

**16<sup>th</sup>**



**International Chemistry Olympiad**

**8 theoretical problems  
2 practical problems**

# THE SIXTEENTH INTERNATIONAL CHEMISTRY OLYMPIAD

FRANKFURT AM MAIN 1984  
GERMAN FEDERAL REPUBLIC

## THEORETICAL PROBLEMS

### PROBLEM 1

A)

The element carbon consists of the stable isotopes  $^{12}\text{C}$  (98.90 percent of atoms) and  $^{13}\text{C}$  (1.10 percent of atoms). In addition, carbon contains a small fraction of the radioisotope  $^{14}\text{C}$  ( $t_{1/2} = 5730$  years), which is continuously formed in the atmosphere by cosmic rays as  $\text{CO}_2$ .  $^{14}\text{C}$  mixes with the isotopes  $^{12}\text{C}$  and  $^{13}\text{C}$  via the natural  $\text{CO}_2$  cycle.

The decay rate of  $^{14}\text{C}$  is described by ( $N$  = number of  $^{14}\text{C}$  atoms;  $t$  = time;  $\lambda$  = decay constant):

$$\text{decay rate} = -\frac{dN}{dt} = \lambda N \quad (1)$$

Integration of (1) leads to the well-known rate law (2) for the radioactive decay:

$$N = N_0 e^{-\lambda t} \quad (2)$$

$N_0$  = number of  $^{14}\text{C}$  atoms at  $t = 0$

- What is the mathematical relationship between the parameters  $\alpha$  and  $t_{1/2}$  (= half life)?
- The decay rate of carbon, which is a part of the natural  $\text{CO}_2$  cycle, is found to be 13.6 disintegrations per minute and gram of carbon. When a plant (e. g. a tree) dies, it no longer takes part in the  $\text{CO}_2$  cycle. As a consequence, the decay rate of carbon decreases.

In 1983, a decay rate of 12.0 disintegrations per minute and gram of carbon was measured for a piece of wood which belongs to a ship of the Vikings. In which year was cut the tree from which this piece of wood originated?

- Assume that the error of the decay rate of 12.0 disintegrations per minute and gram of carbon is 0.2 disintegrations per minute and gram of carbon. What is the corresponding error in the age of the wood in question b)?

- d) What is the isotope  $^{12}\text{C}/^{14}\text{C}$  ratio of carbon, which takes part in the natural  $\text{CO}_2$  cycle (1 year = 365 days)?

B)

The elements strontium and rubidium have the following isotope composition:

Strontium: 0.56 %  $^{84}\text{Sr}$  ; 9.86 %  $^{86}\text{Sr}$  ; 7.00 %  $^{87}\text{Sr}$  ; 82.58 %  $^{88}\text{Sr}$  (these isotopes are all stable).

Rubidium: 72.17 %  $^{85}\text{Rb}$  (stable) ; 27.83 %  $^{87}\text{Rb}$  (radioactive;  $t_{1/2} = 4.7 \times 10^{10}$  years).

The radioactive decay of  $^{87}\text{Rb}$  leads to  $^{87}\text{Sr}$ .

In Greenland one finds a gneiss (= silicate mineral) containing both strontium and rubidium.

- What is the equation rate law describing the formation of  $^{87}\text{Sr}$  from  $^{87}\text{Rb}$  as a function of time?
- Assume that the isotope ratio  $^{87}\text{Sr}/^{86}\text{Sr}$  (as determined by mass spectrometry) and the isotope ratio  $^{87}\text{Rb} : ^{86}\text{Sr}$  are known for the gneiss. What is the mathematical relationship with which one can calculate the age of the gneiss?

## SOLUTION

A)

- The relationship is:

$$\alpha = \frac{\ln 2}{t_{1/2}}$$

b)

$$t = \frac{t_{1/2}}{\ln 2} \times \ln \left( \frac{N_0}{N} \right) = \frac{5730}{0.6930} \times \ln \left( \frac{13.6}{12.0} \right) = 1035 \text{ years}$$

- For  $N_0/N = 13.6/12.0$      $t = 1035$  years

$$\text{For } N_0/N = 13.6/12.2 \quad t = 898 \text{ years}$$

$$\text{For } N_0/N = 13.6/11.8 \quad t = 1174 \text{ years}$$

Thus, the tree was cut 1035 (+ 139/−137) years ago.

d)

$$N = \frac{13.6 \times t_{1/2}}{\ln 2} = 5.91 \times 10^{10} \text{ atoms } ^{14}\text{C} / \text{g carbon}$$

$$1 \text{ g} \approx 0.989 \text{ g } ^{12}\text{C}; \quad 0.989 \text{ g } ^{12}\text{C} \approx (0.989/12) \times 6.023 \times 10^{23} \text{ atoms } ^{12}\text{C}$$

$$^{12}\text{C} / ^{14}\text{C} = \frac{0.989 \times 6.023 \times 10^{23}}{12 \times 5.91 \times 10^{10}} = 8.40 \times 10^{11} : 1$$

**B)**

a) Equation (2) describes the decay of the  $^{87}\text{Rb}$ :

$$^{87}\text{Rb} = ^{87}\text{Rb}_0 \cdot \exp(-\lambda t)$$

The symbol  $^{87}\text{Rb}$  stands for the number of atoms of this nuclide.

Consequently, one obtains for the formation of  $^{87}\text{Sr}$  from  $^{87}\text{Rb}$ :

$$^{87}\text{Sr} = ^{87}\text{Rb}_0 - ^{87}\text{Rb} = ^{87}\text{Rb} \cdot \exp(\lambda t) - ^{87}\text{Rb} \quad (\text{a})$$

b) The formation of the radiogenic  $^{87}\text{Sr}$  follows equation (a).

One has to take into account that at time  $t = 0$ , when the mineral was formed, there was some non-radiogenic strontium in it already:

$$^{87}\text{Sr} = (^{87}\text{Sr})_0 + ^{87}\text{Rb} \cdot [\exp(\lambda t) - 1]$$

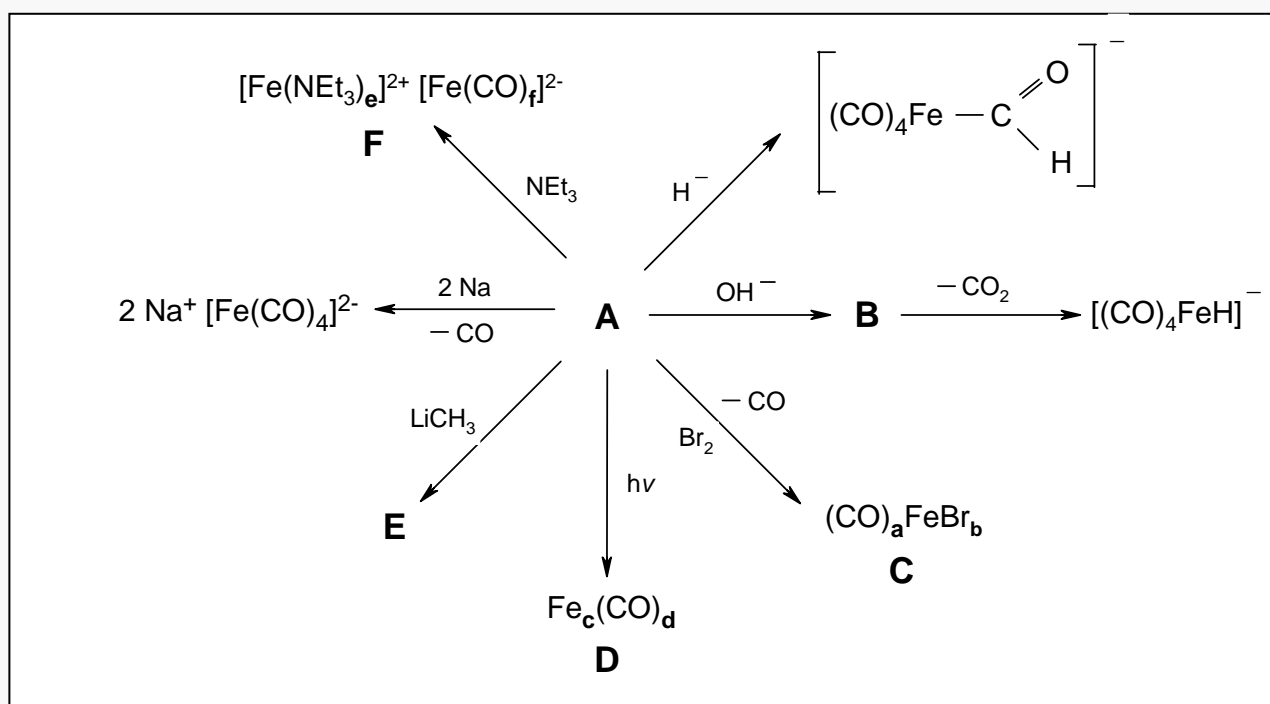
The isotope ratio  $(^{87}\text{Sr} / ^{86}\text{Sr})_0$  follows from the isotope composition of strontium. The time  $t$  in this equation corresponds to the age of the gneiss.

## PROBLEM 2

Ludwig Mond discovered before the turn of this century that finely divided nickel reacts with carbon monoxide forming tetracarbonylnickel,  $\text{Ni(CO)}_4$ , a colourless, very volatile liquid. The composition of  $\text{Ni(CO)}_4$  provides an example of the noble gas rule ("EAN rule").

Problems:

- Use the eighteen-electron rule (noble gas rule) to predict the formula of the binary carbonyls of  $\text{Fe(0)}$  and  $\text{Cr(0)}$ .
- What composition would the eighteen-electron rule predict for the most simple binary chromium(0)-nitrosyl compound?
- Explain why  $\text{Mn(0)}$  and  $\text{Co(0)}$  do not form so-called mononuclear carbonyl complexes of the type  $\text{M(CO)}_x$  ( $\text{M} = \text{metal}$ ), but rather compounds with metal-metal bonding.
- Suggest structures of  $\text{Ni(CO)}_4$ ,  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{Co}_2(\text{CO})_8$ .
- State whether  $\text{V(CO)}_6$  and the compounds mentioned in a) and d) are diamagnetic or paramagnetic.
- Why are the carbon monoxide ligands bound to metals much more strongly than to boron in borane adducts (e.g.  $\text{R}_3\text{B-CO}$ ;  $\text{R} = \text{alkyl}$ )?
- Determine the composition of the compounds labeled **A** - **F** in the following reaction scheme:



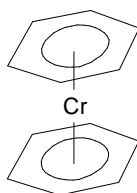
Hints:

- a) **C** has the following analysis: C, 14.75 % ; Br, 48.90 % .
- b) **D** contains 30.70 % Fe; the molecular mass is 363.8 a.m.u.
- c) Excess triethylamine is used for the synthesis of **F**. **F** contains 5.782 % C and 10.11 % N.
- h) Why is the compound **F** formed in the disproportional reaction (given in g)), and not the compositional isomer  $[\text{Fe}(\text{CO})_f]^{2+}[\text{Fe}(\text{NEt}_3)_e]^{2-}$  ?
- i) The eighteen-electron rule is also satisfied by a compound prepared from elementary chromium and benzene.
  - i1) Draw the formula of this complex.
  - i2) Which complex with the analogous structure is prepared by the reaction of iron powder with cyclopentadiene? Write the chemical equation for its formation.

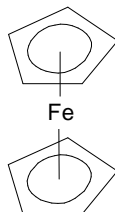
### SOLUTION

- a)  $\text{Fe}(\text{CO})_5$ ,  $\text{Cr}(\text{CO})_6$
- b)  $\text{Cr}(\text{NO})_4$
- c) Explanation: the odd number of electrons in the  $\text{Mn}(\text{CO})_5$  and  $\text{Co}(\text{CO})_4$  fragments.
- d)  $\text{Ni}(\text{CO})_4$ : tetrahedral geometry  
 $\text{Mn}_2(\text{CO})_{10}$ : - octahedral  $\text{Mn}(\text{CO})_5$ -structure having a Mn-Mn bond,  
 - relative orientation (conformation) of the carbonyl groups.  
 $\text{Co}_2(\text{CO})_{10}$ : CO-bridges and Co-Co bond
- e)  $\text{Fe}(\text{CO})_5$ ,  $\text{Cr}(\text{CO})_6$ ,  $\text{Ni}(\text{CO})_4$ ,  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Co}_2(\text{CO})_{10}$  are diamagnetic,  
 $\text{V}(\text{CO})_6$  is paramagnetic.
- f) Explanation using the so-called "back-bonding concept"
- g) **A** =  $[\text{Fe}(\text{CO})_5]$                       **B** =  $[\text{HOCFe}(\text{CO})_4]$                       **C** =  $[\text{FeBr}_2(\text{CO})_4]$   
**D** =  $[\text{Fe}_2(\text{CO})_9]$                       **E** =  $[(\text{CO})_4\text{Fe}=\text{C}(\text{OLi})\text{CH}_3]$                       **F** =  $[\text{Fe}(\text{NEt}_3)_6] [\text{Fe}(\text{CO})_4]$
- h) This observation is due to differing back bonding capability of  $\text{NEt}_3$  and CO.

i1) Structural formula of dibenzenechromium



i2) Structural formula of ferrocene.



### PROBLEM 3

A weak acid of total concentration  $2 \times 10^{-2} \text{ M}$  is dissolved in a buffer of  $\text{pH} = 8.8$ . The anion  $\text{A}^-$  of this acid is coloured and has a molar decadic absorption coefficient  $\varepsilon$  of  $2.1 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$ . A layer  $l$  of the solution with 1.0 cm thickness absorbs 60 percent of the incident luminous intensity  $I_0$ .

- What is the equation relating the extinction to the thickness of the absorbing layer?
- How large is the concentration of the acid anion in the buffer solution?
- How large is the  $\text{p}K_a$  of the acid?

### SOLUTION

- a) The Lambert-Beer law e.g.:

$$\log(I_0/I) = A = \varepsilon \cdot c \cdot l$$

- b)  $\log[(100-60)/100] = -2.1 \times 10^4 \times [\text{A}^-] \times 1$

$$[\text{A}^-] = 1.895 \times 10^{-5} \text{ mol cm}^{-3} = 1.895 \times 10^{-2} \text{ mol dm}^{-3}$$

- c) According to the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]_{\text{eq}}}{[\text{HA}]_{\text{eq}}}$$

and with the total concentration

$$[\text{HA}]_{\text{tot}} = [\text{HA}]_{\text{eq}} + [\text{A}^-]_{\text{eq}} = 2 \times 10^{-2} \text{ mol dm}^{-3}$$

$$8.8 = \text{p}K_a + \log \frac{1.895 \times 10^{-2}}{2 \times 10^{-2} - 1.895 \times 10^{-2}}$$

$$\text{p}K_a = 7.5$$



### PROBLEM 4

15 cm<sup>3</sup> of a gaseous hydrocarbon C<sub>x</sub>H<sub>y</sub> are mixed with 120 cm<sup>3</sup> oxygen and ignited. After the reaction the burned gases are shaken with concentrated aqueous KOH solution. A part of the gases is completely absorbed while 67.5 cm<sup>3</sup> gases remain. It has the same temperature and pressure as the original unburned mixture.

- What is the composition of the remaining gas? Explain.
- How large is the change in the amount of substance per mole of a hydrocarbon C<sub>x</sub>H<sub>y</sub> when this is burned completely?
- What is the chemical formula of the hydrocarbon used for the experiment?  
Give the steps of the calculation.

### SOLUTION

- The remaining gas is oxygen since the burning products CO<sub>2</sub> and H<sub>2</sub>O are completely absorbed in concentrated KOH solution.
- The general stoichiometric equation for complete combustion of a hydrocarbon C<sub>x</sub>H<sub>y</sub> is as follows:  
$$\text{C}_x\text{H}_y + (x + y/4) \text{O}_2 \rightarrow x \text{CO}_2 + (y/2) \text{H}_2\text{O}$$

The change in amount of substance per mole of hydrocarbon is

$$[x + (y/2) - (1 + x + y/4)] \text{ mol} = [(y/4) - 1] \text{ mol}$$
- The equation of chemical conversion at the experimental condition is as follows:  
$$15 \text{C}_x\text{H}_y + 120 \text{O}_2 \rightarrow 15x \text{CO}_2 + (15/2)y \text{H}_2\text{O} + [(120 - 15x - (15/4)y) \text{O}_2]$$

For the residual oxygen:

$$(1) \quad 120 - 15x - (15/4)y = 67.5$$

and for the total balance of amount of substance:

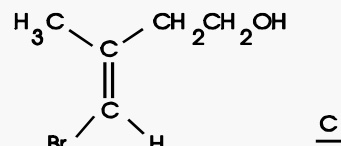
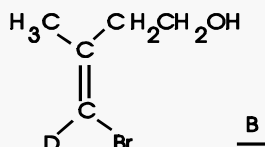
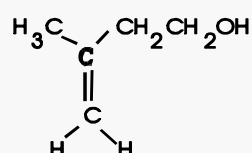
$$(2) \quad 15x + (15/2)y + 67.5 = 15 + 120 + 15[(y/4) - 1]$$

From equation (1) and (2) follows:  $x = 2$  and  $y = 6$ .

The hydrocarbon in question is ethane.

## PROBLEM 5

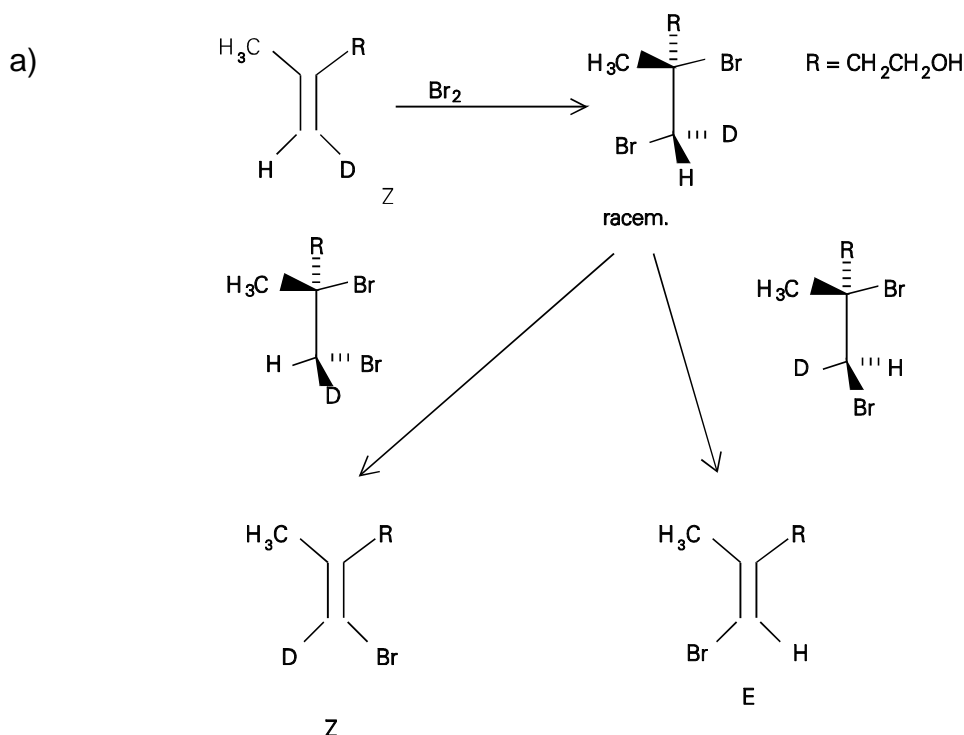
One of the diastereotopic methylene protons at the double bond of **A** was selectively substituted by deuterium. Bromination and subsequent dehydrobromation yields the



deuteriated product **B** and the non-deuteriated product **C**.

- Which configuration follows for the monodeuteriated **A** from the given reaction products?
- The solution of this question requires the formulation of the reaction and a short argumentation why only **B** and **C** are formed.

## SOLUTION



- b) The addition of bromine occurs trans (antarafacial). The elimination of HBr via an E2 mechanism also requires an anti-periplanar (= trans) arrangement of H and Br. The products given in this problem are only formed from a Z-configured adduct.

The bromination of **A** and subsequent dehydrobromination yield both E,Z isomeric bromoolefins that have to be separated. Substitution of the bromine by deuterium in the Z-isomer proceeds by treatment with a metal (best: Na/t-BuOD) under retention to **A**.

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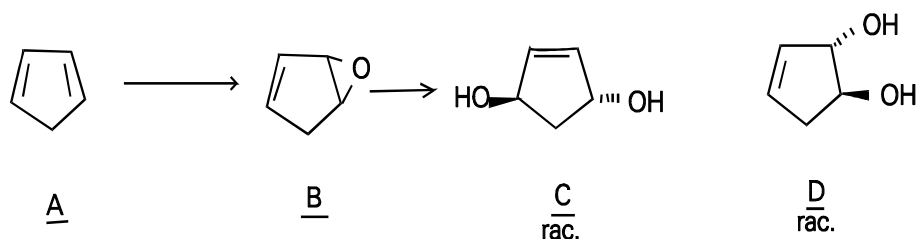
## PROBLEM 6

A technical interesting  $C_5$  hydrocarbon **A** is separated via dimerization from the for-runnings of the benzene-pyrolysis fraction. This is achieved either by heating to  $140 - 150^\circ C$  under pressure or by heating over several hours at  $100^\circ C$ . Then it is distilled out at  $200^\circ C$ . Treatment of **A** with peroxyacetic acid under neutral conditions (sodium acetate and sodium carbonate) in dichloromethane at  $20^\circ C$  yields a product **B**. **B** yields two isomeric products **C** and **D** (summary formula  $C_5H_8O_2$ ) by the reaction with aqueous sodium carbonate solution. The main product **C** contains three different bound carbon atoms whereas in the minor product **D** five different carbon atoms are present. **C** is chiral.

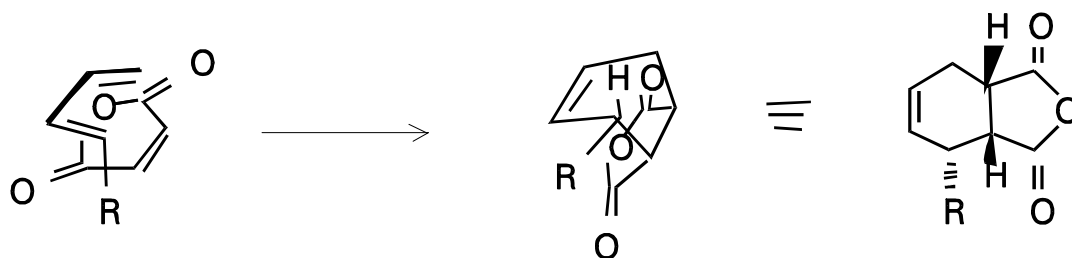
- Write the formulas of **A**, **B**, **C**, and **D** considering the stereochemical representation.
- What is the name of the chemical reaction which is used for the above mentioned separation procedure?
- Which stereochemical rules hold for the dimerization reaction?
- Give the structure of the dimerization product.
- Give the mechanism of the formation of **C** and **D** from **B**.
- Which kind of isomers are **C** and **D**?
- How many stereoisomers of **C** and **D** are principally (regardless of their synthetic availability) possible? Give their mutual stereochemical relations. Write their structural formulas.

## SOLUTION

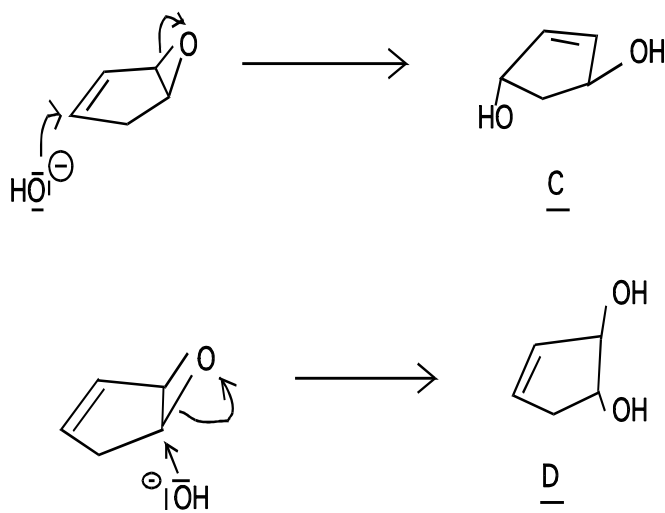
a)



- b) Diels-Alder-reaction, 4+2-cycloaddition  
c) cis-addition = suprafacial addition with respect to diene and dienophile endo-rule: a substituent at the dienophile is oriented primarily toward the diene . E.g.

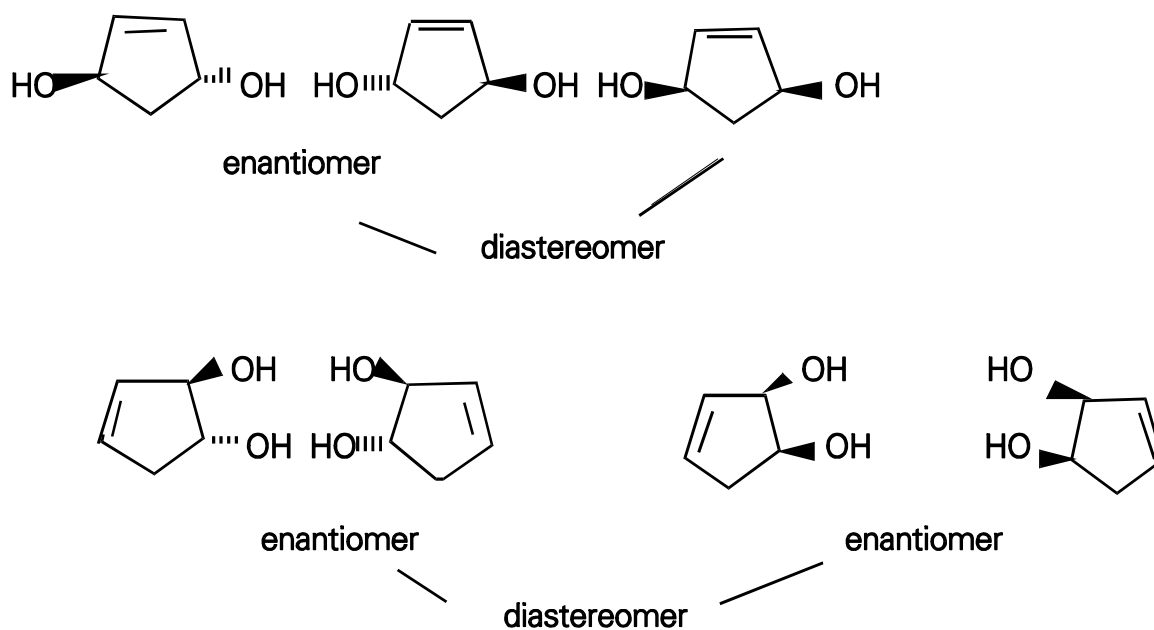


- e) **C** is formed via a  $S_N2$  reaction. This reaction can lead to a cis or a trans product. Because **C** is chiral, the trans product is formed. **D** is formed via  $S_N2$  reaction.



- f) **C** and **D** are constitutional isomers.  
g) There exist two diastereomers (cis and trans) of **C**. The trans form is chiral, i.e. there

exists a pair of enantiomers. The cis form is achiral (reduction of the number of stereoisomers caused by constitutional symmetry, meso-form). **D** forms two diastereomers, each of them is chiral.



## PROBLEM 7

Deoxyribonucleic acid (DNA) represents the genetic program of all living beings. The human genetic program is subdivided into 23 chromosomes.

- a) Calculate the mass of a DNA thread in grams, which reaches from earth to the moon (340,000 km). A mass of 1 g represents 1,000 nucleotide pairs.

One nucleotide pair (base pair) has a length of 0.34 nm.

- b) Give estimation on how many nucleotide pairs are stored in the chromosome set of a human being. Human cells can synthesize 50,000 different proteins, which are on the average 300 amino acids long. Only 2 % of the DNA code for proteins.

- c) The DNA of the bacteriophage M13 shows the following base composition:

A: 23 %, T: 36 %, G: 21 %, C: 20 % (mole %)

What does the base composition tell about the structure of the DNA?

## SOLUTION

- a) 1. Number of nucleotide pairs as calculated from the given length

$$\frac{3.4 \times 10^8 \text{ m}}{3.4 \times 10^{-10} \text{ m}} = 10^{18} \text{ nucleotide pairs}$$

2. Calculation of the mass:

$$1,000 \text{ nucleotide pairs} = 10^{-18} \text{ g}$$

$$10^{18} \text{ nucleotide pairs} = 1 \text{ mg}$$

The mass of 340.000 km DNA is 1 mg.

- b) Human DNA codes for  $50,000 \times 300$  amino acids in form of proteins: Each amino acid is encoded by 3 nucleotides or due to the double stranded structure of DNA by 3 nucleotide pairs. This amounts to  $4.5 \times 10^7$  nucleotide pairs. Since only 2% of the DNA code for proteins one can calculate the number of nucleotide pairs in human DNA to  $2.25 \times 10^9$  nucleotide pairs.
- c) The DNA has to be single stranded, since the ratio of adenine : thymine and guanine : cytosine is different from one.

## PROBLEM 8

The sequence of the amino acids in a peptide can be determined by a combination of chemical and enzymatic methods. The peptide in question functions in the human body as a pain reliever.

1. Hydrolysis of the peptide in 6 M HCl at 110° C followed by an analysis of the liberated amino acids, resulted in a molar ratio of Gly, Leu, and aromatic amino acids Phe, Tyr 2 : 1 : 1 : 1.
2. Reacting the peptide with 2,4-dinitrofluorobenzene (DNFB), followed by hydrolysis and chromatographic analysis, yielded the tyrosine derivative.
3. Partial hydrolysis with chymotrypsin yielded Leu, Tyr and a smaller peptide. After hydrolysis of this peptide Gly and Phe were identified in a ratio 2 : 1. Chymotrypsin is a protease which cleaves a peptide bond following an aromatic amino acid.

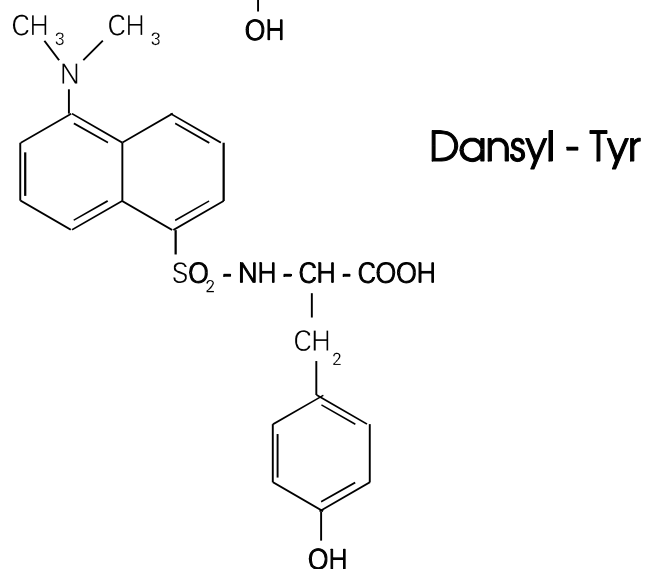
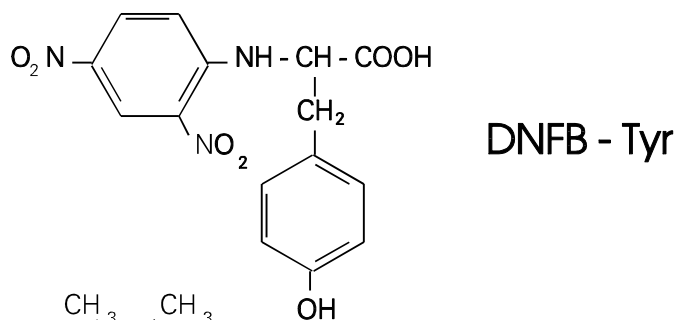
Problems:

- a) Determine the amino acid sequence from the given information.
- b) Write the structural formula of the DNFB- and the dansyl derivative of tyrosine. What is the advantage of the dansylation in comparison to the DNFB-modification?  
Dansyl means 5-N,N-dimethylaminonaphtalene-4-sulphonyl.
- c) In a similar peptide which shows the same biological activity, leucine is replaced by methionine. Explain from the chemical structure of both amino acids why the replacement is possible without loss of biological activity.

## SOLUTION

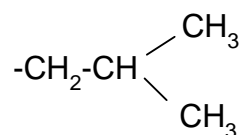
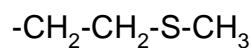
- a) It can be derived from data in part 1 that the net composition of the peptide is 2 Gly, 1 Leu, 1 Phe and 1 Tyr.  
From part 2 one can conclude that the N-terminal amino acid has to be Tyr since DNFB is specific for the N-terminus.  
Part 3 shows that the internal peptide has to be Gly-Gly-Phe.  
The sequence is Tyr-Gly-Gly-Phe-Leu.
- b) The trivial name of the peptide is Leu-Enkephaline. It acts as a pain killer in the human body.





Dansyl derivatives give increased sensitivity since they are highly fluorescent.

- c) The compound is Met-Enkephaline. Leu and Met are both non-polar amino acids. Both side chains show comparable van der Waals radii.



## PRACTICAL PROBLEMS

### PROBLEM 1

Nitration of phenacetine (4-ethoxyacetanilide) with nitric acid in acetic acid as solvent

Caution:

Both acetic acid and 65 % nitric acid attack the skin. If it happens, the skin must be rinsed with water immediately and washed with a saturated aqueous solution of sodium carbonate. Vapours of nitric acid damage the respiratory tract; moreover, nitric gases evolved in the reaction flask are very toxic.

The glass joints of the various apparatus must be only slightly greased.

*Apparatus:*

250 ml four-necked flask with laboratory stirrer, thermometer, reflux condenser with gas vent, water bath, Bunsen burner.

*Preparation:*

40 ml of acetic acid are placed with a glass syringe pipette in the four-necked round bottom flask. 2.0 g of phenacetine are then dissolved in the acetic acid. Also, 2.5 ml 65 % nitric acid are added by using a glass syringe pipette under an effective hood. This mixture is heated for five minutes in a water bath at 90 °C.

*Isolation and purification:*

The hot water bath is replaced by ice water. After ca. 10 minutes the gas vent is removed and ca. 120 ml of distilled water are added through the reflux condenser into the flask in order to dilute the original solution. Stirring is continued until a temperature of ca. 5 °C is reached.

The precipitated solid is filtered off and then washed with a total of 100 ml of cold water and finally dried at 60° C for 2.5 hours in a drying oven.

*Evaluation of the experiment:*

a) Melting points:

The melting point of phenacetine and its reaction product are to be determined and recorded in the note book. The melting point of phenacetine is higher than 120° C and that of the product is higher than 80° C.

b) Thin-layer chromatogram:

The relative position of the spots of the starting compound and its reaction product must be recorded. In order to reach it, little portions of the both samples must be dissolved in 1-2 ml of acetone. The solutions must be placed on the plate by using a capillary tube. To develop the chromatogram, a mixture of 90 ml toluene, 25 ml acetone, and 5 ml acetic acid is used.

After drying the spots are circled with a pen. The  $R_f$ -values must be recorded.

c) Developing reagent:

The developed TLC-plate must be sprayed under a hood with the available reagent solution consisting of iron(III) chloride and potassium hexacyanoferrate(III).

Interpretation of the results:

1. Which nitration product(s) has (have) been formed? The discussion should be focused on the relative position of the spots in your chromatogram; describe your arguments in the note book.
2. Explain why such "mild conditions" have been used here for the nitration reaction. Explain why the nitration reaction has proceeded in spite of these "mild conditions".
3. Explain the observed colour reaction of phenacetine with the developing reagent.
4. Make a brief proposal, how the filtrate should be prepared to avoid environmental damage.

Chemicals:

Acetic acid (analysis grade)

Nitric acid (analysis grade);  $w = 65\%$  by mass

Phenacetine (analysis grade)

Toluene (analysis grade)

Acetone (analysis grade)

Developing reagent: 100 ml solution

200 ml solution

700 ml distilled water.

### SOLUTION

a) Melting points:

4-ethoxy-N-acetylphenylamin (phenacetine) : 135 °C

4-ethoxy-2-nitroacetanilide : 103 °C (theoretical value)

b), c) Documentation, Thin-layer chromatogram

#### Interpretation of the results:

1. The  $R_f$ -value of the nitration product is almost twice as great as that of the starting compound phenacetine. Although nitration has occurred, the molecules exhibit less dipolar character that indicates intramolecular hydrogen bridges. This is only possible if the acetyl amino and nitro groups are located in 1.2-positions.

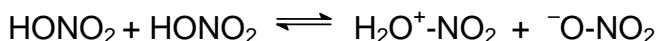
In accordance with the +M-effect of the acetyl amino group one should expect that the nitro group would be favoured in a (free) ortho-position because of the lowered activation energy. On the other hand, one would not expect multiple nitration because of the "mild reaction conditions" (see below) and also because of the electron withdrawing mesomeric effect (-M-effect) and the inductive electron withdrawal (-I-effect) of the nitro group that has entered the molecule.

Nitration product: 4-Ethoxy-2-nitroacetanilide

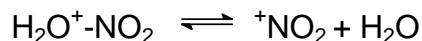
The melting point confirms this observation.

2. The nitration reaction is carried out relatively rapidly, at relatively low temperature in dilute solution and without using fuming nitric acid or "nitration acid".

Instead of sulphuric acid concentrated acetic acid is used. The molecules of the latter compound neither protonate the  $\text{HNO}_3$  sufficiently nor do they do solvate the  $\text{NO}_2^+$  ions. As a result, the equilibrium reactions



and



are shifted far to the left. This effect is counterbalanced by the high reactivity (+M-effect) of phenacetine.

3. Phenacetine is oxidized by iron(III) ions and a molecule of p-quinone type and iron(II) ions are formed. The iron(II) ions react immediately with the hexacyanoferrate(III) ions to give Turnbull's Blue.
  4. Neutralization with sodium or potassium hydroxide solution, use of calcium hydroxide solution and argumentation:  
 $\text{NO}_3^-$ -ions,  $\text{CH}_3\text{COO}^-$  ions and 4-ethoxy-2-nitroacetanilide are removed by biological metabolism.
-

## PROBLEM 2

### Determination of the content of phosphoric acid in a cola drink

#### *Apparatus:*

500 ml round-bottom flask with stirrer, reflux condenser, heating mantle, magnetic stirrer, water bath.

#### *Preparation of the sample:*

The content of a cola drink bottle is stirred for two or three minutes in a round-bottom flask. Afterwards, 6.0 g powdered active charcoal are added. The entire suspension is carefully heated to reflux and is maintained there for ten minutes. The glass joint of the reflux condenser must not be greased!

The heating mantle is then exchanged with an ice water bath. After the sample has been cooled to 20 °C, it is filtered through a double fluted filter paper. The initial filtrate should be recycled several times.

#### *Adjustment of the pH-meter:*

The pH-meter is adjusted to the working electrode by using two buffer solutions.

#### *Titration:*

150 ml of the unknown solution are titrated using pH indication with a standardized sodium hydroxide solution ( $c(\text{NaOH}) = 0.0500 \text{ mol dm}^{-3}$ ).

The first equivalence point of the phosphoric acid is reached after about 6 ml of the NaOH solution have been consumed. The titration is to be continued until more than about 12 ml of sodium hydroxide solution have been added.

#### *Results of the experiment:*

- Draw the titration curve and determine the first equivalence point.
- Determine the pH value of the heated cola drink and the pH value at the first equivalence point.
- Calculate the concentration of phosphoric acid in the cola drink. Write the calculation and the result in your report.

*Interpretation of the experiment:*

1. Describe and explain your observations during the titration.
2. Is it possible that the active charcoal could have influenced your titration result? Give reasons for your presumption.

*Chemicals:*

Powdered active charcoal

Sodium hydroxide solution;  $c(\text{NaOH}) = 0.0500 \text{ mol dm}^{-3}$

Buffer solutions