Hydroxy derivatives

Alcohols

Phenols

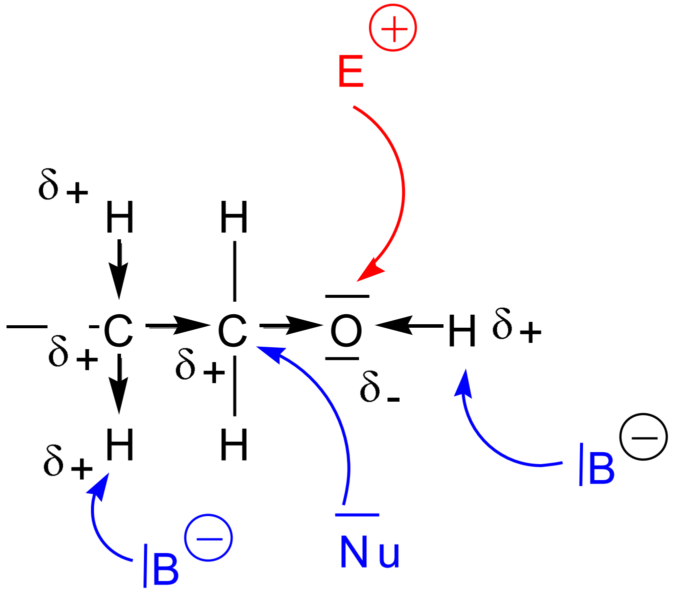
Chemical nomenclature

Hydroxy derivatives

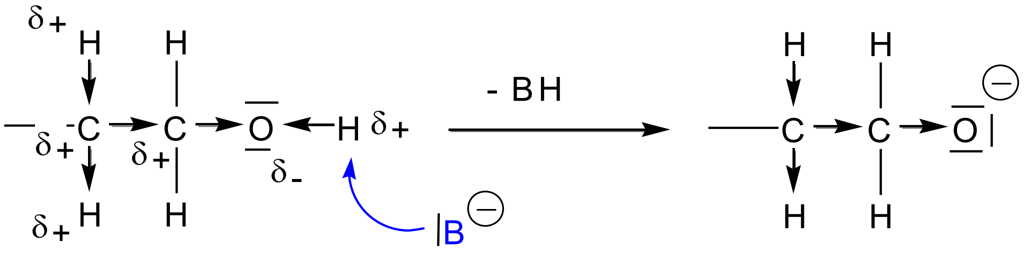
basic reactivity of alcohols:

1. **formation of alcoholates (salts)**

- for removal of proton a stronger base is needed than is basicity of the alcoxide anion



formation of alcoxide



$CH_3CH_2\text{-}OH \xrightarrow{Na} CH_3CH_2\text{-}O^- \; Na^+ + H$ sodium ethoxide

$CH_3CH_2CH_2\text{-}OH + CH_3CH_2\text{-}Mg\text{-}Cl \longrightarrow CH_3CH_2CH_2\text{-}O^- \; MgCl^+ + CH_3CH_3$

propoxide magnesium chloride

$CH_3CH_2\text{-}OH + NaH \longrightarrow CH_3CH_2\text{-}O^- \; Na^+ + H_2$

Hydroxy derivatives

Acidity of alcohols

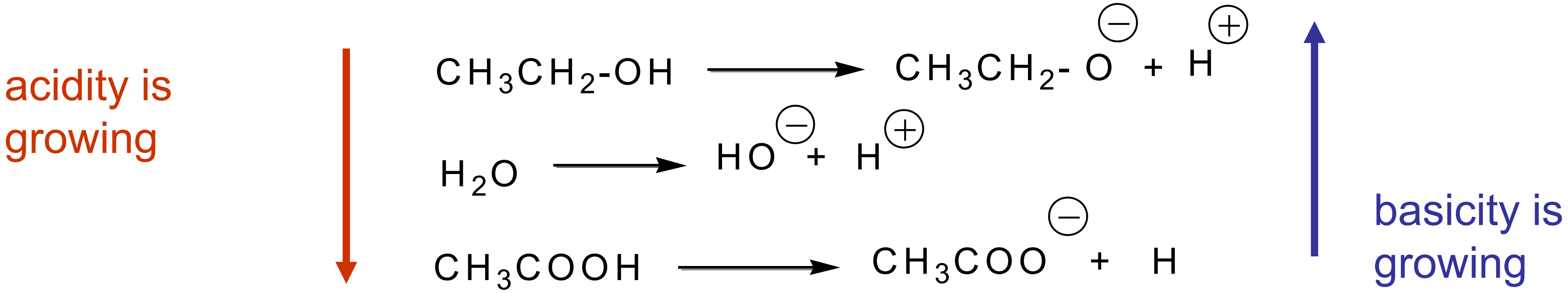
Alkohol	**pK$_a$**
methanol	15,1
ethanol	15,9
propanol	16,1
i- propanol	17,1
t- butanol	19,2

The lower is pK$_a$, the stronger is the acid

Acidity is influenced by the structure of the alcohol

Alcohols are relatively week acids, less acidic than water

Compare the acidity with other acids and take to considation, that the more acidic is the acid, the less acidic is its conjugated base



acidity is growing

$$CH_3CH_2\text{-}OH \longrightarrow CH_3CH_2\text{-}O^{\ominus} + H^{\oplus}$$

$$H_2O \longrightarrow HO^{\ominus} + H^{\oplus}$$

$$CH_3COOH \longrightarrow CH_3COO^{\ominus} + H$$

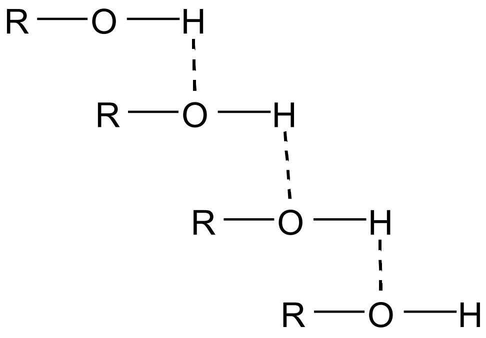
basicity is growing

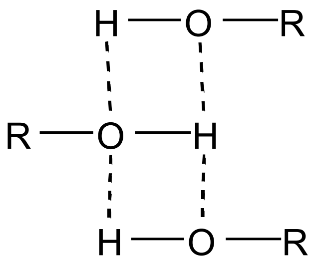
Hydroxy derivatives

Physical properties of alcohols and comparison with hydrocarbons

Uhlovodík	Teplota varu [^{o}C]	Alkohol	Teplota varu [^{o}C]
methan	- 161	methanol	64
ethan	- 88	ethanol	78
propan	- 42	propanol	79
butan	- 0,5	butanol	118
pentan	36	pentanol	138
hexan	68	hexanol	156
heptan	98	heptanol	176

Formation of hydrogen bonding (various types)





formation of agregates

Spektral analysis – Infrared spectrum

During measurement of the spectrum the compound is irradiated and interaction with the radiation is observed. The way the energy interacts with the matter depends upon the wavelength. Relation between wavelenght and energy is given by Planck equation:

$$\boxed{E = h \cdot \nu = h \cdot \frac{c}{\lambda}}$$

E is energy
h Planck constant
c rate of light in vacuum
ν frequence of radiation
λ wavelength

Spectrum is record of absorbance dependence upon the wavelength of radiation

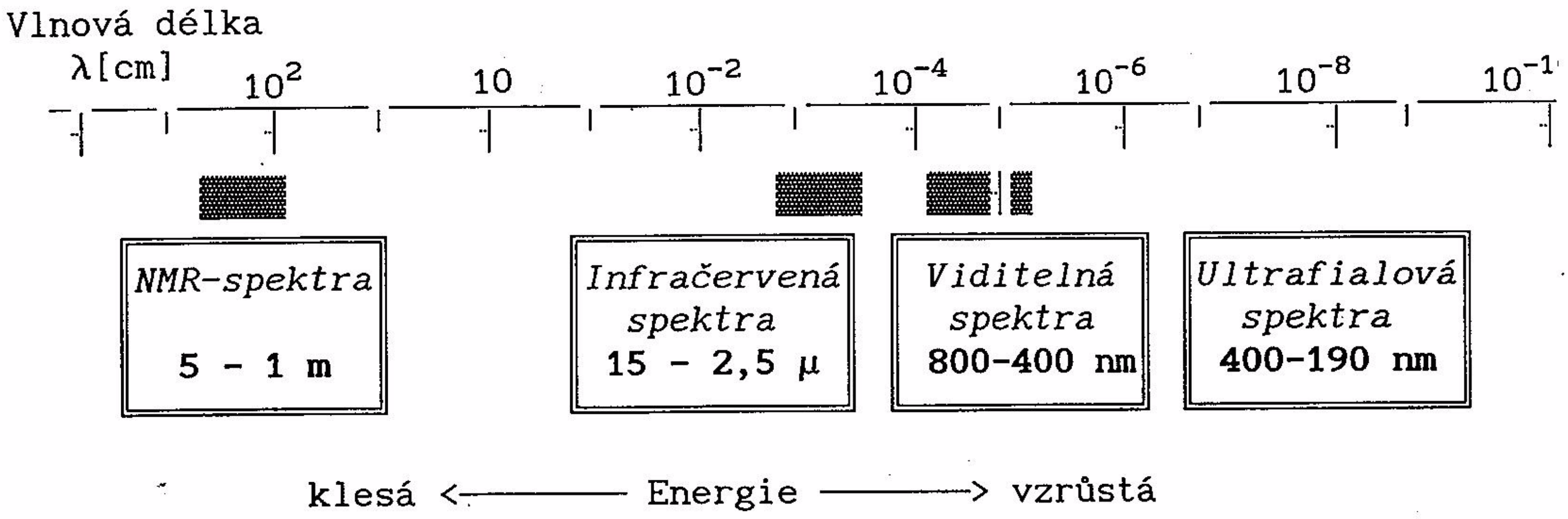
$$A = -\log \frac{I}{I_o} = \varepsilon \cdot c \cdot l$$

$$A = -\log \frac{I}{I_o} = -\log T$$

$$T = \frac{I}{I_o}$$

A is absorbance
I_o,I intensities of light before and after passing the measured matter
ε molar extinction coeficient
c molar concentration of measured matter
l thickness of the meassured layer in cm
T transmittance

Dependence of energy upon the wavelenght and possible spectra in shown regions



Energy of infrared wavelenght is small (between 4-40 kJ/mol) and corresponding is also small interaction of waves with molecules.

After irradiation molecules are exicitated from their basic vibration states to excitated states. Different energy difference corresponds to various bonds, which shows absorption at different wavelength.

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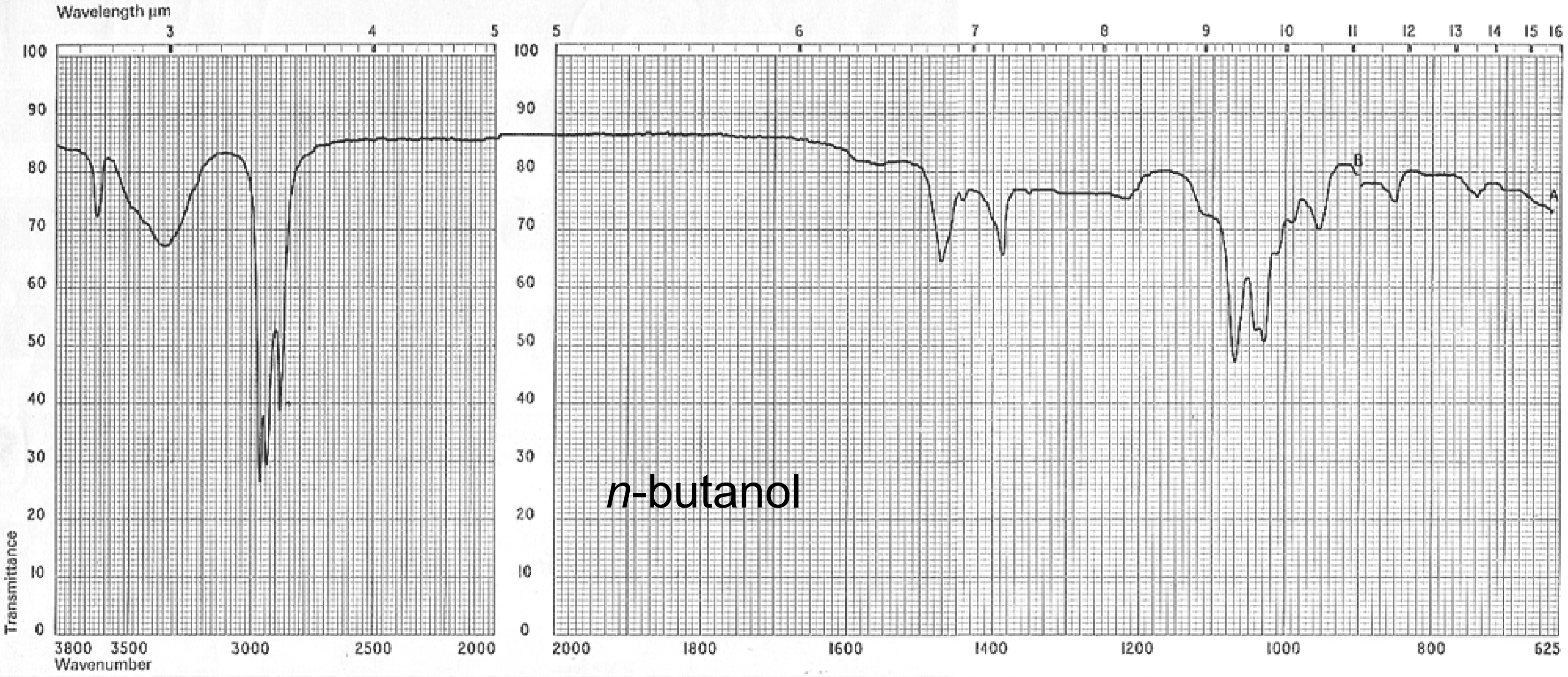
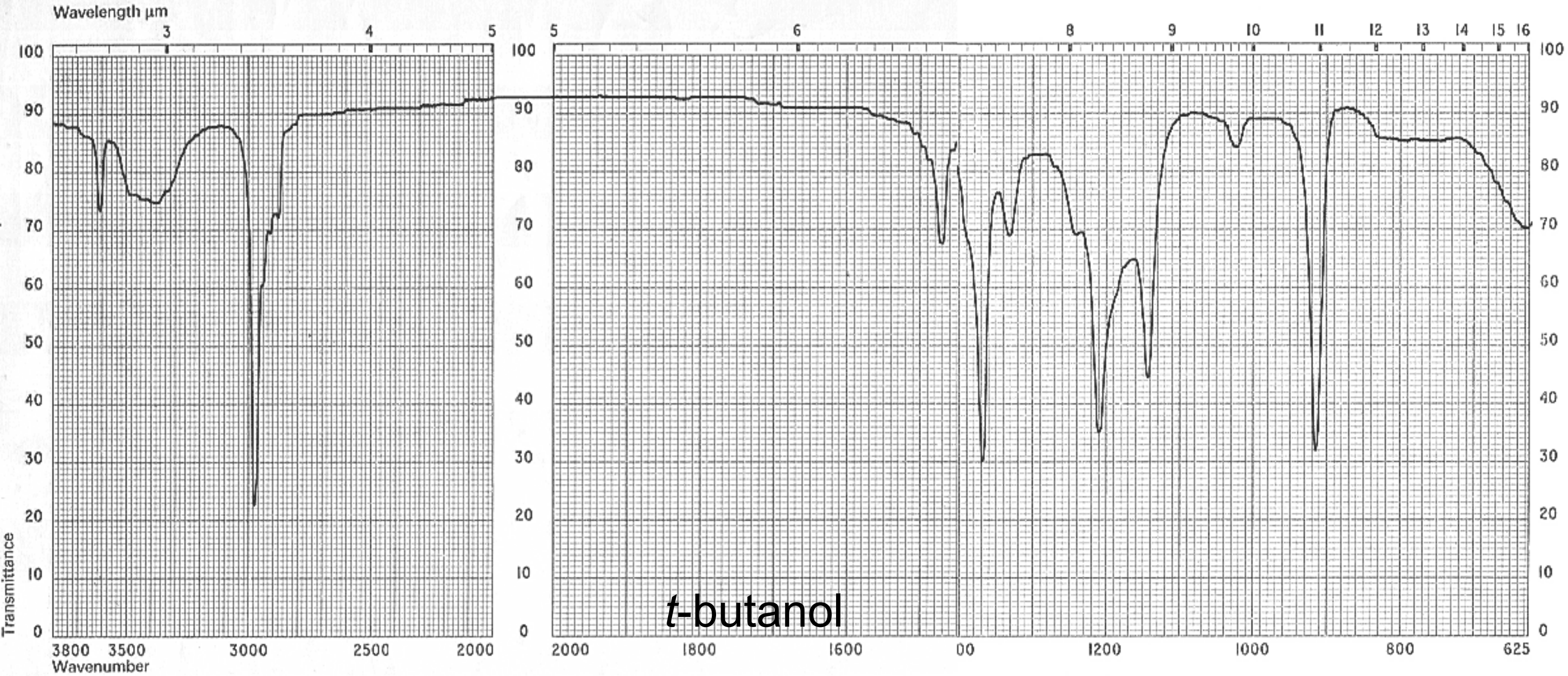


Sample	*n* – BUTANOL A. 2% CS_2 SOLUTION B. 2% CCL_4 SOLUTION
Formula	$CH_3CH_2CH_2CH_2OH$
Phase	LIQUID
Thickness	A. 0·12 m.m. B. 0·15 m.m.
Reference	A. CS_2 , B. CCL_4
Operator	
Date	

8



Sample	tert – BUTANOL 2% CCL_4 SOLUTION
Formula	$CH_3 - \overset{CH_3}{\underset{CH_3}{C}} - OH$
Phase	LIQUID
Thickness	0·2 m.m.
Reference	CCL_4
Operator	
Date	

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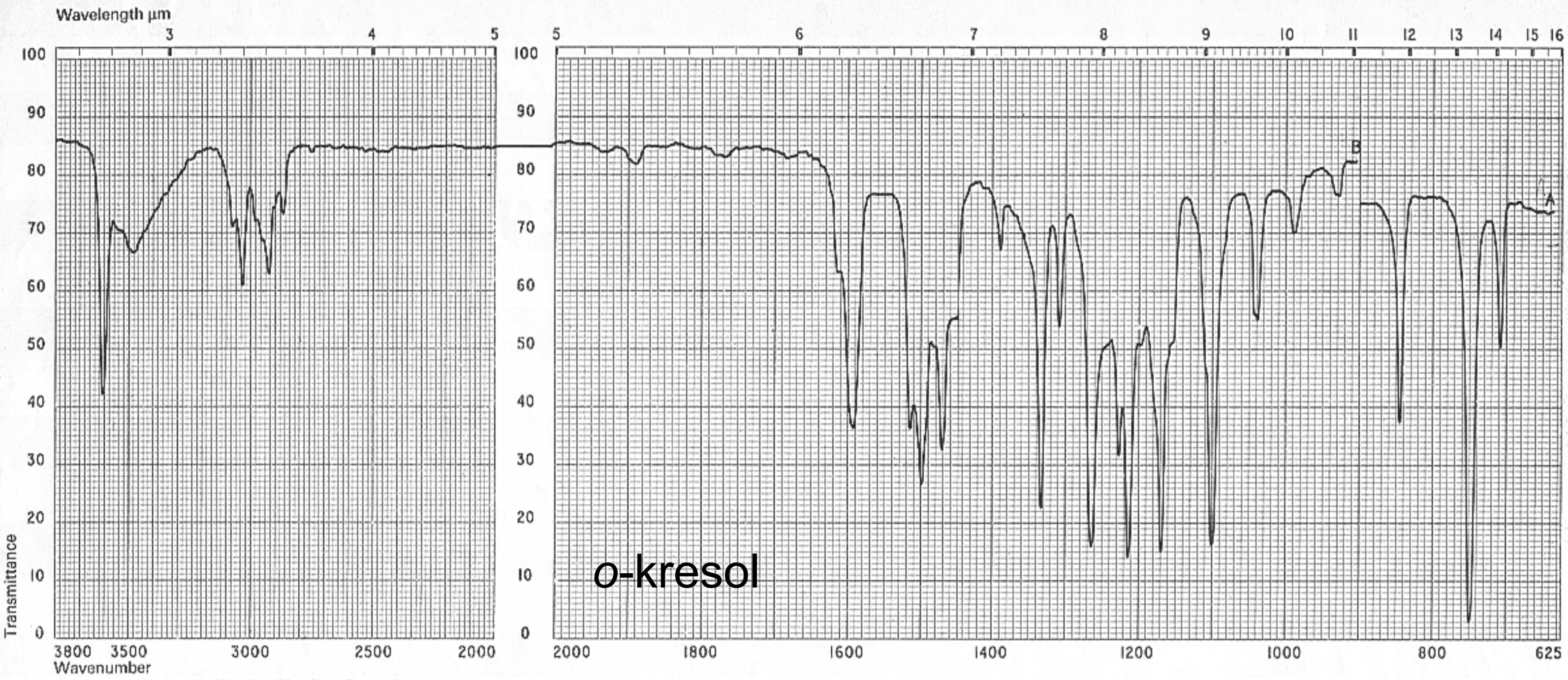
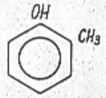


o-kresol

Sample
O-CRESOL
A. 4% CS_2 SOLUTION
B. 4% CCL_4 SOLUTION

Formula



Phase
LIQUID

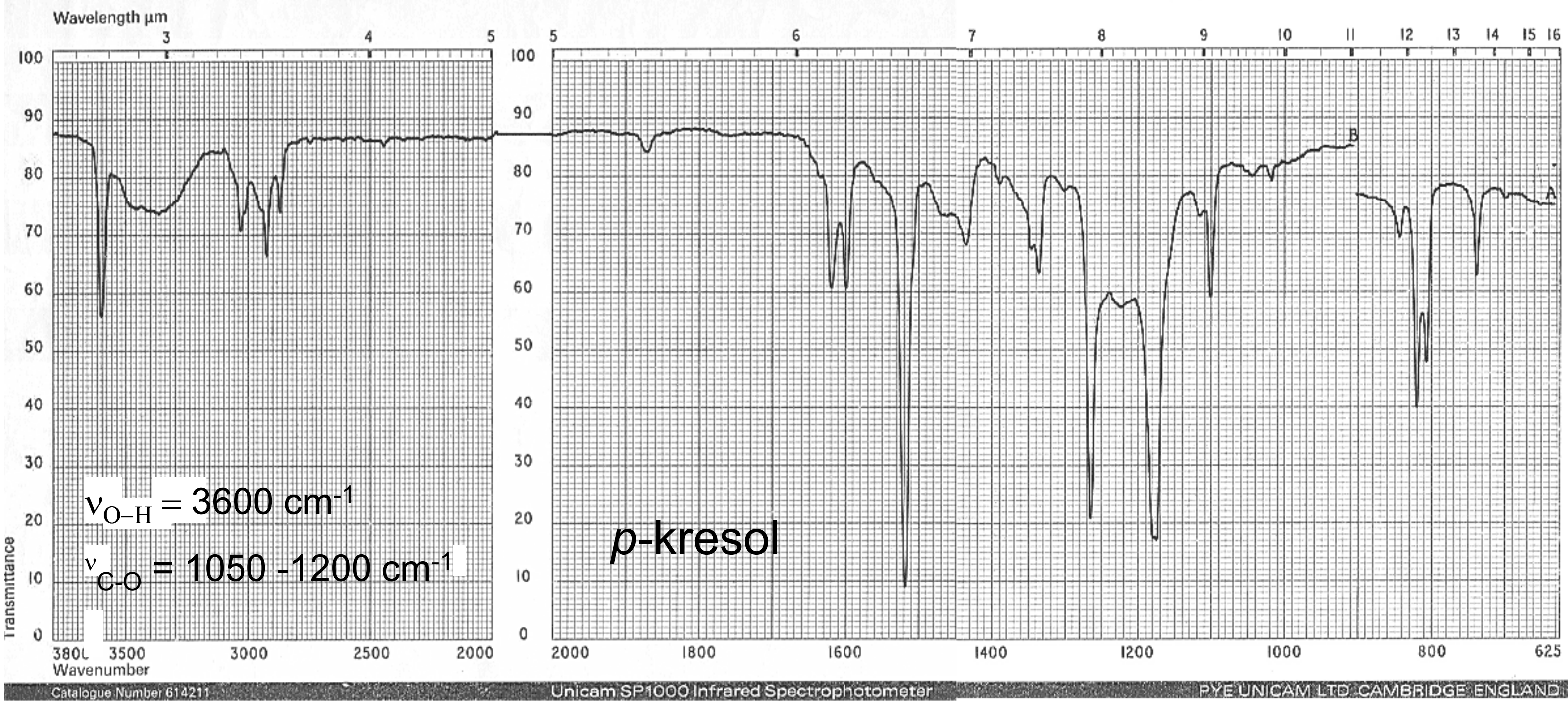
Thickness
A. 0·12 m.m.
B. 0·15 m.m.

Reference
A. CS_2 , B. CCL_4

Operator

Date

11



ν_{O-H} = 3600 cm^{-1}

ν_{C-O} = 1050 -1200 cm^{-1}

p-kresol

Sample
P-CRESOL
A. 2% CS_2 SOLUTION
B. 2% CCL_4 SOLUTION

Formula

Phase
LIQUID

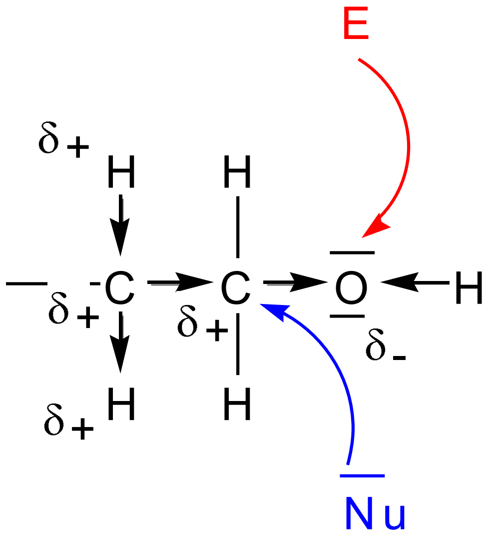
Thickness
A. 0·12 m.m.
B. 0·15 m.m.

Reference
A. CS_2 , B. CCL_4

Operator

Date

Hydroxy derivatives



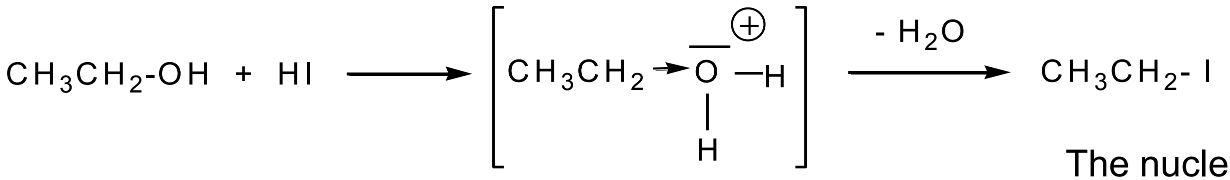
basic reactivity of alcohols:

2. nucleophilic substitution of hydroxy group

for the substitution acid catalyst is needed

$$CH_3CH_2\text{-}OH + Na^+ I^- \rightleftharpoons CH_3CH_2\text{-}I + Na^+ OH^-$$

even strong iodide anion is not able to substitute OH group, because strong leaving nucleophile is pushing the reaction back



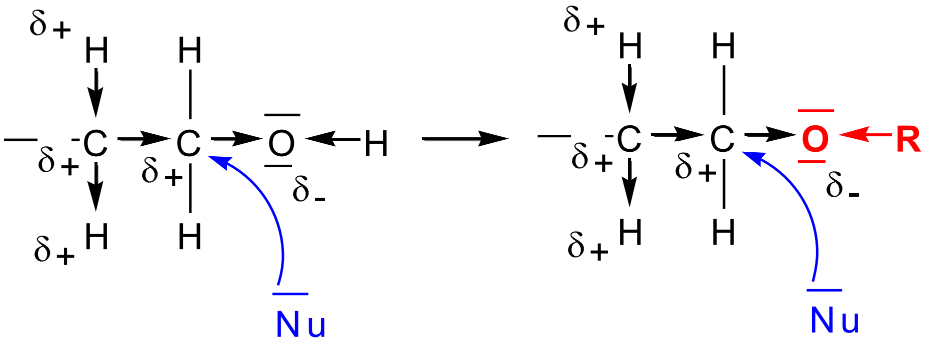
$$CH_3CH_2\text{-}OH + HI \longrightarrow \left[CH_3CH_2 \rightarrow \overset{\oplus}{O}(H)\text{—}H \right] \xrightarrow{-\ H_2O} CH_3CH_2\text{-}I$$

The nucleophility of the leaving OH anion was neutralized by acid (leaving water is a weak nucleophile)

As an acid may serve also Lewis acid:

Al_2O_3, $ZnCl_2$, BF_3 ....

Hydroxy derivatives



basic reactivity of alcohols:

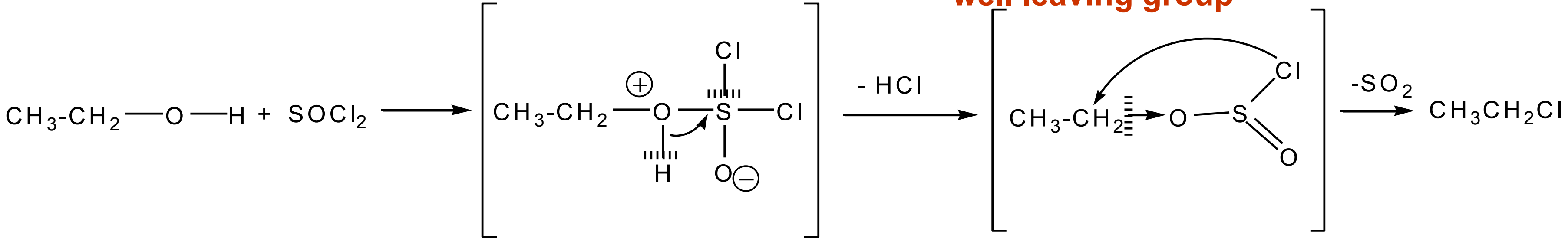
2. nucleophilic substitution of OH group

- OH group can be transferred into an easy leaving group

$R\text{-}CH_2CH_2\text{-}OH + R^1\text{-}SO_2Cl \xrightarrow{-HCl} R\text{-}CH_2CH_2\text{-}OSO_2R^1 \xrightarrow{+Nu} R\text{-}CH_2CH_2\text{-}Nu + R^1\text{-}SO_3^-$

$R^1 = CH_3\text{-}, p\text{-}CH_3\text{-}Ph\text{-}$ ....

alkyl(aryl)sulfonate anion is only very weak nucleophile (it is salt of very strong acid) and therefore **well leaving group**



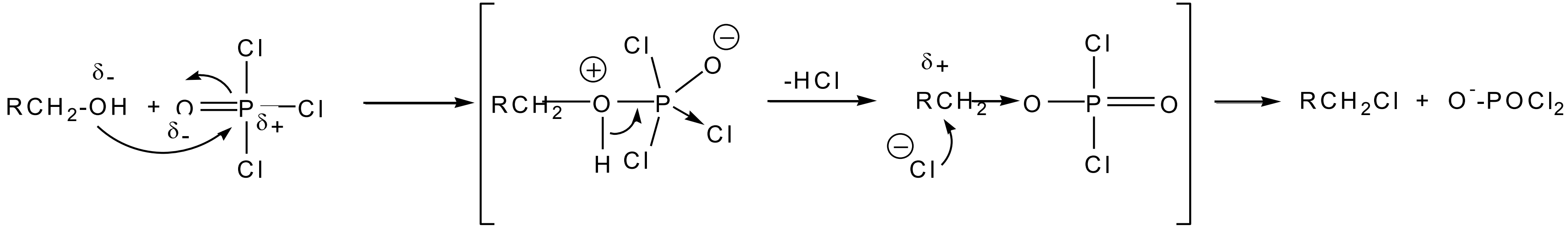
Hydroxy derivatives

For the substitution of hydroxy group for a halogen serve very often halogenides of sulfur and phosphorus (these at first are forming esters with alcohols and released halogen anion). The ester group in the form of anion belong to the very good leaving groups and therefore are substituted by mentioned halogen anion.

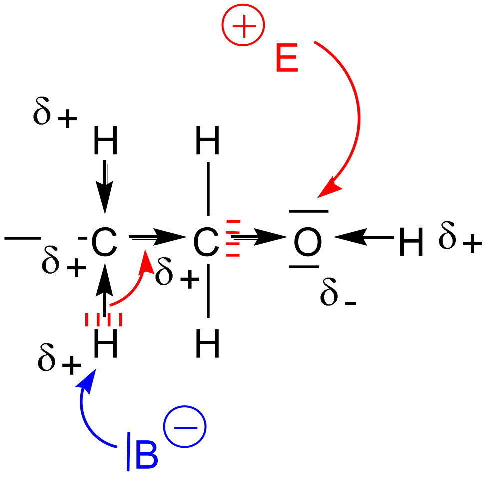
$$RCH_2\text{-}OH + PCl_5 \longrightarrow RCH_2\text{-}Cl + POCl_3 + HCl$$

$$3\ RCH_2\text{-}OH + POCl_3 \longrightarrow 3\ RCH_2\text{-}Cl + H_3PO_4$$

$$3\ RCH_2\text{-}OH + PBr_3 \longrightarrow 3\ RCH_2Br + H_3PO_3$$



Hydroxy derivatives

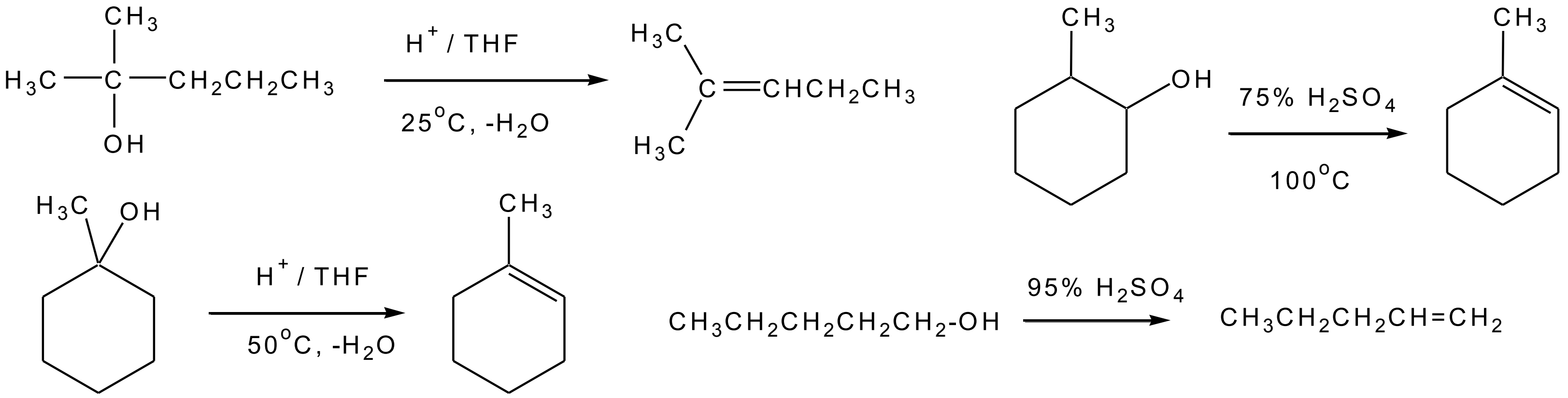


basic ways of transformation:

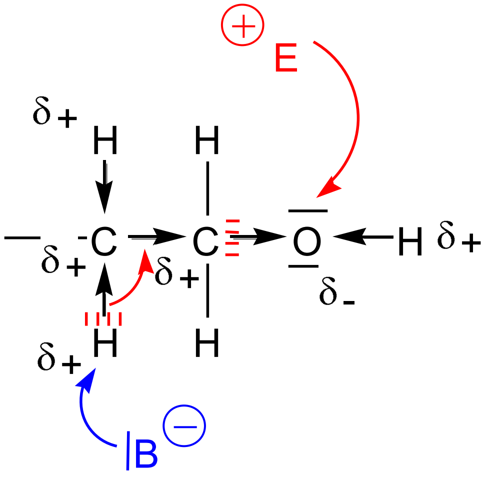
3. water elimination

acid catalysed reactions are characteristic for *t*-alcohols (here they compet with substitution), secondary and primarily need harsh conditions

they obey Saytzeff rule (thermodynamical^{c}olefines are formed)



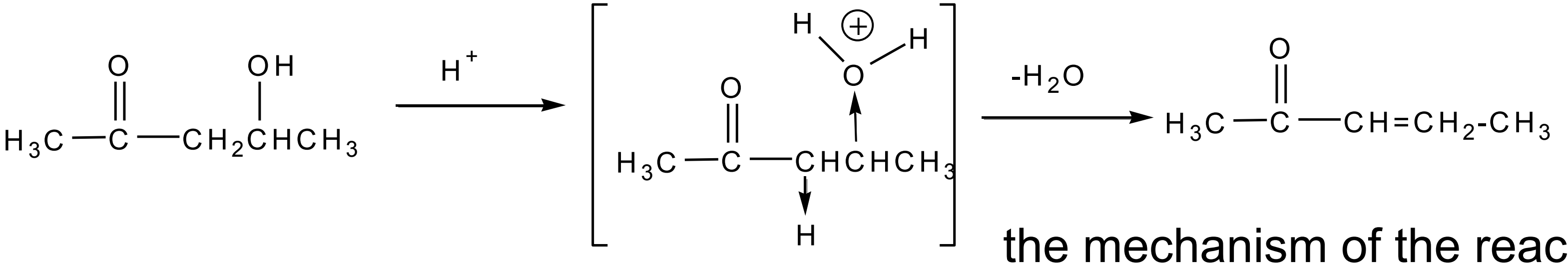
Hydroxy derivatives



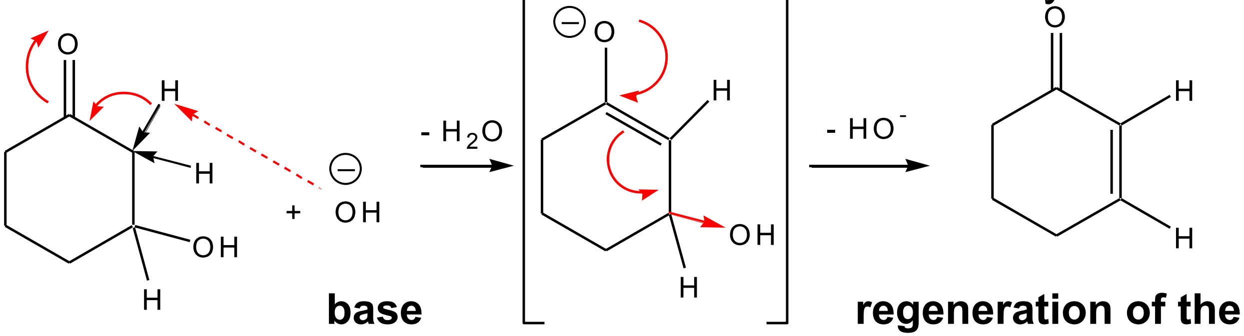
basic ways of transformation:

3. water elimination

acid catalysed dehydratations are characteristic also for the compounds where by elimination can be create a double bond in conjugation with already existing double bond



the mechanism of the reaction may be also E1cB



base

regeneration of the base

Hydroxy compounds

OXIDATION OF ALCOHOL

Primary alcohols $\xrightarrow{\text{oxidation}}$ Aldehydes $\xrightarrow{\text{oxidation}}$ Carboxylic acids

Secondary alcohols $\xrightarrow{\text{oxidation}}$ Ketones

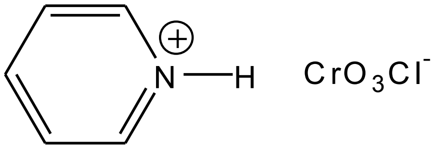
Tertiary alcohols $\xrightarrow{\text{oxidation}}$ they do not oxidace

Oxidation agents:

$Na_2Cr_2O_7$ / acetic acid / water (cheap oxid.agent),

CrO_3/ H_2SO_4 / water

PCC (pyridinium-chlorchromate) / dichlormethane (very good agent)



Hydroxy compounds

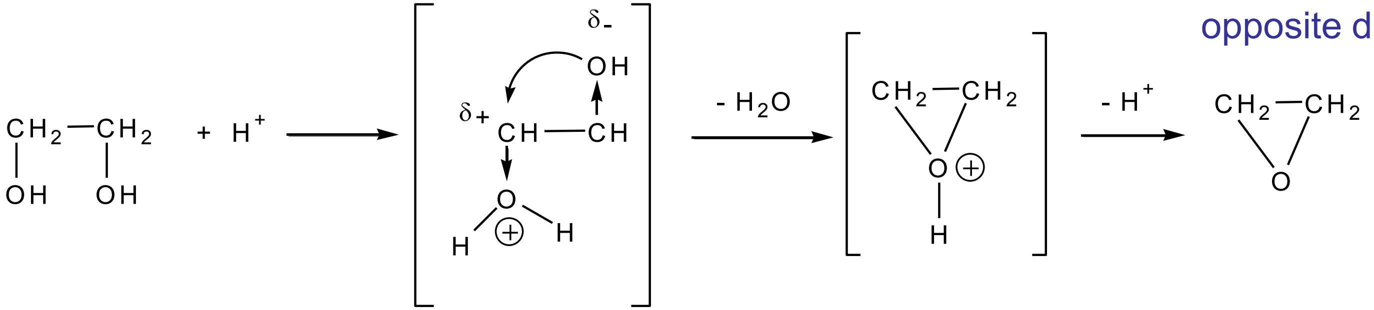
Dioles

1,2 – dioles = glycoles

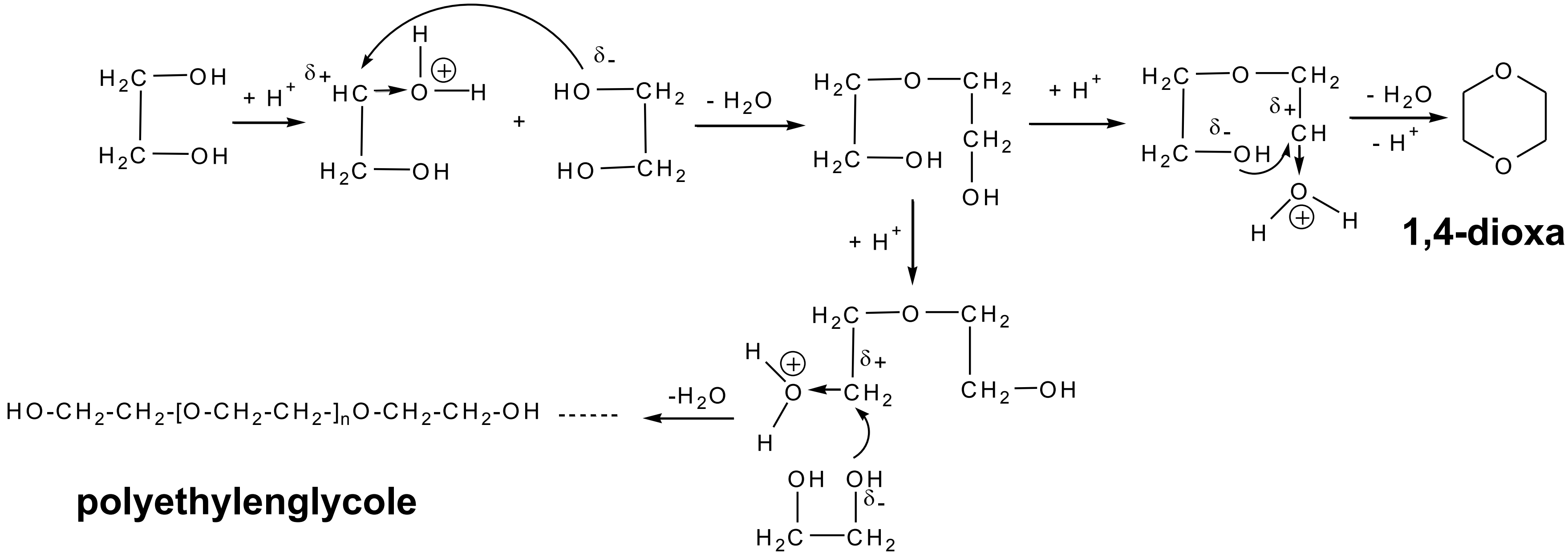
Reactive compound, which under various conditions can create several types of products:

formation of epoxides

reaction can go also by an opposite direction



oxirane
ethylenoxide
epoxyethane



$HO\text{-}CH_2\text{-}CH_2\text{-}[O\text{-}CH_2\text{-}CH_2\text{-}]_nO\text{-}CH_2\text{-}CH_2\text{-}OH$ ------

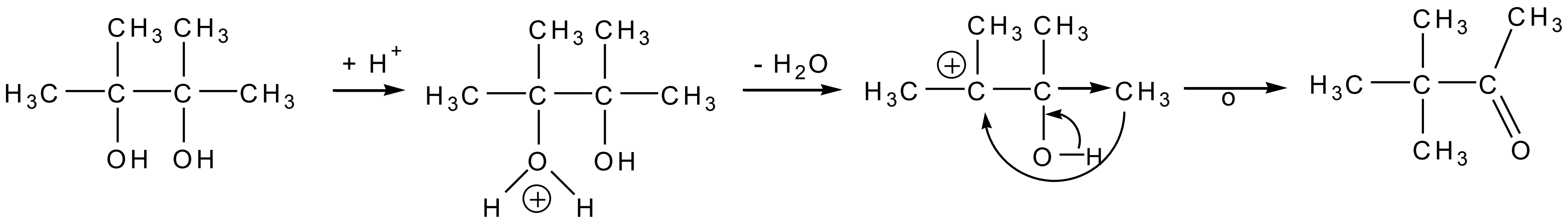
1,4-dioxane

polyethylenglycole

Hydroxy derivatives

glycoles with *t*-carbon atoms can undergo in an acidic medium

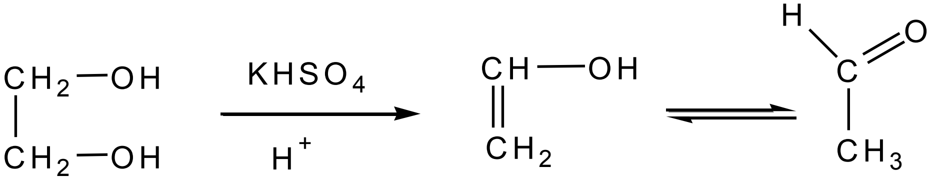
pinacol rearrangement



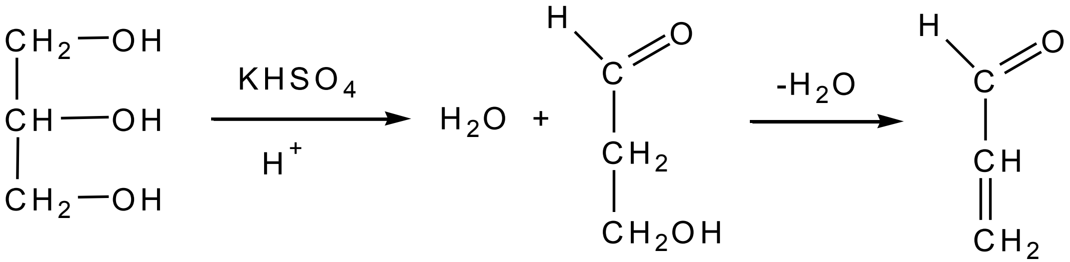
pinacol

pinacolon
pinacoline
3,3-dimethylbutan-2-on

dehydration of vicinal dioles



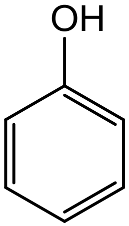
acetaldehyde



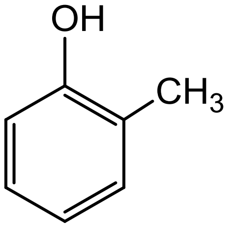
acrolein (propenal)

Hydroxy derivatives

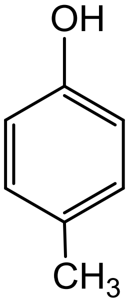
PHENOLES



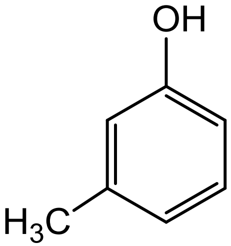
fenol



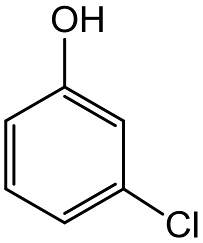
***ortho*-cresol**



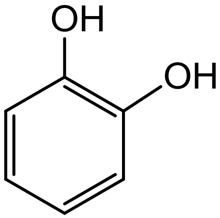
***p*-cresol**



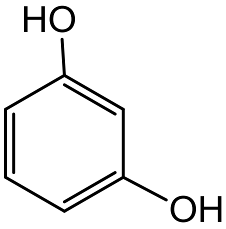
***m*-cresol**



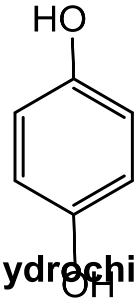
3-chlorophenol



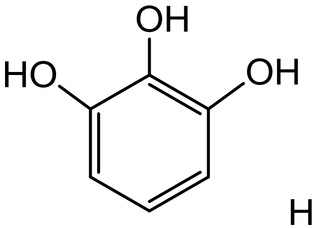
pyrocatechine (-ol)



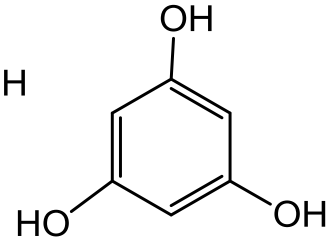
resorcine (-cinol)



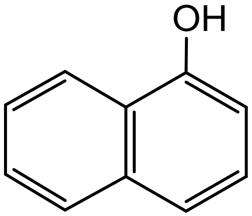
hydrochinone



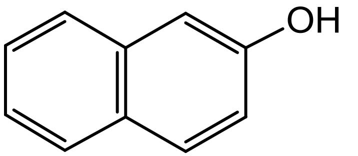
pyrogallole



fluoroglucinol



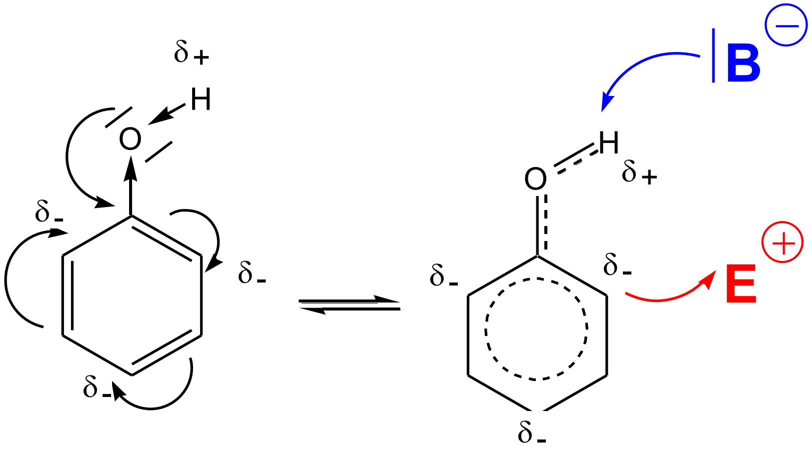
α-naphtole



β- naphtole

Hydroxy derivatives

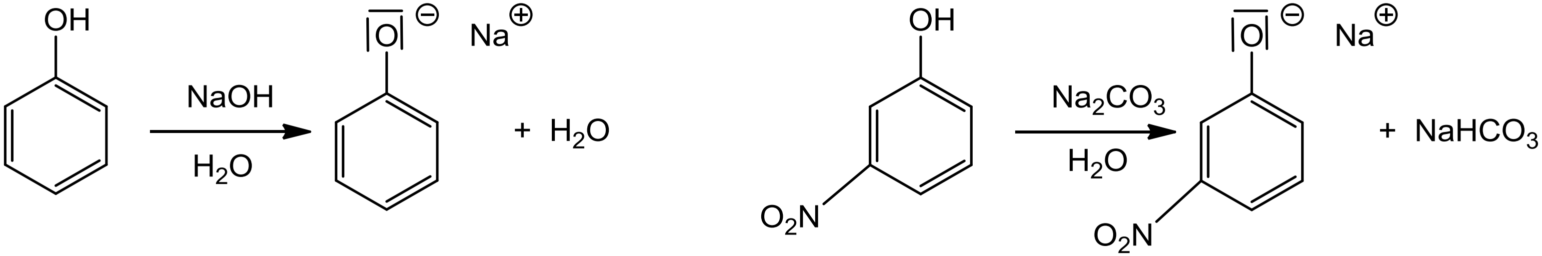
PHENOLES



reactivity of phenols:

1. **acidity of hydrogen atom**
2. ability to react in *o*- and *p*- position activated for S_EAr
3. ability to react with nucleophile in neigbourhood of oxygen atom is very limited

Phenoles are able to form salts – phenolates even with weak bases and in water



sodium phenolate

Hydroxy derivatives

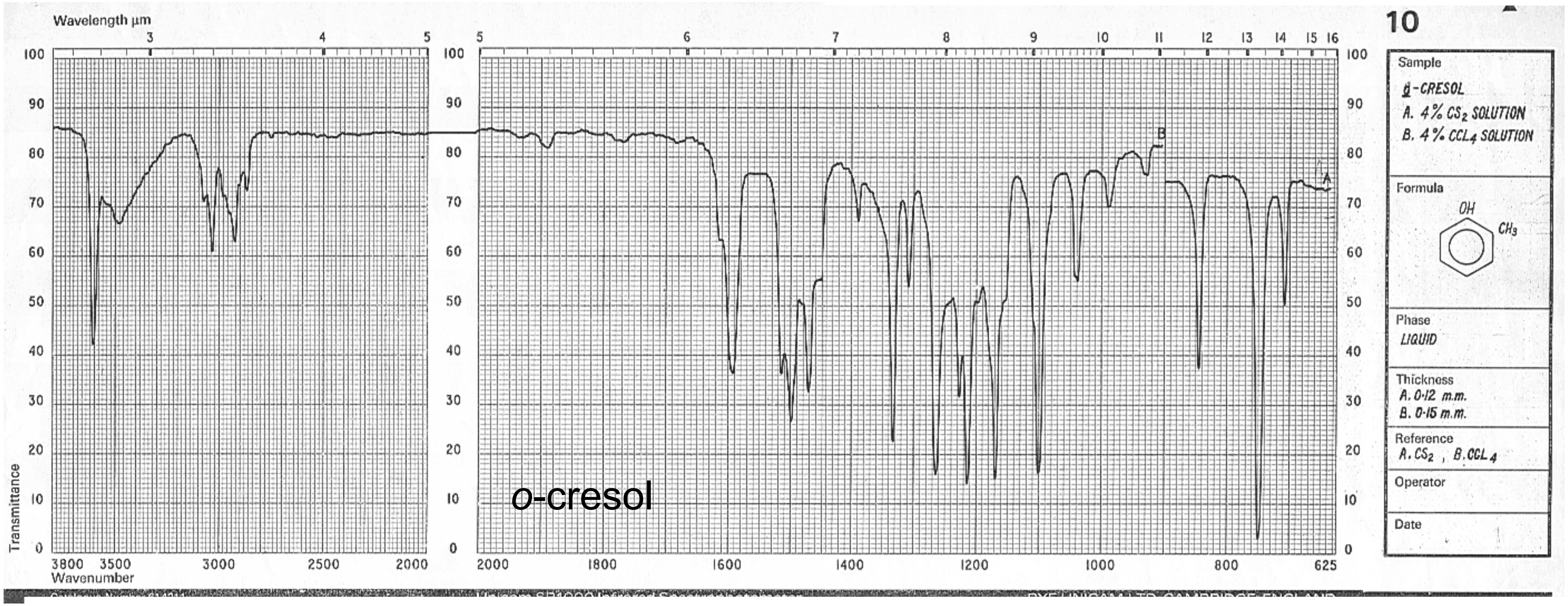
Phenol	pK_a
phenol	9,88
p-cresol	10,17
o-cresol	10,20
p-methoxyphenol	10,21
p-cyanophenol	7,95
p-chlorophenol	9,20
p-nitrophenol	7,15
2,4-dinitrophenol	3,95
2,4,6-trinitrophenol	0,37
1-naphtol	9,30
2-naphtol	9,55

Acidity of phenols

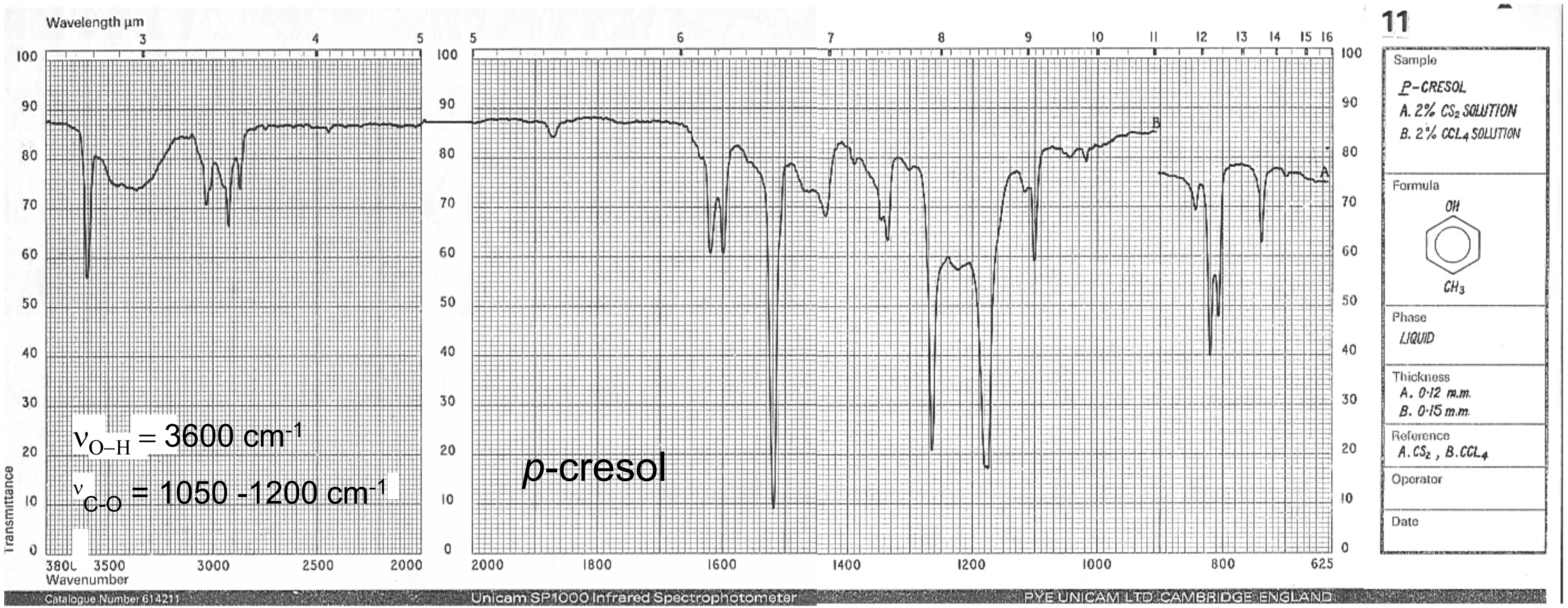
INFLUENCE OF SUBSTITUTION

!!! compare acidity with alcohol !!!

pK_a ethanol 15,9



o-cresol



ν_{O-H} = 3600 cm^{-1}

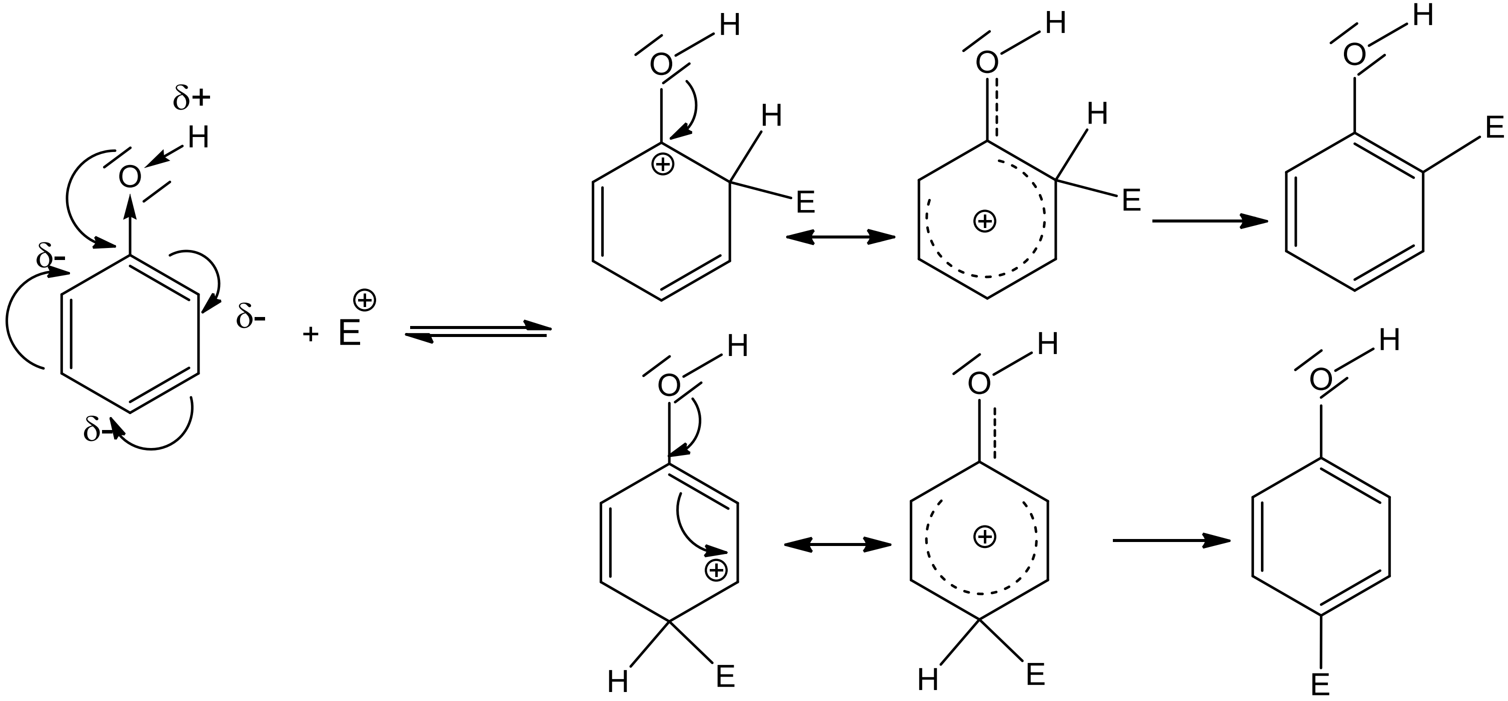
ν_{C-O} = 1050 -1200 cm^{-1}

p-cresol

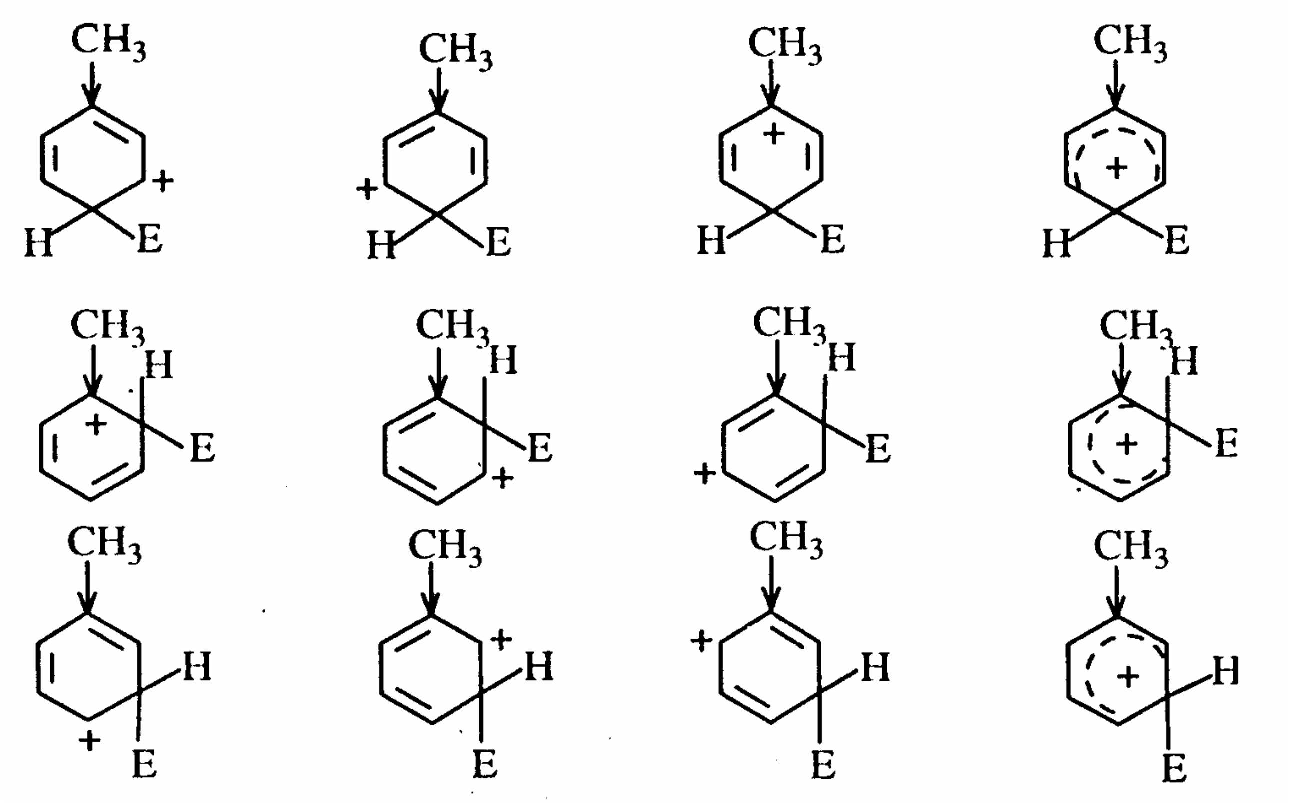
Hydroxy derivatives

reactivity of phenols:

1. acidity of hydrogen atom
2. **ability to react in *o-* and *p-* position activated for S_EAr**
3. ability to react with nucleophile in neigbourhood of oxygen atom is very limited



Hydroxy derivatives



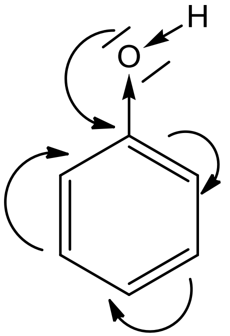
Donating group is directing entrance of electrophile to *ortho*- or *para*-position

Hydroxy group, in comparison with donating methyl group is stronger donor. You can notice **–I efect, but +M efect** is prevailing for **stabilization σ–complex in *ortho* and *para* pozition** and therefore is directing to these positions.

Hydroxy derivatives

reactivity of phenols:

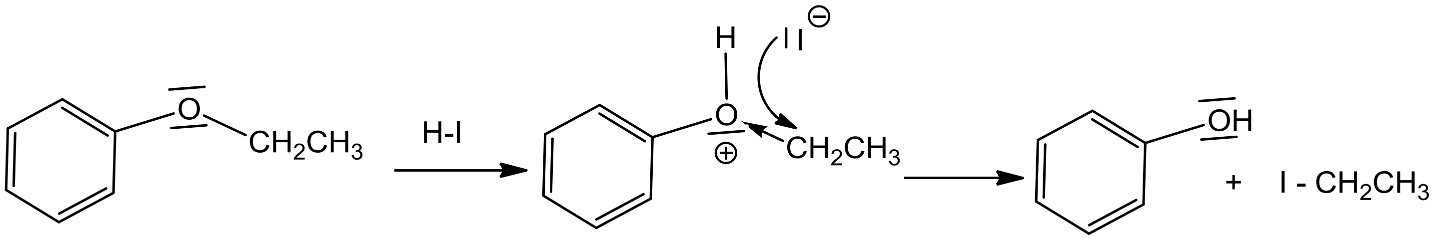
1. acidity of hydrogen atom
2. ability to react in *o*- and *p*- position activated for S_EAr
3. **ability to react with nucleophile in neigbourhood of oxygen atom is very limited**



the bond between oxygen and carbon atom of aromatic system is reinforced by a mesomeric effect of oxygen atom – the bond is difficult to split

$$Ar{-}OH \;+\; PCl_5 \xrightarrow[\Delta T]{\text{melting}} Ar{-}Cl \;+\; POCl_3 \;+\; HCl$$

Proof

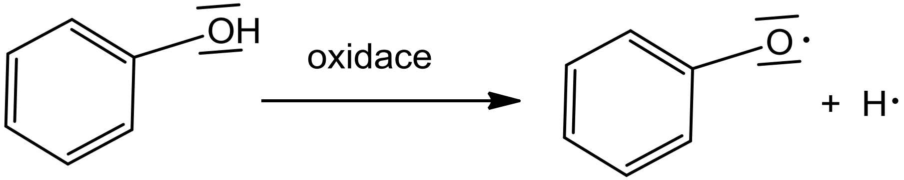


the bond between carbon atom of alifatic system undergoes splitting (but no bond between oxygen and sp^2 carbon atom)

Hydroxy derivatives

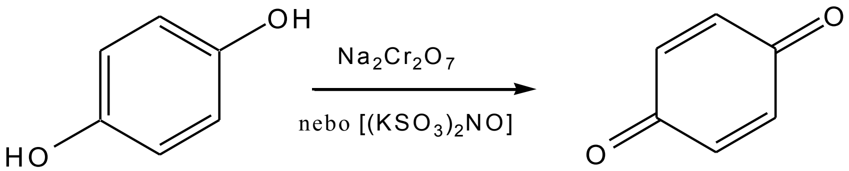
Oxidation of phenols

metal oxides (PbO_2, MnO_2, Fe^{3+}), electrochemically



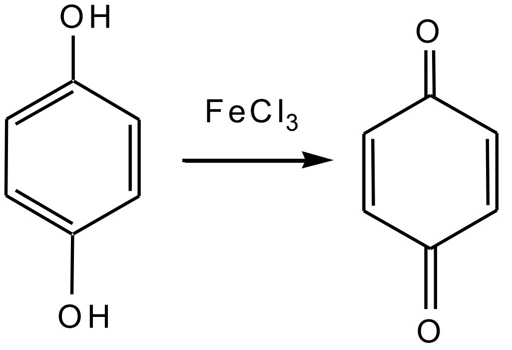
realtively stabil radical is formed

(application as radical scavenger)

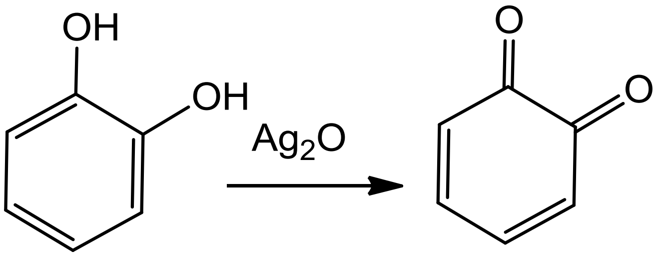


very easy proceeds oxidation of dihydroxy compounds

under formation of **QUINONES**



***p*-benzoquinone**

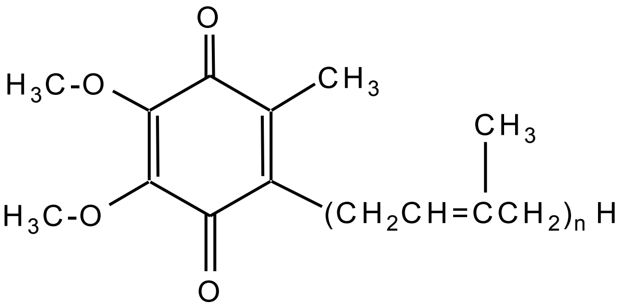


***o*-benzoquinone**

Hydroxy derivatives

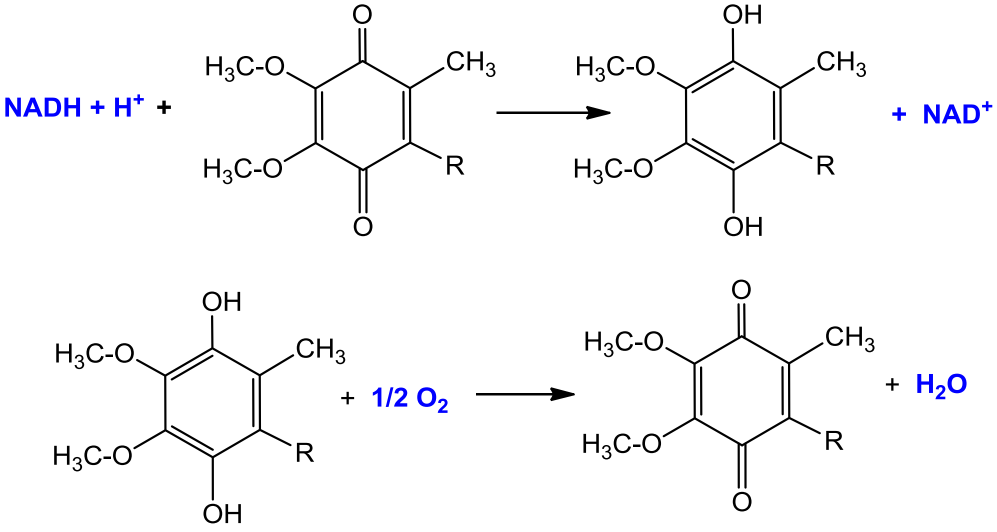
Quinones are important also in biological systems

Their redox properties are playing important role in cells; they are biochemical oxidation agents (they transfer electrones during energy creation)



n = 1 - 10

ubiquinone (coenzym Q)



$$NADH + 1/2\ O_2 \longrightarrow NAD^+ + H_2O$$

Ethers

Nomenclature

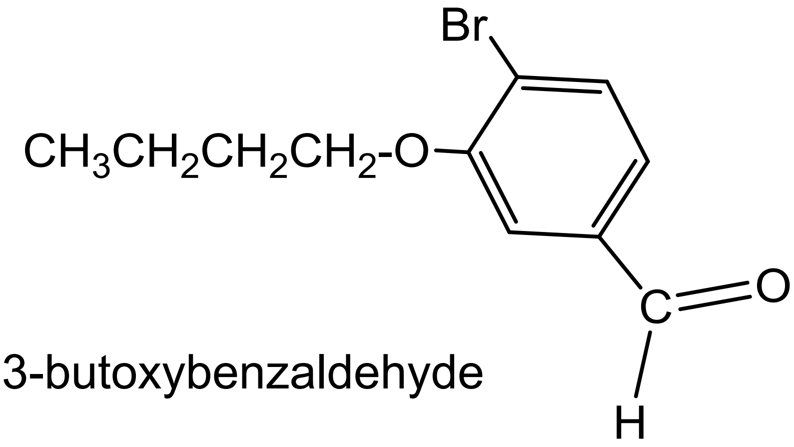
alkylalkylether dimethylether

diethylether $CH_3\text{-}CH_2\text{-}O\text{-}CH_2CH_3$

prefix **alkoxy-** (the base for the name is the bigger part of molecule)

$CH_3 - O - CH_2CH_2CH_2COOCH_2CH_3$

ethyl-4-methoxybutanoate

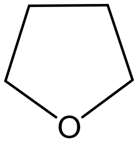


4-bromo-3-butoxybenzaldehyde

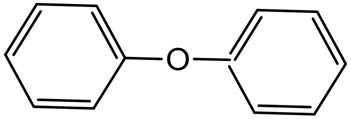
Ethery

Ethery jsou těkavé látky: srovnej teplotu varu s teplotou varu alkoholu

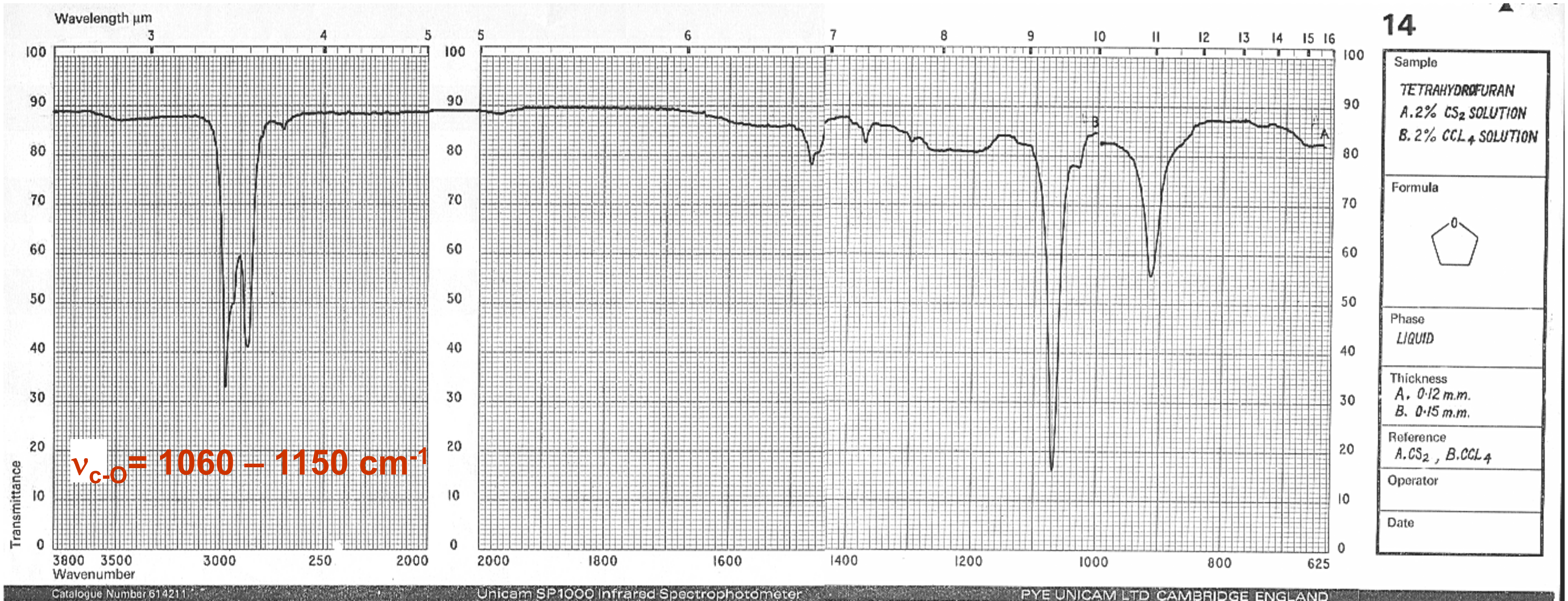
diethylether	b.v. 34°C
ethanol	b.v. 78°C



tetrahydrofuran THF b.v. 67°C

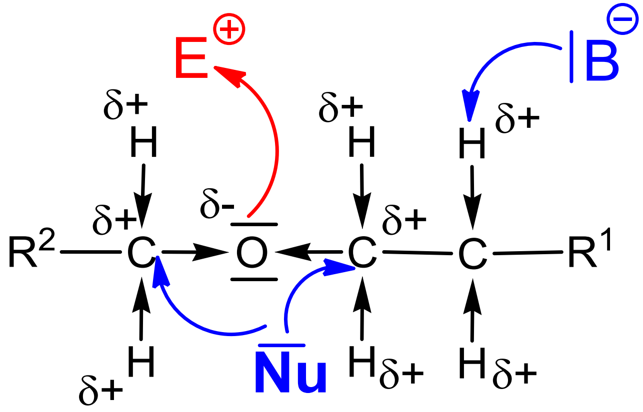


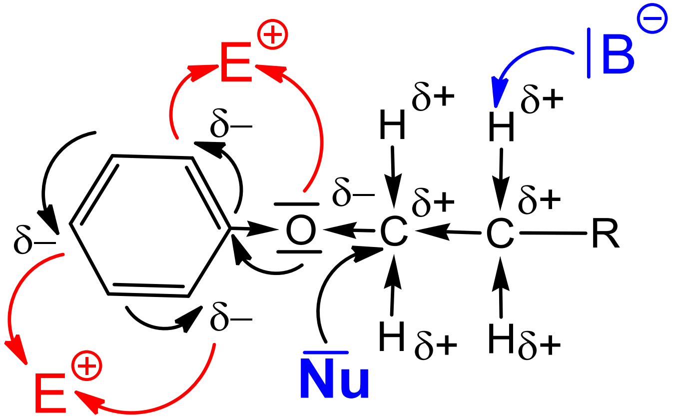
difenylether b.v. 259°C



$\nu_{C\text{-}O} = 1060 – 1150\ cm^{-1}$

Ethers





ethers belong to **low reactive compounds** and therefore are often used as solvents

expected reactivity :

1. interaction of free electron pairs with electrophiles
2. elektron gap at C atom in the neigbourhood of oxygen offers possibility of nucleophilic atack
3. hydrogen atom in β-position may be attacked by a base in elimination reactions