Chem 233

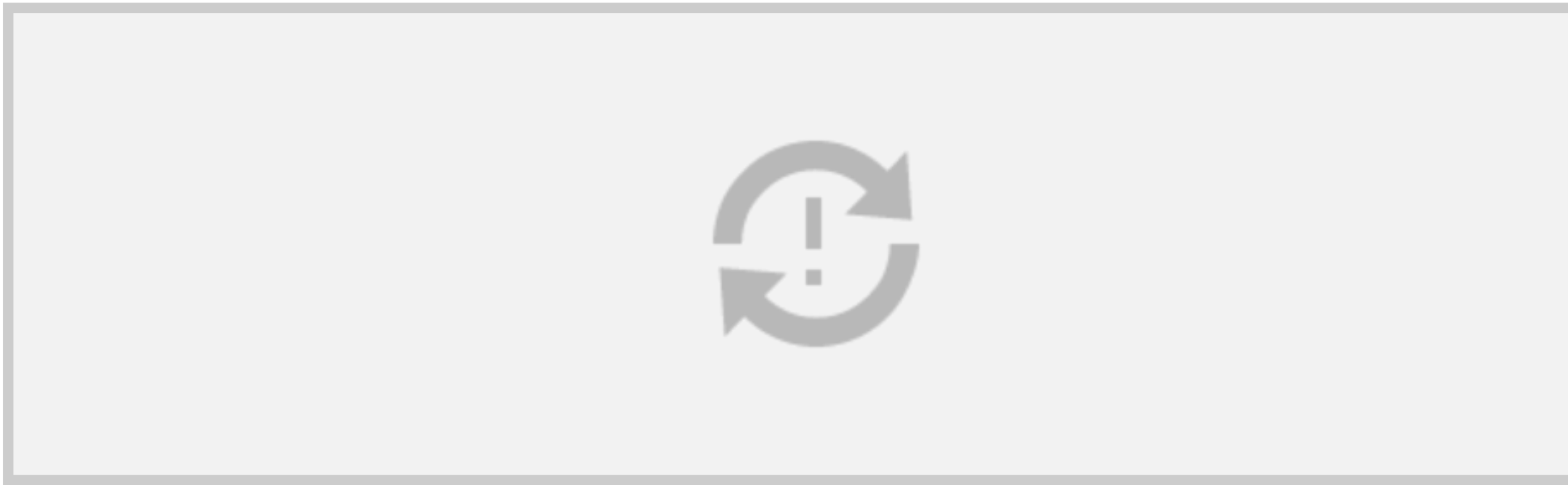
7.5 and .6 Acidity of alcohols and phenols

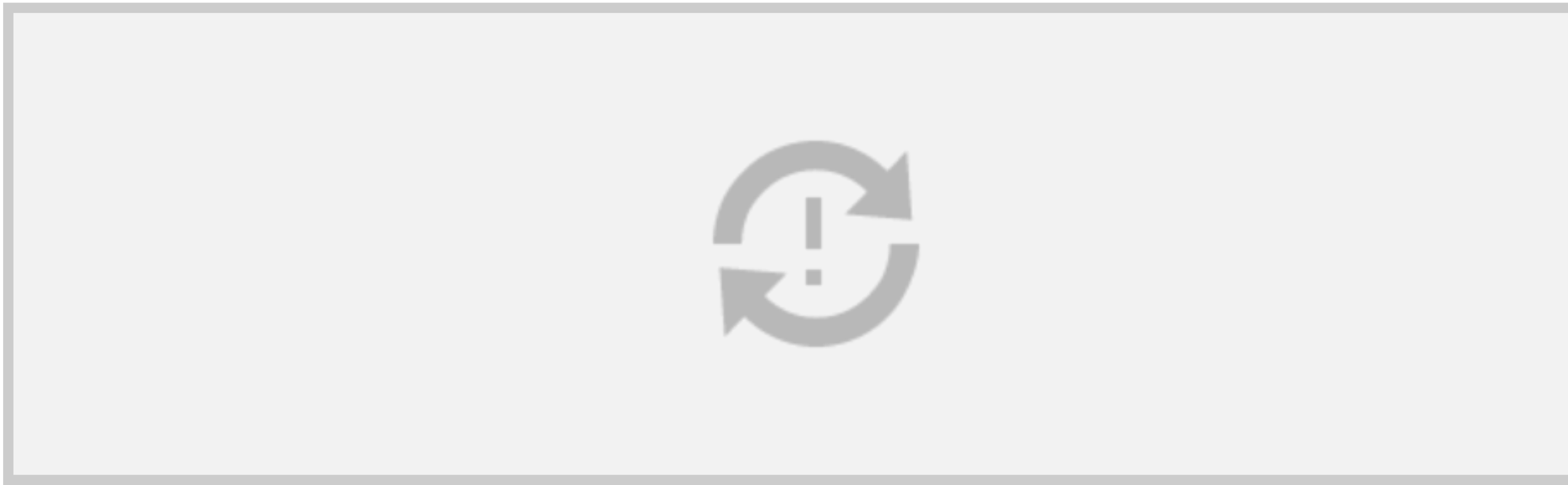
Almeqdad Habashneh

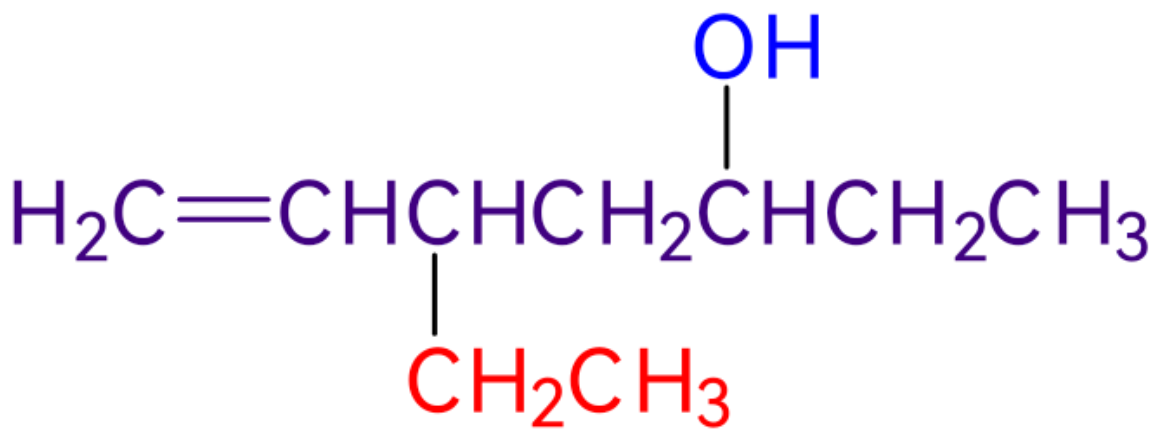
Alcohol and Phenols

Naming of Alcohol and Phenols

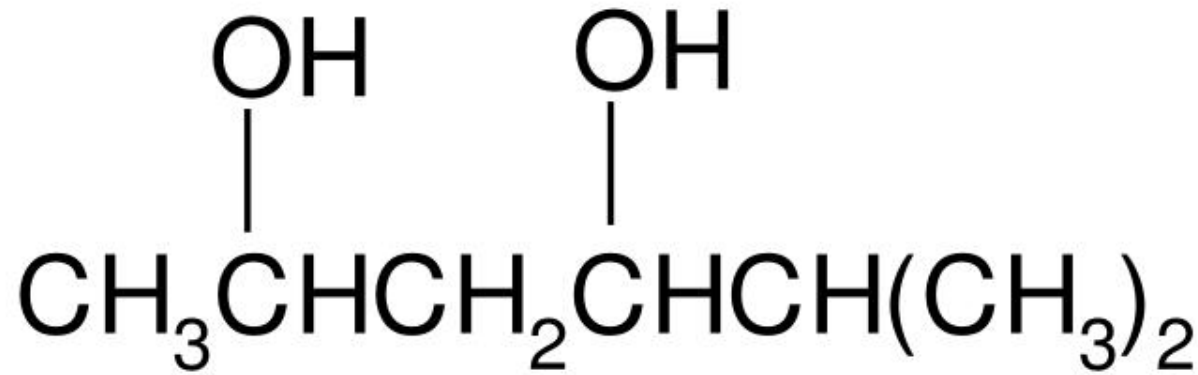
- Select the longest carbon chain containing the hydroxyl group, and derive the parent name by replacing the *-e* ending of the corresponding alkane with *-ol*
- Number the chain from the end nearer the hydroxyl group
- Number substituents according to position on chain, listing the substituents in alphabetical order





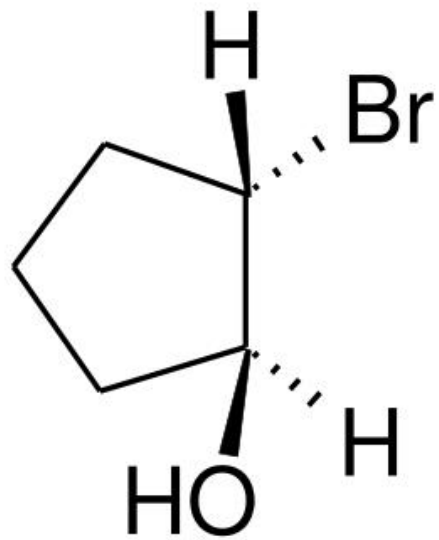


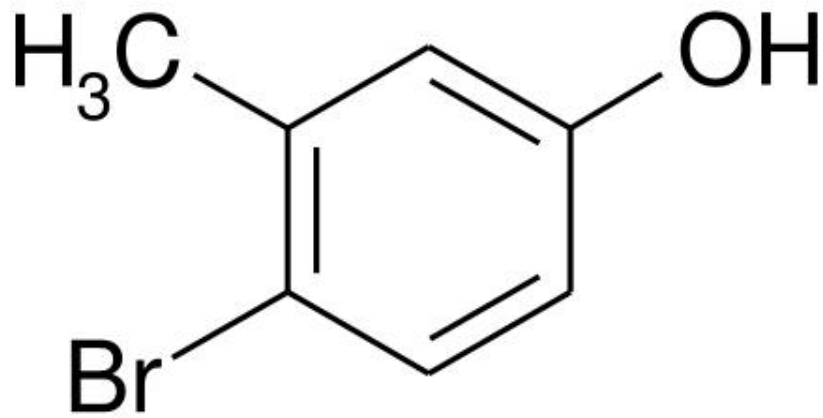
5-ethylhept-6-en-3-ol



5-methyl-2,4-hexanediol

trans-2-Bromocyclopentanol

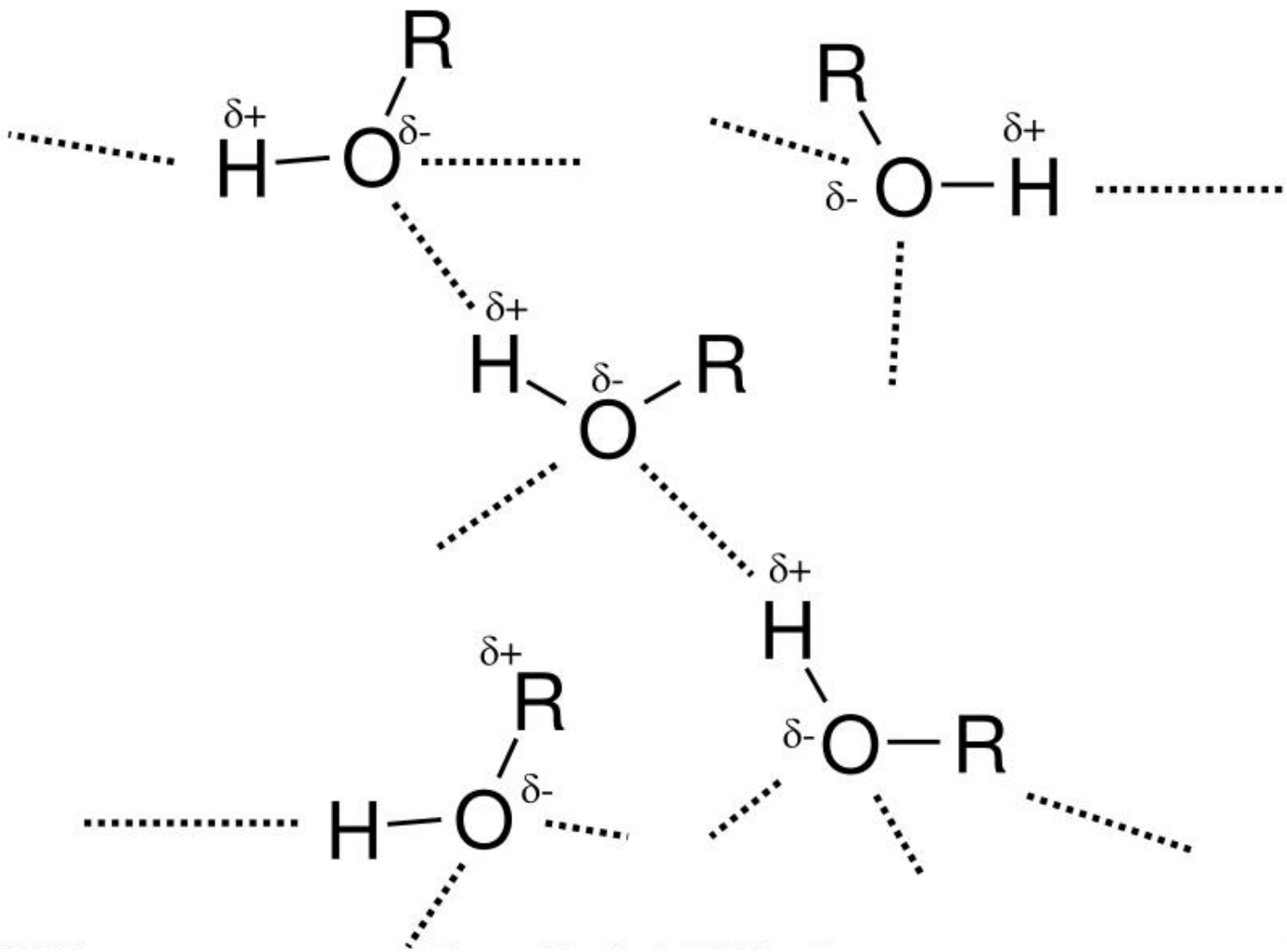


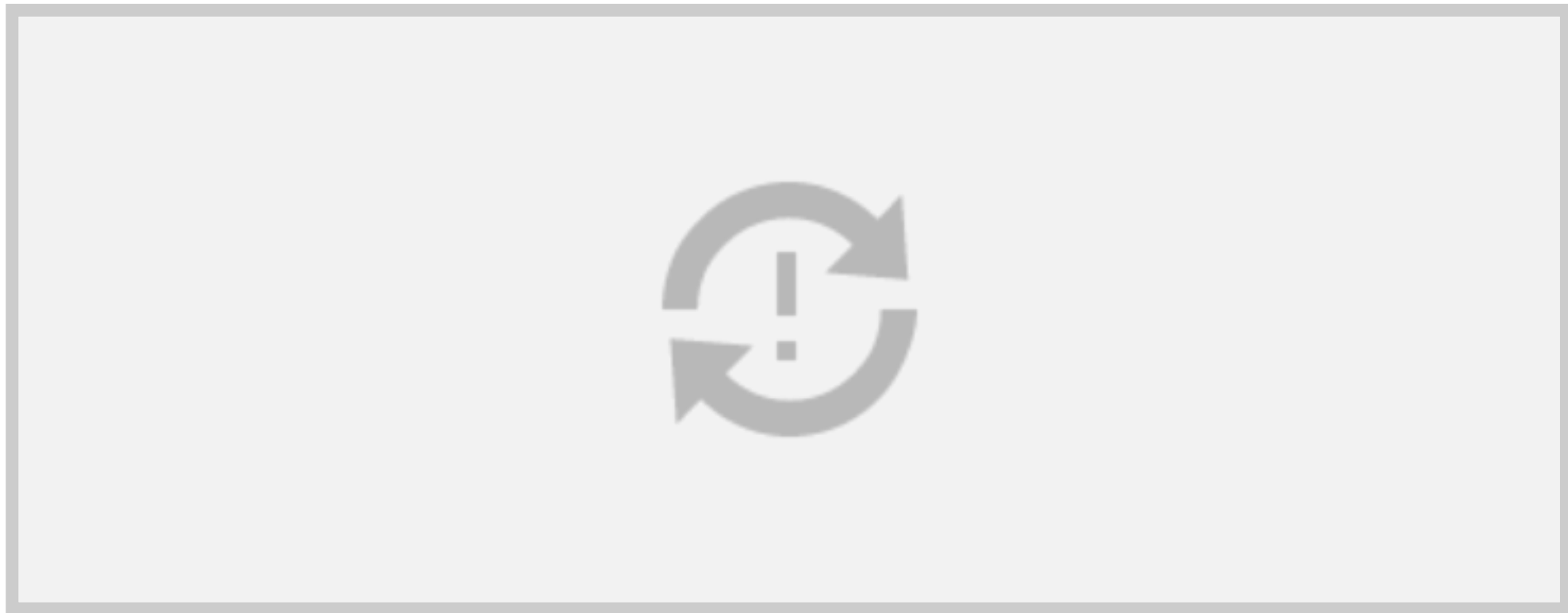


4-Bromo-3-methyl-phenol

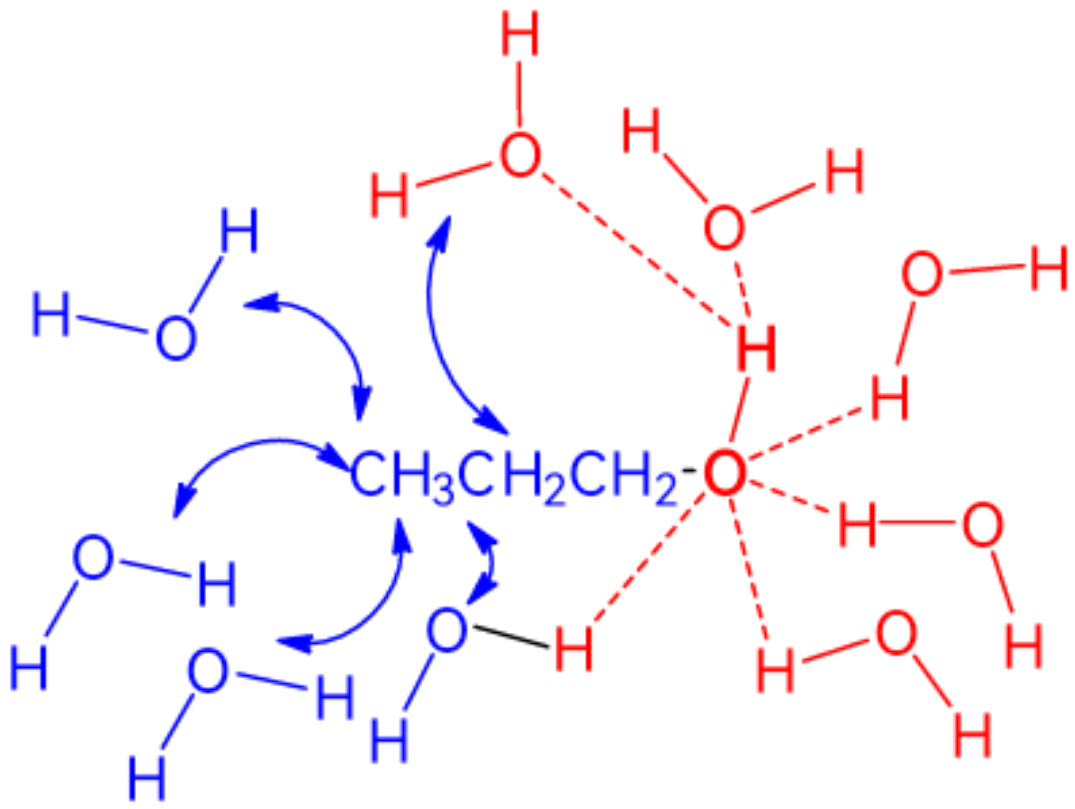
Hydrogen bonding and physical properties of alcohols

Hydrogen Bonding in Alcohol





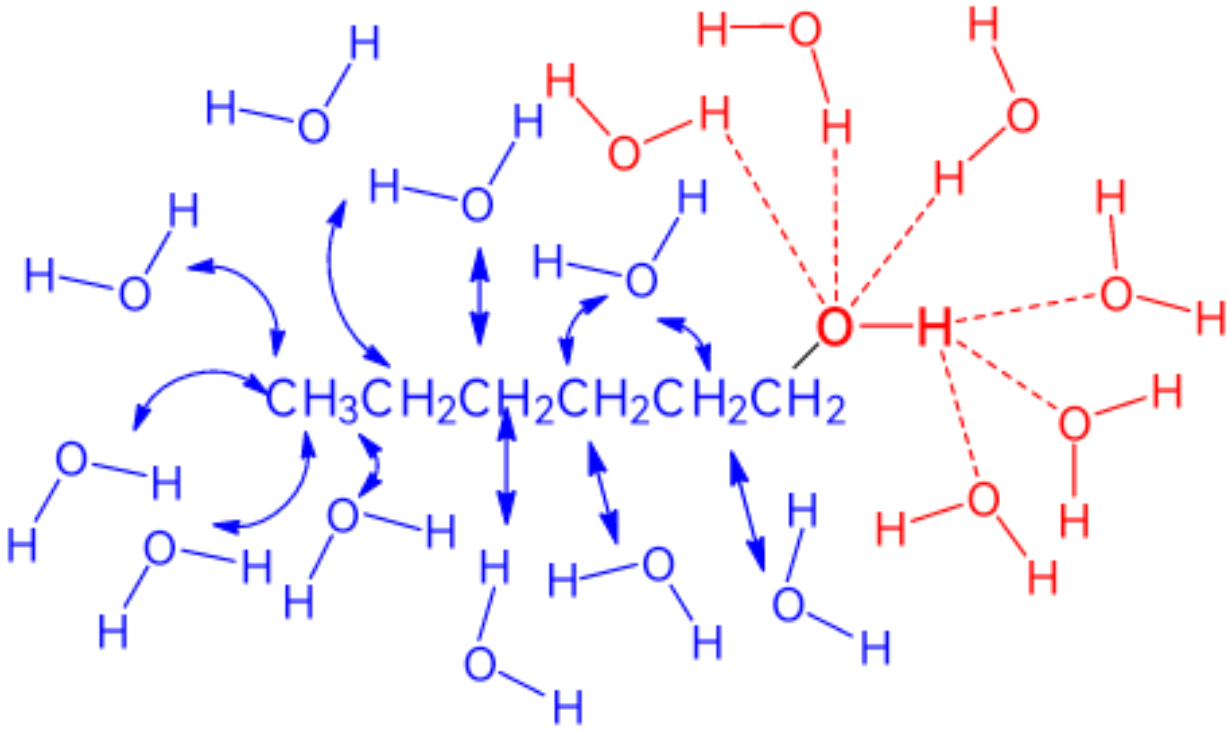
Shorter hydrocarbonic chain



------ Hydrophilic attractive interaction

⟷ Hydrophobic repulsive interaction

Longer hydrocarbonic chain



Hydrophilic attractive interaction

Hydrophobic repulsive interaction

Acidity & Basicity

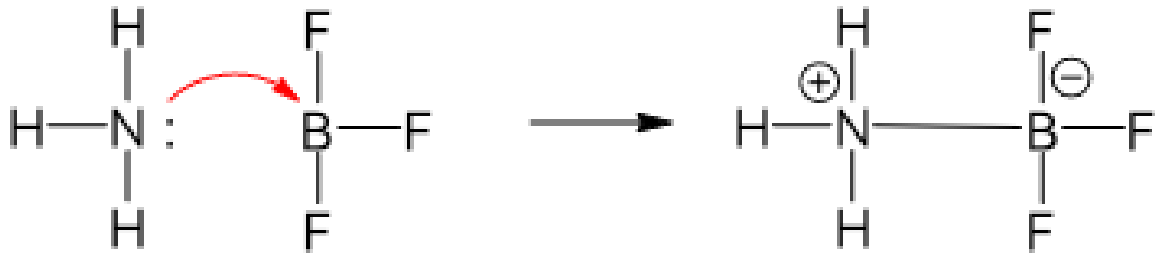
$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

Strong — Weak

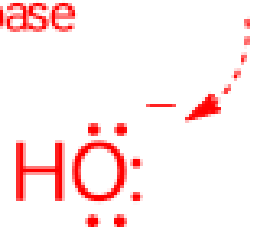
Weak — Strong

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \qquad pK_a = -\log K_a$$

	Ka	pKa
Stronger acid	10^{-3}	3
Weaker acid	10^{-10}	10

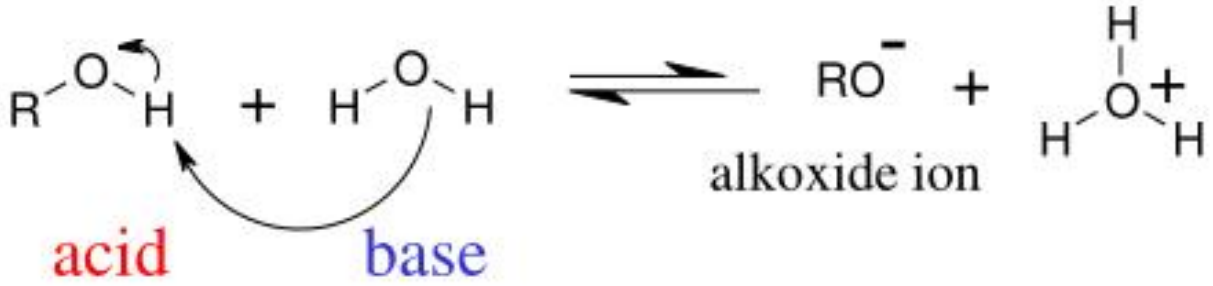


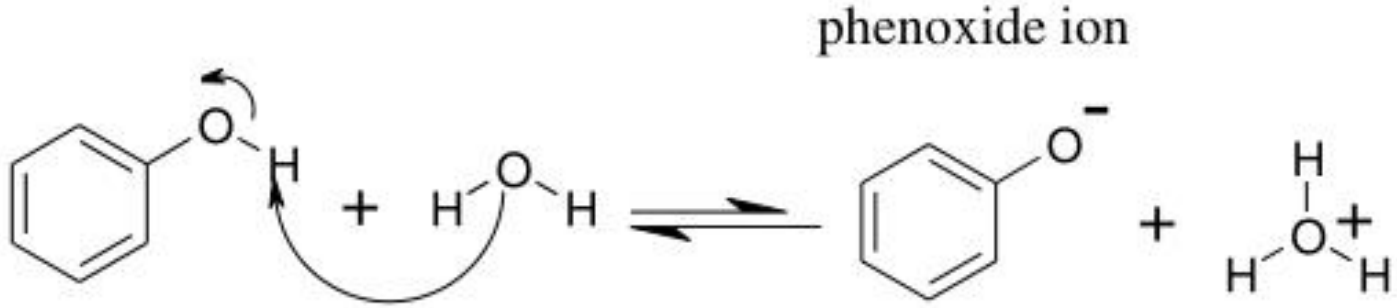
* High electron density on the donating atom
* High repulsive interaction on the donating atom
* Less stable substance
* Easier to donate a lone pair of electrons
* Stronger base



* Lower electron density on the donating atom
* Lower repulsive interaction on the donating atom
* Stable molecule
* No need to donate a lone pair of electrons
* Weaker base

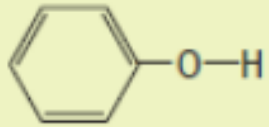
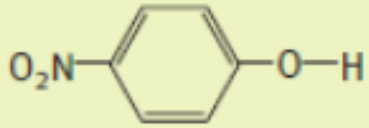
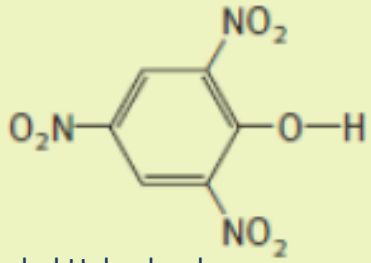
Acidity of alcohols and phenols



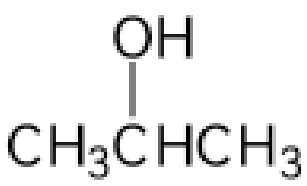
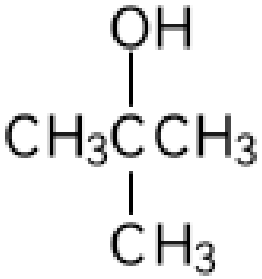


pK_a Values for Typical OH Compounds

Table 7.2 — pK_a's of Selected Alcohols and Phenols in Aqueous Aolution

Name	Formula	pK_a
water	HO—H	15.7
methanol	CH_3O—H	15.5
ethanol	CH_3CH_2O—H	15.9
t-butyl alcohol	$(CH_3)_3CO$—H	18
2,2,2-trifluoroethanol	CF_3CH_2O—H	12.4
phenol		10.0
p-nitrophenol		7.2
picric acid		0.25

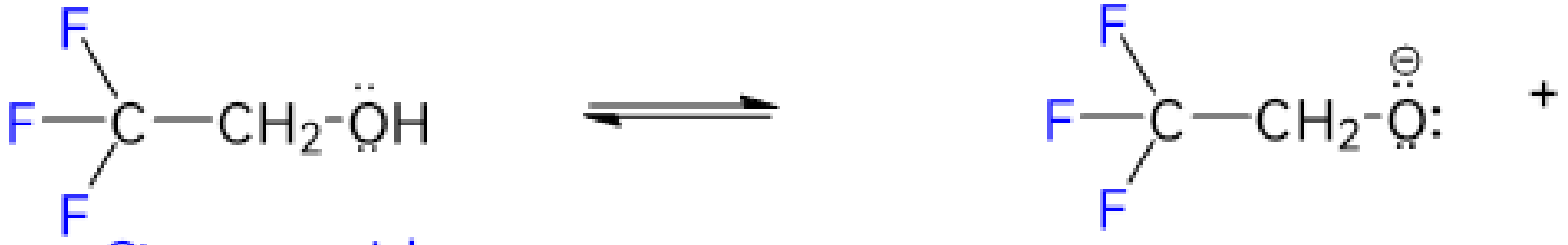
Acidity of Alcohols

	CH_3OH	CH_3CH_2OH		
pKa =	15.5	15.9	16.5	18.0
Acidity	Methanol >	1° >	2° >	3°

Acidity of substituted alcohols

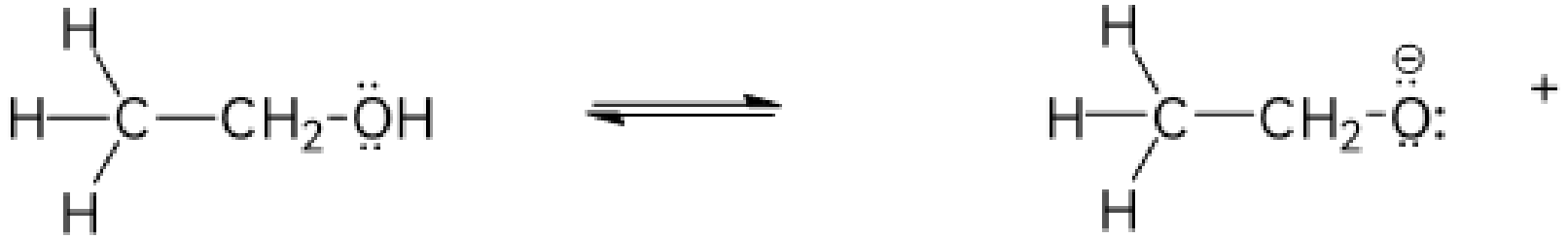
PKa

12.4



Stronger acid

15.9

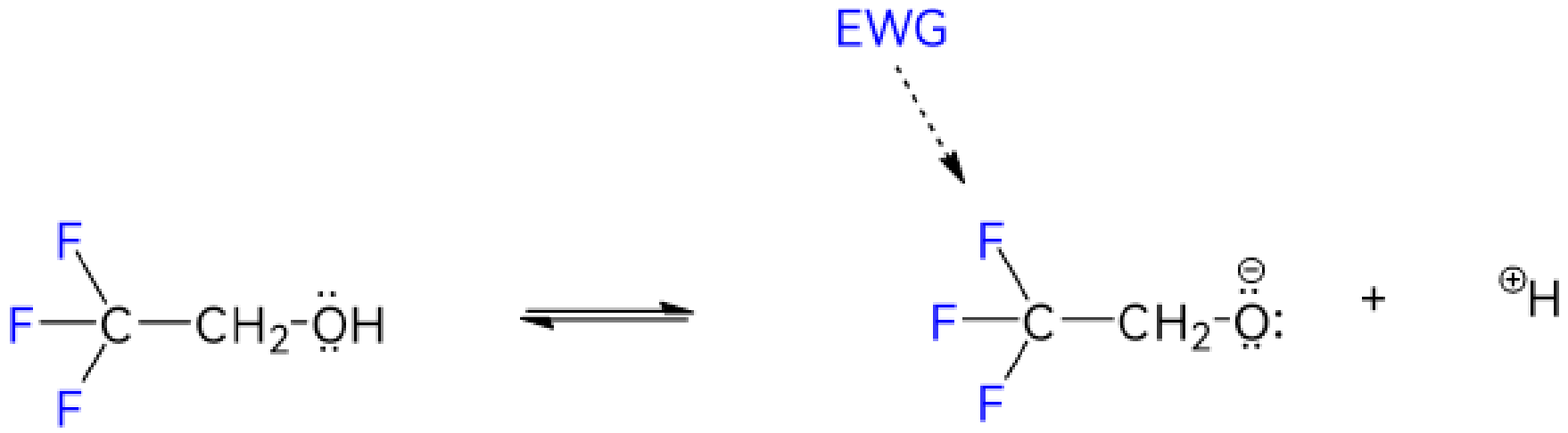


Weaker acid

Acidity of substituted alcohols

PKa

12.4

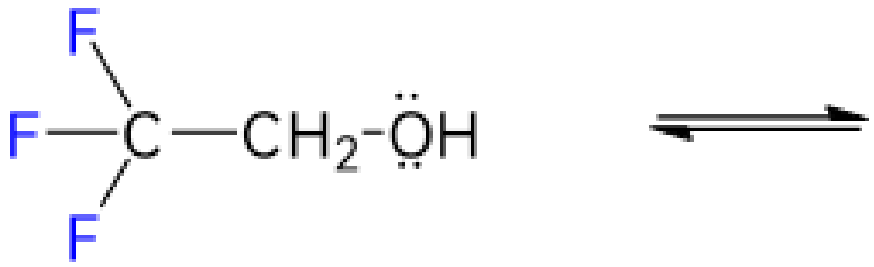


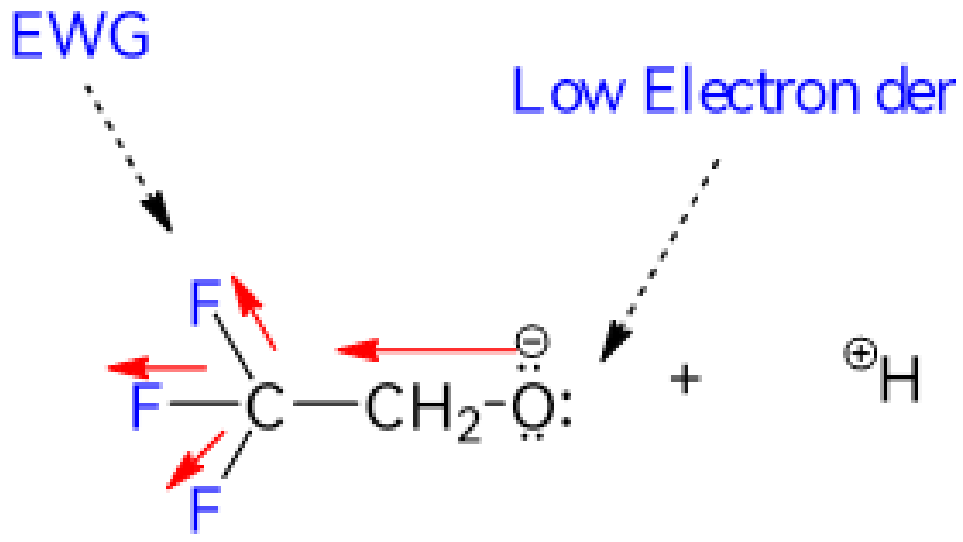
Fluorine is high electronegative atom so it is EWG

Acidity of substituted alcohols

PKa

12.4





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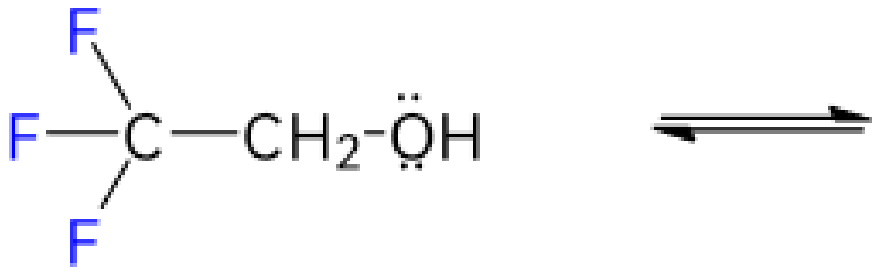
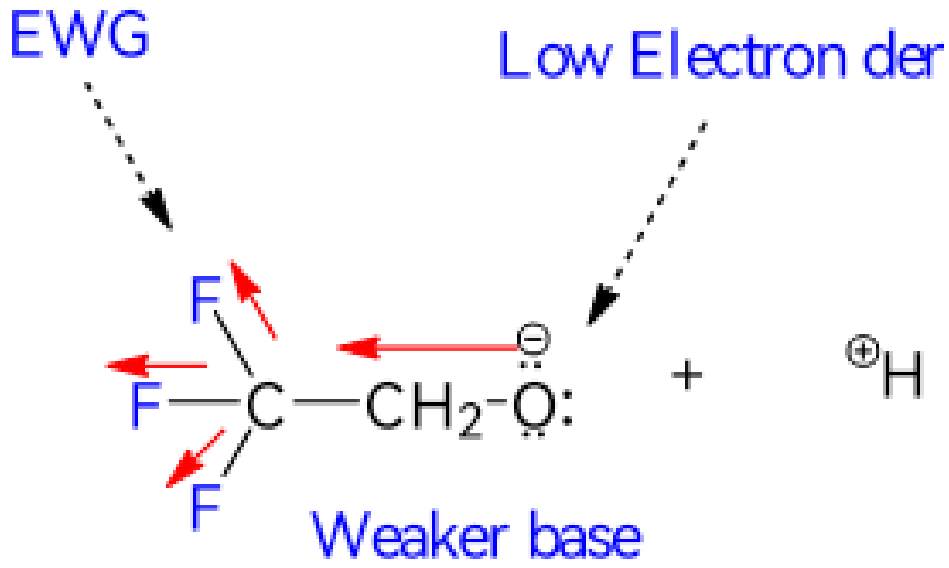
Acidity of substituted alcohols

PKa

12.4



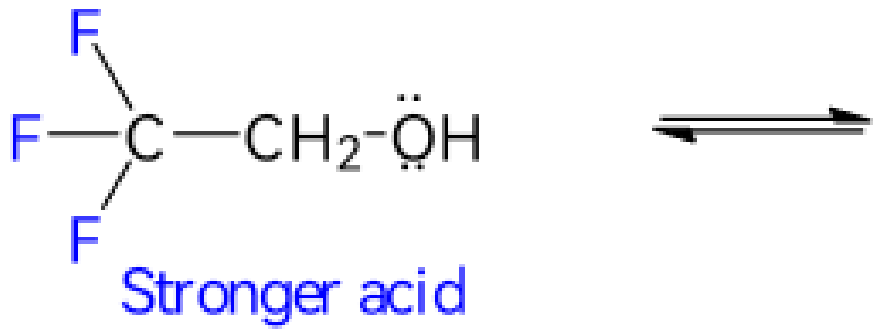


Fluorine is high electronegative atom so it is EWG

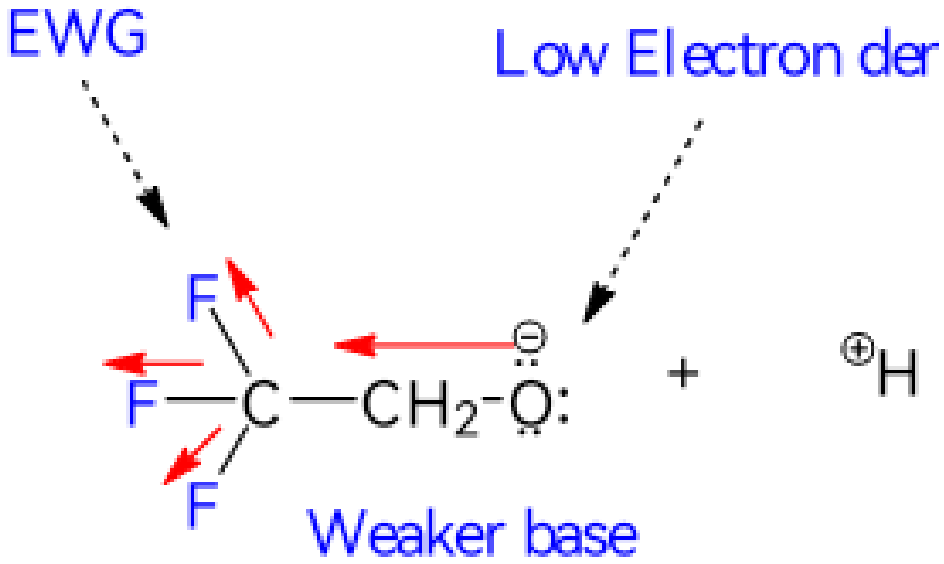
Acidity of substituted alcohols

PKa

12.4



Stronger acid

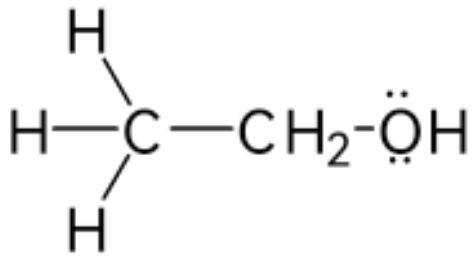


Weaker base

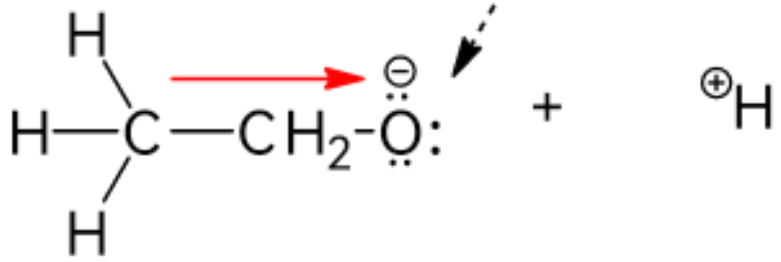
Fluorine is high electronegative atom so it is EWG

Higher Electron density

pKa=15.9



Weaker base



Stronger base

Acidity of Alcohol

* The strength of the EWG

$$FCH_2CH_2OH > ClCH_2CH_2OH > BrCH_2CH_2OH > ICH_2CH_2OH$$

Electronegativity : F > Cl > Br > I

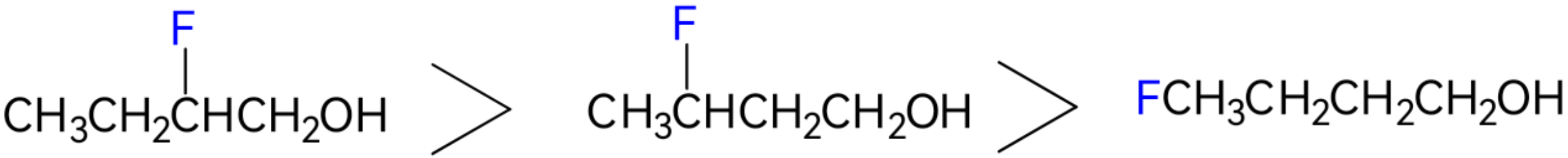
Acidity of Alcohol

* Number of EWG

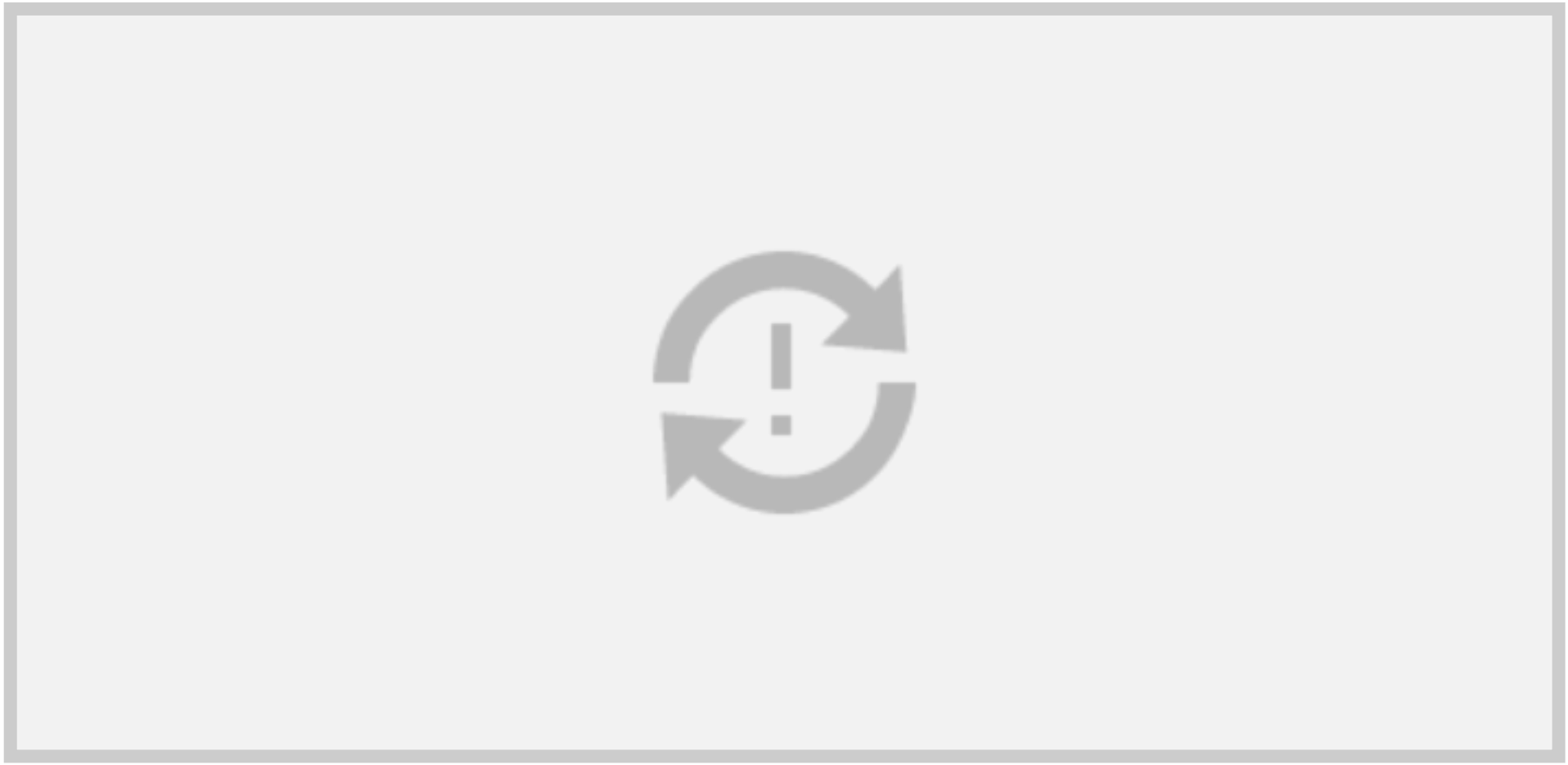
$F_3CCHOH > F_2CHCHOH > FCH_2CHOH$

Acidity of Alcohol

* Position of EWG



Acidity of alcohol and phenol



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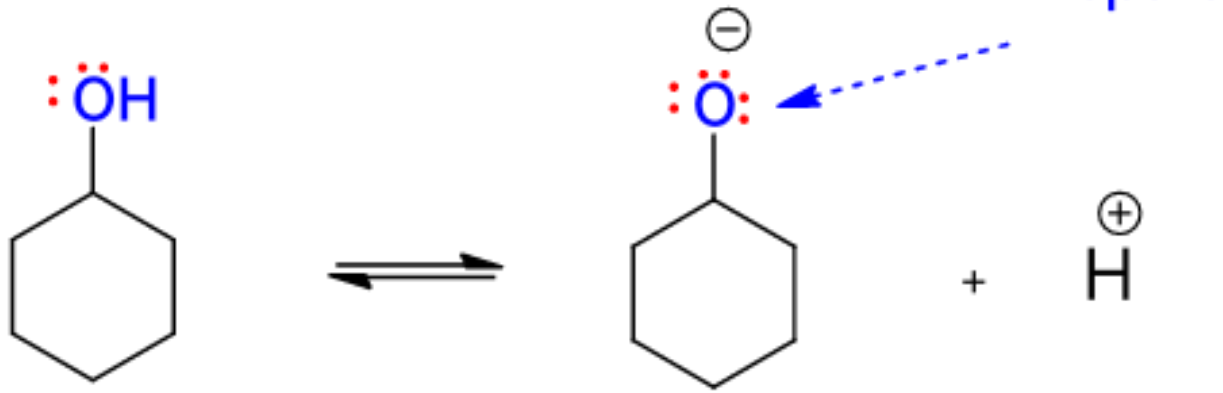
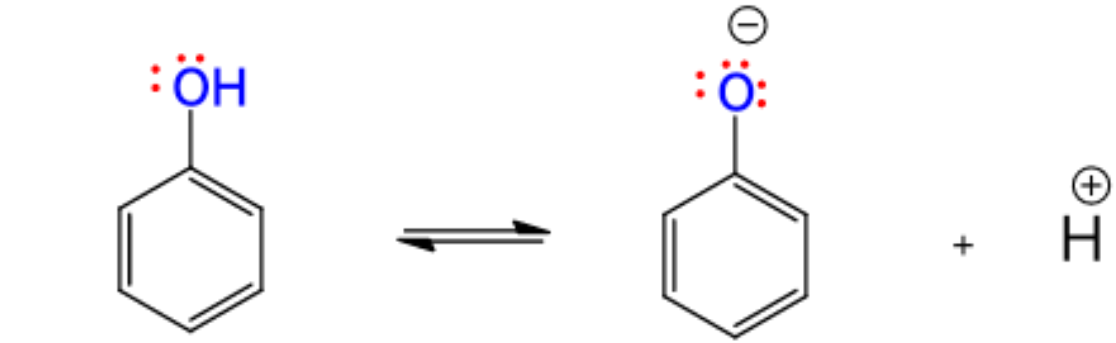
High Electron density with repulsive intreaction



Weaker acid

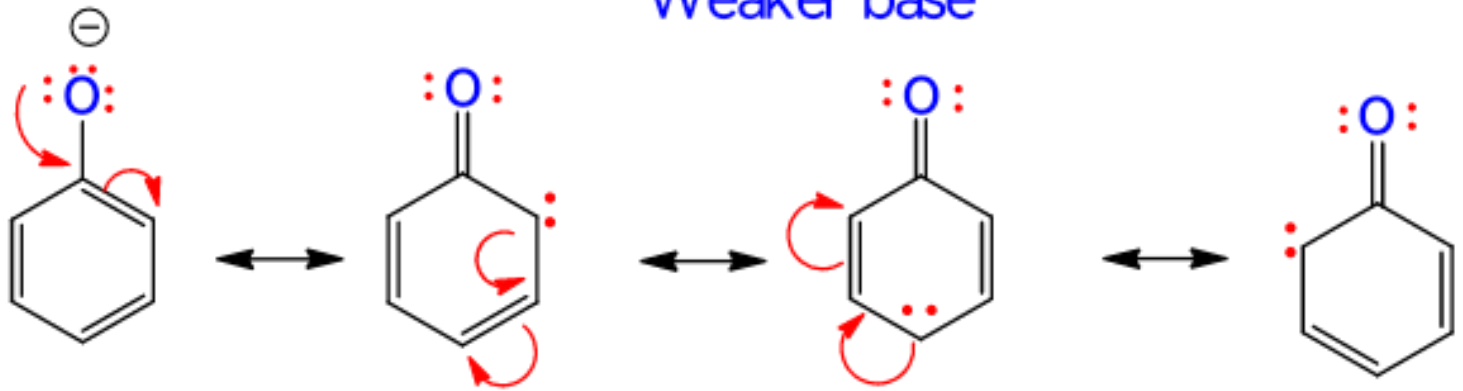
Alkyl oxide anion is
Less stable
Stronger base

Resonance Effect



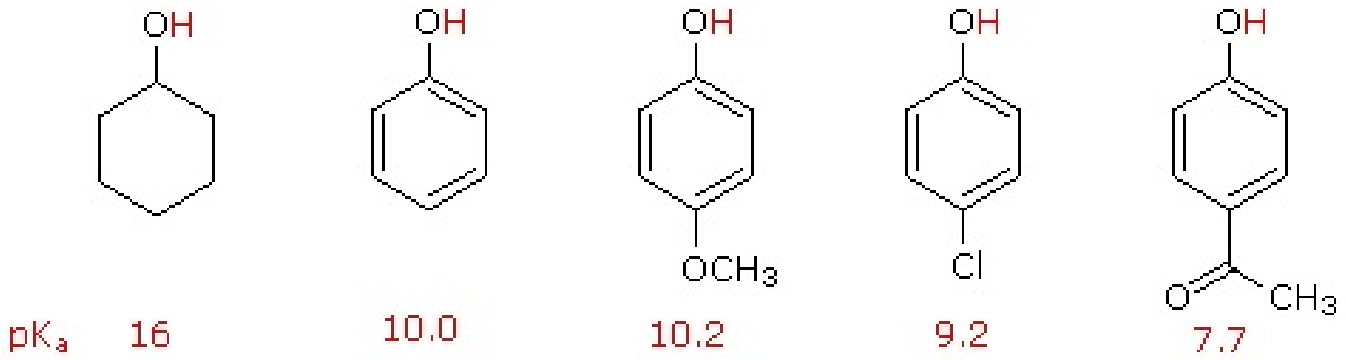
Stronger acid

Phenoxide is
More stable anion
Weaker base

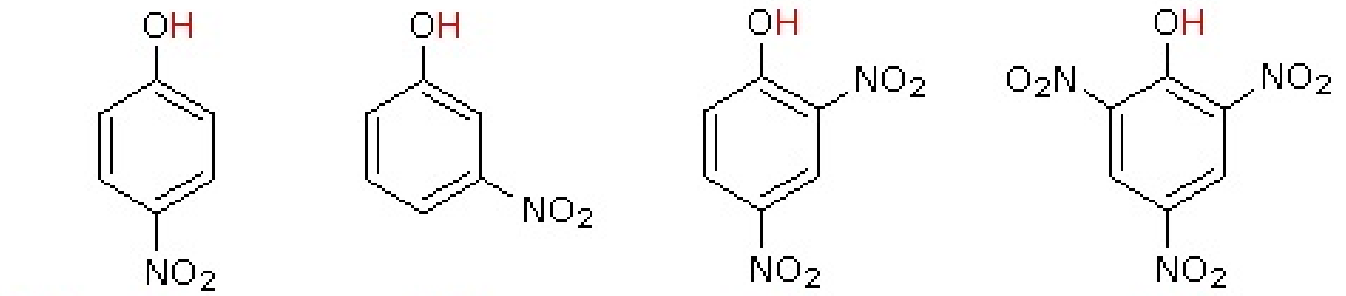


Phenoxide is more stable anion due to resonance effect

The Acidity of substituted phenols

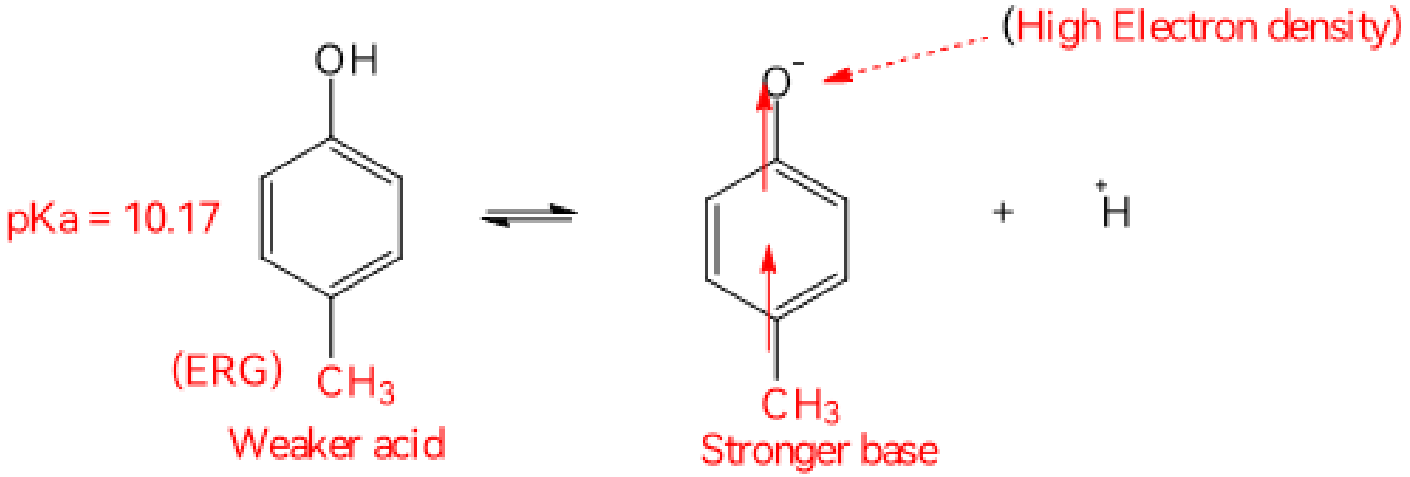


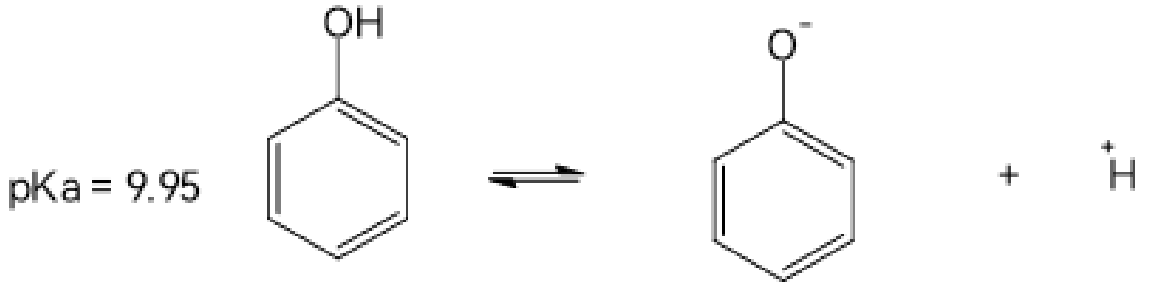
pK_a 16 10.0 10.2 9.2 7.7

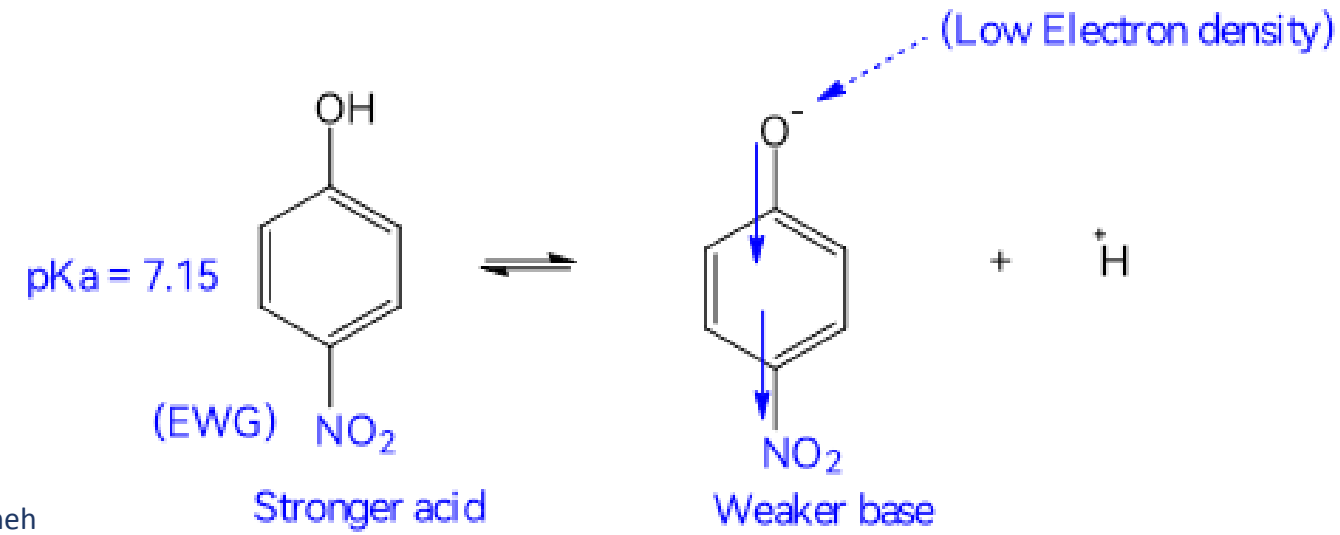


pK_a 7.2 8.3 4.1 0.3

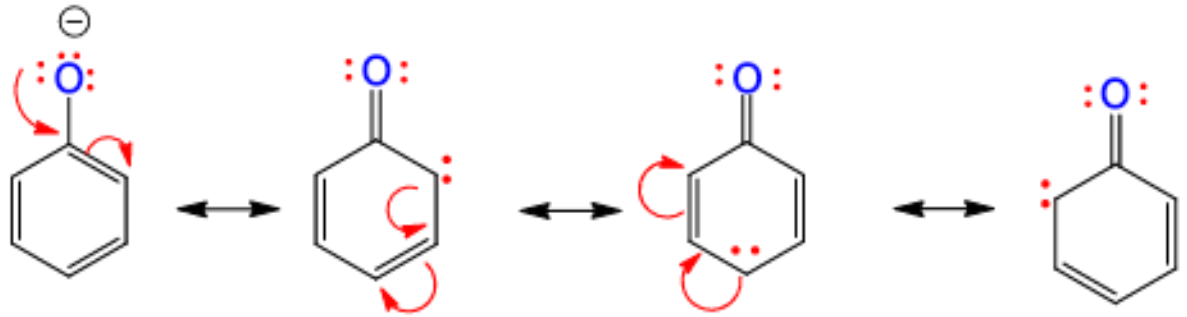
The Acidity of substituted phenols


(High Electron density)
pKa = 10.17
OH
(ERG)
CH3
Weaker acid
O-
CH3
Stronger base
+
H+

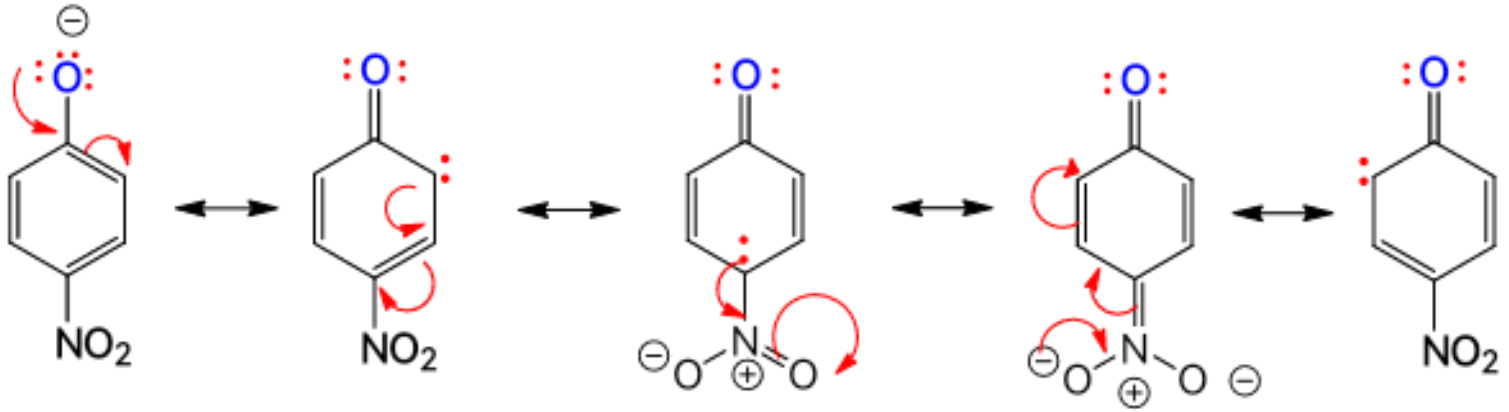

pKa = 9.95
OH
O-
+
H+


(Low Electron density)
pKa = 7.15
OH
(EWG)
NO2
Stronger acid
O-
NO2
Weaker base
+
H+

Resonance effect of the substituent on the acidity of phenol

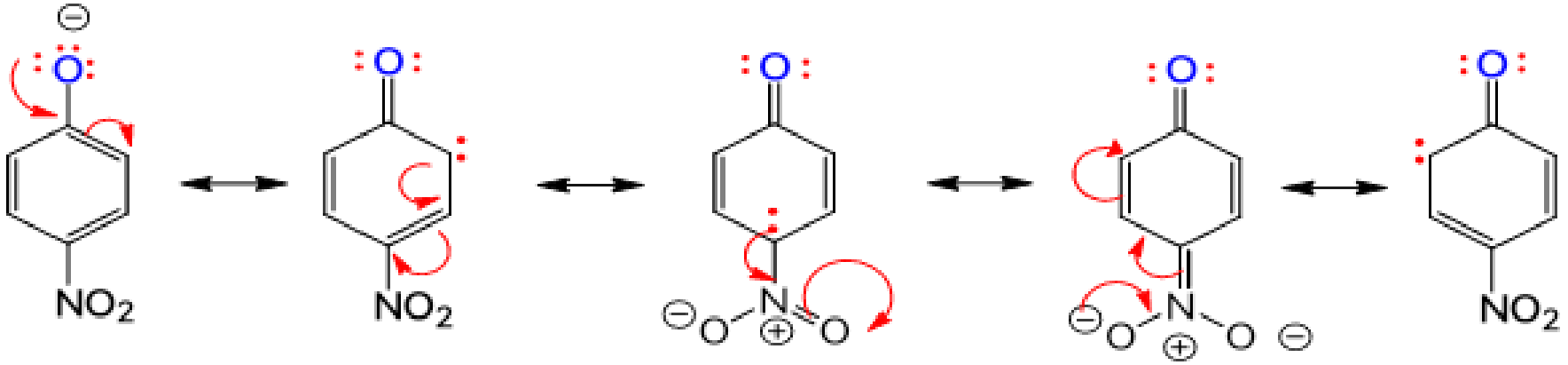


Four resonance structures: less stable phenoxide anion: stronger base

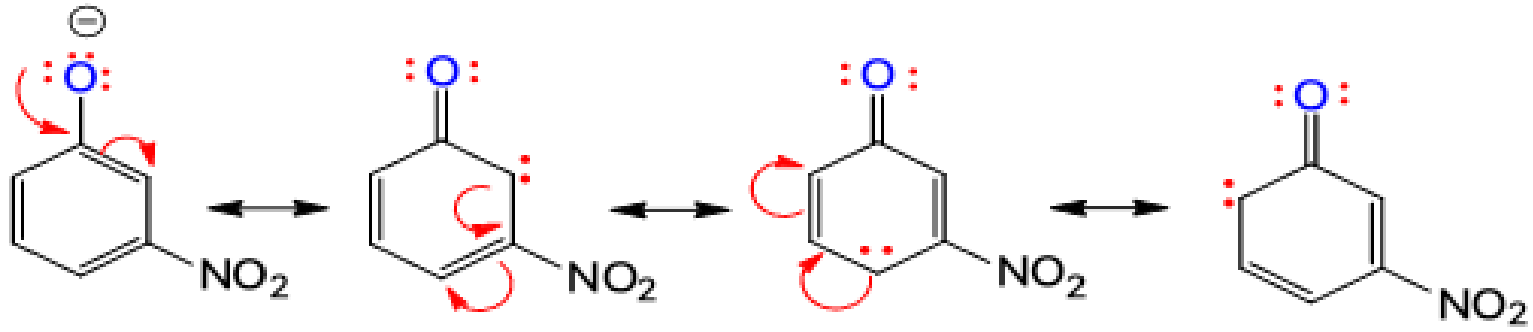


Five resonace structures: more stable phenoxide anion: weaker base

The effect of the position of the substituent on the acidity of phenol



Phenoxide is stabilized by the presnce of nitro group at position para due to resosnace effect



NO_2 never stabilize the phenoxide at posistion meta

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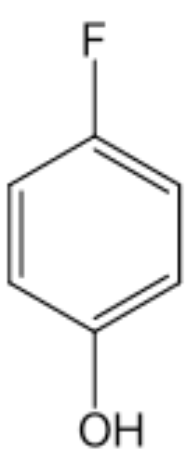
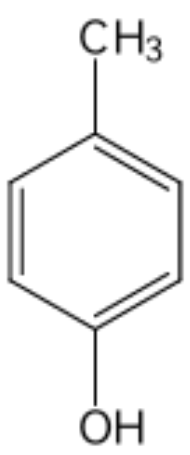
Acidity of different substituted phenol

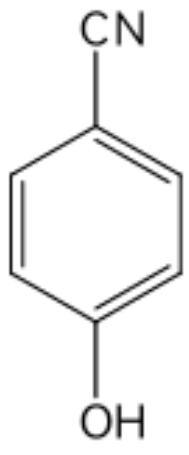
Rank the following compounds according to their acidities



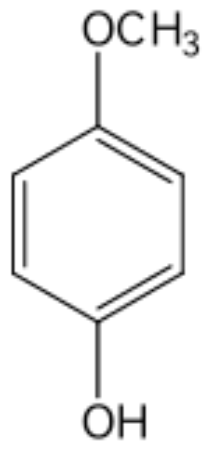
I



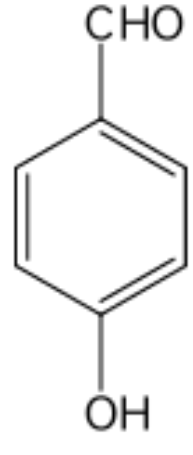
II



III



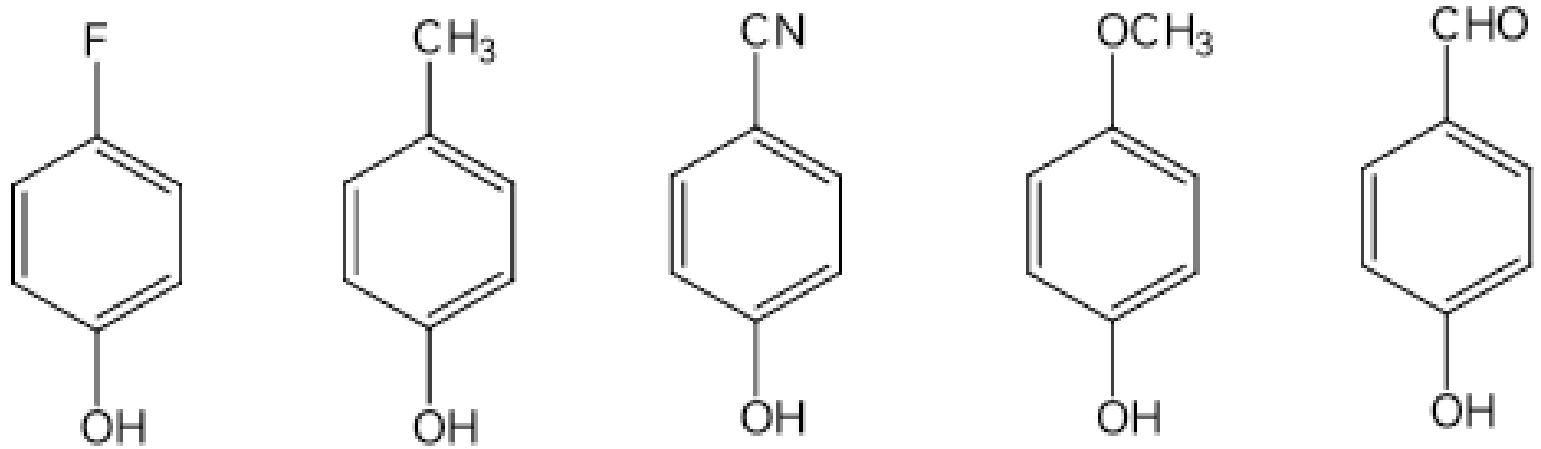
IV



V

Acidity of different substituted phenol

Rank the following compounds according to their acidities



I De

II Ac

III De

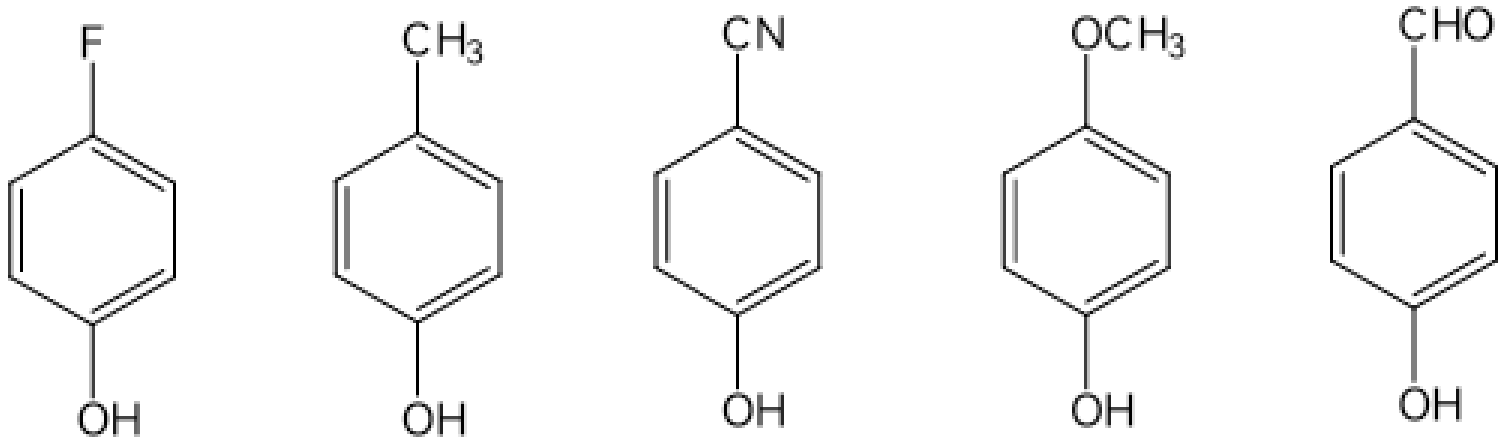
IV Ac

V De

Classify each group substituted on benzene wither is it
Activation or Deactivation

Acidity of different substituted phenol

Rank the following compounds according to their acidities



I De

II Ac

III De

IV Ac

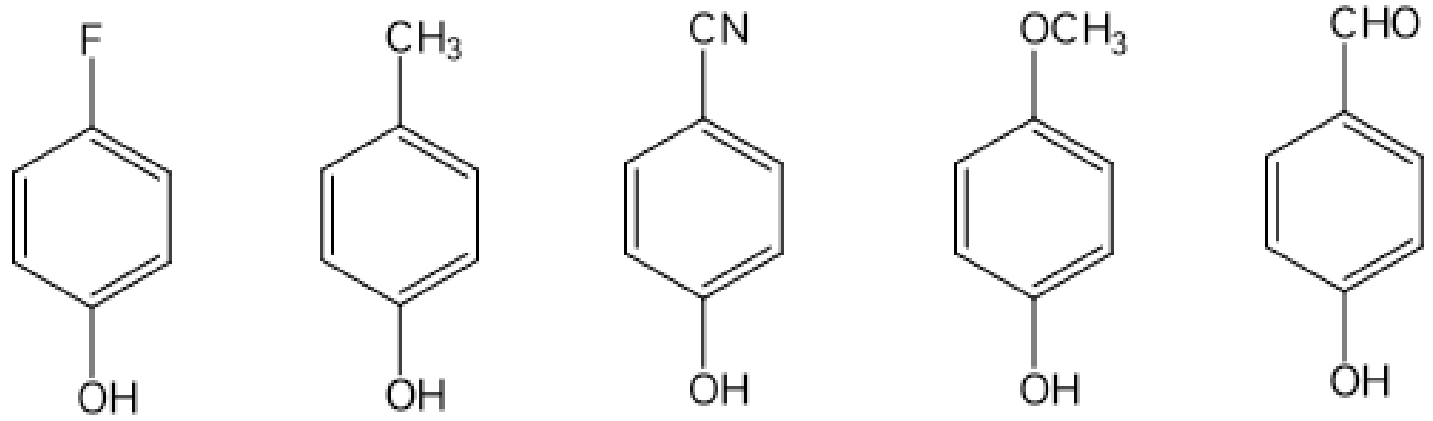
V De

Stronger deactivating group stronger acid

III

Acidity of different substituted phenol

Rank the following compounds according to their acidities



I II III IV V

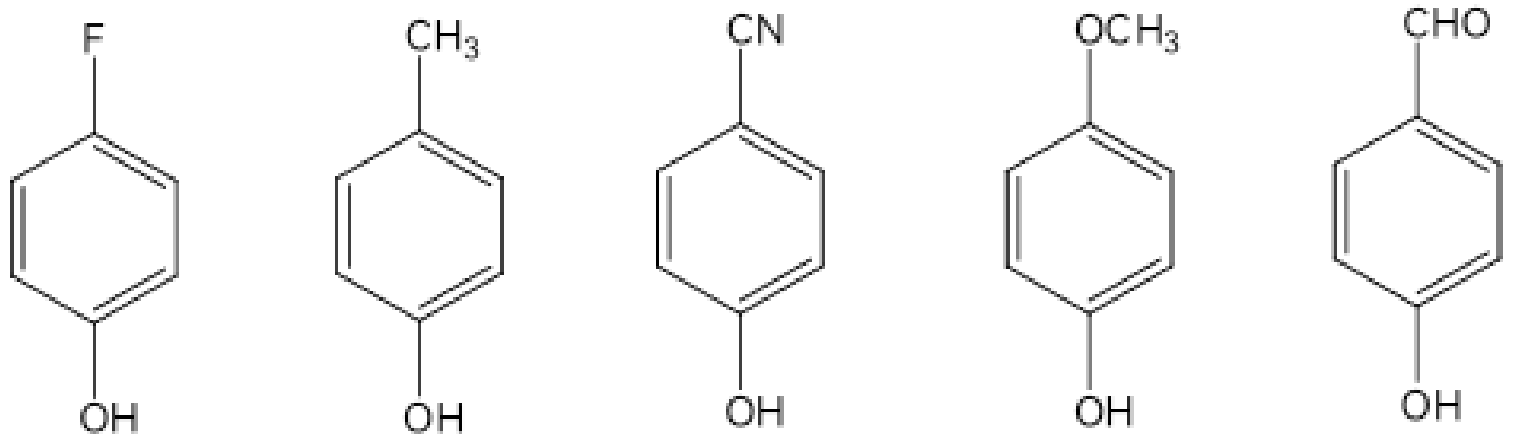
De Ac De Ac De

Stronger deactivating group stronger acid

III > V

Acidity of different substituted phenol

Rank the following compounds according to their acidities



I II III IV V

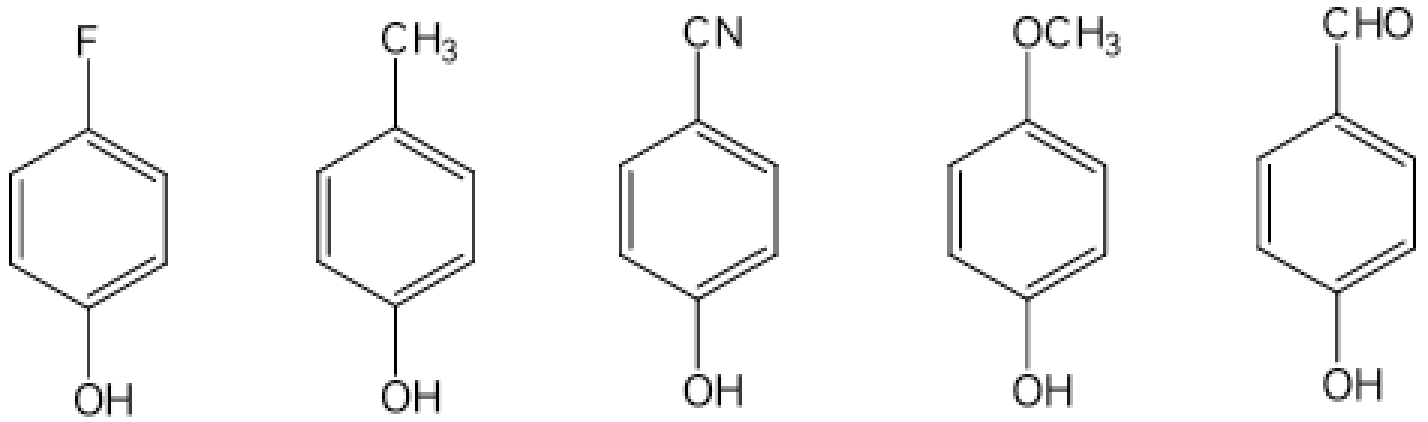
De Ac De Ac De

Stronger deactivating group stronger acid

III > V > I

Acidity of different substituted phenol

Rank the following compounds according to their acidities



I De

II Ac

III De

IV Ac

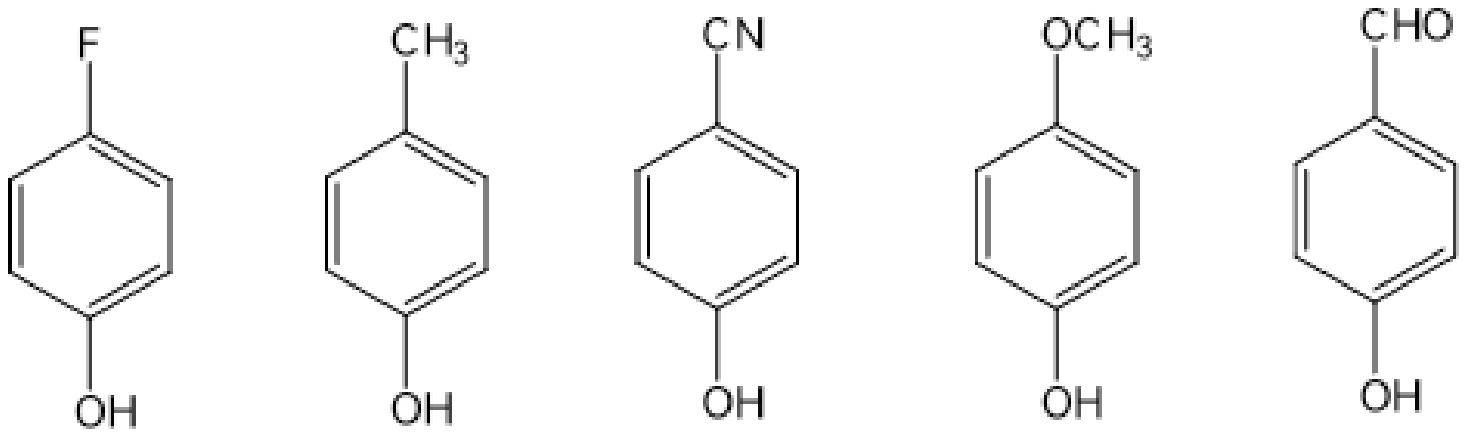
V De

Weaker activating group stronger acid

III > V > I > II

Acidity of different substituted phenol

Rank the following compounds according to their acidities



I De

II Ac

III De

IV Ac

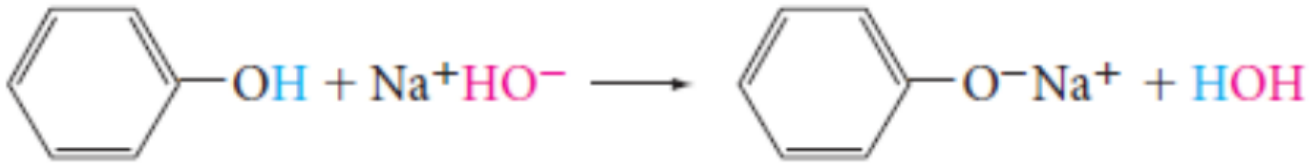
V De

Weaker activating group stronger acid

III > V > I > II > IV

Deprotonating of alcohols and phenols

$$ROH + Na^+HO^- \rightleftharpoons RO^-Na^+ + H_2O$$



phenol — sodium phenoxide

$$2\,RO{-}H + 2\,K \longrightarrow 2\,RO^-\,K^+ + H_2$$

alcohol — potassium alkoxide

$$RO{-}H + NaH \longrightarrow RO^-\,Na^+ + H{-}H$$

sodium hydride — sodium alkoxide

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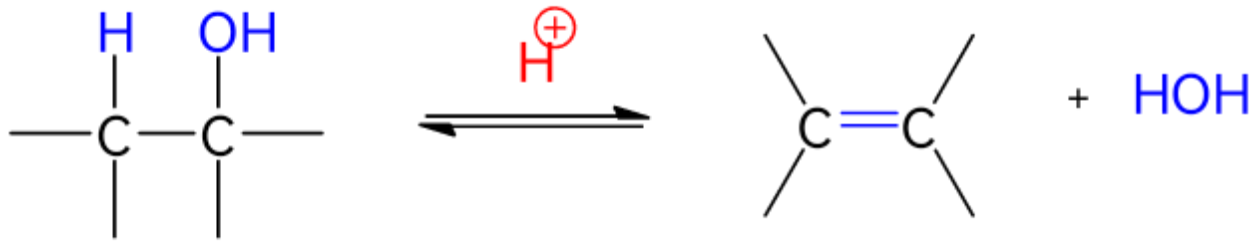
7.8 Dehydration of Alcohols to Yield Alkenes

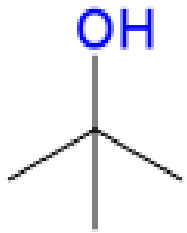
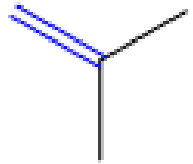
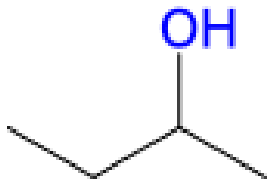
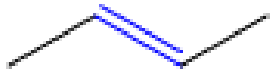
Dehydration of Alcohol



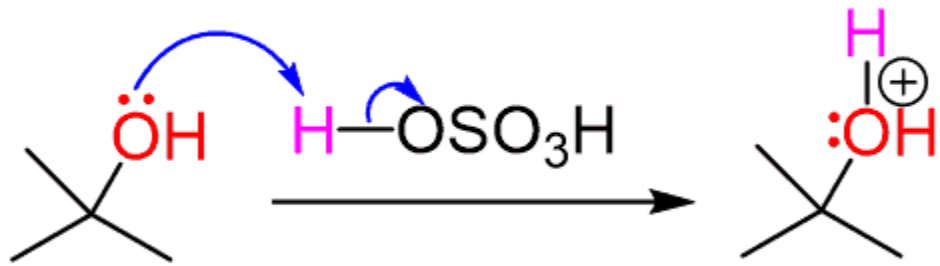
Acid Catalyzed reaction

$\overset{\oplus}{H}$ = H_2SO_4 and H_3PO_4

Dehdydration of Alcochols

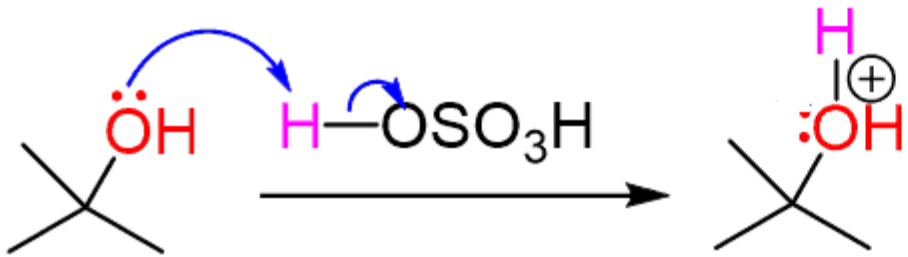
Alcohol				Mechanism
3°		30% H_2SO_4, 90 °C	 + H_2O	E1
2°		75% H_2SO_4, 100 °C	 + H_2O	E1
1°		Conc. H_2SO_4, 150 °C	 + H_2O	E2

protonation of OH



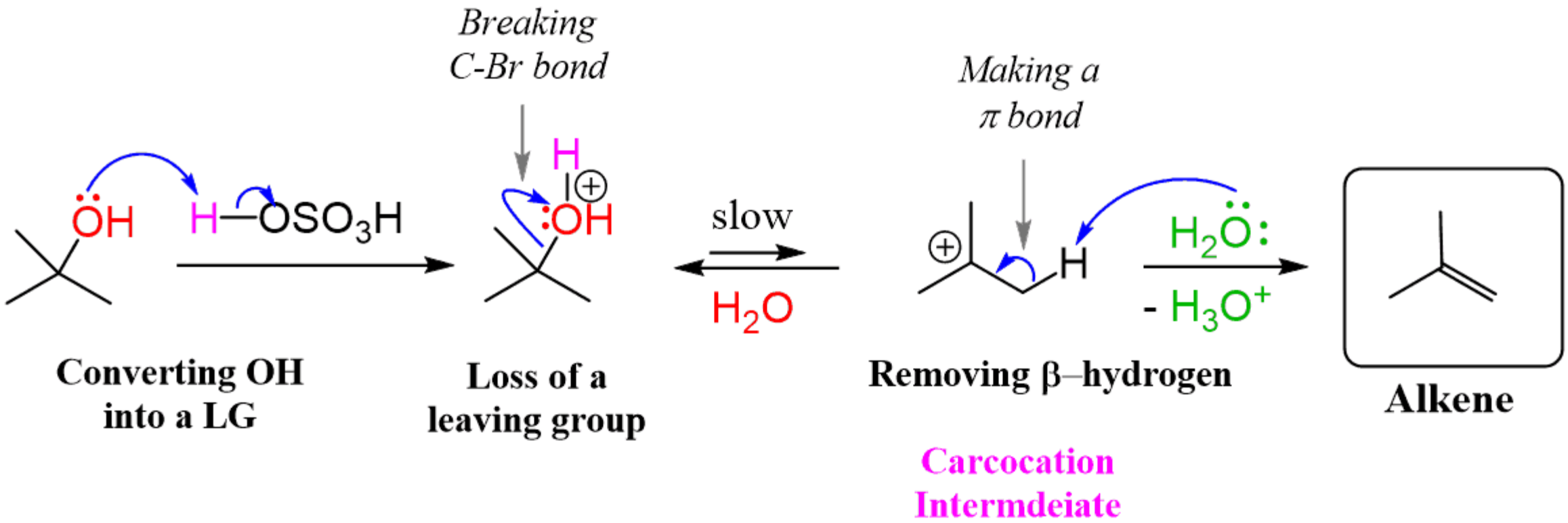
OH has been converted into a good LG

Dehydration of a Tertiary Alcohol thorough a E1 mechanism

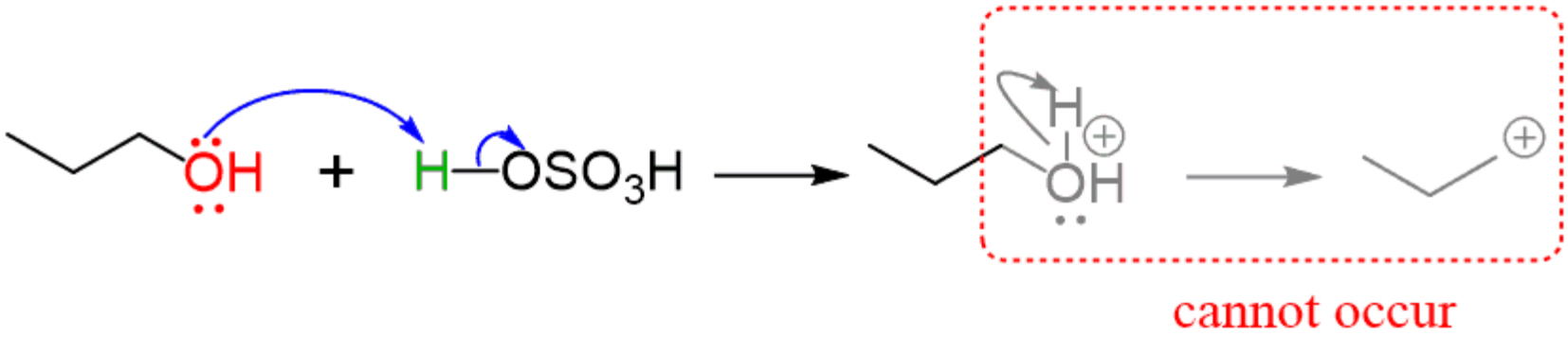


Converting OH into a LG

Dehydration of a Tertiary Alcohol thorough a E1 mechanism

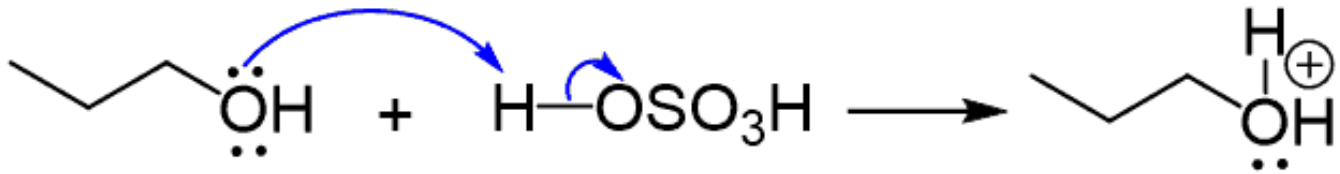


Protonation of Primary Alcochols

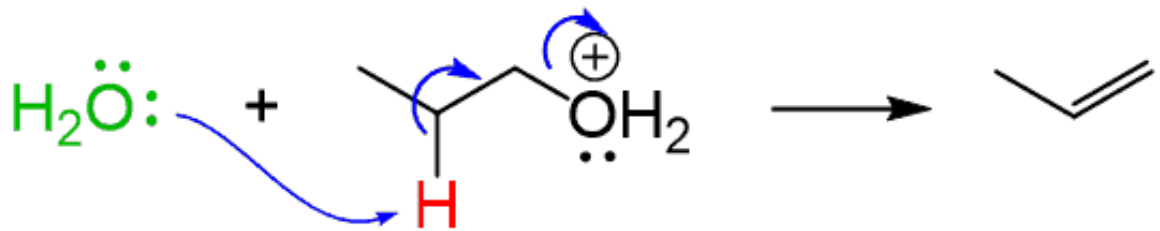


Dehydration of Primary Alcohols by E2 mechanism

Step 1. *Protonation of the hydroxyl group*

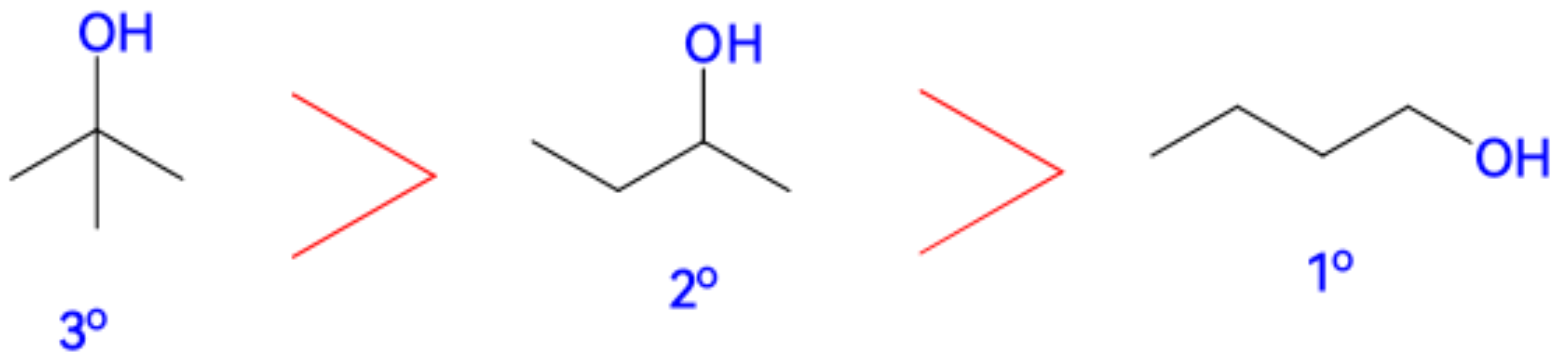


Step 2. *Dehydration of alcohol by E2 mechanism*



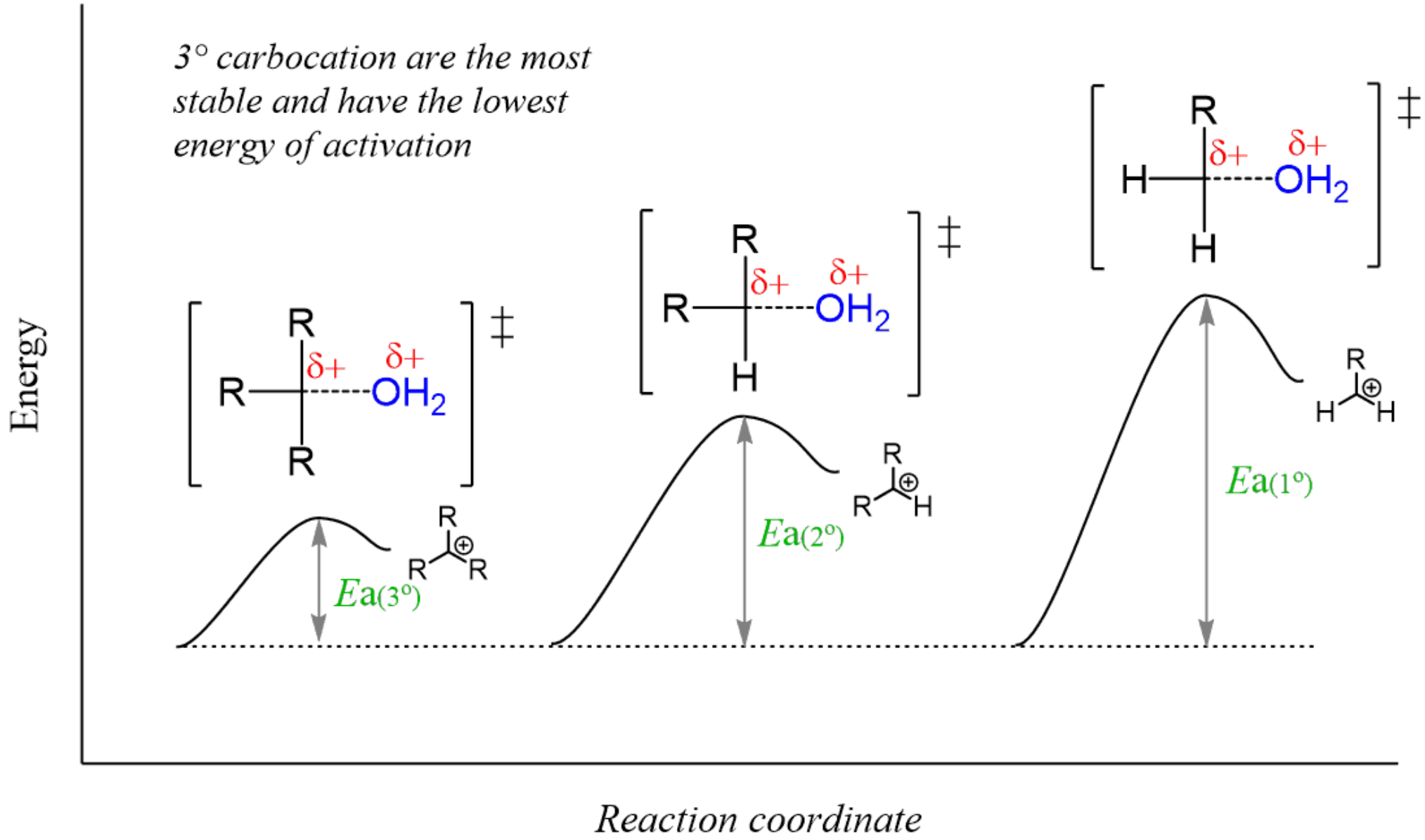
β–hydrogen

Reactivity of Alcochols toward Dehydration reaction

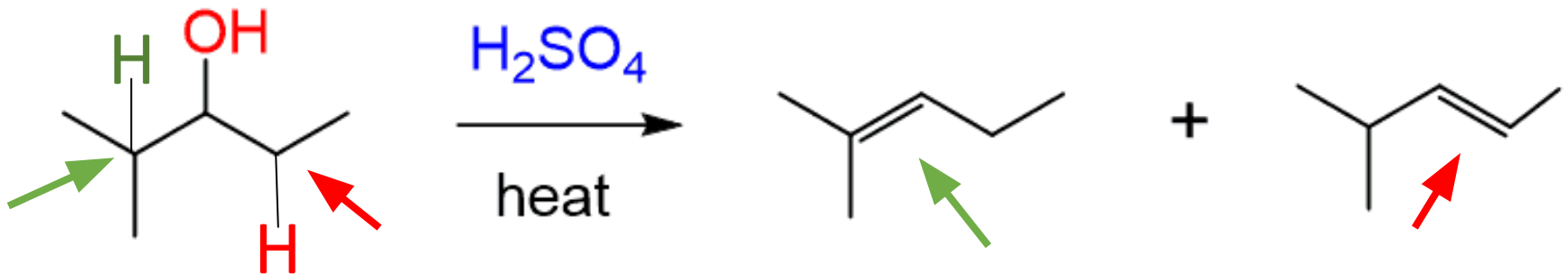


Mechanism	E1	E1	E2

Formation of carbocations from tertiary, secondary, and primary alcohols.



Dehydration is a Regioselective Reaction and it Follows the Zaitsev rule



2-methylpentan-3-ol

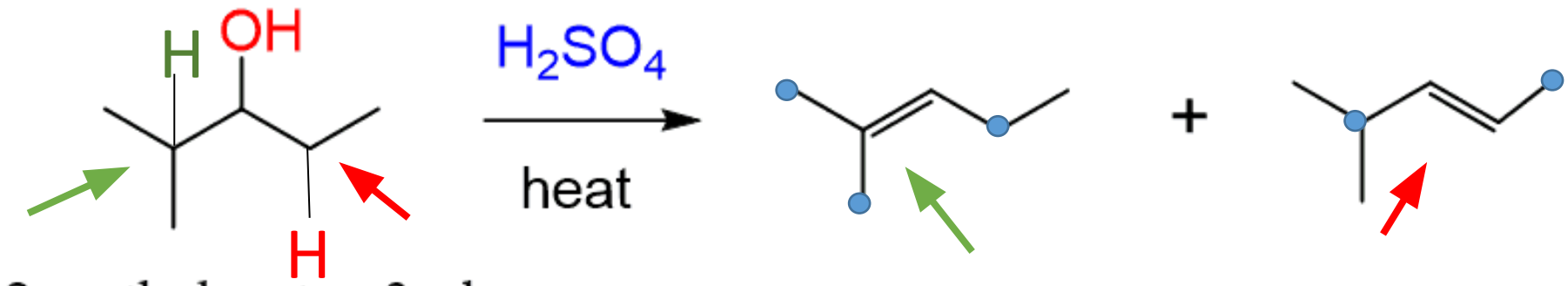
2-methylpent-2-ene

major

Zaitsev's

minor

Dehydration is a Regioselective Reaction and it Follows the Zaitsev rule



2-methylpentan-3-ol

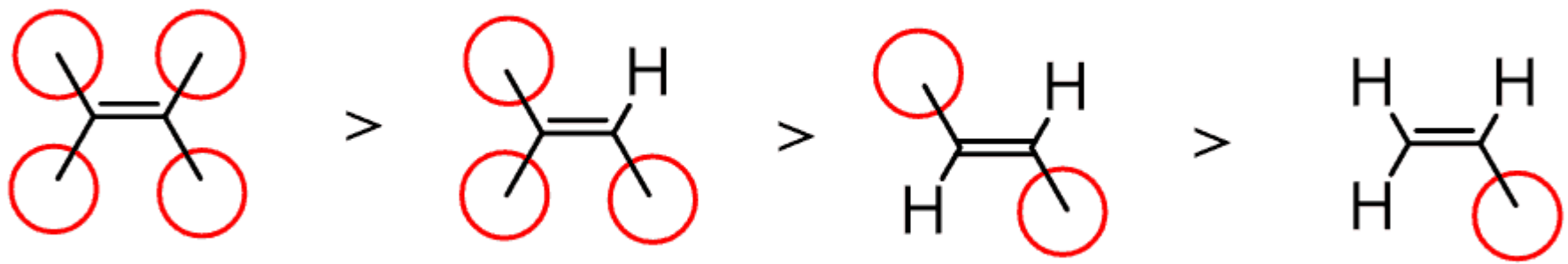
2-methylpent-2-ene

major

Zaitsev's

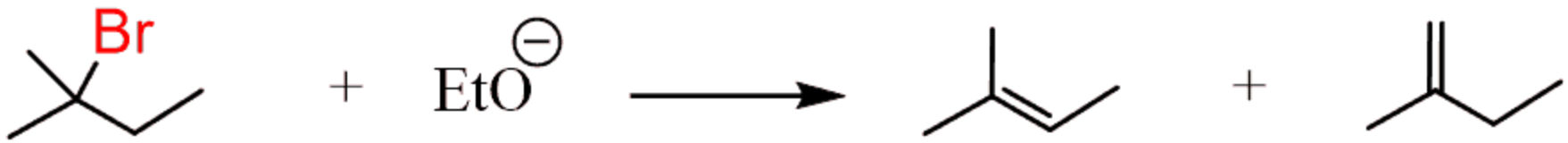
minor

The more substituted alkenes are more stable



Tetrasubstituted > Trisubstituted > Disubstituted > Monosubstituted

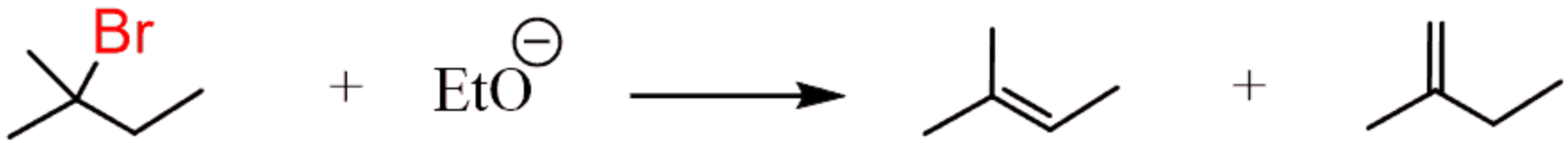
Elimination of Alkyl halide and Zaitsev rule



major minor

80% 20%

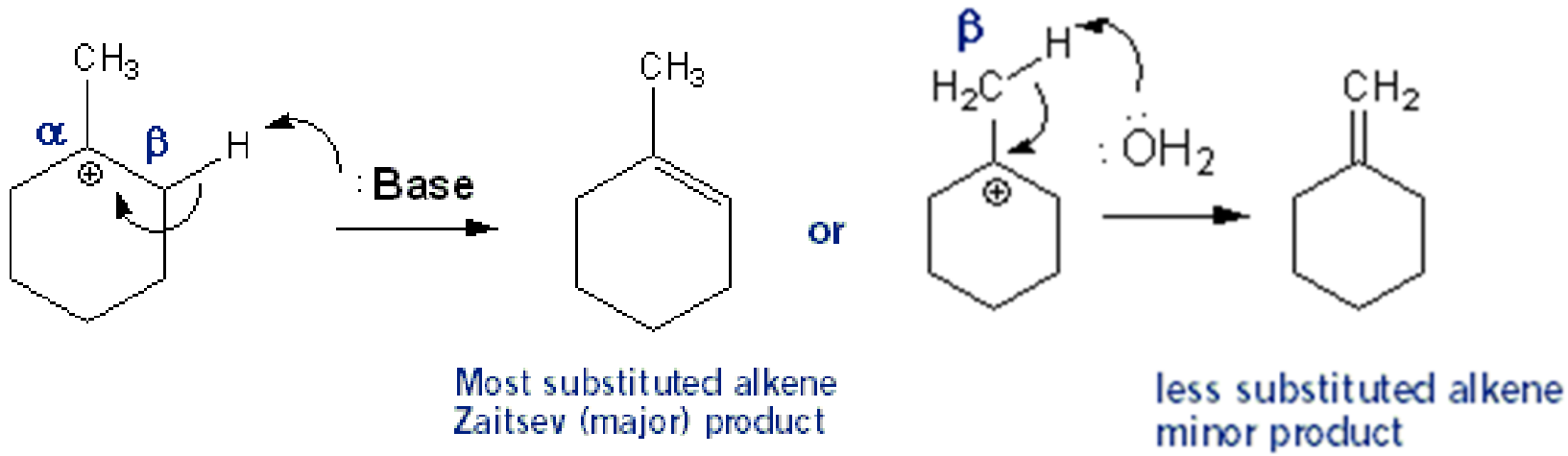
Elimination of Alkyl halide and Zaitsev rule



major minor

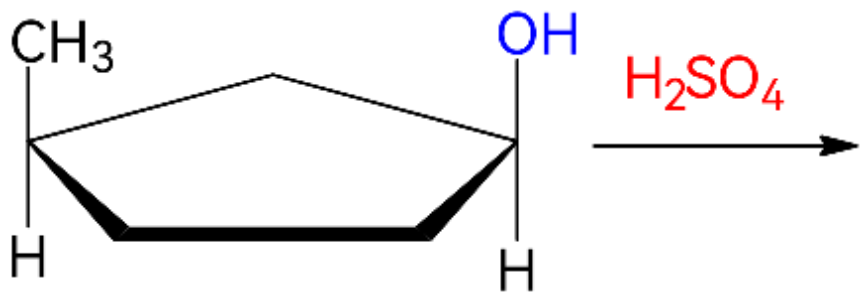
80% 20%

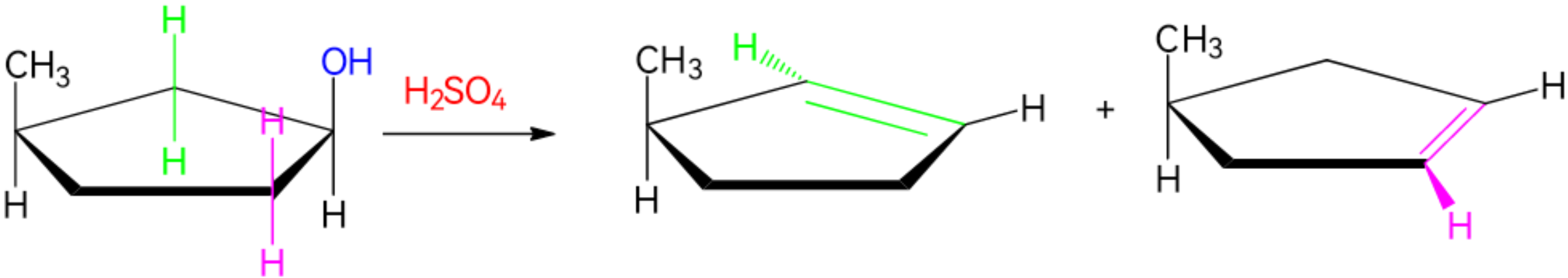
Dehydration of 1-Methylcyclohexanol



Most substituted alkene
Zaitsev (major) product

less substituted alkene
minor product

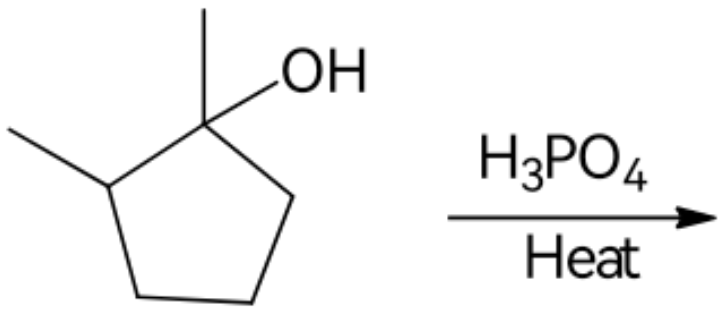

CH3
OH
H2SO4
H
H



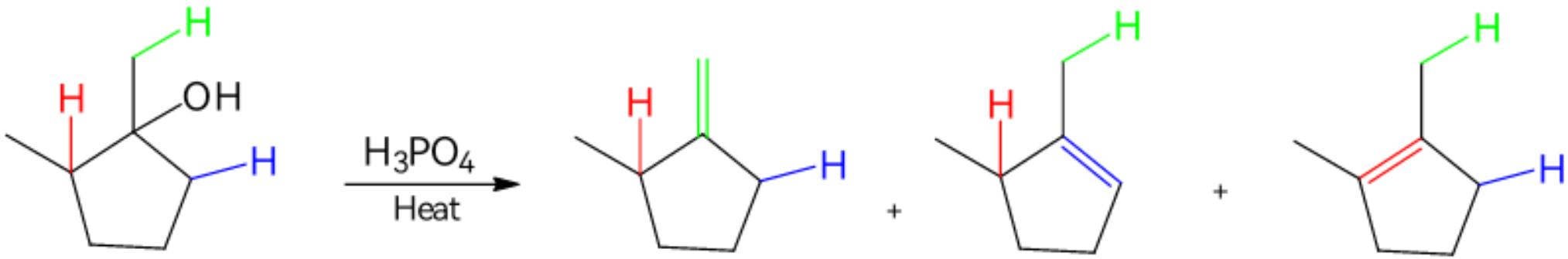
2° Alcohol

E1 Mechanism

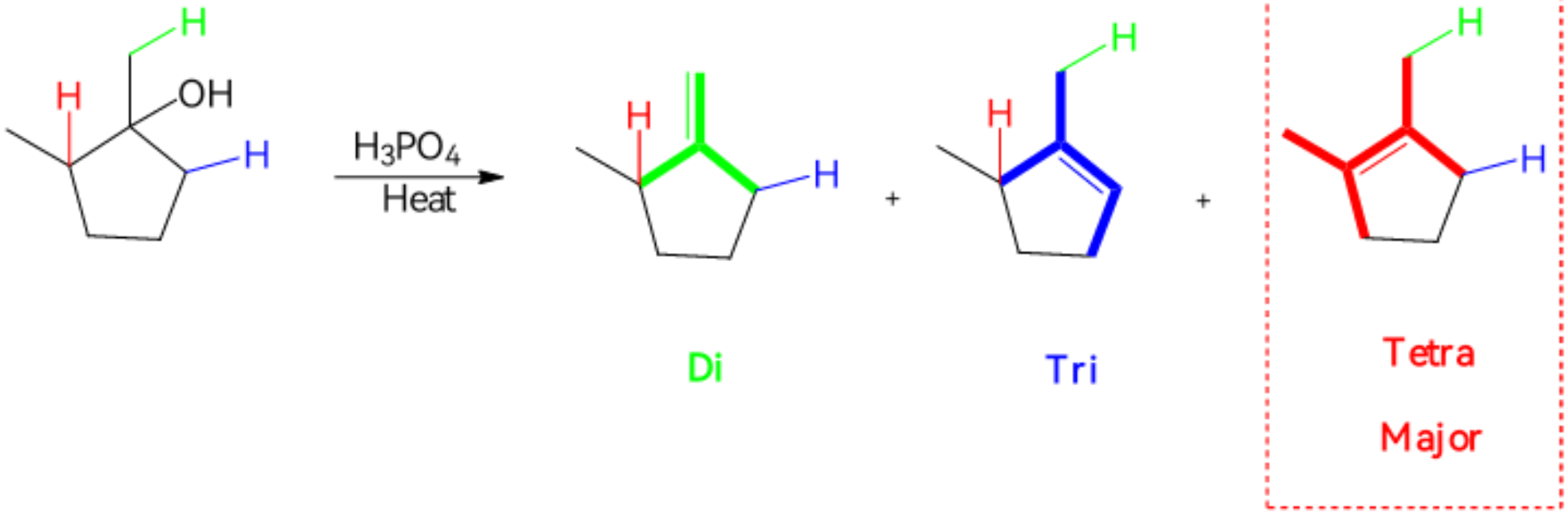
Dehydration of 1,2-Dimethylcyclopetanol



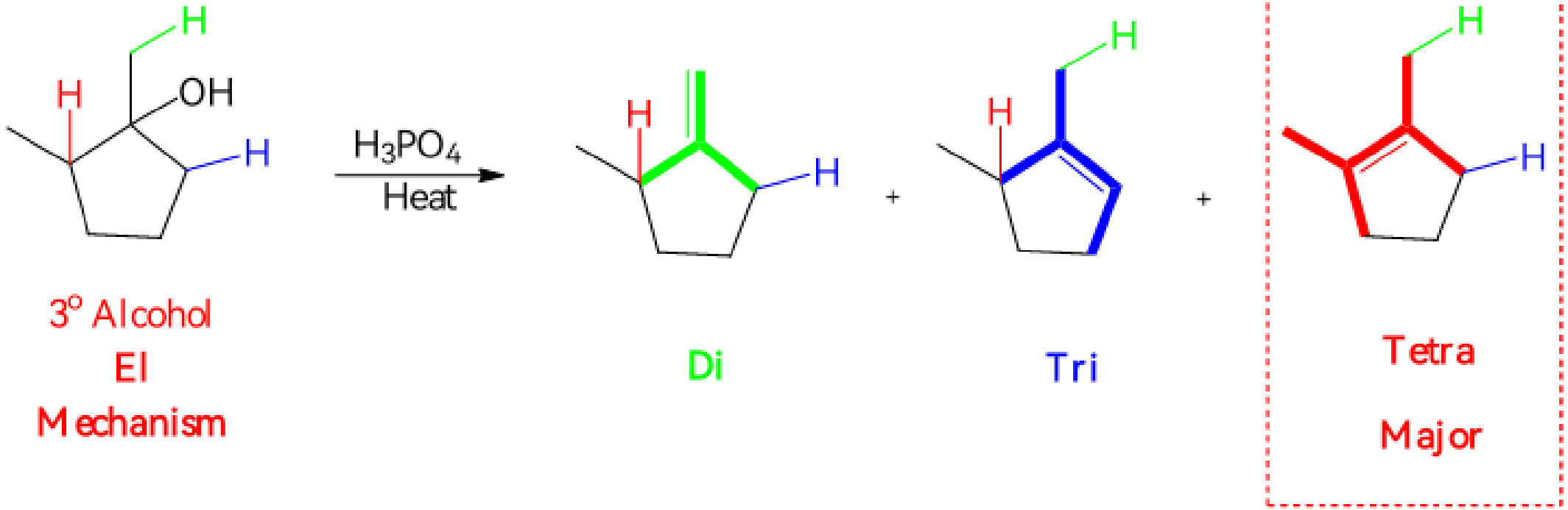
Dehydration of 1,2-Dimethylcyclopetanol



Dehydration of 1,2-Dimethylcyclopetanol



Dehydration of 1,2-Dimethylcyclopetanol



3^{o} Alcohol

E1

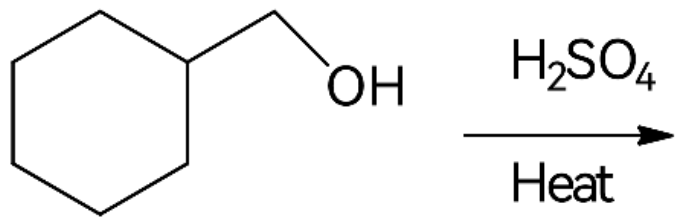
Mechanism

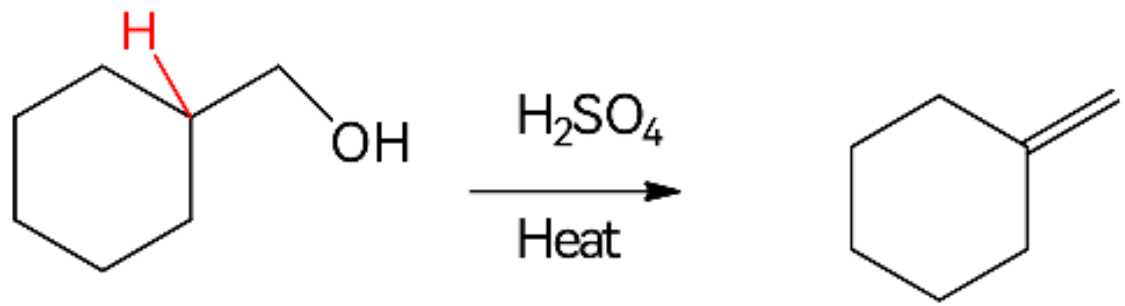
Di

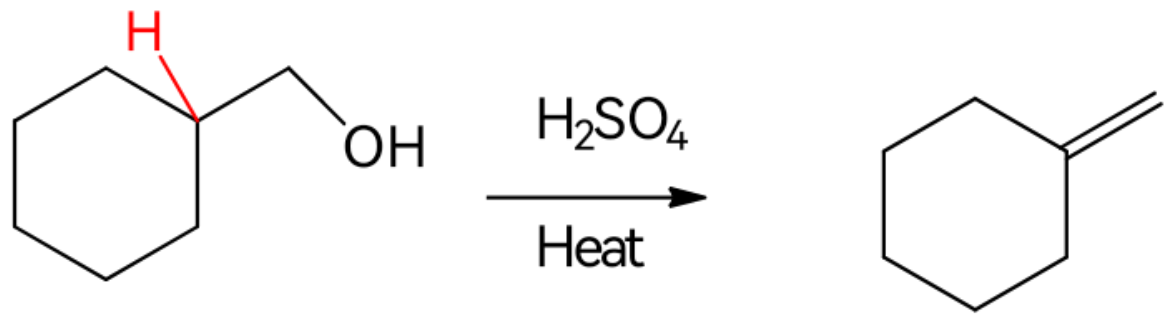
Tri

Tetra

Major


OH
H_2SO_4
Heat


H
OH
H_2SO_4
Heat



1° Alcohol

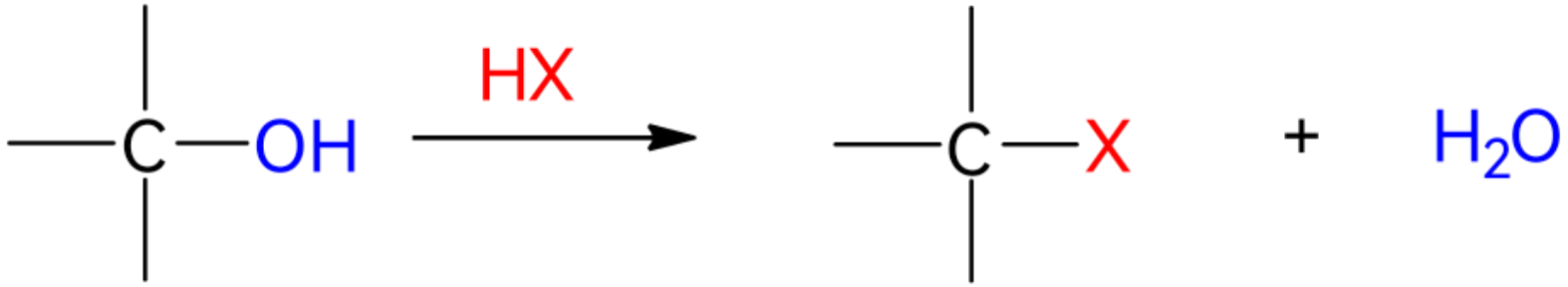
E2

Mechanism

Chem 233

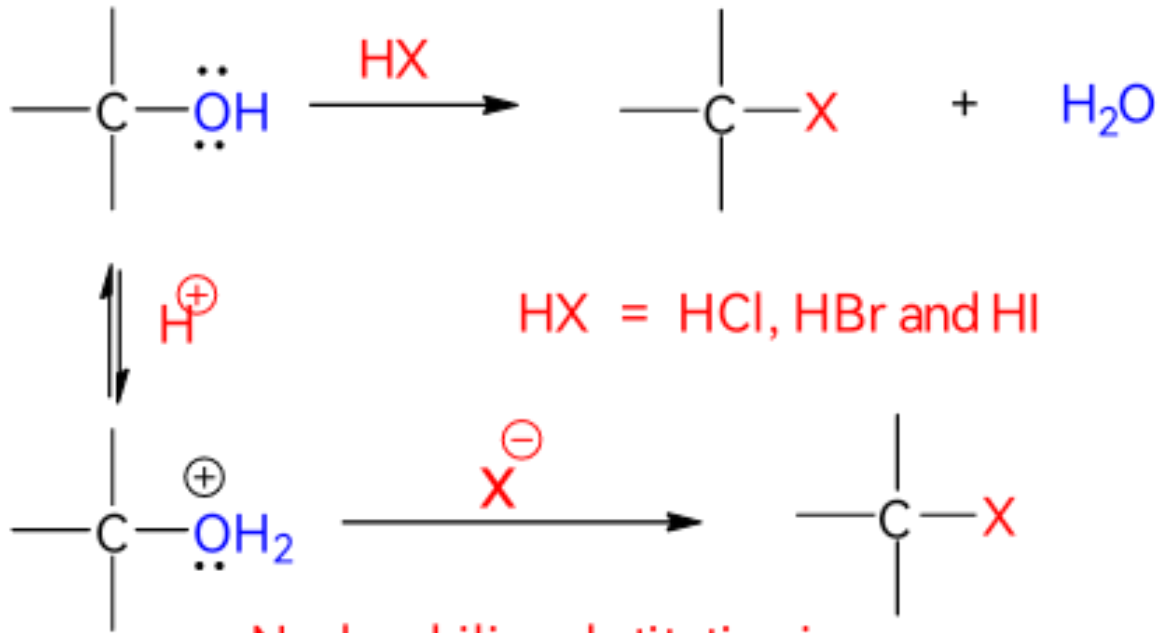
7.9 The Reaction of Alcohols with Hydrogen Halides

Conversion of Alcohols into Alkyl Halides



HX = HCl, HBr and HI

Nucleophilic substitution of alcoholes by a halide



HX = HCl, HBr and HI

Nucleophilic substitution in:

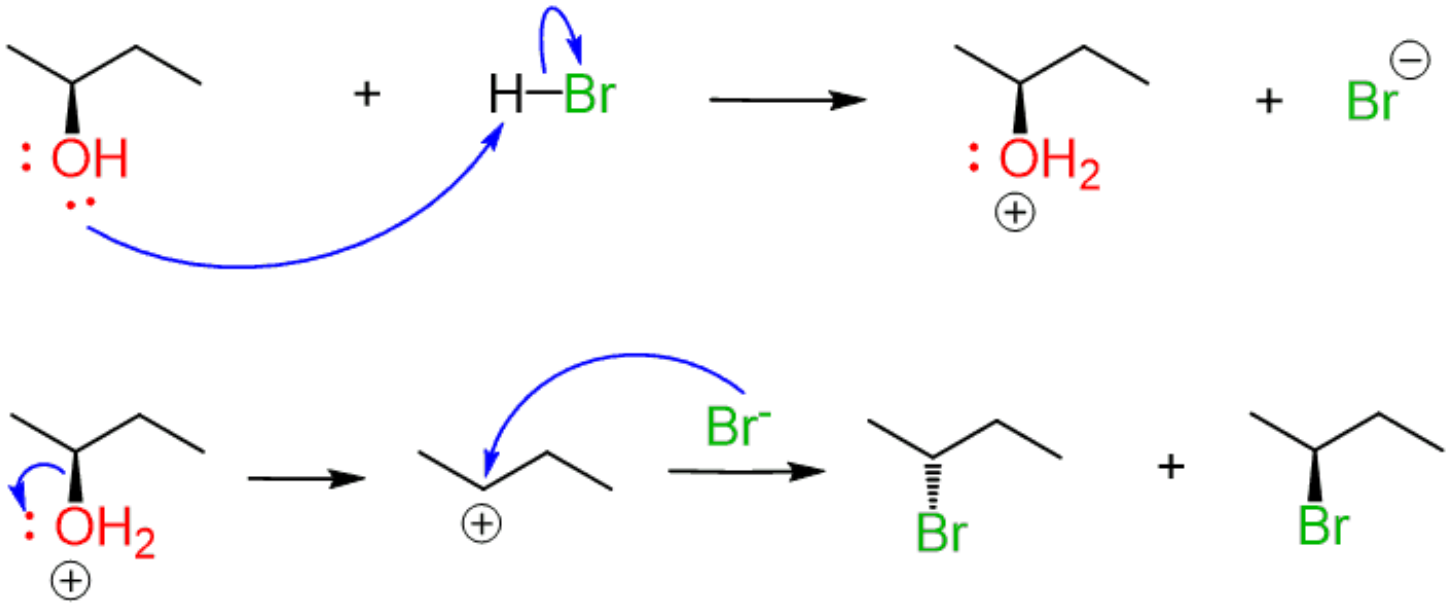
3° and 2° alcohol *via* S_N1

1° alcohol *via* S_N2

-OH Group is not good leaving group

-OH Group is protonated in acidic meadium to form a better leaving group (H_2O)

Stereochemistry is not controlled in S_N1 reactions

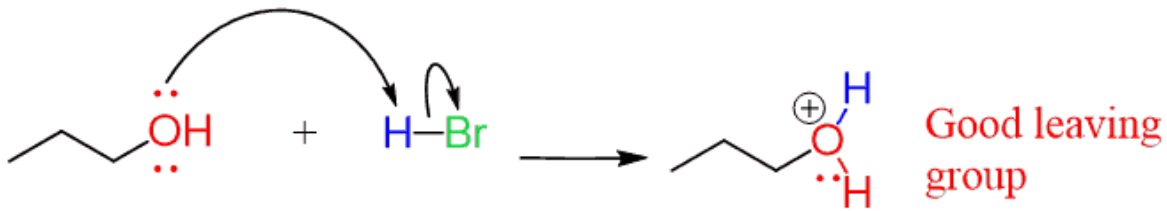


Racemic mixture

Stereochemistry lost

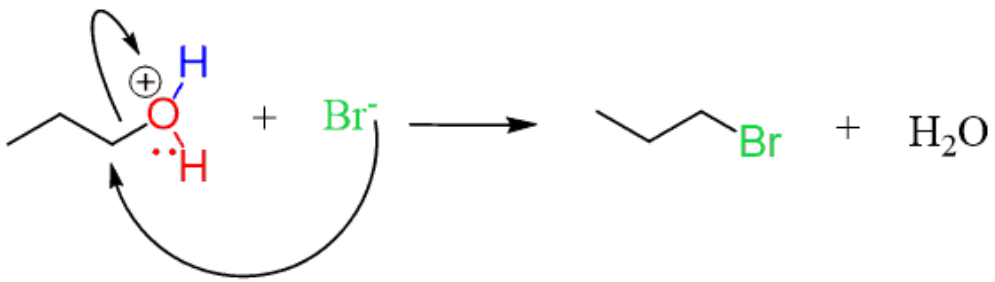
Conversion of Primary Alcohols to Alkyl Halides with HX Acids

Step 1: Prptonation of OH



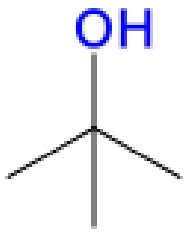
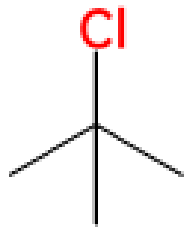
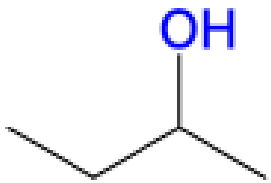
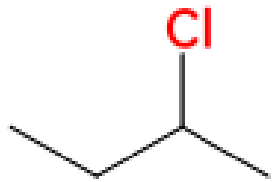
Good leaving group

Step 2: Nucleophilic attack of Br^-

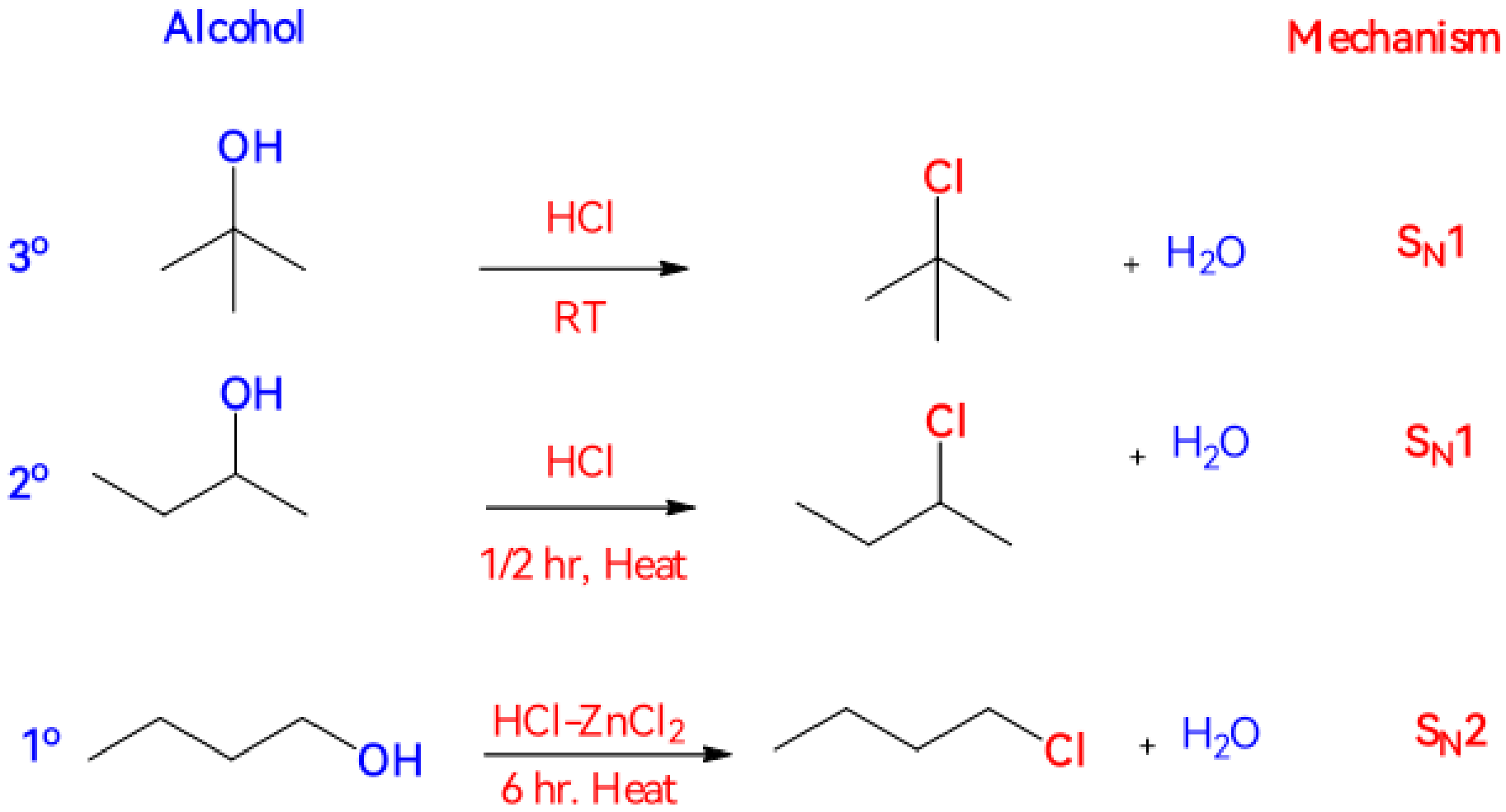


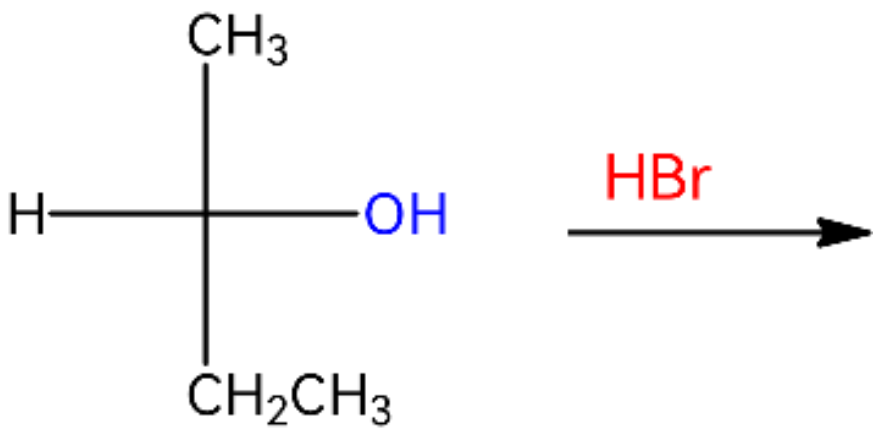
Same for HI and HCl:

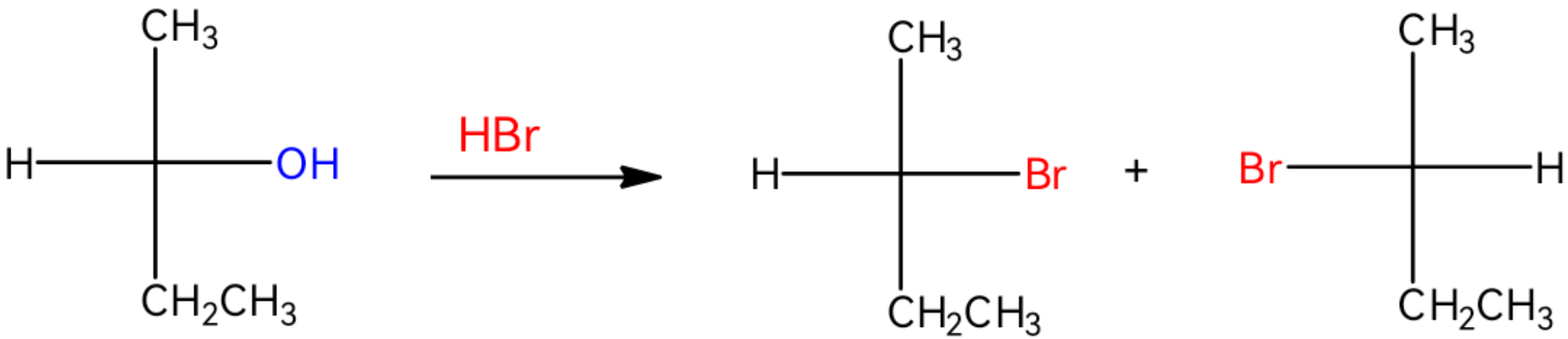
Reactivity of Alcoholes toward substitution reaction with hydrogen halide

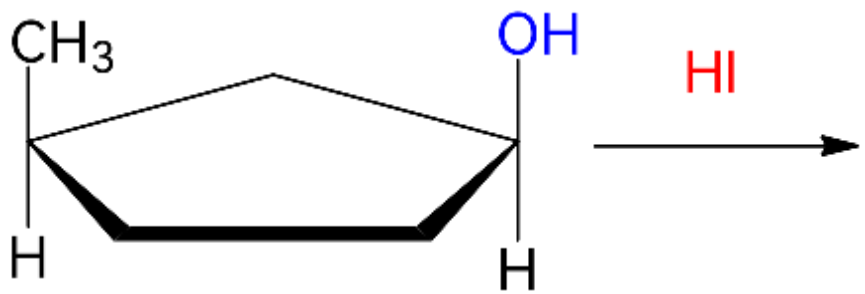
Alcohol				Mechanism
3°		HCl, RT	 + H_2O	S_N1
2°		HCl, 1/2 hr, Heat	 + H_2O	S_N1
1°		HCl	No Reaction	

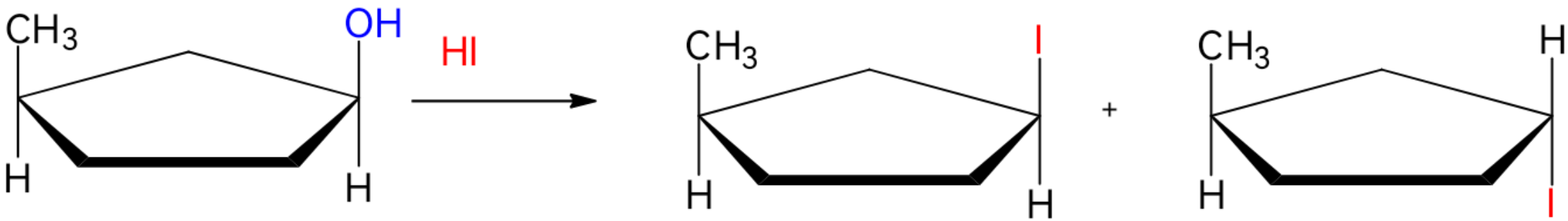
Reactivity of Alcoholes toward substitution reaction with hydrogen halide

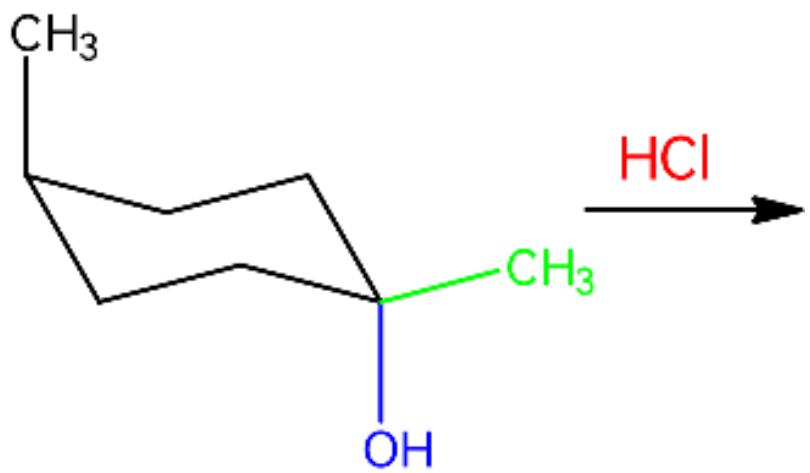


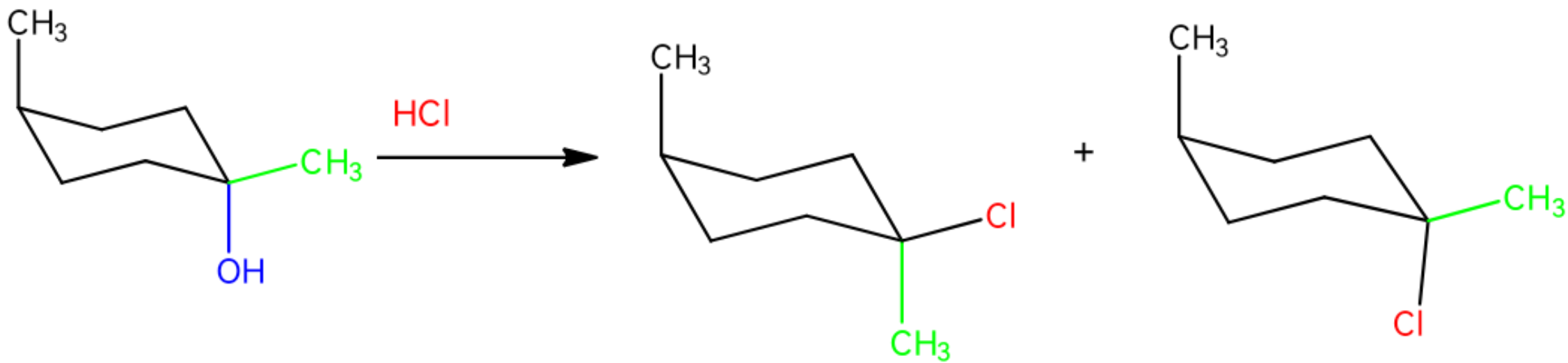

CH3
H
OH
CH2CH3
HBr


CH3
H
OH
CH2CH3
HBr
CH3
H
Br
CH2CH3
+
CH3
Br
H
CH2CH3

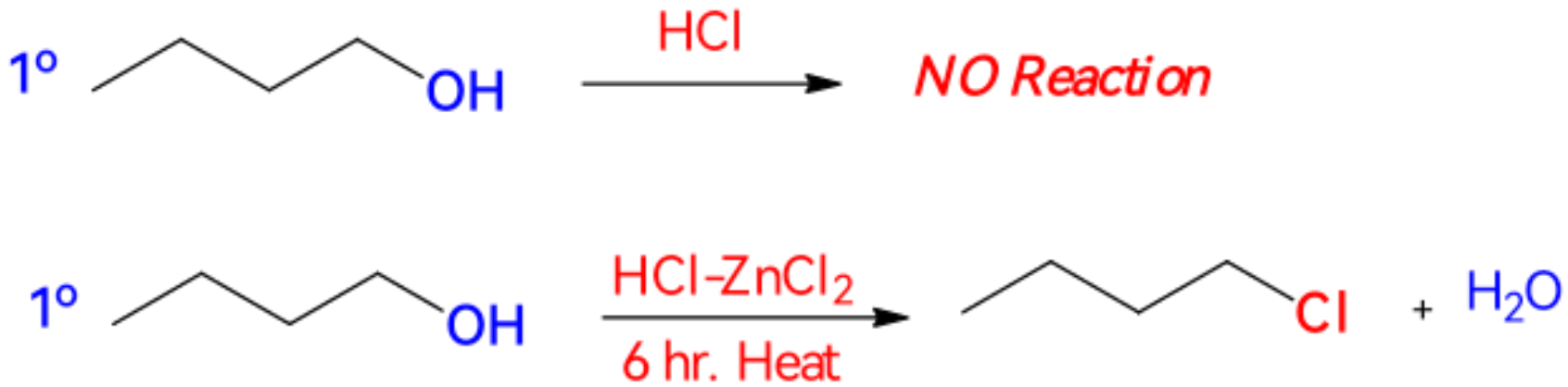

CH3
OH
HI
H
H


CH3
OH
H
H
HI
CH3
I
H
H
+
CH3
H
H
I


CH3
HCl
CH3
OH

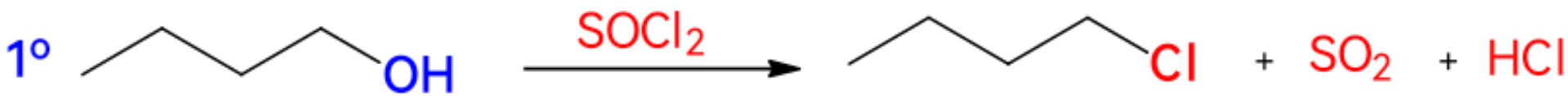

CH3
CH3
OH
HCl
CH3
Cl
CH3
+
CH3
CH3
Cl

Substitution of primary alcohols by Chloride

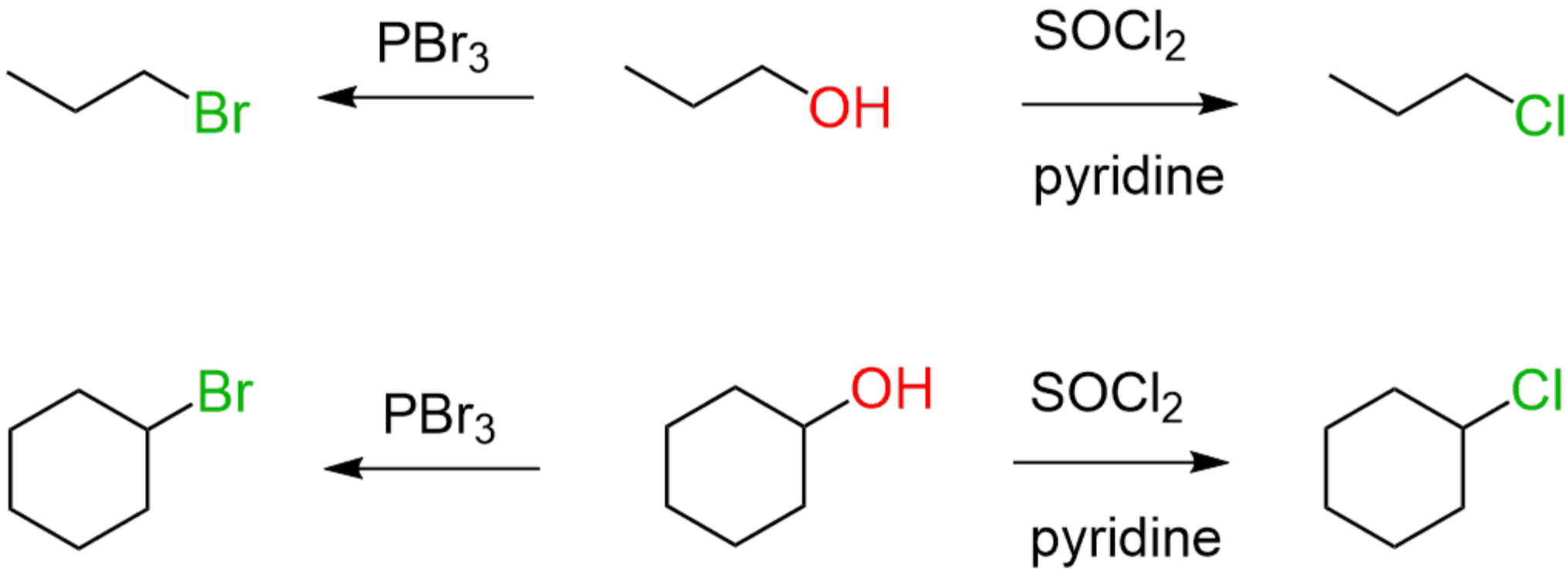


Sevier conditions are used to prepare primary chloroalkane from primary alcohol

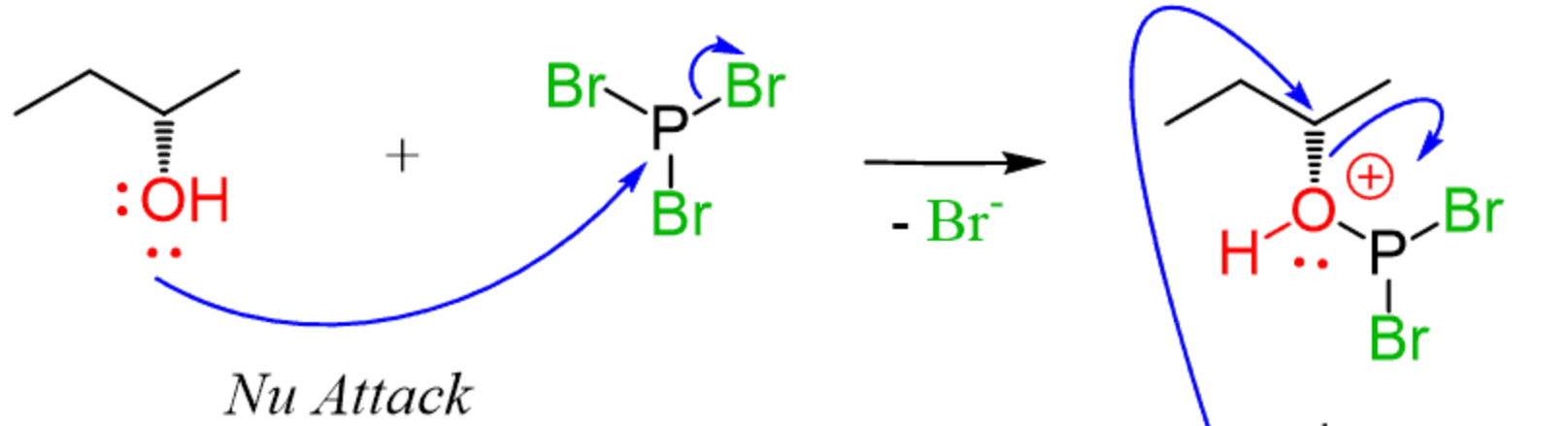
Mild conditions of Thionyl chloride to prepare Alkyl chloride



1° and 2° alcohols can be converted to alkyl halides with $SOCl_2$ and PBr_3

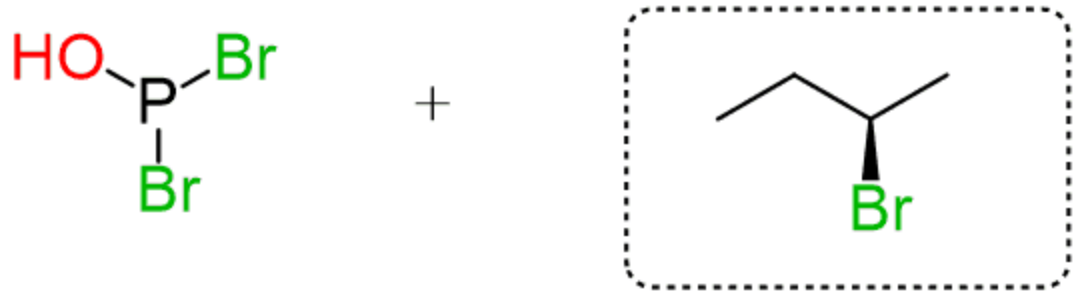


Reaction of Alcohols with PBr_3 via S_N2 Mechanism



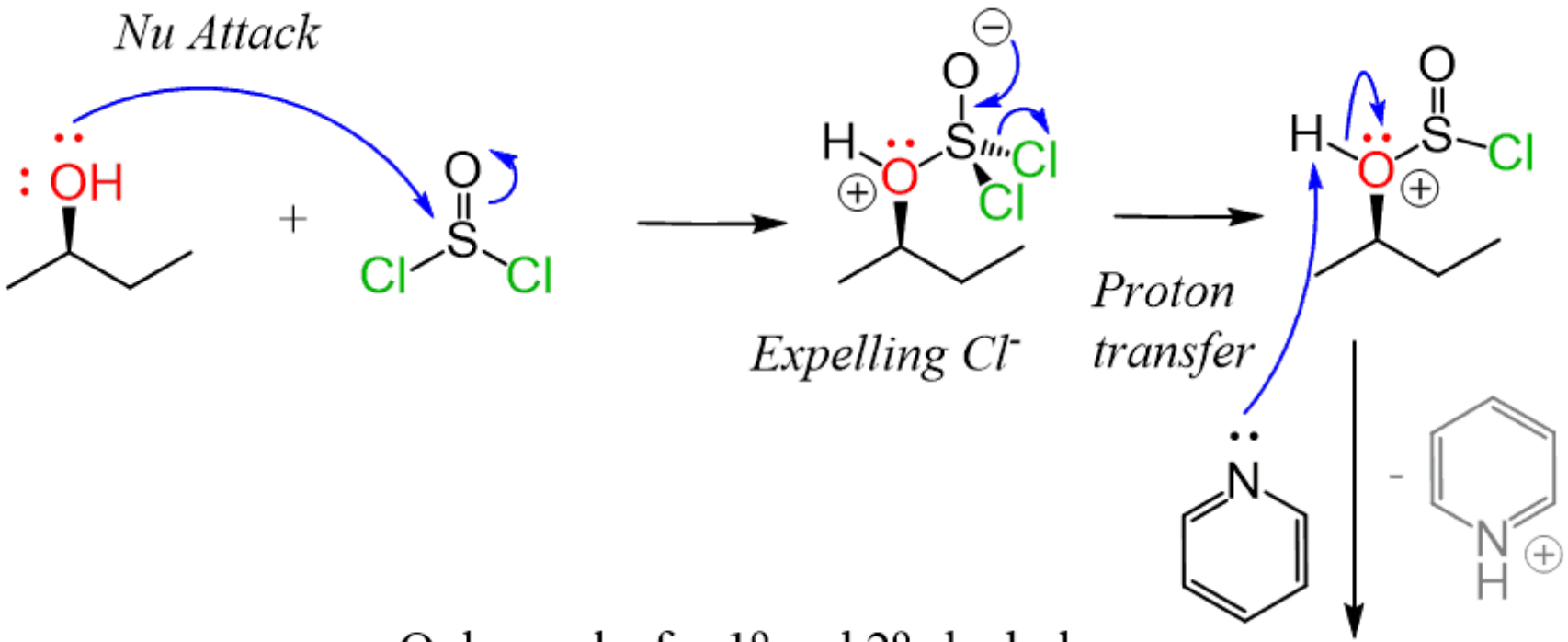
Only works for 1° and 2° alcohols

S_N2

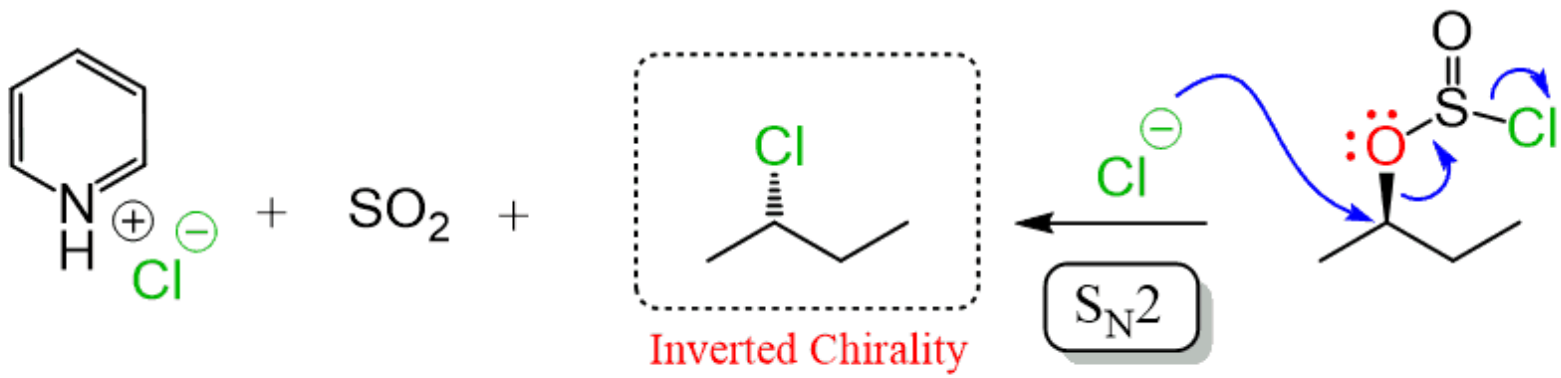


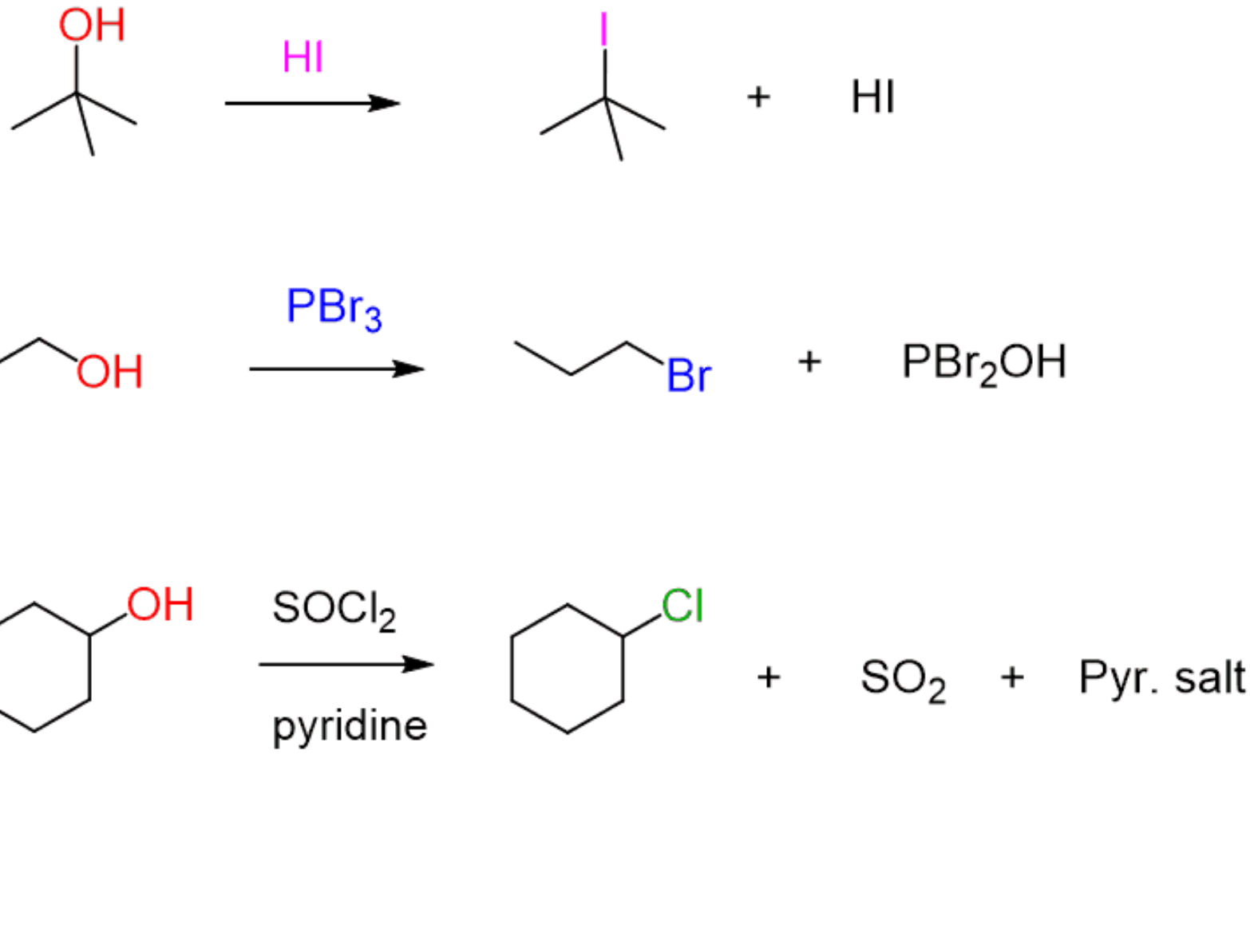
Inverted Chirality

Reaction of Alcohols with $SOCl_2$ and Pyridine via an S_N2 Mechanism



Only works for 1° and 2° alcohols



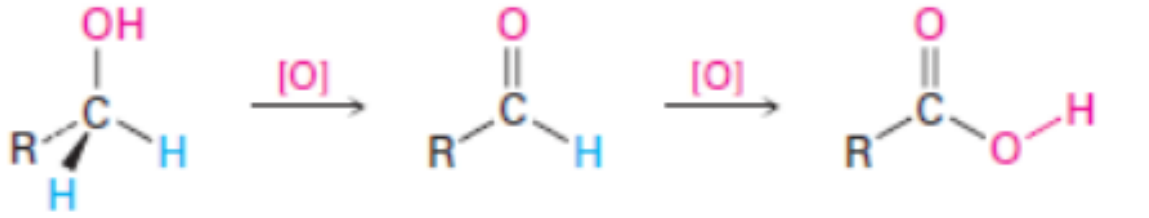

OH
HI
I
+ HI
PBr3
OH
Br
+ PBr2OH
OH
SOCl2
pyridine
Cl
+ SO2 + Pyr. salt

Organic Chemistry for nonmajor students
Chem 233

7.12 Oxidation of Alcohols

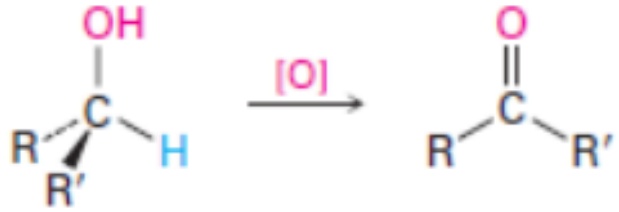
Oxidation of Alcohols

Primary alcohol



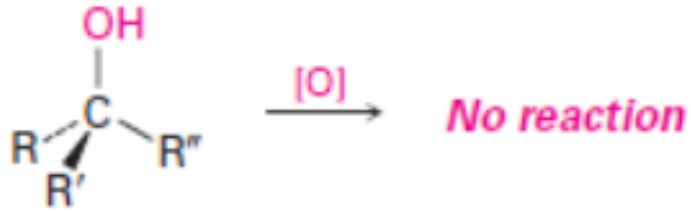
An aldehyde **A carboxylic acid**

Secondary alcohol



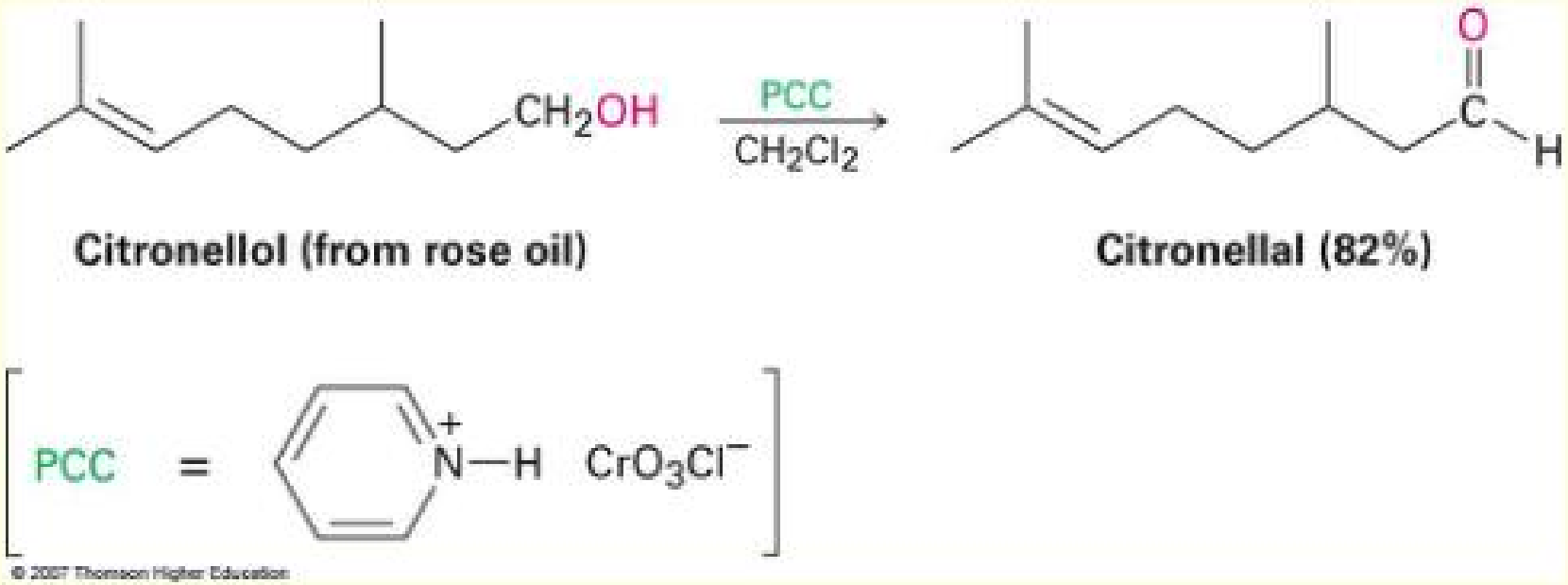
A ketone

Tertiary alcohol

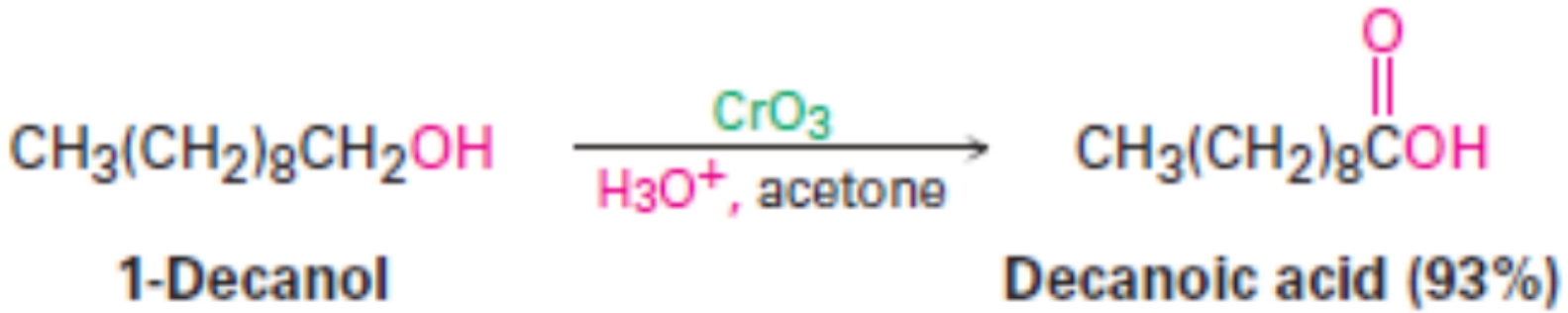


No reaction

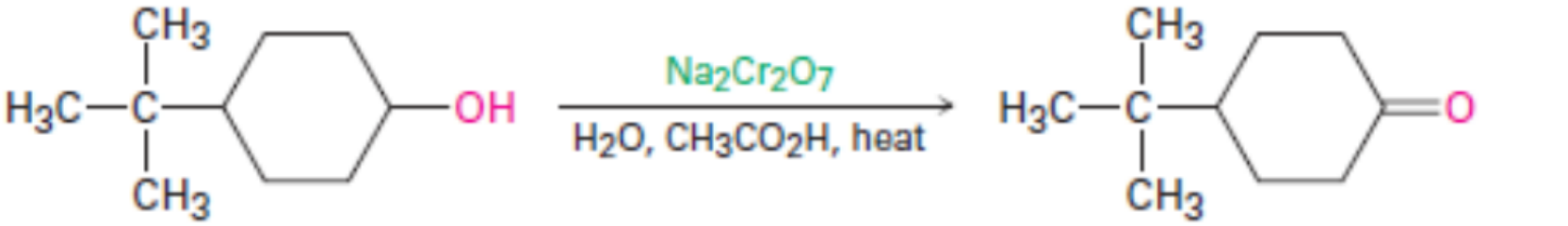
PCC Oxidation



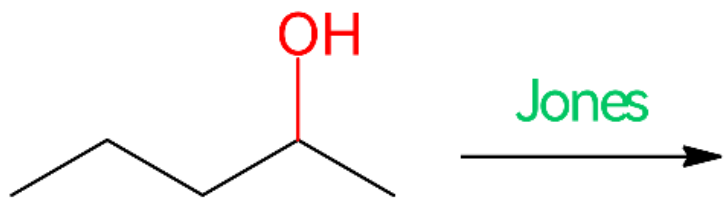
Oxidation primary alcohol by Jones

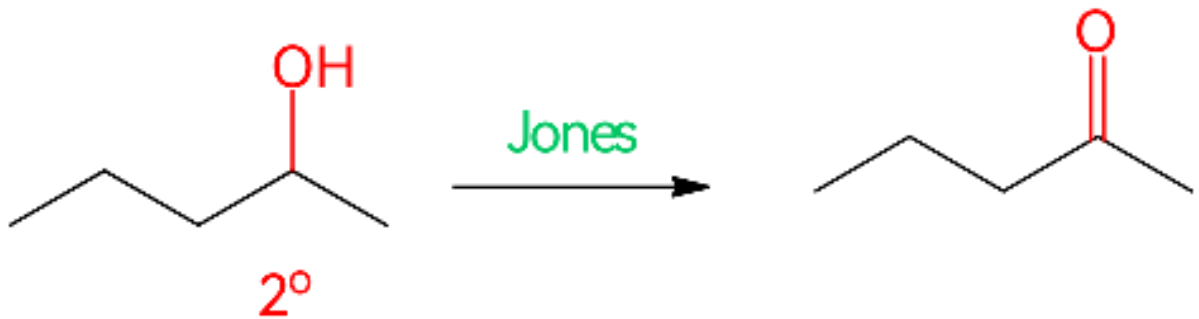


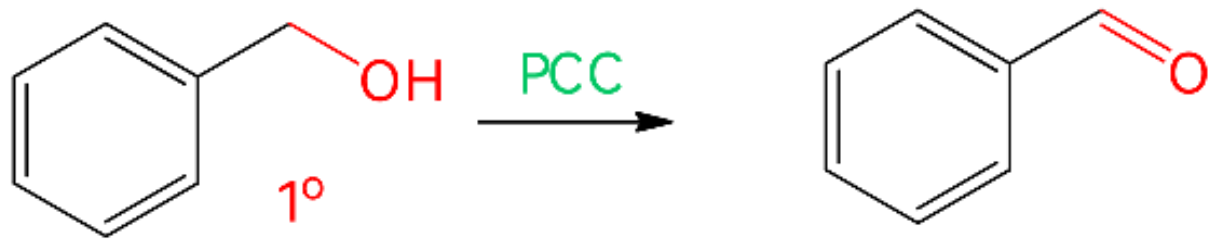
Oxidation by inexpensive reagent $Na_2Cr_2O_7$

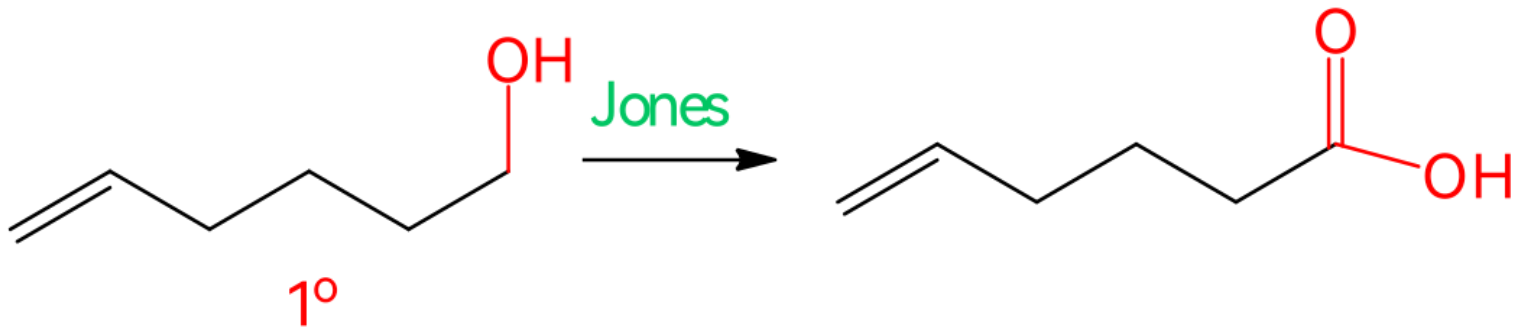


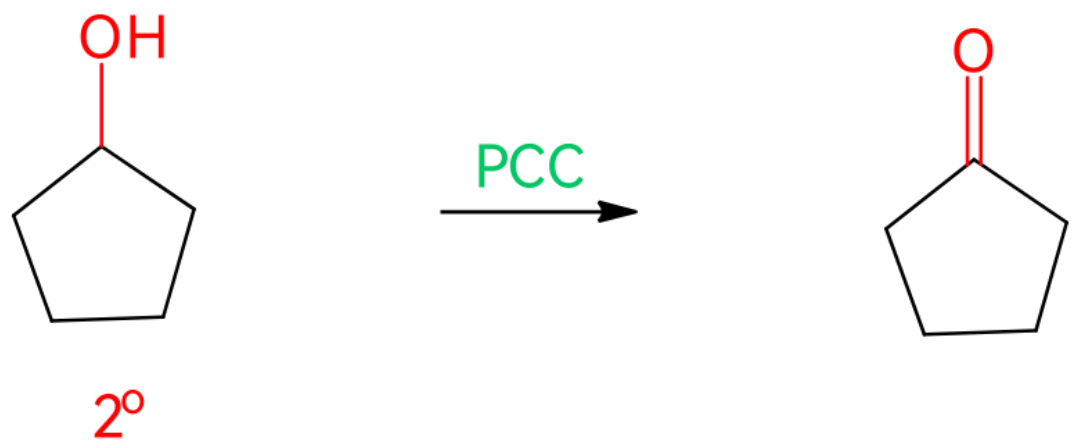
4-*tert*-Butylcyclohexanol **4-*tert*-Butylcyclohexanone (91%)**


OH
Jones

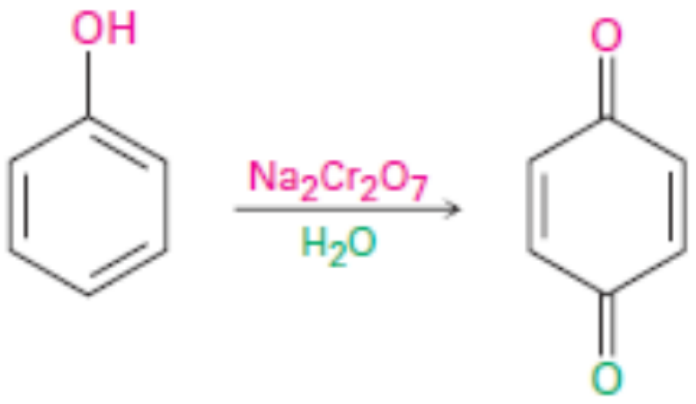

OH
Jones
O
2°


OH
PCC
1°
O


OH
Jones
O
OH
1º


OH
PCC
O
2°

Oxidation of Phenols: Quinones



Phenol **Benzoquinone**

Thanks to chemistrysteps.com
for their valued schemes