Ethers

Nomenclature

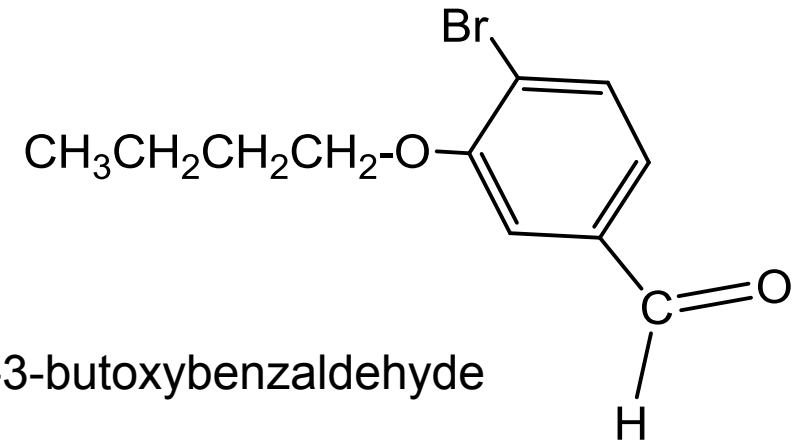
alkylalkylether dimethylether

diethylether CH_3-CH_2-O-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



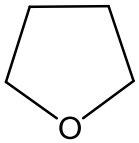
4-bromo-3-butoxybenzaldehyde

Ethers

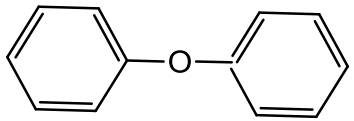
Ethers are very volatile: compare boiling temperature with alcohol

diethylether b.p. 34°C

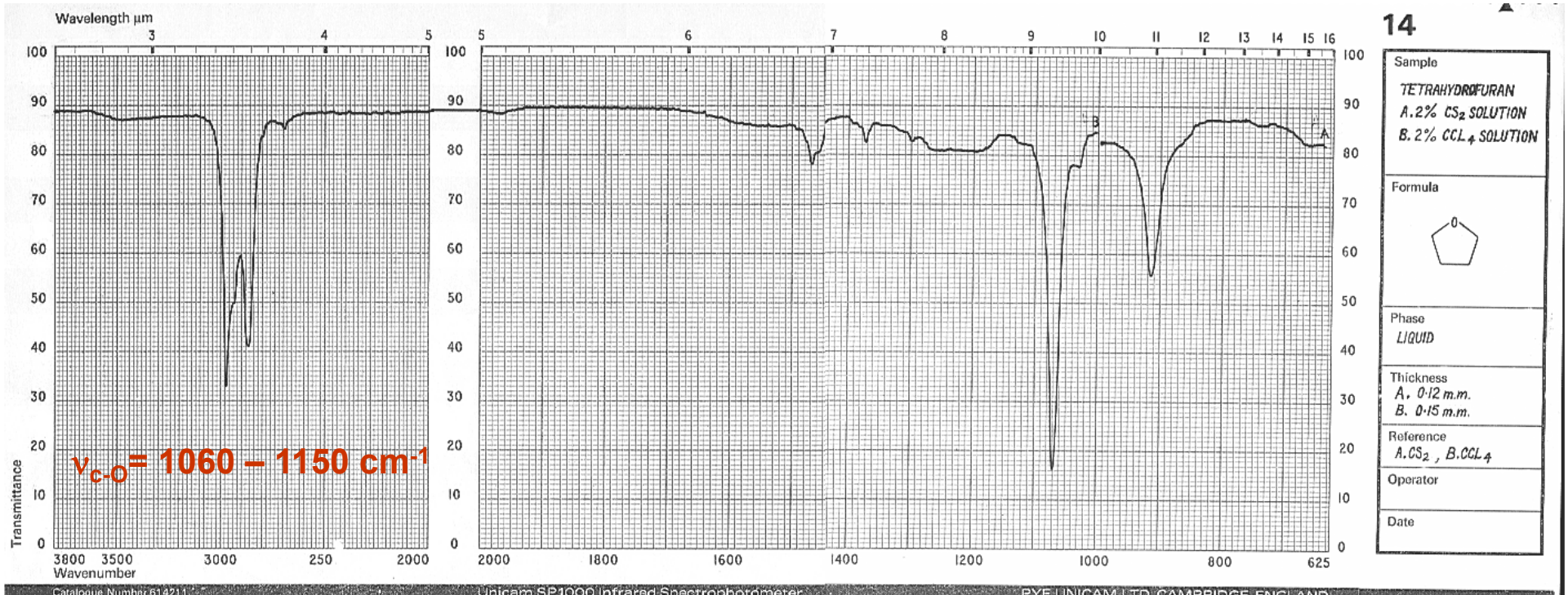
ethanol b.p. 78°C



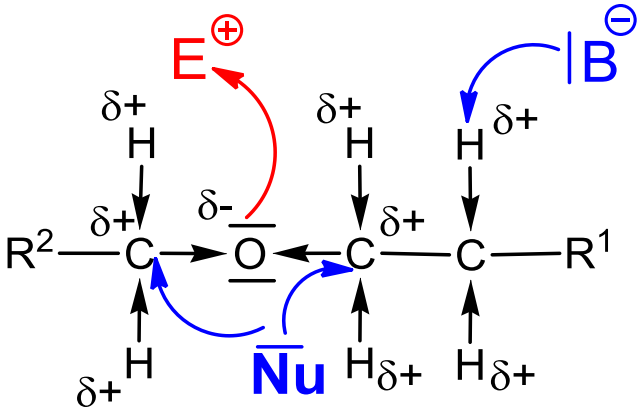
tetrahydrofuran THF b.p. 67°C

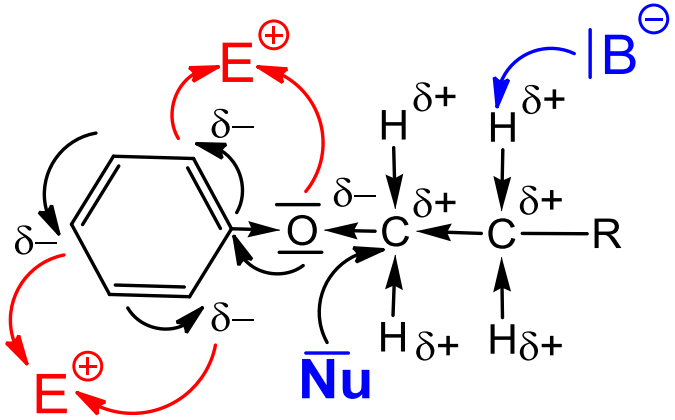


diphenylether b.p. 259°C



Ethers



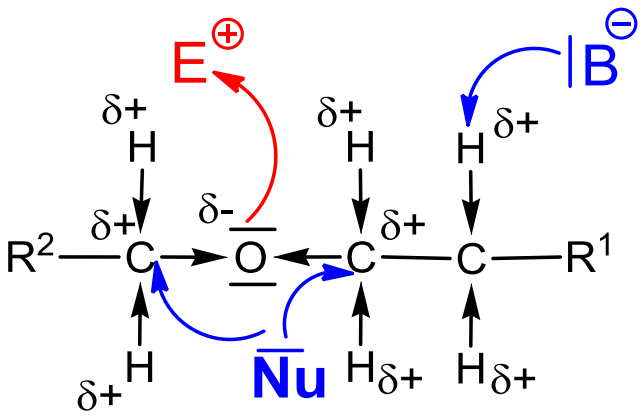


ethers belong to **low reactive compounds** and therefore are often used as solvents

expected reactivity :

1. interaction of free electron pairs with electrophiles
2. electron 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

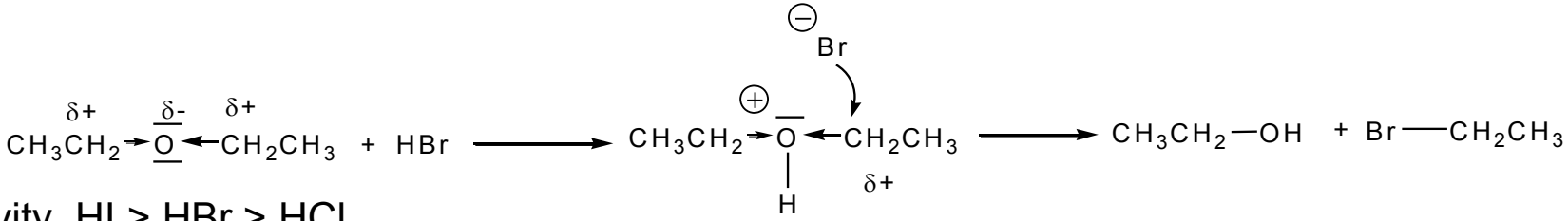
Ethers



expected reactivity :

1. interaction of free electron pairs with electrophiles
2. electron gap at C atom in the neigbourhood of oxygen offers possibility of nucleophilic atack

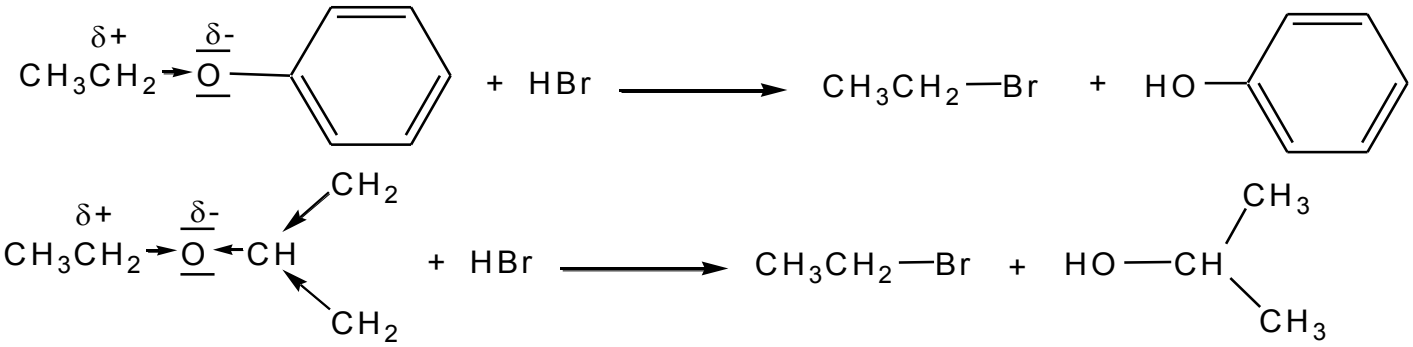
for reaction concentrated acids are needed



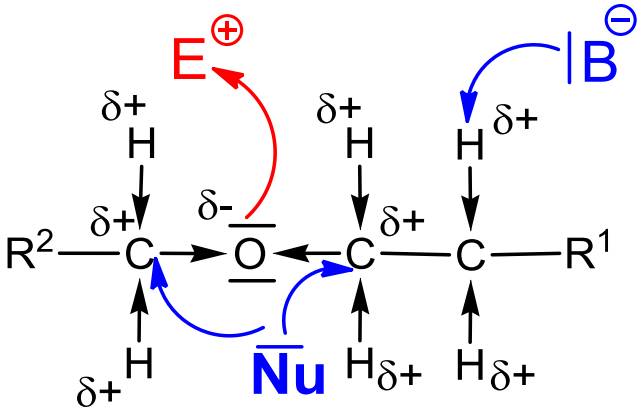
reactivity HI > HBr > HCl

temperature = 120° – 140°C (press vessels)

!!Nonsymmestrical ethers splitting!!



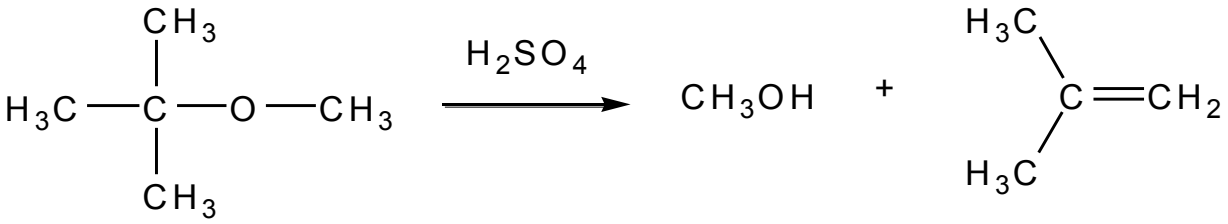
Ethers



expected reactivity :

1. interaction of free electron pairs with electrophiles
2. electron 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

tert. ethers rather undergo elimination reaction than substitution



Ethers

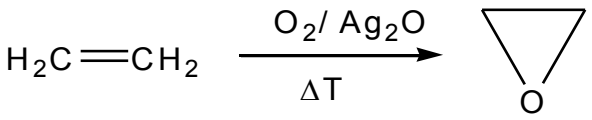
!!!Ethers often form peroxides – dangerous explosives compounds!!!

Ethers

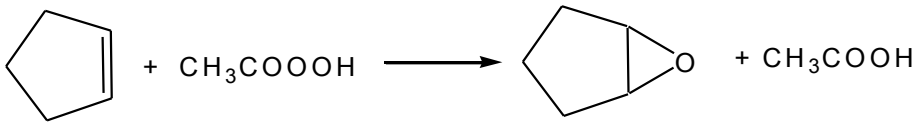
Cyclic ethers:

Oxiranes (epoxides) show other reactivity connectes with a bond angle strain in small three member ring **– the ring can be easily split**

Preparation: oxidation of olefins



oxiran (ethylenoxid, epoxide)

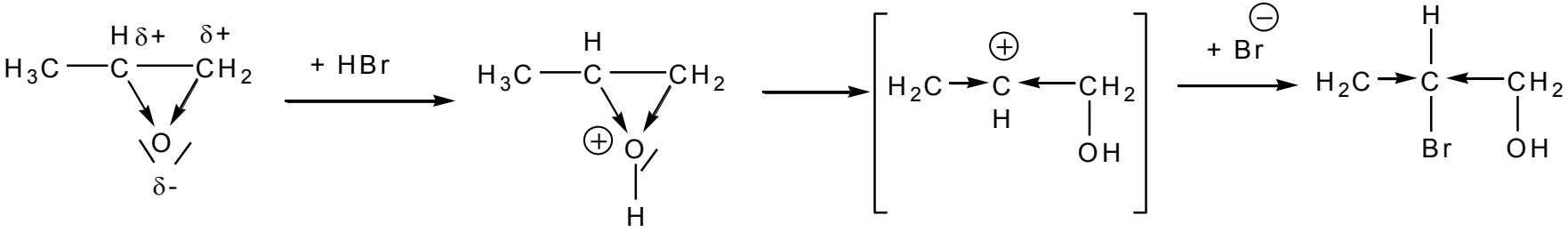


1,2-epoxycyklopentane

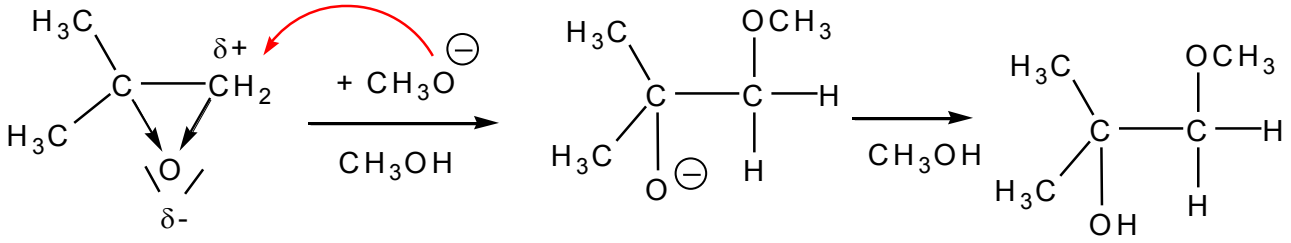
Priležajev oxidation = (*cis* – addition)

Ethers

The oxirane ring may be opened either under acid or base catalysis, results at nonsymmetrical oxiranes then may differ



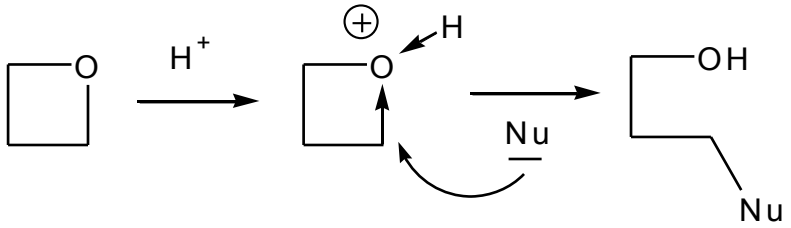
After protonation of oxirane oxygen atom the ring is opened in direction to form a stable cation, which in following step is attacked by the present anion

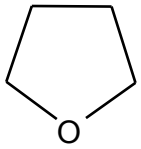


Opening in the presence of a base takes place from the less sterically hindered side, where the nucleophile is bound and proceeds the ring opening. The alkoxide this way formed is stabilized by proton from reaction medium.

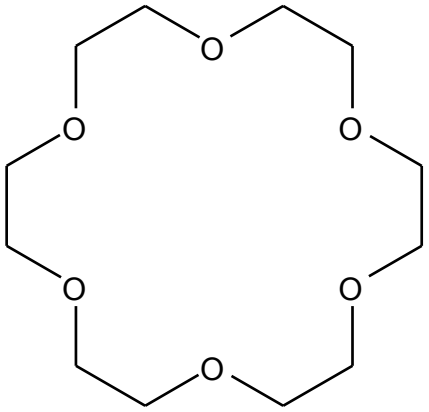
Ethers

oxetan is more resistant against acid action, but finaly the ring may be open





tetrahydrofuran is resistant against acids and is opened only by concentrated acids

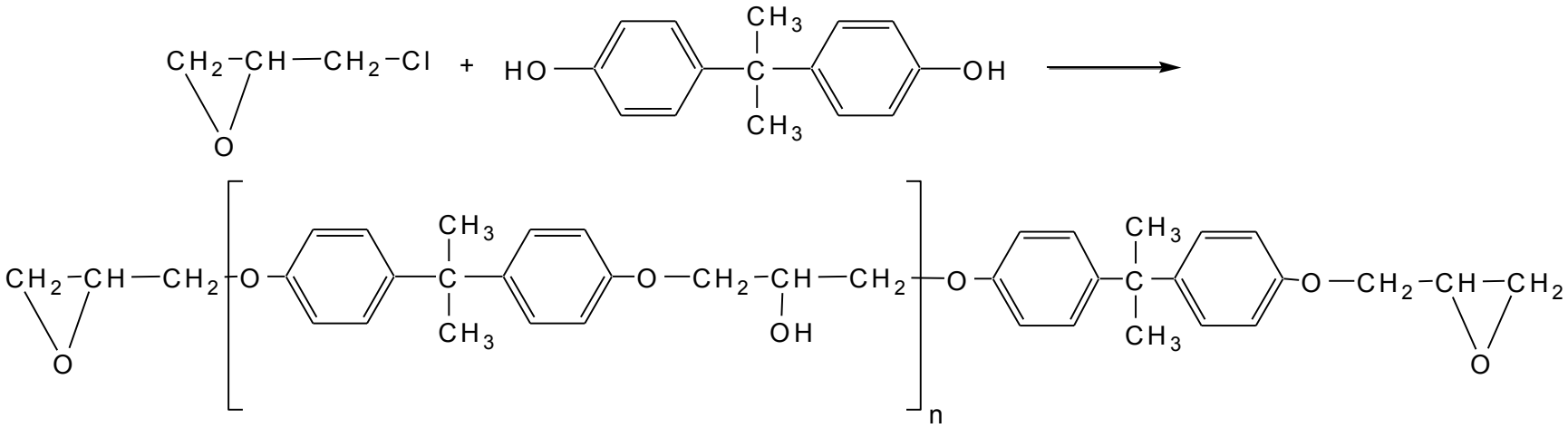


crown –ethers

18-crown-6 is able to complexate K^+ cation

Ethers

Epoxides resines epichlorhydrine + dian (2,2-bis-(4-hydroxyfenyl)propane)



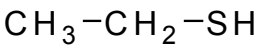
two component glue: 1. the polymer above

2. component - hardener

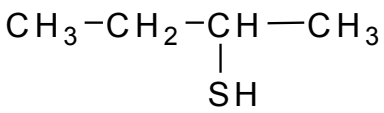
As a hardener are used: diamines, glycoles, dicarboxylic acids anhydrides, or other acids and bases

They are opening the epoxide ring and binding chains of prepolymer together into hard mass with netlike structure of resin

Sulfur analogs of alcohols, phenols and ethers

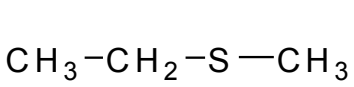


ethanthiol

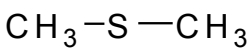


butan-2-thiol

thioles (earlier mercaptanes)



ethylmethylsulfid

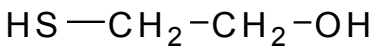


dimethylsulfid

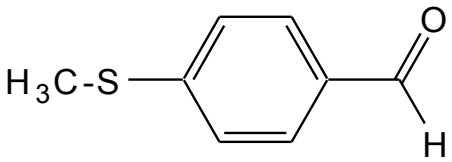
sulfides

Prefix -- **sulfanyl**

event. **alkylsulfanyl**



2-sulfanylethanol



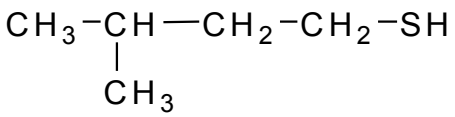
4-methylsulfanylbenzaldehyd

Sulfur analogs of alcohols, phenols and ethers

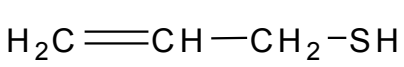
When compared with alcohols they are more volatile (the hydrogen bonds formed here are not so strong) and therefore smell also in small quantity

Ethanol b.v. 78°C

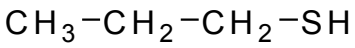
Ethanthiol b.v. 37°C



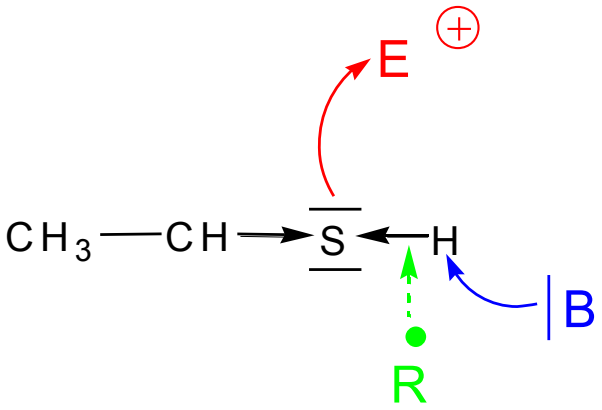
3-methylbutanthiol



diallylsulfid



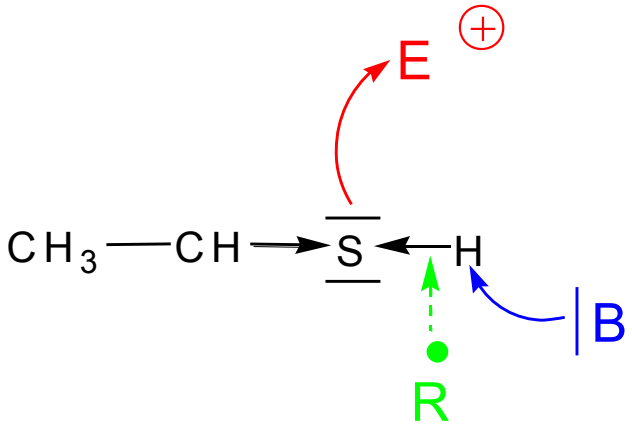
propanthiol



General reactivity:

1. Sulfur atom is nucleophilic and reacts very well with all electrophilic centra
2. Hydrogen atom at sulfur is acidic
3. The bond S-H is only little polar and therefore radical splitting is possible to expect

Sulfur analogs of alcohols, phenols and ethers



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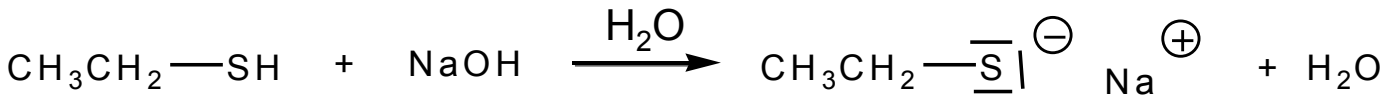
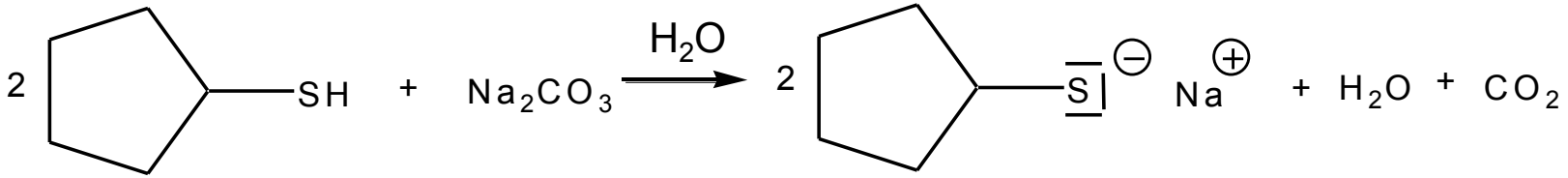
Hydrogen atom is more acidic than in alcohols and therefore can be removed even by a weak base and in water

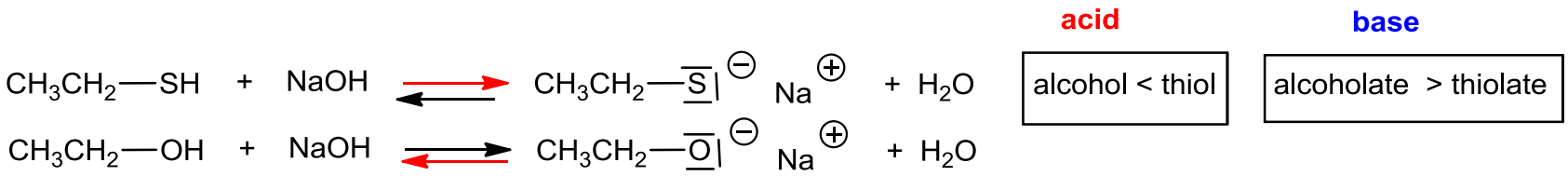
$pK_a = 10$ (thiol) compare $pK_a = 16$ (alcoholes)





Sulfur analogs of alcohols, phenols and ethers

thiol is stronger acid than **alcohol**

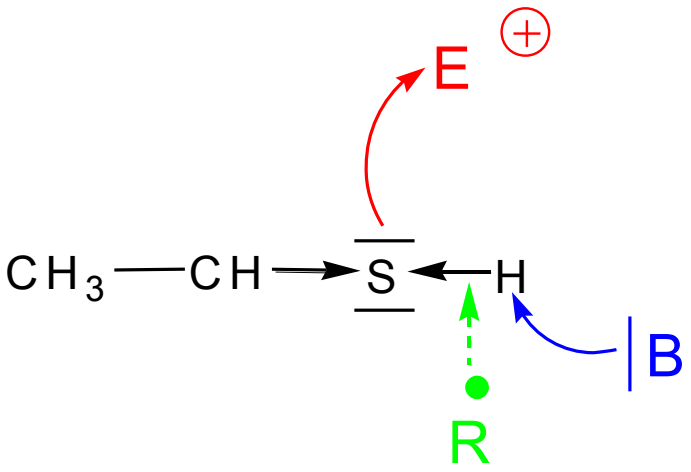


!Be carefull! Thiolate is stronger nucleophile than alkoholate

It is caused by better polarizibility of sulfur

Alcoholates rather enter into elimination reactions and thiolates prefer nucleophilic substitution reactions

Sulfur analogs of alcohols, phenols and ethers



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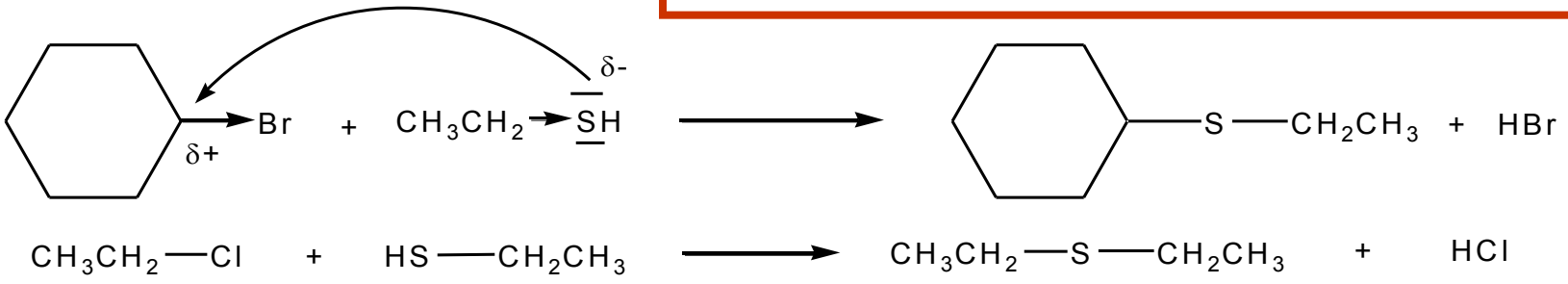
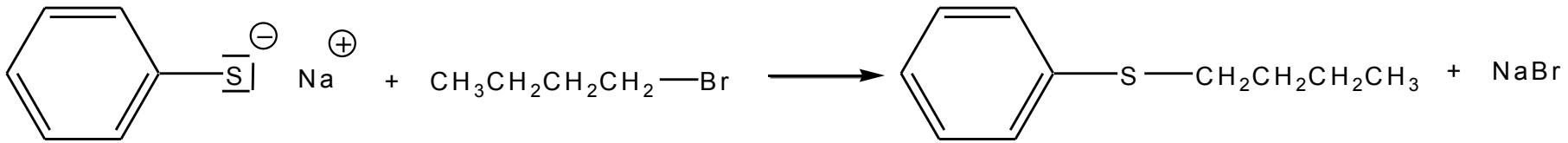
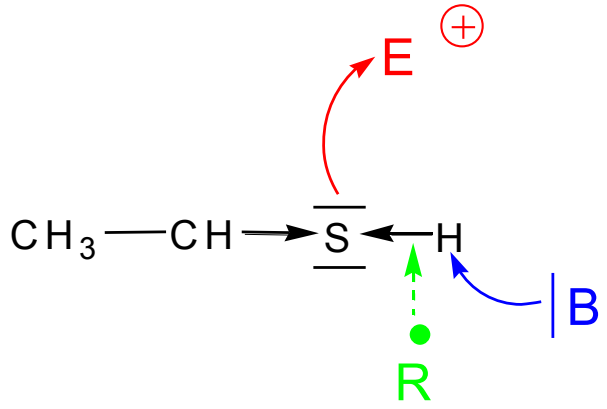




Sulfur analogs of alcohols, phenols and ethers



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2. Hydrogen atom at sulfur is acidic
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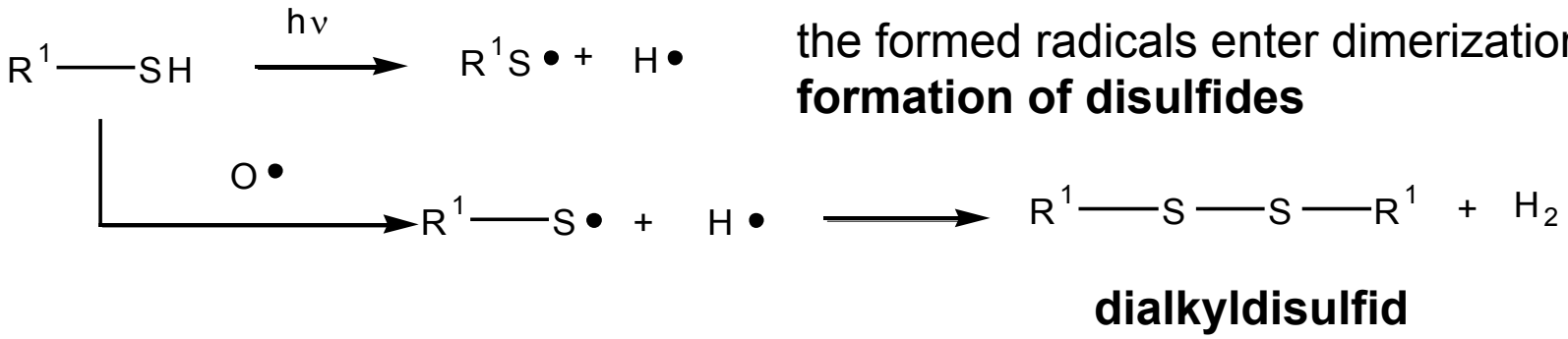
Bond **C – S is less polar than bond C – O** (oxygen atom is more electronegative)

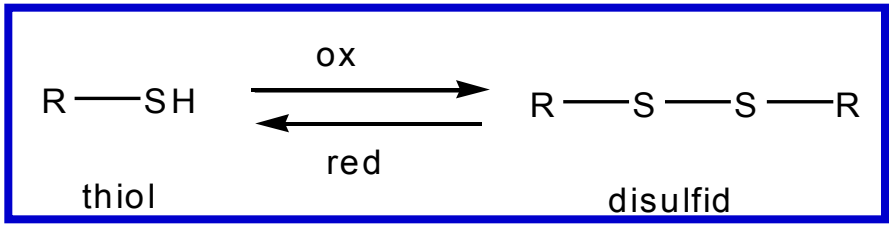
the bond is difficult to split
– substitution is difficult



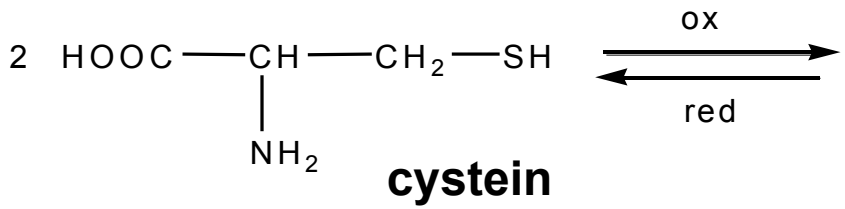
the formed radicals enter dimerization - **formation of disulfides**

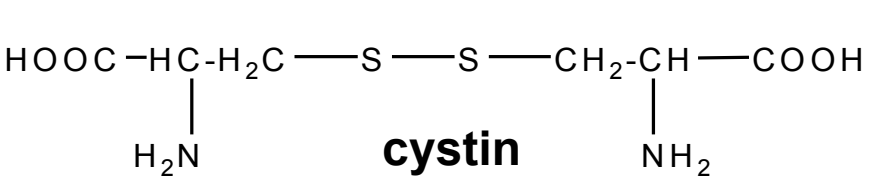
dialkyldisulfid

Sulfur analogs of alcohols, phenols and ethers

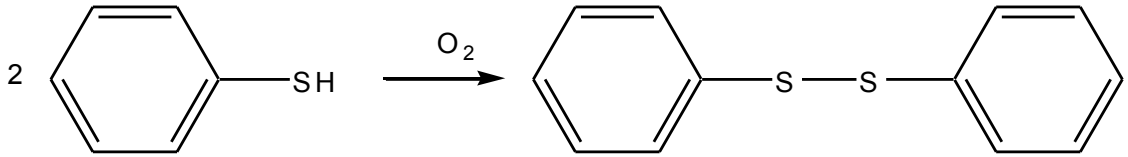


reversible process in a brain – responsible for process of remembering

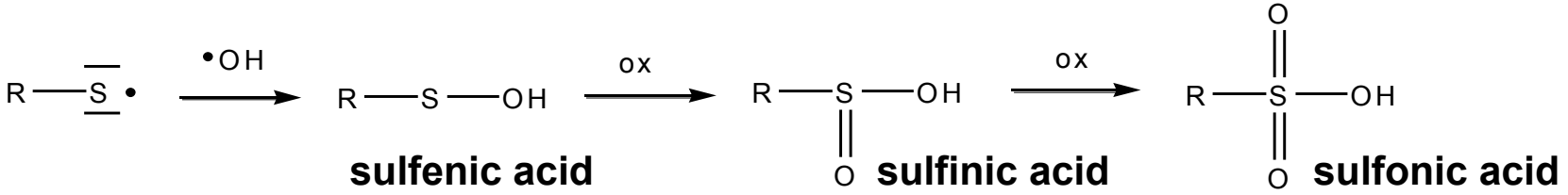




sulfur derivatives undergo easy oxidation

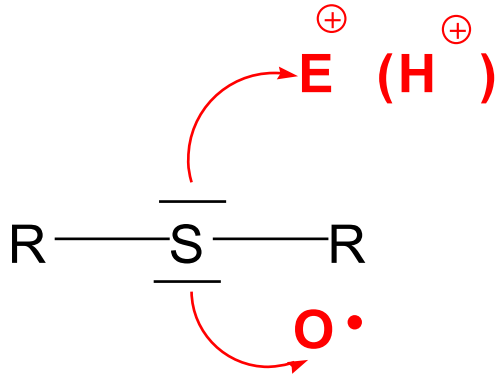


gentle oxidation reagents



strong oxidation reagents (HNO_3, $KMnO_4$ ….)

Sulfur analogs of alcohols, phenols and ethers

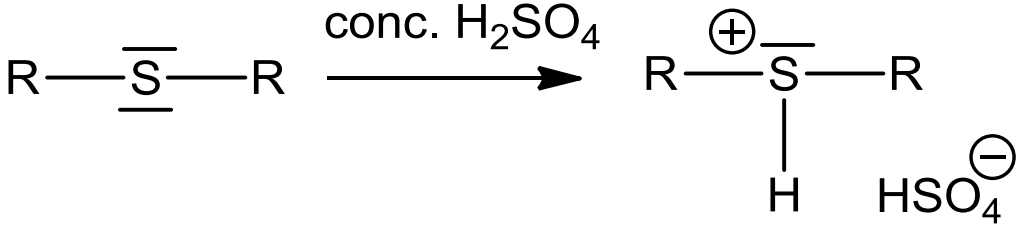


General reactivity :

1. **basic properties**
2. high nucleophility
3. sensitivity against oxidation

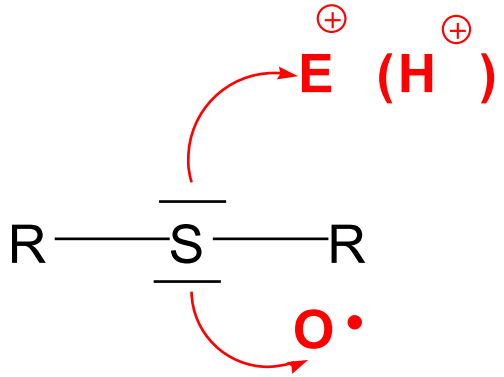
SULFIDES

in properties similar to ethers, but they have higher boiling temperatures then ethers



in acids they dissolve under formation of sulfonium salts, which in water split back

Sulfur analogs of alcohols, phenols and ethers



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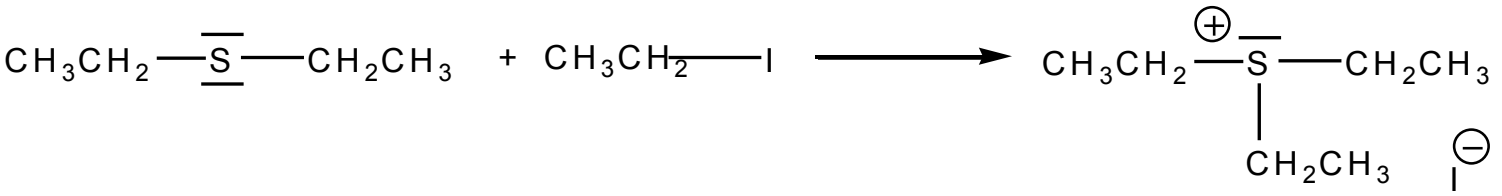

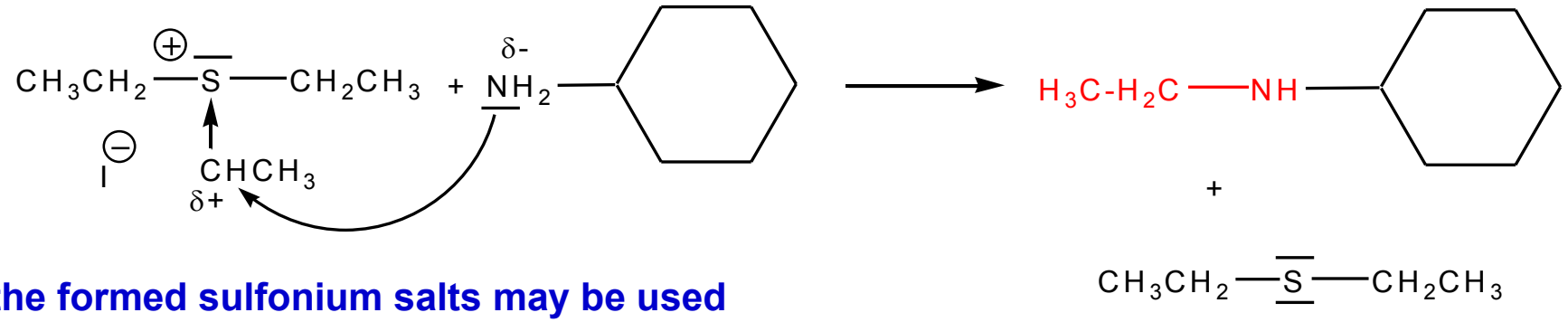

the formed sulfonium salts may be used for alkylation of nucleophiles