



University of  
Zurich<sup>UZH</sup>

MNF — Chemistry/Biochemistry

# General Practical Course in Chemistry

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Grundlagenpraktikum der Chemie

Part 2

Organic and  
Physical Chemistry

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Edited by

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for the *General Practical Course in Chemistry Part 2* (CHE112) and the *Practical Course for General and Inorganic Chemistry for Biologists* (CHE173) of the University of Zurich directed by Prof. Dr. R. Sigel, Prof. Dr. S. Bienz, Dr. K. Abou-Hadeed, Dr. J. Helbing, and Dr. F. Wild

# 10 Functional Groups of Organic Compounds

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Organic Chemistry deals with compounds that are primarily based on the element carbon. In these compounds, carbon atoms are usually bonded to additional carbon atoms but also to atoms of other elements, most often hydrogen, oxygen, and nitrogen but also sulfur, the halogens, and, less frequently, also any of the other elements of the periodic table. The variety of the linking possibilities of carbon is additionally increased by the fact that carbon cannot only form stable single bonds but also double and triple bonds to other carbon atoms and a variety of heteroatoms.

The diversity of structural possibilities of carbon results in the fact that by now already more than 25 million of organic compounds are known, which all differ in their physical and chemical properties. Therefore, a certain classification of the compounds is required.

Organic compounds can be classified according to a variety of criteria. For instance, naturally occurring compounds (natural products) can be distinguished from synthetic substances, or toxic from non-toxic compounds, volatile from less volatile compounds, etc. From the perspective of chemistry it makes sense to classify substances primarily on the basis of common chemical reactivities. The chemical reactivities of organic compounds, however, are closely related to certain structural elements, the functional groups, for which reason we will focus on these functional groups at the beginning of this part of the practical course.

The following experiments deal with the distinction and identification of some important functional groups of organic compounds. We will not go here into the details of their chemical behaviors; this will be done in the lecture courses. At this point we will focus primarily on the acid-base properties of compounds, following up the concepts already taught last semester. The chemistry of the “tests for functional groups” is going beyond this, and we do not ask you to understand it fully. Nevertheless, we provide chemical explanations for the reactions performed with the several tests, not wanting to withhold information you are interested into. For performing the experiments properly and to be able to do the required evaluation, however, the knowledge of the theory (except of the acid-base theory) is not crucial.

The individual experiments in Chapter 10 are:

Experiment 10 A	Solubility and Acidity/Basicity of Organic Compounds
Experiment 10 B	Tests for Functional Groups
Experiment 10 C	Analysis of an Unknown Mixture

## Experiment 10 A Solubility and Acidity/Basicity of Organic Compounds

### Objective

Important information about organic compounds and their functional groups can already be obtained by means of simple solubility tests. In Experiment 10 A, you will acquire a technique that allows you to quickly characterize unknown compounds and to classify them on the basis of their polarity and acid/base properties, respectively. You will become acquainted with a “solubility theory”, which you need as a basis to understand and apply the most common working-up procedure in Organic Chemistry — the extraction. You already performed a separation of two organic compounds by the extraction procedure (Experiment 5 A, fall semester); here you learn more about the respective chemistry behind it. Additionally, you will recollect the most important functional groups that you already (might) have encountered in lecture courses or at the *Gymnasium*.

### Solubility of Organic Compounds

We have already dealt extensively with the solubility of chemical substances in the first part of this course. In Chapter 4 you were given a set of solubility rules for inorganic salts enabling you to estimate the solubility properties of a given inorganic compound quickly. For organic compounds — *e.g.*, with regard to their functional groups —, similar generally applicable rules do not exist. In Organic Chemistry we primarily rely on the rule “*like dissolves like*” already introduced in Experiment 4 B (see also table on the next page).

The following table shows that the hydrophobic/hydrophilic properties of an organic compound can be correlated rather directly to its functional groups. However, the table does not consider the total structure of a molecule and merely indicates a “local polarity” in the vicinity of a functional group. This means, *e.g.*, a carboxylic acid always contains a strongly polar and hydrophilic group enabling good interaction with water. However, the acid might also have a significant apolar (hydrophobic, lipophilic) hydrocarbon part so that the properties of the latter can prevail with regard to the overall solubility properties of the substance. This is the case, *e.g.*, with fatty acids (cf. Experiment 11 E) that are sparingly soluble in water but very readily soluble in a variety of organic solvents, even in hydrocarbons, which are very apolar.

Generally, most organic compounds are (very) readily soluble in diethyl ether ( $\text{Et}_2\text{O}$ , frequently called just ether) and only sparingly soluble in water. Exceptions from this rule are functionalized compounds with only a few carbon atoms (1 to about 5 C atoms, depending on the functional group), polyfunctionalized compounds, and organic salts. Some of them are very poorly soluble in organic solvents but, as a rule, readily soluble in water instead.



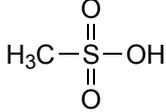
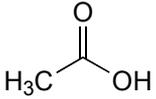
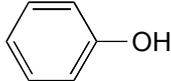
On the basis of the different solubilities of compounds in neutral, basic, and acidic environments, we can easily distinguish between organic acids, bases, and neutral substances (whose solubility depends only slightly on the pH of the environment). Which organic substances are acids, which are bases, and which are neutral substances, though?

## Organic Acids

In principle, all compounds that bear at least one hydrogen atom are acids because they all can be deprotonated with a sufficiently strong base. In the proper sense, however, we only call compounds acids when they dissociate relatively easily into  $H^+$  and the conjugate base ( $A^-$ ) in an aqueous environment (see Chapter 6, Part 1); when their  $pK_a$  value is similar to or smaller than that of water ( $pK_a(H_2O) = 15.7$ ). Within a period of the periodic table, the acidity of an  $XH$  compound increases with increasing polarization of the corresponding  $X-H$  bond, i.e. with increasing electronegativity of the element  $X$ . Stabilization of the anions formed by deprotonation plays an important role, and anion stabilization by resonance is often considered as the source of the acidity of many organic acids. The following compound classes belong, among others, to the typical organic acids:

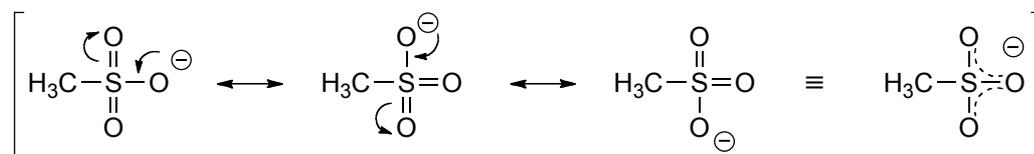
### Compounds with Acidic OH Groups

The OH functionality contains a polarized bond between the strongly electronegative O atom and the less electronegative H atom. This promotes dissociation as a principle. Nevertheless, the most typical compounds with OH groups, the alcohols, do not belong to the actual organic acids. Their  $pK_a$  values usually lie about 1–3  $pK_a$  units above that of water; alcohols are, thus, only marginally dissociated in water. Typical organic acids are sulfonic acids and carboxylic acids; phenols and 1,3-diketones (in the enol form, see below) are acidic as well, but to a considerably lesser degree.

compounds	$pK_a$	example	
sulfonic acids $RSO_3H$	$< 0$		$pK_a = -2.3$
carboxylic acids $RCO_2H$	$< 5$		$pK_a = 4.8$
phenols $ArOH$	$10 \pm 3$ (approx.)		$pK_a = 10.0$

Sulfonic acids, carboxylic acids, and phenols are stronger acids than alcohols because the charges of the anions formed by dissociation (of the conjugate bases = sulfonates, carboxylates, and phenolates) are stabilized by resonance (= delocalization). The corresponding resonance

formulae (= mesomeric forms or resonance structures) for sulfonate (= the deprotonated sulfonic acid) are shown in the following:

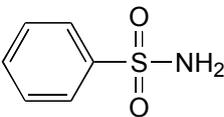
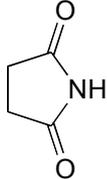


While the strongly acidic sulfonic acids dissociate in water almost completely, the considerably less acidic carboxylic acids only dissociate partially (cf. Experiment 6 B, Part 1). Aqueous solutions of both compound types show acidic pH values, though. On the other hand, solutions of phenols usually react neutral. Only hydroxyls attached to very electron poor aromatic frameworks dissociate sufficiently to yield a  $\text{pH} < 7$ .

The carboxylic acids, having  $\text{pK}_a$  values of  $< \text{ca. } 5$ , get usually fully deprotonated by relatively weak bases. Therefore, they generally dissolve already in 0.5 M aqueous  $\text{NaHCO}_3$  solution in the form of the carboxylates. To fully deprotonate phenols, stronger bases are required: normally, however, they already dissolve in 0.5 M aqueous  $\text{NaOH}$  in the form of phenolates.

#### Compounds with Acidic NH Groups

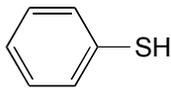
Nitrogen-containing compounds in low oxidation states, except for protonated species like protonated amines, normally are basic and therefore only release their protons reluctantly (see below). However, if the anions that are formed by deprotonation of NH groups are very well stabilized, NH compounds can also be weak acids. The conjugate bases of sulfonamides and of imides show a particularly high resonance stabilization; the respective parent compounds are, thus, rather acidic.

compounds	$\text{pK}_a$	example	
sulfonamides $\text{RSO}_2\text{NHR}'$	$10 \pm 3$		$\text{pK}_a = 10$
imides $(\text{RCO})_2\text{NH}$	$10 \pm 3$		$\text{pK}_a = 9.7$

Sulfonamides and imides having  $\text{pK}_a$  values of about 10, are significantly weaker acids than sulfonic or carboxylic acids. They are comparable in their acidity to phenols, though, and, like them, are usually deprotonated by aqueous  $\text{NaOH}$ , but generally not by aqueous  $\text{NaHCO}_3$ .

## Compounds with Acidic SH Groups

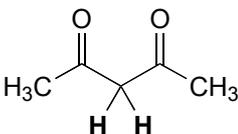
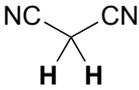
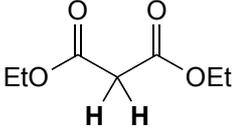
In principle, the acidity of XH compounds increases when X (within the same group) is of a higher period. Accordingly, SH compounds generally are more acidic than the analogous OH compounds. The  $pK_a$  values here are lower by about 4–7 units.

compounds	$pK_a$	example	
thiophenols ArSH	$6.5 \pm 3$		$pK_a = 6.5$
thiols RSH	approx. 11	$H_3C-SH$	$pK_a = 10.5$

Thiophenols are often already deprotonated by  $NaHCO_3$ ; thiols by  $NaOH$ .

## Compounds with Acidic CH Groups

The CH bond is only slightly polarized *per se* and so the  $pK_a$  values of hydrocarbons are very high (*e.g.*, ethane:  $pK_a = 52$ ). In the vicinity of strongly electron withdrawing groups, however, the H atoms bound to C atoms become acidic. Possible electron withdrawing groups are, among others, nitro, carbonyl, nitrile, and carboxyl groups (according to decreasing CH activation). Whereas a single nitro group is sufficient to effect a  $pK_a$  value of about 10 for the corresponding  $\alpha$ -CH atoms, two carbonyl, nitrile, or carboxyl groups are required to achieve the same result (double activation).

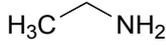
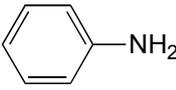
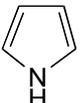
compounds	$pK_a$	example	
nitroalkanes $R_2CHNO_2$	$10 \pm 3$	$H_3C-NO_2$	$pK_a = 10.2$
1,3-diketones $RCOCHR'COR$	$9 \pm 3$ (cyclic: up to $5 \pm 2$ )		$pK_a = 9.0$
malononitriles $NCCHR'CN$	$11 \pm 2$		$pK_a = 12.9$
malonates $RO_2CCHR'CO_2R$	$13 \pm 2$		$pK_a = 11.3$

The acidity of the above compounds is due, on the one hand, to the polarization of the CH bond as a consequence of the inductive ( $\sigma$  acceptor) effect of the  $NO_2$  and the CO/CN groups, respectively; on the other hand, the resonance stabilization of the deprotonated forms contribute markedly ( $\pi$  acceptor effect of the groups, see questions to Experiment 10 A below).

## Organic Bases

Possible bases generally are all organic compounds that have functional groups with high electron density, *e.g.*, electron lone pairs. However, here we again consider as bases only those charge-neutral compounds that can be converted into salts by protonation in an aqueous environment. Thus, the compounds must be comparable or even stronger bases than water.

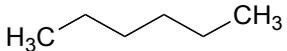
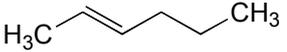
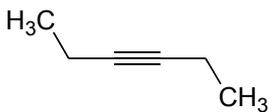
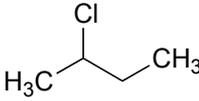
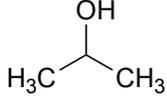
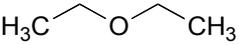
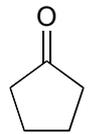
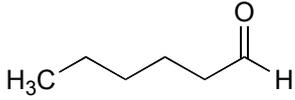
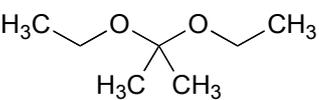
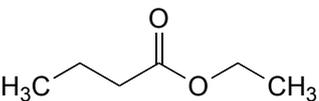
The strength of a base depends on two factors: on the availability of the electron lone pair and on the stabilization of the cation produced by protonation. The availability of the electron lone pair is closely related to its orbital energy. The higher the orbital energy is, the more reactive and, consequently, the more basic the electron pair is. Because the orbital energies decrease with increasing electronegativity of the elements, it is obvious that amines ( $EN_N = 3.1$ ) must be more basic than alcohols ( $EN_O = 3.5$ ). The basicity of N-containing organic compounds varies in a wide range, though, because the availability of the electron lone pair can be limited due to conjugation. Possible basic compounds that get fully protonated by 0.5 M aqueous HCl and, therefore, can often (but not always) be dissolved in water in form of their ammonium salts are alkyl amines (primary, secondary, and tertiary, cf. the table), aryl amines, and heterocyclic nitrogen compounds. Other N- (and O-) containing functional groups can also be protonated, if the acids used are sufficiently strong and concentrated, *e.g.*, conc.  $H_2SO_4$  (see below).

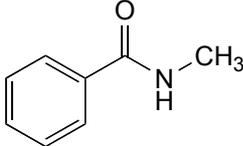
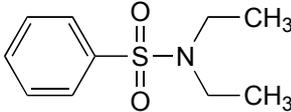
compounds	$pK_b$	example	
alkyl amines $RNH_2$ (prim.) $R_2NH$ (sec.) $R_3N$ (tert.)	$3.5 \pm 1$		$pK_b = 3.19$
aryl amines $ArNH_2$	$9 \pm 3$		aniline $pK_b = 9.27$
pyridine type	$8 \pm 3$		pyridine $pK_b = 8.75$
pyrrole type	$15 \pm 3$		pyrrole $pK_b = 15.0$

## Neutral Substances

We regard as neutral substances all those organic compounds that are not converted, for the major part, into a deprotonated or protonated form by the action of diluted aqueous HCl or NaOH, respectively. Nevertheless, many of these substances react as acids and bases — but not completely, just to a minor degree. Because protonated or deprotonated neutral substances usually are very reactive, they are of great chemical importance in spite of the low amounts in

which they are produced. They are, *e.g.*, the reactive intermediates in acid- and base-catalyzed reactions (see later in this manual and lecture courses). Moreover, many neutral substances can be completely protonated and deprotonated, respectively, in an anhydrous environment by very strong acids or very strong bases. For this reason, almost all N- and O-containing compounds (except for diaryl ethers and nitro compounds) as well as unsaturated hydrocarbons (except for aromatic compounds) can be converted into the conjugate acids by conc.  $\text{H}_2\text{SO}_4$ . On the other hand, almost all carbonyl and carboxyl compounds can be deprotonated to the corresponding enolates by amide bases (= deprotonated amides). Typical neutral substance classes are compiled in the following table, with one example for each.

compounds	example	
alkanes	hexane	
alkenes	( <i>E</i> )-hex-2-ene	
alkynes	hex-3-yne	
aromatic hydrocarbons	benzene	
alkyl and aryl halides	2-chlorobutane (an alkyl halide)	
alcohols	propan-2-ol	
ethers	diethyl ether	
ketones	cyclopentanone	
aldehydes	hexanal	
acetals	2,2-diethoxypropane acetone diethyl acetal	
esters	ethyl butanoate butanoic acid ethyl ester	

amides	<i>N</i> -methylbenzamide	
<i>N,N</i> -disubstituted sulfonamides	<i>N,N</i> -diethylbenzene sulfonamide	

### Solubility Groups, Solubility Tree

On the basis of their solubilities, organic compounds can be classified as follows:

**Group I:** soluble in water and ether.

Monofunctionalized, polar substances with neutral charge and up to about 5 C atoms. This group includes acidic, basic, and neutral compounds in sub-groups.

**Group II:** soluble in water; not or only sparingly soluble in ether.

Very polar substances with neutral charge containing several functional groups or organic salts. This group includes acidic, basic, and neutral compounds in sub-groups.

**Group III:** soluble in ether; not or only sparingly soluble in water and acid; readily soluble in weak or strong base.

Relatively *strong organic acids* ( $\text{p}K_a \leq \text{ca. } 7-8$ ) with sufficiently large apolar structural parts: carboxylic acids with larger hydrocarbon residues and substituted electron-deficient phenols.

**Group IV:** soluble in ether; not or only sparingly soluble in water, acid, and weak base; readily soluble in strong base.

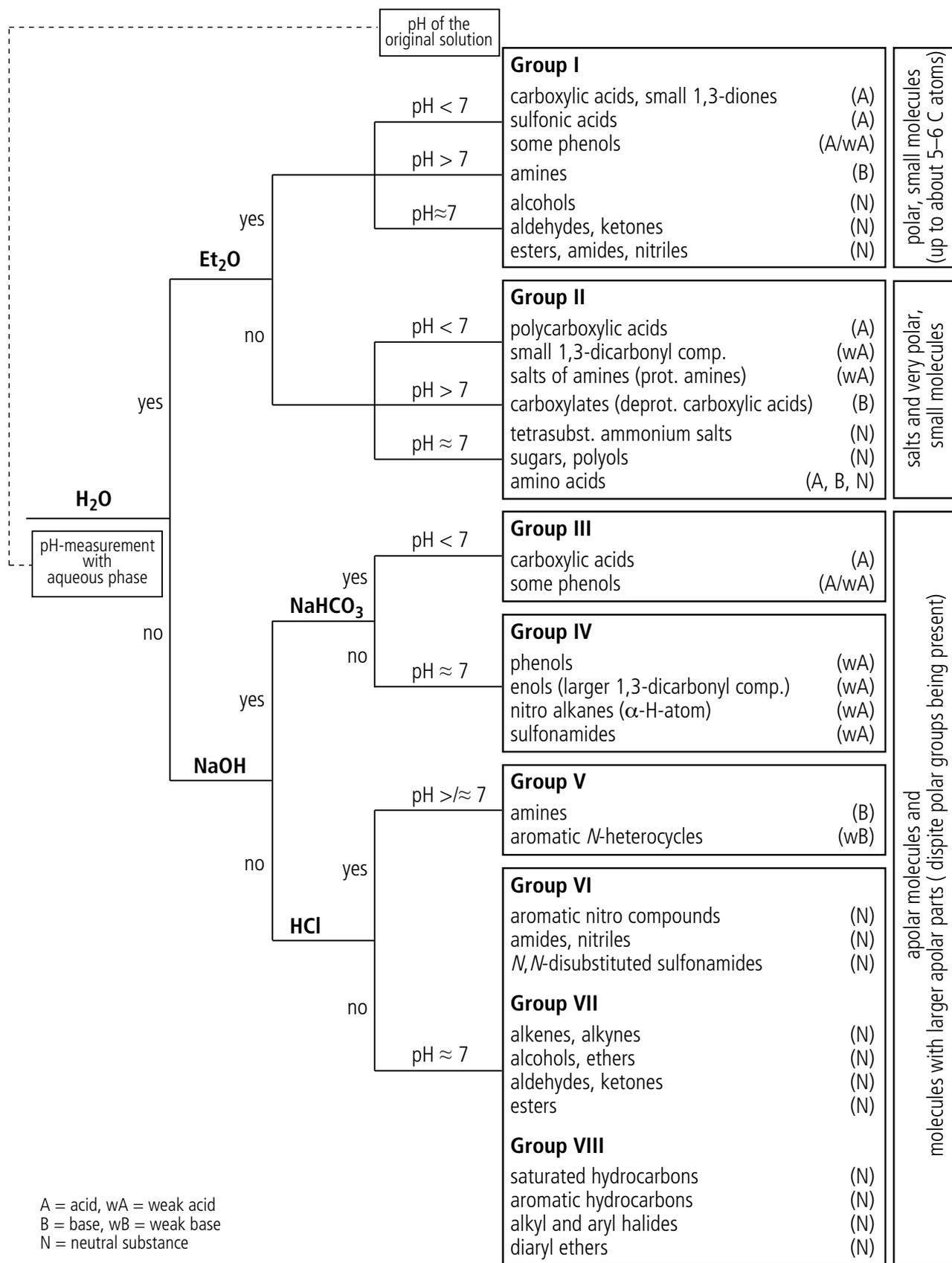
*Weak organic acids* (approx.  $8 \leq \text{p}K_a \leq \text{ca. } 14$ ) with sufficiently large apolar structural parts: substituted electron-rich phenols, enols (dicarbonyl compounds), primary and secondary nitroalkanes, and *N*-mono/*N*-unsubstituted sulfonamides.

**Group V:** soluble in ether; not or only sparingly soluble in water and base; readily soluble in diluted acid.

*Organic bases* ( $\text{p}K_b \leq \text{approx. } 15$ , mostly N-containing compounds) with sufficiently large apolar structural parts: amines, aryl amines, and aromatic heterocycles.

**Group VI-VIII:** soluble in ether; not or only sparingly soluble in aqueous systems.

*Neutral substances:* little polar compounds that can be further classified due to their N/S content and their ability to be protonated by conc.  $\text{H}_2\text{SO}_4$  (see below).



## Classification of the Neutral Substances

The neutral substances can be subclassified into compounds of the groups VI–VIII. For this, not only the solubility arguments are taken into account. At first, the samples are analyzed qualitatively for their content of N and S (group VI), and the N/S-free compounds are further classified into the groups VII (receptive towards protonation by conc.  $\text{H}_2\text{SO}_4$ ) and VIII (inert):

**Group VI:** not or only sparingly soluble in water, diluted acid, or base; often soluble in ether; contains N and/or S.

Neutral substances with N- and/or S-containing groups and sufficiently large apolar residues.

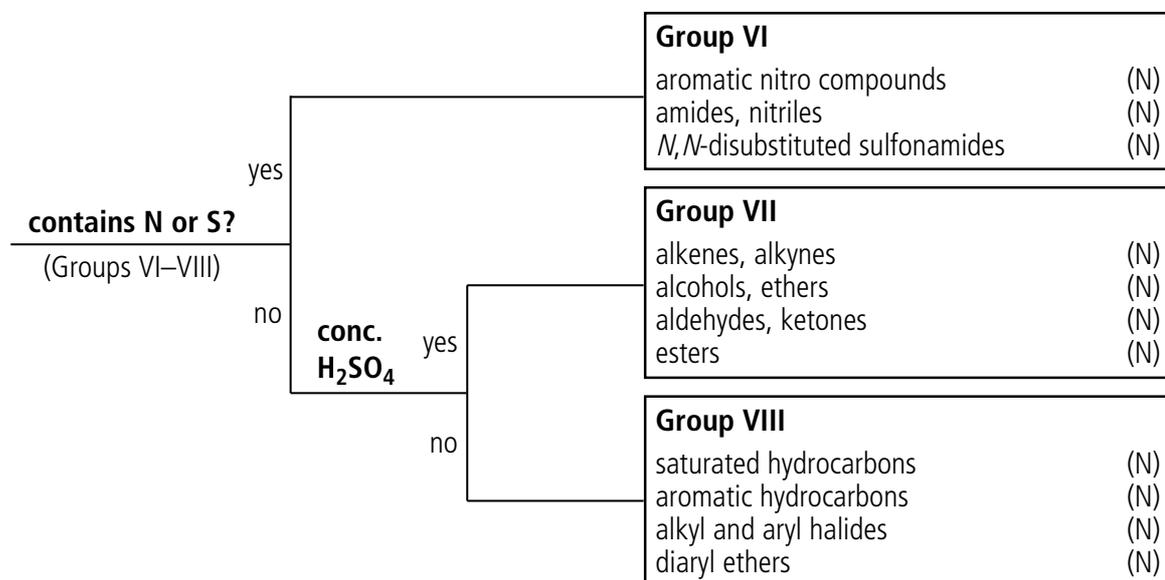
**Group VII:** not or only sparingly soluble in water, diluted acid, or base; often soluble in ether; contains neither N nor S; soluble in conc.  $\text{H}_2\text{SO}_4$ .

Neutral substances containing O, double and/or triple bonds that can be protonated by conc.  $\text{H}_2\text{SO}_4$  (mostly with decomposition!).

**Group VIII:** not or only sparingly soluble in water, diluted acid, or base; often soluble in ether; contains neither N nor S; insoluble in conc.  $\text{H}_2\text{SO}_4$ .

Neutral compounds that are inert even towards strong acid.

The “solubility tree” is supplemented, thus, as follows:



To analyze the sample for nitrogen and sulfur (and halogens), the compound is fused with sodium. N-containing compounds produce  $\text{CN}^-$  in the sodium fusion, S-containing compounds produce  $\text{S}^{2-}$  (and  $\text{SCN}^-$ , provided that N is contained as well), and halogen-containing substances produce the corresponding halides. The anions can then be detected specifically as learned with Experiment 9 C, Part 1 of this course.

## Preparative Tasks to Experiment 10 A

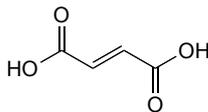
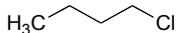
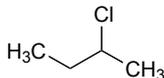
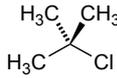
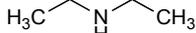
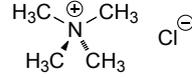
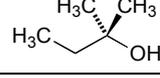
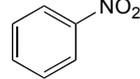
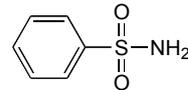
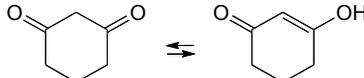
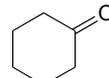
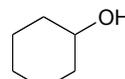
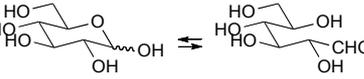
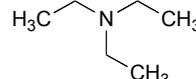
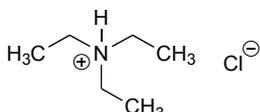
1. Indicate for each of the substances of the following list (= possible compounds you might receive in Experiment 10 A/B for analysis) the functional group(s).
2. Assign them to the Groups I–VIII (incl. subgroups) as far as possible.

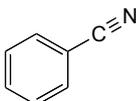
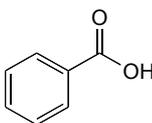
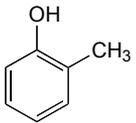
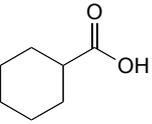
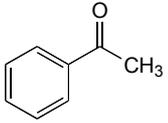
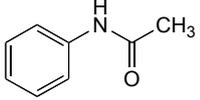
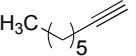
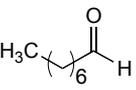
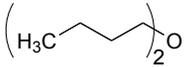
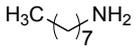
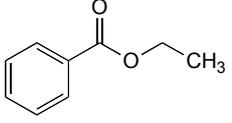
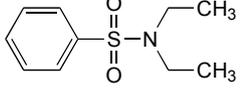
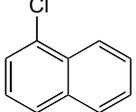
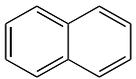
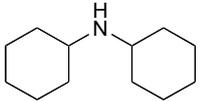
Specify in particular those compounds whose assignment seems difficult for you on the basis of the given criteria. You shall discuss these compounds specifically in the course of the introductory meeting for Experiment 10 A with the teaching assistants and make sure that your assignments are correct (this is crucial for later in the experiment!).

### List of the Compounds for Analysis in the Experiments 10A and 10B

(sorted according to their molecular formulae)

molecular formula	name	structure	grp
$C_2H_2O_4$	oxalic acid (ethanedioic acid)		
$C_2H_3ClO_2$	chloroacetic acid (chloroethanoic acid)		
$C_2H_3N$	acetonitrile (methyl cyanide)	$H_3C-C\equiv N$	
$C_2H_3NaO_2$	sodium acetate (sodium ethanoate)		
$C_2H_4O_2$	acetic acid (ethanoic acid)		
$C_2H_6O$	ethanol		
$C_2H_8N_2$	ethylenediamine		
$C_3H_6O$	acetone (propanone)		
$C_3H_6O$	allyl alcohol (propenol)		
$C_3H_6O$	propionaldehyde propanal		
$C_3H_7NO_2$	L-alanine		
$CH_3NO_2$	nitromethane	$H_3C-NO_2$	
$C_3H_8O$	isopropanol (propan-2-ol)		

molecular formula	name	structure	grp
$C_4H_4O_4$	fumaric acid ( <i>E</i> -butenedioic acid)		
$C_4H_9Cl$	chlorobutane (butyl chloride)		
$C_4H_9Cl$	2-chlorobutane ( <i>sec</i> -butyl chloride)		
$C_4H_9Cl$	<i>tert</i> -butyl chloride (2-chloro-2-methylpropane)		
$C_4H_{11}N$	diethylamine		
$C_4H_{12}ClN$	tetramethylammonium chloride		
$C_5H_{12}O$	2-methylbutan-2-ol ( <i>tert</i> -pentanol)		
$C_6H_5NO_2$	nitrobenzene		
$C_6H_7NO_2S$	benzene sulfonamide		
$C_6H_8O_2$	cyclohexa-1,3-dione		
$C_6H_{10}$	cyclohexene		
$C_6H_{10}O$	cyclohexanone		
$C_6H_{12}$	cyclohexane		
$C_6H_{12}O$	cyclohexanol		
$C_6H_{12}O_6$	D-glucose		
$C_6H_{14}O$	hexanol		
$C_6H_{15}N$	triethylamine		
$C_6H_{16}ClN$	triethylamine hydrochloride		

molecular formula	name	structure	grp
$C_7H_5N$	benzonitrile (phenyl cyanide)		
$C_7H_6O_2$	benzoic acid (benzene carboxylic acid)		
$C_7H_8O$	<i>o</i> -cresol (2-methylphenol)		
$C_7H_{12}O_2$	cyclohexane carboxylic acid		
$C_8H_8O$	acetophenone (methyl phenyl ketone)		
$C_8H_9NO$	acetanilide ( <i>N</i> -phenylacetamide)		
$C_8H_{14}$	oct-1-yne		
$C_8H_{16}O$	octanal		
$C_8H_{18}O$	dibutylether		
$C_8H_{19}N$	octylamine		
$C_9H_{10}O_2$	ethyl benzoate (benzoic acid ethyl ester)		
$C_{10}H_{15}NO_2S$	<i>N,N</i> -diethylbenzene sulfonamide		
$C_{10}H_7Cl$	1-chloronaphthalene		
$C_{10}H_8$	naphthalene		
$C_{12}H_{23}N$	dicyclohexylamine		

## Experimental Instructions

### Problem

You will receive four unknown compounds, about 10 g of each, from the substances given in the table on p. 32ff. You are to characterize these four compounds on the basis of solubility tests and, where appropriate, by sodium fusion and tests for nitrogen, sulfur, and halogens. Finally the compounds have to be assigned to the Groups I–VIII.

### Accessories

Combustion tubes, Et<sub>2</sub>O, aqueous solutions of HCl (0.5 M), NaHCO<sub>3</sub> (0.5 M), NaOH (2 M), AgNO<sub>3</sub> (0.5 M), Na<sub>2</sub>[Fe(CN)<sub>5</sub>NO] (1 M, sodium nitroprusside), FeSO<sub>4</sub>·7 H<sub>2</sub>O (pure, solid), Na (pure, solid, under oil), H<sub>2</sub>SO<sub>4</sub> (2 M), HNO<sub>3</sub> (2 M).

### Safety Instructions

Be aware that you usually do not know anything about the safety risks connected to unknown compounds. Most of the samples provided in this practical course are harmless, but some are not (especially in concentrated form)! Therefore, always handle all of your samples, particularly if you do not know what they are, as if they were dangerous substances: Avoid skin contact and uncontrolled inhalation of the vapors. (Hence, what do you do in practice?)

Elemental Na reacts violently and exothermically with H<sub>2</sub>O or O<sub>2</sub>, producing strongly corrosive NaOH and H<sub>2</sub> gas. The latter can ignite spontaneously in this exothermic reaction. Therefore, never leave unprotected Na anywhere and avoid allowing it to come in contact with H<sub>2</sub>O. Always work in the fume hood, with the sash closed as good as possible.

### Preliminary Remarks

The results of chemical tests are not always easily assessed. You probably have had this experience already with the Experiments 9 in Part 1 of this course. It generally applies that only “positive results” (*e.g.*, the observation of a reaction typical for a functional group) are really significant. “Negative results” (*e.g.*, the absence of a reaction that normally is typical for a functional group) do not allow unambiguous interpretation. Chemical reactions often are complex and can be affected by many parameters — *e.g.*, by the presence of contaminants, the effective concentrations of the reaction partners, etc. —, which remain often concealed. Therefore, consider “negative results” as indications at best, but never as proof.

## Procedure

### Solubility Tests 1

Test the solubility of each compound individually for each of the 5 solvents:

H<sub>2</sub>O, aqueous solutions of NaOH (2 M), NaHCO<sub>3</sub> (0.5 M), HCl (0.5 M), and Et<sub>2</sub>O

For this purpose, add 5 drops of the liquid substance (or the amount that fits on the tip of a spatula; about 20–50 mg) of the pulverized solid substance into a small test tube. Then add dropwise the individual solvent (to max. 0.5 ml) while you shake thoroughly and observe the dissolving progress (enter your observations into a table).

*Readily soluble compounds dissolve immediately within the first drops of solvent; insoluble compounds do not dissolve even in 0.5 ml. For many compounds, the solubility lies somewhere in-between.*

*At this point it must be added that the solubility rules only apply roughly. It is possible that acid-base reactions do effect the formation of a salt but that the corresponding salt is not readily soluble in water (as we would expect). In such cases, the observation of a reaction (e.g., the formation of a precipitate) is sufficient to be interpreted! It indicates "reaction with the base/acid" and is thus an indicator for the nature of the compound as strong as the "change in solubility". Thus, the "formation of salt" can be interpreted as equivalent to "soluble".*

When you have the impression that a substance dissolves more readily in acid or in base than in pure water, you may confirm this observation by neutralization of the solution. If the amount of solvent is not too high, the dissolved material should precipitate again in its original form upon neutralization, which can be observed as cloudiness (or the formation of a second phase).

Measure the pH of the solutions, emulsions, or suspensions you have obtained upon mixing the samples with pure H<sub>2</sub>O, and add this information into your table.

### Preliminary Evaluation

On the basis of the information collected in your table, classify each of your samples as belonging to the groups I, II, III, IV, V, or VI–VIII. Confirm your results with your teaching assistant before proceeding.

*For some of the samples, the classification might not be unambiguous. Make sure that you discuss these cases with your teaching assistant and that your teaching as-*

*stant confirms the correct assignment (or decides, to which group you have to assign the sample). It is decisive for the next steps that you know to which group your compound belongs!*

### **Sodium Fusion and Detection of Nitrogen, Sulfur, and Halogen**

To assign the compounds that were found to belong to the groups VI–VIII (only these!) to group VI or to the groups VII/VIII, they are analyzed for their content of N and/or S (group VI). For this purpose, sodium fusion and subsequent anion analysis is performed.

#### *Sodium Fusion*

Add about 15 drops of the liquid (or 20–30 mg of the solid sample) into a combustion tube. Hold the tube with the crucible tongs slightly inclined and introduce a freshly cut piece of Na (about 4×1×1 mm) by means of tweezers so that it lies about 5 mm above the substance. Then heat the Na in the tube, which is still kept inclined, with the small sharp flame of your *Bunsen* burner to melting — avoid heating your sample too strongly. Allow the liquid metal to flow into the sample where it reacts (often violently). Heat the Na and the substance until the glass tube becomes red by heat and the sample got charred. Drop the still hot tube into a test tube with about 5 ml of deionized H<sub>2</sub>O, where the combustion tube should break into pieces. Shake shortly to dissolve the Na salts, filter off the solution (= sodium fusion solution); if appropriate, rinse the test tube with 2–3 ml of H<sub>2</sub>O and supplement the sodium fusion solution with it.

*Attention: There might be some Na left in the combustion tube that will violently react with the water. Therefore, perform this experiment with the appropriate care in the fume hood, with the sash pulled down. Never keep any organic solvent in the immediate proximity of your experiment!*

Organic compounds that contain N form upon sodium fusion CN<sup>−</sup> (particularly amides, imides, imines — to a lesser extent alkyl amines and their ammonium salts). Organic compound with S-content form S<sup>2−</sup> and those with halogen-content Hal<sup>−</sup>. The several ions can be detected by specific test reactions:

#### *Detection of Nitrogen (Lassaigne Test for CN<sup>−</sup>)*

Add a small amount of FeSO<sub>4</sub>·7 H<sub>2</sub>O (tip of the spatula; about 20 mg) to 1 ml of the sodium fusion solution and heat the mixture. The iron(II) salt dissolves, the color of the solution turns yellow to dark green, and iron hydroxides precipitate. Acidify the mixture with a few drops of 2 M H<sub>2</sub>SO<sub>4</sub>. In the presence of CN<sup>−</sup>, *Prussian blue*, a deeply blue complex salt of the formula Fe(III)[Fe(III)Fe(II)(CN)<sub>6</sub>]<sub>3</sub>, forms, which you can easily observe when you give some drops of the thoroughly shaken solution onto a filter paper. Attention: the

*Lassaigne* test is not very reliable! It frequently gives only very small amounts (or even none) of the expected colored species, particularly if aliphatic amines and their hydrochlorides are analyzed! Thus, do not overrate a negative result!

*Fe(II) is oxidized partially to Fe(III) by atmospheric oxygen (cf. Part 1).*

#### *Detection of Sulfur*

Add a few drops of 1 M aq. sodium nitroprusside solution ( $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ ) to 0.5 ml of the sodium fusion solution. A purple-violet color indicates the presence of  $\text{S}^{2-}$ .

*The  $\text{NO}^+$  of the prusside reacts with  $\text{S}^{2-}$  to  $\text{NOS}^-$  (sulfur analog of  $\text{NO}_2^-$ ) and the purple colored complex anion  $[\text{Fe}(\text{CN})_5\text{NOS}]^{4-}$  is formed.*

#### *Detection of Chloride (and other Halides)*

To decide to which of the three groups VI–VIII your sample belongs, the knowledge of its halogen-content is not necessary. However, having the sodium fusion solution at hand, the additional information can be used for further characterization of the product. For halogen detection:

Acidify 0.5 ml of the sodium fusion solution with 2 M  $\text{HNO}_3$ , and, in case you have detected N or S, boil the solution in the fume hood to expel HCN (prussic acid!) and/or  $\text{H}_2\text{S}$ . Then add several drops of 0.5 M  $\text{AgNO}_3$ . The formation of a colorless precipitate indicates the presence of a halogenide — in our case this would be  $\text{Cl}^-$ . (For the differentiation of  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  cf. Experiment 9 C, Part 1)

### **Distinction of Groups VII and VIII**

To assign the compounds of the groups VII and VIII, their solubility in conc.  $\text{H}_2\text{SO}_4$  is investigated.

Thus, place 5 drops of the liquid substance (or the amount that fits on the tip of a spatula; about 20–50 mg) of the pulverized solid substance into a small test tube and add then dropwise the acid to your sample. Shake carefully and observe dissolution ( $\rightarrow$  group VII) or other effects. It is important to know that apart from protonation also other reactions might occur under the strongly acidic conditions (most often subsequent reactions with the protonated species). These reactions are often irreversible. Significant changes of color indicate reactions and, therefore, the presence of functional groups. The respective sample is then also assigned to group VII.

*Attention: conc.  $\text{H}_2\text{SO}_4$  is aggressive and highly corrosive. Avoid contact with skin. In case of spilling, dilute immediately with cold water.*

## Collection

You will need the remnants of your samples for Experiment 10 B!

Groupwise combine all solutions in a large beaker while stirring. Basify the mixture with NaOH solution, transfer it into a large separatory funnel, and extract it three times with ether (do not forget the ice!). Then acidify and extract again three times with ether. The aqueous phase can be disposed of down the sink. The organic extracts are collected in the provided container.

## Evaluation

In the laboratory notebook: assign your compounds to the groups I–VIII (incl. subgroups) and characterize them as far as possible (e.g., contains halogen). Obtain a confirmation for this before leaving the laboratory!

List for each of your samples those substances from the table given on p. 32 that are, based on your acquired information, possible candidates for your unknowns. This information is important for the next experiment!

## Experiment 10 B Tests for Functional Groups

### Objective

You are to learn that you can get an idea about the most important structural elements of organic compounds — the functional groups, which determine the reactivity of the molecules — by simple means already. The tests presented here often are the basis for spraying reagents that you can use in the daily laboratory work for visualizing chromatographic spots.

### Preparative Questions to Experiment 10 B

1. You have assigned in the evaluation of Experiment 10 A each of your four samples to a solubility group and determined for each of the samples the possible candidates for your unknowns. These compounds should have functional groups (some solely one, others more) that can be assigned unambiguously by means of the following tests.

Indicate for each of your sample compounds of Experiment 10 A those tests that should enable you to assign the substances unambiguously to one of the suggested possible candidate structures. Indicate first the functional groups of the candidate structures and look up the corresponding detection or exclusion tests in the experimental part of this experiment.

2. When performing the *Lucas* test (test **7**), you recognize a reaction but you are not sure whether your sample is a secondary or a tertiary alcohol because you cannot really rate the reaction as fast or very fast. What do you do? Hint: a set of compounds with known structures is provided in the laboratory.

## Experimental Instructions

### Problem

Identify the functional groups of your samples from Experiment 10 A with chemical tests and assign the correct structures to the compounds.

### Accessories

#### Utensils

New small test tubes, Cu wire.

**Solvents**

EtOH	(pure)
Acetone	(pure, not recycled)
Diethylene glycol	(pure, HOCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH)

**Acids**

HCl	(conc. = 12 M, 2 M)
HNO <sub>3</sub>	(conc. = 14 M, 2 M)
H <sub>2</sub> SO <sub>4</sub>	(conc. = 18 M, 2 M)
Glacial acetic acid (AcOH)	(acetic acid, conc.)

**Bases**

KOH	(pure, as pellets)
NaOH	(6 M, 2 M, 0.5 M)
NH <sub>3</sub>	(conc. = 13 M)

**Solutions of Salts and Pure Substances**

AgNO <sub>3</sub>	(0.5 M)
Benzenesulfonyl chloride	(pure, PhSO <sub>2</sub> Cl)
FeCl <sub>3</sub>	(0.5 M)
FeSO <sub>4</sub> · 7 H <sub>2</sub> O	(pure, solid)
KMnO <sub>4</sub>	(0.05 M)
Na	(pure, solid, under oil)
Na <sub>2</sub> [Fe(CN) <sub>5</sub> NO]	(1 M, sodium nitroprussiate)
Ninhydrin	(1%)
Phenolphthalein	(0.1% in EtOH)

**Reagent Solutions**

Ce(NH <sub>4</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>6</sub> reagent	(9.0 g in 22.5 ml of 2 M HNO <sub>3</sub> )
2,4-Dinitrophenylhydrazine reagent	(3.0 g of 2,4-dinitrophenylhydrazine in 15 ml of conc. H <sub>2</sub> SO <sub>4</sub> /90 ml of H <sub>2</sub> O/EtOH (2:7))
Lucas reagent	(1:1 anhydrous ZnCl <sub>2</sub> /conc. HCl)
Fehling I	(3.5 g of CuSO <sub>4</sub> · 5 H <sub>2</sub> O in 50 ml of H <sub>2</sub> O)
Fehling II	(19.23 g of sodium potassium tartrate · 4 H <sub>2</sub> O and 5.0 g of NaOH in 50 ml of H <sub>2</sub> O)

**Reference Samples**

alkane, alkene, aromatic compound  
 prim., sec., tert. alkyl chloride  
 prim., sec., tert. alcohol  
 prim., sec., tert. amine

more reference samples upon request

## Safety Instructions

Mind that your samples and the reagents can be toxic and corrosive. Avoid skin contact and inhalation of vapors.

## Preliminary Remarks

Mind the remarks concerning "negative results" in Experiment 10 A.

Consider carefully which tests are appropriate for your compounds due to their belonging to a solubility group and their potential structures (*Preparative Question 1*).

In the individual experiments, the sample amounts are indicated as drops. For solid substances use the amount fitting of the tip of a spatula (about 10 mg) instead of one drop.

To find the appropriate tests, consult the following table:

<b>Compound Type</b>	<b>Tests</b>
Alkanes	no specific tests, exclusion principle
Alkenes	<b>1</b>
Alkynes	<b>1, 2</b>
Aromatic compounds	<b>3</b>
Halides	halogen detection with soln. of sodium fusion, <b>4</b>
Alcohols	<b>5, 6, 7</b>
Phenols	<b>8</b>
CH acidic comp.	<b>3, 8</b>
Ethers	no specific tests, exclusion principle
Aldehydes	<b>9, 10, 11</b>
Ketones	<b>9</b>
Carboxylic acids	<b>12</b>
Esters	<b>13</b>
Amines	basic, N detection with soln. of sodium fusion, <b>14</b>
N-Heterocycles	slightly basic, N detection with soln. of sodium fusion, <b>3</b>
Amides/Nitriles	N detection with soln. of sodium fusion, <b>15</b>
Amino acids	N detection with soln. of sodium fusion, <b>16</b>
Nitro compounds	N detection with soln. of sodium fusion, <b>17</b>
Sulfonamides	N/S detection with soln. of sodium fusion, <b>18</b>

To unambiguously characterize certain compounds, several tests might be necessary. It is possible, for example, that a compound is an alcohol and at the same time contains an aromatic part.

## Procedures

### Hydrocarbons

#### *Alkanes (Saturated Hydrocarbons)*

Alkanes are extraordinarily inert and cannot be detected in a chemically specific manner (apart from this, most organic compounds contain an “alkane part” and its detection would be rather meaningless for the substance class). So, pure alkanes are revealed best by the exclusion principle.

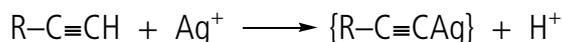
#### *Alkenes (Hydrocarbons with Double Bonds, except Aromatic Compounds)*

1. *Test for Oxidizable Double Bonds (Baeyer Test):* Dissolve 2–3 drops of the sample in about 0.5 ml of H<sub>2</sub>O or pure acetone (the sample must be dissolved completely!), and dropwise add 0.05 M KMnO<sub>4</sub>. If you need more than one drop of the reagent to turn the color of the solution to violet, the presence of double or triple bonds (but not of aromatic compounds) is indicated. Attention: other oxidizable groups react as well, *e.g.*, phenols react quite quickly, alcohols and other substances more slowly; perform a comparison test with an alkene!

*Collection:* collect the solutions in a “waste beaker”. The waste will be extracted at the end of the afternoon collectively.

#### *Alkynes (Hydrocarbons with Triple Bonds)*

Alkynes react with oxidants (*e.g.*, KMnO<sub>4</sub>, test **1**) just like alkenes, but require more oxidant for a complete reaction due to the double unsaturation. Terminal alkynes can be converted into sparingly soluble silver or copper acetylides.



2. *Test for Terminal Alkynes:* Preparation of the reagent (the *Tollens* reagent is also used for test **10**): Mix 5 ml of 0.5 M AgNO<sub>3</sub> with 1 ml of 2 M NaOH and then re-dissolve the obtained precipitates by adding conc. NH<sub>3</sub>. Detection: Add 2–3 drops of your sample, dissolved in ca. 0.5 ml of acetone, to 1 ml of the freshly prepared reagent and mix thoroughly. Formation of a precipitate indicates the presence of a terminal alkyne.

*Caution:* Silver acetylides are explosive in the dry state! Decompose the acetylide immediately after you have observed it by addition of 2 M H<sub>2</sub>SO<sub>4</sub>.

*Collection:* collect the solutions in a “waste beaker”. The waste will be extracted at the end of the afternoon collectively.

*Aromatic Compounds*

- 3.** *Beilstein Test (Flame Test for Aromatic Compounds and Halides):* Form a small ring from the end of a copper wire. Dip this into a beaker with conc.  $\text{HNO}_3$  for a short time, rinse it with deionized  $\text{H}_2\text{O}$ , and heat it in the flame of the *Bunsen* burner until the flame no longer shows a green color. After the ring has cooled down, moisten it with your sample and subsequently hold it into the non-luminous flame of the burner. Formation of soot during the combustion indicates aromatic compounds. Organic chlorides yield a deep green coloring of the flame, bromides a bluish one with a green edge. The color differences are characteristic but are really apparent only with a comparison test.

*Caution: The combustion of halides on copper wire yields toxic products (dioxines)!*

*Collection:* the copper wires are returned; they will be used again.

**Compounds with Halogens***Alkyl and Aryl Halides*

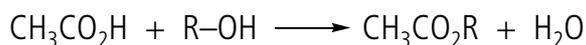
All organic halides show precipitation of  $\{\text{AgHal}\}$  in the solution of the sodium fusion upon addition of  $\text{AgNO}_3$ . The precipitate also allows a differentiation of the halogens — Cl, Br, and I — (see Experiment 9 C, Part 1). The *Beilstein* test (test **3**) confirms the presence and the type of halogen. The following test **4** allows the differentiation of primary, secondary, and tertiary alkyl chlorides.

- 4.** *Differentiation of Primary, Secondary, and Tertiary Alkyl Chlorides ( $\text{AgNO}_3$  Test):* Dissolve 5–10 drops of your sample in 1 ml of EtOH. Add 1 drop of 2 M  $\text{HNO}_3$  and about 0.5 ml of 0.5 M  $\text{AgNO}_3$  and shake vigorously. If a precipitate forms within 2 min, this indicates alkyl bromides (greenish yellow), alkyl iodides (yellow), or tertiary alkyl chlorides (a positive test can be obtained by other activated alkyl chlorides as well). In case of small amounts, the colors cannot be observed very well: the precipitate is recognized as a milky cloudiness of the solution only (cf. Experiment 11 A). If you do not observe a precipitate within 2 min, heat the mixture in a boiling water bath for 5–10 min to 50–60 °C. In the case of primary (slowly) and secondary alkyl chlorides, a precipitate of  $\{\text{AgCl}\}$  forms; aryl chlorides and vinyl chlorides do not react. Also see Experiment 11 A. (Comparison tests with known halides are indispensable for this test!)

*Collection:* collect the solutions in a “waste beaker”. The waste will be extracted at the end of the afternoon collectively.

**Functional Groups with Oxygen** (without any further Elements)*Alcohols*

5. *Esterification Test:* Mix about 0.5 ml of your sample with about 0.5 ml of glacial acetic acid and add 5–10 drops of conc.  $\text{H}_2\text{SO}_4$ . Warm the pungent smelling mixture for 5–10 min in a boiling water bath to 50–60 °C. Allow to cool down, add about 2 ml of  $\text{H}_2\text{O}$ , and basify with 6 M NaOH. Primary and secondary alcohols form esters (fruity smell, sometimes weak and masked by other smells); tertiary alcohols often eliminate  $\text{H}_2\text{O}$  producing alkenes (pungent smell).

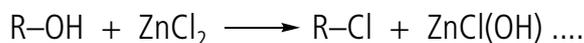


*Collection:* collect the solutions in a “waste beaker”. The waste will be extracted at the end of the afternoon collectively.

6.  *$\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$  Test (for Alcohols with < ca. 10 C Atoms):* Add 4–5 drops of your sample to 1 ml of  $\text{H}_2\text{O}$  and add such an amount of acetone that the sample is completely dissolved. Then add about 0.5 ml of the Ce(IV) reagent and mix thoroughly. In the presence of alcohols, a complex of  $[\text{Ce}(\text{NO}_3)_x(\text{OR})_y]$  ( $x + y = 8$ ) is formed, and the color of the solution turns from yellow to red.

*Collection:* collect the solutions in a “waste beaker”. The waste will be extracted at the end of the afternoon collectively.

7. *Differentiation of Primary, Secondary, and Tertiary Alcohols (Lucas Test):* Add 2–3 drops of your sample to 10 drops of Lucas reagent, shake thoroughly and then allow the mixture to rest. Tertiary alcohols react immediately, secondary within several minutes, primary only after several hours to the corresponding alkyl chlorides. You observe a cloudiness and subsequent phase separation. If too much of the alcohol is employed, the reaction proceeds slowly and indistinctly.



*Collection:* collect the solutions in a “waste beaker”. The waste will be extracted at the end of the afternoon collectively.

*Phenols and CH-Acidic Compounds*

8.  *$\text{FeCl}_3$  Test for Phenols and Enols:* Dissolve 2–3 drops of your sample in 1 ml of  $\text{H}_2\text{O}$  or 1 ml of a mixture of  $\text{H}_2\text{O}/\text{EtOH}$  and add 1 drop of 0.5 M  $\text{FeCl}_3$ . If the color turns to red, blue, green, or purple, this indicates phenols or enols (formation of an Fe(III) complex). Primary and secondary nitro alkanes might be indicated positively as well; normally, however, these have to be converted into the correspond-

ing *aci*-forms (see test **17**). Basic compounds yield sparingly soluble  $\text{Fe}^{3+}$  precipitates, and carboxylates often yield red colored solutions that might be mistaken for Fe(III) enolate/phenolate complexes.

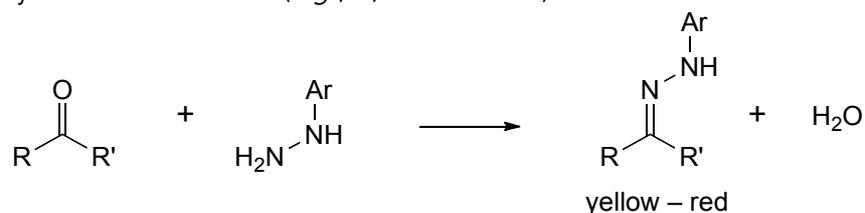
*Collection:* collect the solutions in a "waste beaker". The waste will be extracted at the end of the afternoon collectively.

### Ethers

Ethers are inert. They are recognized by the fact that they can be protonated by conc.  $\text{H}_2\text{SO}_4$  and by exclusion of alkenes (neg. test **1**).

### Aldehydes/Ketones

- 9.** *2,4-Dinitrophenylhydrazone Test for Carbonyl Compounds:* Dissolve 2–3 drops of your sample in 2 ml of EtOH and add 3 ml of the 2,4-dinitrophenylhydrazine reagent. Mix thoroughly and allow the mixture to rest. A yellow to red precipitate indicates a carbonyl compound (aldehyde or ketone); the test is often negative for easily enolizable ketones (e.g., 1,3-diketones!).



*Collection:* collect the solutions in a "waste beaker". The waste will be extracted at the end of the afternoon collectively.

### Aldehydes

- 10.** *Tollens Test* (cf. Experiment 8 D, Part 1): Mix 5 ml of 0.5 M  $\text{AgNO}_3$  with 1 ml of 2 M NaOH and then completely re-dissolve the precipitates by adding conc.  $\text{NH}_3$  (is also used in test **2**). Add 3–5 drops of your sample to 1 ml of this *Tollens* solution in a new test tube and warm the mixture in the water bath. Formation of a silver mirror indicates the presence of an aldehyde.

*Collection:* collect the solutions in a "waste beaker". The waste will be extracted at the end of the afternoon collectively.

- 11.** *Fehling Test:* Mix 1 ml of each of the solutions "*Fehling I*" and "*Fehling II*" to obtain the *Fehling* reagent. Add 3–5 drops of your sample (if necessary dissolved in EtOH) to this reagent, and warm the mixture in the water bath for 2–3 min. A yellow to orange precipitate of  $\{\text{Cu}_2\text{O}\}$  indicates an aldehyde.

*Collection:* collect the solutions in a “waste beaker”. The waste will be extracted at the end of the afternoon collectively.

*In the Tollens and Fehling tests, the aldehydes are converted to the corresponding carboxylic acids by mild oxidation. The reactions are specific for aldehydes (also for the cyclic forms of sugars that are in equilibrium with the open aldehyde forms). Alcohols or ketones do not react.*

### Carboxylic Acids

- 12.** *Esterification Test* (cf. test 5): Mix about 0.5 ml of your sample with about 0.5 ml of EtOH (maybe a little more, until the sample is completely dissolved) and add 5–10 drops of conc.  $\text{H}_2\text{SO}_4$ . Warm the mixture for 5–10 min in a hot water bath to 50–60 °C. Allow the mixture to cool down, add about 2 ml of  $\text{H}_2\text{O}$ , and basify with 6 M NaOH. Carboxylic acids form fruity smelling esters (the smell is sometimes weak and masked by other smells).

*Collection:* collect the solutions in a “waste beaker”. The waste will be extracted at the end of the afternoon collectively.

### Esters

- 13.** *Rojahn Test for Alkaline Hydrolyzable Compounds:* Dissolve 10 drops of your sample in about 1 ml of EtOH and add 1 drop of phenolphthalein solution (0.1% in EtOH) as well as 1 drop of 0.5 M NaOH (you obtain a red solution). Mix thoroughly and warm the mixture with occasional shaking in the water bath for at least 5 min. Decoloration (even if not really completely) indicates the presence of an ester. The test is also positive for lactones, anhydrides, and readily hydrolyzable halides, amides, and nitriles. (Question: What does the decoloration mean?)

*Collection:* collect the solutions in a “waste beaker”. The waste will be extracted at the end of the afternoon collectively.

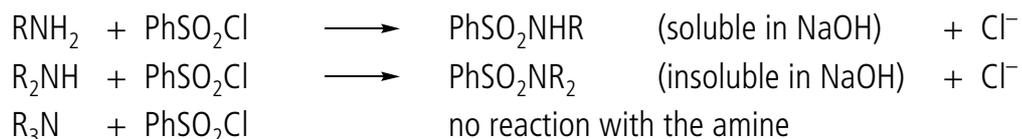
## Functional Groups with Nitrogen and Sulfur

### Amines and Aromatic N-Heterocycles

Amines and aromatic N-heterocycles are recognized by their basicity and their belonging to group V. But you can further distinguish primary, secondary, and tertiary amines from one another.

- 14.** *Differentiation of Primary, Secondary, and Tertiary Amines (Hinsberg Test):* Add 5 ml of 2 M NaOH and 0.4 ml of benzene sulfonyl chloride (caution: corrosive and

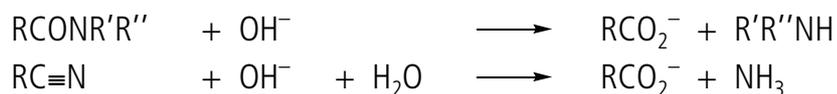
volatile; produces HCl and stinks. Definitely work in the fume hood!) to 0.5 ml of your sample. Warm for 3–4 min in a boiling water bath and shake vigorously: primary and secondary amines react to form the corresponding sulfonamides; tertiary amines and aromatic *N*-heterocycles do not react. If a clear solution is formed, this indicates a primary amine (*N*-monosubstituted sulfonamide, cf. test **18**). A heterogeneous mixture indicates a secondary amine (the amine reacts to insoluble *N,N*-disubstituted sulfonamide, which most often is a solid) or a tertiary amine (you observe unreacted sulfonyl chloride that hydrolyzes only slowly).



*Collection:* collect the solutions in a “waste beaker”. The waste will be extracted at the end of the afternoon collectively.

### Amides and Nitriles

- 15.** *Hydrolysis:* Dissolve 4–5 pellets of KOH in 5–10 drops of H<sub>2</sub>O and 2 ml of diethylene glycol and add 8–10 drops of your sample. Heat cautiously in a boiling water bath, and check the vapor for evaporating basic compounds (amine or NH<sub>3</sub>) with a moistened pH paper (maybe check with your nose). Amides react more quickly (formation of amines or NH<sub>3</sub> in about 1 min) than nitriles (formation of NH<sub>3</sub> after about 3–5 min). Comparison test!



The carboxylic acid that may have also formed upon hydrolyzation (as carboxylate) might be made visible by acidifying the solution (observation of cloudiness; works only with carboxylic acids with sufficiently nonpolar residues).

*Collection:* collect the solutions in a “waste beaker”. The waste will be extracted at the end of the afternoon collectively.

### Amino Acids

- 16.** *Ninhydrin Test:*  $\alpha$ -Amino acids react specifically with ninhydrin to a blue-violet dye: Dissolve 1 drop of your sample in 5–6 drops of H<sub>2</sub>O and add 5 drops of ninhydrin solution (1%). A blue-violet coloring of the solution indicates an  $\alpha$ -amino acid; NH<sub>3</sub>, primary amines, and their salts turn the solution to red brown.

*Collection:* collect the solutions in a “waste beaker”. The waste will be extracted at the end of the afternoon collectively.

*Nitro Compounds*

- 17.** *FeCl<sub>3</sub> Test* (cf. test **8**): In contrast to phenols and dicarbonyl compounds (enols), enolizable nitro compounds do not react spontaneously to colored FeCl<sub>3</sub> complexes. They must be converted into their *aci*-forms at first: Dissolve 8–10 drops of the sample in 1 ml of EtOH and add 20 drops of 2 M NaOH to this mixture. Dilute 20 drops of 2 M HCl with 40 drops of H<sub>2</sub>O in a separate test tube and add 2 drops of 0.5 M FeCl<sub>3</sub> to this solution. Cool both solutions in an ice bath and mix them thoroughly afterwards. Brown to red coloring indicates enolizable nitro compounds. Tertiary nitro compounds (and aromatic nitro compounds) do not show a coloring.

*Collection:* collect the solutions in a “waste beaker”. The waste will be extracted at the end of the afternoon collectively.

*Sulfonamides*

- 18.** *Solubility Test* (to distinguish *N*-unsubstituted and *N*-monosubstituted from *N,N*-disubstituted sulfonamides): Mix 3–5 drops of your sample (that you have already recognized as a sulfonamide!) with 0.5 ml of H<sub>2</sub>O and add 0.5 ml of 2 M NaOH. If the sample dissolves, this indicates an *N*-unsubstituted or an *N*-monosubstituted sulfonamide. Addition of 0.5 ml of 2 M HCl results in re-protonation and reformation of the sparingly soluble sulfonamide (can often be observed as a clouding of the solution). *N,N*-Disubstituted sulfonamides (without NH) cannot be deprotonated and therefore do not react (dissolve).

*Collection:* collect the solutions in a “waste beaker”. The waste will be extracted at the end of the afternoon collectively.

**Collection**

Collect all waste solutions within the group in a large separating funnel. Extract the solution under basic and acidic conditions three times with 50–100 ml of Et<sub>2</sub>O. Collect both the organic and aqueous phases in the provided collecting containers; they will be disposed of properly by us. The excess of the samples are to be returned.

**Evaluation**

Summarize the results of your tests in a separate evaluation section at the end of your notebook entry. Draw a final conclusion about the nature of your sample compounds. Before leaving the laboratory, make sure — by consulting your teaching assistant — that your assignments are correct. You may not leave the laboratory before this is the case.

## Experiment 10 C Analysis of an Unknown Mixture

### Objective

You are to show that you are able to separate two unknown compounds handed out as a mixture, to purify them, and to derive their functional groups on the basis of the knowledge acquired in the Experiments 10 A and 10 B. To develop a separation strategy, to perform the separation, and to determine the purity of the components by TLC, the techniques you have acquired with Experiments 5 A (Extraction) and 5 B (Chromatography) have to be recalled.

The separated samples will be re-used in the Physicochemical Practical Course 1 (CHE213, third semester) for further analysis.

### Preparative Questions to Experiment 10 C

1. The two-component mixture you obtain in Experiment 10 C can be separated by the means of the extraction procedure (cf. Experiment 5 A, Part 1). What can you deduce from this for the components of your sample with regard to their acidity/basicity?
2. You find in the preliminary tests that your sample reacts acidic as a whole. Schematically sketch the reasonable procedure to separate the components by extraction. Indicate at each step which component should be present in which fraction in which form.
3. How would you proceed if the sample reacted basic? Sketch the procedure for this case in the same manner as above.
4. What could be deduced if your samples were neutral? Which types of components — the components still must be separable by the extraction procedure! — are possible for your sample? How do you proceed in order to find out whether you must extract acidically or basically in shaking out?

### Preparation for the Experiment

Study the Experiments 5 A (Extraction, Extraction Procedure) and 5 B (Chromatography) in the course manual of the fall semester and your notes to these experiments in your laboratory notebook as well. Take with you the respective documentations as a reference.

We expect that you are acquainted with the techniques and the theoretical basics of extraction and of TLC. This will be checked by the teaching assistants! If you are not familiar with it, you have to expect getting excluded from the experiment.

## Experimental Instructions

### Problem

You will receive a mixture of two components belonging to different solubility groups, but not to group I. You are to separate these two substances quantitatively, to purify them, to check their purity, and to determine their functional groups.

### Accessories

NaHCO<sub>3</sub> (pure), NaOH (pure), drying agents: Na<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub>, (NaOH (2 M for extraction), HCl (conc.), HCl (2 M for extraction), reagents of Experiment 10 A and 10 B, Et<sub>2</sub>O, hexane, CH<sub>2</sub>Cl<sub>2</sub>, AcOEt, MeOH, TLC plates, several staining reagents for TLC.

### Safety Instructions

Mind the safety instructions for the Experiments 10 A and 10 B that apply also for the separation of your mixture and for the characterization of the separated samples.

### Procedure

*1<sup>st</sup> afternoon:*

Start with preliminary tests, just like in Experiment 10 A, in order to determine the conditions (acidic or basic) you have to employ for the extraction procedure (cf. also *Preparative Questions*). The task is somewhat more complex for Experiment 10 C because you no longer work with pure samples but with a mixture of two samples. In the context of the preparative questions, you have already considered appropriate procedures for different cases. Notify your teaching assistants about the results of your preliminary tests and how you intend to proceed with the extraction.

Perform the extractions as soon as the teaching assistants have approved your intended procedure. Check the result of the separation by means of TLC, which you show to the teaching assistants. (You have to evaluate the appropriate solvent system for the TLC with the provided solvents by yourself.)

*If you perform chemical analyses, you usually employ only partial amounts of the samples so that a repetition of the analysis with the original sample is guaranteed. However, for ecological reasons — so that no unnecessary chemical residues are*

*produced —, use in this experiment the total amount of the sample you were given for the separation and analysis.*

Preliminary evaluation: Before disposing of any solutions and leaving the laboratory, calculate the mass balance. If the mass balance is not satisfying (for you: less than 80% of the mass recovered), look for the missing material. It might still be dissolved in one of your solutions. Check your notes and discuss, if necessary, the possible fate of your compounds with your teaching assistant. If the material is not found, the extraction/separation has to be repeated with a new sample (maybe the next afternoon).

*2<sup>nd</sup> afternoon:*

Perform tests for functional groups with your separated samples analogously to those performed in Experiment 10 B. Take into account that your samples (usually) are not completely pure (TLC?) and that the detection reactions might be potentially falsified by impurities. The aim of this analysis is to gather as much information about the structures of your samples as possible. However, you will not be able to derive the complete structures yet by the techniques at hand. The final structures will be revealed by you in the subsequent Physicochemical Practical Course 1 (CHE213) by spectroscopic analysis.

## Collection

Hand over your separated samples to your teaching assistants — placed into vials (solids) or screw-cap vials (liquids) that are neatly labeled. You will get them back in the Physicochemical Practical Course 1 (third semester) for further analysis.

Recover the rather large amounts of solvents that you used for the extraction ( $\text{Et}_2\text{O}$ , maybe  $\text{CH}_2\text{Cl}_2$ ) by means of the rotary evaporator and collect them sorted by type. Use always the same rotary evaporator for the same type of solvent! The recovered solvents will be further purified by us and re-used in the practical course.

Solvents from chromatography are disposed of in the collecting container for solvent waste.

## Evaluation

Summarize your results in a short and lucid way in the evaluation section at the end of your notebook entry. Be aware that you will need this information again next semester (PCP1).