SATHYABAMA
INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)
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SCHOOL OF SCIENCE AND HUMANITIES

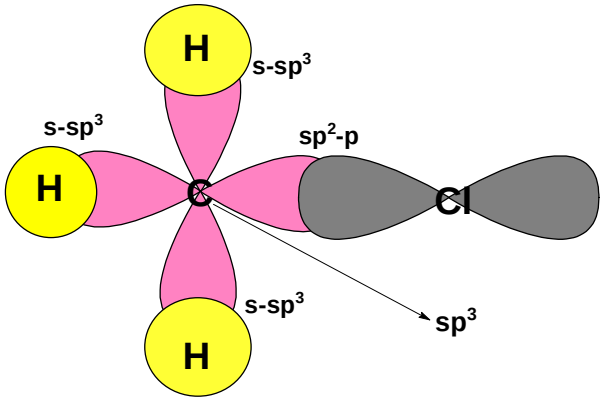
DEPARTMENT OF CHEMISTRY

UNIT - 1 – ALKYL AND ARYL HALIDES – SCY 1312

UNIT 1: ALKYL AND ARYL HALIDES

Alkyl halides are organic molecules containing a halogen atom bonded to an sp^3 hybridized carbon atom. Alkyl halides are classified as primary (1°), secondary (2°), or tertiary (3°), depending on the number of carbons bonded to the carbon with the halogen atom. The halogen atom in halides is often denoted by the symbol "X".

Structure of alkyl halides



Chemical Reactivity of RX

With respect to halide group

$CH_3I > CH_3Br > CH_3Cl > CH_3F$

With respect to alkyl group

$(CH_3)_3CBr > (CH_3)_2CHBr > CH_3CH_2Br > CH_3Br$

Chemical Properties of Alkyl halides

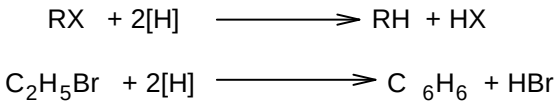
1. Displacement or Substitution reactions

   $$\text{Nucleophile} + R\,X \longrightarrow Nu - R + X$$

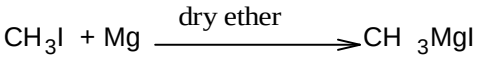
2. Elimination reactions

   $$R\,CH_2CH_2\,X \longrightarrow RCH{=}CH_2 + H_2O + KX$$

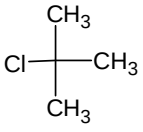
3. Reduction Reaction



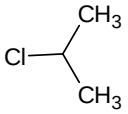
4. Reactions with metals



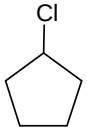
Nomenclature of alkyl halides



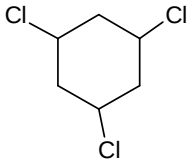
2-chloro-2-methylpropane



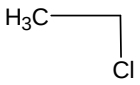
2-chloropropane



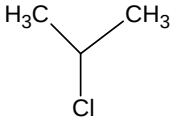
chlorocyclopentane



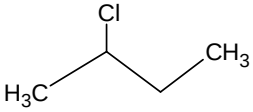
1,3,5-trichlorocyclohexane



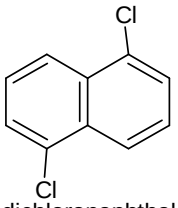
chloroethane



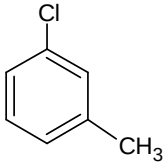
2-chloropropane



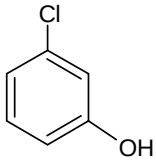
2-chlorobutane



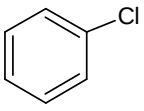
1,5-dichloronaphthalene



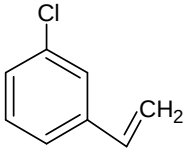
1-chloro-3-methylbenzene



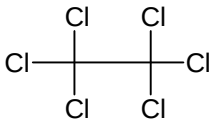
3-chlorophenol



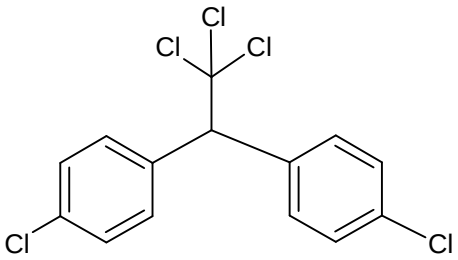
chlorobenzene



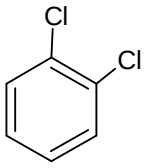
1-chloro-3-ethenylbenzene



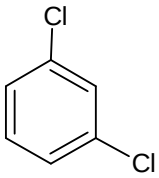
hexachloroethane



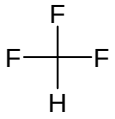
1,1'-(2,2,2-trichloroethane-1,1-diyl)bis(4-chlorobenzene)



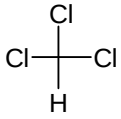
1,2-dichlorobenzene



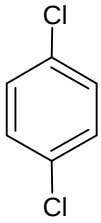
1,3-dichlorobenzene



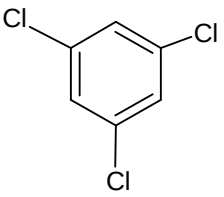
trifluoromethane



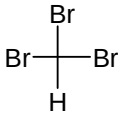
trichloromethane



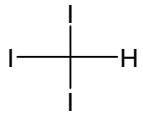
1,4-dichlorobenzene



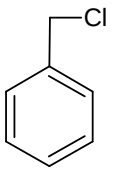
1,3,5-trichlorobenzene



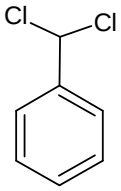
tribromomethane



triiodomethane

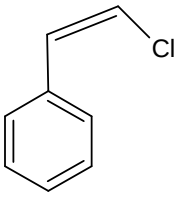


(chloromethyl)benzene

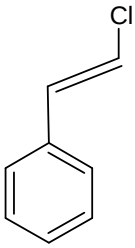


(dichloromethyl)benzene

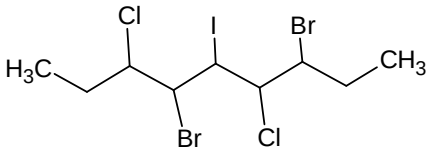
3-chloroprop-1-ene



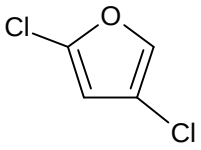
[(*Z*)-2-chloroethenyl]benzene



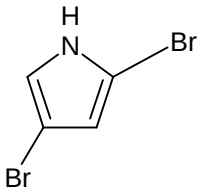
[(*E*)-2-chloroethenyl]benzene



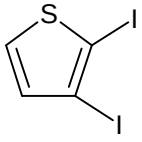
3,6-dibromo-4,7-dichloro-5-iodononane



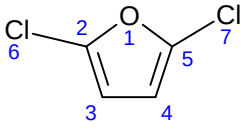
2,4-dichlorofuran



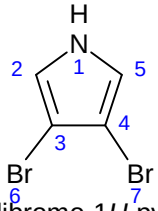
2,4-dibromo-1*H*-pyrrole



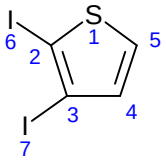
2,3-diiodothiophene



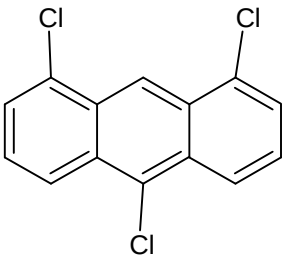
2,5-dichlorofuran



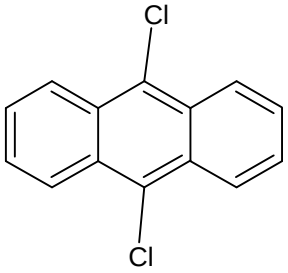
3,4-dibromo-1*H*-pyrrole



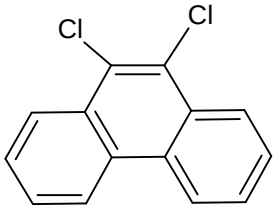
2,3-diiodothiophene



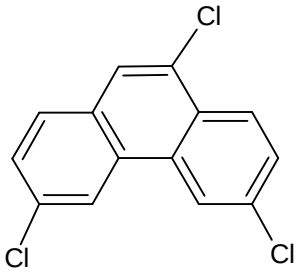
1,8,10-trichloroanthracene



9,10-dichloroanthracene



9,10-dichlorophenanthrene

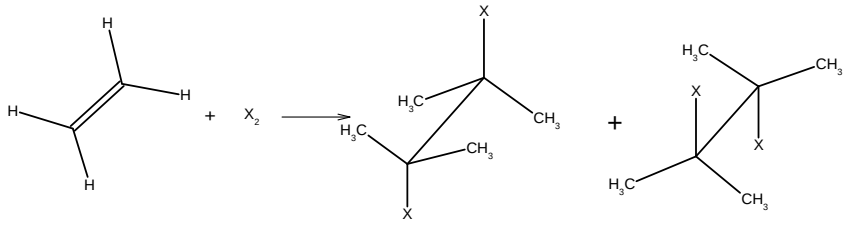


3,6,9-trichlorophenanthrene

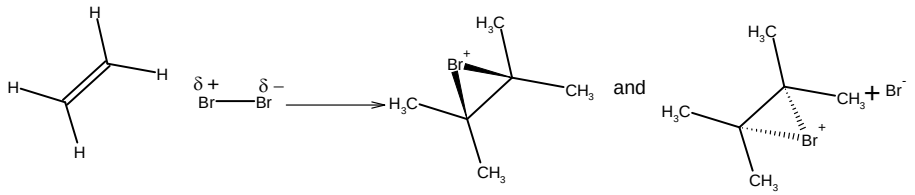
Preparation methods

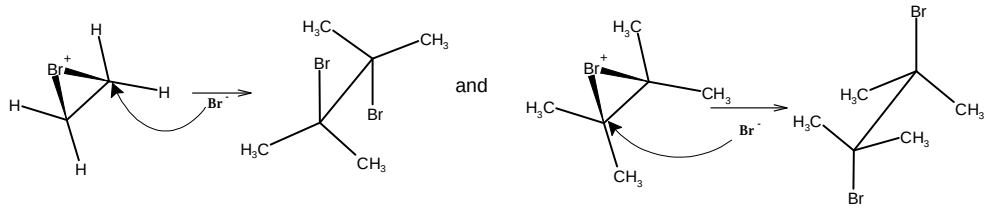
1. Halogenation of alkanes
2. Electrophilic addition to alkenes
3. Halogination of alcohol

Addition of symmetrical reagents

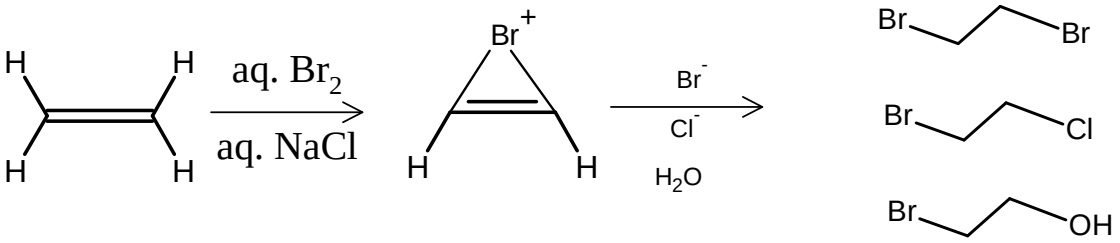


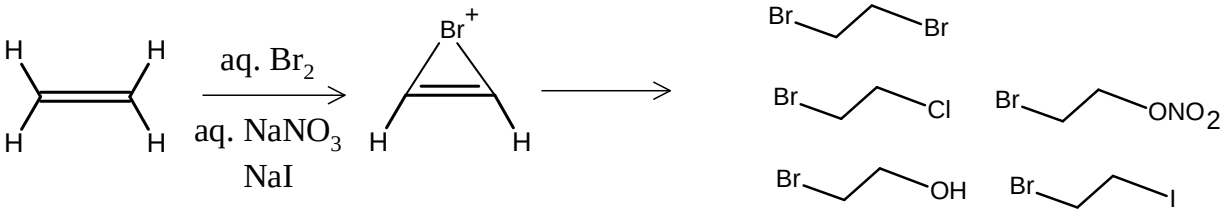
Addition of symmetrical reagents



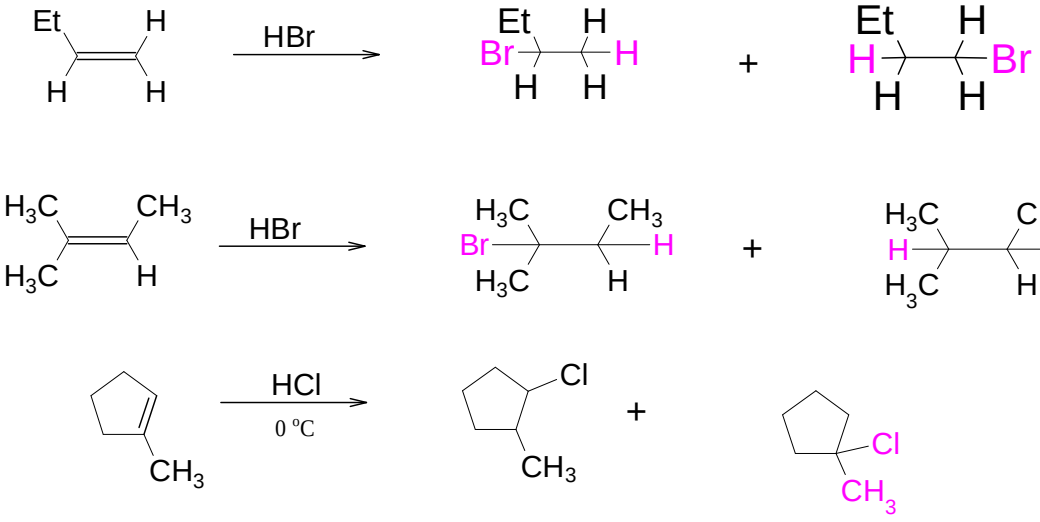


Factors affecting the addition of halogen to olefin: Effect of added nucleophiles

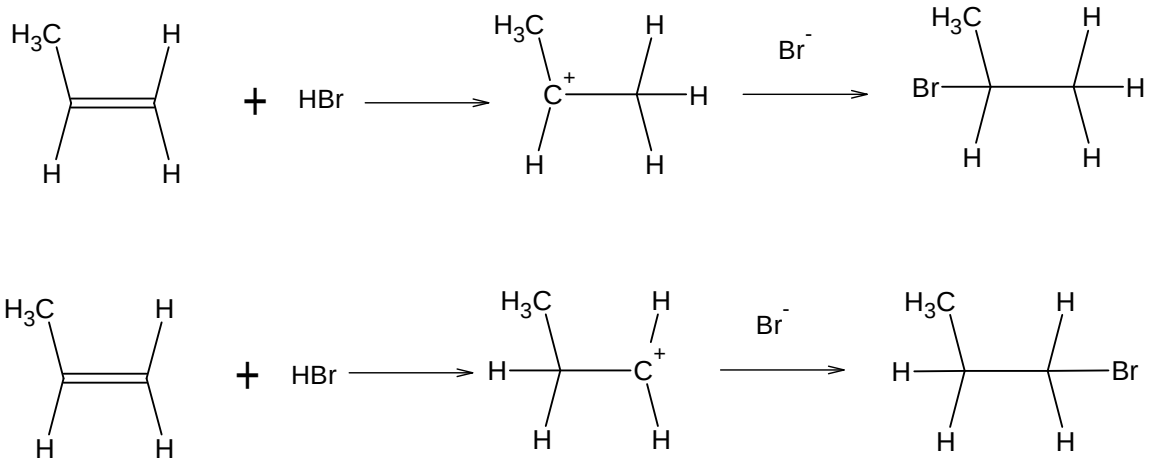




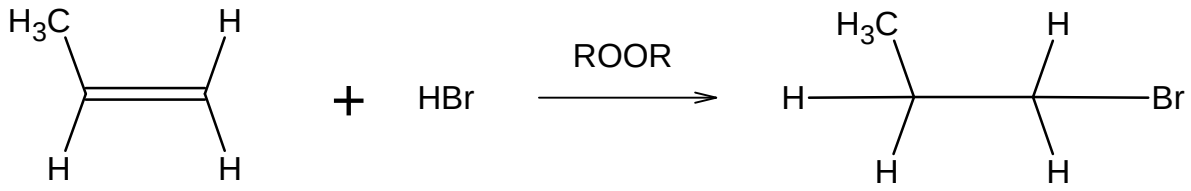
Unsymmetrical Olefines - Markovnikov Rule



Mechanism of Markonikov Rule

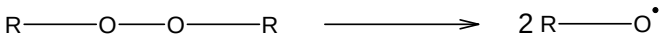


Antimarkovnikov Rule or Karasch effect

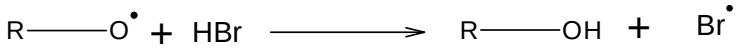


Mechanism of Karasch effect

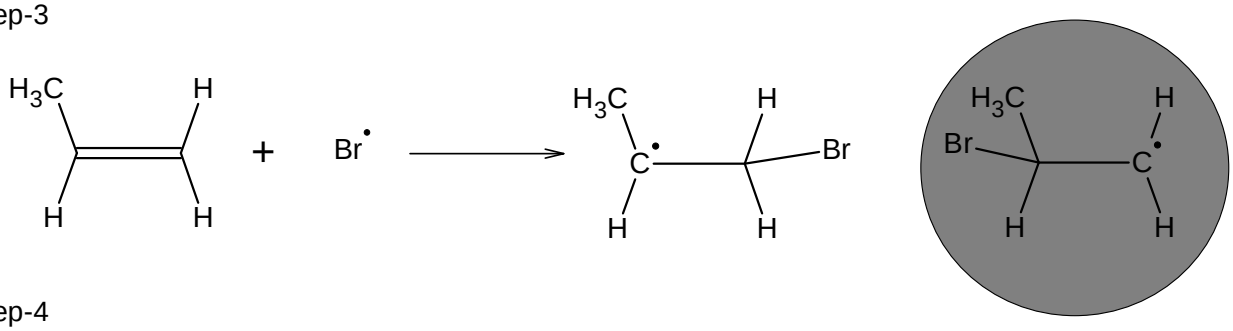
Step-1



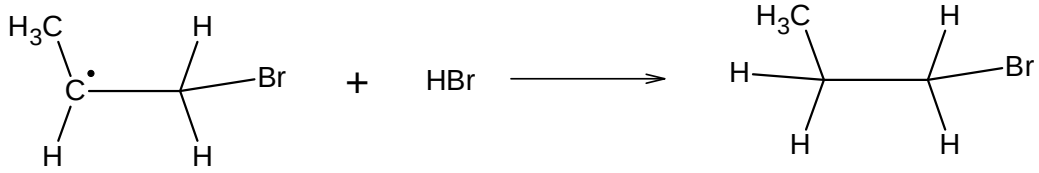
Step-2



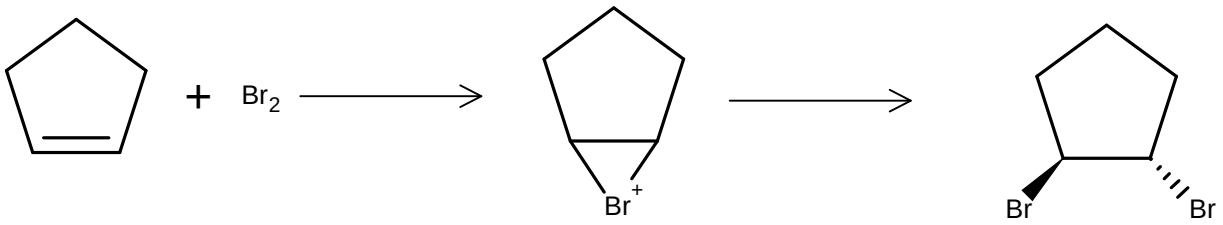
Step-3



Step-4



Addition of hydrogen to cycloalkenes



Grignard Reagent

Oranomagnesium halides are called Grignard Reagents.

General Formulae: RMgX

Where R = alkyl or aryl group

X = Cl, Br, I

Preparation of Grignard Reagent

The Grignard reagents are produced by dropping a solution of the alkyl halide in dry ether into the reaction flask containing magnesium ribbon suspended in dry ether. The ether solution of the Grignard reagent thus obtained is used immediately in the flask. These are explosives.

$$CH_3I + Mg \xrightarrow{\text{dry ether}} CH_3MgI$$

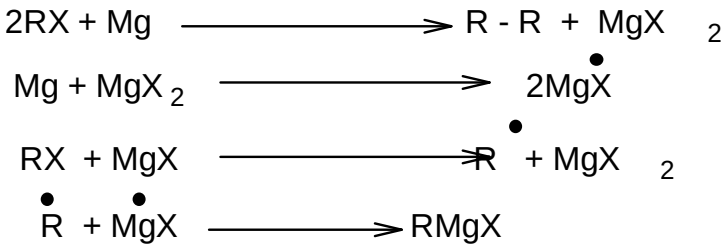
For given alkyl group the formation order is

RI > RBr > RCl

For a given halogen the formation order is

$CH_3I > C_2H_5I > C_3H_7I$

Formation mechanism



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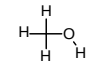
SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

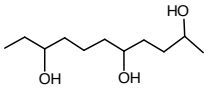
UNIT - 2 – ALCOHOLS AND PHENOLS – SCY 1312

UNIT 2 ALCOHOLS AND PHENOLS

Nomenclature of Alcohols

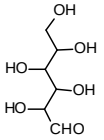


methanol



undecane-2,5,9-triol

cyclopentanol



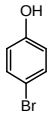
2,3,4,5,6-pentahydroxyhexanal

cyclohexanol

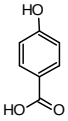
ethane-1,2-diol

propane-1,2,3-triol

phenol



4-bromophenol

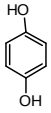


4-hydroxybenzoic acid

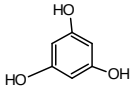
2-methylpropan-2-ol

propan-2-ol

benzene-1,2-diol



benzene-1,4-diol



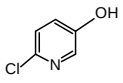
benzene-1,3,5-triol

benzene-1,3-diol

furan-3-ol

1*H*-pyrrol-3-ol

pyridine

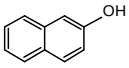


6-chloropyridin-3-ol

ethenol

prop-2-en-1-ol

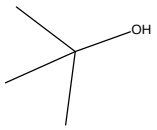
naphthalen-1-ol



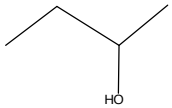
naphthalen-2-ol

cyclohepta-2,4,6-trien-1-ol

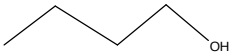
Physical Properties of Alcohol



B.P = 83 °C

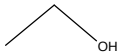


B.P = 99 °C

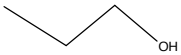


B.P = 119 °C

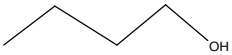
B.P.= 64 °C



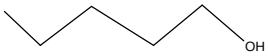
B.P.= 78 °C



B.P.= 97 °C

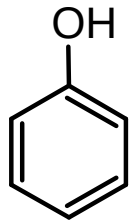


B.P.= 118 °C

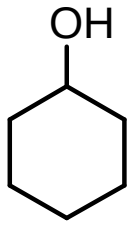


B.P.= 138 °C

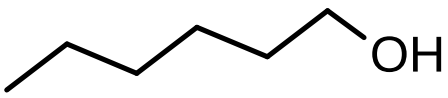
Aromatic compounds



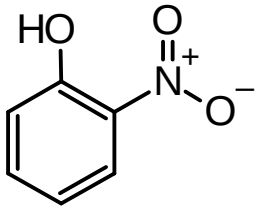
M.P.= 94 °C
B.P.= 182 °C



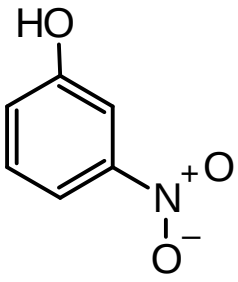
M.P.= 100 °C
B.P.= 162 °C

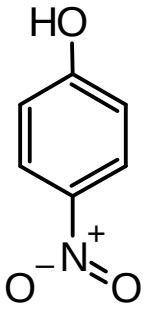


M.P.= 102 °C
B.P.= 152 °C



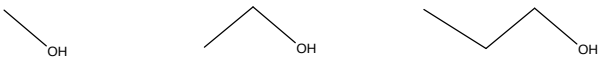
M.P.= 45 °C
B.P.= 1217 °C





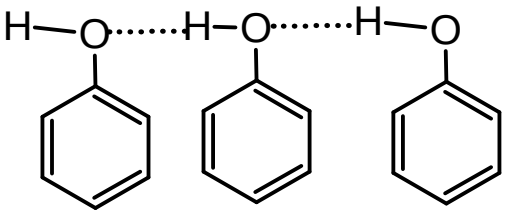
M.P.= 114 °C
B.P.= 279 °C

Solubilitly of Alcohols

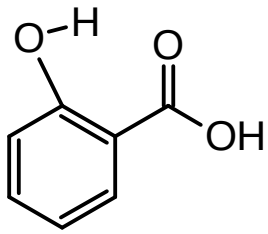


SOLUBLE IN WATER

Intermolecular Hydrogen Bonding



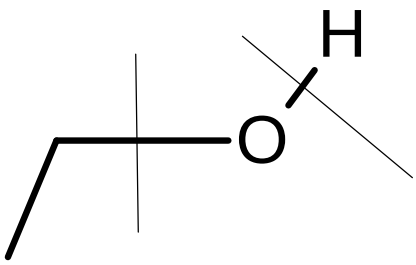
Intramolecular Hydrogen Bonding



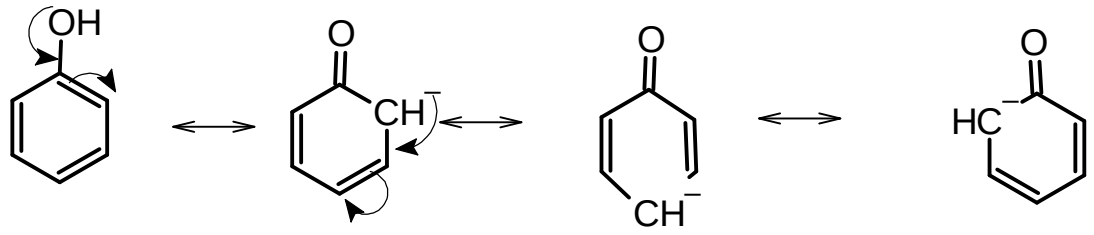
Acidity of alcohols:

$$ROH < H_2O < ArOH$$

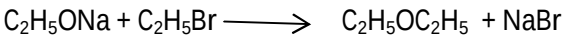
Chemical Properties of Alcohols



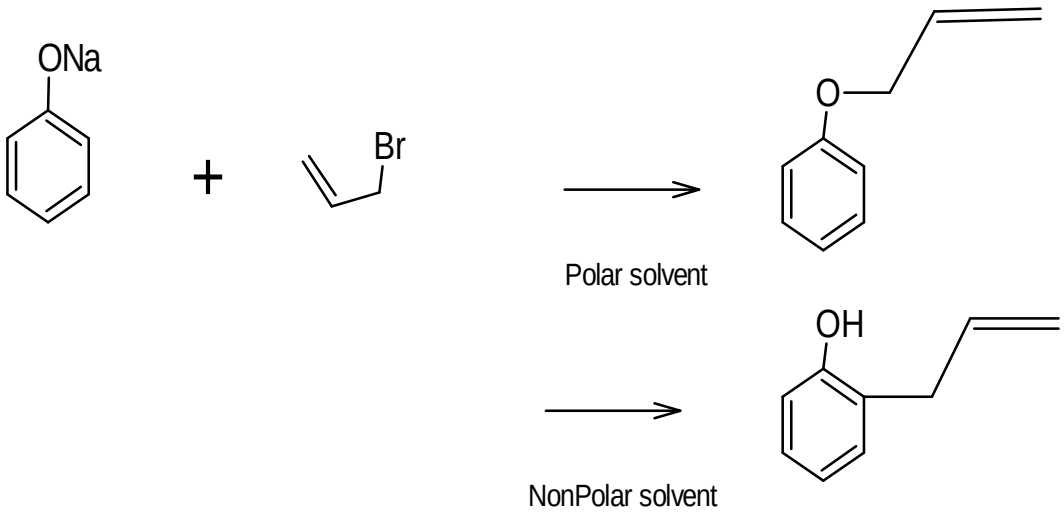
O-H Cleavage:



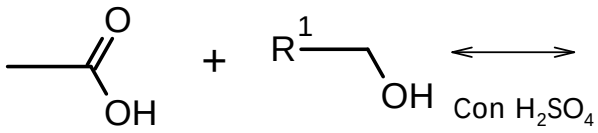
1. Reaction with Alkyl halides



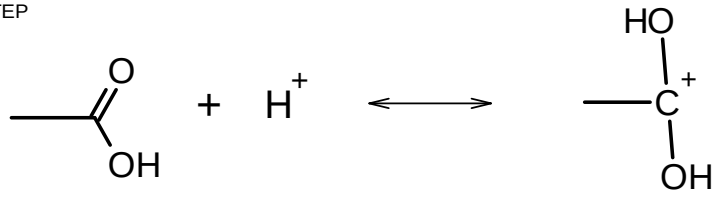
2. Reaction with aryl halides



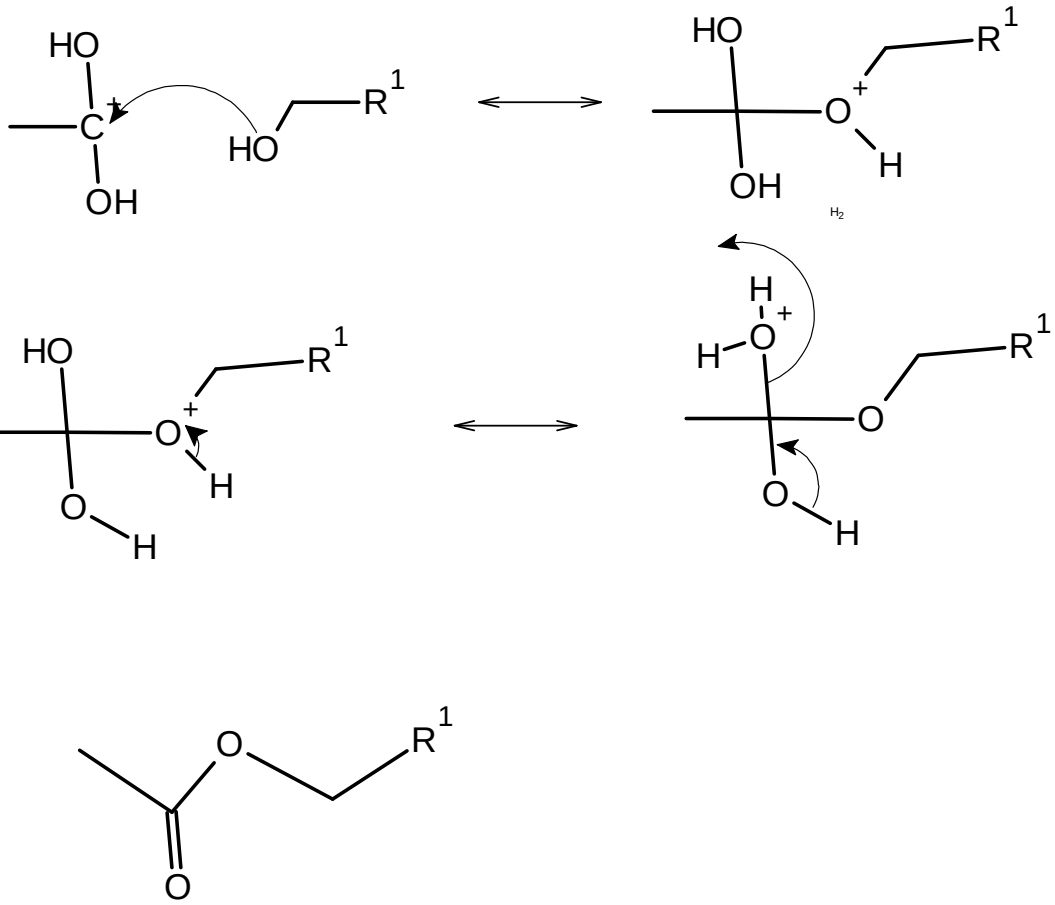
3. Esterification reaction



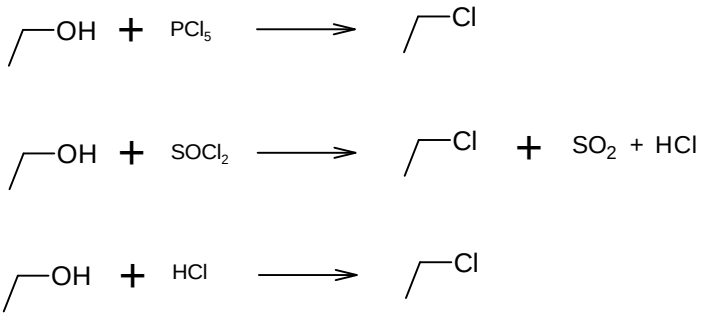
FIRST STEP



SECOND STEP



4. Halogination of alcohols



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DEPARTMENT OF CHEMISTRY

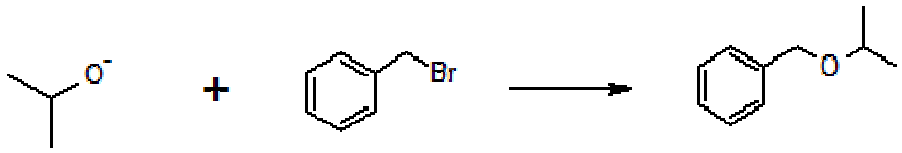
UNIT - 3 – ETHERS AND EPOXIDES – SCY 1312

UNIT 3 ETHERS AND EPOXIDES

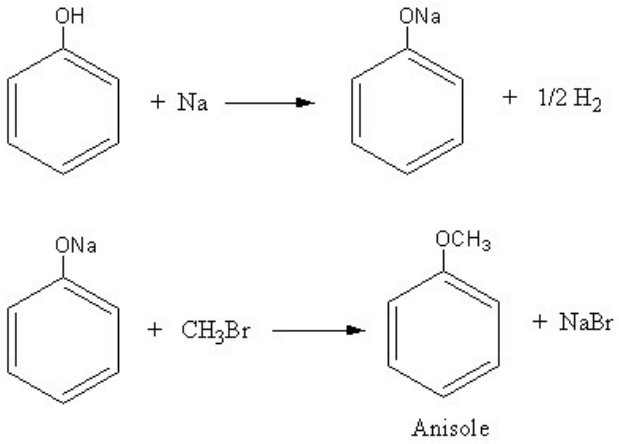
Preparation of Ethers

Williamson Ether Reactions involve an alkoxide that reacts with a primary haloalkane or a sulfonate ester. Alkoxides consist of the conjugate base of an alcohol and are comprised of an R group bonded to an oxygen atom. They are often written as RO^-, where R is the organic substituent.

Example:



Example:



Acid-Catalyzed Cleavage of Ethers

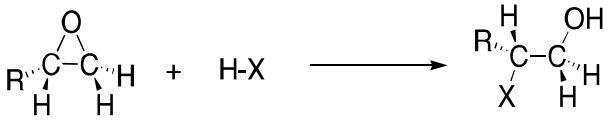
Recall the reaction of an alcohol with HX to give a halide (Ch. 4.12)

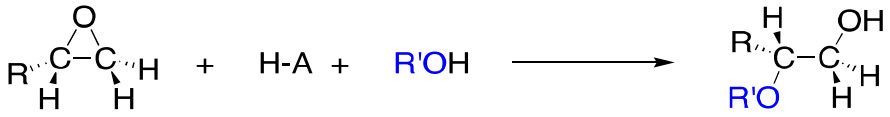
$$RCH_2\text{-}OH + H\text{-}X \longrightarrow RCH_2\text{-}X + H_2O$$

The mechanism for the acid clevage of ethers is similar

$$RCH_2\text{-}O\text{-}R' + H\text{-}X \longrightarrow RCH_2\text{-}X + HO\text{-}R'$$

Acid-Catalyzed Ring Opening of Epoxides





THIOETHERS

Thioalcohols are more properly called thiols. The old name for this class of molecules is the mercaptans. These are alcohols where the oxygen has been replaced by sulfur and they smell incredibly bad. Natural gas (methane) has no odor.

A thioether or sulfide is a compound that has the following general structural formula.

$$R^1 - S - R^2$$

R^1, R^2 = alkyl groups and/or aryl groups

Another class of sulfur containing molecule has important biological implications, the disulfides. The molecules have the generic formula R-S-S-R and correspond to the peroxide class of oxygen containing molecules. Organic peroxides are high energy molecules, not found in nature.

Hydrogen peroxide (H_2O_2, H-O-O-H) is the inorganic analogue and if you've ever put some on an open wound to disinfect it, you have some understanding by what is meant by the phrase "high energy molecule." While still comparatively reactive, disulfides are much more stable than peroxides and are found in nature. They form from the oxidation of thiols.

$2\ RSH + [O] \rightarrow R\text{-}S\text{-}S\text{-}R + H_2O$

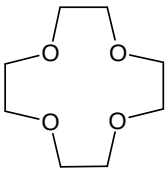
In the presence of a reducing agent (source of hydrogen) the reaction runs basically in reverse:

$R\text{-}S\text{-}S\text{-}R + 2[H] \rightarrow 2RSH$

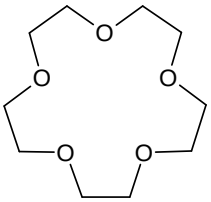
Protein molecules frequently contain disulfide linkages. When a perm is done, two solutions are used. The first reduces the disulfide linkages to thiols, the hair is then set, and an oxidizing solution is then used to generate new disulfide bonds to hold the hair in place

CROWN ETHERS

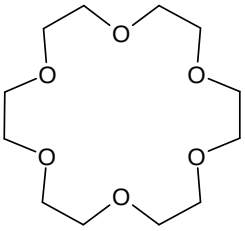
Crown ethers are cyclic compounds that have several ether linkages. A Crown ether specifically binds certain metal ions or organic molecules, depending on the size of its cavity.



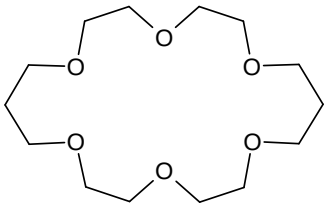
[12]-Crown-4



[15]-Crown-5



[18]-Crown-6

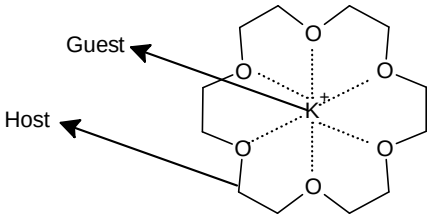


[20]-Crown-6

Representation of Crown ethers

Applications of Crown Ethers

1. The crown–guest complex is called an inclusion compound. The Nonactin will bind selectively to potassium ion. The [15]-Crown-5 will bind selectively to sodium ion.

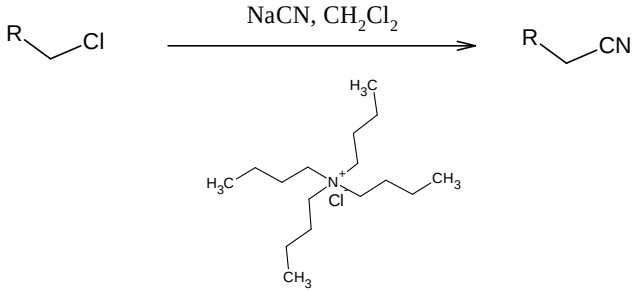


Host Guest complexation of [18]-crwon-6

Crown Ether	Cavity Size /Å	Alkali Ion	Ion Radii/Å
[12]-crown-4	0.6-0.75	Li^+	0.76
[15]-crown-5	0.86-0.92	Na^+	1.02
[18]-crown-6	1.34-1.55	K^+	1.38
[21]-crown-7	1.7-2.1	Cs^+	1.67

Fig. The Cavity size and radii of alkali ions

2. The crown ether is acting as a phase-transfer catalyst. A phase-transfer catalyst or PTC is a catalyst that facilitates the migration of a reactant from one phase into another phase where reaction occurs.



The Quarternery ammonium salt as Phase transfer catalyst and its role in organic reaction

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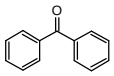
DEPARTMENT OF CHEMISTRY

UNIT - 4 – CARBONYL COMPOUNDS – SCY 1312

UNIT 4 CARBONYL COMPOUNDS

Nomenclature of Carbonyl Compounds

benzaldehyde



diphenylmethanone

Methanal

propan-2-one

butanal

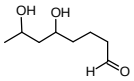
3-chlorobutanal

butanedial

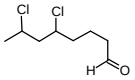
hexane-2,5-dione

butan-2-one

pentan-2-one

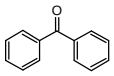


5,7-dihydroxyoctanal

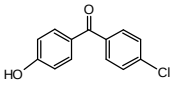


5,7-dichlorooctanal

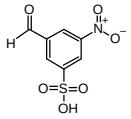
benzaldehyde



diphenylmethanone

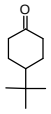


(4-chlorophenyl)(4-hydroxyphenyl)methanone

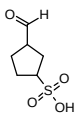


3-formyl-5-nitrobenzene-1-sulfonic acid

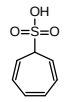
cyclohexanone



4-*tert*-butylcyclohexan-1-one



3-formylcyclopentane-1-sulfonic acid



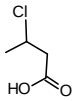
cyclohepta-2,4,6-triene-1-sulfonic acid

Nomenclature of carbonyl compounds

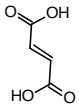
formic acid

acetic acid

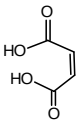
butanoic acid



3-chlorobutanoic acid

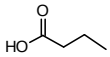


(2*E*)-but-2-enedioic acid

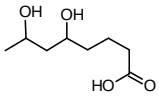


(2*Z*)-but-2-enedioic acid

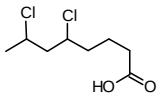
propanoic acid



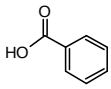
butanoic acid



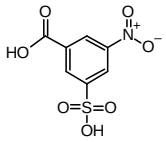
5,7-dihydroxyoctanoic acid



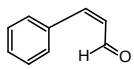
5,7-dichlorooctanoic acid



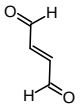
benzoic acid



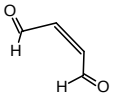
3-nitro-5-sulfobenzoic acid



(2*Z*)-3-phenylprop-2-enal

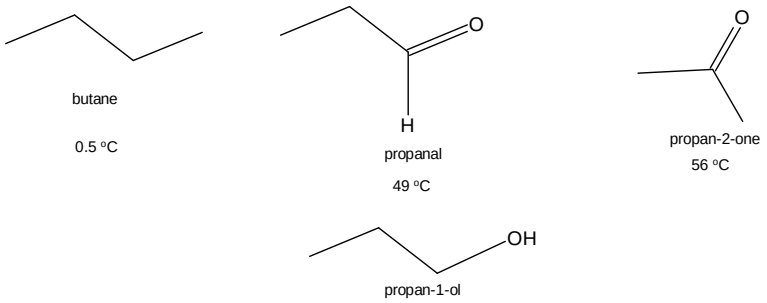


(2*E*)-but-2-enedial



(2*Z*)-but-2-enedial

Physical properties of carbonyl compounds



PREPARATION METHODS

1. Acid Chlorides & Nitrile

2. 1,3 Dithianes

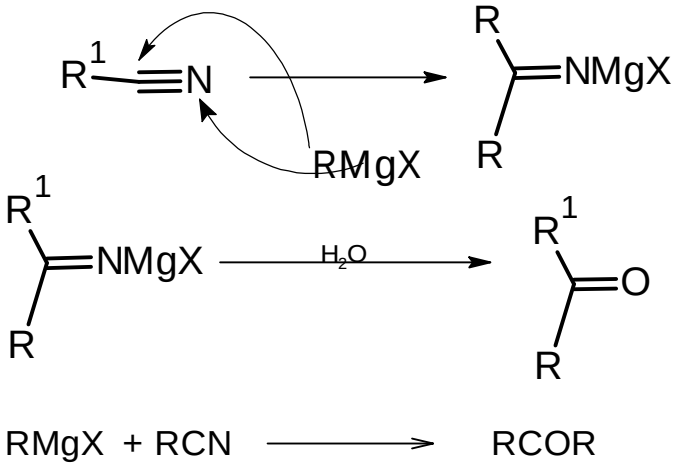
3. From Carboxylic Acids

4. Oxidation

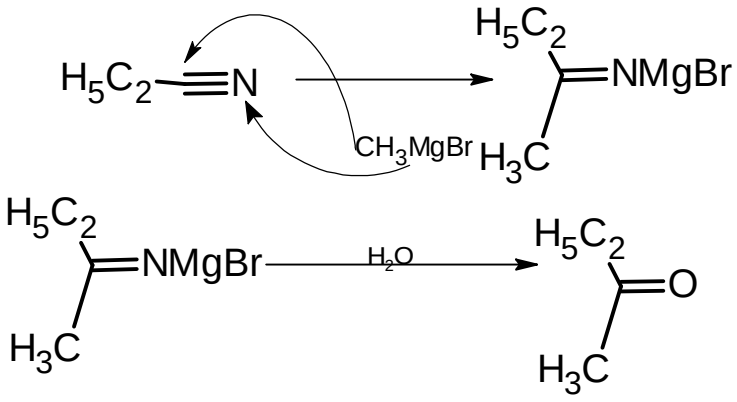
5. Friedal Craft Acylation

Preparation of Carbonyl Compounds

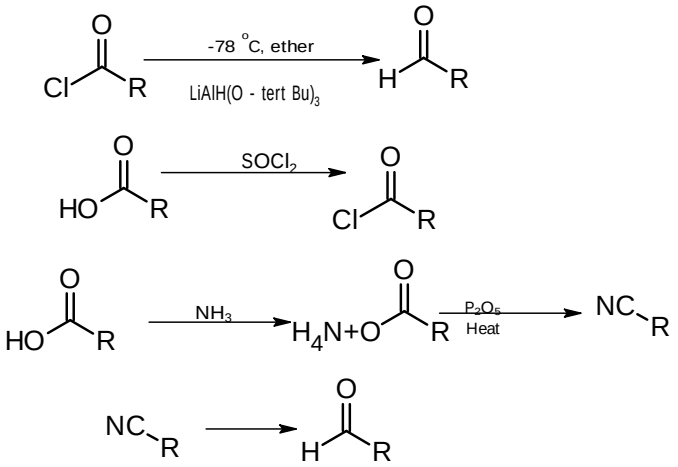
1. Acid chloride and Nitrile compounds



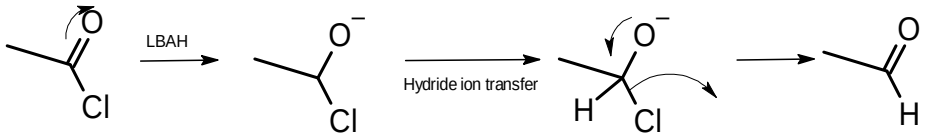
Example:



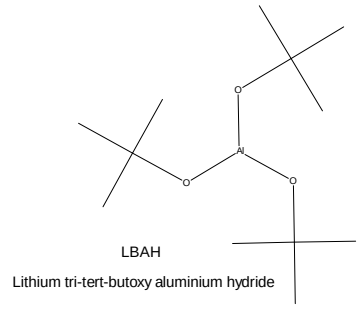
Acid chlorides to carbonyl compounds



Acid chloride to aldehydes

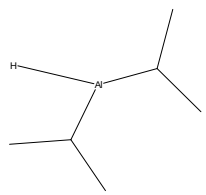


Reducing Agents



LBAH

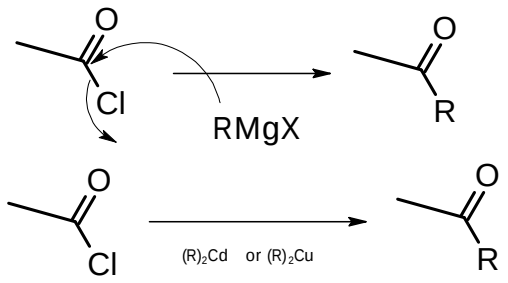
Lithium tri-tert-butoxy aluminium hydride



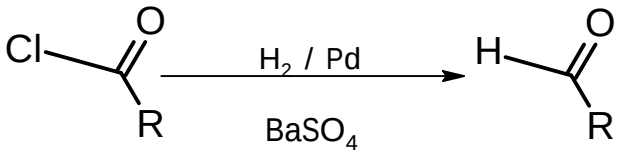
DBAH

Diisobutyl aluminium hydride

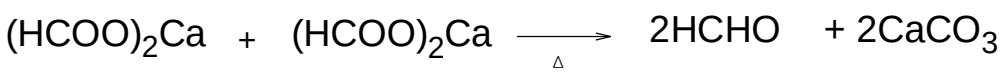
2. Grignard Reagents

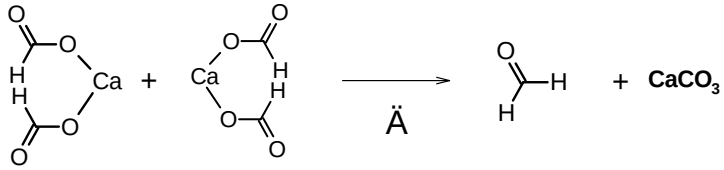


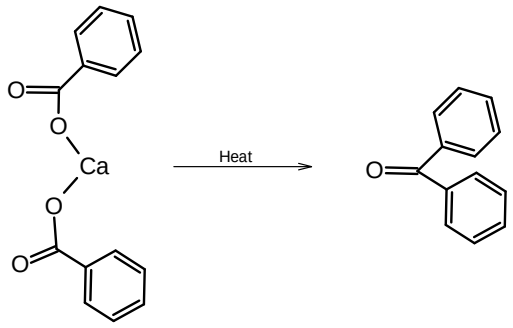
3. Rosenmunds Reduction



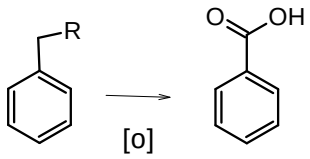
4. Calcium salts of Carboxilic acids



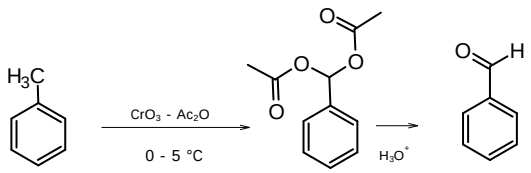




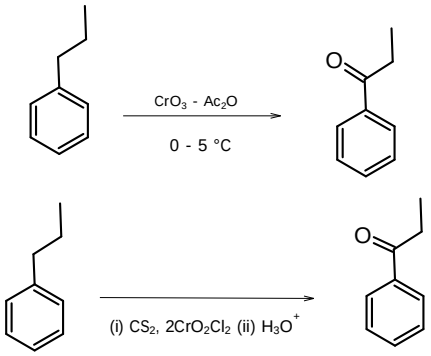
5. Oxidation of benzilic position



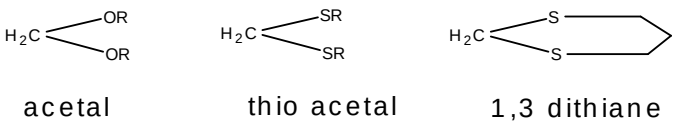
6. Oxidation of Toluene



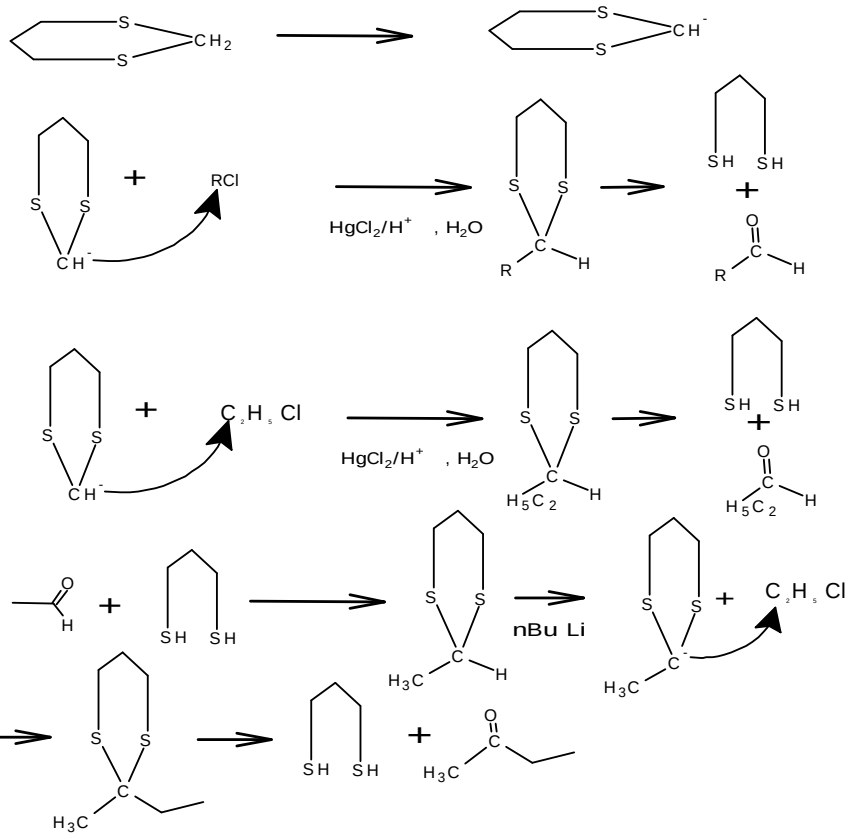
Oxidation of Benzilic position



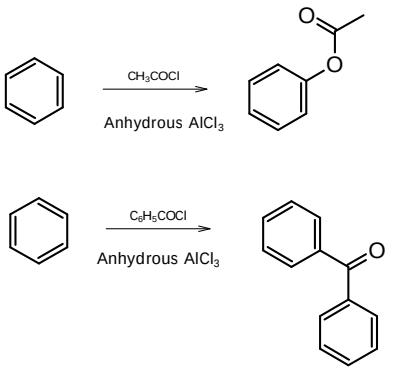
7. Dithianes



acetal thio acetal 1,3 dithiane



8. Friedal Crafts Acylation



Ketoenol isomerism of Carbonyl compounds

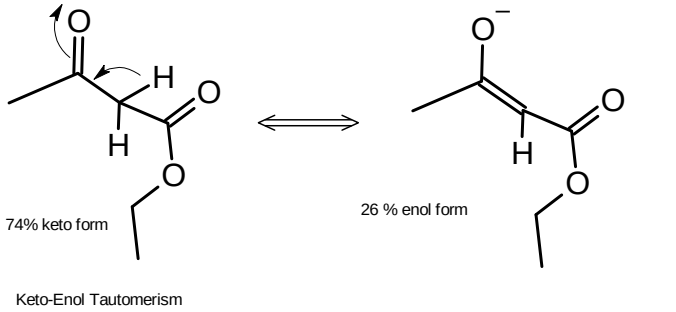
1. Carbonyl with alpha hydrogen

2. Reversible intramolecular change

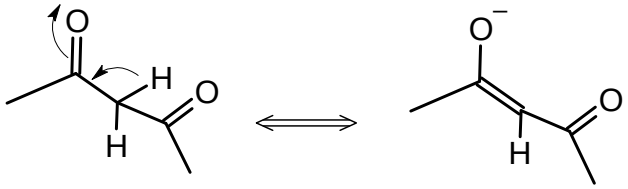
3. Difficult to separate

4. The conversion keto form to enol form is called enolization

5. The % of these forms will be different for different compounds

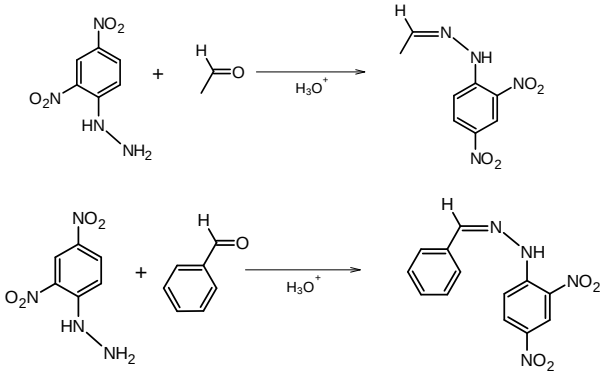


Keto-Enol Tautomerism



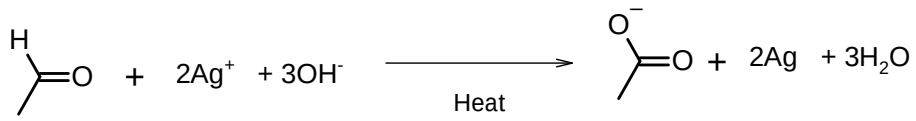
Analysis of Aldehydes and Ketones

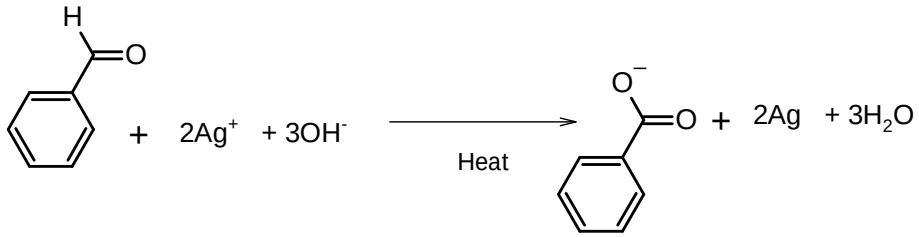
1. 2,4 DNP Test:



2. Tollens Reagent

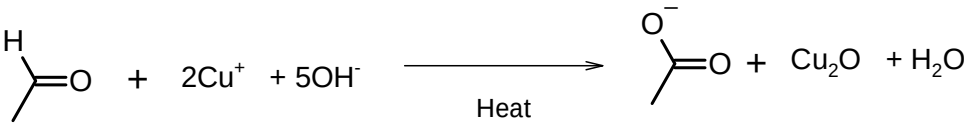
Ammonical Silver Nitrate solution is called Tollen's Reagent





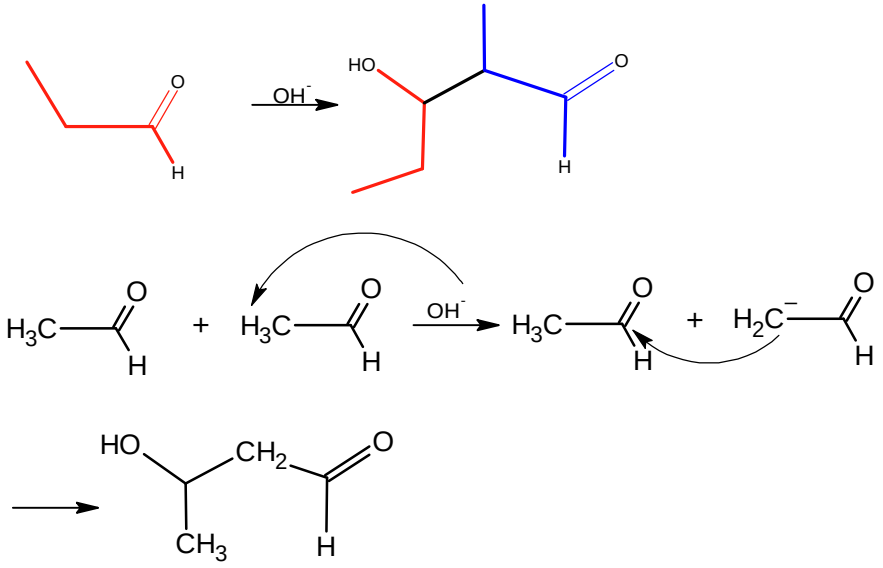
3. Fehlings solution test

An alkaline solution of cupric ion complexed with sodium potassium tratrate (Rochelle salt) ions. The deep blue complexed cupric ion is reduced to red cuprous oxide.

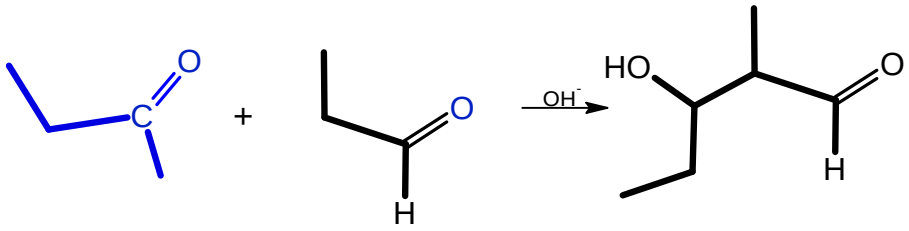


Chemical Reactions of Carbonyl compounds

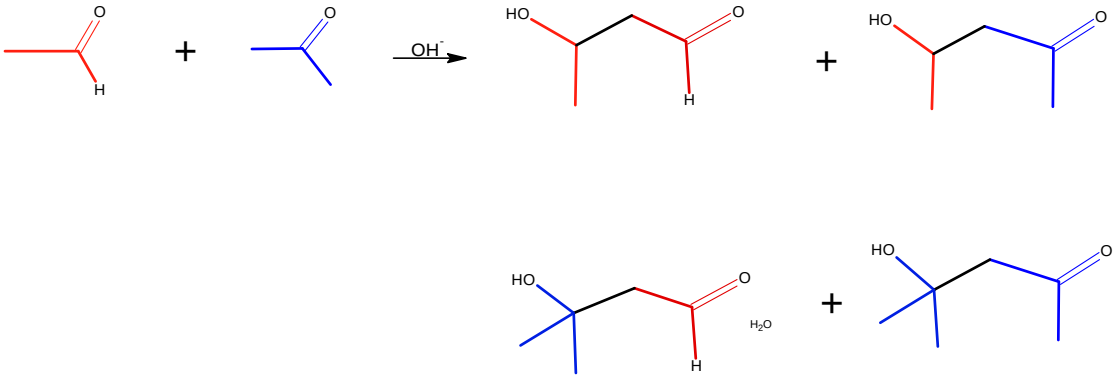
1. Aldol condensation



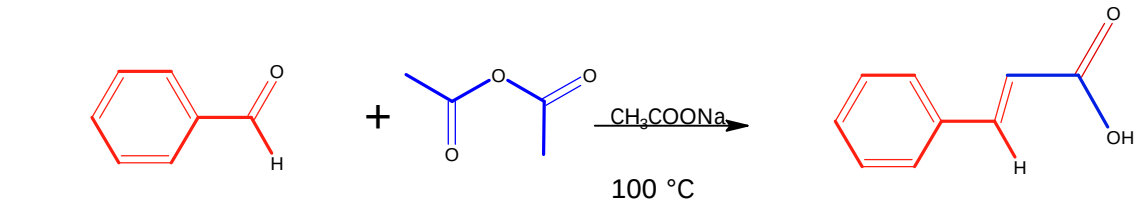
Example:



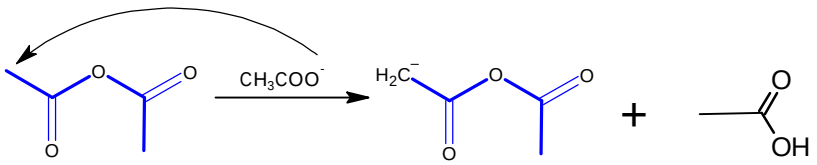
Cross aldol condensation

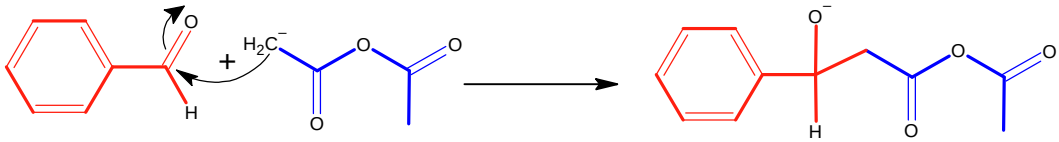


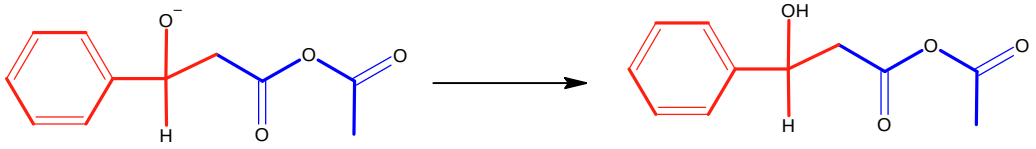
2. Perkin Reaction

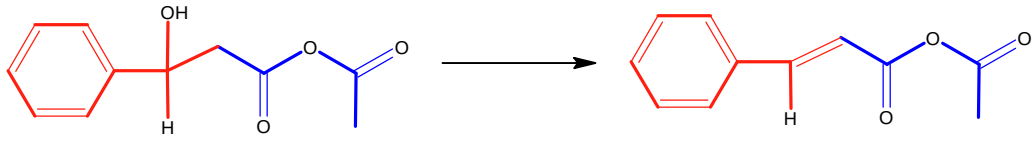


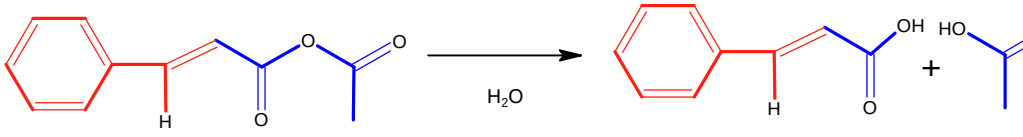
MECHANISM:
STEP - I



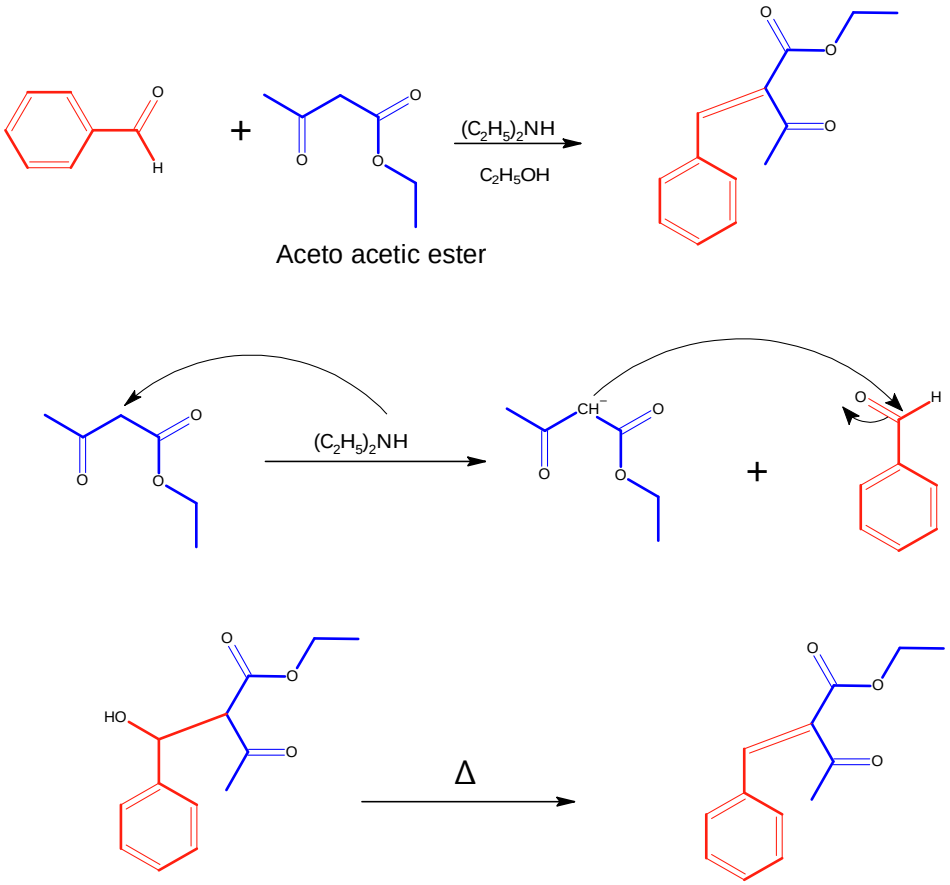




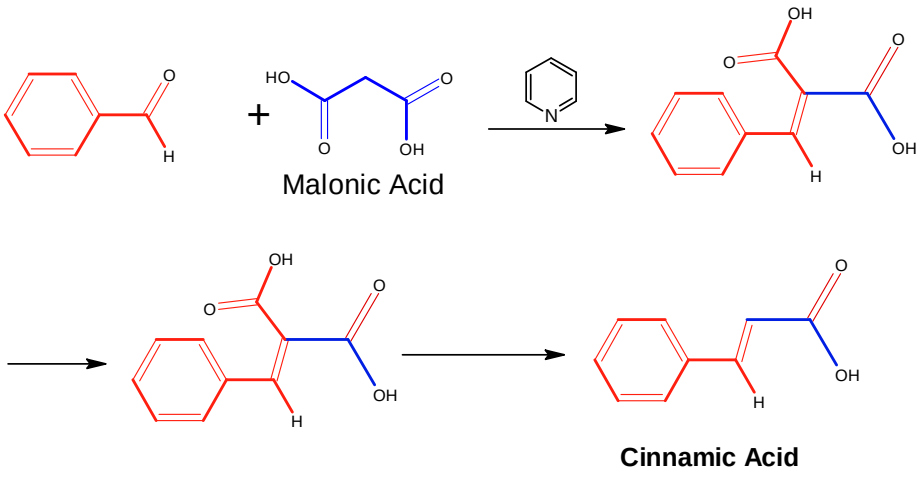




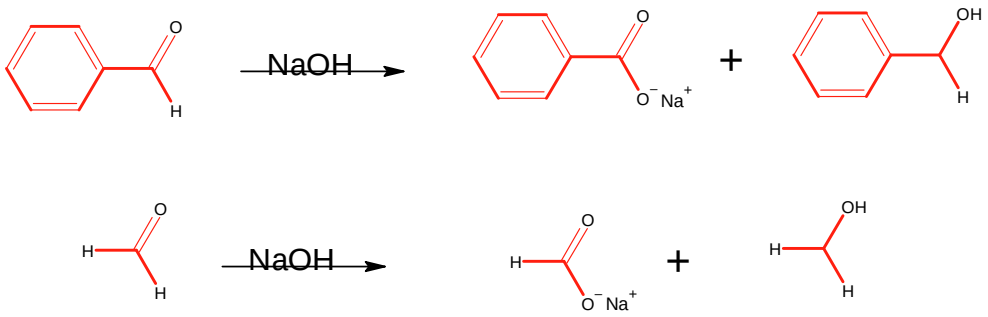
3. Knovenagen condensation



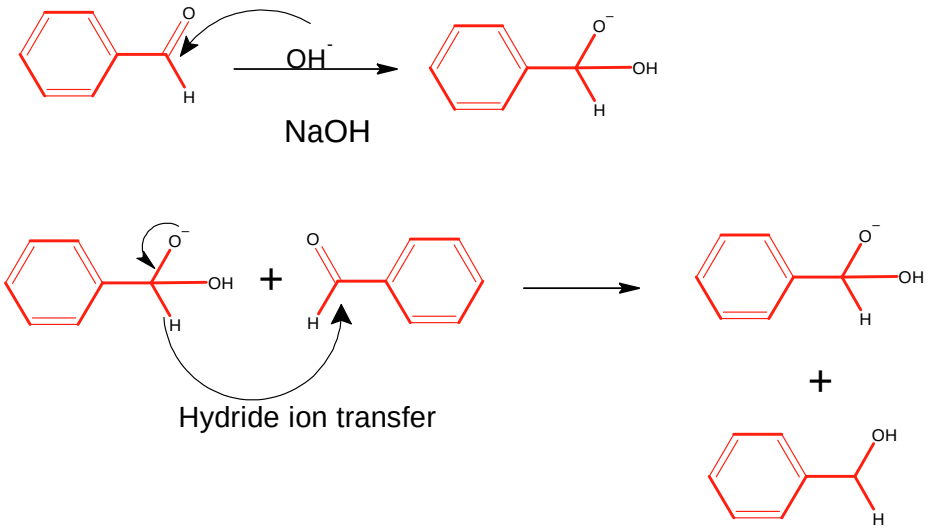
Example:



4. Benzoin condensation

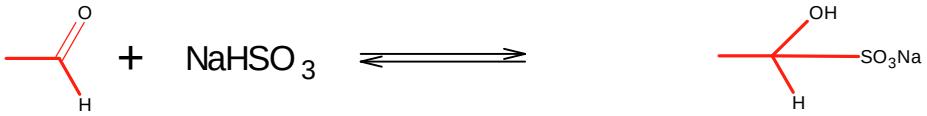


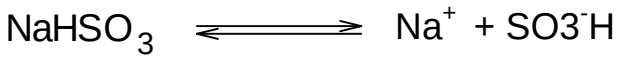
Mechanism

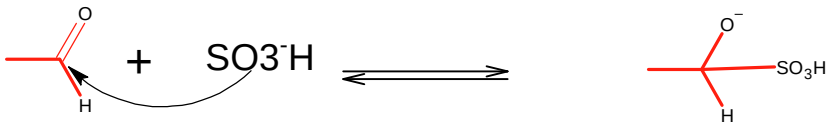


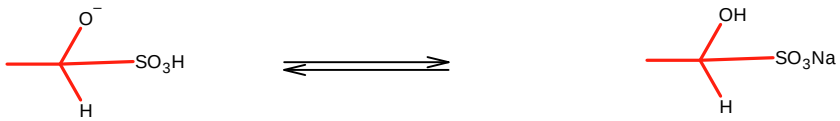
Nucleophilic addition reactions

1. Addition of sodium bisulphite

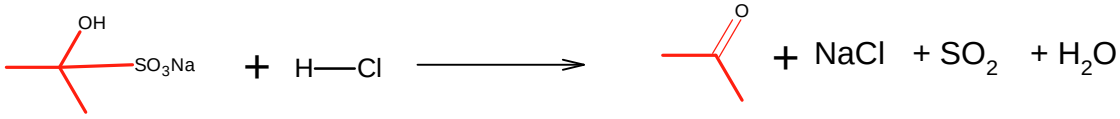




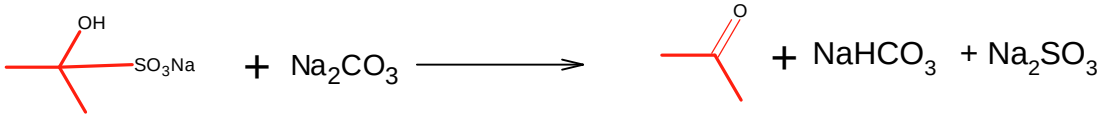




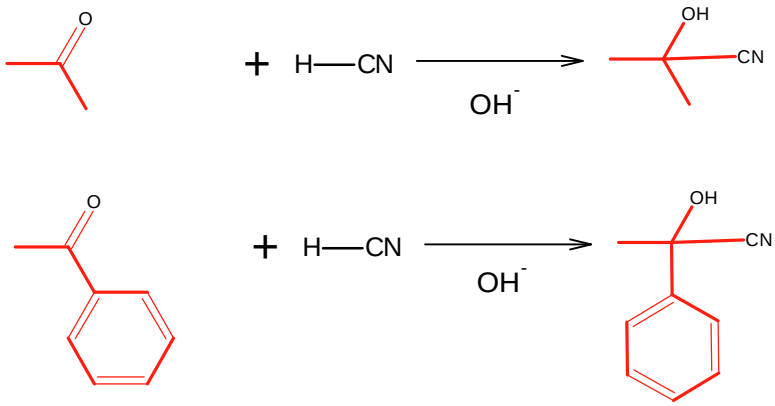
2. Addition of HCl



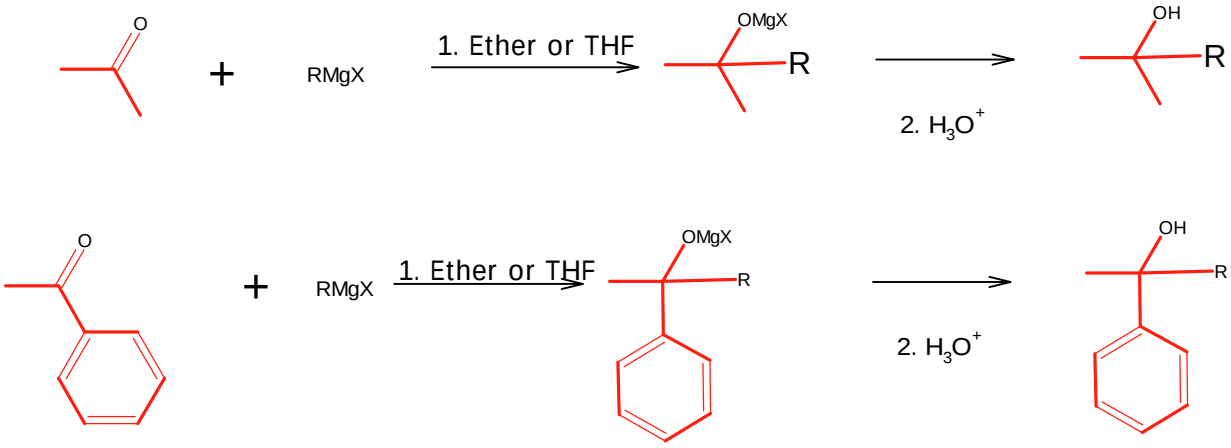
3. Addition of sodium carbonate



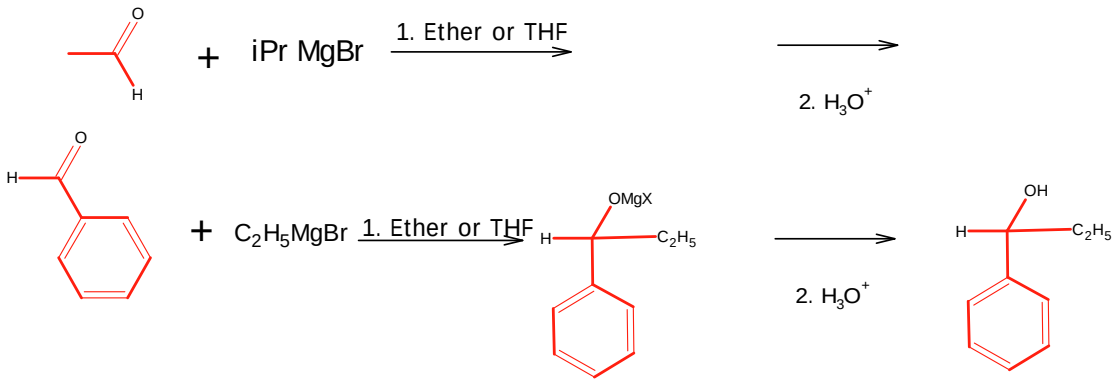
4. Addition of HCN



5. Addition of RMgX

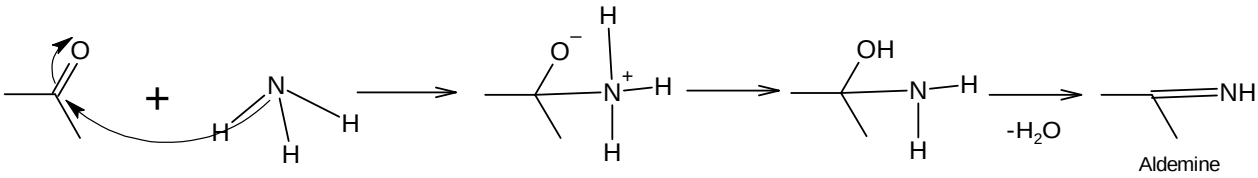


Example:

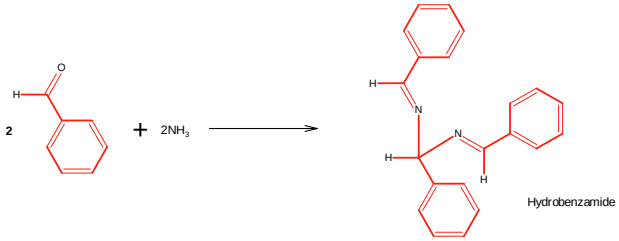


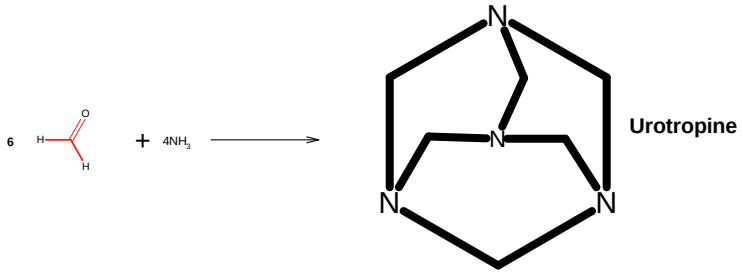
6. Addition of Ammonia

a. With Ammonia

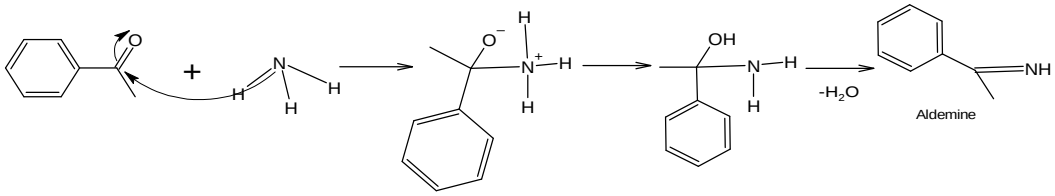


Example

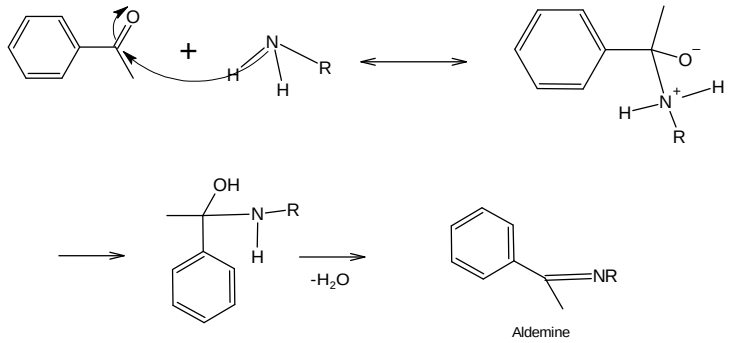




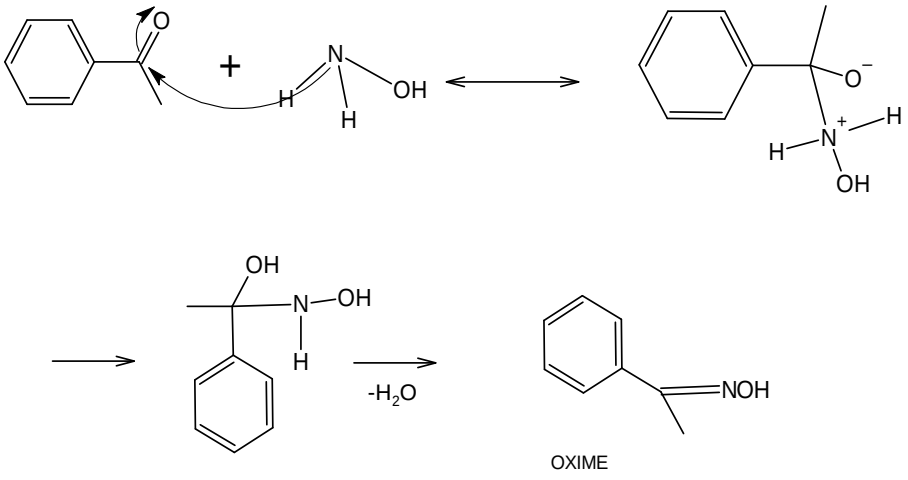
Mechanism:



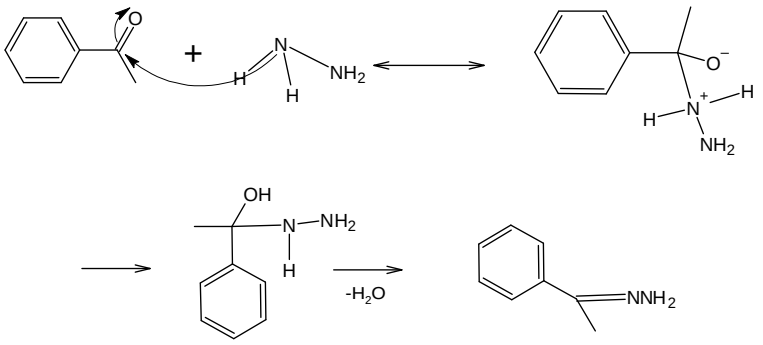
Reaction with ketone



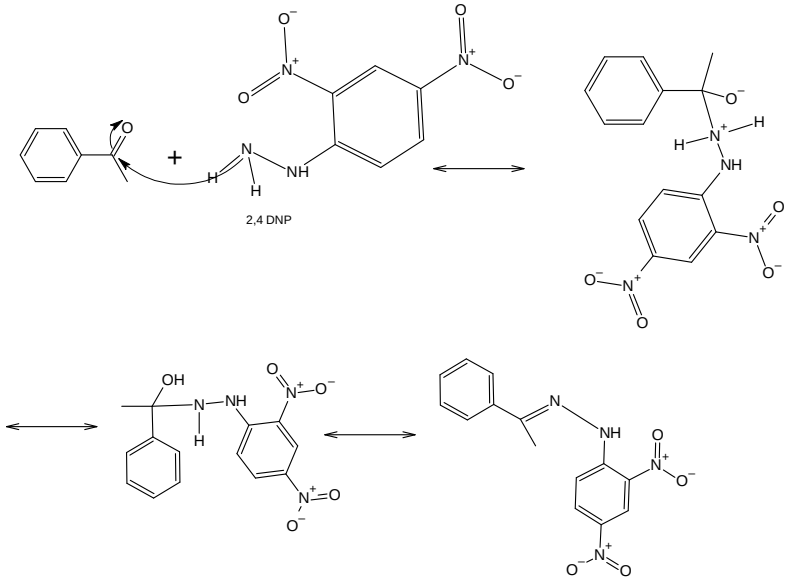
b. Reaction with hydroxyl amine



c. Reaction with hydrazine

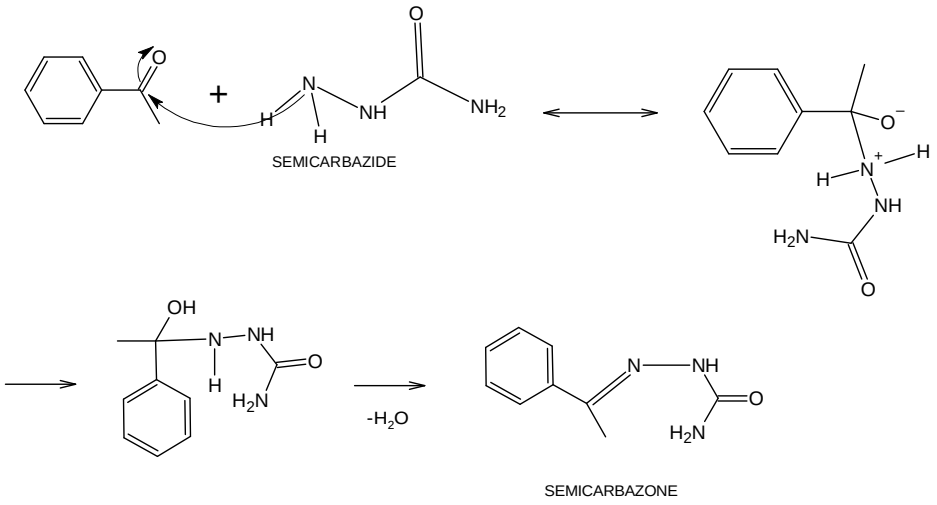


d. Reaction with 2,4 DNP

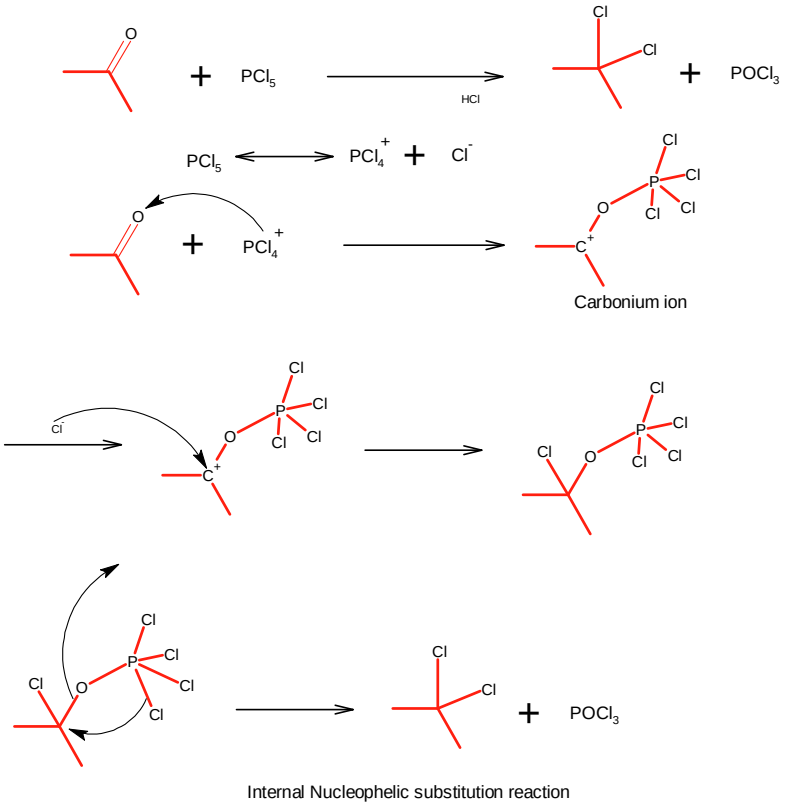


2,4 DINITRO PHENYL HYDRAZONE

e. Reaction with Semicarbazide



7. Halogination of carbonyl compounds



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INSTITUTE OF SCIENCE AND TECHNOLOGY
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SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT - 5 – CARBOHYDRATES – SCY 1312

UNIT 5 CARBOHYDRATES

1. Mono saccharides - simple sugars with multiple OH groups. Based on number of carbons (3, 4, 5, 6), a monosaccharide is a triose, tetrose, pentose or hexose.
2. Disaccharides - 2 mono saccharides covalently linked.
3. Oligosaccharides - a few mono saccharides covalently linked.
4. Polysaccharides - polymers consisting of chains of monosaccharide or disaccharide units.

Polysaccharides have a general formula $(C_6H_{10}O_5)_n$ where n may have value from 12 to few thousands.

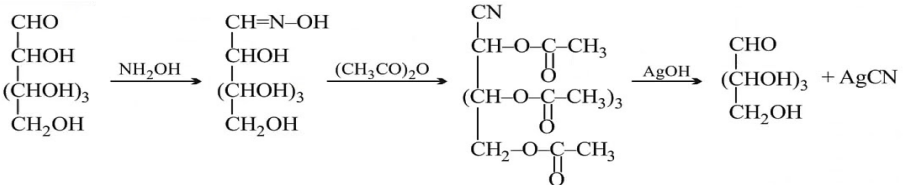
They are tasteless, amorphous compounds and are insoluble in water.

They form colloidal solution.

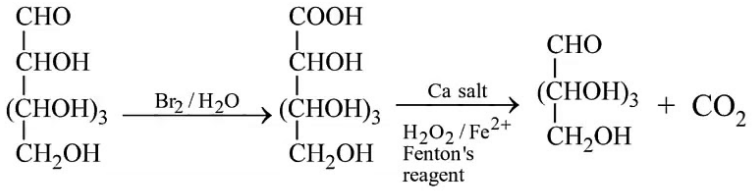
When hydrolysed with dilute acids or enzymes they yield monosaccharides and various oligosaccharide intermediates.

Preparation of Carbohydrate:

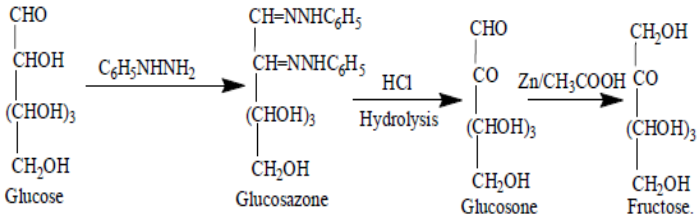
Wohl's method:



Ruff's method:

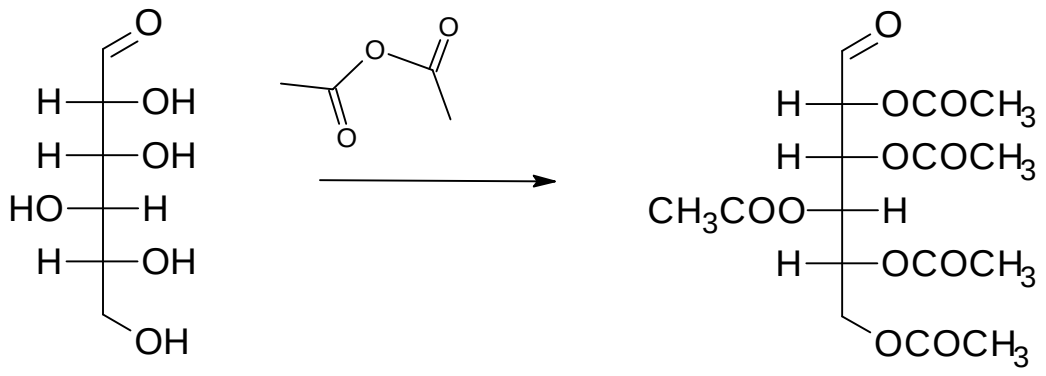


Aldose to ketose conversion:

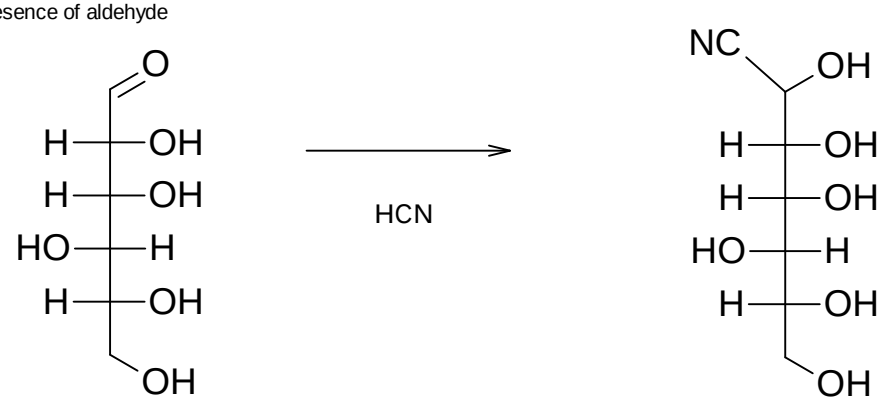


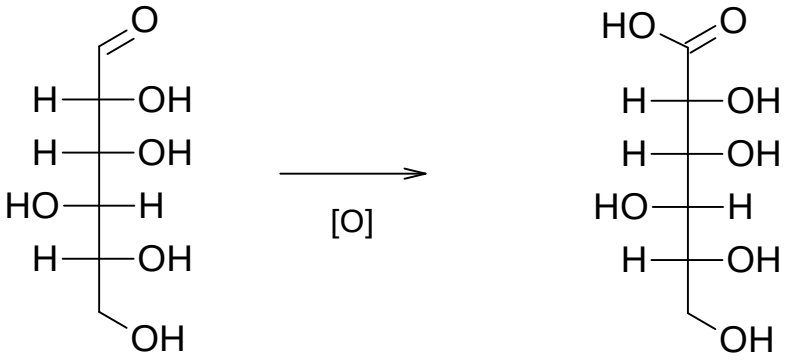
STRUCTURAL ELUCIDATION :

1. M. F: $C_6H_{12}O_6$
2. PRESENCE OF 5 HYDROXYL GROUPS

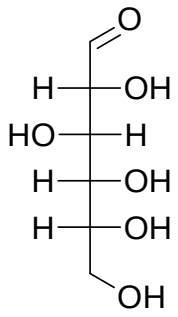


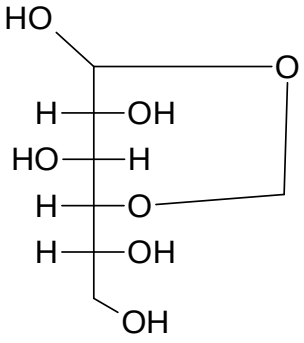
3. Presence of aldehyde

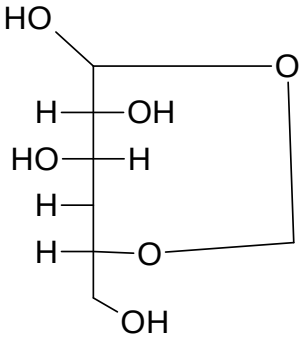


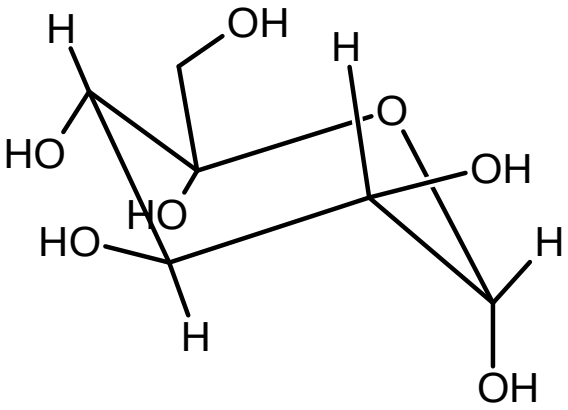


Presence of cyclic ring

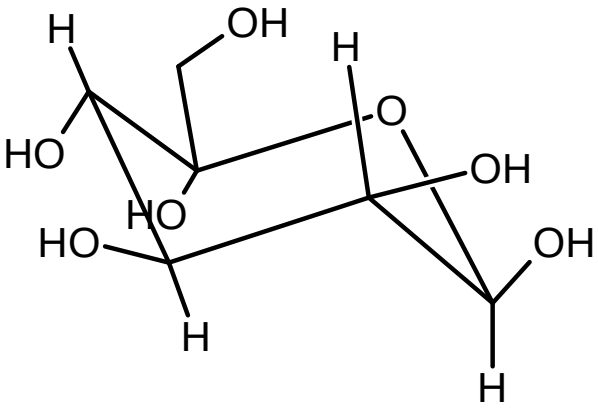




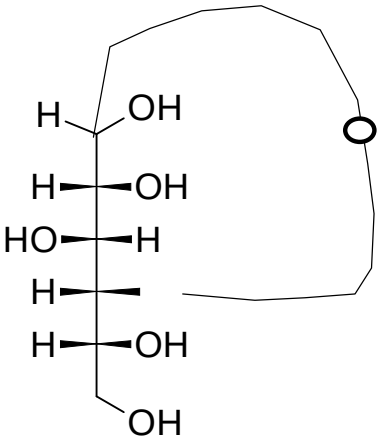




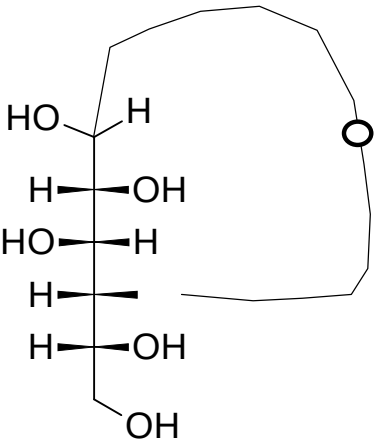
α – D GLUCOSE



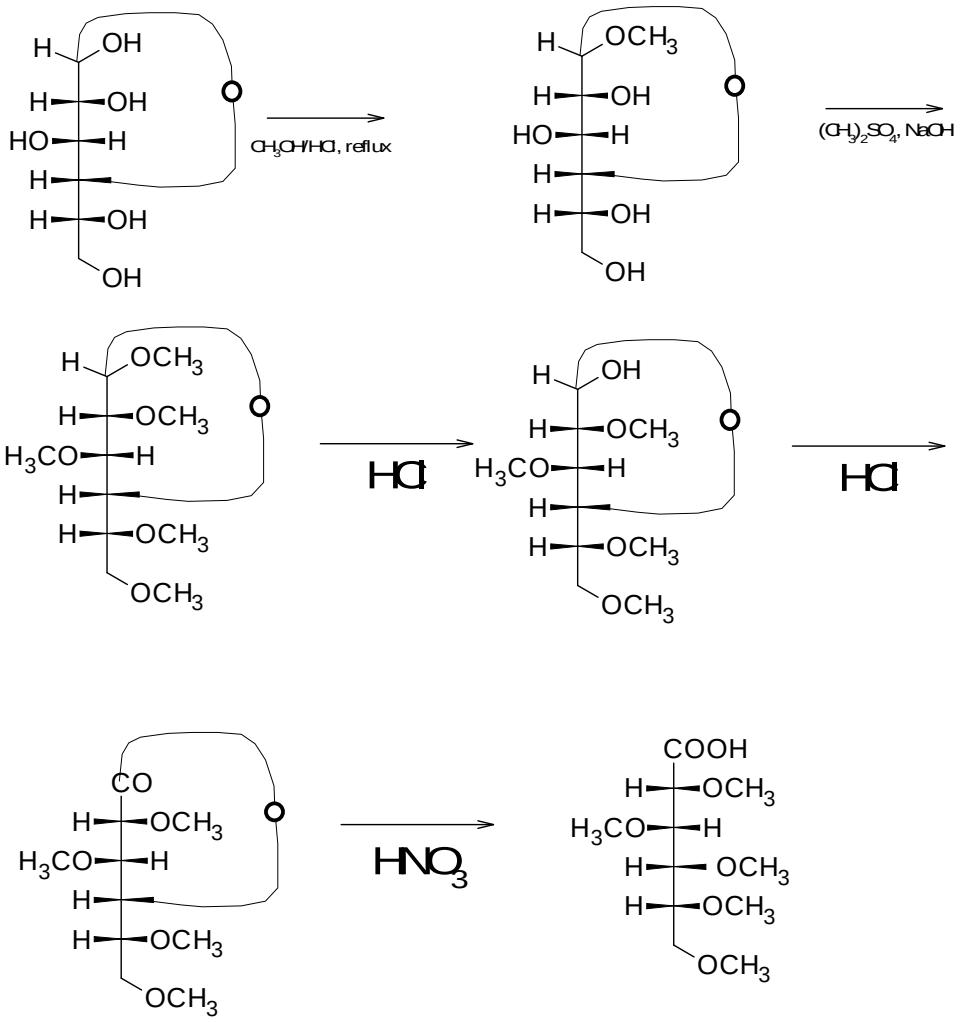
β – D GLUCOSE



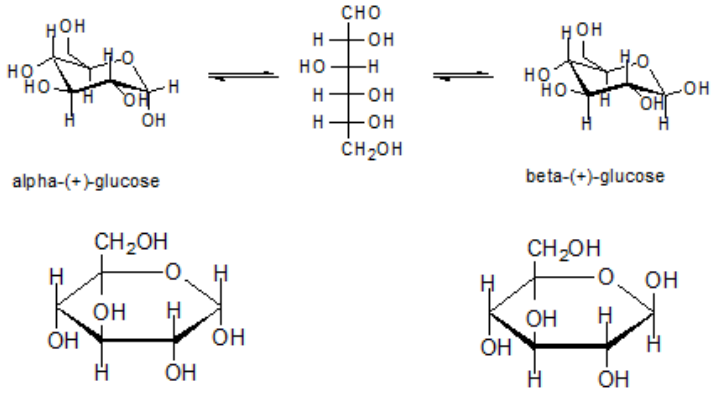
36% , α–D - Glucose



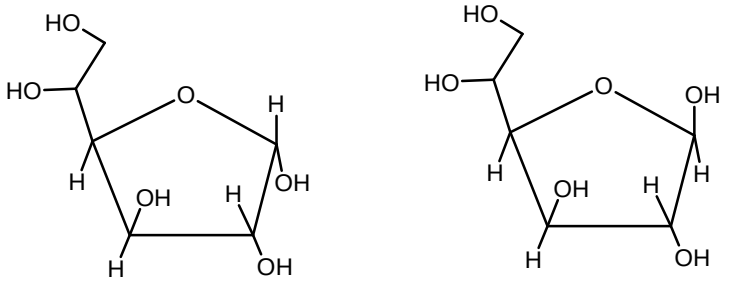
64% , β–D - Glucose



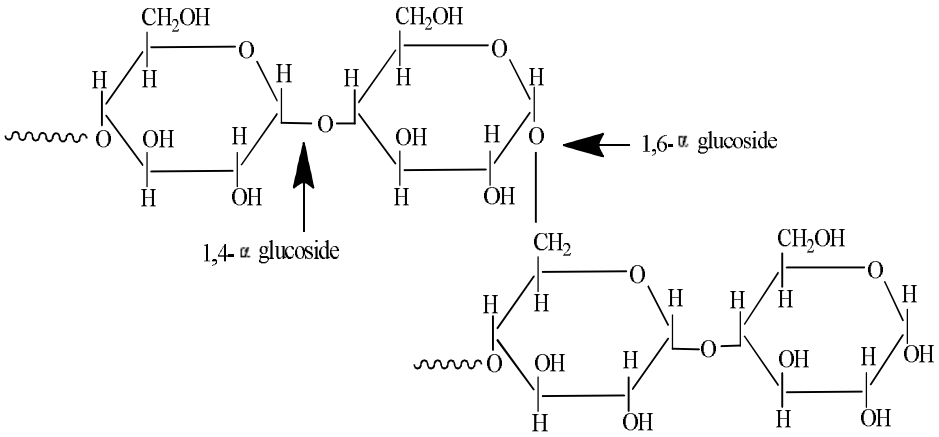
Glucose isomeric conversion



Presence five membered ring

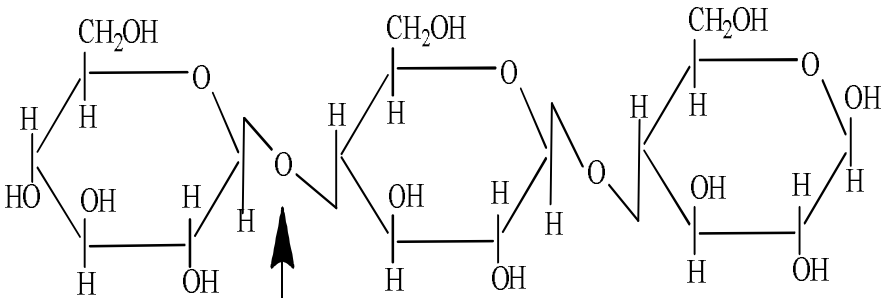


Structure of Starch



α Amylopectin

Structure of Cellulose



1,4 β glycosidic linkage

Cellulose