Aliphatic Chemistry

1st Year Biology and Geology Students

Faculty of Education

2021/2022

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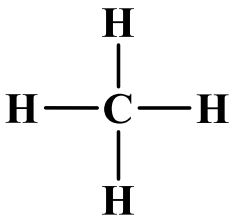
Contents

- Hydrocarbons.
- Alkyl halides.
- Alcohols.
- Ethers.
- Thiols.
- Thioethers.
- Aldehydes and ketones.
- Carboxylic acids and their derivatives.
- Amines.

Hydrocarbons

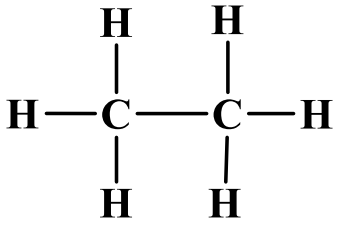
The simplest organic compounds are those composed of only two elements: carbon and hydrogen. These compounds are called hydrocarbons. Hydrocarbons themselves are separated into two types: aliphatic hydrocarbons and aromatic hydrocarbons. Aliphatic hydrocarbons are hydrocarbons based on chains of C atoms. There are three types of aliphatic hydrocarbons.

A- Alkanes are aliphatic hydrocarbons with only single covalent bonds.



CH_4

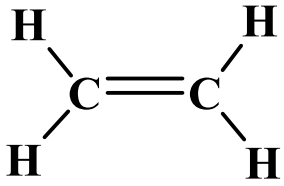
methane



C_2H_6

ethane

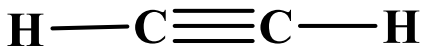
B- Alkenes are hydrocarbons that contain at least one C–C double bond.



C_2H_4

ethylene

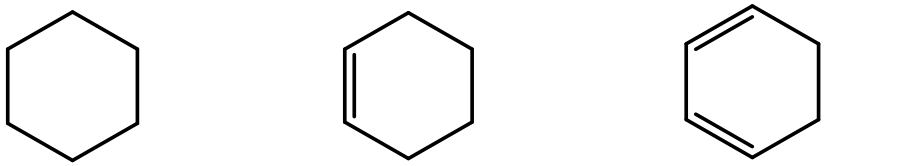
C- Alkynes are hydrocarbons that contain C-C triple bond.



C_2H_2

acetylene

D- An aliphatic hydrocarbon with a ring or C atoms; these hydrocarbons are called cycloalkanes (or cycloalkenes or cycloalkynes).



cyclohexane cyclohexene cyclohexadiene

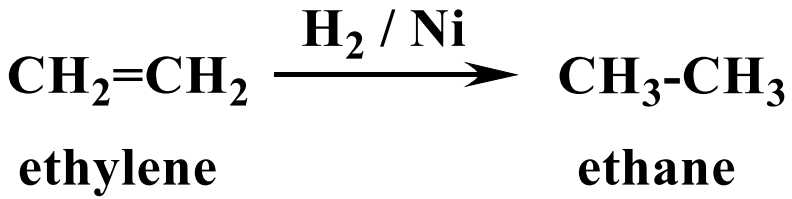
Because alkanes have the maximum number of H atoms possible according to the rules of covalent bonds, alkanes are also referred to as saturated hydrocarbons.

A- Alkanes

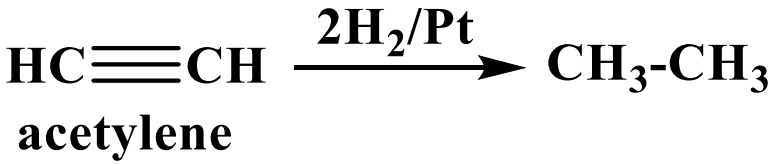
All bonds between carbon atoms are single.

Synthesis

1- From alkenes (by catalytic hydrogenation).



2- From alkynes (by catalytic hydrogenation).

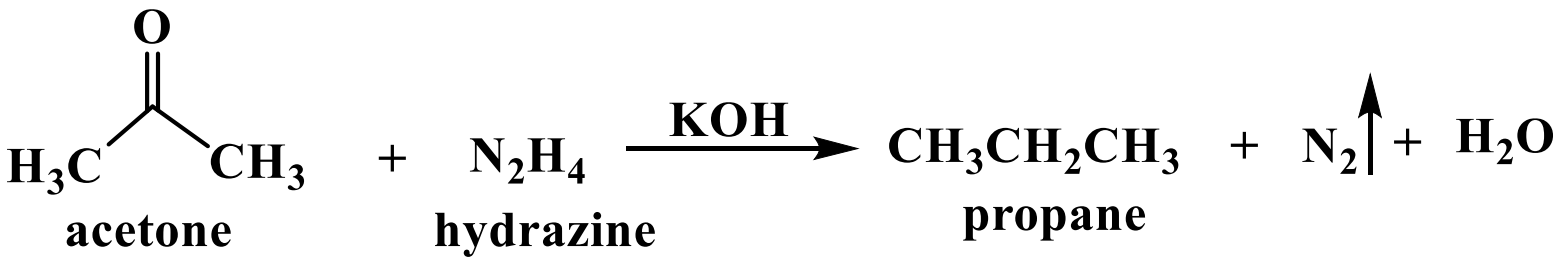


3- From alkyl halides (RX).

R= alkyl X= halogen= F, Cl, Br, I

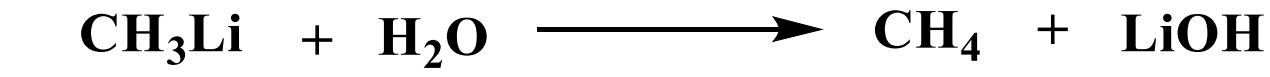
methyl bromide — **methane**

4- From Wolff Kishner's reaction.



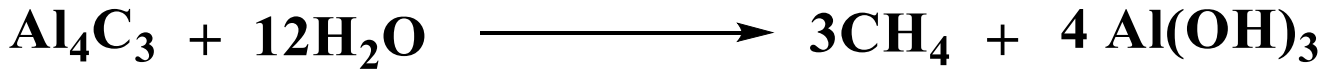
acetone — **hydrazine** — **propane**

5- From organometalic reagents.



methyl lithium

6- Hydrolysis of metal carbides.



aluminium carbide

Reactions

1- Halogenation.

$$CH_4 + X_2 \xrightarrow[250\text{-}400^oC]{\text{light or}} CH_3X + HX$$

$$CH_4 \xrightarrow{Cl_2/\,h\nu} CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$$

CH_3Cl: methyl chloride

CH_2Cl_2: dichloromethane or methylene chloride

$CHCl_3$: chloroform

CCl_4: carbon tetrachloride

hv= energy

2- Nitration.

$$CH_4 + HNO_3 \xrightarrow[150\text{-}475\ ^oC]{\text{vapour phase}} CH_3NO_2 + H_2O$$

nitromethane

3- Oxidation.

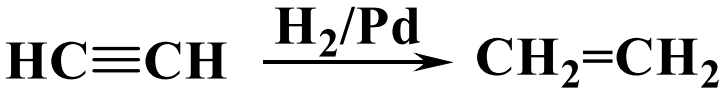
$$CH_4 + O_2 \longrightarrow CO_2 + 2H_2O$$

B- Alkenes

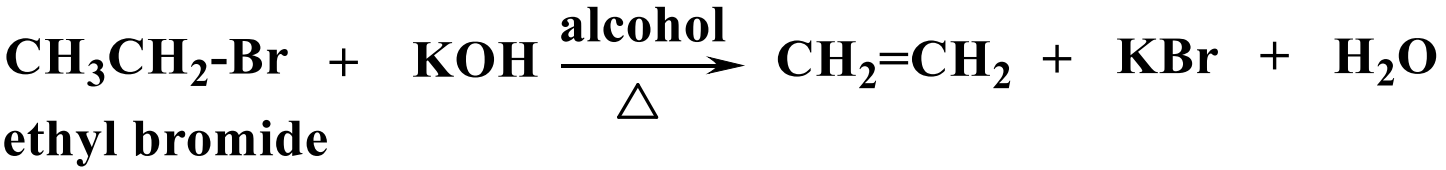
Unsaturated hydrocarbons (contain double bonds).

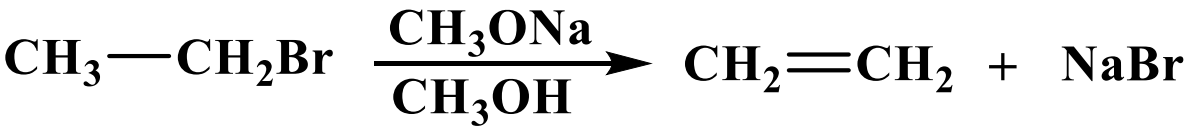
Synthesis

1- From alkynes (*via* catalytic hydrogenation).

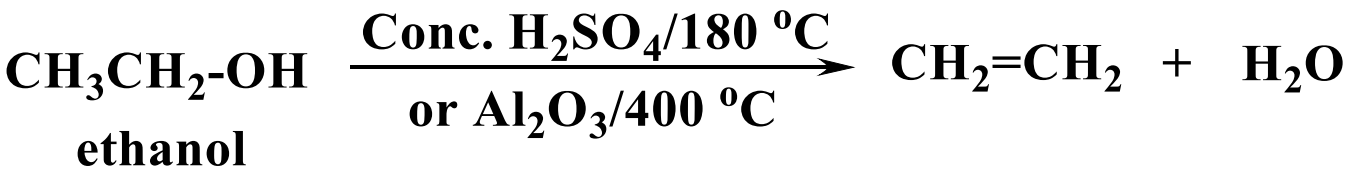


2- From alkyl halides (*via* dehydrohalogenation).

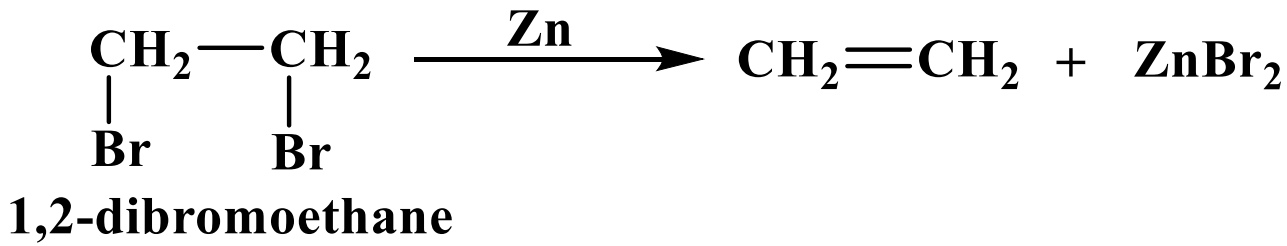




3- From alcohols (*via* dehydration).

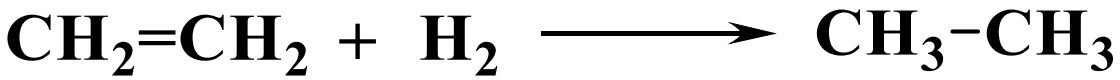


4- Dehalogenation of vicinal dihalides.

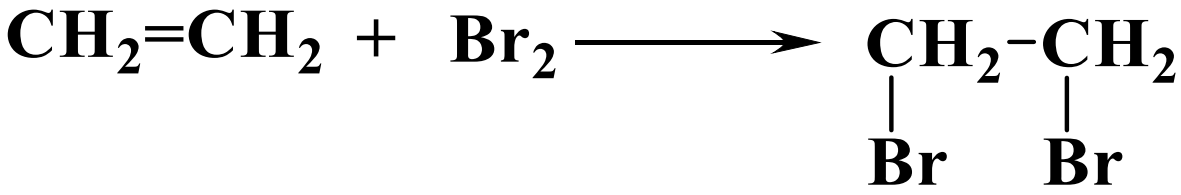


Reactions

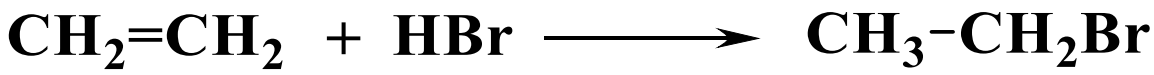
1- Addition of hydrogen.



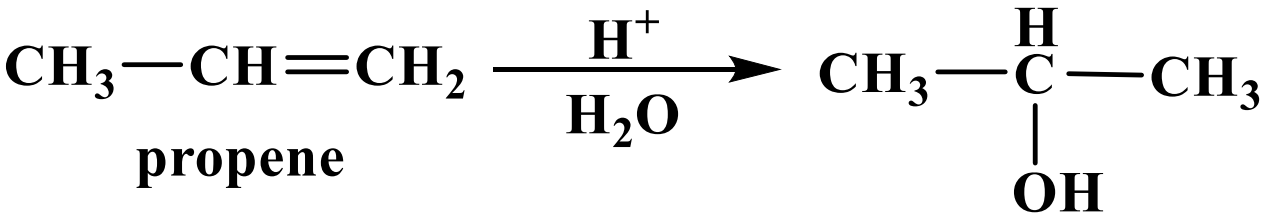
2- Addition of halogens.



3- Addition of halogen acids.



4- Addition of water.



propene

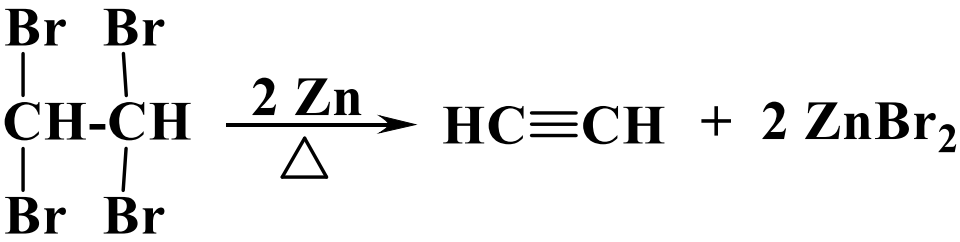
propan-2-ol

C-Alkynes

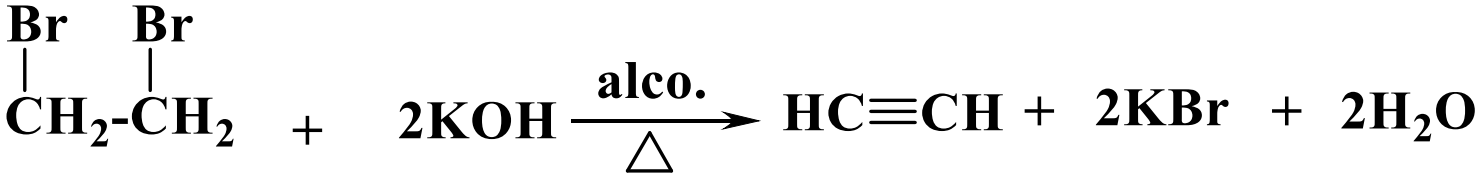
Unsaturated hydrocarbons (contain triple bond).

Synthesis

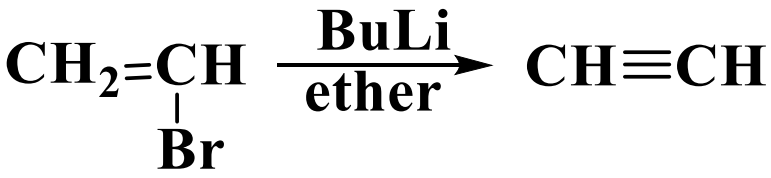
From alkyl halides.



1,1,2,2-tetrabromoethane



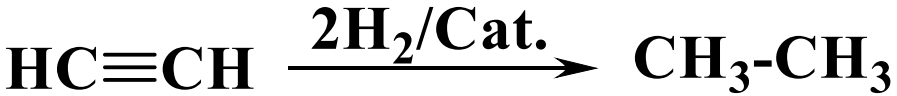
1,2-dibromoethane

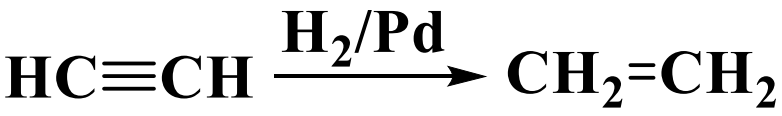


bromoethylene

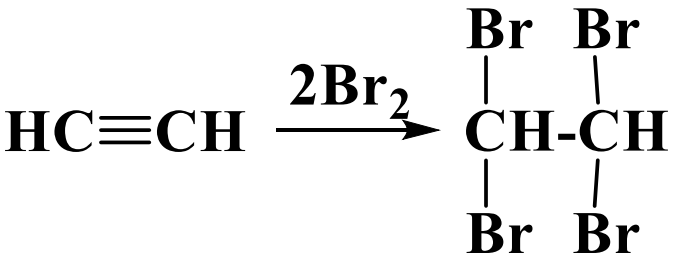
Reactions

1- Addition of hydrogen.





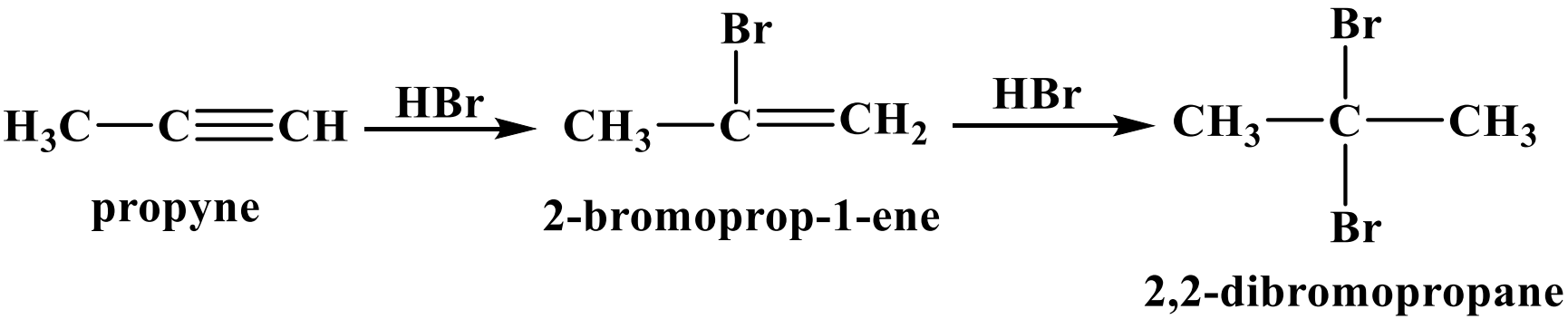
2- Addition of bromine.



3- Addition of hydrogen cyanide (HCN).

vinyl cyanide

4- Addition of HBr.



propyne

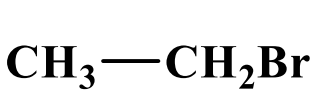
2-bromoprop-1-ene

2,2-dibromopropane

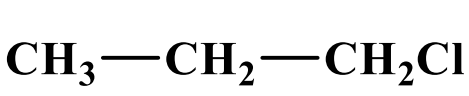
Halogen derivatives of saturated hydrocarbons

(Alkyl halides)

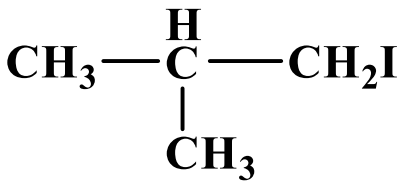
Alkyl halides are also known as haloalkanes. Alkyl halides are compounds in which one or more hydrogen atoms in an alkane have been replaced by halogen atoms (fluorine, chlorine, bromine or iodine). Alkyl halides can be classified as primary, secondary, or tertiary.



bromoethane

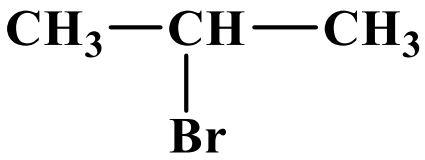


1-chloropropane

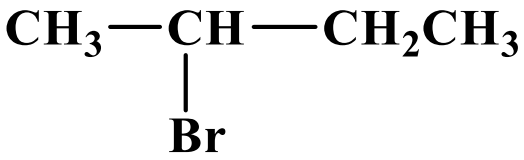


1-iodo-2-methylpropane

primary alkyl halide

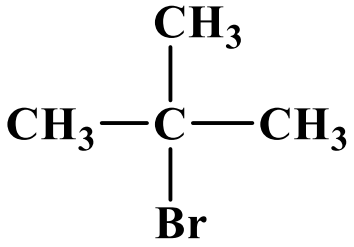


2-bromopropane

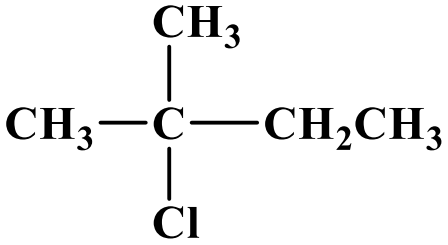


2-bromobutane

secondary alkyl halide



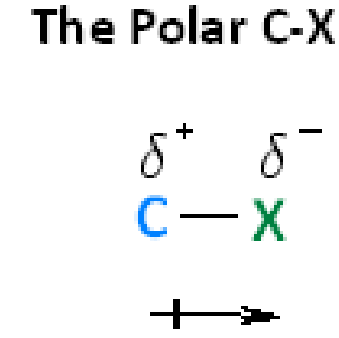
2-bromo-2-methylpropane



2-chloro-2-methylbutane

tertiary alkyl halide

With respect to electronegativity, halogens are more electronegative than carbons. This results in a carbon-halogen bond that is polarized. As shown in the image below, carbon atom has a partial positive charge, while the halogen has a partial negative charge.



The following image shows the relationships between bond length, bond strength, and molecular size. As we progress down the periodic table from fluorine to iodine, molecular size increases. As a result, we also see an increase in bond length. Conversely, as molecular size increases and we get longer bonds, the strength of those bonds decreases.

Bond length	C-F	<	C-Cl	<	C-Br	< C-I
Bond strength	C-I	<	C-Br	<	C-Cl	< C-F
Molecular size	F	<	Cl	<	Br	< I

Synthesis

1- From alkanes.

$$RH + X_2 \xrightarrow{h\nu} RX + HX$$

2- From alkenes.

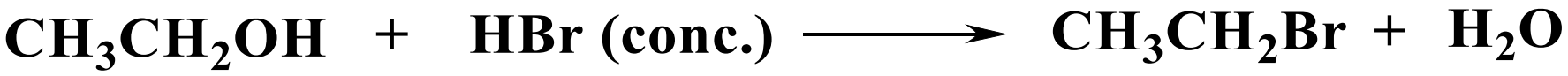
i) *Via* addition of halogen acids

$$CH_2{=}CH_2 + HX \longrightarrow CH_3{-}CH_2X$$

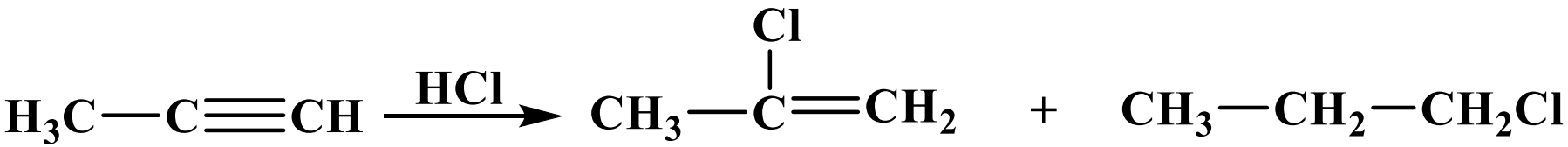
ii) *Via* addition of halogen

$$CH_2{=}CH_2 + X_2 \longrightarrow CH_2X{-}CH_2X \text{ (vicinal dihalides)}$$

3- From alcohols.



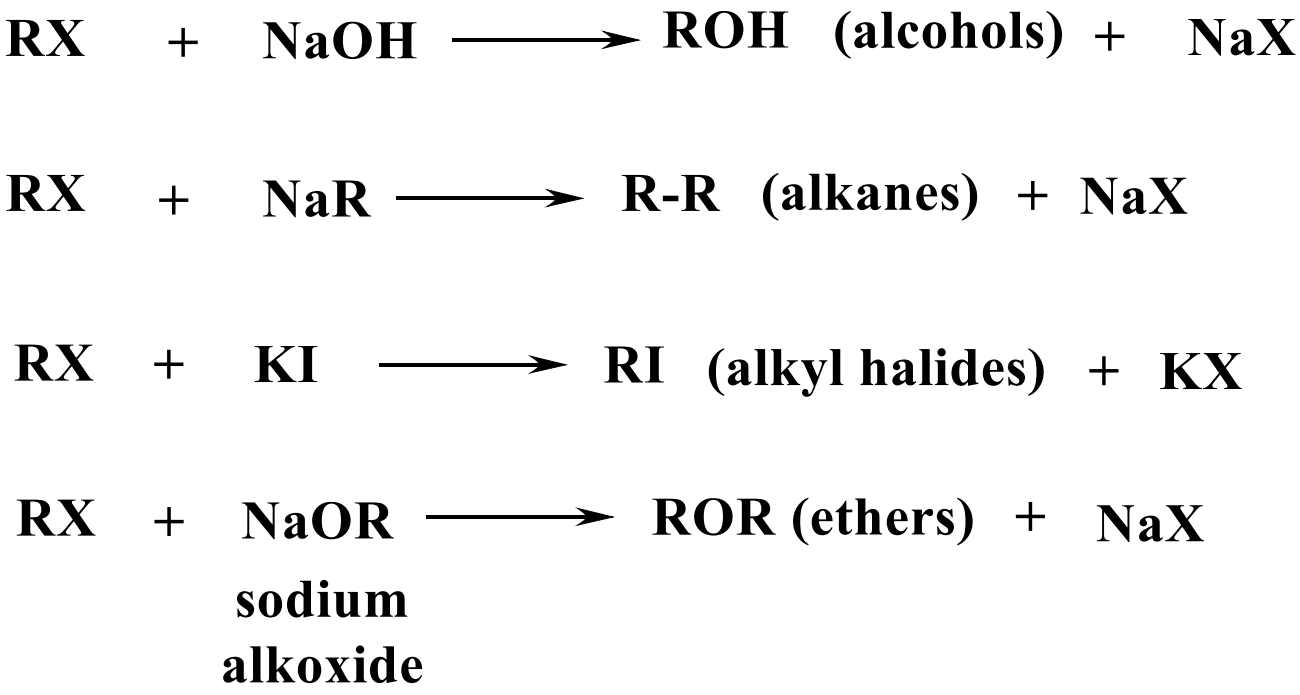
4- Addition of hydrogen halides to alkenes.



propyne | 2-chloroprop-1-ene | 1-chloropropane

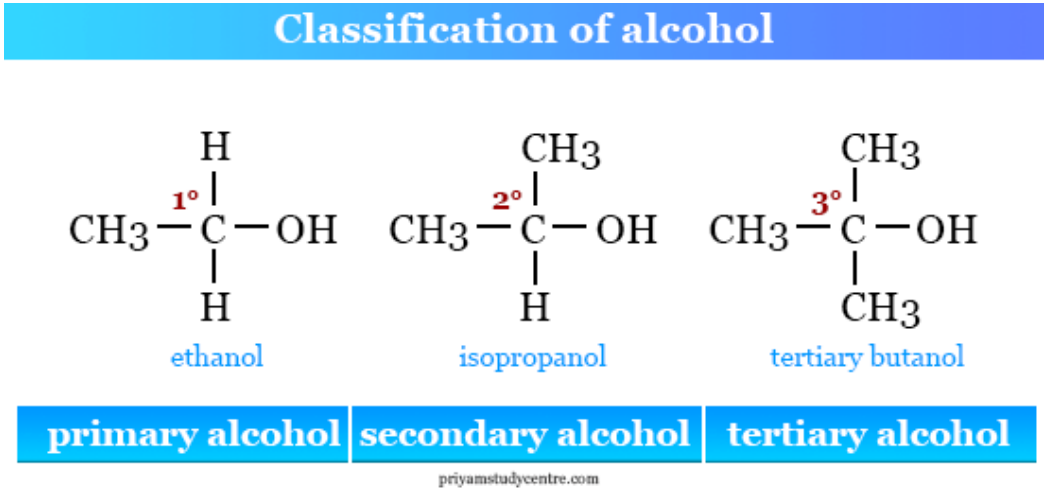
Reactions

Nucleophilic substitution.



Alcohols

Aliphatic alcohols are organic chemical compounds. They are flammable liquids and are highly soluble in water and many organic solvents. Highly volatile liquids, they are stable in water under typical use conditions.



-Types of aliphatic alcohol

1- Methanol, ethanol, propanol, isopropyl alcohol, butanol, isobutanol, etc are examples of monohydric alcohols because these contain only one hydroxyl group.

2- Ethylene glycol, trimethylene glycol, pentamethylene glycol, isobutene glycol are dihydric types of aliphatic alcohols. These chemicals contain two alcoholic groups.

3- The only important trihydric aliphatic organic compound is glycerol or propane-1-2-2-triol because these contain three alcoholic groups. Glycerol occurs in almost all animals and vegetable oils.

4- D-sorbitol, D-mannitol, and dulcitol are the polyhydric aliphatic alcohols that occur naturally contain more than three hydroxyl groups.

Examples of alcohol Names and Formula

methanol CH_3OH

***n*-propanol $CH_3CH_2CH_2OH$**

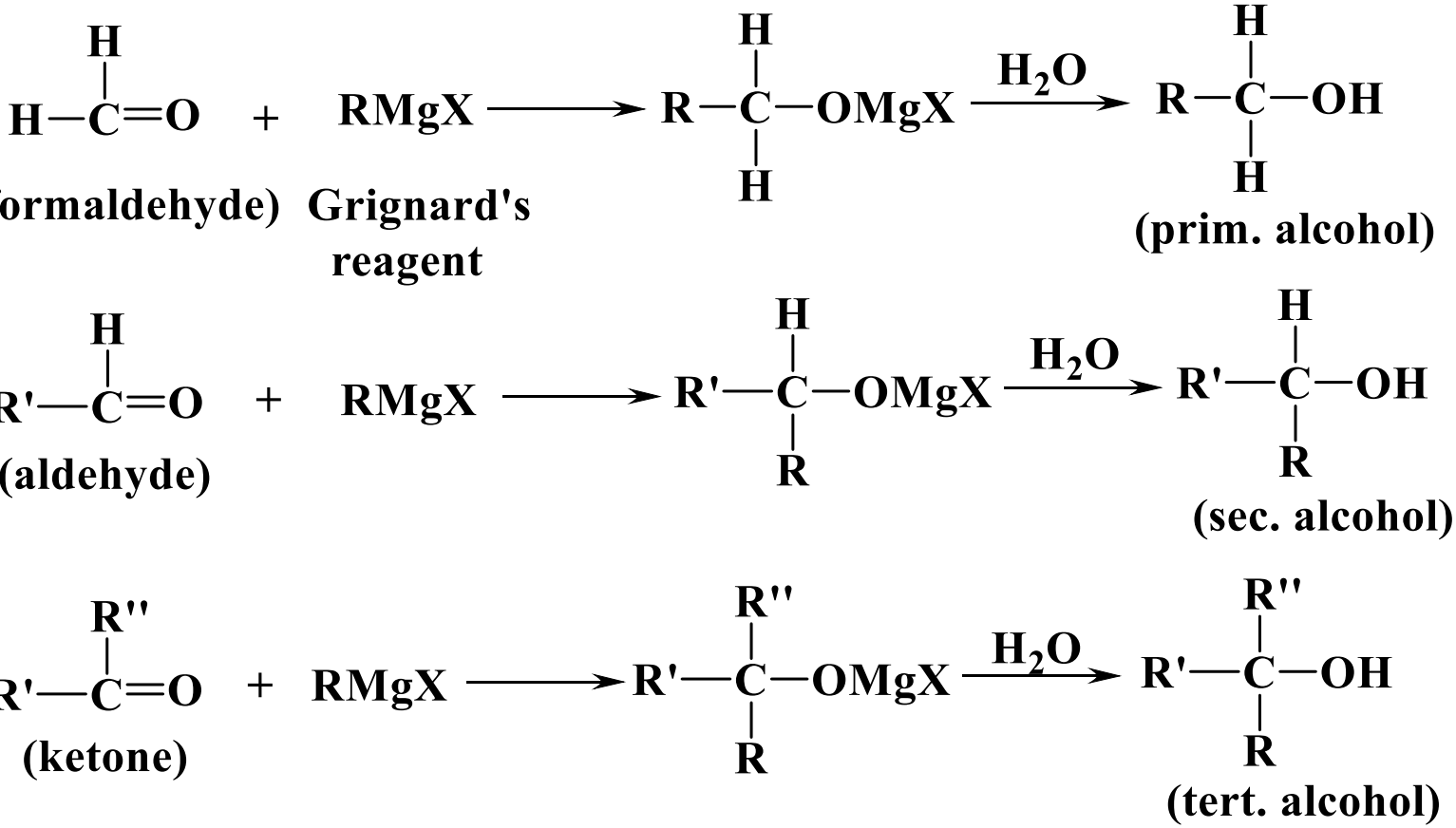
***iso*-propanol$CH_3CH(OH)CH_3$**

***t*-butanol $(CH_3)_3COH$**

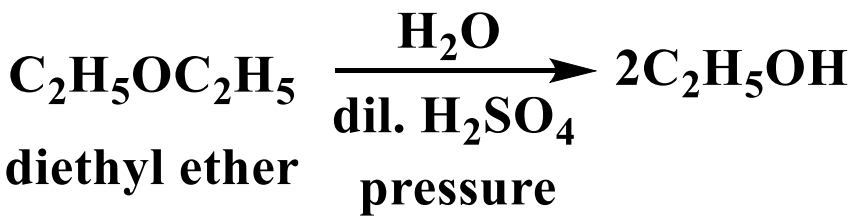
Synthesis

1- From alkyl halides by hydrolysis.

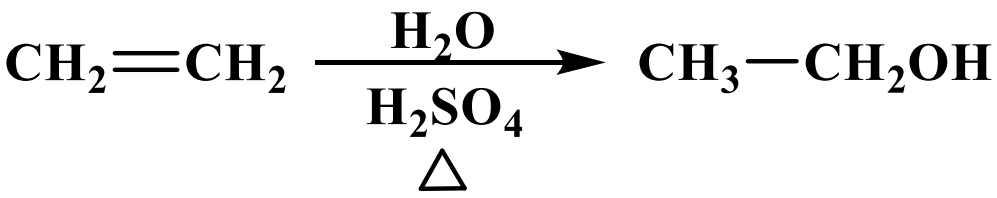
2- From aldehydes and ketones.



3- From ethers.



4- From alkenes.



Reactions

1- Reaction with halogen acids.

$$CH_3CH_2OH + HBr\ (conc.) \longrightarrow CH_3CH_2Br + H_2O$$

2- Dehydration.

$$CH_3CH_2\text{-}OH \xrightarrow[\text{or } Al_2O_3/400\ ^oC]{\text{Conc. } H_2SO_4/180\ ^oC} CH_2{=}CH_2 + H_2O$$

3- Esterification.

$$CH_3CH_2OH + CH_3COOH \xrightleftharpoons{\text{conc. } H_2SO_4} \underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

4-Reaction with ammonium.

$$ROH + NH_3 \xrightarrow{\text{pressure}} \underset{\text{primary amines}}{RNH_2} + H_2O$$

$$ROH + ROH \xrightarrow{\text{pressure}} \underset{\text{secondary amines}}{(R)_2NH} + H_2O$$

$$(R)_2NH + ROH \xrightarrow{\text{pressure}} \underset{\text{tertiary amines}}{R_3N} + H_2O$$

5- Reaction with phosphorus pentasulphide (P_2S_5).

$$5ROH + P_2S_5 \longrightarrow \underset{\text{thiol}}{5RSH} + P_2O_5$$

Ethers

Ethers are a class of organic compounds that contain an ether group - an oxygen atom connected to two alkyl or aryl groups. They have the general formula R–O–R′, where R and R′ represent the alkyl or aryl groups. Ethers can again be classified into two varieties: if the alkyl groups are the same on both sides of the oxygen atom, then it is simple or symmetrical ether, whereas if they are different, the ethers are called mixed or unsymmetrical ethers. A typical example of the first group is the solvent and anaethetic diethyl ether, commonly referred to simply as "ether" ($CH_3–CH_2–O–CH_2–CH_3$).

Synthesis

1- From alkyl halides (Williamson Synthesis).

$$RX + NaOR \longrightarrow ROR \text{ (ethers)} + NaX$$

2- By dehydration of alcohols.

$$2C_2H_5OH \xrightarrow[-\ H_2O]{H_2SO_4} C_2H_5OC_2H_5$$

diethyl ether

Reactions

1- Cleavage by halogen acids.

$$ROR + HX \xrightarrow[\text{high temp.}]{\text{conc.}} RX + ROH$$

$$(CH_3CH_2)_2O + HI \xrightarrow{\text{high temp.}} CH_3CH_2I + CH_3CH_2OH$$

$$(CH_3CH_2)_2O + 2HI\ (conc.) \xrightarrow{\text{high temp.}} 2CH_3CH_2I + H_2O$$

2- Reaction with phosphorus pentasulphide P_2S_5.

$$5C_2H_5OC_2H_5 + P_2S_5 \xrightarrow{\triangle} 5C_2H_5SC_2H_5 + P_2O_5$$

diethylthioether

3- Oxidation.

$$C_2H_5OC_2H_5 \xrightarrow{6O_2} 4CO_2 + 5H_2O$$

4- Halogenation.

a- In dark gives the substituted ether.

$$C_2H_5OC_2H_5 \xrightarrow{Cl_2,\ dark} CH_3CHClOCHClCH_3$$

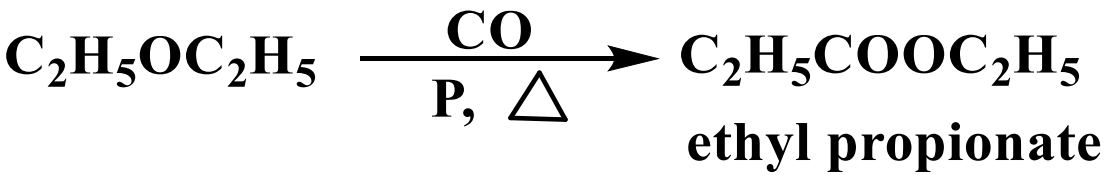
1,1'- dichloro diethyl ether

b- In sunlight it substitutes all hydrogen atoms present.

$$C_2H_5OC_2H_5 \xrightarrow{Cl_2,\ sunlight} C_2Cl_5OC_2Cl_5$$

perchloro diethyl ether

5- Reaction with carbon monoxide.

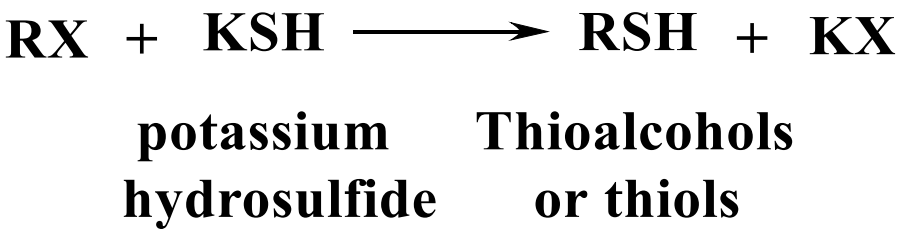


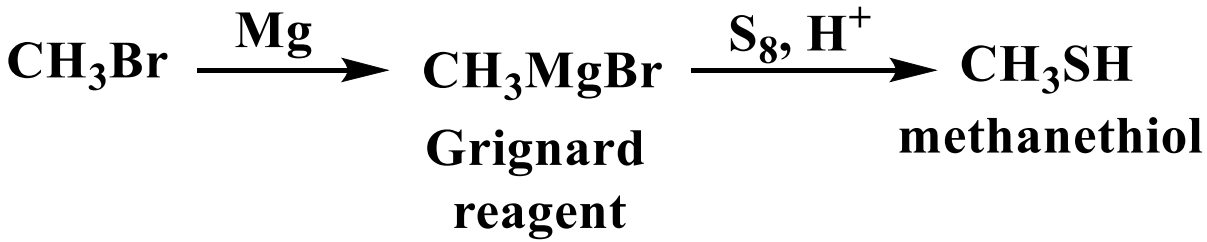
Thioalcohols

A thiol or thiol derivative is any organosulfur compound with the form R−SH, where R represents an alkyl or other organic substituent. The –SH functional group itself is referred to as either a thiol group or a sulfhydryl group, or a sulfanyl group. Thiols are the sulfur analogue of alcohols (that is, sulfur takes the place of oxygen in the hydroxyl group of an alcohol). Thiols are sometimes referred to as mercaptans.

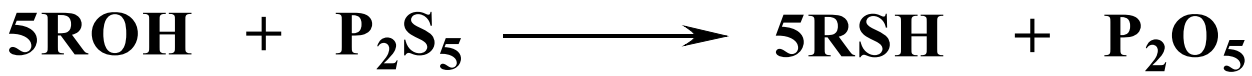
Synthesis

1- From alkyl halides.



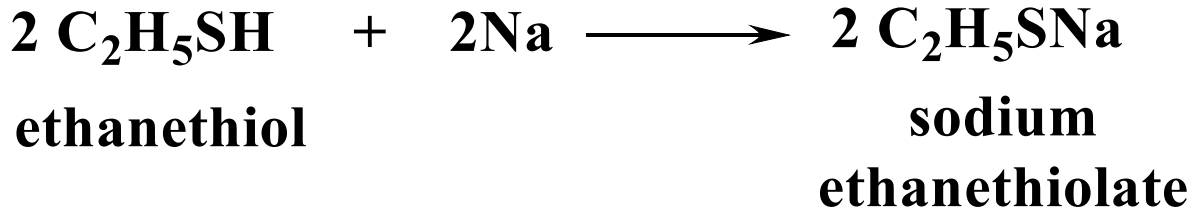


2- From alcohols.

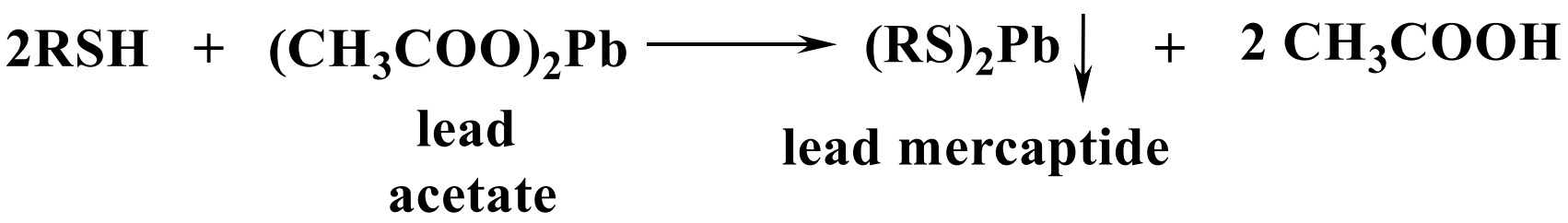


Reactions

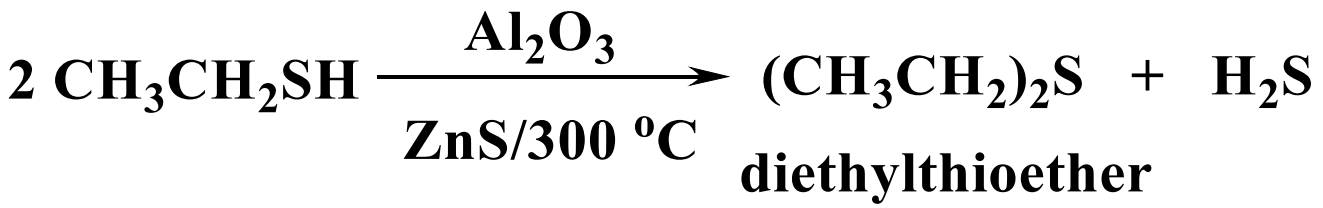
1- With sodium.



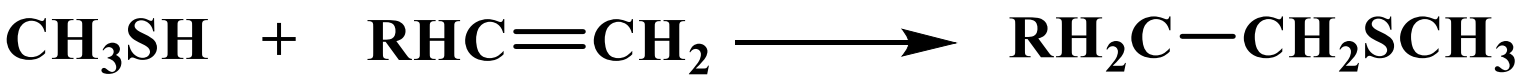
2- Reaction with lead acetate.



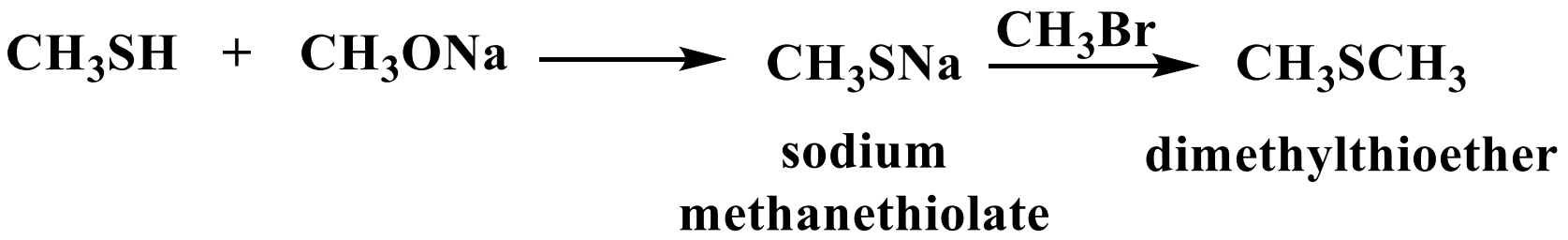
3- Reaction with alumina/zinc sulphide.



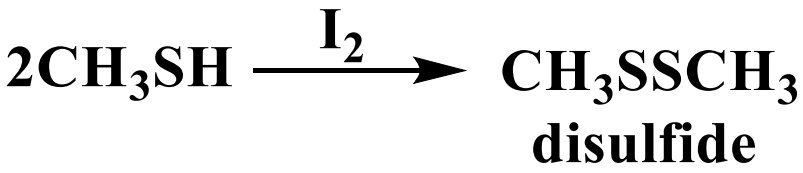
4- Reaction with alkenes.



5- Formation of thioethers.



6- Oxidation by iodine.



Thioethers

(Alkyl sulphides)

An organic sulfide or thioether is a functional group in organosulfur chemistry with the connectivity C–S–C. Like many other sulfur-containing compounds, volatile sulfides have foul odors. A sulfide is similar to an ether except that it contains a sulfur atom in place of the oxygen. The grouping of oxygen and sulfur in the periodic table suggests that the chemical properties of ethers and sulfides are somewhat similar.

Synthesis

1- From alkyl halides (*via* heating with K_2S).

$$RX + KSR \longrightarrow RSR + KX$$

potassium alkanethiolate — thioethers

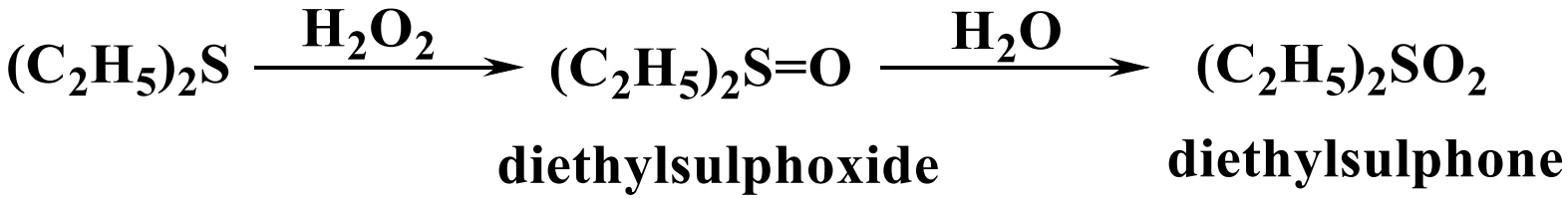
2- From ethers (*via* reaction with P_2S_5).

$$5\ ROR + P_2S_5 \longrightarrow 5\ RSR + P_2O_5$$

Reactions

1- Desulphurization.

2- Oxidation.



Aldehydes and ketones

Aliphatic aldehydes and ketones are essential building blocks for the synthesis of more complex organic compounds.

e.g.

Formaldehyde HCHO

Acetaldehyde CH_3CHO

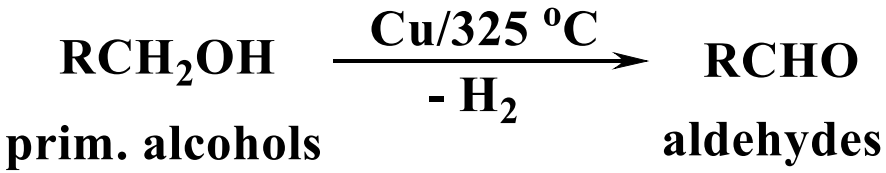
Acetone CH_3COCH_3

A- Aldehydes

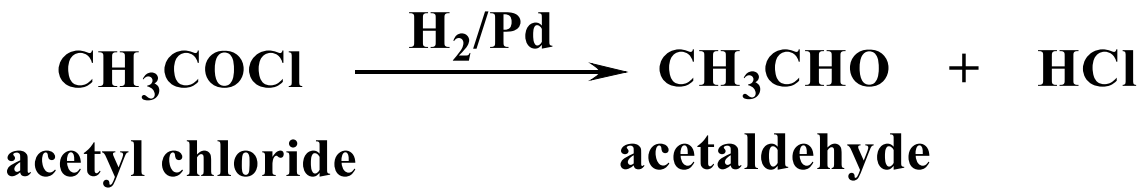
Chemically, an aldehyde is a compound containing a functional group with the structure -CHO, consisting of a carbonyl center (a carbon double-bonded to oxygen) with the carbon atom also bonded to hydrogen and to any generic alkyl or side chain R group. The functional group itself (i.e. without the "R" side chain) is known as an aldehyde or formyl group. Aldehydes, which are generally created by removing hydrogen from an alcohol, are common in organic chemistry; the most well-known is formaldehyde. As they are frequently strongly scented, many fragrances are or contain aldehydes.

Synthesis

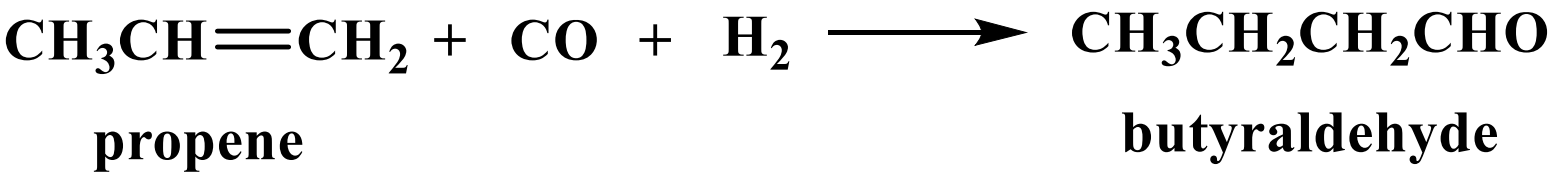
1- *Via* dehydrogenation of alcohols.



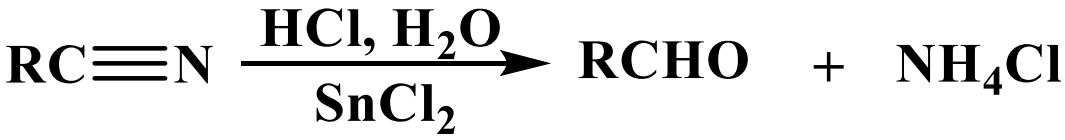
2- From acid derivatives (from acetyl chlorides).



3- From alkenes (by hydroformylation).



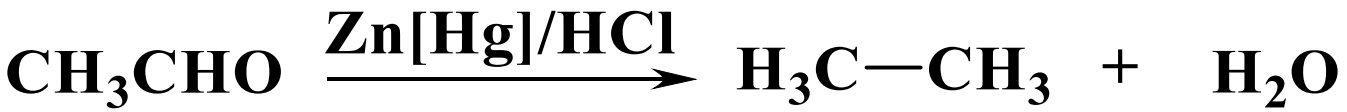
4- From nitriles.



5- From geminal halide hydrolysis.

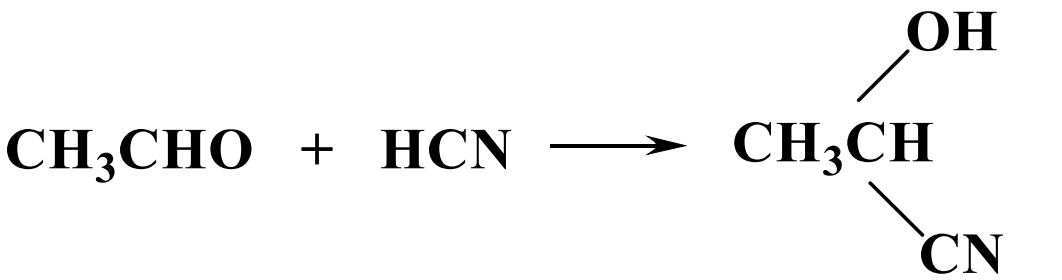
Reactions

1- Addition of hydrogen.



a- Reduction to alkanes (Clemensen reduction).

2- Addition of hydrogen cyanide.



acetaldehyde cyanohydrine

3- Addition of hydrazine (H_2N-NH_2).

$$CH_3CHO + H_2NNH_2 \longrightarrow CH_3CH{=}NNH_2 + H_2O$$

acetaldehyde hydrazone

$$\xrightarrow[-\,H_2O]{CH_3CHO} CH_3CH{=}N\text{-}NCHCH_3$$

4- Oxidation with potassium dichromate $K_2Cr_2O_7$/conc H_2SO_4.

$$RCHO \xrightarrow{K_2Cr_2O_7/\ \text{conc}\ H_2SO_4} RCOOH$$

carboxylic acid

B- Ketones

In chemistry, a ketone is a functional group with the structure $R_2C=O$, where R can be a variety of carbon-containing substituents. Ketones contain a cabonyl group (a carbon-oxygen double bond). The simplest ketone is acetone (R= R'= methyl), with the formula $CH_3C(O)CH_3$. Many ketones are of great importance in biology and in industry. Examples include many sugars (ketones), many steroids (e.g., testosterone), and the solvent acetone.

Synthesis

From alcohols by

a- Oxidation.

$$(R)_2CHOH \xrightarrow[K_2Cr_2O_7/H_2SO_4]{\text{oxidtion}} (R)_2C{=}O$$

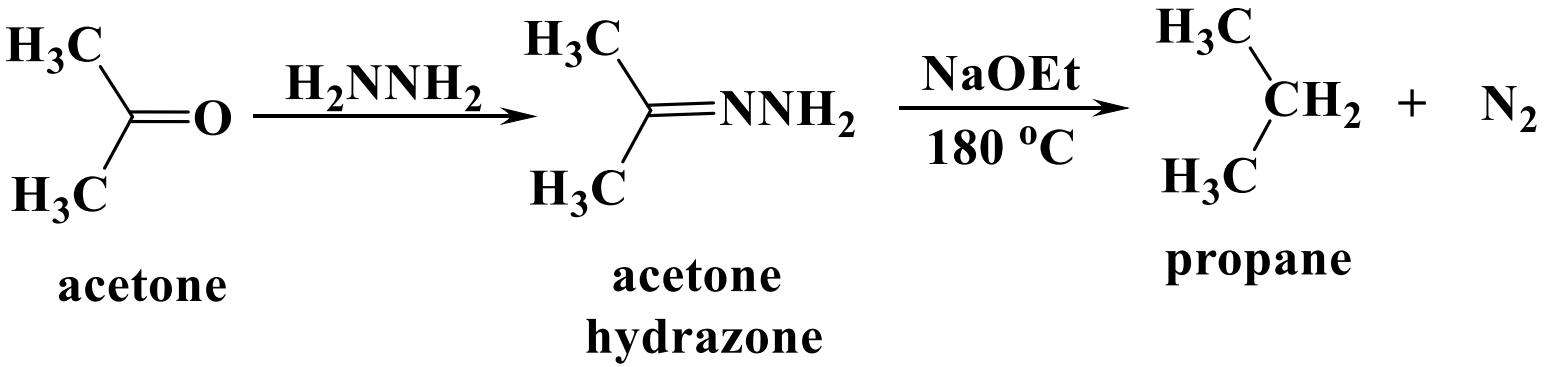
sec. alcohols — ketones

b- Dehydrogenation.

$$(R)_2CHOH \xrightarrow[-\ H_2]{Cu/325\ ^oC} (R)_2C{=}O$$

Reactions

1- Reduction to alkanes.



acetone

acetone hydrazone

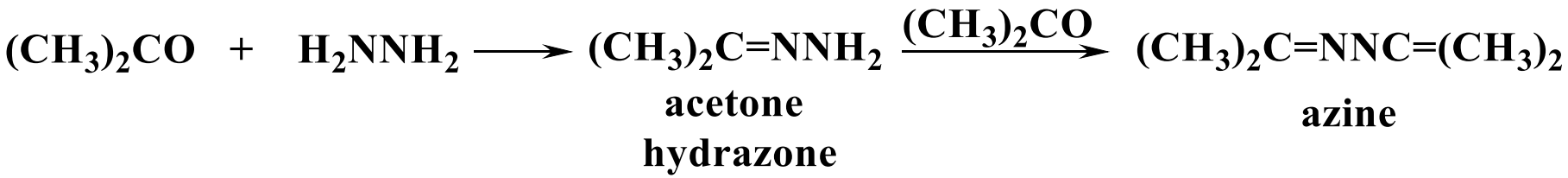
propane

2- Addition of ammonia derivatives

a- With hydroxyl amine.

acetone oxime

b- With hydrazine.



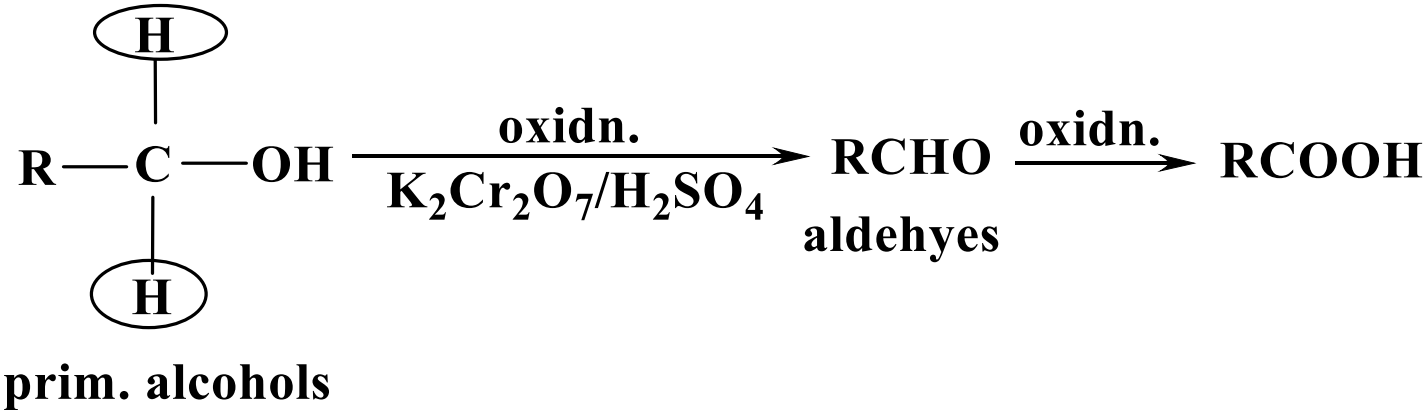
Carboxylic acids and their derivatives

A- Carboxylic acids

A carboxylic acid is an organic acid that contains a carboxyl group (C(=O)OH) attached to a R-group. The general formula of a carboxylic acid is R−COOH or R−CO_2H, with R referring to the alkyl, alkenyl, aryl, or other group. Carboxylic acids occur widely. Important examples include the amino acids and fatty acids. Deprotonation of a carboxylic acid gives a carboxylate anion COO^-.

Synthesis

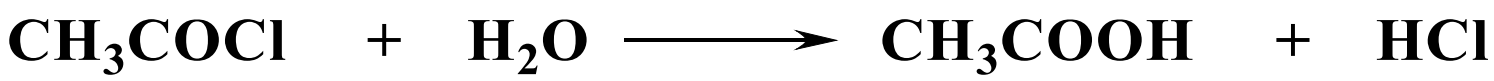
1- From primary alcohols by oxidation.



prim. alcohols

2- From aldehydes by oxidation.

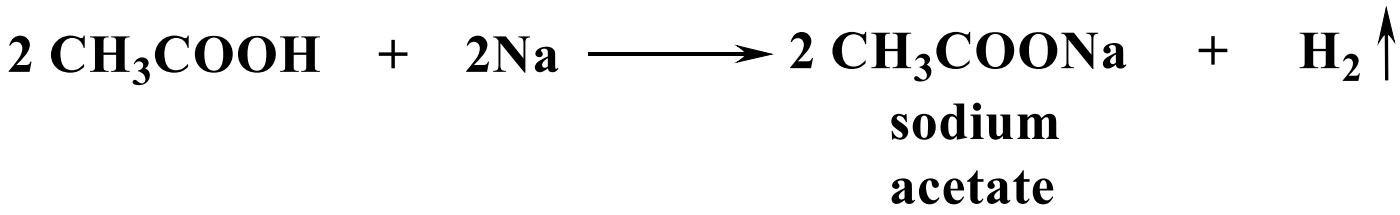
3- Hydrolysis of acid derivatives.

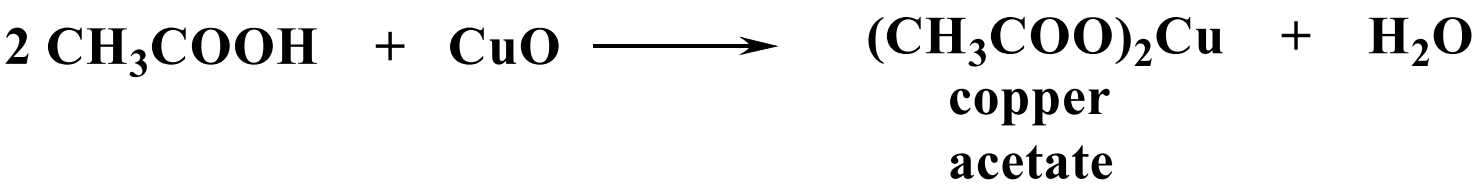


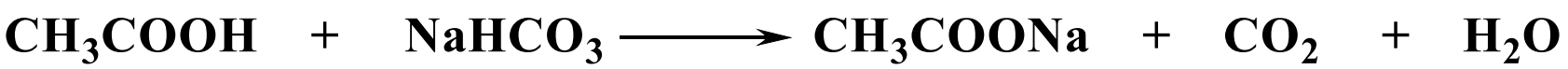
Reactions

1- Salt formation.

Acids react with metals, metal oxides, hydroxides, carbonates to form salts of carboxylic acids.

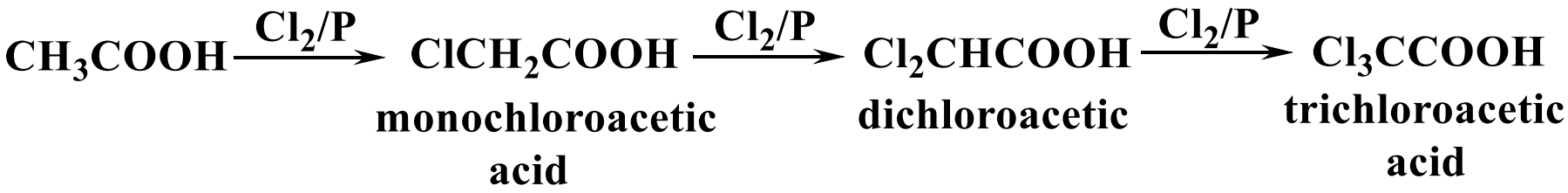




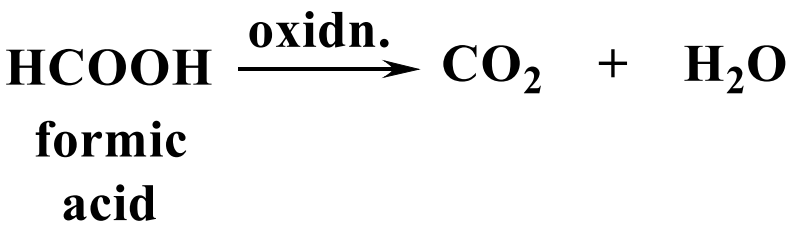


2- Esterification.

3- Halogenation.

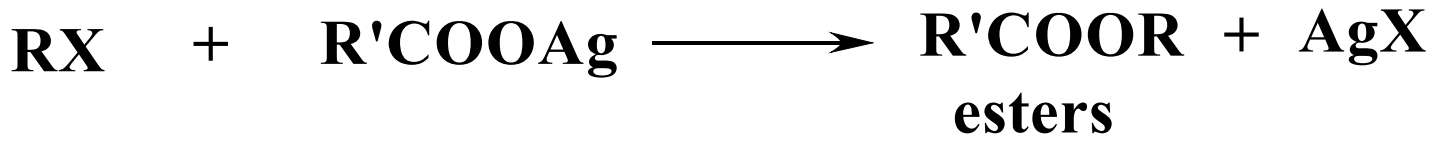


4- Oxidation (only formic acid).

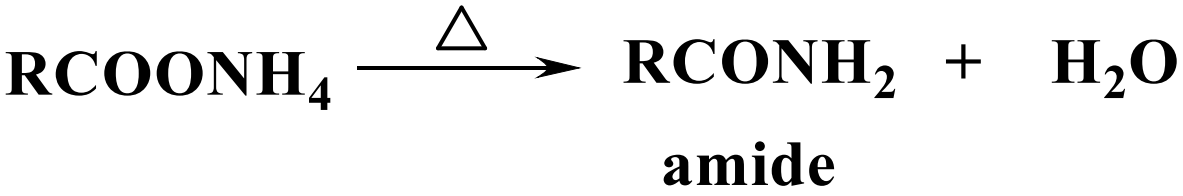


Reactions of carboxylic acid salts.

1- Silver salts.



2- Heating of ammonium salts.



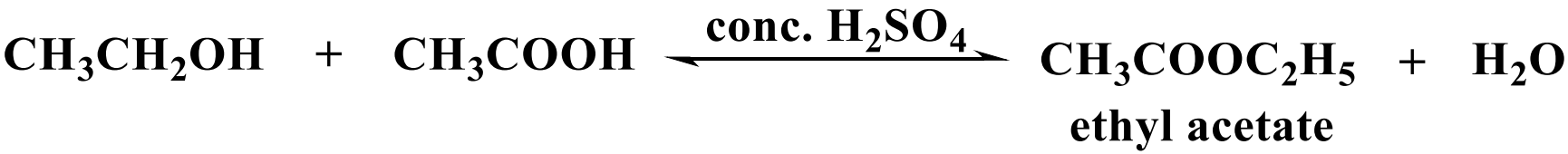
B- Acid derivatives

1- Esters

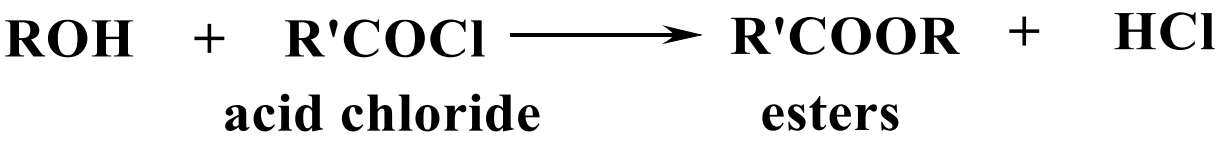
An ester is a chemical compound derived from an acid (organic or inorganic) in which at least one –OH hydroxyl group is replaced by an –O– alkyl (alkoxy) group, as in the substitution reaction of a carboxylic acid and an alcohol.

Synthesis

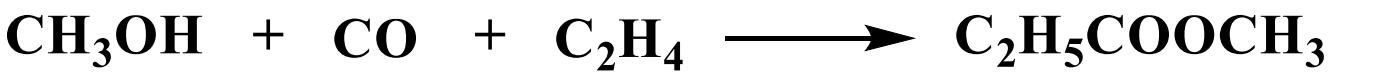
1- From acids.



2- From acylhalides.



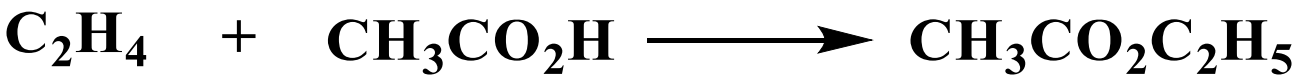
3- Carbonylation of alkenes and/or alcohols.



methyl propionate

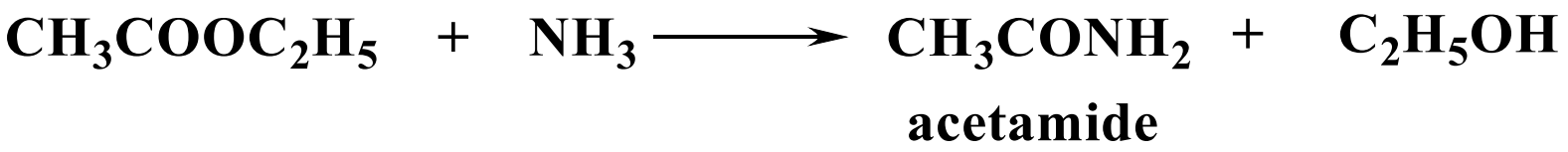
methyl formate

4- Addition of carboxylic acid to alkenes.

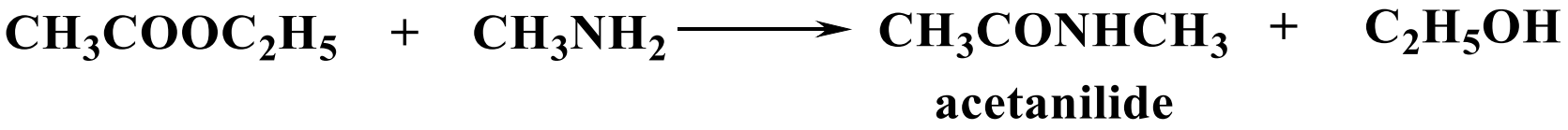


Reactions

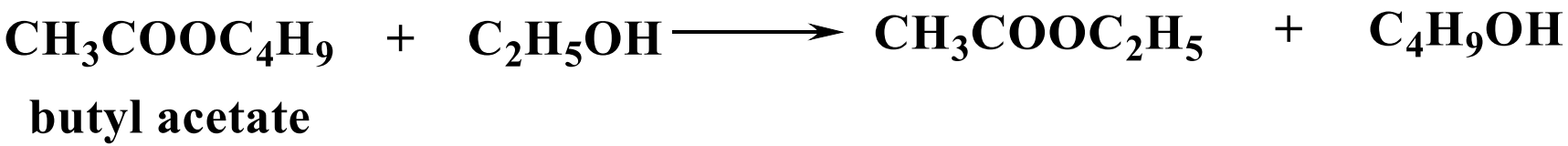
1- Ammonolysis.



2- Aminolysis.



3- Transesterfication (with lower alcohols).

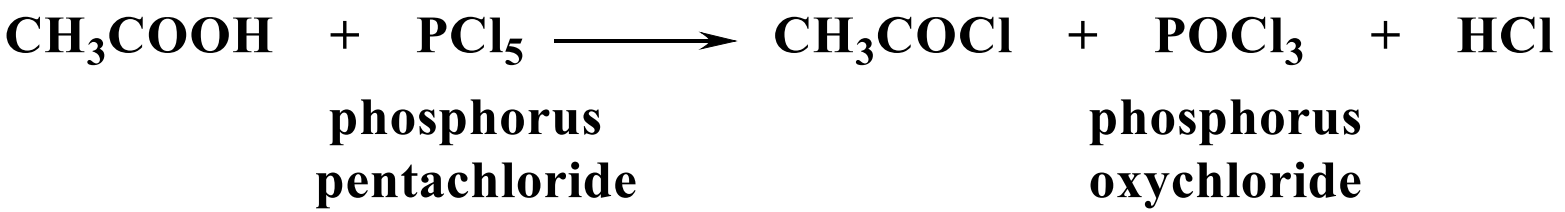


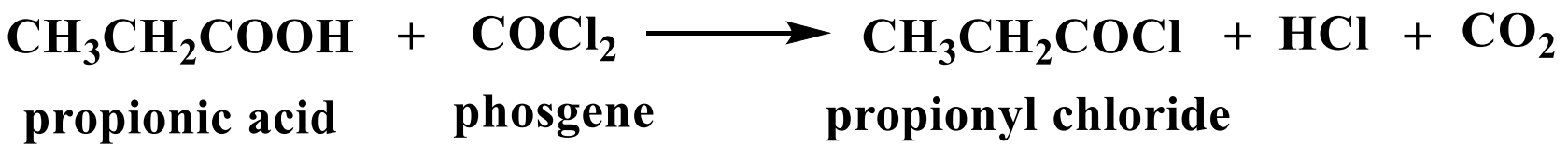
2- Acylchlorides

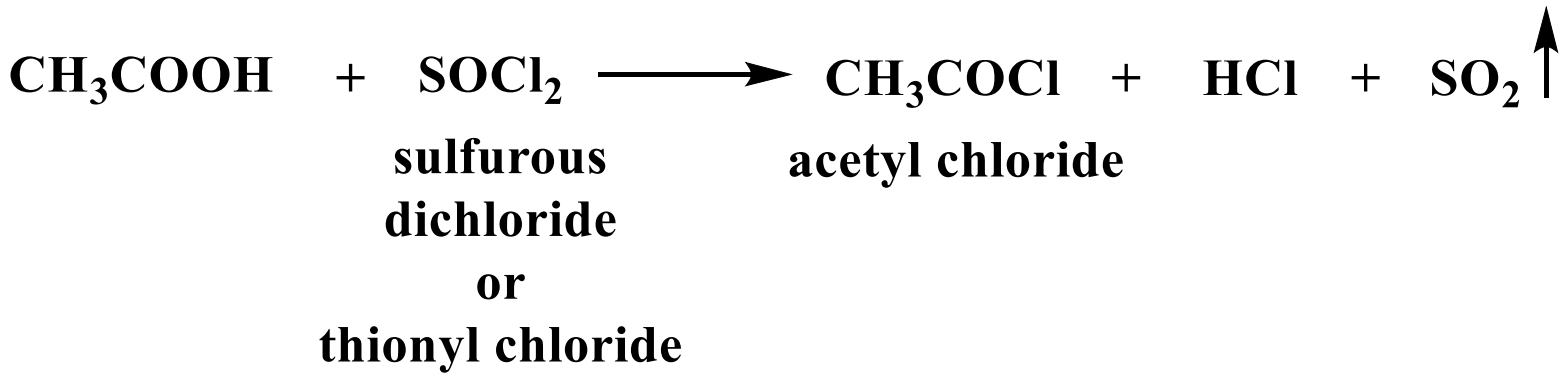
In organic chemistry, an acyl chloride (or acid chloride) is an organic compound with the functional group -COCl. Their formula is usually written RCOCl, where R is a side chain. They are reactive derivatives of carboxylic acids. A specific example of an acyl chloride is acetyl chloride, CH_3COCl. Acyl chlorides are the most important subset of acyl halides.

Synthesis

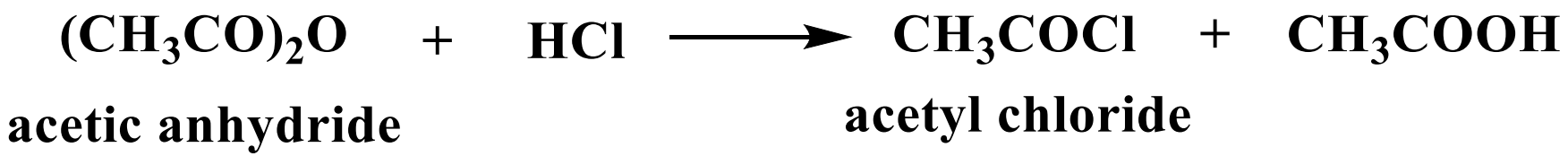
1- From carboxylic acids.





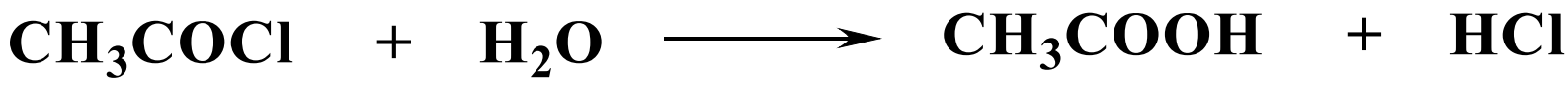


2- From anhydrides.

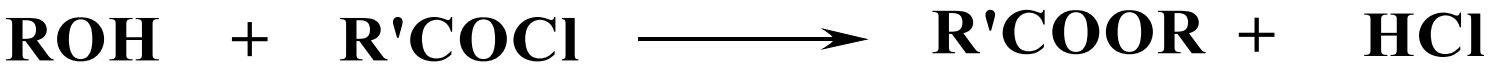


Reactions

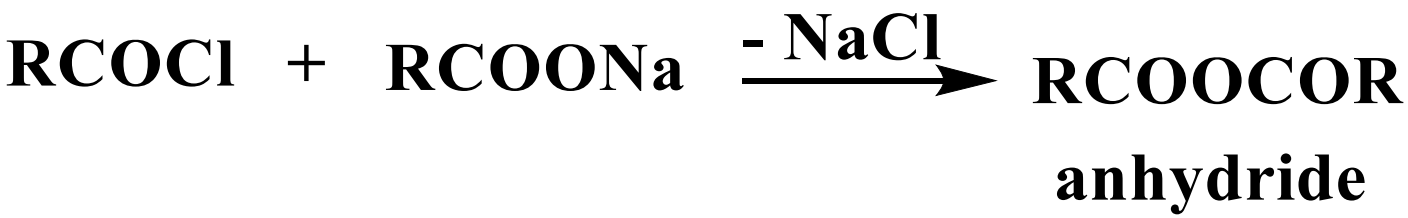
1- Hydrolysis to acid.



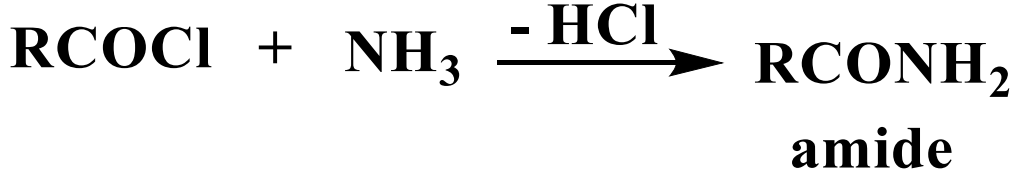
2- Alcoholysis to esters.



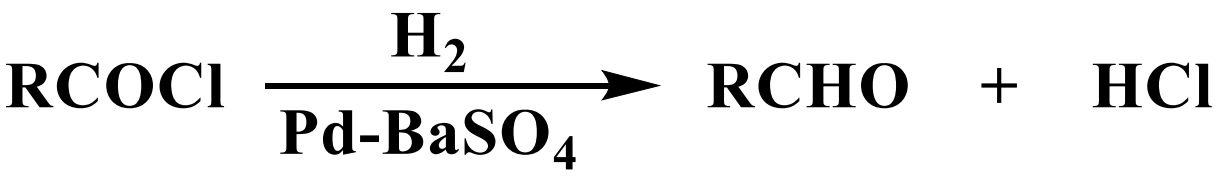
3- Synthesis of anhydrides.



4- Formation of amides.



5- Reduction to aldehydes.

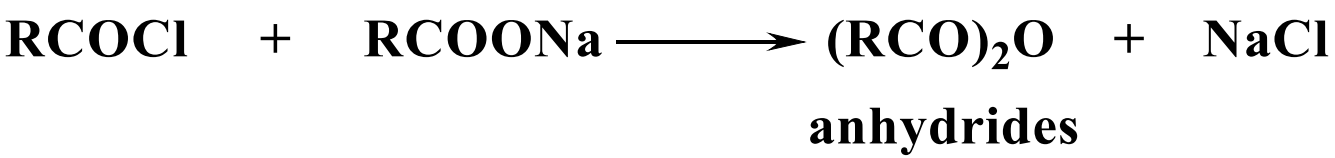


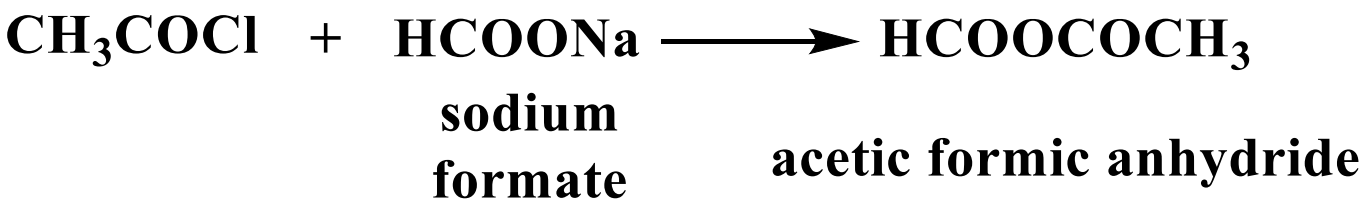
3-Anhydrides

An acid anhydride is a compound that has two acyl groups bonded to the same oxygen atom. A common type of organic acid anhydride is a carboxylic anhydride, where the parent acid is a carboxylic acid, the formula of the anhydride being $(RC(O))_2O$. Symmetrical acid anhydrides of this type are named by replacing the word acid in the name of the parent carboxylic acid by the word anhydride. Thus, $(CH_3CO)_2O$ is called acetic anhydride. Mixed (or unsymmetrical) acid anhydrides, such as acetic formic anhydride, are known, whereby reaction occurs between two different carboxylic acids. Nomenclature of unsymmetrical acid anhydrides list the names of both of the reacted carboxylic acids before the word "anhydride" (for example, the dehydration reaction between benzoic acid and propanoic acid would yield "benzoic propanoic anhydride").

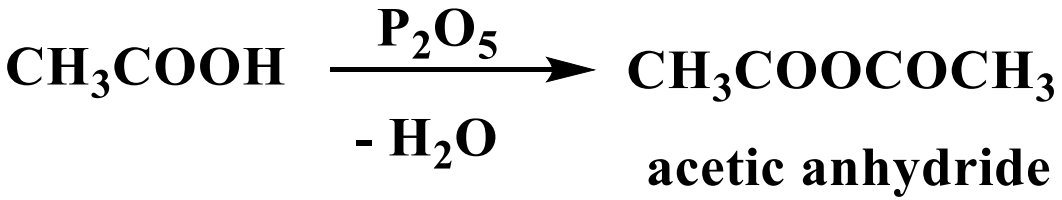
Synthesis

1- From acyl halides.



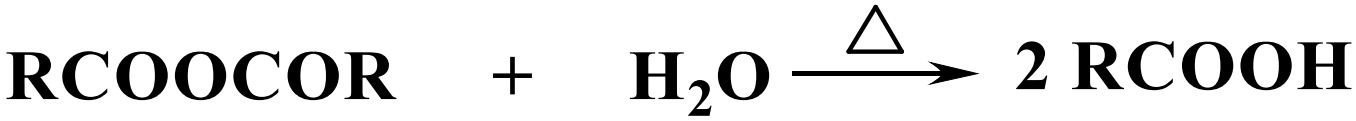


2- From carboxylic acids by dehydration.

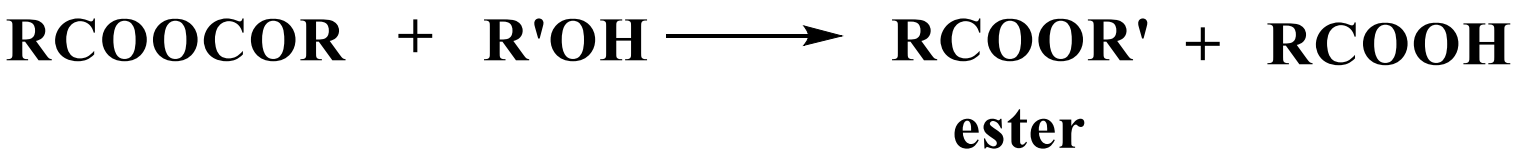


Reactions

1- Hydrolysis to acids.

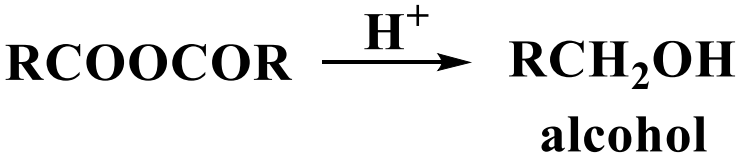


2- With alcohols.



3- With ammonia.

4- Reduction.



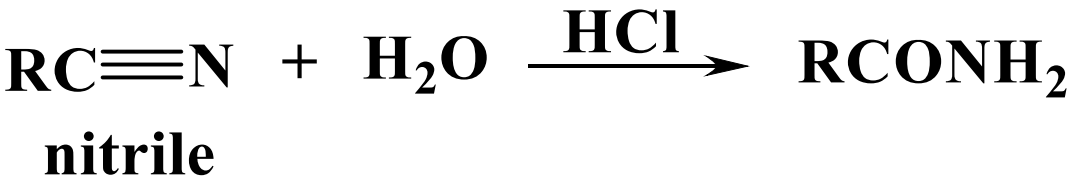
4- Amides

In organic chemistry, an amide also known as an organic amide or a carboxamide, is a compound with the general formula RC(=O)NR′R″, where R, R', and R″ represent organic groups or hydrogen atoms. It can be viewed as a derivative of a carboxylic acid RC(=O)OH with the hydroxyl group –OH replaced by an amine group –NR′R″; or, equivalently, an acyl (alkanoyl) group RC(=O)– joined to an amine group. Common examples of amides are acetamide $H_3C–CONH_2$, benzamide $C_6H_5–CONH_2$, and dimethylformamide $HCON(–CH_3)_2$. Amides are qualified as primary, secondary, and tertiary according to whether the amine subgroup has the form $–NH_2$, –NHR, or –NRR', where R and R' are groups other than hydrogen. The core –C(=O)N= of amides is called the amide group (specifically, carboxamide group).

Synthesis

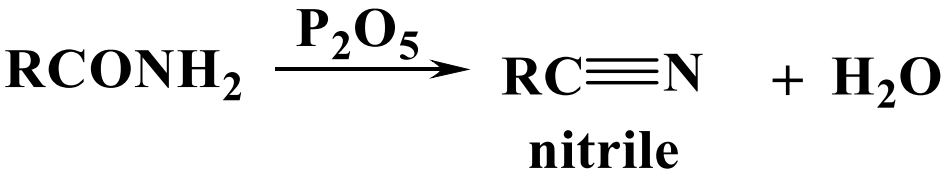
1- From ammonium salts by pyrolysis.

2- Partial hydrolysis of nitriles.

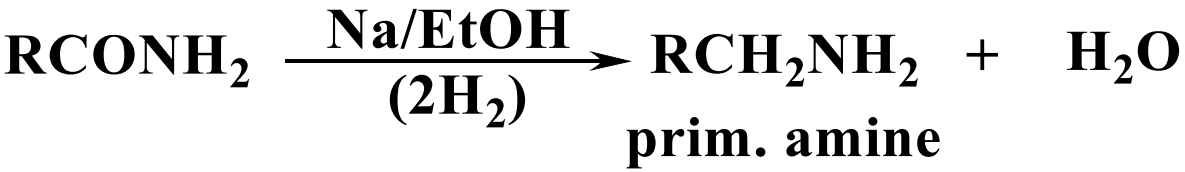


Reactions

1- Dehydration to nitriles.



2- Reduction to primary amines.



Amines

In organic chemistry, amines are compounds and functional groups that contain a basic nitrogen atom with a lone pair. Amines are formally derivatives of ammonia, wherein one or more hydrogen atoms have been replaced by a substituent such as an alkyl or aryl group (these may respectively be called alkylamines and arylamines; amines in which both types of substituent are attached to one nitrogen atom may be called alkylarylamines). Important amines include amino acids, biogenic amines, trimethylamine, and aniline; inorganic derivatives of ammonia are also called amines, such as monochloramine ($NClH_2$). The substituent -NH_2 is called an amino group. Compounds with a nitrogen atom attached to a carbonyl group, thus having the structure R–CO–NR′R″, are called amides and have different chemical properties from amines.

Synthesis

Synthesis of primary, secondary and tertiary amines from alcohols (mixture).

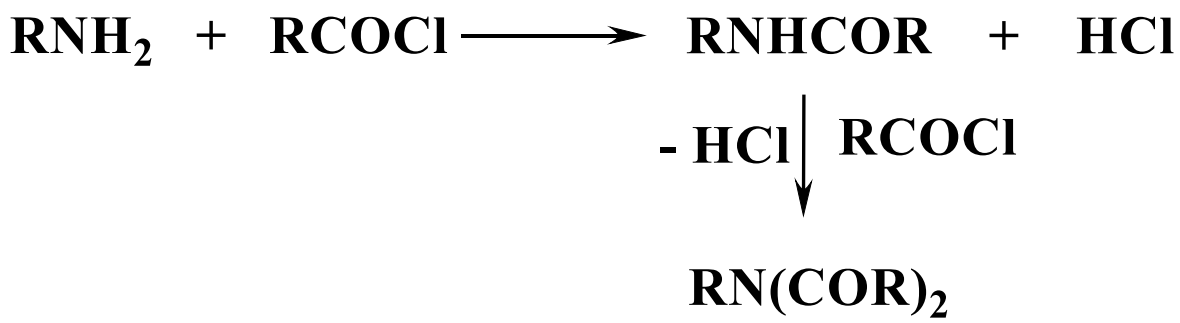
$$ROH + NH_3 \xrightarrow{\text{pressure}} RNH_2 + H_2O$$

$$ROH + RNH_2 \xrightarrow{\text{pressure}} R_2NH + H_2O$$

$$ROH + R_2NH \xrightarrow{\text{pressure}} R_3N + H_2O$$

Reactions

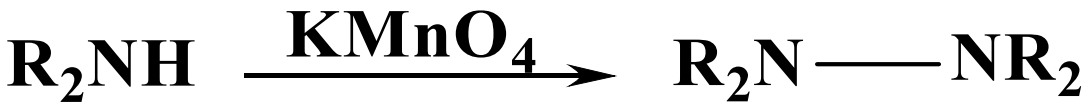
1- Acylation.



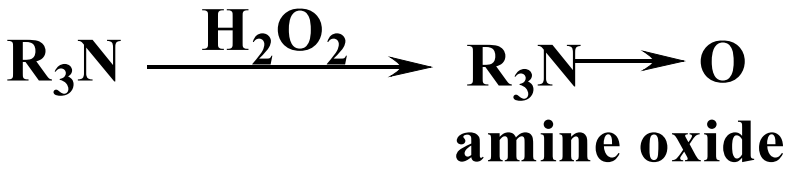
2- Oxidation.

a- Primary amines.

b- Secondary amines.



c- Tertiary amines.



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South Valley University

Faculty of Science

Aromatic Chemistry

For 1st Year Students

Biology and Geology

Faculty of Education

Prepared by

Dr. Entesar A. Hassan

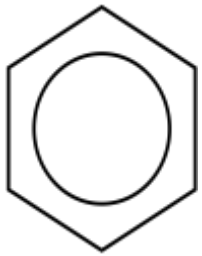
Aromatic compounds

Aromatic compounds, also known as "mono- and polycyclic aromatic hydrocarbons“, are organic compounds containing one or more aromatic rings. The parent member is benzene. Heteroarenes are closely related, since at least one carbon atom of CH group is replaced by one of the heteroatoms oxygen, nitrogen, or sulfur. Examples of non-benzene compounds with aromatic properties are furan, a heterocyclic compound with a five-membered ring that includes a single oxygen atom, and pyridine, a heterocyclic compound,with a six-membered ring containing one nitrogen atom hydrocarbons without an aromatic ring are called aliphatic.

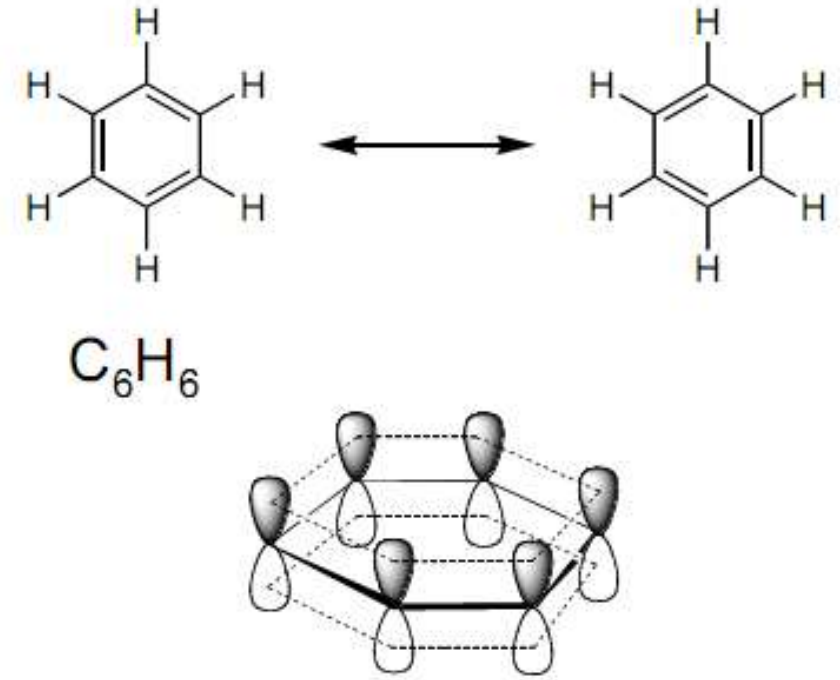
Benzene ring

Benzene, , is the least complex aromatic hydrocarbon, and it was the fisrt first one recognized by August Kekulé named as such.

The nature of its bonding was first in the 19th century. Each carbon atom in the hexagonal cycle has four electrons to share. One goes to the hydrogen atom, and one to each of the two neighboring carbons. This leaves one electron to share with one of the two neighboring carbon atoms, thus creating a double bond with one carbon and leaving a single bond with theother, which is why some representations of the benzene molecule portray it as a hexagon with alternating single and double bonds.



Other depictions of the structure portray the hexagon with a circle inside it, to indicate that the six electrons are floating around in delocalized molecular orbitals the size of the ring itself. This represents the equivalent nature of the six carbon-carbon bonds all of bond order 1.5; the equivalency is explained by resonance forms. The electrons are visualized as floating above and below the ring, with the electromagnetic fields they generate acting to keep the ring flat.



General properties of aromatic hydrocarbons

1- They display aromaticity

2- The carbon-hydrogen ratio is high.

3- They burn with a strong sooty yellow flame because of the high carbon–hydrogen ratio.

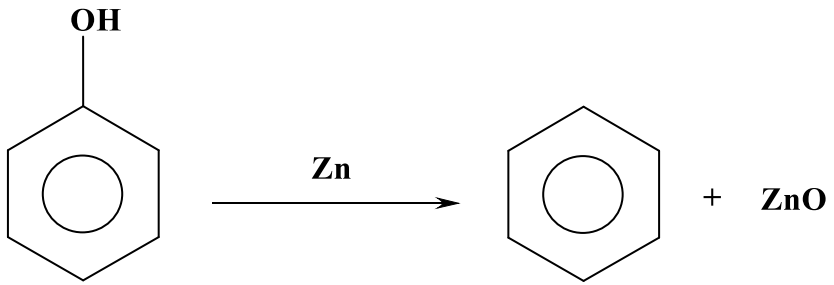
4- They undergo electrophilic substitution reactions and nucleophilic aromatic substitutions.

The circle symbol for aromaticity was introduced by Sir Robert Robinson and his student James Armit in 1925 and popularized starting in 1959 by the Morrison & Boyd textbook on organic chemistry. The proper use of the symbol is debated: some publications use it to *any* cyclic π system, while others use it only for those π systems that obey Hückel's rule. Jensen argues that, in line with Robinson's original proposal, the use of the circle symbol should be limited to monocyclic 6 π-electron systems. In this way the circle symbol for a six-center six-electron bond can be compared to the Y symbol for a three-center two-electron bond.

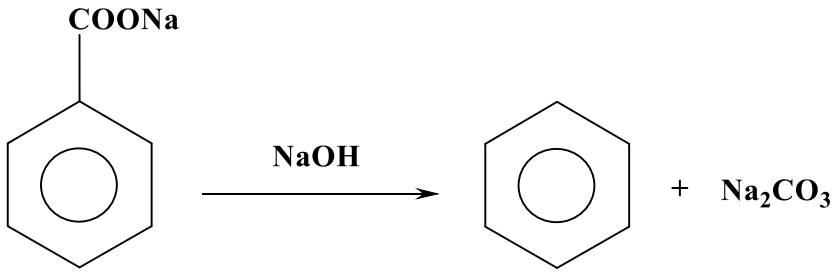
The chemistry of benzene

Preparation

1- by the reaction of phenol with zinc dust

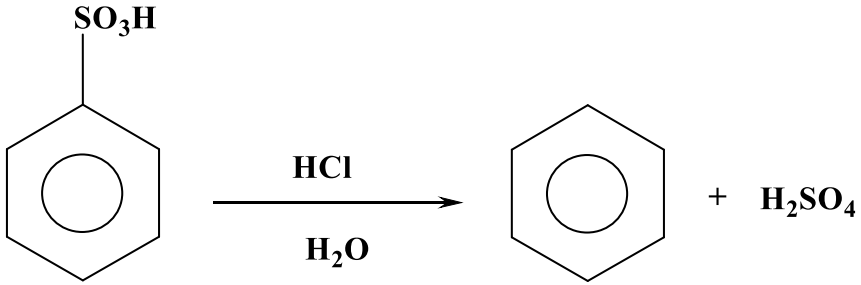


2- by the reaction of sodium benzoate with sodium metal



3- by passing acetylene in a hot red tube at 400-500 ^{o}C

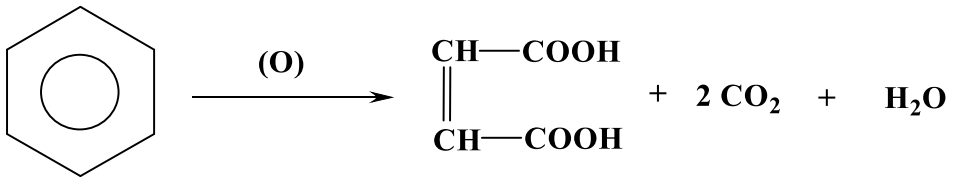
4- by boiling benzene sulfonic acid in HCl/H_2O



The chemical properties of benzene

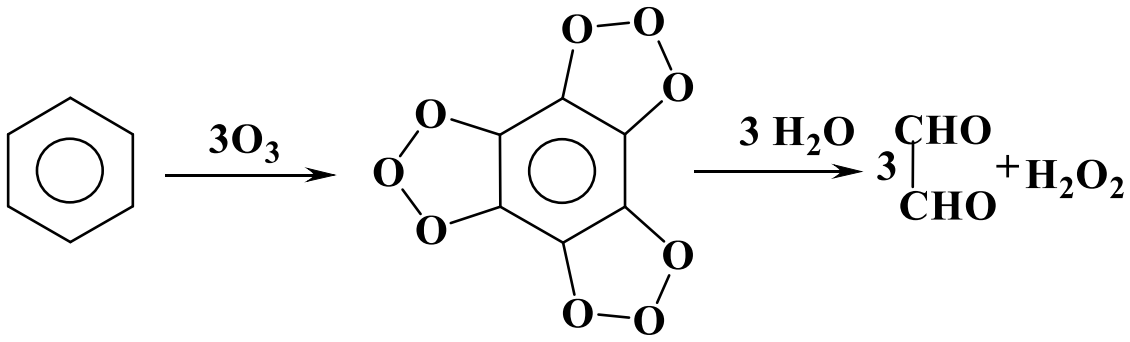
a- chemical reactions lead to destroying of the ring

1- formation of maleic acid by the reaction with O_2



2- ozonolysis

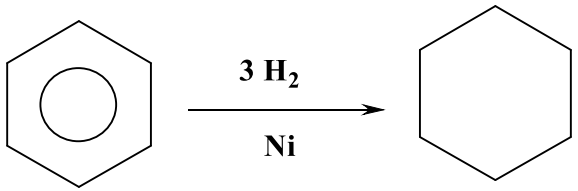
It forms glyoxal by the reaction with ozone



b- addition reactions

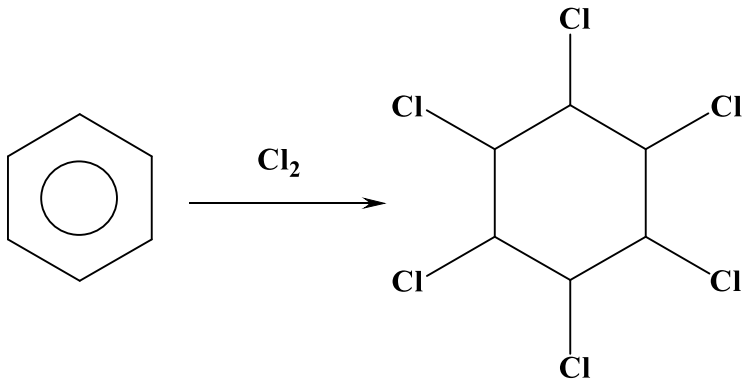
1- addition of hydrogen

Cyclohexane results from the catalytic hydrogenation of benzene in high temperatures.



2- addition of chlorine

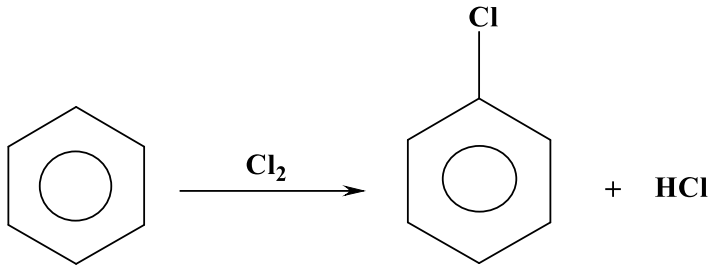
In direct sun light, chlorine reacts with benzene to afford hexachloro cyclohexane



c- substitution reaction

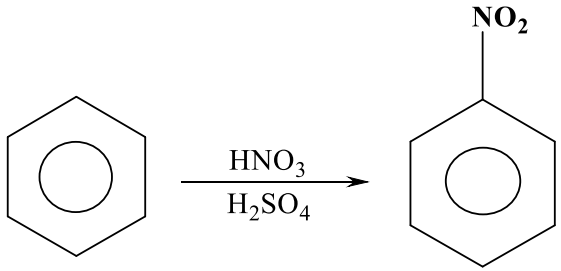
1- halogenation

In absence of the sun light and in the presence of a catalyst, a substitution reaction occurs between chlorine and/or bromine with benzene ring to gather mono- chloro or bromo benzene.



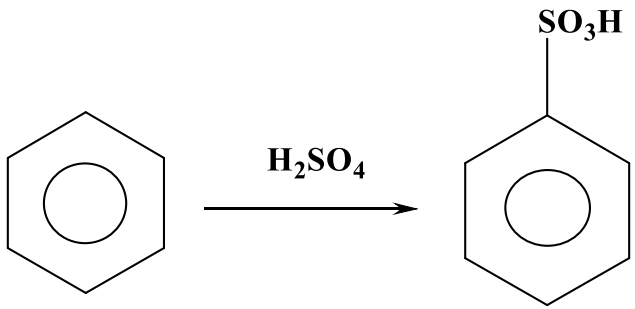
2-nitration reaction

By the reaction of nitric acid with benzene in the presence of sulforic acid to give nitrobenzene.

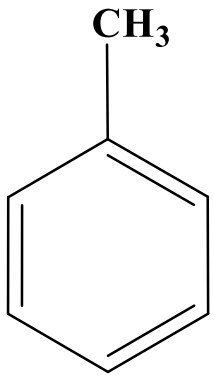


3- sulfonation reaction

By the heating of benzene with conc. sulforic acid to give benzene sulfonic acid.



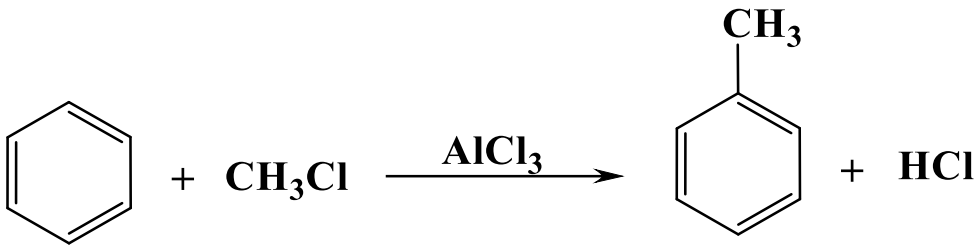
Toluene



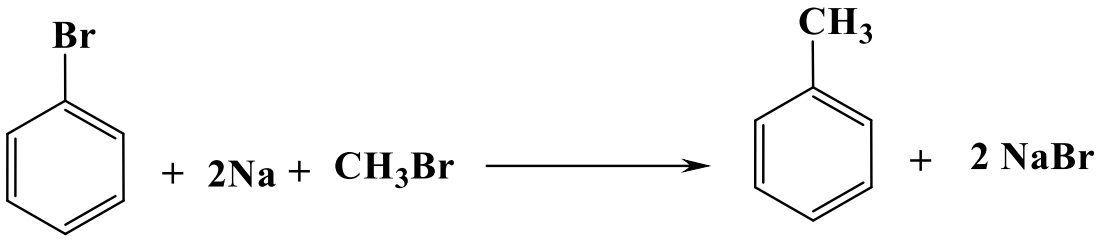
C_7H_8

Preparation

1- Friedel- Craft reaction

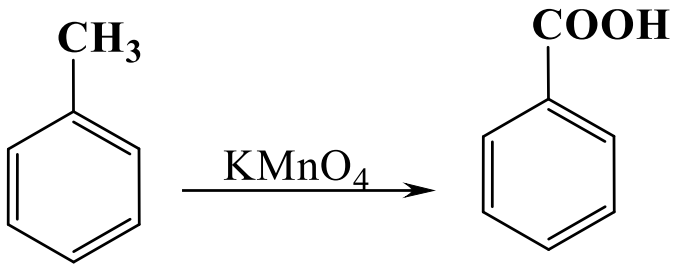


2- Wurtz-Fitting

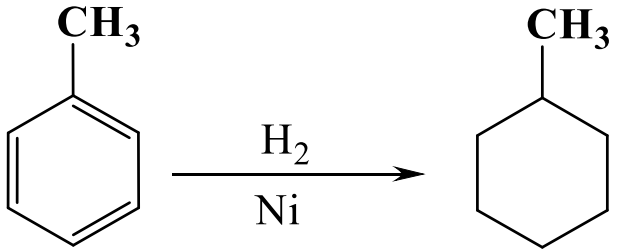


Reactions

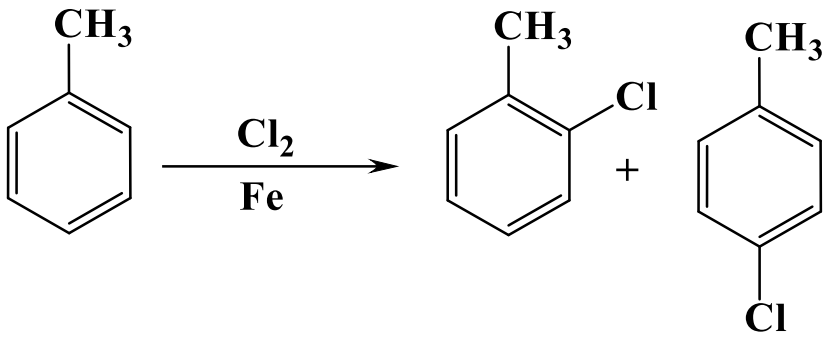
1- oxidation by $KMnO_4$



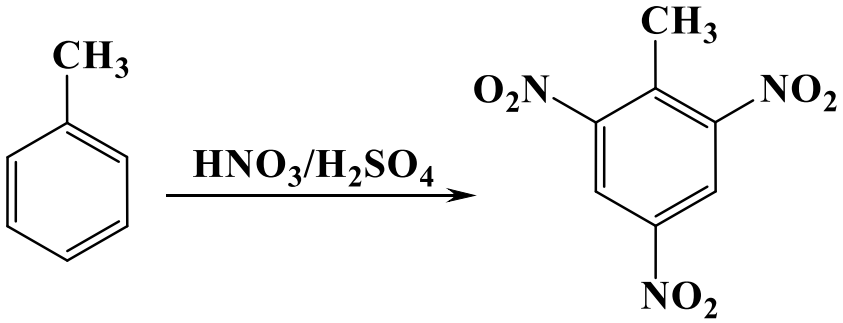
2- reduction



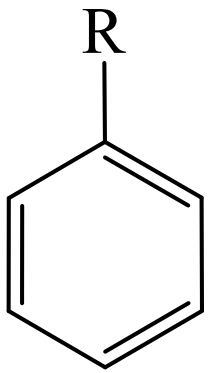
3- halogenation



4- nitration

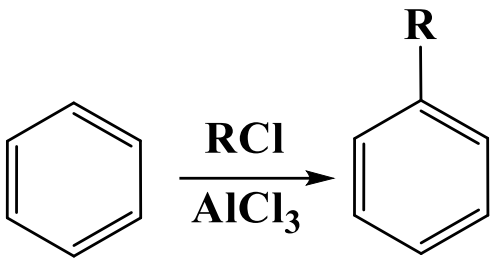


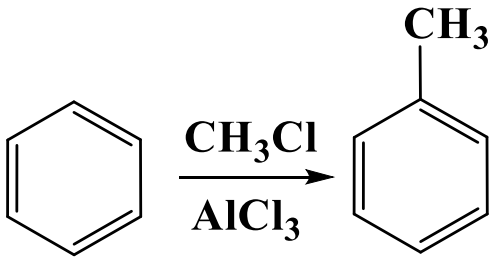
Alkylbenzene



Synthesis of alkylbenzene

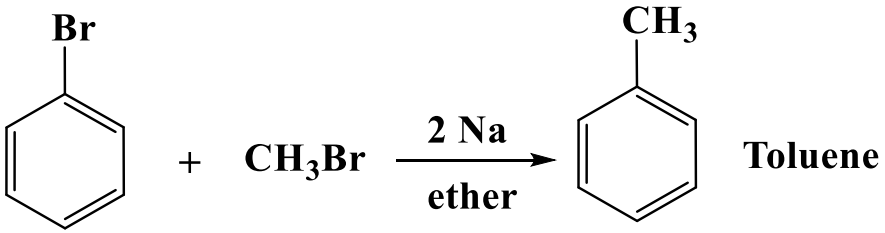
1- Via Friedel-Crafts reaction

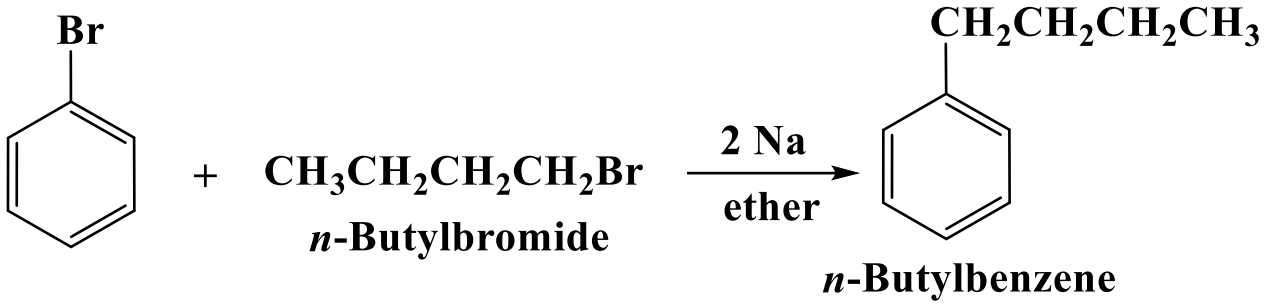




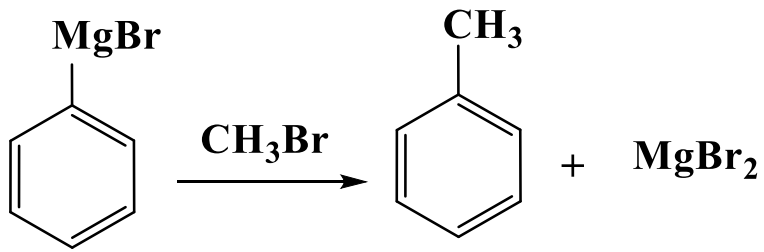
Toluene

2- Wurtz-Fittig reaction



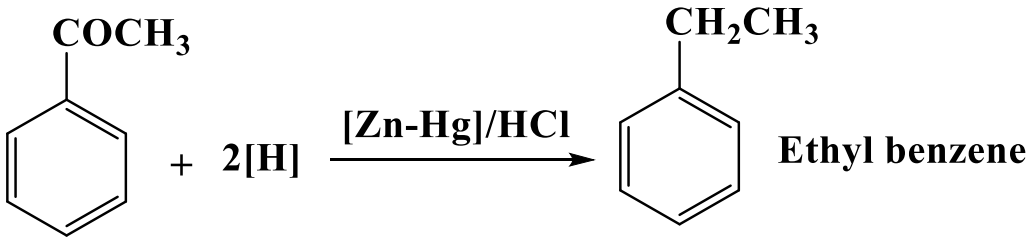


3- From Grignard reagents



Phenyl magnesium bromide
Grignard reagent

4- Via Clemensen reduction

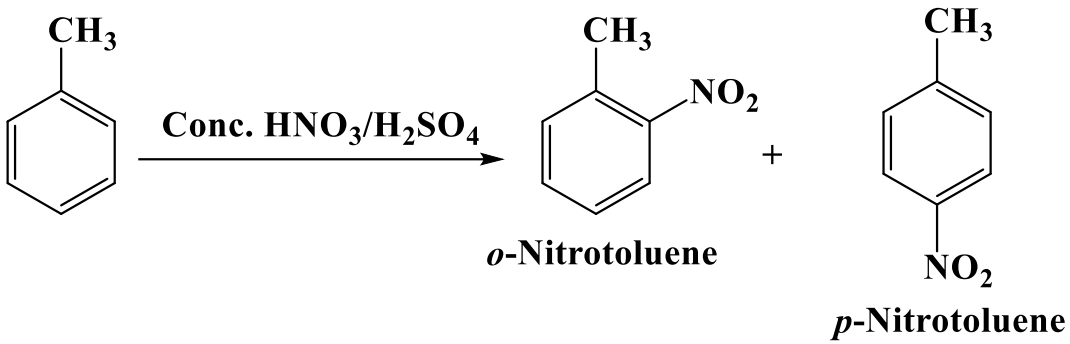


Acetophenone

Reactions of alkylbenzene

A- reaction in benzene ring

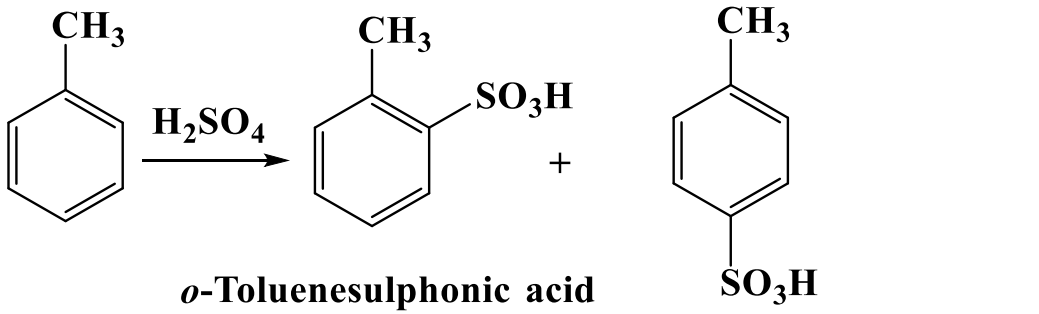
1- Nitration



o-Nitrotoluene

p-Nitrotoluene

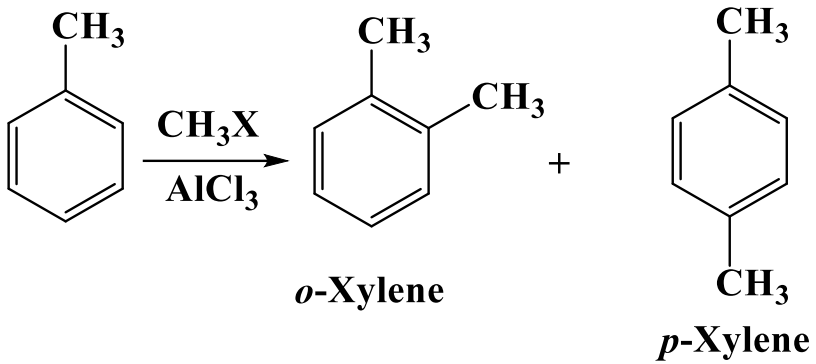
2- Reaction with H_2SO_4



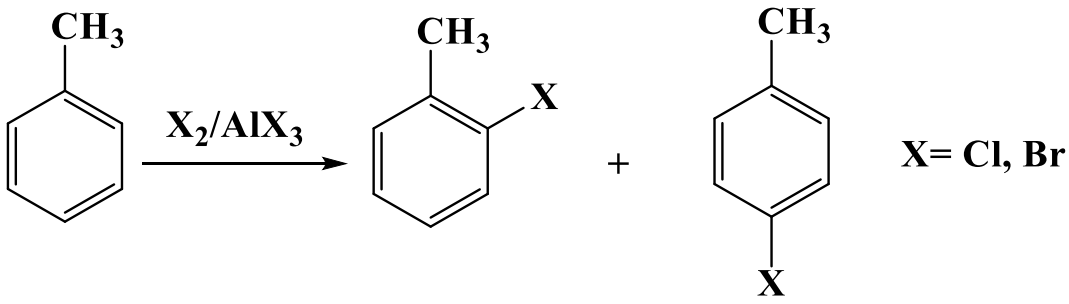
o-Toluenesulphonic acid

p-Toluenesulphonic acid

3- Friedel-Craft alkylation

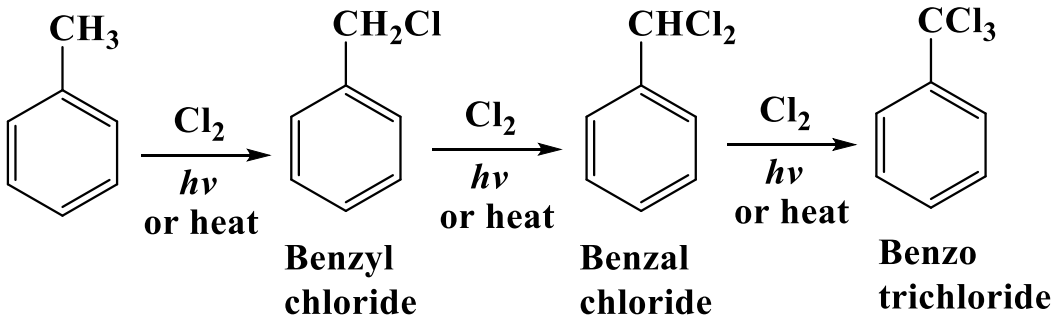


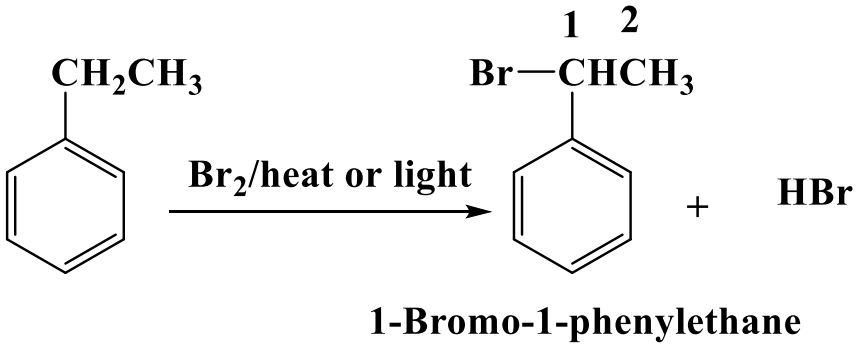
4- Reaction with halogens



B- Reaction of the side chain

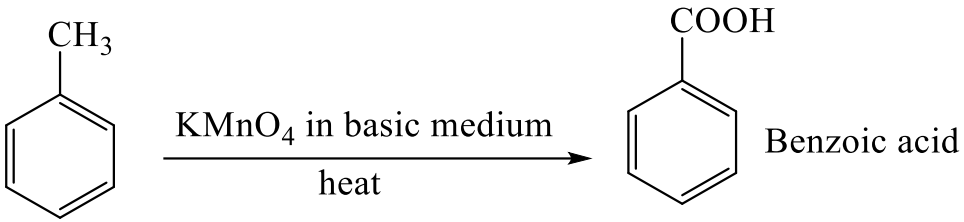
1- Halogenation



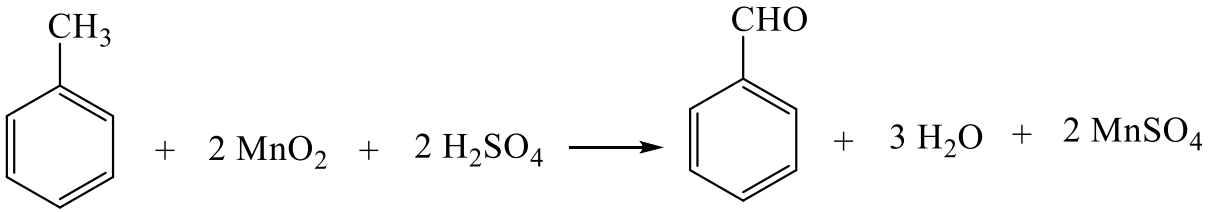


2- Oxidation of the side chain

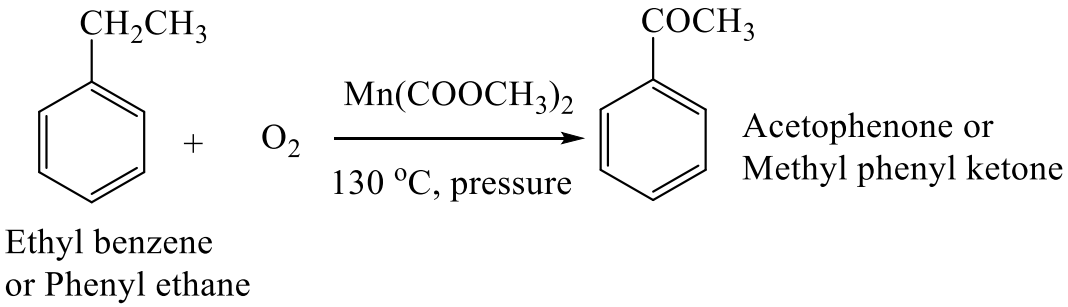
a- Oxidation by $KMnO_4$



b- Oxidation with MnO_2/H_2SO_4



c- Catalytic oxidation by air

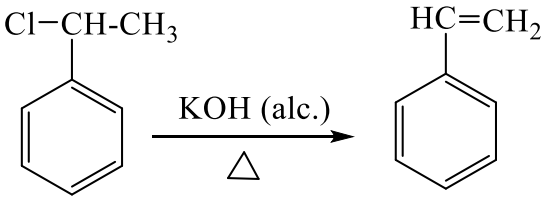


Alkenylbenzene

Alkenylbenzene

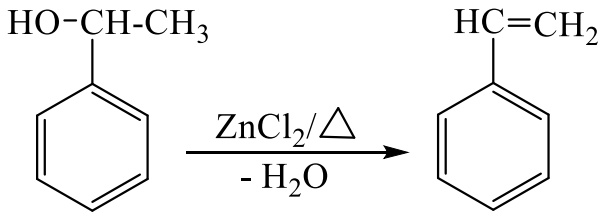
Synthesis

1- From halides



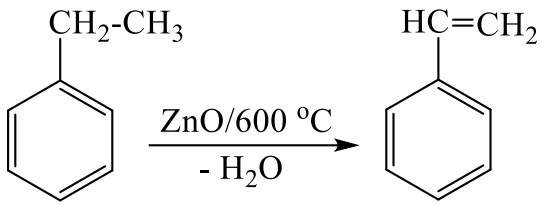
1-Chloro-1-phenylethane Styrene or 1-Phenylethylene

2- From alcohols



1-Phenylethanol Styrene or 1-Phenylethylene

3- From ethylbenzene

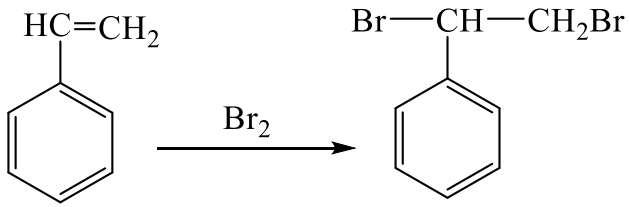


1-Phenylethane
or ethylbenzene

Styrene or 1-Phenylethylene

Reactions

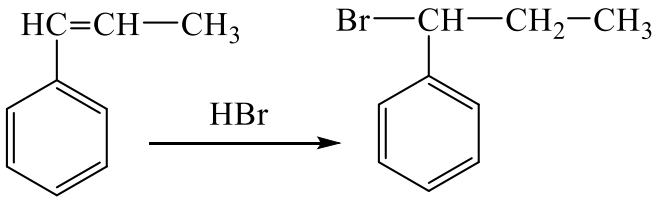
1- Addition of halogens



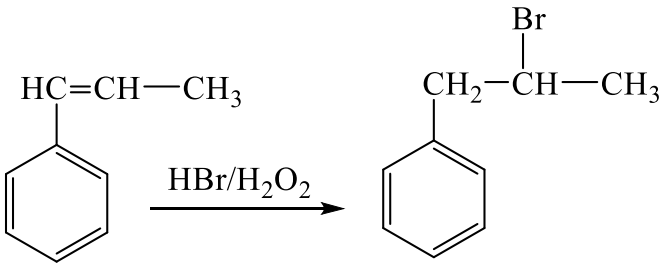
Styrene or 1-Phenylethylene

1-Phenyl-1,2-dibromoethane

2- Addition of halogen acids

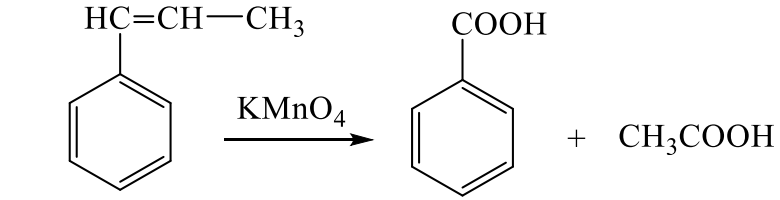


1-Phenylpropene 1-Phenyl-1-brompropane



1-Phenylpropene 1-Phenyl-2-brompropane

3- Oxidation



1-Phenylpropene Benzoic acid

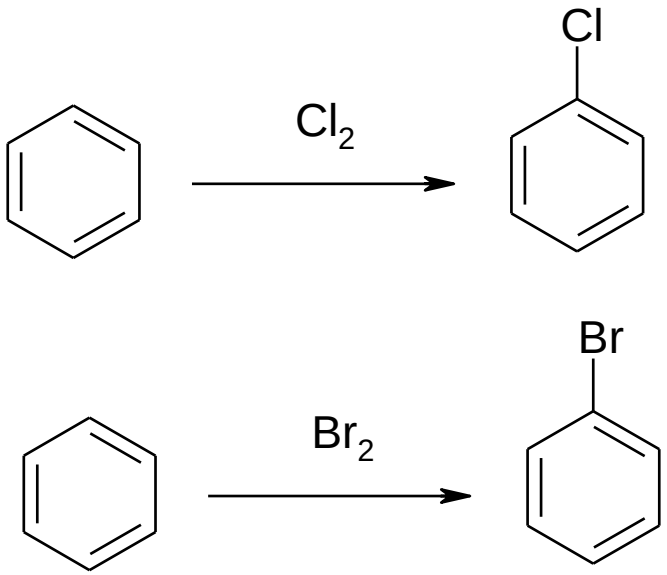
Aryl halides

ArX

Chloro- and bromobenzene

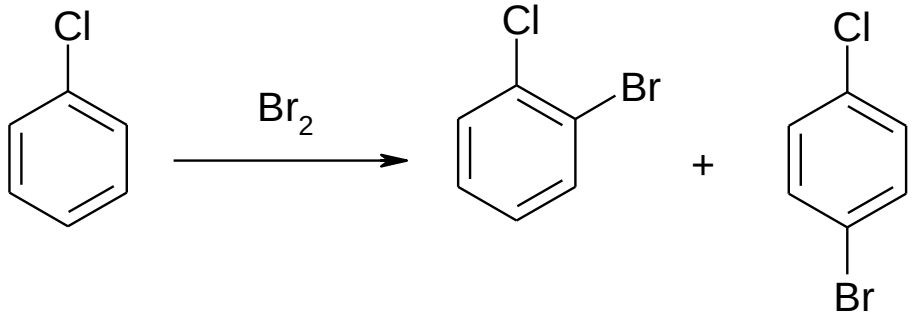
Synthesis

1- from the reaction of benzene with chlorine or bromine

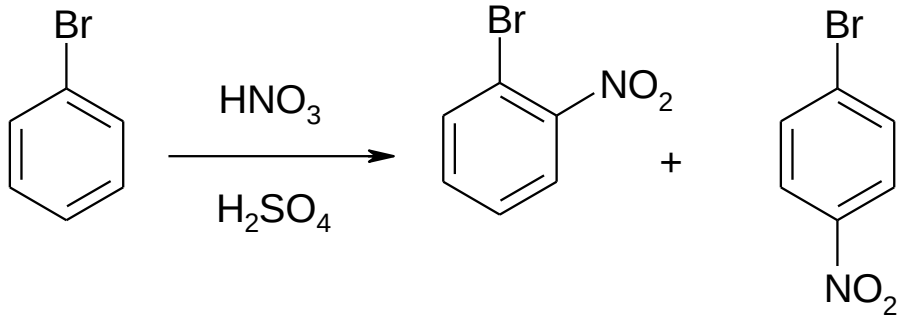


Reactions

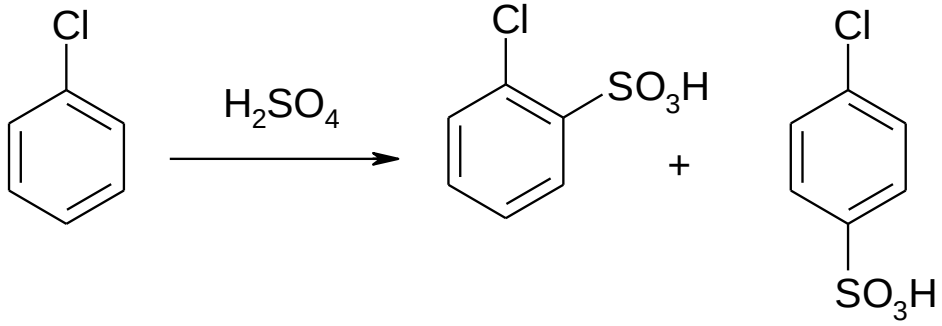
1- halogenation



2- nitration



3- sulfonation

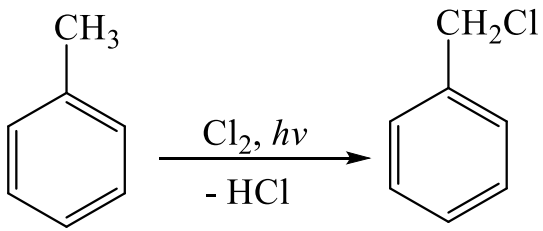


Benzyl halides

Benzyl chloride

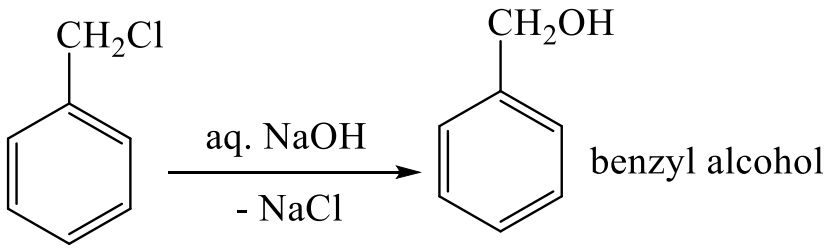
Synthesis

From toluene

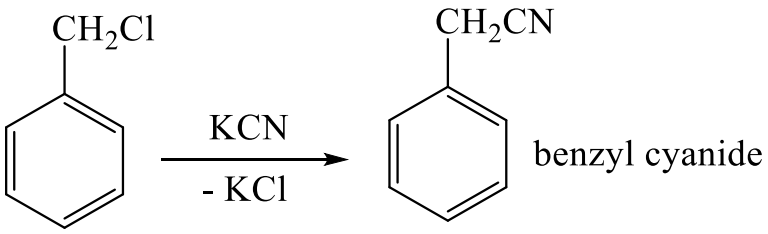


Reactions

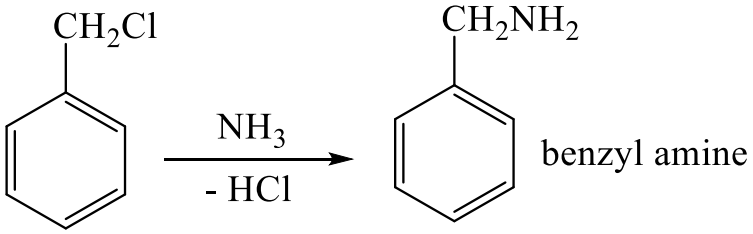
1- With aqueous NaOH



2- With potassium cyanide KCN



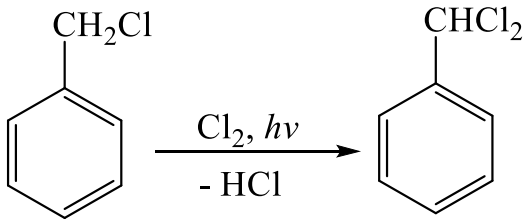
3- With ammonia NH_3



Benzal chloride

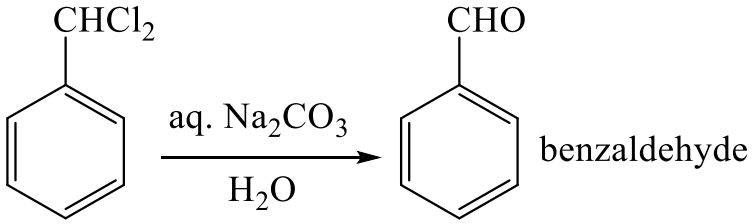
Synthesis

From benzyl chloride



Reactions

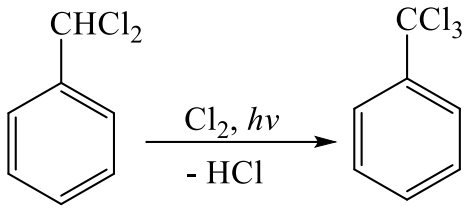
With aq. Na_2CO_3



Benzotrichloride

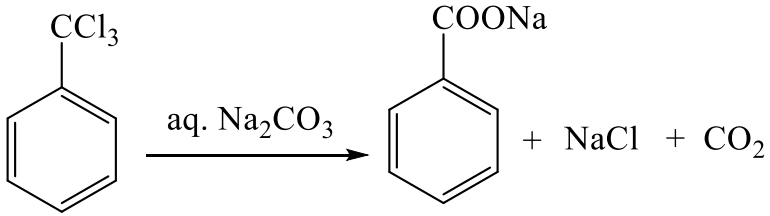
Synthesis

From benzal chloride

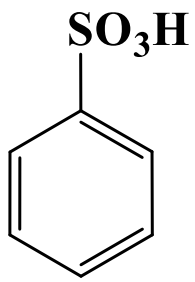


Reactions

With aq. Na_2CO_3

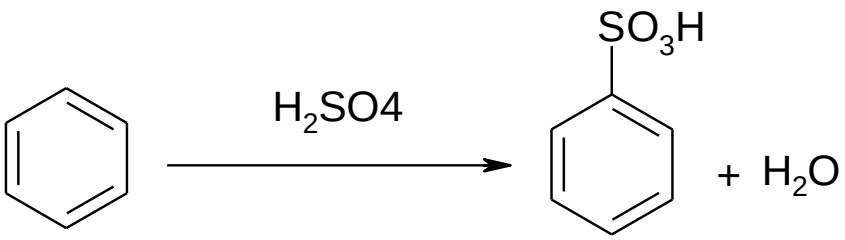


Benzene sulfonic acid



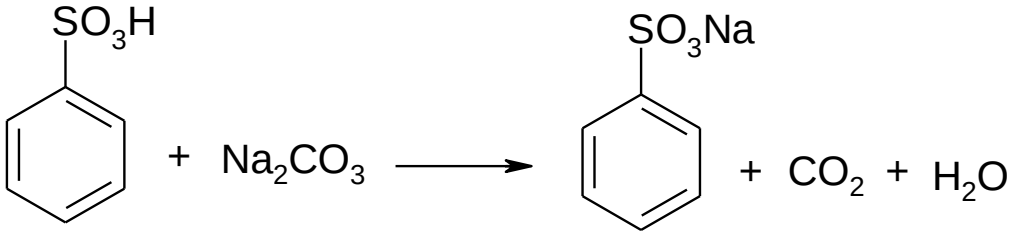
Preparation

1- by the reaction of benzene with sulforic acid

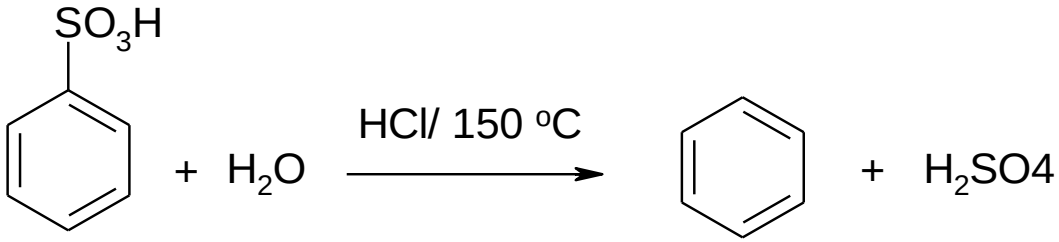


Reactions

1- with sodium carbonate

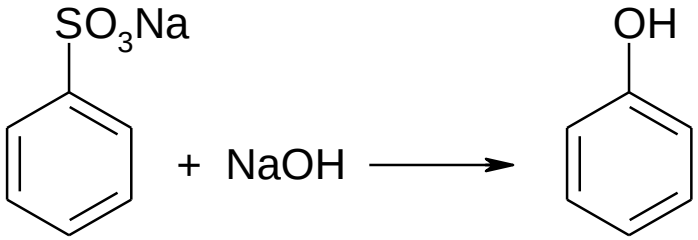


2- elimination of the sulfonic acid group

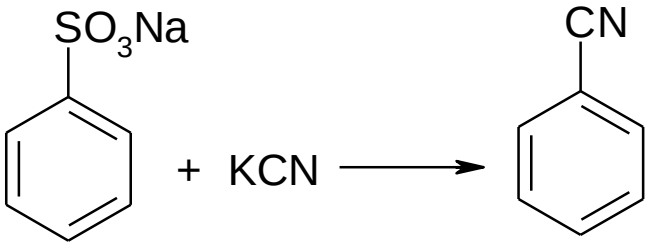


3- replacement of the sulfonic acid group

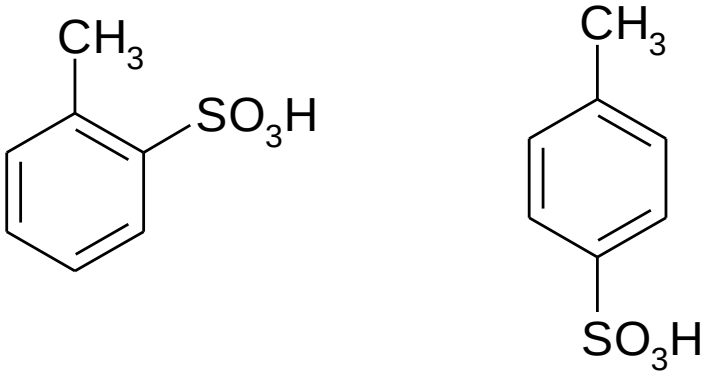
a- with NaoH



b- with KCN



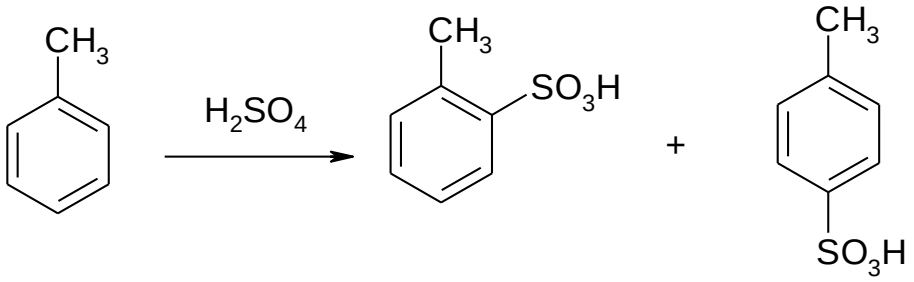
Toluene sulfonic acids



Toluene sulfonic acids

Preparation

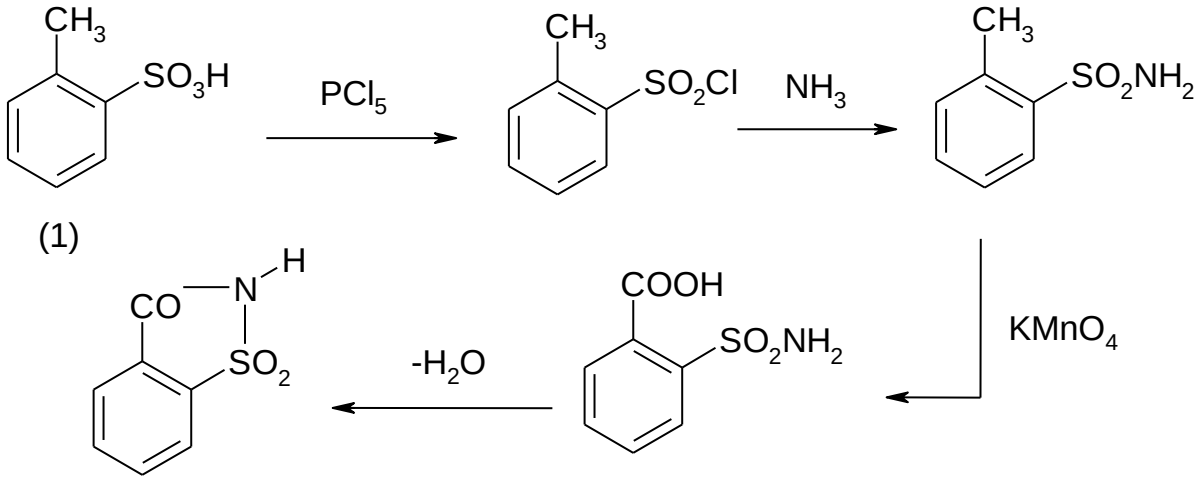
By the reaction of benzene with conc. sulforic acid



(1) (2)

Preparation of saccharin

By the reaction of *o*-toluene sulfonic acid with phosphorus pentafluoride (PCl_5) and subsequently with ammonia (NH_3). On oxidation with $KMnO_4$, and elimination of H_2O, saccharin is obtained. It is used in diabetics treatment. Its sweeten 500 times like sugar.



(1) (3)

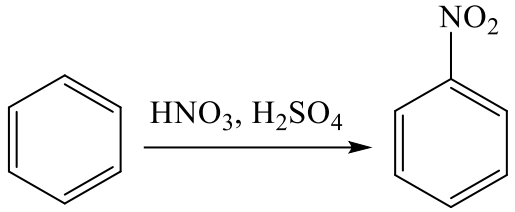
Aromatic nitro compounds

$ArNO_2$

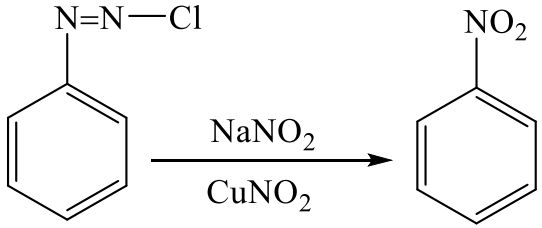
Aromatic nitro compounds

Synthesis

1- From direct nitration of benzene

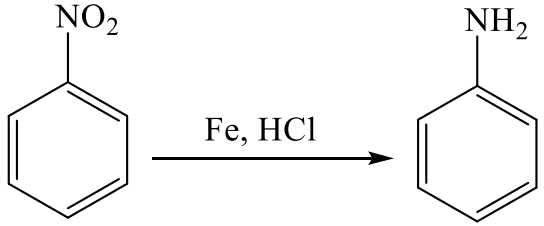


2- From diazonium salt



Reactions

Reduction to aniline



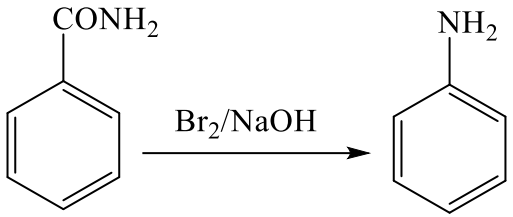
Aromatic amines

$ArNH_2$

Aromatic amines

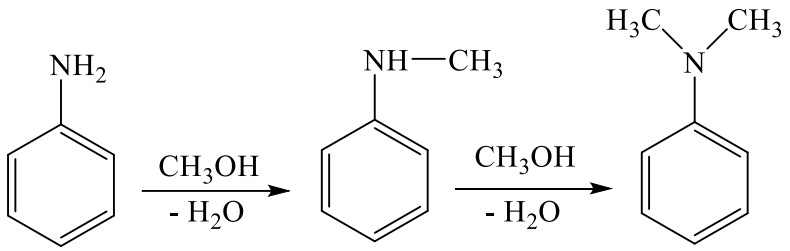
Synthesis

From benzamide



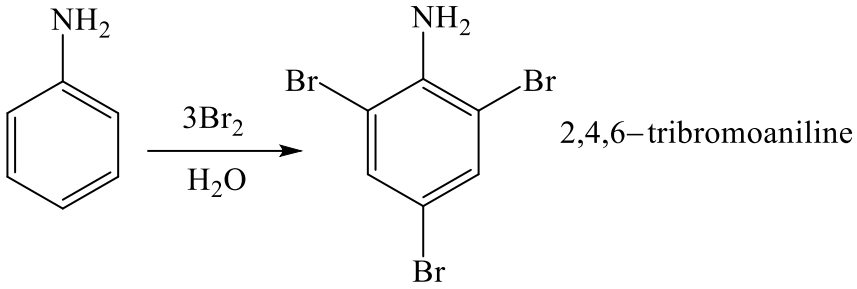
Reactions

1- With methanol



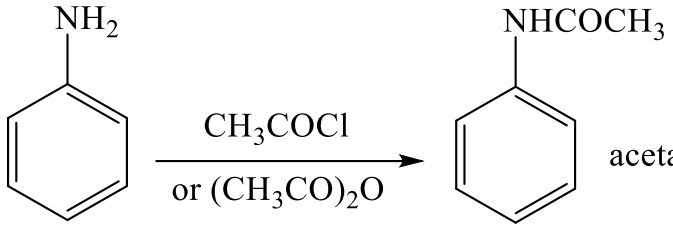
N-methylaniline *N,N*-dimethylaniline

2- Reaction with bromine



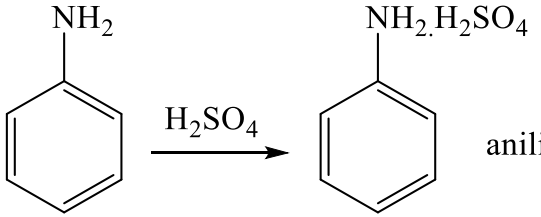
2,4,6−tribromoaniline

3- Reaction with acetyl chloride or acetic anhydride



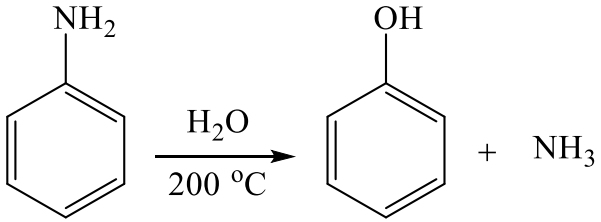
acetanilide

4- Reaction with sulphoric acid



aniline sulphate

5- Boiling with water



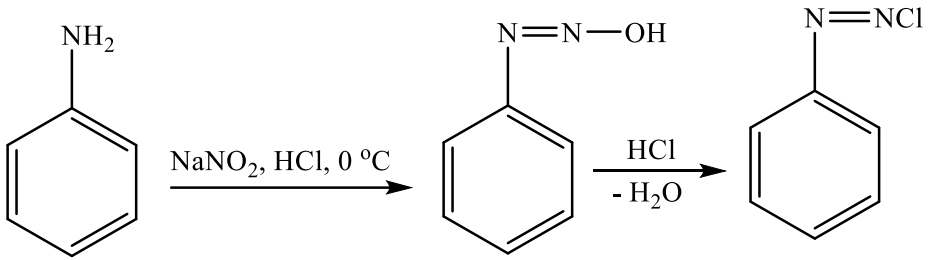
Aromatic diazonium salts

ArN=N-Cl

Aromatic diazonium salts

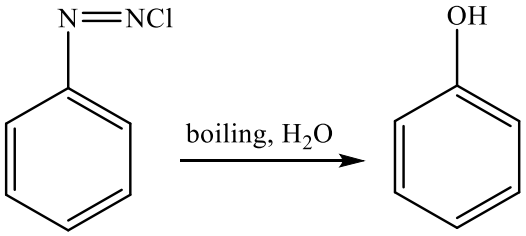
Synthesis

From aniline

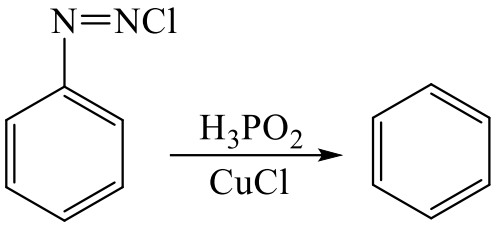


Reactions

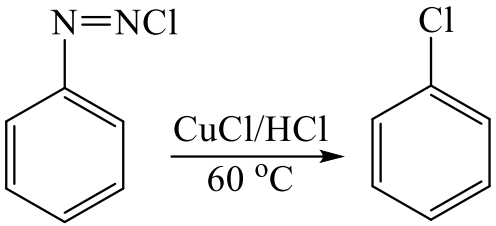
1- Boiling with water



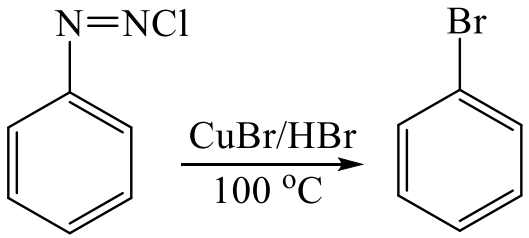
2- With hypophosphorous acid



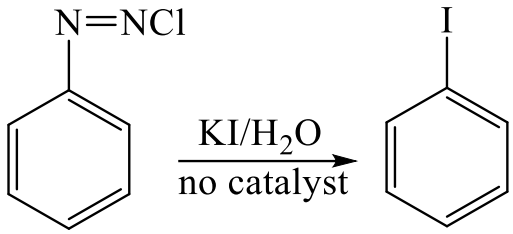
3- With copper chloride



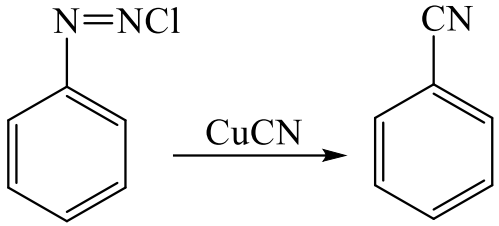
4- With copper bromide



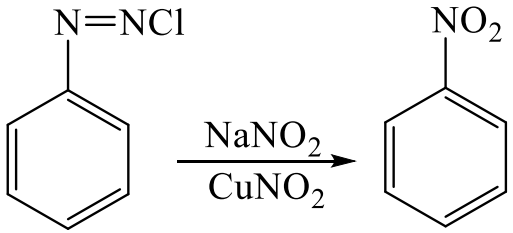
5- With potassium iodide



6- With copper cyanide



7- With sodium nitrite and copper nitrite



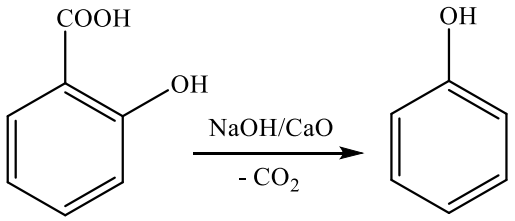
Phenols

ArOH

Phenols

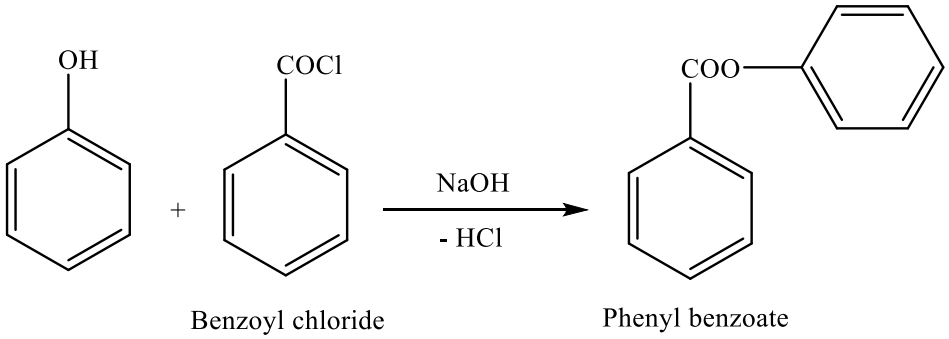
Synthesis

From salicylic acid

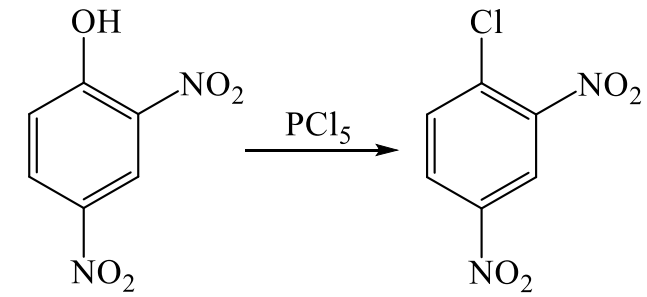


Reactions

1- Ester formation

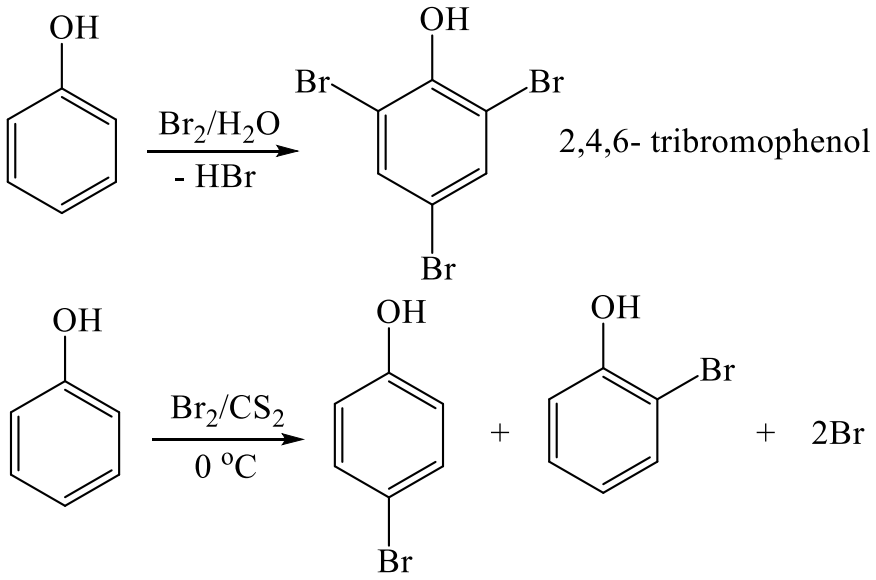


2- With phosphorous pentachloride

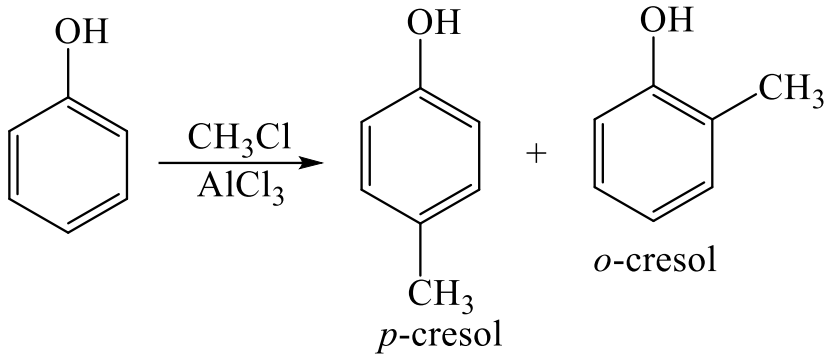


2,4-dinitrophenol

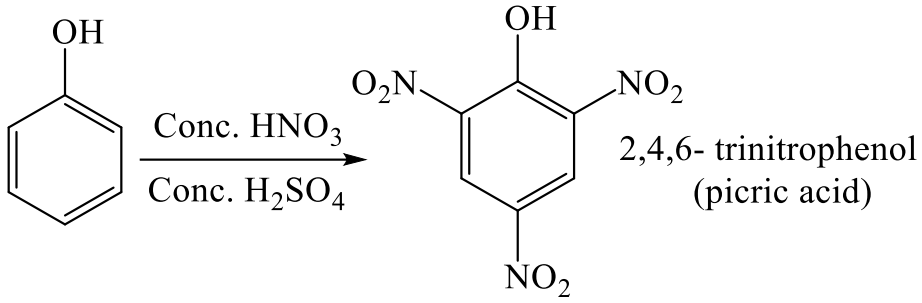
3- With bromine



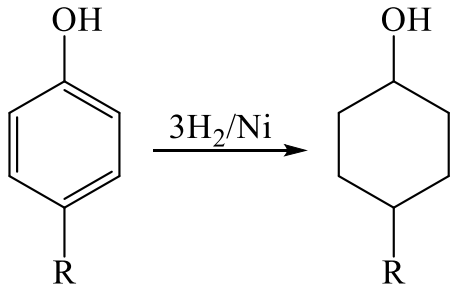
4- Alkylation



5- Nitration



6- Reduction



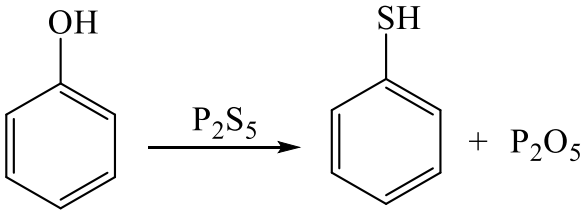
Aryl thiols

ArSH

Aryl thiols

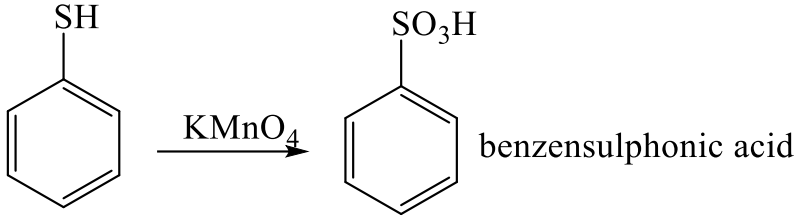
Synthesis

From phenols

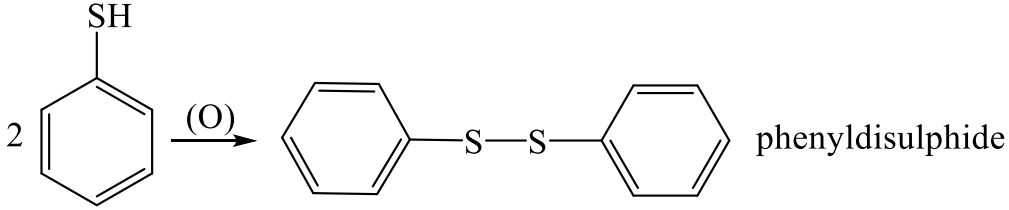


Reactions

1- With mild oxidizing agent



2- With strong $KMnO_4$

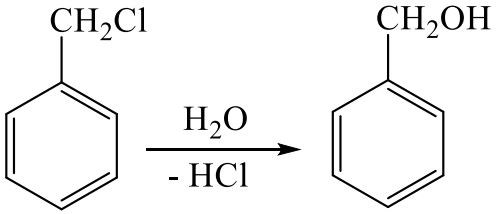


Aromatic alcohols

Aromatic alcohols

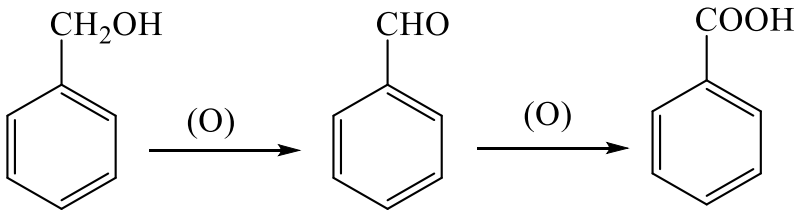
Synthesis

From benzyl chloride

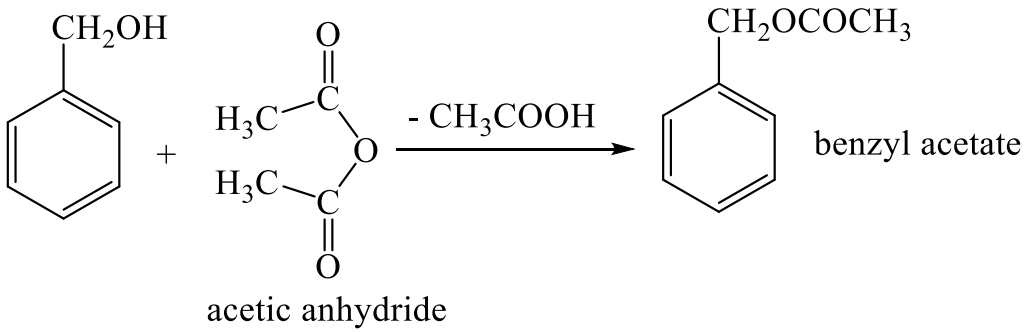


Reactions

1- Oxidation



2- Esterformation



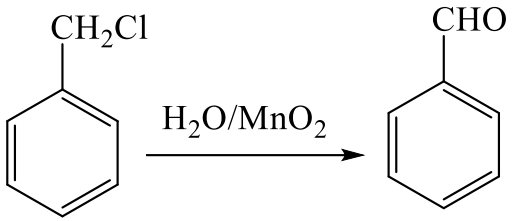
Aromatic aldehydes

ArCHO

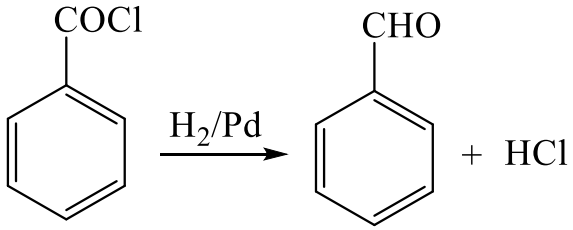
Aromatic aldehydes

Synthesis

1- From benzyl chloride

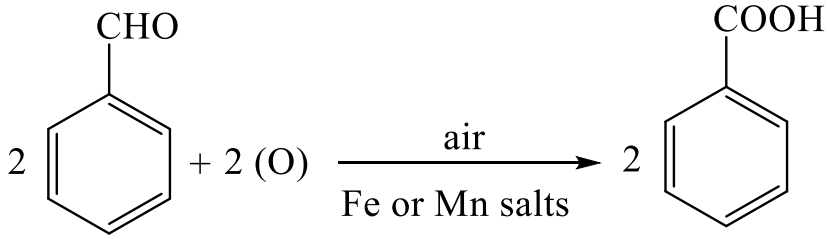


2- From benzoyl chloride

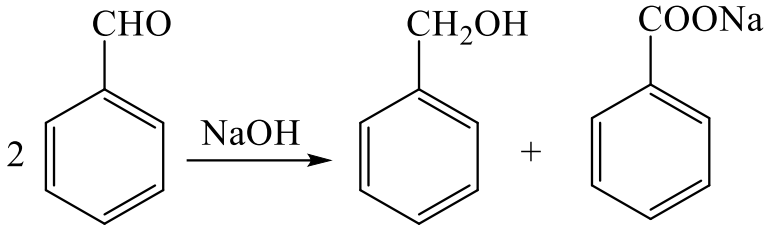


Reactions

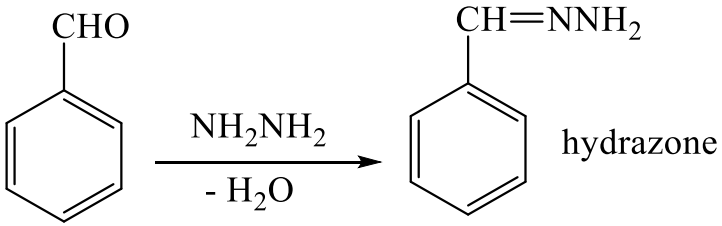
1- Oxidation



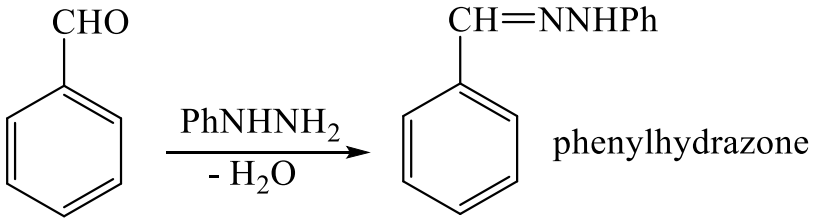
2- Cannizaro reaction



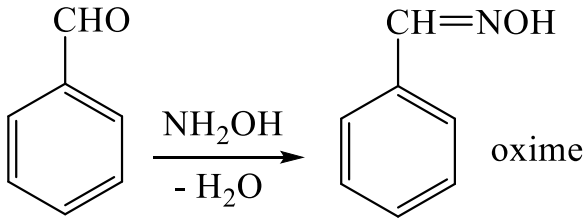
3- With hydrazine



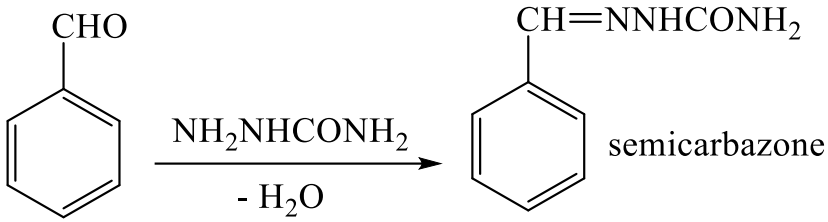
4- With phenylhydrazine



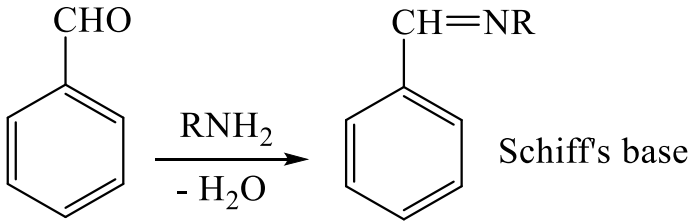
5- With hydroxyl amine



6- With semicarbazide



7- With amines

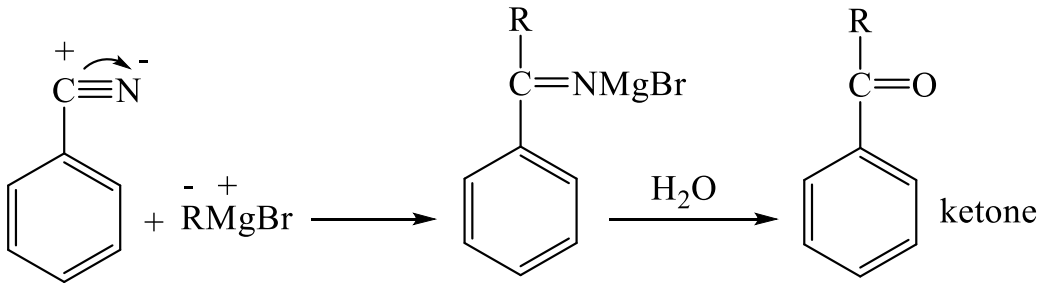


Aromatic ketones

Aromatic ketones

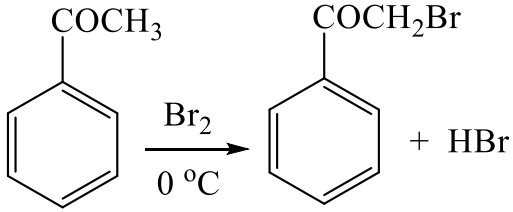
Synthesis

By the reaction of Grignar reagents benzonitrile

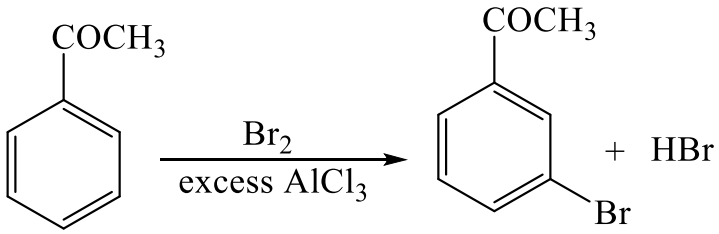


Reactions

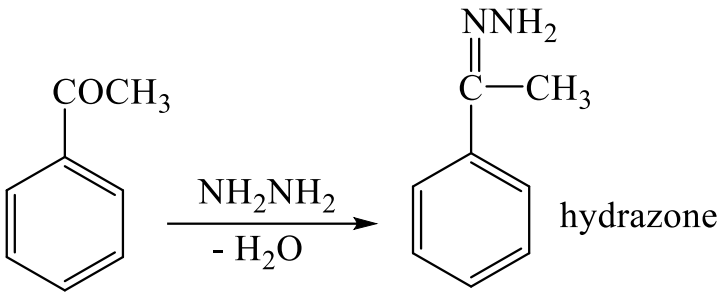
1- With bromine



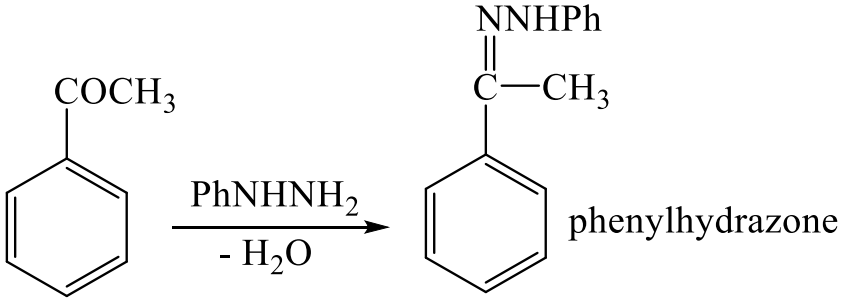
phenacyl bromide



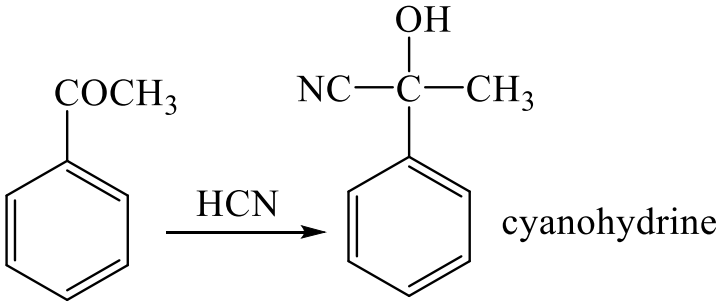
2- With hydrazine



3- With phenyl hydrazine



4- With hydrogen cyanide



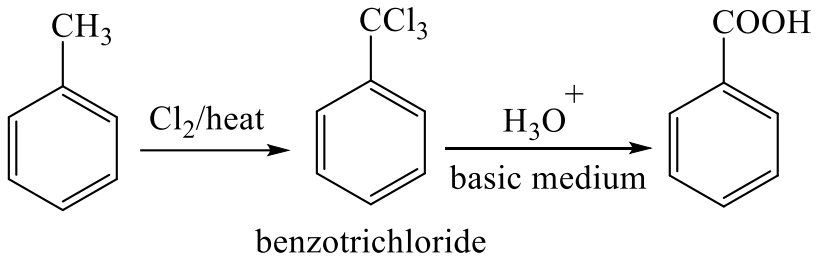
Aromatic carboxylic acids

ArCOOH

Aromatic carboxylic acids

Synthesis

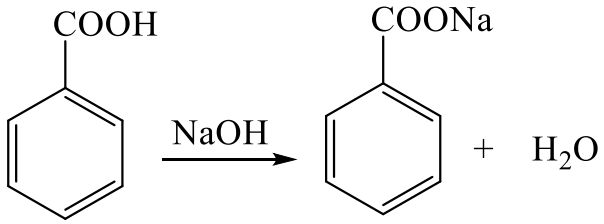
From toluene



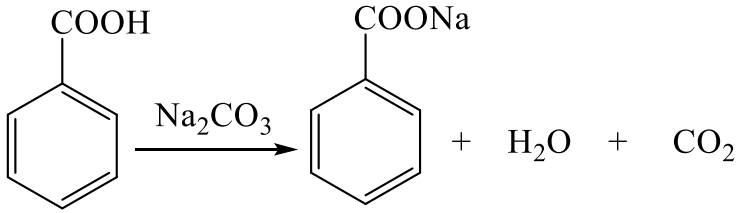
benzotrichloride

Reactions

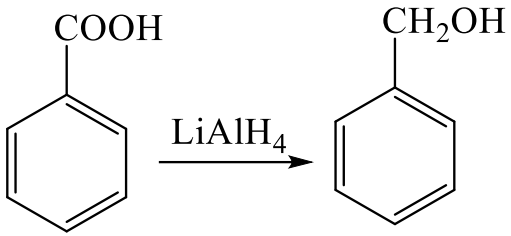
1- With NaOH



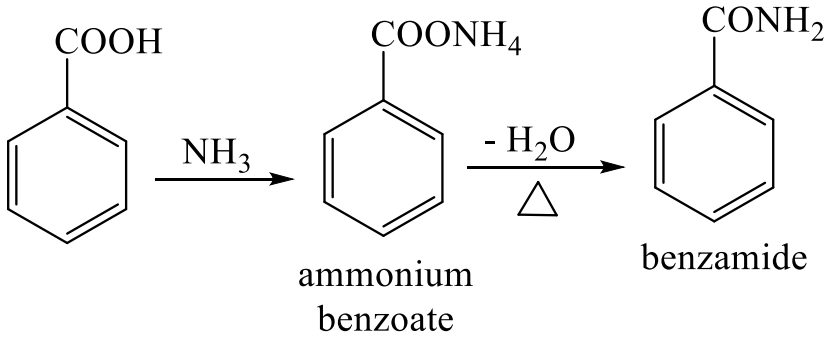
2- With Na_2CO_3



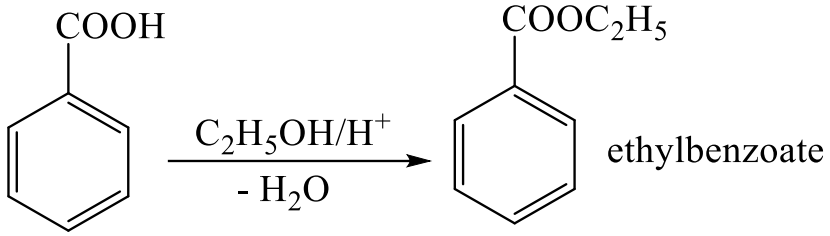
3- With lithium aluminium hydride



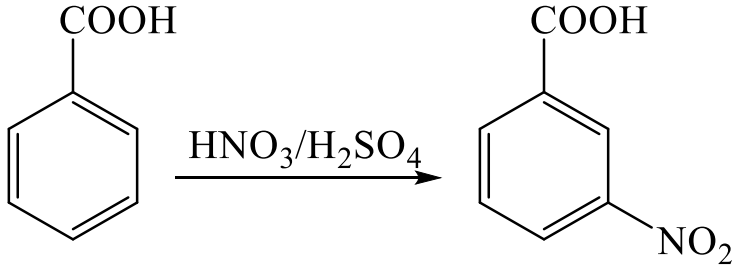
4- With ammonia



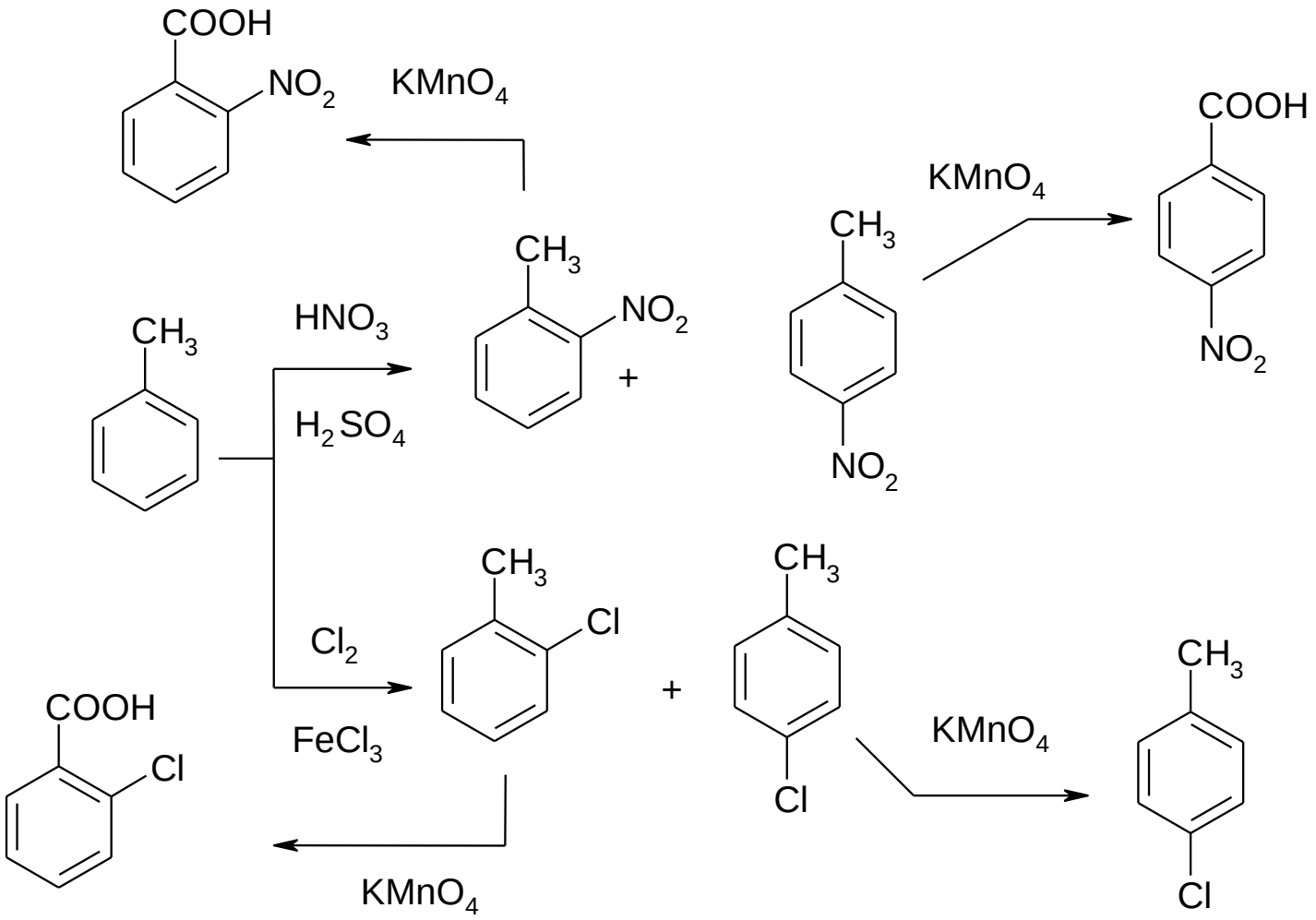
5- Ester formation



6- Nitration



Preparation of *o*- and *p*- derivatives of benzoic acid



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- Armit, James Wilkins; Robinson, Robert (1925). "Polynuclear heterocyclic aromatic types. Part II. Some anhydronium bases". J. Chem. Soc. Trans. 127: 1604–1618. doi:10.1039/CT9252701604.
- Jensen, William B. (April 2009). "The circle symbol for aromaticity" (PDF). J. Chem. Educ. 86 (4): 423–424. Bibcode:2009JChEd..86..423J. doi:10.1021/ed086p423. Archived (PDF) from the original on 2022-10-09.
- Reaction of aromatic compound book
- Text book of organic chemistry