them.

3-Methylhexane and 2,3-dimethylpentane (C_7H_{16}) are hydrocarbons with one stereogenic center. FISCHER and tetrahedral projections formulas specify the absolute configurations following the FISCHER and CIP convention.



(44.4) Draw the appropriate projection formulas of *(R)*- and *(S)*-2,3-dibromopropanoic acid. Is L = *(S)* and D = *(R)* a rule?

FISCHER and tetrahedral projection formulas specify the absolute configurations following the FISCHER- and the CIP convention, exemplifying that L = *(S)*- and D = *(R)*- *is not a general rule*.

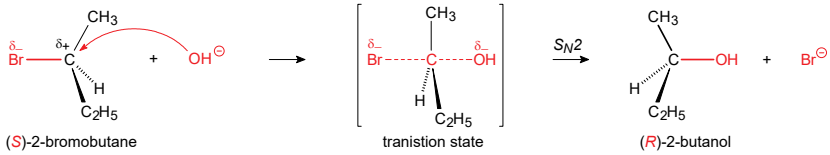


(44.5) What is a racemic mixture? Suggest a method to resolve racemic 2-butanol.

Chapter **44.3.4**: Set R = 2-butyl in the scheme and read the introduction of Chapter **46**.

(44.6) What product is expected from reacting *(S)*-2-bromooctane with sodium hydroxide? Characterize this reaction.

Chapter **44.4**: *(S)*-2-Bromobutane is expected to undergo a stereospecific S_N2 reaction, producing *(R)*-2-butanol (WALDEN inversion of the absolute configuration; but dehydrobromination to *E*- and *Z*-2-butene may compete).



(45.1) Which kinds of chiral compounds with heteroatoms as stereogenic centers do you know? Draw example formulas.

Chapter **45.1**

(45.2) Which kinds of chiral compounds without stereogenic centers do you know? Draw example formulas.

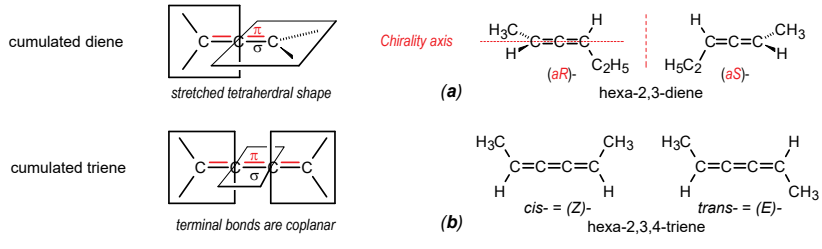
Chapter **45.1**

(45.3) Enantiomers of 1,3-diphenylallene exist. Why? Look at the molecular orbital model in Chapter **17.2.3**.

Chapters **45.2**, **17.2.3**

(45.4) Which one of ***(a)*** hexa-2,3-diene and ***(b)*** hexa-2,3,4-triene exists as *(E)*- and *(Z)*-isomers, and which one as enantiomers? Specify the enantiomers.

Chapter **45.2**: ***(a)*** *(aR)*- or *M*- and *(aS)*- or *P*- enantiomers are expected for hexa-2,3-diene with an even number of cumulated double bonds; ***(b)*** *cis*- and *trans*-isomers, however, are expected for hexa-2,3,4-triene with an odd number of double bonds. The molecular orbital model provides an explanation (Chapter **17.2.3**).



(45.5) What are atropisomers? Draw formulas of a pair of enantiomers and specify their absolute configuration.
Chapter **45.2**, last section

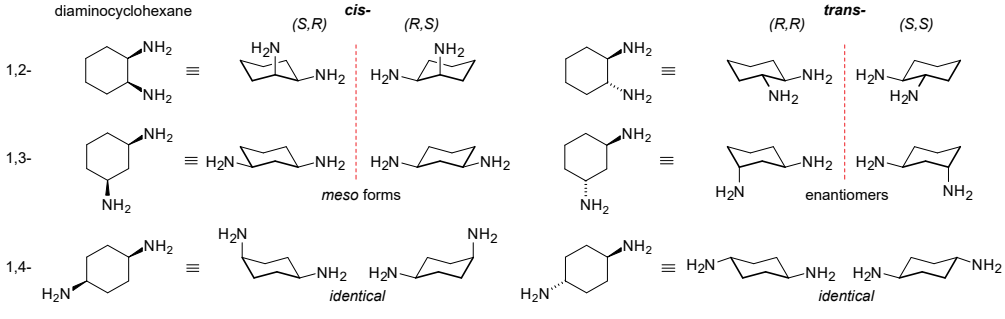
(46.1) How do enantiomers and diastereomers differ?
Chapter **46.1**

(46.2) Which stereoisomers exist for 3-bromo-2-butanol? Specify their configurations and classify them.
Chapter **46.1**

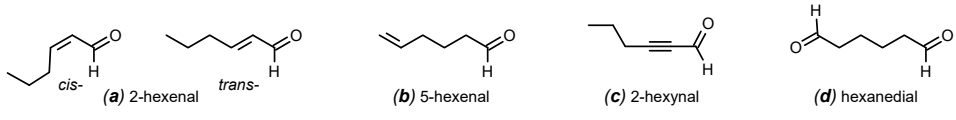
(46.3) Which stereoisomers exist for 2,3,4-trihydroxybutanoic acid? Specify their configurations and classify them.
Chapter **46.1**: Replace the aldehyde function by a carboxy group in threose and erythrose.

(46.4) Which stereoisomers exist for 2,3-dihydroxybutanedioic acid? Characterize a *meso*-isomer.
Chapter **46.2** (tartaric acids)

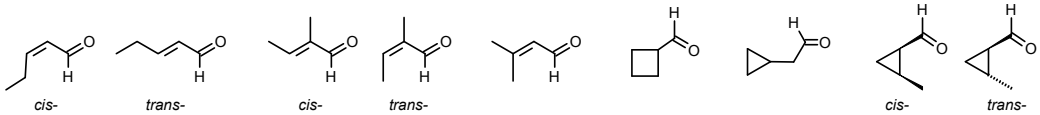
(46.5) Draw all stereoisomers of ***(a)*** 1,2-, ***(b)*** 1,3-, and ***(c)*** 1,4-diaminocyclohexane and fully name them.
Chapter **46.2**, last section: ***(a)*** 1,2-, ***(b)*** 1,3- and ***(c)*** 1,4-diaminocyclohexane exist as *cis*- and *trans*-isomers. Mirror images of *cis*-1,2- and 1,3-diaminocyclohexane are *meso* forms; mirror images of *trans*-1,2- and 1,3-diaminocyclohexane are enantiomers.



(47.1) Draw the structural formulas of ***(a)*** *cis*- and *trans*-2-hexenal, ***(b)*** 5-hexenal, ***(c)*** 2-hexynal, and ***(d)*** hexanedial.
Skeletal formulas (Chapter **8.2**) of unsaturated C_6 aldehydes portray the molecular shape, *e.g.* for ***(a)*** and ***(c)***.

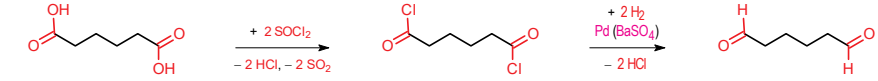


(47.2) Draw the structural formulas of all aldehydes with the molecular formula C_5H_8O and name them.
There are nine aldehydes with the molecular formula C_5H_8O; *cis*- and *trans*-2-methylcyclopropanecarbaldehyde (1-formyl-2-methylcyclopropane) are diastereomers; each one of those is a pair of enantiomers.



(47.3) Formulate equations to describe the preparation of benzaldehyde from toluene.
Chapter **47.2.2**

(47.4) Formulate equations to describe the preparation of hexanedial from adipic acid (hexanedioic acid).
Chapter **47.2.3**: Hexanedial is expected to be produced by ROSENMUND reduction of adipic acid dichloride.



adipic acid (hexanedioic acid) — adipic acid dichloride — hexanedial

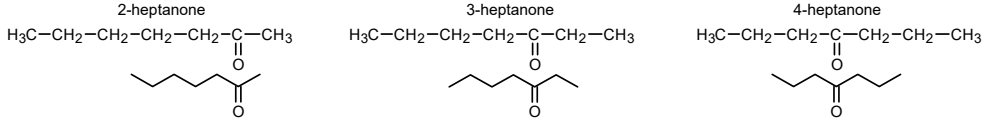
Reduction of the bis-*N*-methylanilide of adipic acid with $LiAlH_4$ (Chapter **47.2.3**) would require an additional step.

(47.5) Which reactions permit preparation of *p*-methoxybenzaldehyde from methyl phenyl ether (methoxybenzene)?
Chapter **47.2.4**: *p*-Methoxybenzaldehyde (anisaldehyde) is expected to arise from electrophilic formylation of anisol (methyl phenyl ether, methoxybenzene) by following the GATTERMANN-KOCH or the VILSMEIER method.

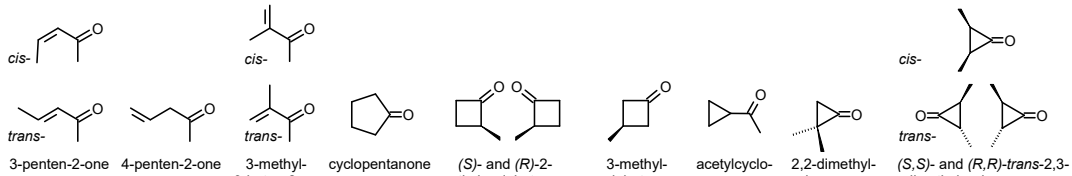
(47.6) One test tube contains butanal, the other butanone (C_4H_8O, Table 48.1). Formulate three test tube reactions to identify the aldehyde.
Chapter **47.4.1**: Unlike butanone, butanal *reduces*: TOLLENS-, FEHLING- and NYLANDER reactions are positive.

(47.7) What happens when *p*-tolualdehyde (*p*-methylbenzaldehyde) is reacted with sodium hydroxide? Formulate the mechanism.
Chapter **47.4.2**: CANNIZZARO disproportionation of *p*-tolualdehyde is expected to produce *p*-methylbenzoic acid (toluic acid, product of oxidation) and *p*-methylbenzylalcohol (α-hydroxy-*p*-xylene, product of reduction). Set Ar = *p*-methylphenyl in the reaction equations.

(48.1) Draw the structural formulas of all unbranched heptanones and name these compounds.
Chapter **48.1**: Three unbranched heptanones exist.

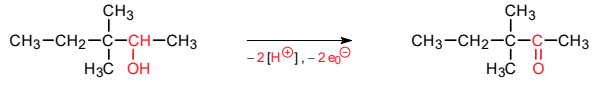


(48.2) Draw structural formulas of all isomeric ketones with the molecular formula C_5H_8O and name them.
There are 14 isomeric ketones with the molecular formula C_5H_8O; three of those are *cis*- and *trans*-isomers, two are enantiomers *(R)*- and *(S)*- and *(R,R)*- and *(S,S)*-, respectively. Enol tautomers are not considered here.



3-penten-2-one — 4-penten-2-one — 3-methyl-3-buten-2-one — cyclopentanone — *(S)*- and *(R)*-2-methylcyclobutanone — 3-methylcyclobutanone — acetylcyclopropanone — 2,2-dimethylcyclopropanone — *(S,S)*- and *(R,R)*-*trans*-2,3-dimethylcyclopropanone

(48.3) Which secondary alcohol can be oxidized to 3,3-dimethyl-2-pentanone? Formulate the reaction.
Chapter **48.2.1**: 3,3-Dimethyl-2-pentanol undergoes oxidation to yield 3,3-dimethyl-2-pentanone.



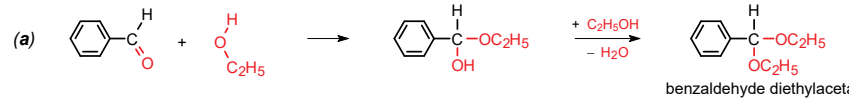
(48.4) Write equations which suggest methods to prepare 1,2-cyclopentanedione from an appropriate *(**a**)* diol and *(**b**)* ketone.
Chapters **48.2.1**, **48.2.3**: 1,2-Cyclopentanedione can be prepared by *(**a**)* oxidation of cyclopentanediol (*cis*- and/or *trans*-) and *(**b**)* oxidation of cyclopentanone with selenium dioxide (RILEY oxidation).

(48.5) Acetylation of 1,3-dimethoxybenzene gives 2,4-dimethoxyacetophenone as the major product. Why?
Chapters **48.2.4, 26.2**: Owing to their *(+M)* effect, both methoxy groups direct electrophilic acetylation to the *o*-, *o´*- and *p*-positions (positions 2-, 4- and 6-), but the bulky methoxy groups shield the 2-position. 5-Acetyl-2,4-dimethoxyacetophenone is expected to be a minor product.

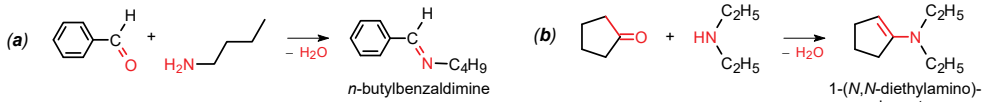
(48.6) Look again at Chapter **36.2** and suggest a method to prepare *t*-butyl methyl ketone (3,3-dimethyl-2-butanone).
Chapter **36.2**: Pinacol rearrangement of 2,3-dimethyl-2,3-butandiol will produce 3,3-dimethyl-2-butanone.

(49.1) Formulate a general equation that accounts for the typical reactions of aldehydes and ketones.
Chapter **49**, first section

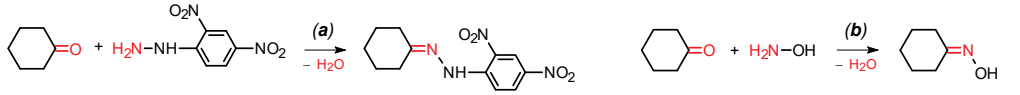
(49.2) What products arise from the acid-catalyzed reaction of ethanol with ***(a)*** benzaldehyde and ***(b)*** propanone (acetone)?
Chapter **49.1.2**, analogous reaction: Acid-catalyzed reaction of ethanol with ***(a)*** benzaldehyde produces benzaldehyde diethyl acetal *via* the hemiacetal; with ***(b)*** acetone (propanone), acetone diethyl ketal (2,2,-diethyoxpropane) is expected *via* the hemiketal (2-ethoxy-2-hydroxypropane).



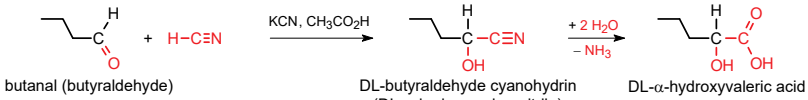
(49.3) Formulate the reactions of ***(a)*** benzaldehyde with *n*-butylamine and ***(b)*** cyclopentanone with diethylamine.
Chapter **49.2**, analogous reactions: ***(a)*** Benzaldehyde and the *primary* amine *n*-butylamine react to produce *n*-butylbenzaldimine (an azomethine, SCHIFF base). ***(b)*** Cyclopentanone and the *secondary* amine diethylamine undergo dehydration to produce the enamine 1-(*N*,*N*-diethylamino)cyclopentene.



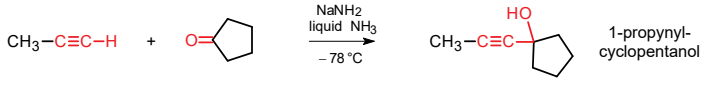
(49.4) Formulate the reactions of cyclohexanone with ***(a)*** 2,4-dinitrophenylhydrazine and ***(b)*** hydroxylamine.
Chapter **49.2**, analogous reactions: Cyclohexanone reacts with ***(a)*** 2,4-dinitrophenylhydrazine to yield the 2,4-dinitrophenylhydrazone and with ***(b)*** hydroxylamine to produce cyclohexanone oxime.



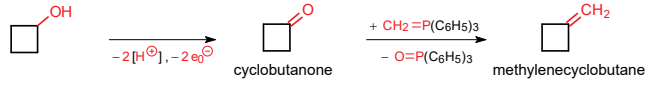
(49.5) Formulate the cyanohydrin reaction of butanal. Which kind of isomers are formed?
Chapter **49.3.2**, analogous reaction: Cyanohydrin reaction of butanal generates a stereogenic center (chirogenic reaction), producing both enantiomers of the cyanohydrin (DL-1-cyano-1-hydroxybutane = α-hydroxyvaleric acid nitrile) as a racemic mixture (DL).

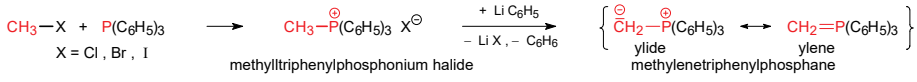


(49.6) Propyne reacts with cyclopentanone in liquid NH_3 and $NaNH_2$ as base. Write the equation and name the product.
Chapter **49.3.1**, analogous reaction: Nucleophilic alkynylation of cyclopentanone with propyne in liquid ammonia and with sodium amide as deprotonating reagent is expected to produce 1-propynylcyclopentanol.

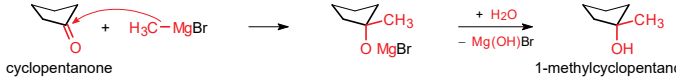


(49.7) Formulate all steps necessary to convert cyclobutanol into methylenecyclobutane, using the WITTIG alkenylation.
Chapter **49.3.4**, analogous reaction: The secondary alcohol cyclobutanol is oxidized to the ketone cyclobutanone which is reacted with meth**ylene**triphenylphosphane to undergo WITTIG alkenylation to produce methylene-cyclobutane. The "ylene" arises from deprotonation of methyltriphenylphosphonium iodide, obtained by methylation of triphenylphosphane with methyl iodide.

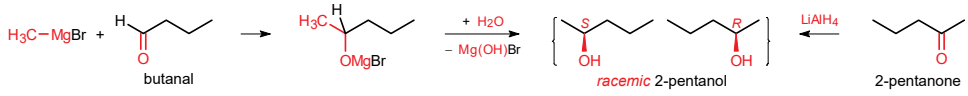




(49.8) Suggest reactions for the preparation of *(**a**)* 1-methylcyclopentanol and *(**b**)* racemic 2-pentanol from appropriate carbonyl compounds.
Chapters **49.3.3**, **49.4**, analogous reactions: 1-Methylcyclopentanol *(**a**)* can be prepared by methylation of cyclopentanone with methylmagnesium bromide.



Racemic 2-pentanol *(**b**)* is accessible by reduction of 2-pentanone with complex metal hydride such as $LiAlH_4$ or by methylation of butanal (butyraldehyde) with methylmagnesium bromide.

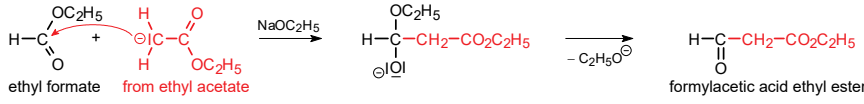


(49.9) Which methods are available to convert butyrophenone into *n*-butylbenzene?
Chapter **49.4**: CLEMMENSEN- and WOLFF-KISHNER reductions of butyrophenone

(50.1) Explain why carboxylic acid derivatives, aldehydes, and ketones are CH acidic.
Chapters **50.1**, **50.2**

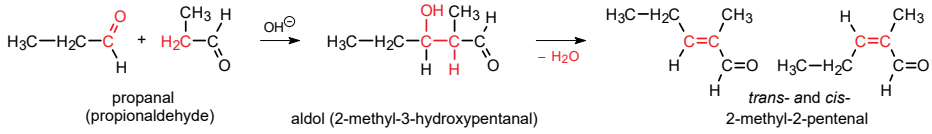
(50.2) Write equations for *(**a**)* a CLAISEN condensation and *(**b**)* an aldol reaction with subsequent dehydration.
Chapters **50.1.1**, **50.2.1**

(50.3) Formulate the reaction of ethyl formate and ethyl acetate in the presence of sodium ethoxide and name the product.
Chapter **50.1.1**, analogous reaction: CLAISEN condensation of ethyl formate (formic acid ethyl ester) and ethyl acetate (acetic acid ethyl ester) in the presence of a base is expected to produce formylacetic acid ethyl ester.

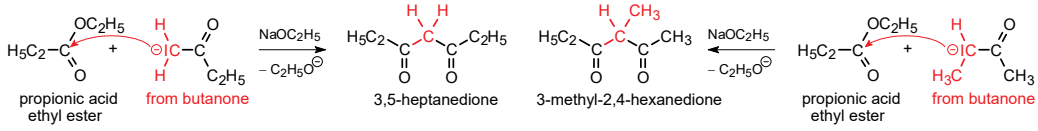


(50.4) Write equations to describe a synthesis of cyclopentanone from adipic acid.
Chapter **50.1.2**, last section

(50.5) Suggest a simple synthesis of 2-methyl-2-pentenal (*trans*- and *cis*-isomers) by aldol reaction and dehydration.
Chapter **50.2.1**, analogous reaction: Propanal (propionaldehyde) undergoes aldol reaction and subsequent dehydration to produce *trans*- and *cis*- 2-methyl-2-pentenal.



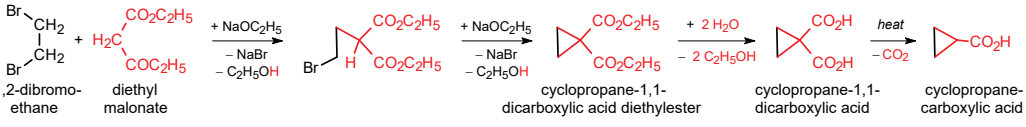
(50.6) Which reaction permits production of 2,4-pentanedione? Suggest an analogous preparation of 3,5-heptanedione.
Chapter **50.2.2**, analogous reaction: 3,5-Heptanedione is accessible by CLAISEN condensation of ethyl propanoate (propionic acid ethyl ester) and butanone. Two regioisomeric diketones may be produced. 3,5-Heptanedione as desired (major product) arises from deprotonation of the *methyl* group of butanone by the base; 3-methyl-2,4-hexanedione is obtained when deprotonation of the *methylene* group of butanone takes place (regioselectivity: Chapter **78.2**).



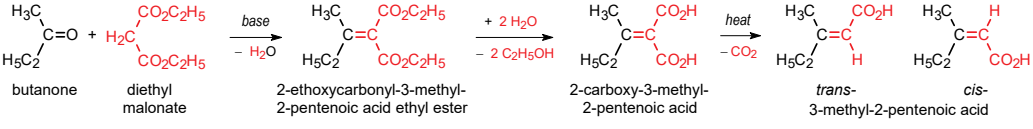
(51.1) Draw the structural formulas of all kinds of 1,3-dicarbonyl compounds you know.
Chapter **51**, first section

(51.2) Formulate and explain the CH acidity of 1,3-dicarbonyl compounds.
Chapter **51.1**

(51.3) Formulate a sequence of reactions that permits the synthesis of cyclopropanecarboxylic acid.
Chapter **51.2.1**, analogous reaction: Cyclopropanation is achieved by cycloalkylation of diethyl malonate with 1,2-dibromoethane. Hydrolysis (saponification) of the diester and decarboxylation of the cyclopropane-1,1-dicarboxylic acid produces the target cyclopropane carboxylic acid.



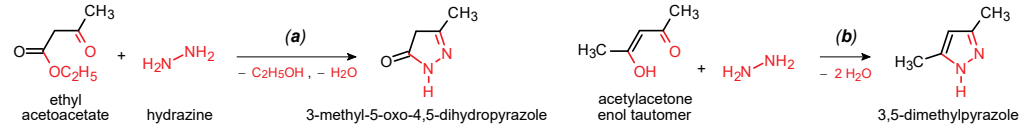
(51.4) Propose a synthesis of 3-methyl-2-pentenoic acid. Which isomers can be formed?
Chapter **51.2.2**, analogous reaction: KNOEVENAGEL alkenylation of butanone with diethyl malonate is the key step of the synthesis. Primarily formed 2-ethoxycarbonyl-3-methyl-2-pentenoic acid ethyl ester is hydrolyzed to the dicarboxylic acid wich undergoes thermal decarboxylation to *trans*- and *cis*-3-methyl-2-pentenoic acid.



(51.5) What product is obtained by MICHAEL addition of acetylacetone to butenone?
Chapter **51.2.3**, last section

(51.6) Which test tube reactions indicate the presence of enol tautomers in samples of 1,3-dicarbonyl compounds?
Chapter **51.2.4**

(51.7) What products are formed by reaction of hydrazine with ***(a)*** ethyl acetoacetate and ***(b)*** acetylacetone?
Chapter **51.2.5**, analogous reactions: Binucleophilic hydrazine undergoes cyclodehydration with ***(a)*** ethyl acetoacetate, yielding 3-methyl-5-oxo-4,5-dihydropyrazole, and with ***(b)*** acetylacetone (2,4-pentanedione), yielding 3,5-dimethylpyrazole.



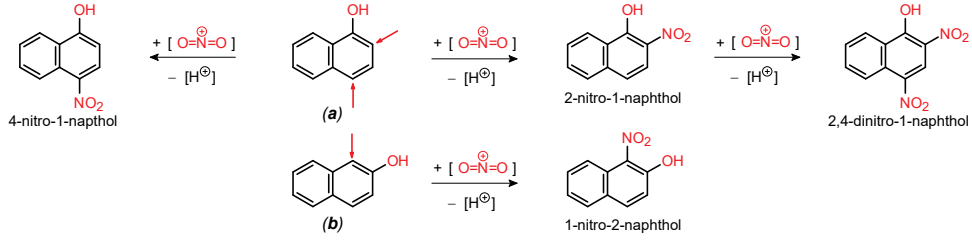
(52.1) Why are phenols much stronger acids than alcohols? Explain your reasoning with resonance formulas.
Chapter **52.2**

(52.2) Formulate all equations necessary to outline the production of phenol and acetone from cumene.
Chapter **52.3.1**

(52.3) What products are formed by reaction of acetic anhydride with ***(a)*** phenol and $AlCl_3$, and ***(b)*** salicylic acid?
Chapter **52.4.2**, answering ***(a)*** and ***(b)***

(52.4) What product is formed by reaction of phenol with 3-bromo-1-propene (allyl bromide) in sodium hydroxide?
Chapter **37.3.2**, last reaction equation

(52.5) What products are likely to be formed by nitration of ***(a)*** α-naphthol and ***(b)*** β-naphthol? Look at Chapter **28.3**.
Chapter **28.3**, analogous reaction: ***(a)*** α-Naphthol undergoes electrophilic nitration with concentrated nitric acid and sulfuric acid at positions 2 and 4; ***(b)*** nitration of β-naphthol is expected to occur at position 1.



(52.6) What product is expected from the oxidation of 2,4,6-tri-*t*-butylphenol? Account for the stability of the product.
Chapter **52.4.4**

(53.1) Which isomeric benzo- and naphthoquinones exist? Draw the structural formulas.
Chapter **53.1**, Table 53.1

(53.2) Formulate the tautomerism of resorcinol.
Chapter **53.1**

(53.3) Formulate the preparation of ***(a)*** *o*-benzoquinone, ***(b)*** *p*-benzoquinone, and ***(c)*** 1,4-naphthoquinone, using appropriate phenols as starting material.
Chapter **53.2.1**: Oxidation of ***(a)*** catechol, ***(b)*** hydroquinone, and ***(c)*** 1,4-dihydroxynaphthalene

(53.4) What is an *EDA* or *CT* complex? Draw the formula of quinhydrone to explain.
Chapter **53.3.1**

(53.5) Formulate ***(a)*** the redox equilibrium between hydroquinone and *p*-benzoquinone and ***(b)*** the mechanism of the electron transfer in quinhydrone.
Chapter **53.3.1**, answering ***(a)*** and ***(b)***

(53.6) Which reactions can be used to prepare 9,10-anthraquinone?
Chapters **53.2.3**, **53.3.3**, last section

(53.7) Formulate an industrial method to produce hydrogen peroxide.
Chapter **53.3.2**

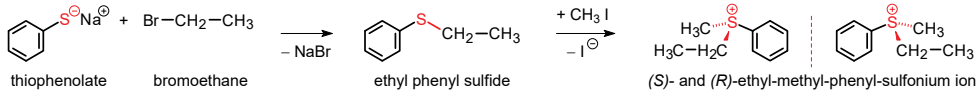
(53.8) What products are expected from the electrophilic sulfonation of 9,10-anthraquinone? Outline a synthesis of 1,2-dihydroxy-9,10-anthraquinone (known as alizarin).
Chapter **53.3.4**

(54.1) Which organosulfur compounds do you know? Which ones have oxygen analogues?
Chapter **54.1**, Table 54.1

(54.2) Formulate equations to suggest preparations of ***(a)*** 1-butanethiol and ***(b)*** thiophenol.
Chapter **54.2.1**

(54.3) What happens when thiols are exposed to air? Why are thiols much stronger acids than alcohols?
Chapter **54.2.1**, last sections

(54.4) Suggest a preparation of ethyl phenyl sulfide. Ethyl phenyl sulfide reacts with iodomethane. Specify the product.
Chapter **54.2.2**: Ethyl phenyl sulfide is prepared by WILLIAMSON synthesis from thiophenolate as nucleophile and bromoethane (S_N2) but not from ethane thiolate and bromobenzene (Chapter **27.1**). Methylation of ethyl phenyl sulfide with iodomethane produces *(R)*- and *(S)*-enantiomers of ethyl-methyl-phenyl-sulfonium iodide.



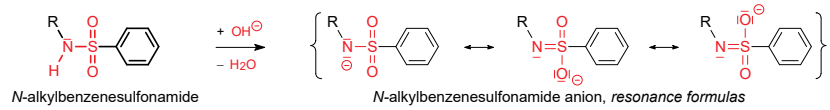
thiophenolate bromoethane ethyl phenyl sulfide *(S)*- and *(R)*-ethyl-methyl-phenyl-sulfonium ion

(54.5) Which products are obtained by the oxidation of thioethers with hydrogen peroxide? Formulate the reactions.
Chapter **54.3.1**

(54.6) Which reactions open access to *(**a**)* sulfinic acids and *(**b**)* sulfonic acids?
Chapter **54.3.2**, answering *(**a**)* and *(**b**)*

(54.7) Formulate equations to outline preparations of *(**a**)* sulfochlorides, *(**b**)* alkyl sulfonates, and *(**c**)* sulfonamides.
Chapter **54.3.3**

(54.8) Sulfonamides and *N*-alkylsulfonamides dissolve in aqueous sodium hydroxide. Explain with resonance formulas.
Chapter **54.3.3**, last section: Dissociation of an NH-proton from a sulfonamide leaves a resonance-stabilized sulfonamide anion; the negative charge is distributed (delocalized) among the N-atom and both O-atoms.



N-alkylbenzenesulfonamide *N*-alkylbenzenesulfonamide anion, *resonance formulas*

(54.9) Which thiocarbonyl compounds exist? Suggest syntheses of *(**a**)* thiobenzophenone and *(**b**)* phenyldithioacetic acid.
Chapter **54.2.4**, answering *(**a**)*; Chapter **54.2.5**, answering *(**b**)*, last reaction equation, set R = C_6H_5–CH_2– (benzyl).

(55.1) Which stable derivatives of carbonic acid do you know?
Chapter **55.1**

(55.2) What products are obtained from the reaction of phosgene and *(**a**)* ammonia, *(**b**)* ethanol with and without base, and *(**c**)* potassium *t*-butylmonocarbonate?
*(**a**)* Chapter **55.4.1**, product: urea; *(**b**)* Chapters **55.2.2**, **55.3.1**, set R = C_2H_5, products: ethyl chlorocarbonate and diethyl carbonate; *(**c**)* Chapter **55.3.1**, second reaction equation, set R = $C(CH_3)_3$, product: di-*t*-butyl tricarbonate

(55.3) Explain why all CN bonds of the guanidinium cation have equal length.
Chapter **55.4.2**

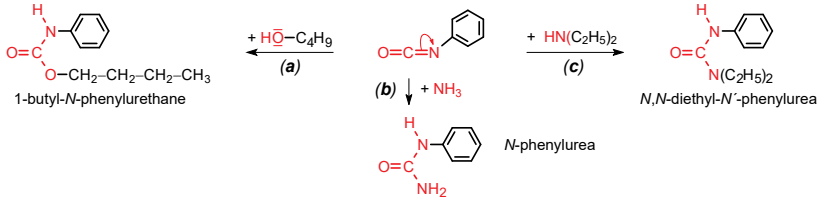
(55.4) Formulate equations to outline the syntheses of *(**a**)* tetramethylurea, *(**b**)* guanidine, and *(**c**)* thiourea.
Chapter **55.4.1**, last reaction equation, answering *(**a**)*, set R_2 = $(CH_3)_2$; Chapter **55.4.2**, last scheme, answering *(**b**)*; Chapter **55.4.2**, last scheme, answering *(**c**)*

(55.5) What are the parent compounds of *(**a**)* urethanes and *(**b**)* ureides?
*(**a**)* Chapter **55.3.2**: *Urethanes* are esters of *carbamic acid*. *(**b**)* Chapter **55.4.1**: *Ureides* are acylated *ureas*.

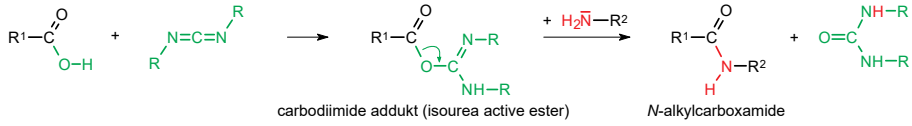
(56.1) What is a heterocumulene? Give examples. How are carbodiimide and cyanamide related to each other?
Chapter **56.1**: heterocumulenes; Chapter **56.4**: cyanamide-carbodiimide-tautomerism

(56.2) Formulate the preparation of *(**a**)* phenyl isocyanate, *(**b**)* phenyl isothiocyanate, and *(**c**)* DCC.
*(**a**)* Chapter **56.3**, first reaction equation: set R = C_6H_5 (phenyl); *(**b**)* Chapter **56.3**, second reaction equation: set Ar = C_6H_5 (phenyl); *(**c**)* Chapter **56.4**, second and third reaction equation: set R = cyclohexyl

(56.3) Formulate the reactions of phenyl isocyanate with *(**a**)* 1-butanol, *(**b**)* ammonia, and *(**c**)* diethylamine.
Chapter **56.3**, analogous reactions: phenylisocyanate adds *(**a**)* 1-butanol to produce 1-butyl-*N*-phenylurethane, *(**b**)* ammonia to produce *N*-phenylurea and *(**c**)* diethylamine to produce *N*,*N*-diethyl-*N´*-phenylurea.



(56.4) React DCC, first with a carboxylic acid, then with *(**a**)* an alcohol and *(**b**)* a primary amine. Formulate all reactions.
*(**a**)* Chapter **56.4**, last reaction equation: *activated esterification* of the carboxylic acid;
*(**b**)* same reaction equation: *activated amidation* of the carboxylic acid (Chapter **69.4**, peptide synthesis)



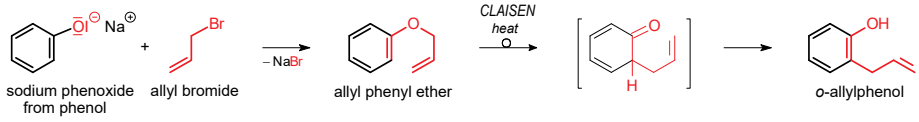
(57.1) Formulate the general mechanisms of *(**a**)* anionotropic and *(**b**)* cationotropic 1,2-shifts.
Chapter **57.1.1**, answering *(**a**)*; Chapter **57.2**, answering *(**b**)*

(57.2) Formulate a sequence of reactions which results in homologization of a carboxylic acid (R–CO_2H → R–CH_2–CO_2H).
Chapter **57.1.2** (WOLFF rearrangement, ARNDT-EISTERT homologization of carboxylic acids)

(57.3) Formulate all reactions which can be used to convert a carboxylic acid into a primary amine.
Chapter **57.1.4**, Fig. 57.1

(57.4) Write equations for the reactions of *(**a**)* 2-bromocyclohexanone, *(**b**)* benzyltrimethylammonium salt, and *(**c**)* benzyl methyl ether with a base.
*(**a**)* Chapter **57.2.1**: FAVORSKII rearrangement to yield cyclopentanecarboxylic acid ester, replace Cl by Br;
*(**b**)* Chapter **57.3**: SOMMELET-HAUSER rearrangement to give *N*,*N*-dimethyl-2-methylbenzylamine, set R = CH_3;
*(**c**)* Chapter **57.2.3**: WITTIG rearrangement to produce 1-phenylethanol, set R = phenyl and R´ = CH_3

(57.5) Sodium phenoxide is reacted with 3-bromo-1-propene, and the product is heated (200 °C). What happens?
Chapters **57.4**, **37.3.2**: 3-Bromo-1-propene (allyl bromide) reacts with phenoxide to produce allyl phenyl ether which undergoes CLAISEN rearrangement to give *o*-allylphenol upon heating.



(58.1) What is a polymer?
Chapter **58.1**

(58.2) What are *(**a**)* vinyl polymers and *(**b**)* diene polymers? How do they differ? Formulate examples.
Chapter **58.2**, answering *(**a**)* and *(**b**)*

(58.3) What kinds of reactions are *(**a**)* polymerizations, *(**b**)* polycondensations, and *(**c**)* polyadditions? Formulate examples.
Chapters **58.1**, **58.2**, answering *(**a**)*; Chapters **58.4**, **58.5**, answering *(**b**)*; Chapter **58.6**, answering *(**c**)*

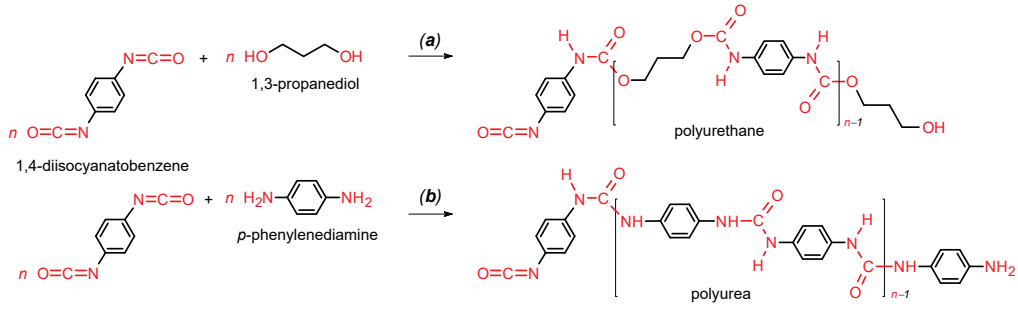
(58.4) Formulate equations to explain the mechanism of a radical polymerization.
Chapter **58.2**, p. 165

(58.5) Formulate equations to outline the formation of polyethers from oxiranes.
Chapter **58.3**

(58.6) Draw the structure of a polylactide. Which reactions permit the production of polyesters? Formulate examples.
Chapter **58.4**

(58.7) Which types of polymers are *(**a**)* polyamides and *(**b**)* polyurethanes? What kinds of reactions permit their production?
*(**a**)* Chapter **58.5**: polyamides by polycondensation; *(**b**)* Chapter **58.6**: polyurethanes by polyaddition

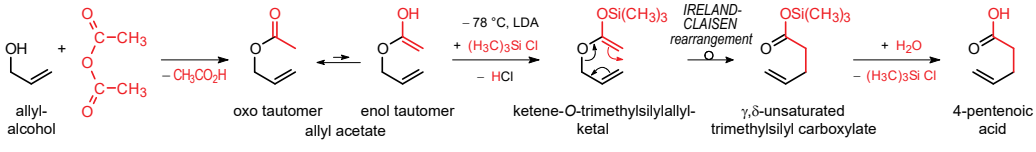
(58.8) Which types of polymers are formed from the reaction of 1,4-diisocyanatobenzene with *(**a**)* 1,3-propanediol and *(**b**)* 1,4-diaminobenzene (*p*-phenylenediamine)?
Chapter **58.6**: Polyaddition of 1,4-diisocyanatobenzene and 1,3-propanediol *(**a**)* produces a polyurethane; the analogous polyaddition with *p*-phenylenediamine *(**b**)* produces a polyurea.



(59.1) Which organosilicon compounds do you know? Why don't silacarbonyl compounds exist? What are silicones?
Chapters **59.1**, **59.4** (silicones)

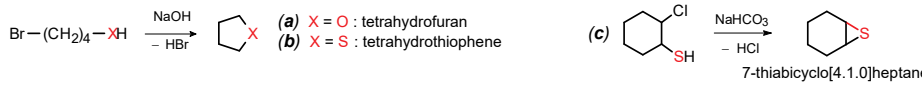
(59.2) Formulate all reactions you know to describe the preparative significance of chlorotrimethylsilane.
Chapter **59.3** (trimethylsilylations, reactions of silylenolethers)

(59.3) Design a synthesis of 4-pentenoic acid from 2-propen-1-ol and acetic anhydride.
Chapter **59.3.2**, typical reaction: The IRELAND-CLAISEN rearrangement of allyl acetate (acetic acid allyl ester), accessible by acetylation of allyl alcohol with acetic anhydride, is the key step of a synthesis of 4-pentenoic acid.



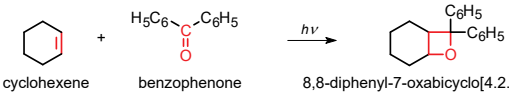
(60.1) Which heteroalicycles in Table 60.2 are *(**a**)* peroxides, *(**b**)* disulfides, *(**c**)* acetals, *(**d**)* thioacetals, *(**e**)* secondary amines, *(**f**)* enol ethers, and *(**g**)* enamines?
*(**a**)* peroxide: 1,2-dioxolane; *(**b**)* disulfide: 1,2-dithiolane; *(**c**)* acetals: 1,3-dioxolane, 1,3-dioxane; *(**d**)* thioacetals: 1,3-dithiolane, 1,3-dithiane; *(**e**)* secondary amines: azirane, azetane, pyrrolidine, imidazolidine, piperidine, piperazine, azepane; *(**f**)* enolethers: oxirene, oxete, furan, 2*H*-pyran, 4*H*-pyran, 1,4-dioxine, oxepine; *(**g**)* enamines: 1*H*-azirine, azete (an imine as well), pyrrole, imidazole, 1,4-dihydropyridine, 1*H*-azepine

(60.2) Write equations to prepare *(**a**)* tetrahydrofuran, *(**b**)* tetrahydrothiophene, and *(**c**)* 7-thiabicyclo[4.1.0]heptane.
Chapter **60.2.1**: *(**a**)* Tetrahydrofuran and *(**b**)* tetrahydrothiophene are obtained by intramolecular S_N reaction of 4-halobutanol or 4-halobutanethiol, respectively. Tetrahydrofuran is industrially produced by cyclodehydration of butane-1,4-diol. *(**c**)* 7-Thiabicyclo[4.1.0]heptane is the product of an intramolecular S_N reaction (dehydrochlorination) of 2-chlorocyclohexanethiol.



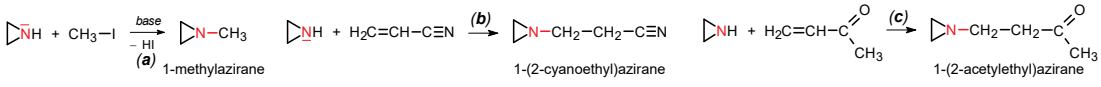
(60.3) What product is expected from the reaction of cyclohexene and benzophenone under UV light? Write the equation?

Chapter **60.2.2**, analogous reaction: When irradiated by UV, cyclohexene and benzophenone undergo [2+2]-cycloaddition to produce 8,8-diphenyl-7-oxabicyclo[4.2.0]octane (PATERNO-BÜCHI reaction).



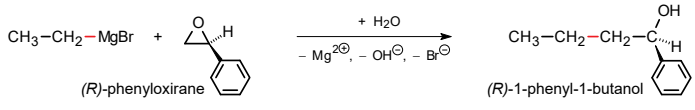
(60.4) What products are obtained from the reaction of azirane with *(**a**)* iodomethane, *(**b**)* acrylonitrile, and *(**c**)* butenone?

Chapter **60.3.1**, analogous reaction: Azirane as a nitrogen nucleophile is *N*-methylated by *(**a**)* methyl iodide and adds to the electron-deficient CC double bonds of *(**b**)* acrylonitrile and *(**c**)* butenone (MICHAEL addditions, Chapter **51.2.3**).



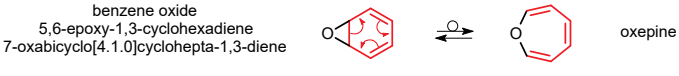
(60.5) Ethylmagnesium bromide is reacted with *(R)*-phenyloxirane. Draw the equation and name the product.

Chapter **60.3.2**, analogous reaction: Ethylmagnesium bromide reacts with *(R)*-phenyloxirane to produce *(R)*-1-phenyl-1-butanol.



(60.6) 5,6-Epoxy-1,3-cyclohexadiene and oxepine equilibrate at 25 °C. Formulate and provide an explanation.

Chapter **60.3.3**, analogous reaction: Benzene oxide and oxepine arise from each other by COPE rearrangement.



(60.7) What happens when 2-hydroxymethyl)tetrahydrofuran reacts with an acid? Write the mechanism.

Chapter **60.3.3**, last section

(61.1) Explain the term π-excessive heteroaromatic compounds. Which representatives do you know?

Chapter **61.2**

(61.2) Account for the acidity of pyrrole and cyclopentadiene in terms of resonance stabilization of the anions.

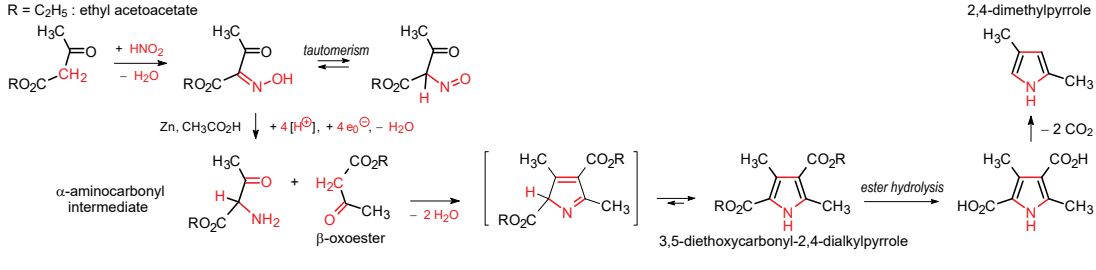
Chapters **61.4.1**, **29.1.2**

(61.3) Which aromatic heterocycles can be prepared by the PAAL-KNORR synthesis? Write the equations.

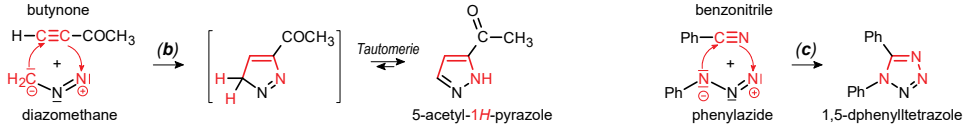
Chapter **61.3.1**

(61.4) Devise syntheses of *(**a**)* 2,4-dimethylpyrrole, *(**b**)* 5-acetylpyrazole, and *(**c**)* 1,5-diphenyltetrazole.

Chapters **61.3.1**, **61.3.2**, analogous reactions: 2,4-Dimethylpyrrole *(**a**)* is accessible by KNORR synthesis from ethyl acetoacetate.



1,3-Dipolar cycloaddition of diazomethane and butynone produces 5-acetyl-1*H*-pyrazole (***b***); analogous reaction of phenyl azide and benzonitrile affords 1,5-diphenyltetrazole (***c***), Ph = C_6H_5.



(61.5) What products are obtained from (***a***) acetylation and (***b***) nitration of *N*-methylpyrrole?
Chapter **61.4.2**, analogous reactions: (***a***) 2-Acetyl-*N*-methylpyrrole and (***b***) 2-nitro-*N*-methylpyrrole are expected.

(61.6) Formulate two mechanisms for the nitration of furan in anhydrous acetic acid. Which one is more likely?
Chapters **61.4.2**, **61.4.3**

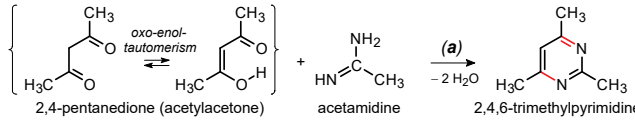
(61.7) What product arises from reaction of furan with (***a***) bromine in methanol and (***b***) butynedioic acid dimethyl ester?
Chapter **61.4.3**

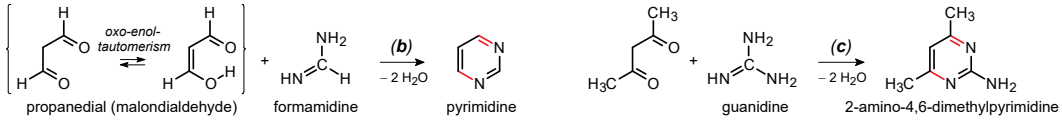
(61.8) Formulate the hydrolysis of furan in aqueous acid. What is the name of the reverse reaction?
Chapter **61.4.5**

(62.1) Explain the term π-deficient heteroaromatic compound, using pyridine and the pyrylium ion as examples.
Chapter **62.2**

(62.2) Formulate equations for the preparations of (***a***) 2,2´-bipyridine and (***b***) 2,4,6-trimethylpyridine.
Chapter **62.3.1**, answering (***a***); 2,4,6-trimethylpyridine (***b***) is obtained by HANTZSCH synthesis starting from ethyl acetoacetate, acetaldehyde and ammonia; set $R^1 = R^3 = CH_3$ and $R^2 = C_2H_5$ in the scheme.

(62.3) Devise syntheses of (***a***) 2,4,6-trimethylpyrimidine, (***b***) unsubstituted pyrimidine, and (***c***) 2-amino-4,6-dimethylpyrimidine.
Chapter **62.3.2**, analogous reactions: Pyrimidines are prepared by cyclodehydration of 1,3-dicarbonyl compounds with amidines, *e.g.* 2,4,6-trimethylpyrimidine (***a***) from 2,4-pentanedione and acetamidine, unsubstituted pyrimidine (***b***) from malondialdehyde (or the tetraethyl acetal) and formamidine, 2-amino-4,6-dimethylpyrimidine (***c***) from 2,4-pentanedione and guanidine.





(62.4) Outline a synthesis of 2-phenyl-4,6-dimethylpyrylium perchlorate.
Chapter **62.3.3**, analogous reaction: Insert R = CH_3 (for 2,4-pentanedione, enol tautomer) in the reaction equation.

(62.5) 4-*N*,*N*-Dimethylaminopyridine (DMAP) is much more basic than pyridine. Give an explanation.
Chapter **62.4.1**: Replace NH_2 in 4-aminopyridine by $N(CH_3)_2$.

(62.6) Formulate the reaction of pyridine with (***a***) sodium amide in liquid NH_3 and (***b***) butyllithium under nitrogen.
Chapter **62.4.2**, (***a***): first reaction equation; (***b***): second reaction equation: Replace phenyllithium by butyllithium, C_6H_5 by *n*-C_4H_9, and obtain 2-*n*-butylpyridine.

(62.7) Draw the resonance formulas of pyridine *N*-oxide. What can be concluded concerning reactivity?
Chapter **62.4.1**

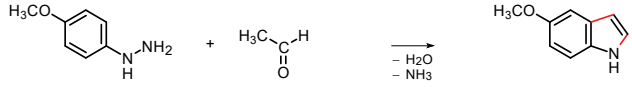
(62.8) Suggest reactions to prepare (***a***) 3-nitropyridine and (***b***) 4-nitropyridine.
Chapter **62.4.3**, answering (***a***) and (***b***)

(62.9) Draw resonance formulas of the intermediates resulting from deprotonation of ***(a)*** acetone and ***(b)*** 2-methylpyridine.
Chapter **50.2**, concerning ***(a)*** and Chapter **62.4.4**, concerning ***(b)***

(62.10) 2-Methylpyrimidine is reacted with benzaldehyde in the presence of $ZnCl_2$. Which *(E)*-isomer is the major product?
Chapter **62.4.4**

(63.1) Why are benzo[*c*]furan and its analogues not aromatic? Write the equation for their reaction with maleic anhydride.
Chapters **63.3**, **63.3.2**

(63.2) Which reactants are required to synthesize 5-methoxyindole? Write the mechanism of the reaction.
Chapter **63.2.2**: Following the mechanism of FISCHER´s indole synthesis, 5-methoxyindole can be synthesized from *p*-methoxyphenylhydrazine and acetaldehyde (or acetaldehyde diethylacetal).



p-methoxyphenylhydrazine acetaldehyde 5-methoxyindole

(63.3) What products are obtained by nitration of ***(a)*** benzo[*b*]furan and ***(b)*** benzo[*b*]thiophene? Explain your answer.
Chapter **63.3.1**, answering ***(a)*** and ***(b)***

(63.4) Suggest reactions to prepare ***(a)*** indole-3-carboxylic acid and ***(b)*** 3-(*N*,*N*-dimethylaminomethyl)indole from indole.
Chapter **63.3.1**, answering ***(a)***; Chapter **50.2.3** and Fig. 63.1, answering ***(b)***

(63.5) Propose a reaction to convert a substituted indole into a substituted quinoline.
Chapter **63.3.2**

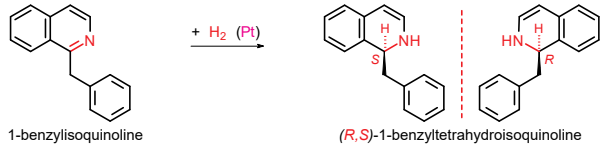
(63.6) Formulate ***(a)*** the tautomerism and oxidation of 3-hydroxyindole and ***(b)*** the dyeing of fabrics with indigo.
Chapter **63.3.3**, answering ***(a)*** and ***(b)***

(64.1) Draw the structural formulas of all benzodiazines with the molecular formula $C_8H_6N_2$ and name them.
Chapter **64.1**, Table 64.1; [$C_8H_6N_2$ includes 1,5-, 1,6-, 1,7-, 1,8-, 2,6-, and 2,7-naphthyridine (diazanaphthalenes) with nitrogen atoms *in different rings*, representing structural isomers containing differently fused pyridine rings.]

(64.2) What compound arises from reacting aniline and butenone in nitrobenzene with $ZnCl_2$? Write the mechanism.
Chapter **64.2.1**: SKRAUP´s quinoline synthesis with butenone ($R^1 = R^2 = H$, $R^3 = CH_3$) produces 4-methylquinoline.

(64.3) Write equations to suggest two syntheses of the alkaloid parent compound 1-benzylisoquinoline (Chapter **70.1**).
Chapter **64.2.2**: analogous reactions: 1-Benzylisoquinoline can be prepared from phenylethylamine and phenylacetyl chloride (BISCHLER-NAPIERALSKY synthesis, R = CH_2–C_6H_5, benzyl) or from phenylethylamine and phenylacetaldehyde (PICTET-SPENGLER synthesis, R = CH_2–C_6H_5).

(64.4) Recalling Chapter 44, two products are obtained by the catalytic hydrogenation of 1-benzylisoquinoline? Draw them.
Catalytic hydrogenation of 1-benzylisoquinoline produces the racemate (*R*,*S*)-1-benzyltetrahydroisoquinoline.



1-benzylisoquinoline (*R*,*S*)-1-benzyltetrahydroisoquinoline

(64.5) Isoquinoline reacts with ***(a)*** $NaNH_2$ in liquid NH_3 and ***(b)*** *n*-butyllithium under nitrogen. What are the products?
Chapter **64.3.4**, answering ***(a)***; Chapter **64.3.3**, answering ***(b)***: *n*-butyllithium is expected to undergo nucleophilic addition to isoquinoline, producing *(R,S)*-1-*n*-butyl-1,2-dihydroisoquinoline upon addition of water.

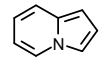
(64.6) 2-Chloroquinoline reacts with ***(a)*** water and ***(b)*** sodium ethoxide. Formulate the reactions and name the products.
Chapter **64.3.4**, answering ***(a)*** and ***(b)***

(64.7) What products arise from the nitration of ***(a)*** quinoline and ***(b)*** isoquinoline?
Chapter **64.3.5**, answering ***(a)***; ***(b)*** electrophilic nitration of isoquinoline is expected to produce 5-nitroisoquinoline.

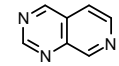
(64.8) Write an equation to propose a synthesis of 2-quinolylacetone.
Chapter **64.3.6**: 2-Quinolylacetone (quinolin-2-yl-propanone) is expected to arise from the ester condensation of 2-methylquinoline with ethyl acetate in the presence of sodium ethoxide as a base.

(65.1) Draw the structural formulas of ***(a)*** 3*H*-pyrrolo[1,2-*a*]pyrrole, ***(b)*** pyrrolo[1,2-*a*]pyridine, and ***(c)*** pyrido[2,3-*d*]pyrimidine.
Structural formulas of the heterobicycles are:

(a) 3*H*-pyrrolo[1,2-*a*]pyrrole



(b) pyrrolo[1,2-*a*]pyridine

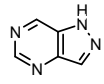


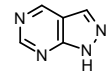
(c) pyrido[3,4-*d*]pyrimidine

(65.2) Which of the heterobicycles in Table 65.1 are aromatic?
Chapter **65.1**, Table 65.1: 3*H*-Pyrrolizine (π electron sextet in one pyrrole ring), indolizine (π electron sextet in one pyrrole ring) and dehydroquinolizinium ion (π electron sextet in one pyridine ring) are aromatic.

(65.3) Design a synthesis of 2-methylindolizine.
Chapter **65.1**, analogous reaction: 2-Methylindolizine can be synthesized from α-picoline (2-methylpyridine) and bromoacetone. Set R = CH_3 in the reaction equation.

(65.4) Draw the structural formulas of two purine isomers that contain a fused pyrazole instead of an imidazole ring, and name them.
Chapter **65.2.1**: Pyrazol[4,3-*d*]pyrimidine and pyrazolo[3,4-*d*]pyrimidine are isomers of purine containing a fused pyrazole instead of the imidazole ring. Provided ring numbering is the same as in purine, the bicycles are more precisely denoted as 9*H*-pyrazolo[4,3-*d*]pyrimidine and 7*H*-pyrazolo[3,4-*d*]pyrimidine.

pyrazolo[4,3-*d*]pyrimidine 

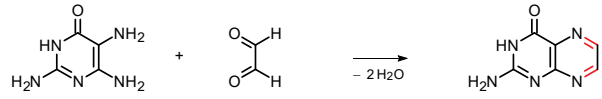
pyrazolo[3,4-*d*]pyrimidine 

(65.5) Which tautomers exist for ***(a)*** purine and ***(b)*** 2,4,5,6-tetraoxohexahydropyrimidine (alloxan)?
Chapter **65.2.1**, concerning purine ***(a)***; Chapter **65.2.3**, concerning alloxan ***(b)***

(65.6) Which ***(a)*** purine nucleobases and ***(b)*** purine stimulants do you know?
Chapter **65.2.1**, Table 65.2, answering ***(a)*** and ***(b)***

(65.7) Formulate equations to describe TRAUBE's guanine synthesis.
Chapter **65.2.2**

(65.8) Formulate an equation to suggest the preparation of pterine from an intermediate in TRAUBE's guanine synthesis.
Chapter **65.3.2**, analogous reaction: Pterine is synthesized by cyclodehydration of 2,4,5-triamino-6-oxo-1,6-dihydropyrimidine and glyoxal (ethanedial or the mono- or diacetal).



2,4,5-triamino-6-oxo-1,6-dihydropyrimidine + glyoxal $\xrightarrow{-\,2\,H_2O}$ pterine

(65.9) Formulate equations to describe the preparations of ***(a)*** adenine and ***(b)*** 6,7-dimethyl-2-aminopteridine.
Chapter **65.2.2**, concerning adenine ***(a)***; Chapter **65.3.2**, concerning 6,7-dimethyl-2-aminopteridine ***(b)***, obtained from 2,4,5-triaminopyrimidine and diacetyl (butanedione); set $R^1 = R^2 = CH_3$ in the second reaction equation.

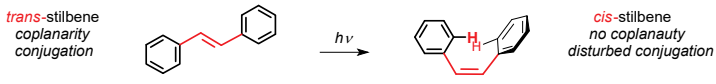
(65.10) Formulate an equation to synthesize the heterocycle of riboflavin (Table 65.3).
Chapter **65.3.2**, last reaction equation

(66.1) Which structural features cause the color of a compound?
Chapter **66.1**

(66.2) List the chromophores in organic compounds giving rise to UV and visible light absorption and classify them with respect to the electronic transitions they may undergo upon excitation.
Chapter **66.1**

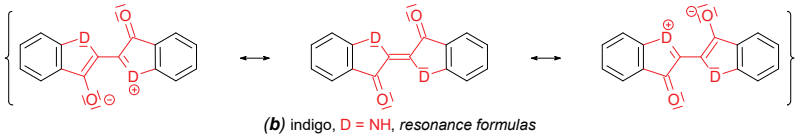
(66.3) Explain why *trans*-stilbene (1,2-diphenylethene) has a longer wavelength UV absorption than the *cis*-isomer.
Chapter **66.1**: As described for azobenzene, steric repulsion of the hydrogen atoms at the *o*-positions of the

phenyl rings in *cis*-stilbene prevents coplanarity required for undisturbed conjugation of all double bonds and the smaller λ_{max} (278 nm instead of 298 nm for *trans*-stilbene) reflects this.

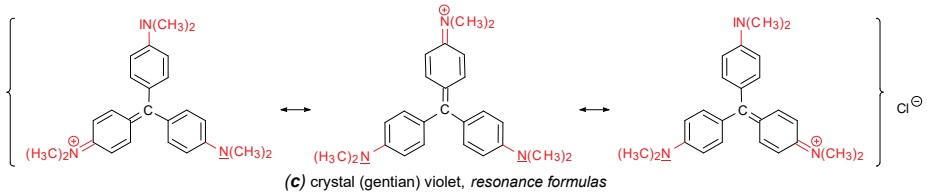


(66.4) What are the structural elements of a dye? Draw the structural formulas of some azobenzene derivatives to explain.
Chapter **66.3.1**

(66.5) Draw resonance formulas of ***(a)*** pinacyanol, ***(b)*** indigo, ***(c)*** crystal violet (= gentian violet), and ***(d)*** phenolphthalein at pH > 8. Classify these dyes.
Chapter **66.3.2**, answering ***(a)***; Chapter **66.3.4**, answering ***(b)*** as follows; Chapter **66.3.3**, answering ***(c)*** as follows and ***(d)***



(b) indigo, D = NH, *resonance formulas*



(c) crystal (gentian) violet, *resonance formulas*

(66.6) How do dyes differ from pigments?
Chapter **66.2**

(67.1) How do you account for the outstanding stability of porphyrins and phthalocyanines?
Chapter **67.1**

(67.2) What is the difference between heme and hemin? How is hemin obtained?
Chapter **67.2.1**

(67.3) What is the difference between porphine and chlorin? Draw formulas.
Chapters **67.2.1**, **67.2.2**

(67.4) Briefly outline the biological function of ***(a)*** heme and ***(b)*** chlorophyll.
Chapters **67.2.1**, **67.2.2**

(68.1) How do you account for the high melting points of amino acids?
Chapter **68.1**

(68.2) What are essential amino acids and which ones do you know?
Chapter **68.1**, Table 68.1

(68.3) Specify the absolute configuration of ***(a)*** L-serine and ***(b)*** L-cysteine following the CIP convention.
Chapter **68.1**, Table 68.1: ***(a)*** L-serine = *(S)*-serine, but ***(b)*** L-cysteine = *(R)*-cysteine (S-atom > O-atoms)

(68.4) Write equations to suggest a synthesis of racemic phenylalanine from a derivative of diethyl malonate.
Chapter **68.2**, first reaction equation: set R = C_6H_5–CH_2 and X = Br for benzyl bromide.

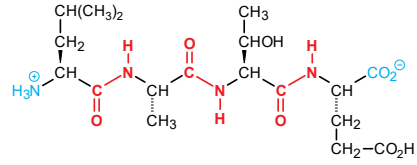
(68.5) Write equations to suggest a synthesis of *(R)*-phenylalanine from benzyl bromide (α-bromotoluene).
Chapter **68.2**, second reaction equation: set R = C_6H_5–CH_2 , X = Br and start with the dioxopiperazine of L-valine.

(69.1) The C–N bond in amides and peptides is shorter (132.5 pm) than in amines (148.7 pm). Why?
Chapter **69.1**

(69.2) What is an α-helix? Explain the terms primary, secondary, tertiary, and quaternary structure of a protein.
Chapter **69.3**, Fig. 69.2

(69.3) Look at Table 68.1 to draw the structural formula of the peptide with the sequence LATE.
The sequence LATE abbreviates the following (primary) structure:

LATE = Leu-Ala-Thr-Glu



(69.4) Which protective groups are used for ***(a)*** amino and ***(b)*** carboxy functions? Outline their introduction and removal.
Chapter **69.4.1**, answering ***(a)*** and ***(b)***

(69.5) Formulate the reaction of a Boc-amino acid with an amino acid ester. Explain the purpose of ester activation.
Chapter **69.4.2**

(69.6) Write the equations for all steps necessary to synthesize the dipeptide Phe-Leu (FL).
Chapter **69.4.3**, Fig. 69.3: Set phenylalanine for *N*-terminal, leucine for C-terminal amino acid.
Find formulas of the amino acids in Table 68.1.

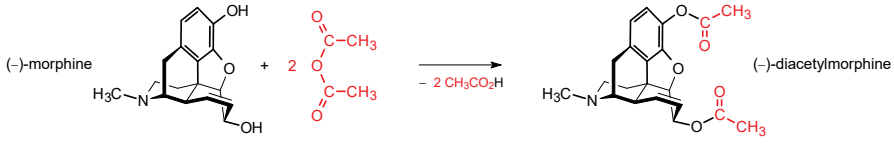
(70.1) What are alkaloids and which biological functions do they perform?
Chapter **70.1**

(70.2) Which amino acids are alkaloid precursors and which alkaloid classes are derived from them?
Chapter **70.1**, Table 70.1

(70.3) Draw the structural formulas of ***(a)*** (–)-cocaine, ***(b)*** (–)-nicotine, and ***(c)*** (+)-LSD. Classify these alkaloids.
Chapter **70.2**, Table 70.2, answering ***(a)***, ***(b)*** and ***(c)***

(70.4) Which alkaloid subunit do you recognize in the illegal drugs "speed" and "ecstasy"?
Chapter **70.2**, last section, the phenylethylamine alkaloids and "drugs"

(70.5) Formulate the reaction of (–)-morphine with acetic anhydride.
Acetylation of morphine with acetic anhydride produces diacetylmorphine, known as heroin.

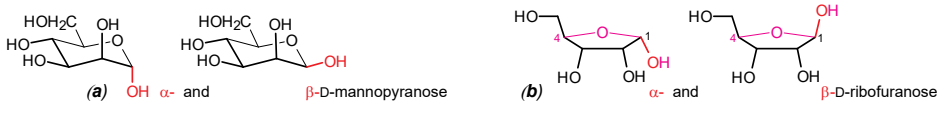


(70.6) Count the number of stereogenic centers in morphine. How many stereoisomers are possible? Look at Chapter **46.1**.
Five carbon atoms and the nitrogen atom in morphine are stereogenic centers. Thus, $2^6 = 64$ stereoisomers are possible, comprising 32 diastereomers which are pairs of enantiomers.

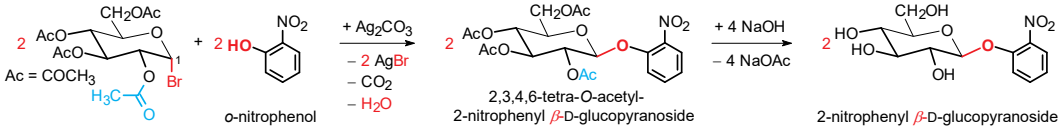
(71.1) Which compound is named (+)-(2*R*,3*S*,4*R*,5*R*)-2,3,4,5,6-pentahydroxyhexanal? How many stereoisomers exist?
Chapter **71.1**

(71.2) Write FISCHER projections of all ***(a)*** aldohexoses, ***(b)*** aldopentoses, and ***(c)*** hexuloses, all with the D configuration.
Chapter **71.1**, **71.2**, answering ***(a)*** and ***(b)*** in Fig. 71.1, answering ***(c)*** in Fig. 71.2

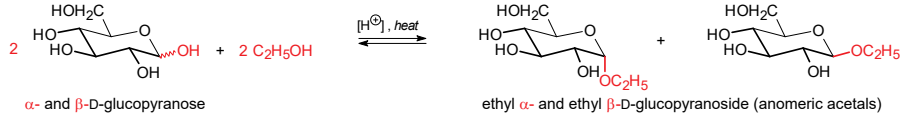
(71.3) Draw the formulas of ***(a)*** α- and β-D-mannopyranose and ***(b)*** α- and β-D-ribofuranose. Define the term mutarotation.
Chapters **71.3**, **71.4** (mutarotation)
(a) α- and β-D-mannopyranose and ***(b)*** α- and β-D-ribofuranose (Chapter **71.3**) can be clearly depicted by means of their skeletal formulas.



(71.4) What is a glucoside? Draw the structural formula of 2-nitrophenyl *β*-D-glucopyranoside and design a synthesis.
Chapter **71.5.1**, analogous reaction: Glycosidation of *o*-nitrophenol (2-nitrophenol) with acetobromo-α-D-glucose produces 2-nitrophenyl β-D-glucopyranoside (KÖNIGS-KNORR glycosidation). *SN2*: dictates inversion of configuration at C-1 (β glycosidation because of stereospecificity). *SN1*: The O-acetyl group at C-2 shields the α position of the intermediate carbenium ion from nucleophilic attack (β glyosidation because of stereoselectivity).



(71.5) D-Glucose is exposed to ethanol containing some anhydrous hydrogen chloride. What products are formed?
Chapter **71.5.1**, analogous reaction: Glycosidation of D-glucose with ethanol and anhydrous hydrogen chloride is expected to produce a mixture of ethyl α- and ethyl β-D-glucopyranoside (FISCHER glycosidation).



(71.6) What products are obtained from glucose by *(**a**)* reduction and *(**b**)* oxidation?
Chapter **71.5.3**

(72.1) What compound is named *β*-D-fructofuranosyl-*α*-D-glucopyranoside? Draw the structural formula.
Chapter **72.1**, Fig. 72.1

(72.2) What is the difference between maltose and cellobiose? Draw the structural formulas to explain.
Chapter **72.1**, Fig. 72.1

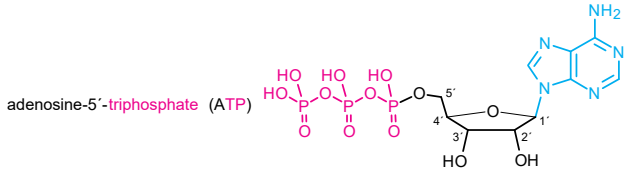
(72.3) What is the difference between maltose and trehalose? Suggest a test tube reaction to identify one of them.
Chapter **72.1**, Fig. 72.1

(72.4) What products are obtained by enzymatic degradation (hydrolysis) of starch?
Chapter **72.1**, last section

(72.5) Draw the structures of *(**a**)* amylose, *(**b**)* cellulose, and *(**c**)* chitin. What are the sources of these polysaccharides?
Chapter **72.2**, answering ***(a)***, ***(b)*** and ***(c)***

(73.1) Disconnect a nucleic acid stepwise *via* larger fragments to the monomeric components. Formulate and name them.
Chapter **73.1**

(73.2) Adenosine 5´-triphosphate (ATP) is an energy source, phosphorylation reagent, and coenzyme in biosyntheses. Draw the structural formula and classify this compound.
Chapter **73.1**, Fig. 73.1: Adenosine-5´-triphosphate (ATP) is a mononucleotide.



(73.3) Draw the DNA sequence ACGT in detail and abbreviated.
Chapter **73.1**, Fig. 73.1: Exchange thymine (T) and guanine (G).

(73.4) What are base pairs and how are they held together?
Chapter **73.2**, Fig. 73.2

(73.5) An open-chain DNA strand would have a length of about 2 m. In fact, the length is in the nm range. Why?
Chapter **72.2**, last section

(74.1) *(**a**)* Explain the term lipid. *(**b**)* What are fats and which kinds of other lipids do you know? *(**c**)* What are RMEs?
Chapter **74.1**, Table 74.1, answering *(**a**)* and *(**b**)*; Chapter **74.2.2**, answering *(**c**)*

(74.2) Which compound is described by the abbreviation $C_{18:2(9c,12c)}$? Draw the formula. What is an *ω6* fatty acid?
Chapter **74.2.1**, Table 74.2: linoleic acid, 18 C atoms, 2 double bonds, 9-*cis*-, 12-*cis*-, ω6

(74.3) Suggest a test tube reaction to distinguish a saturated from an unsaturated fatty acid. Look at Chapter **16.2**.
Unsaturated fatty acids decolorize a solution of bromine (addition of Br_2 to CC double bonds, Chapter **16.2**).

(74.4) What is the difference between a fat and a wax? How are soaps related to fats and how does a soap clean?
Chapters **74,2.1**, **74.2.2**

(75.1) Polyketide is a misleading term. Why? Explain your reasoning by briefly formulating the polyketide pathway.
Chapter **75**, introducing section and Chapter **75.1**

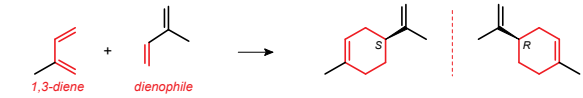
(75.2) Explain the biogenetic relationship of polyketides and fatty acids.
Chapter **75.1**

(75.3) What is the smallest polyketide? Which biologically active tetraketides do you know?
Chapter **75.2**, first section, Table 75.1

(75.4) How are the benzenoid rings of naturally occurring aromatic compounds and quinones formed?
Chapter **75.2**, Table 75.1

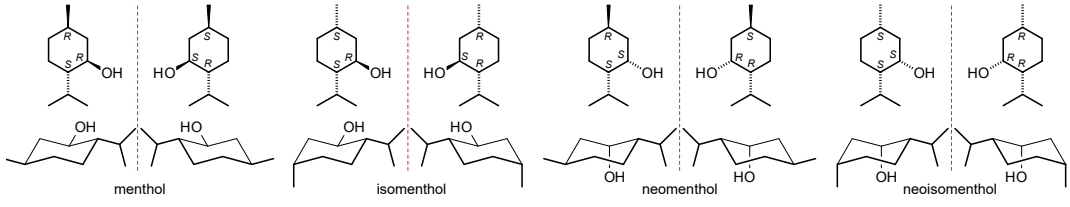
(76.1) What is a terpenoid structure? Which classes of terpenes do you know?
Chapter **76.1**, Table 76.1

(76.2) Suggest a synthesis of limonene (Chapter **21.4**). Specify which stereoisomers are formed.
Chapters **21.4**, **76.3.1**: [4+2]-Cycloaddition (DIELS-ALDER reaction) of isoprene (2-methyl-1,3-butadiene) produces the racemate *(R,S)*-limonene.



isoprene (2-methyl-1,3-butadiene) *(R,S)*-limonene (racemate)

(76.3) How many diastereomers and enantiomers of menthol exist? Draw the structures and specify configurations.
Chapter **76.3.1**: Three C atoms of menthol are stereogenic centers. Thus, $2^3 = 8$ stereoisomers exist, comprising four diastereomers which are pairs of enantiomers. Diastereomers are referred to as isomenthol, neomenthol and neoisomenthol.



(76.4) What is squalene? How is it related to tetracyclic triterpenes and to steroids? Try to formulate.
Chapter **76.3.4**

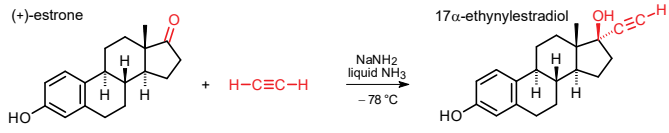
(76.5) What is a carotenoid? What causes the color of carotenoids? Look again at Chapter **66.1**.
Chapters **76.3.5**, **66.1**

(77.1) (Almost) all steroids possess a hydroxy or carbonyl function at position 3. Why?
Chapter **76.3.4**: 2,3-Epoxysqualene is the biogenetic precursor of tetracyclic triterpenes and steroids with the gonane skeleton; it introduces the hydroxy function at position 3 of the steroids.

(77.2) Briefly formulate the genesis of cholesterol in mammals.
Chapter **77.2**

(77.3) Which steroid hormones do you know and what are their biological functions?
Chapter **77.4**

(77.4) Look at Chapter **49.3.1** to suggest a partial synthesis of 17α-ethynylestradiol, a component of contraceptives.
Alkynylation of estrone with ethyne (acetylene) and sodium amide as a base in liquid ammonia (Chapter **49.3.1**) produces 17α-ethynylestradiol. Spacefilling of the methyl group at C-18 shields the β position from nucleophilic addition.



(78.1) Explain *(**a**)* chemoselectivity, *(**b**)* regioselectivity, *(**c**)* stereoselectivity, and *(**d**)* stereospecificity. Provide examples.
Chapter **78.1**, answering *(**a**)*; Chapter **78.2**, answering *(**b**)*; Chapter **78.3**, answering *(**c**)*; Chapter **78.4**, answering *(**d**)*

(78.2) 2-Pentanone and allyl bromide yield 1-octen-5-one when reacted with LDA. Formulate and characterize this reaction.
Chapter **78.2**

(78.3) Formulate examples for the *(**a**)* regioselectivity, *(**b**)* stereoselectivity, and *(**c**)* stereospecificity of [4+2]-cycloadditions.
Chapter **78.2**, answering *(**a**)*; Chapter **78.3**, answering *(**b**)*; Chapter **78.4**, answering *(**c**)*

(78.4) (*S*)-2-Bromobutane yields (*R*)-2-butanol when reacted with hydroxide. Formulate and characterize this reaction.
Chapters **31.1**, **44.4** and **78.4**

(79.1) Explain the term prochirality at a tetrahedral and a trigonal carbon atom.
Chapters **79.1**, **79.2**

(79.2) Draw the tetrahedral projection formula of the methylene C of ethanol and assign the enantiotopic H atoms.
Chapter **79.1**

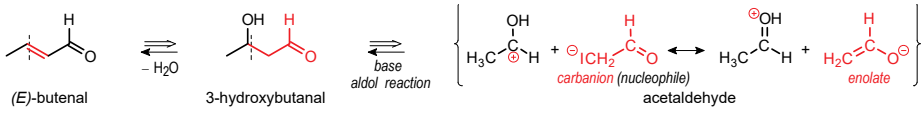
(79.3) Formulate a reaction which converts enantiotopic groups into diastereotopic ones.
Chapter **79.1**, last section

(79.4) Chirogenic reactions produce racemic mixtures under usual conditions. Why? Formulate examples.
Chapters **79.1**, **79.2**

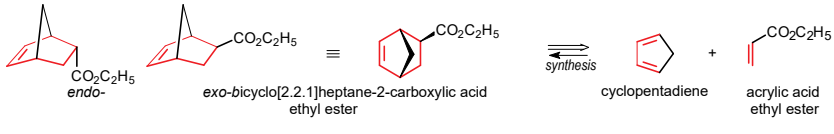
(79.5) Formulate examples of enantioselective catalytic hydrogenations.
Chapter **79.3**

Design syntheses of the following target compounds:

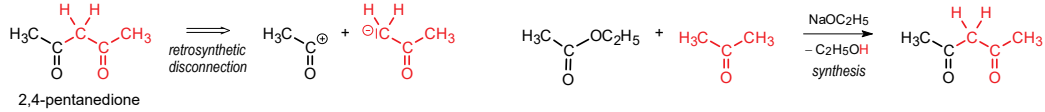
(80.1) *(**a**)* (*E*)-Butenal and *(**b**)* (*E*)-2-ethyl-2-hexenal;
Chapter **80.3.1**, answering *(**b**)*
(a) In analogy to *(**b**)*, retrosynthetic disconnection of (*E*)-butenal *via* racemic aldol 3-hydroxybutanal exposes aetaldehyde as the starting compound, exemplified in Chapter **80.2**.



(80.2) *(**a**)* 1-methylcyclohexene-4-carboxylic acid methyl ester and *(**b**)* bicyclo[2.2.1]heptane-2-carboxylic acid ethyl ester;
Chapter **80.2**, Table 80.2: 1-Methylcyclohexene-4-carboxylic acid methyl ester *(**a**)* arises from a [4+2]-cycloaddition of methyl acrylate to 2-methyl-1,3-butadiene (isoprene) as exemplified. *(**b**)* Bicyclo[2.2.2]heptane-2-carboxylic acid ethyl ester (*endo*- or *exo*-) is produced by [4+2]-cycloaddition of ethyl acrylate (dienophile) to cyclopentadiene (1,3-diene):



(80.3) *(**a**)* ethyl 2,4-dioxoheptanoate, *(**b**)* 2,4-pentanedione, and *(**c**)* 2-(4-isobutylphenyl)propanoic acid;
Chapter **80.3.2**, answering *(**a**)*; Chapter **80.3.3**, answering *(**c**)*
Retrosynthetic disconnection of 2,4-pentandione *(**b**)* to the acetyl cation (from ethyl acetate) and the acetylmethyl carbanion (from acetone) explains the synthesis of the target by CLAISEN condensation of ethyl acetate and acetone as outlined in Chapter **50.2.2**.



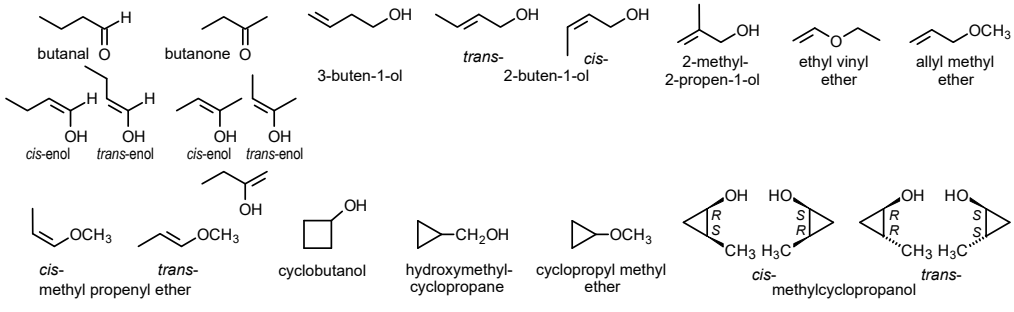
2,4-pentanedione

(80.4) Δ^9-tetrahydrocannabinol from (*R*)-*p*-mentha-2,8-dien-1-ol.
Chapter **80.3.4**

(81.1) How many double bond equivalents hide behind the molecular formulas *(**a**)* C_5H_5N, *(**b**)* $C_6H_{12}O_6$, and *(**c**)* $C_6H_7NO_2$?
Chapter **81.1**: The numbers of double bond equivalents are *(**a**)* 4, *(**b**)* 1 and *(**c**)* 4.

(81.2) Give examples of *(**a**)* all kinds of skeletal isomers and *(**b**)* all kinds of stereoisomers.
Chapter **81.2**, answering *(**a**)*; Chapters **81.4**, **81.5**, answering *(**b**)*

(81.3) Which *(**a**)* skeletal isomers and *(**b**)* stereoisomers exist for C_4H_8O? Draw and classify all of them.
*(**a**)* 22 skeletal and configurational isomers with the molecular formula C_4H_8O exist, also comprising three enol tautomers of butanal (one, *cis*- and *trans*-) and butanone (two, one *cis*- and *trans*-); *(**b**) cis*- and *trans*-isomers exist for 2-buten-1-ol, methyl propenyl ether and methylcyclopropanol (different *relative* configuration); *cis*- and *trans*-methylcyclopropanol are diastereomers, and each one of those is a pair of enantiomers (with different *absolute* configurations).



(81.4) What significance does the absolute configuration have in biochemical processes? Give examples.
Chapter **81.5**

(82.1) The molecular formula of a compound can be determined by mass spectrometry. Explain how.
Chapter **82.2**, second and third section

(82.2) Explain how you recognize a nitrogen compound with an odd number of nitrogen atoms in a molecule.
Chapter **82.2**, last section

(82.3) Formulate *(**a**)* the generation of the molecular ion, *(**b**)* an α fragmentation, and *(**c**)* a benzyl fragmentation.
Chapters **82.2**, **82.3**, answering *(**a**)*; Chapter **82.3**, answering *(**b**)* and *(**c**)*

(82.4) Comprehend the elucidation of the skeletal structure from Fig. 82.1. Which structural aspect remains unresolved?
Chapter **82.3**: The *absolute* configuration of amphetamine (racemate, pure enantiomer, enantiomeric excess) cannot be decoded by mass spectrometry and other methods of molecular spectroscopy (in non-chiral environment). Specific rotation and other chiroptic methods (Chapter **44.2**) are appropriate methods to solve this problem.

(83.1) Which molecular vibrations do you know and what property is required for them to be IR-active?
Chapter **83.2**

(83.2) IR absorptions of alkynes ($\nu_{C\equiv C}$ 2200 cm^{-1}) are very weak; those of nitriles ($\nu_{C\equiv N}$ 2250 cm^{-1}) are very strong. Why?
Chapter **83.2**: Nitrile groups display much more intense IR absorption bands because the polar CN triple bonds are *vibrating dipoles* in contrast to the unpolar CC triple bonds of alkynes.

(83.3) Which IR absorption bands can be used to identify a primary amino group?
Chapter **83.3**, first section

(83.4) Which IR absorption bands characterize a carboxylic acid ester?
Chapter **83.3**, Fig. 83.4, last section

(84.1) Measure the integral steps (mm) in Figs. 84.2, 84.3, and 84.6 and evaluate the results.
Chapter **84.3**, Fig. 84.2

(84.2) Try to predict the proton NMR spectra of 2- and 3-pentanone. All coupling constants are 7 Hz (why?).
Chapters **84.4.1**, **84.4.2**, Figs. 84.4, 84.5
2-Pentanone displays four signals: one intense singlet for the protons of the methyl group attached to the carbonyl function; one triplet for the protons of CH_2 attached to carbonyl (X_2), one sextet (n = 5 coupling protons so that n+1 = 6) for the protons of the central CH_2 group (M_2) and one triplet for the protons of the terminal CH_3 group (A_3) belong to the *n*-propyl group (CH_3–CH_2–CH_2–, an $A_3M_2X_2$ spin system, ratio of integral steps: 3:2:2). Because of molecular symmetry, 3-pentanone displays only two signals for two chemically equivalent ethyl groups, comprising one triplet for the methyl protons and one quartet for the methylene groups of ethyl (CH_3–CH_2–, A_3X_2 spin system, ratio of intergral step heights: 3:2). Look at Chapter **84.4.2** and Fig. 84.5 to explain the averaged coupling constant (7 Hz) of chemically non-equivalent alkyl protons.

(84.3) Specify the spin systems in Figs. 84.3 and 84.6. Assign all coupling constants.
Chapters **84.4.1**, **84.4.2**: *AMX* spin systems characterize vinyl in acrylic acid ethyl ester (Fig. 84.3) and ethynyl attached to ethenyl in 1-methoxy-1-buten-3-yne (Fig. 84.6)

(84.4) Which kind of NMR data reflects the relative configuration? Provide some examples.
Chapters **84.4.2**, **85.3** including examples

(85.1) Homonuclear $^{13}C^{13}C$ couplings are usually not observed in ^{13}C NMR spectra. Why?
Chapter **85.1**

(85.2) How do aldehydes and ketones differ in carbon-13 NMR spectroscopy?
Chapters **85.2**, **85.3**: Unlike ketones ($R_2C{=}O$), aldehydes display a doublet splitting of the ^{13}C signal (R–CH=O) in the ^{13}C NMR spectrum with coupling constant $J_{CH} \approx 190$ Hz due to their CH bonds.

(85.3) How do ethyl, ethenyl and ethynyl groups differ with respect to ***(a)*** ^{13}C chemical shifts and ***(b)*** C*H* couplings?
Chapter **85.2**, Fig. 85.1, answering ***(a)***: ^{13}C chemical shifts increase in the order ethyl < ethynyl < ethenyl;
Chapter **85.3**, answering ***(b)***: CH coupling constants of ethyl: $J_{CH} \approx 125$ Hz, ethenyl: $J_{CH} \approx 165$ Hz and ethynyl: $J_{CH} \approx 250$ Hz follow the rule $J_{CH} = 500\ s$, where $s = 0.25$, 0.33 and 0.5 for sp^3, sp^2 and sp hybridized C atoms, respectively.

(85.4) Summate all C, C*H*, CH_2, and CH_3 in Fig. 85.2. Why is the result different to the molecular formula?
Chapter **85.3**, last section

(86.1) Briefly describe the concept of two-dimensional shift correlations and their use in molecular structure elucidation.
Chapter **86**, introduction

(86.2) Evaluate the HH COSY plot in Fig. 86.1 including the integral steps (on top) to decode the skeletal structure.
Chapter **86.1.1**, Fig. 86.1

(86.3) Evaluate the CC shift correlations in Fig. 86.2 in order to establish the carbocyclic molecular structure.
Chapter **86.1.2**, Fig. 86.2

(86.4) Assign all C*H* bonds of the sample molecule in Fig. 86.3. One proton does not give a cross signal. Why?
Chapter **86.2**, Fig. 86.3