الكيمياء الاروماتية

Aromatic Chemistry

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South Valley University

Faculty of Science

Aromatic Chemistry

For 1st Year Students

Biology and Geology

Faculty of Education

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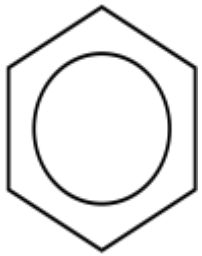
Aromatic compounds

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.

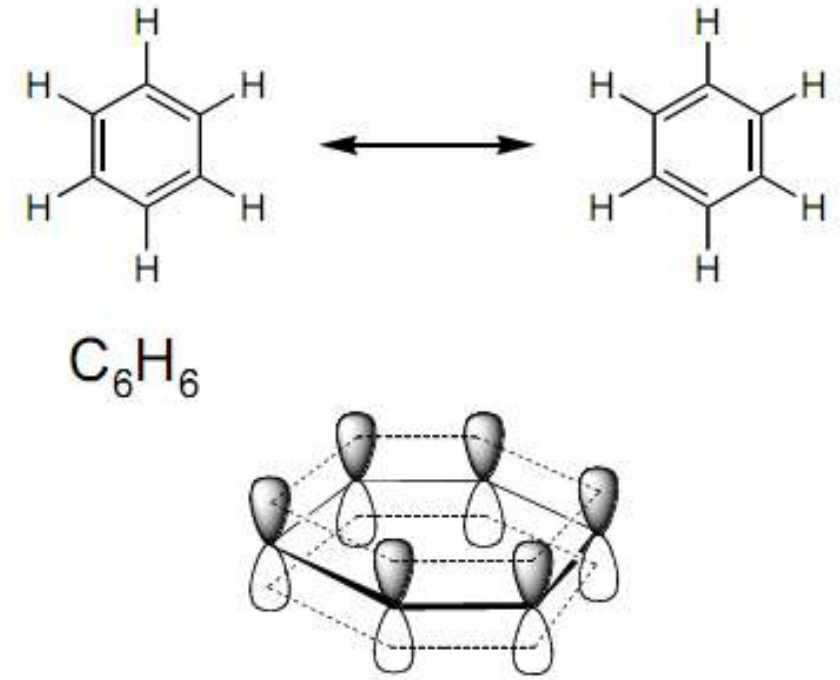
Benzene ring

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.

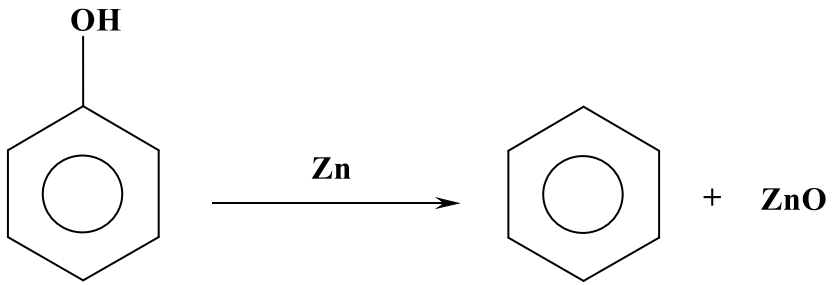
4- They undergo electrophilic substitution reactions and nucleophilic aromatic substitutions.

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.

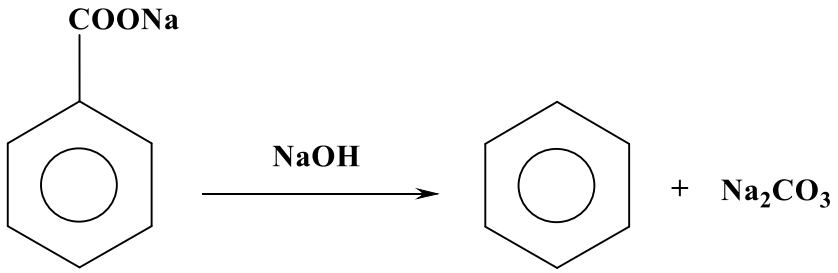
The chemistry of benzene

Preparation

1- by the reaction of phenol with zinc dust

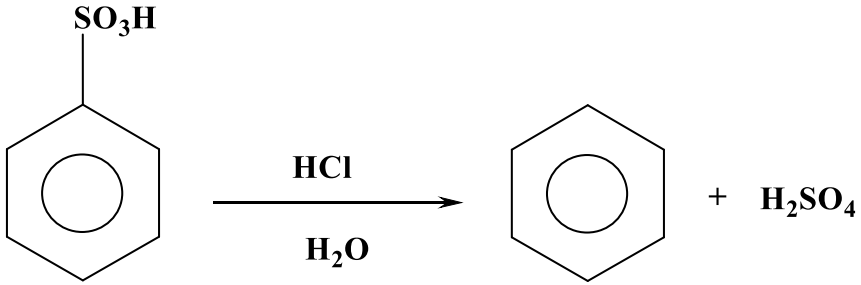


2- by the reaction of sodium benzoate with sodium metal



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

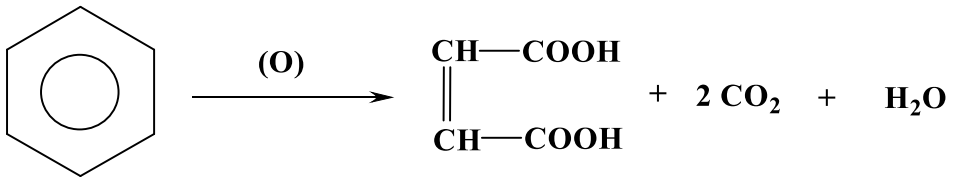
4- by boiling benzene sulfonic acid in HCl/H_2O



The chemical properties of benzene

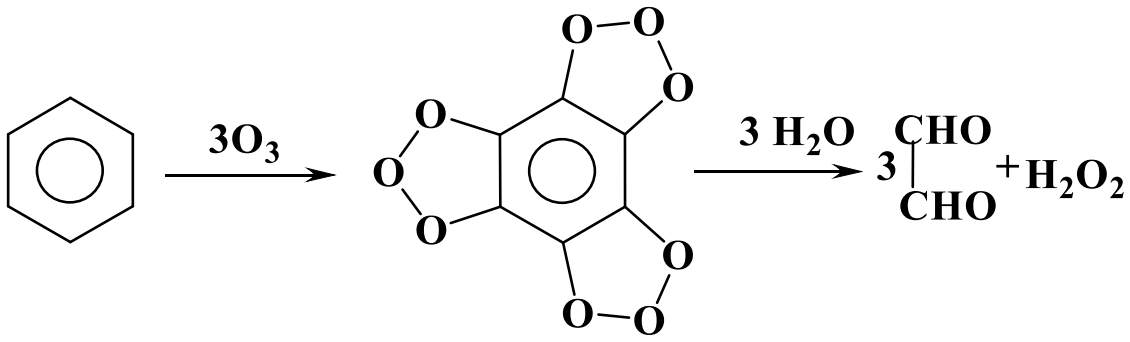
a- chemical reactions lead to destroying of the ring

1- formation of maleic acid by the reaction with O_2



2- ozonolysis

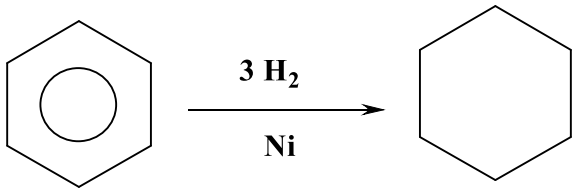
It forms glyoxal by the reaction with ozone



b- addition reactions

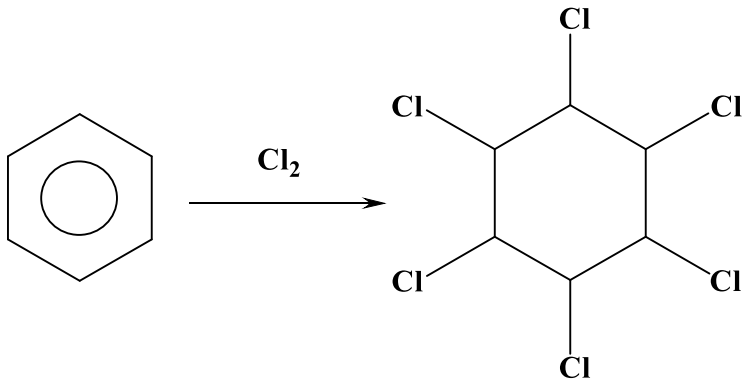
1- addition of hydrogen

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



2- addition of chlorine

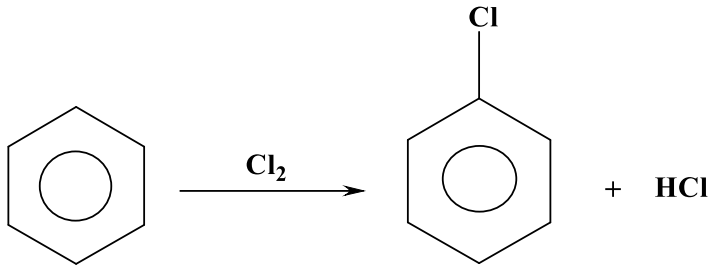
In direct sun light, chlorine reacts with benzene to afford hexachloro cyclohexane



c- substitution reaction

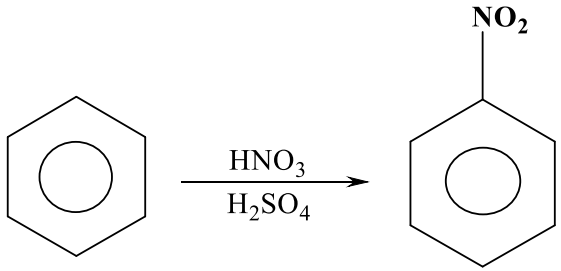
1- halogenation

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.



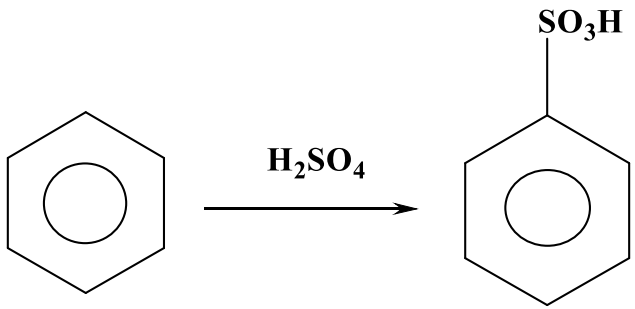
2-nitration reaction

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

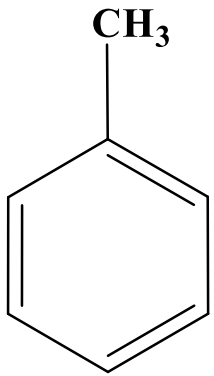


3- sulfonation reaction

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



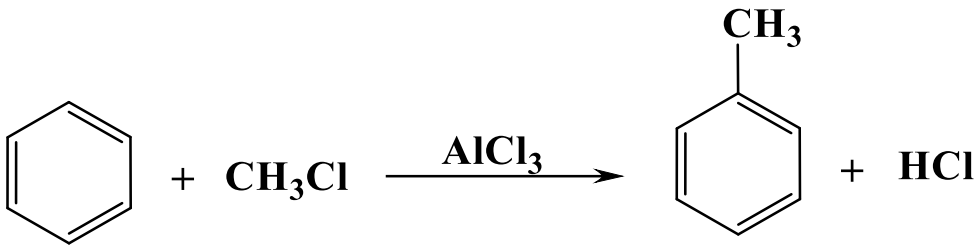
Toluene



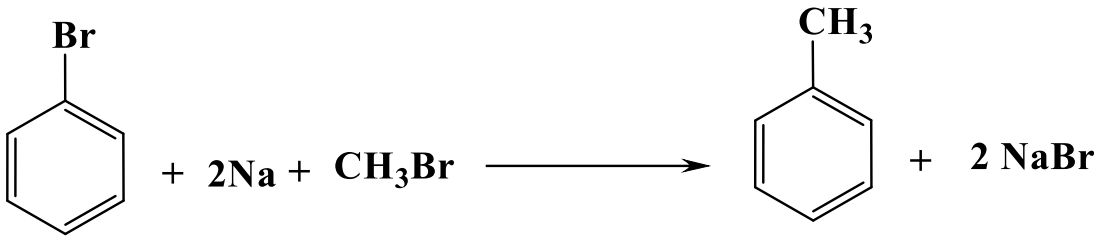
C_7H_8

Preparation

1- Friedel- Craft reaction

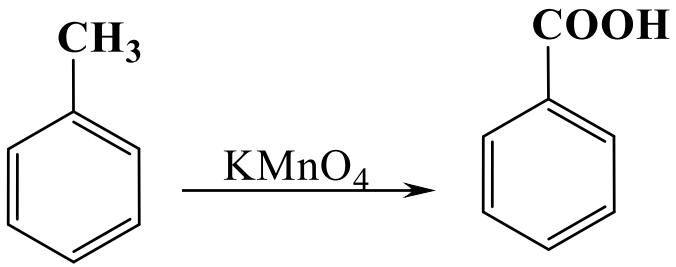


2- Wurtz-Fitting

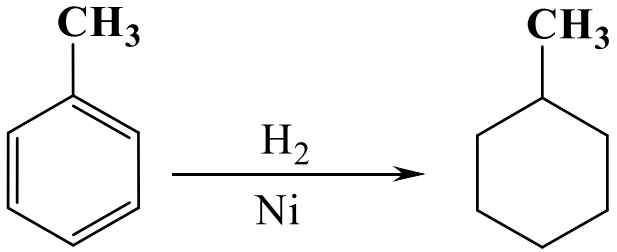


Reactions

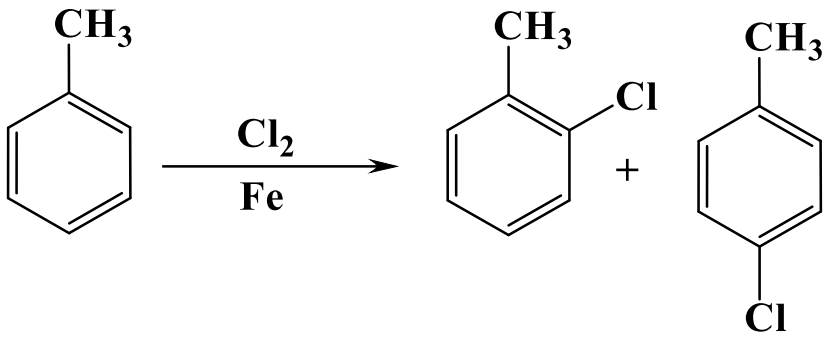
1- oxidation by $KMnO_4$



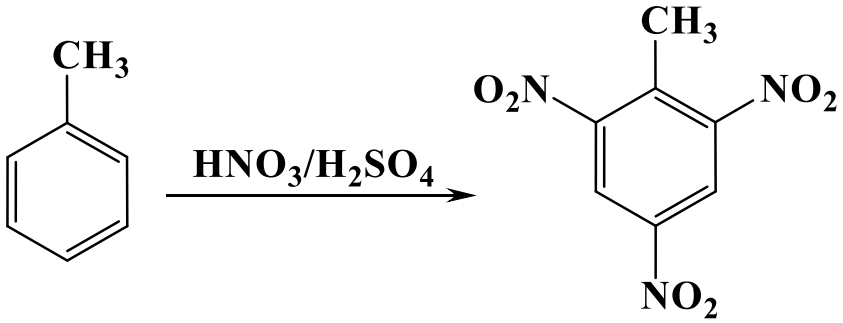
2- reduction



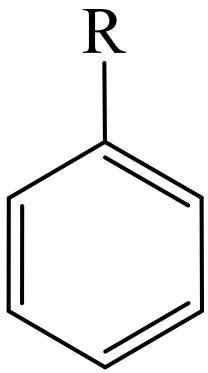
3- halogenation



4- nitration

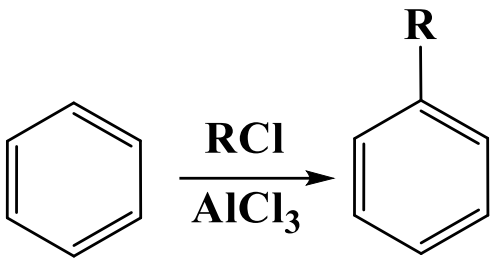


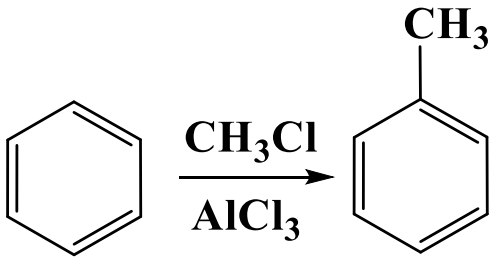
Alkylbenzene



Synthesis of alkylbenzene

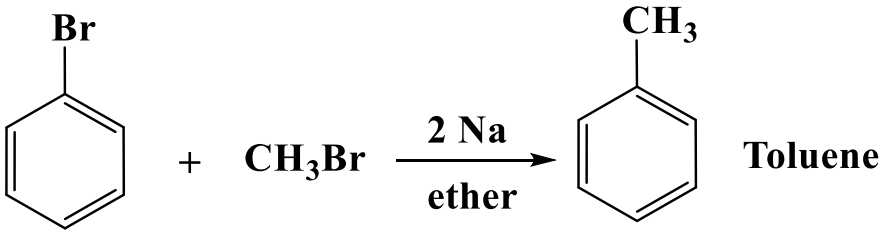
1- Via Friedel-Crafts reaction

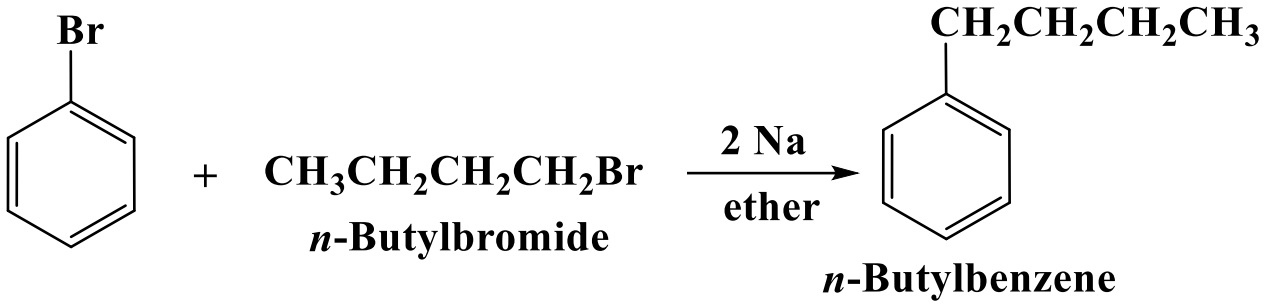




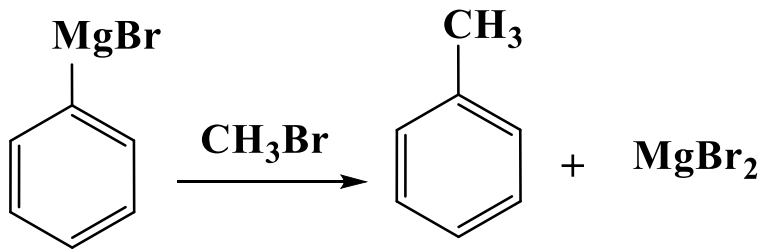
Toluene

2- Wurtz-Fittig reaction



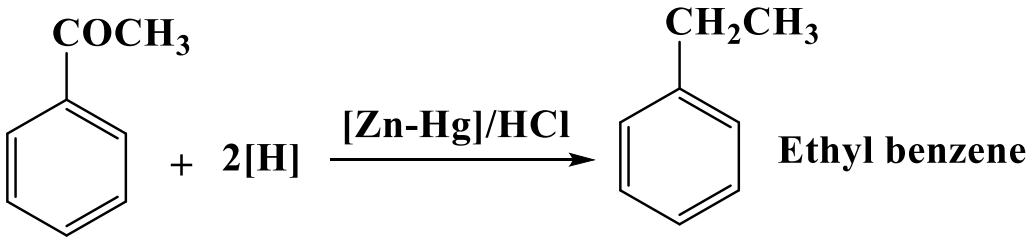


3- From Grignard reagents



Phenyl magnesium bromide
Grignard reagent

4- Via Clemensen reduction

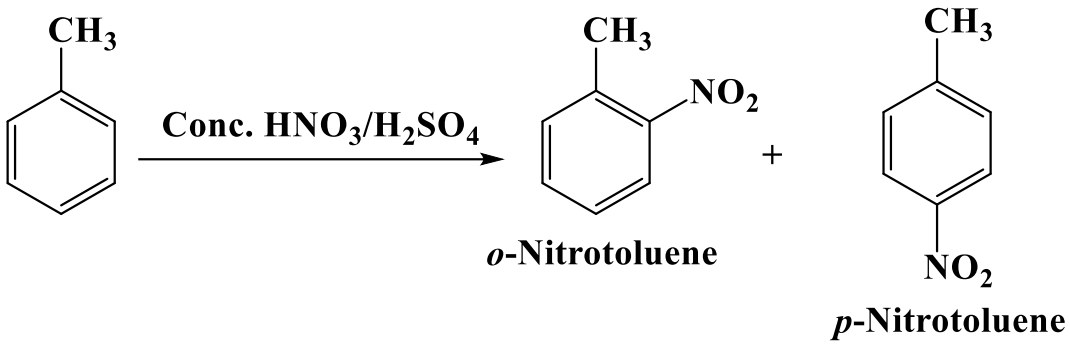


Acetophenone

Reactions of alkylbenzene

A- reaction in benzene ring

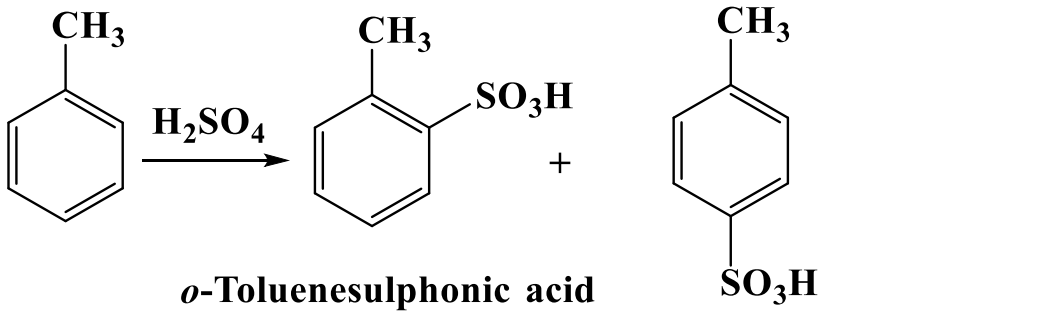
1- Nitration



o-Nitrotoluene

p-Nitrotoluene

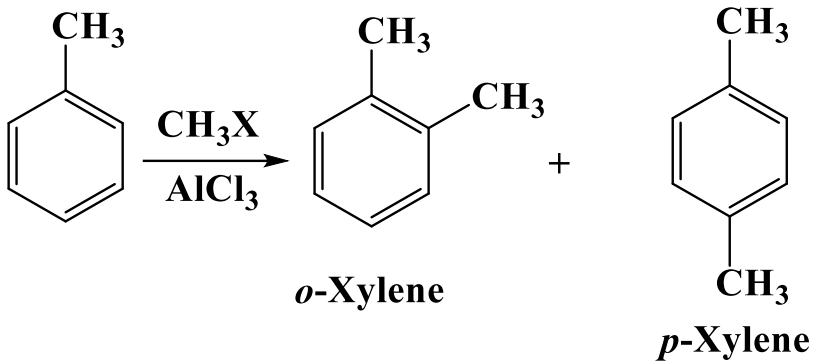
2- Reaction with H_2SO_4



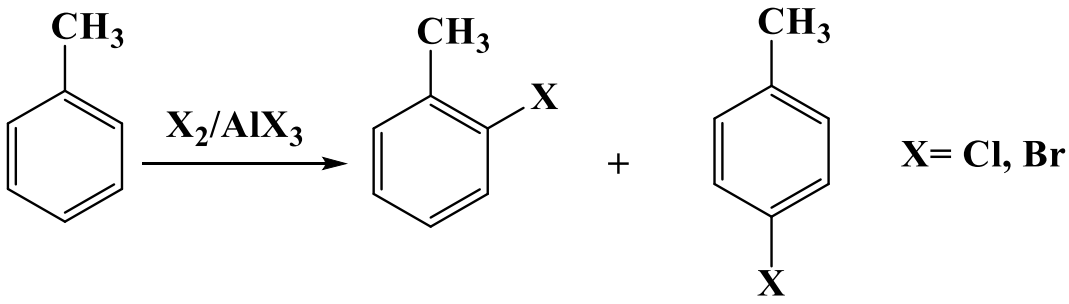
o-Toluenesulphonic acid

p-Toluenesulphonic acid

3- Friedel-Craft alkylation

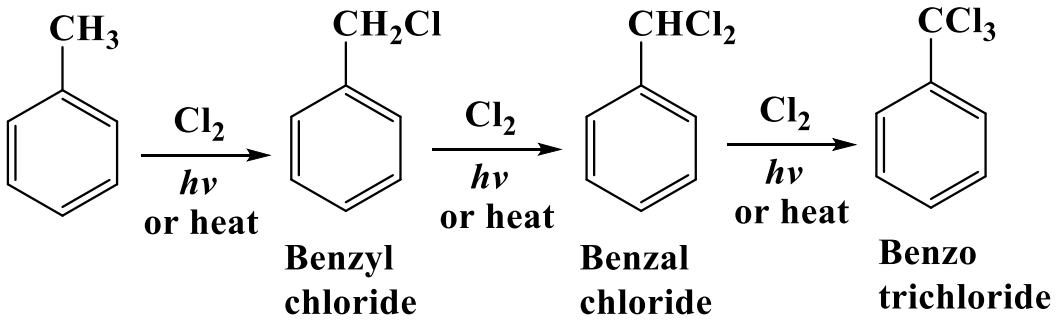


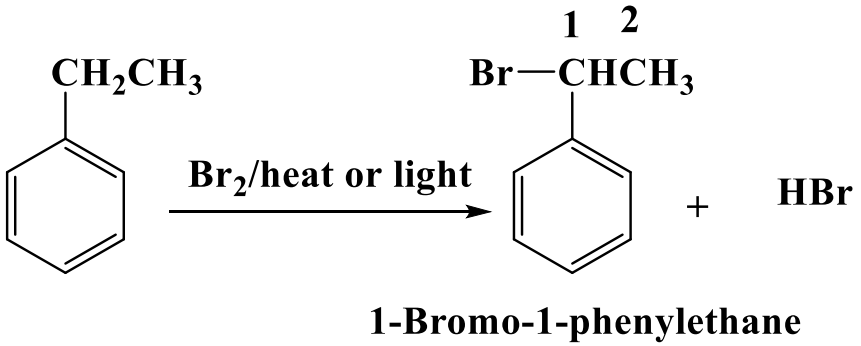
4- Reaction with halogens



B- Reaction of the side chain

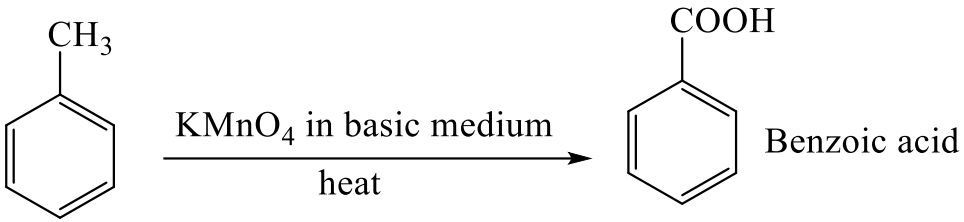
1- Halogenation



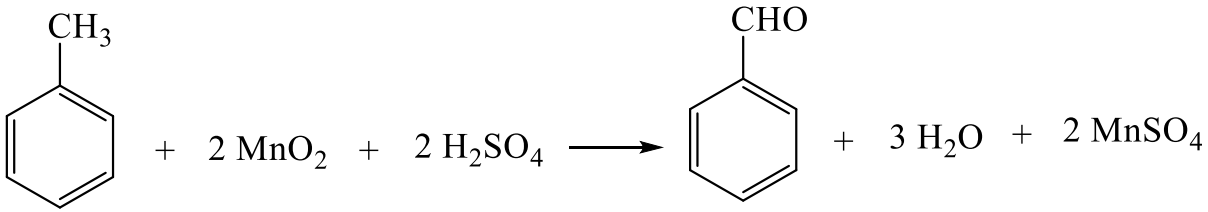


2- Oxidation of the side chain

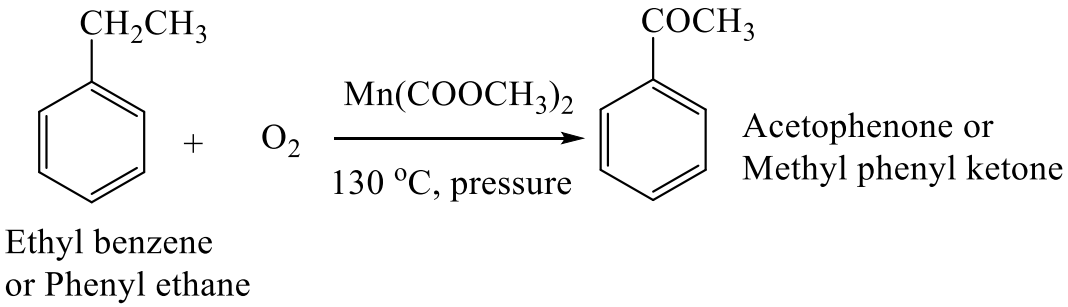
a- Oxidation by $KMnO_4$



b- Oxidation with MnO_2/H_2SO_4



c- Catalytic oxidation by air

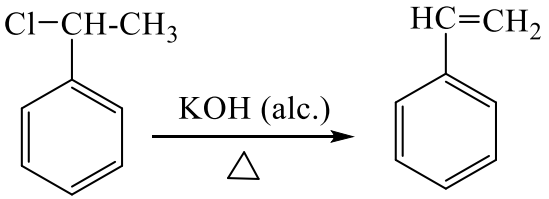


Alkenylbenzene

Alkenylbenzene

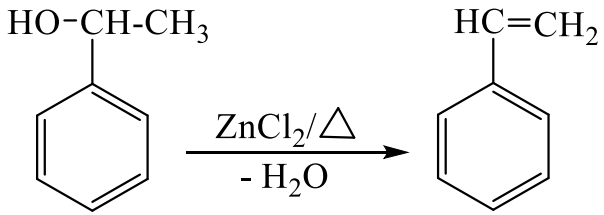
Synthesis

1- From halides



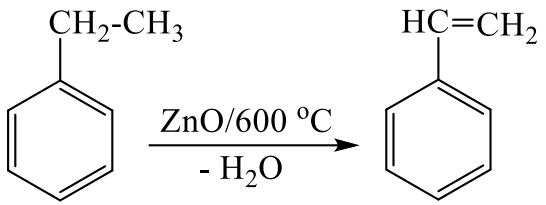
1-Chloro-1-phenylethane Styrene or 1-Phenylethylene

2- From alcohols



1-Phenylethanol Styrene or 1-Phenylethylene

3- From ethylbenzene

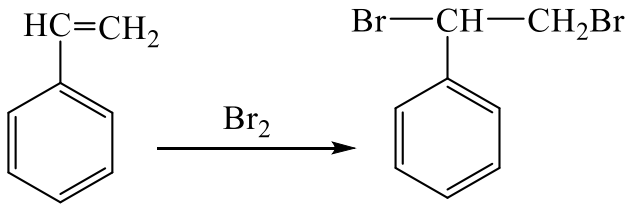


1-Phenylethane
or ethylbenzene

Styrene or 1-Phenylethylene

Reactions

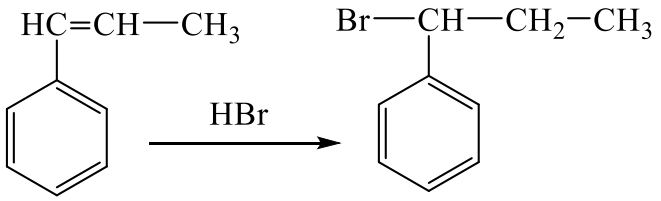
1- Addition of halogens



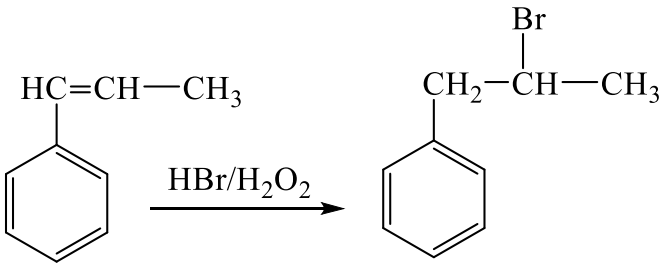
Styrene or 1-Phenylethylene

1-Phenyl-1,2-dibromoethane

2- Addition of halogen acids

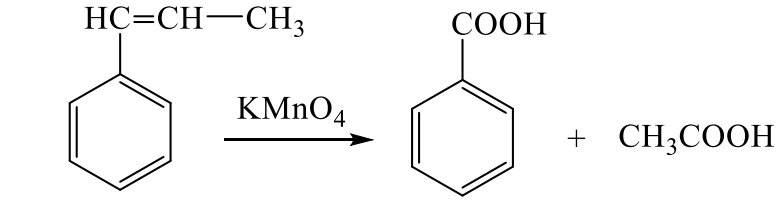


1-Phenylpropene 1-Phenyl-1-brompropane



1-Phenylpropene 1-Phenyl-2-brompropane

3- Oxidation



1-Phenylpropene Benzoic acid

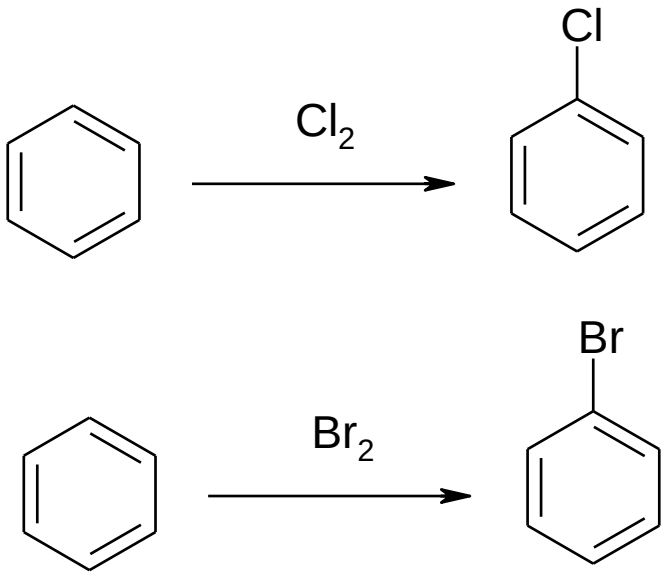
Aryl halides

ArX

Chloro- and bromobenzene

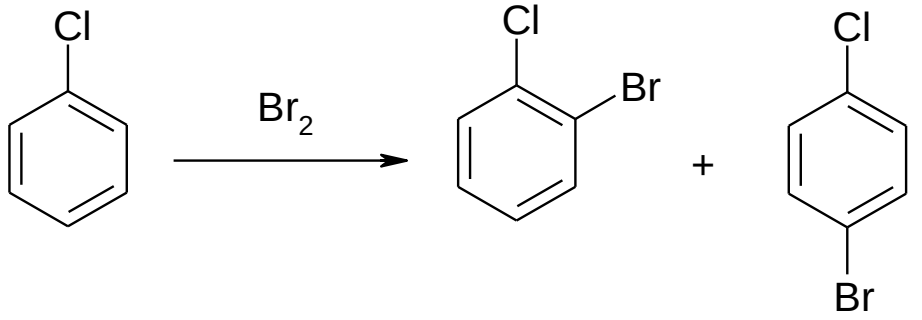
Synthesis

1- from the reaction of benzene with chlorine or bromine

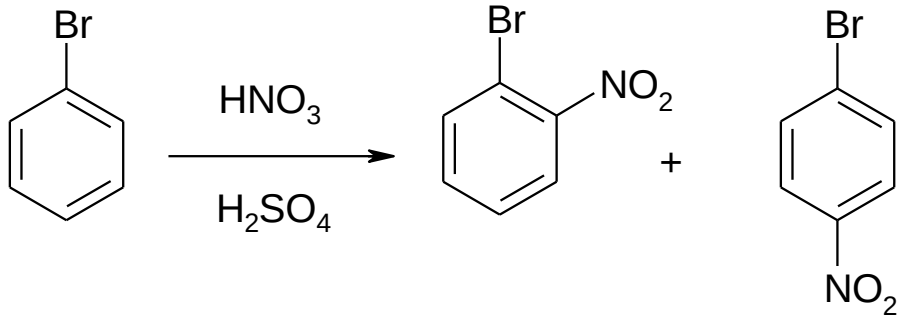


Reactions

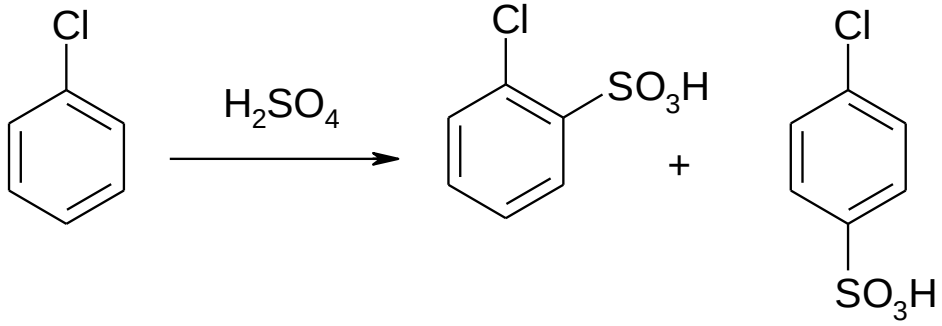
1- halogenation



2- nitration



3- sulfonation

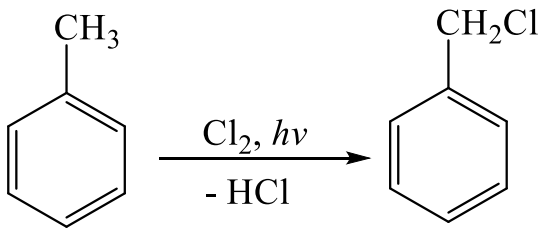


Benzyl halides

Benzyl chloride

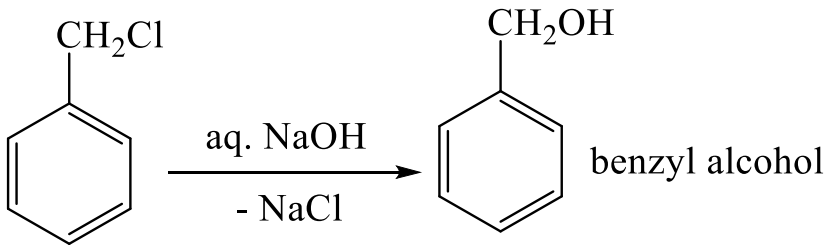
Synthesis

From toluene

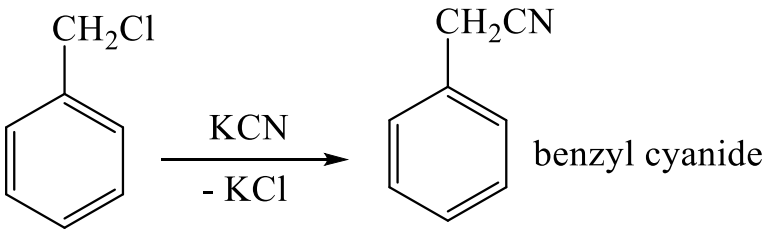


Reactions

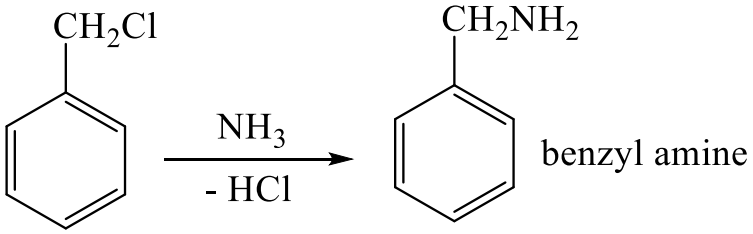
1- With aqueous NaOH



2- With potassium cyanide KCN



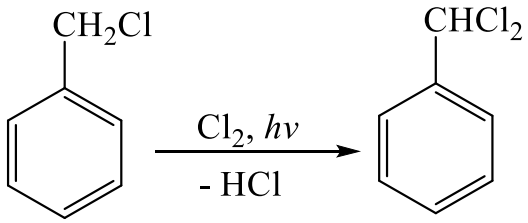
3- With ammonia NH_3



Benzal chloride

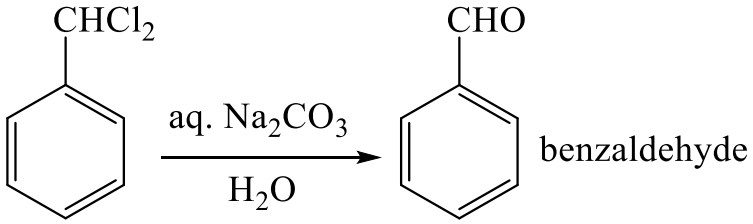
Synthesis

From benzyl chloride



Reactions

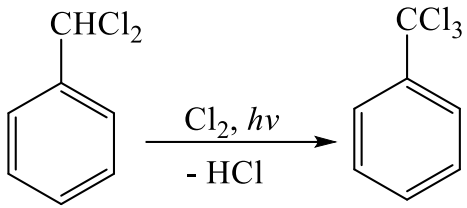
With aq. Na_2CO_3



Benzotrichloride

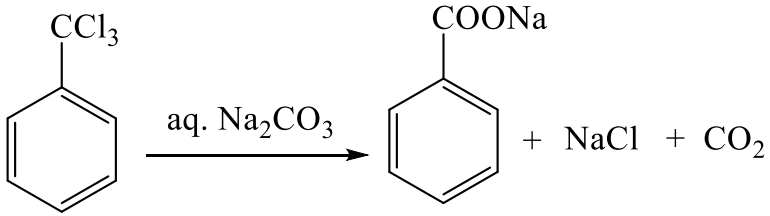
Synthesis

From benzal chloride

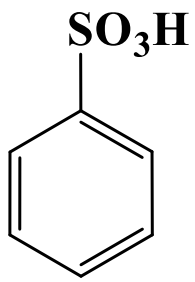


Reactions

With aq. Na_2CO_3

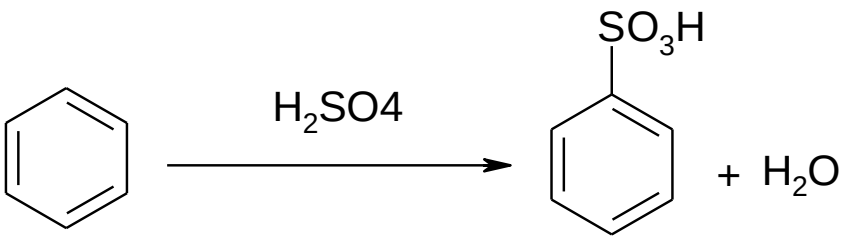


Benzene sulfonic acid



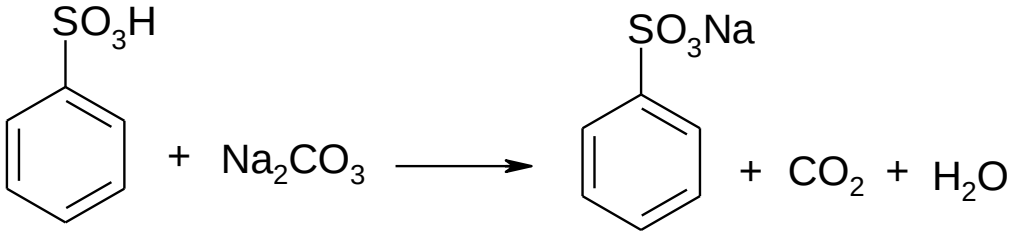
Preparation

1- by the reaction of benzene with sulforic acid

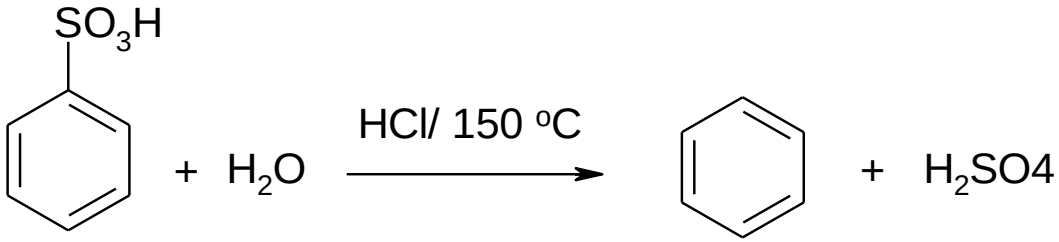


Reactions

1- with sodium carbonate

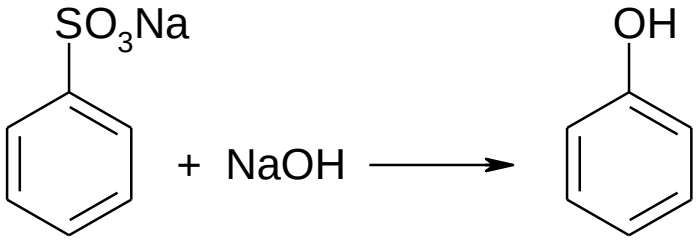


2- elimination of the sulfonic acid group

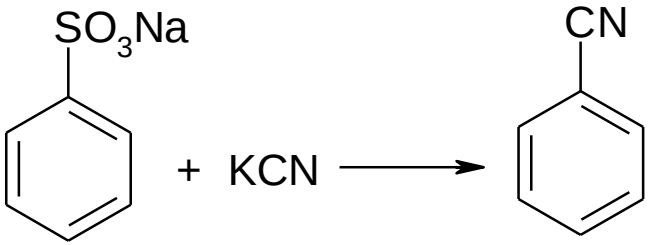


3- replacement of the sulfonic acid group

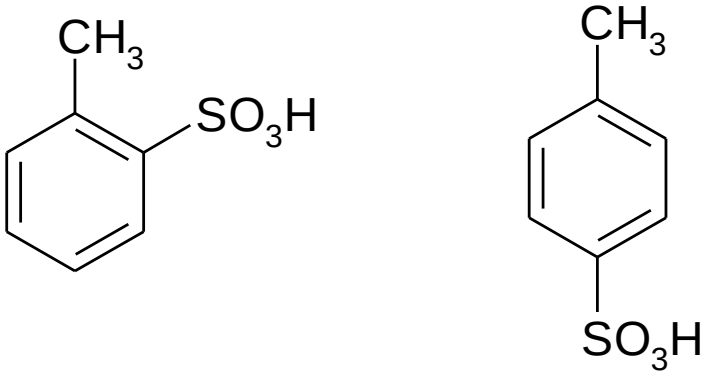
a- with NaoH



b- with KCN



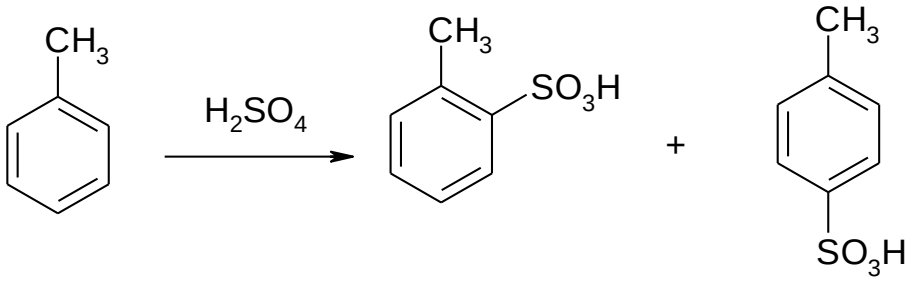
Toluene sulfonic acids



Toluene sulfonic acids

Preparation

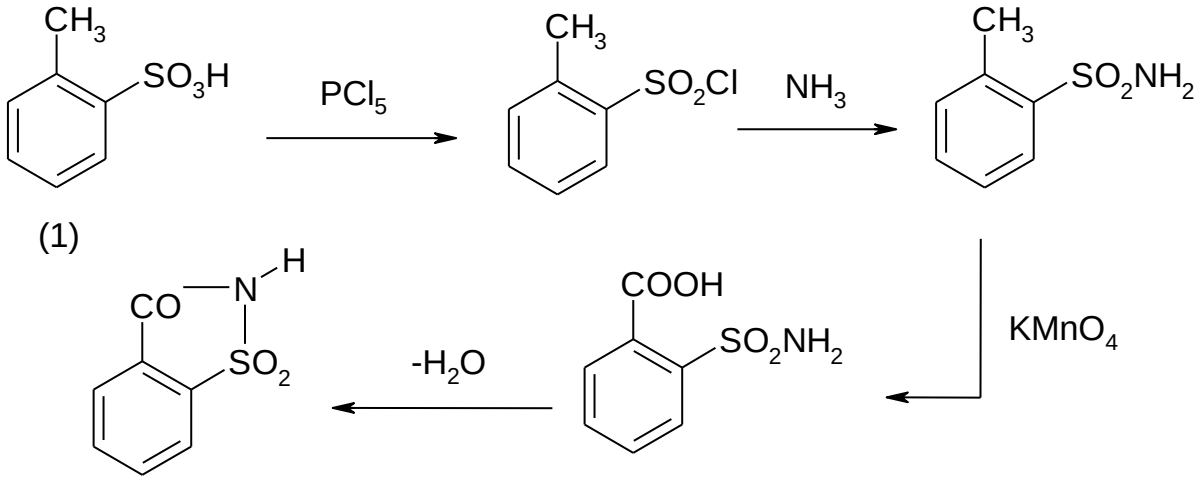
By the reaction of benzene with conc. sulforic acid



(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)

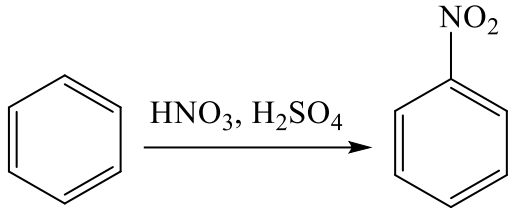
Aromatic nitro compounds

$ArNO_2$

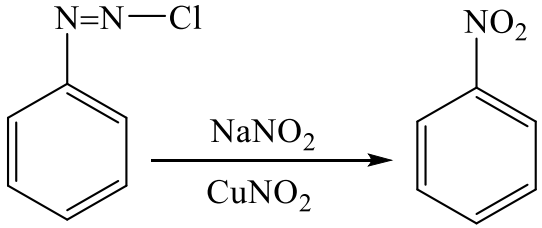
Aromatic nitro compounds

Synthesis

1- From direct nitration of benzene

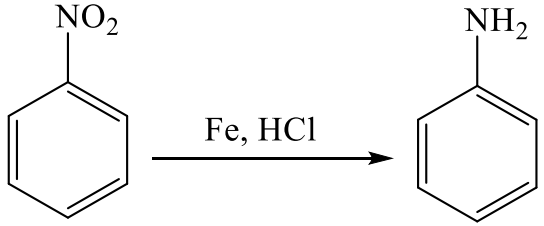


2- From diazonium salt



Reactions

Reduction to aniline



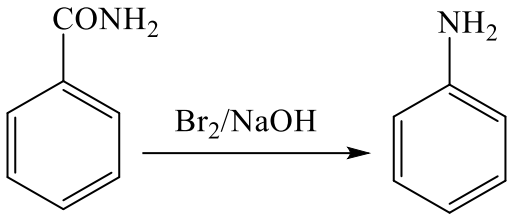
Aromatic amines

$ArNH_2$

Aromatic amines

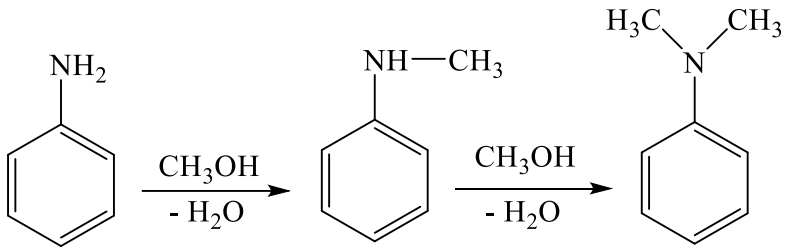
Synthesis

From benzamide



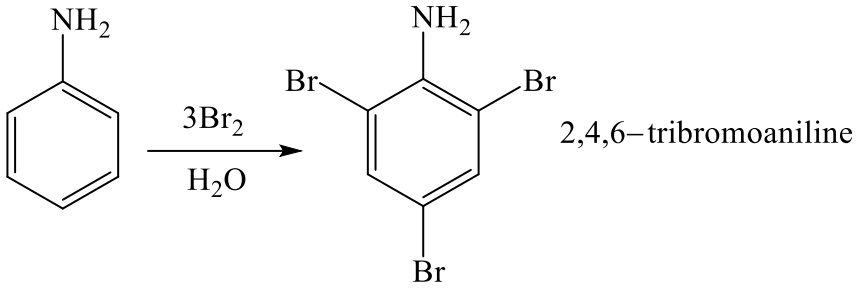
Reactions

1- With methanol



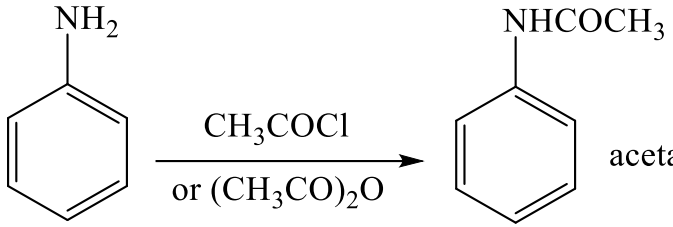
N-methylaniline *N,N*-dimethylaniline

2- Reaction with bromine



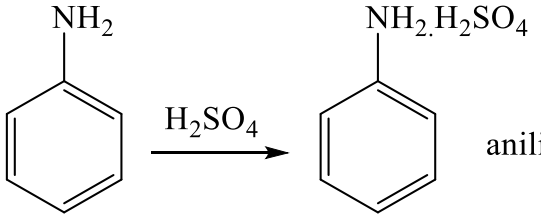
2,4,6−tribromoaniline

3- Reaction with acetyl chloride or acetic anhydride



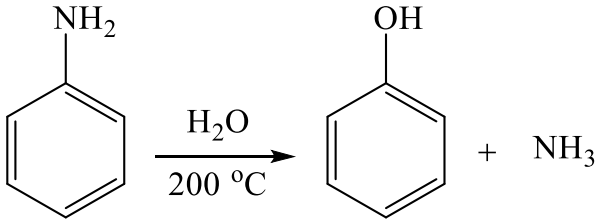
acetanilide

4- Reaction with sulphoric acid



aniline sulphate

5- Boiling with water



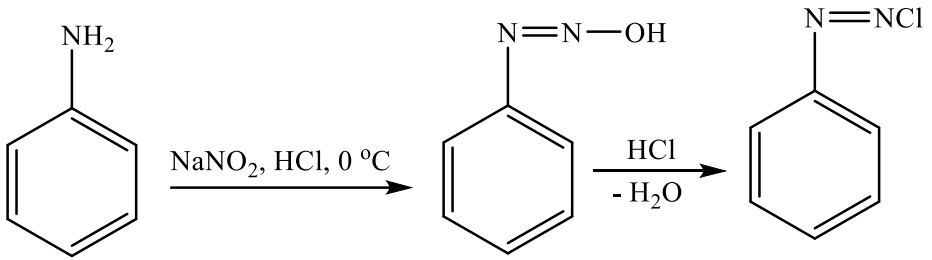
Aromatic diazonium salts

ArN=N-Cl

Aromatic diazonium salts

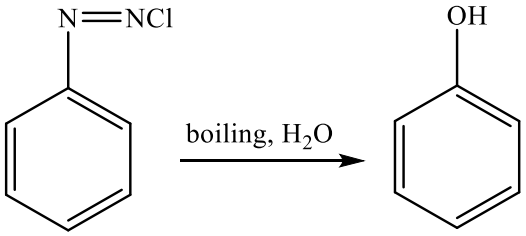
Synthesis

From aniline

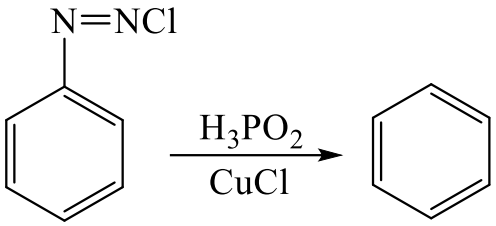


Reactions

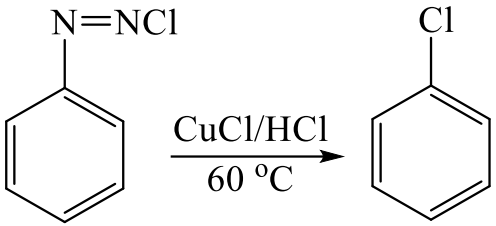
1- Boiling with water



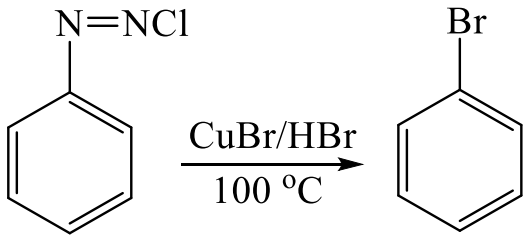
2- With hypophosphorous acid



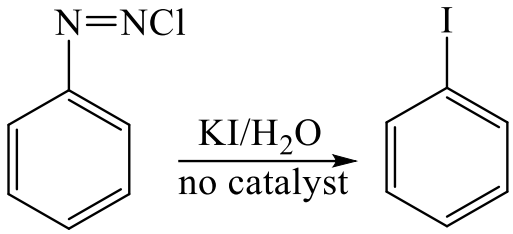
3- With copper chloride



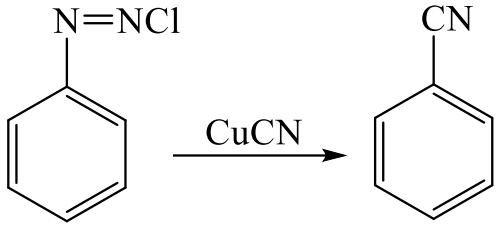
4- With copper bromide



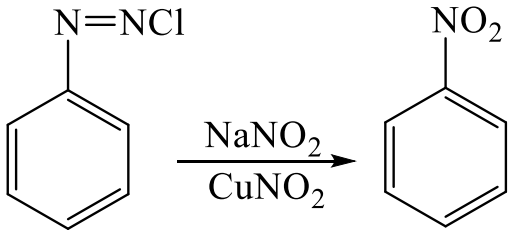
5- With potassium iodide



6- With copper cyanide



7- With sodium nitrite and copper nitrite



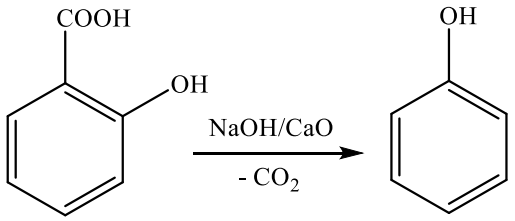
Phenols

ArOH

Phenols

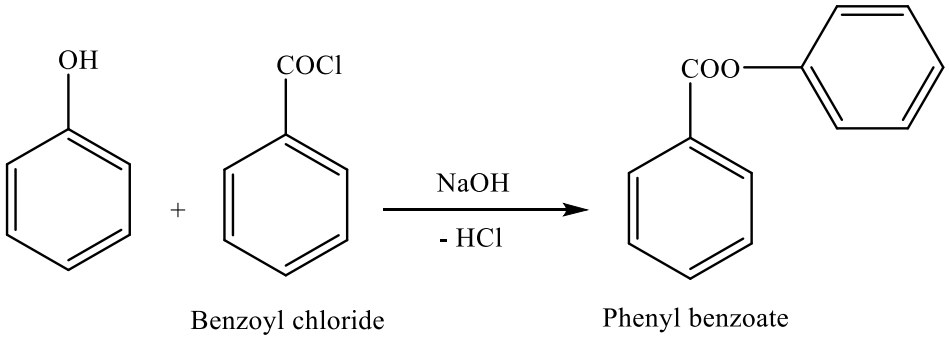
Synthesis

From salicylic acid

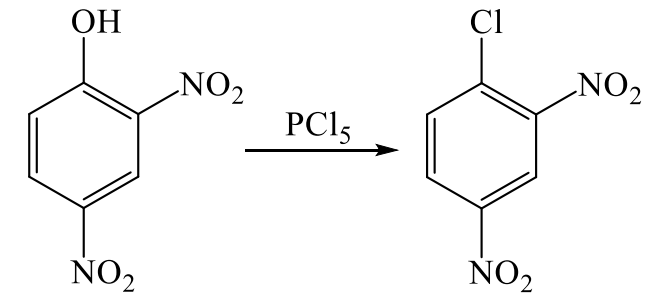


Reactions

1- Ester formation

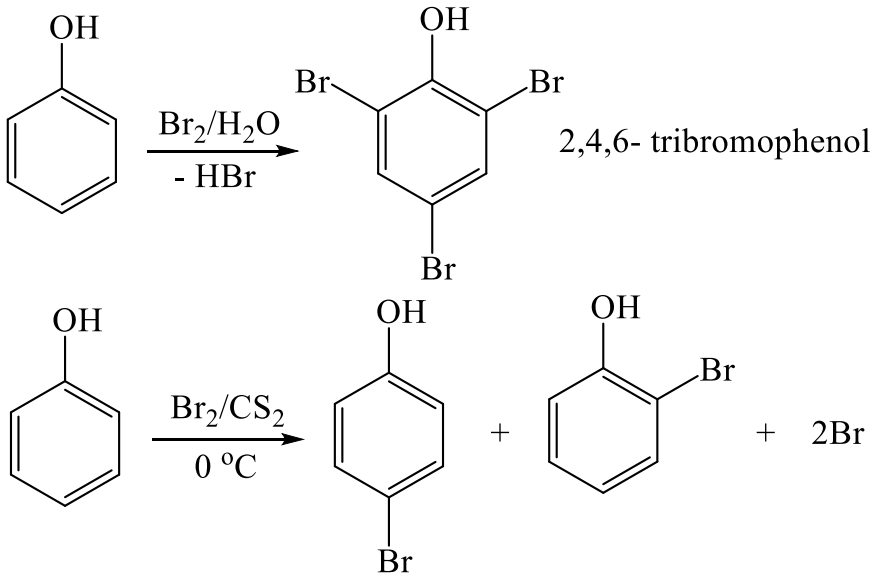


2- With phosphorous pentachloride

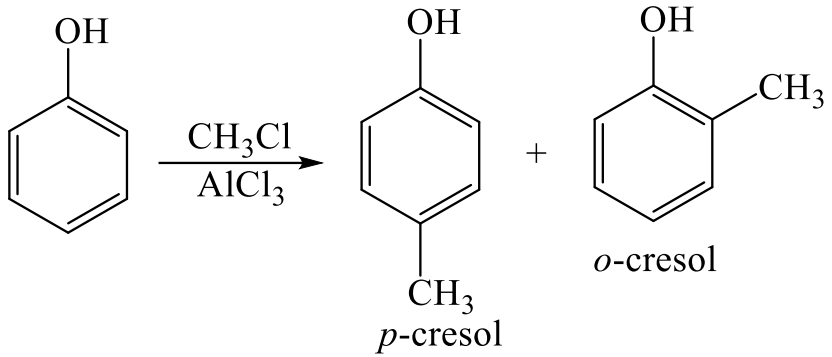


2,4-dinitrophenol

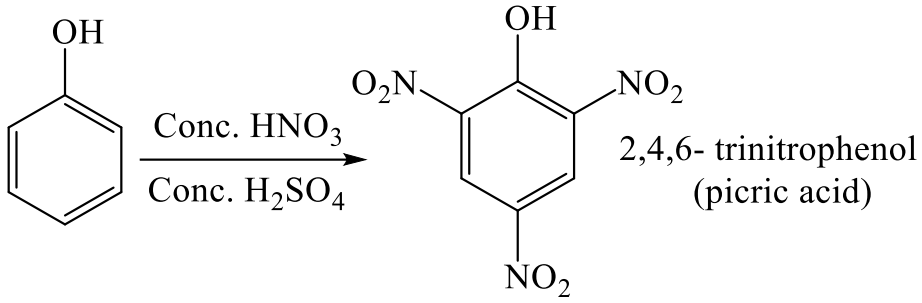
3- With bromine



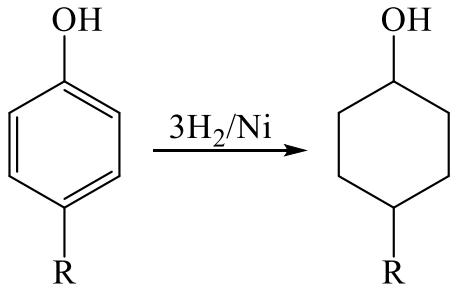
4- Alkylation



5- Nitration



6- Reduction



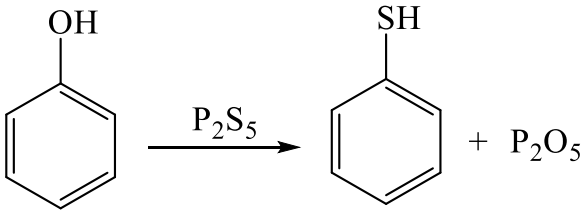
Aryl thiols

ArSH

Aryl thiols

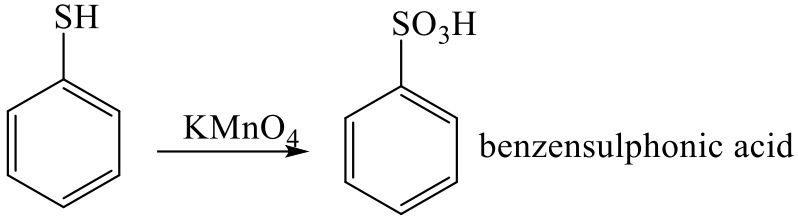
Synthesis

From phenols

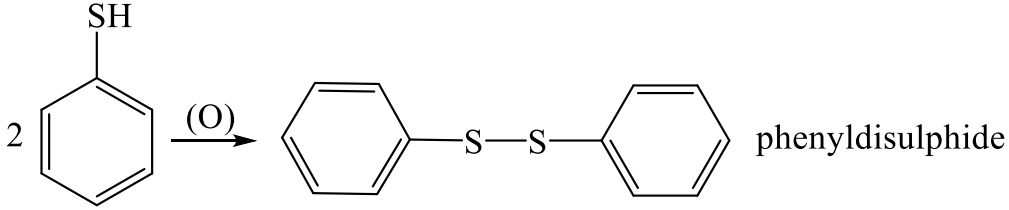


Reactions

1- With mild oxidizing agent



2- With strong $KMnO_4$

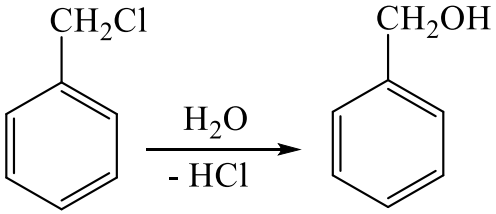


Aromatic alcohols

Aromatic alcohols

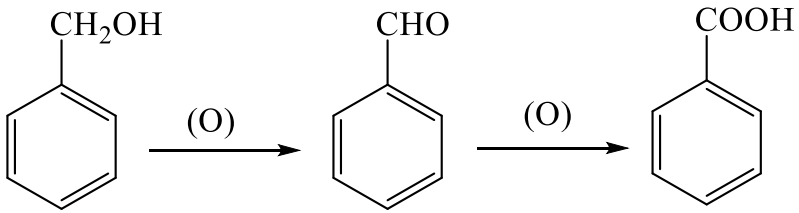
Synthesis

From benzyl chloride

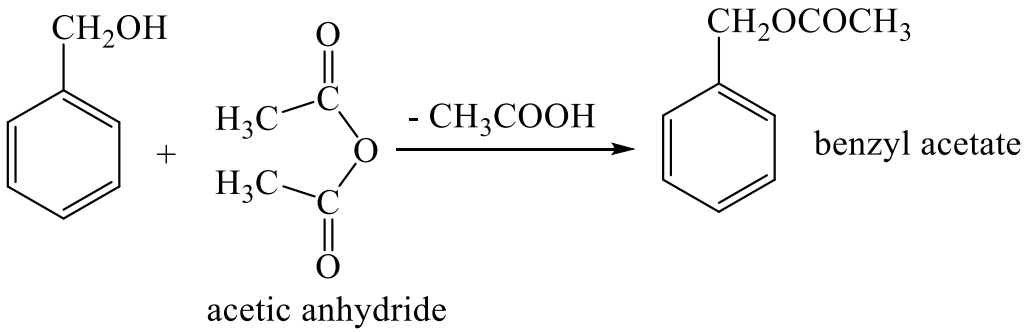


Reactions

1- Oxidation



2- Esterformation



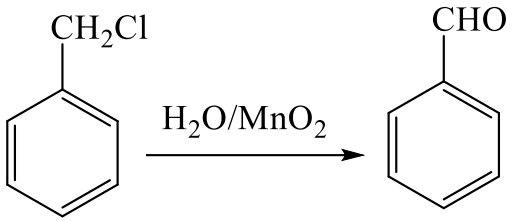
Aromatic aldehydes

ArCHO

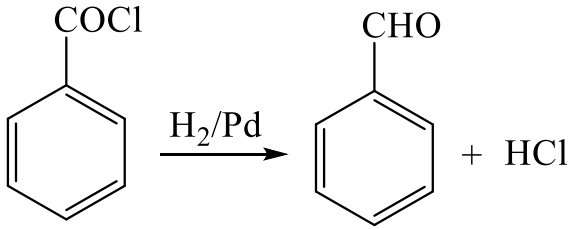
Aromatic aldehydes

Synthesis

1- From benzyl chloride

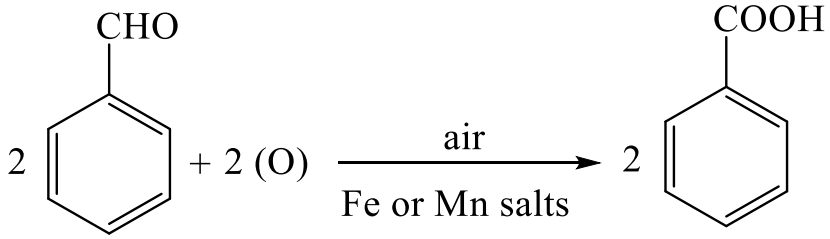


2- From benzoyl chloride

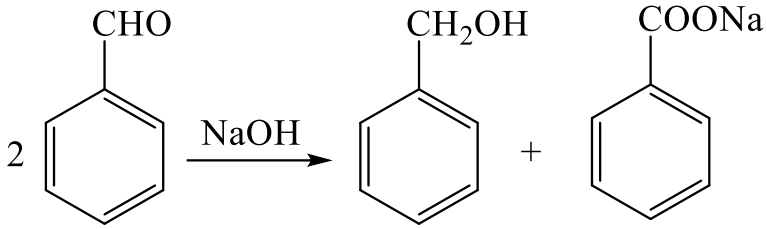


Reactions

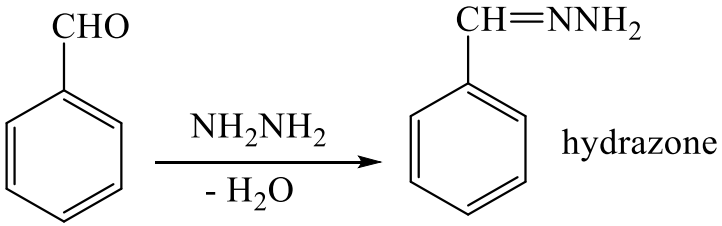
1- Oxidation



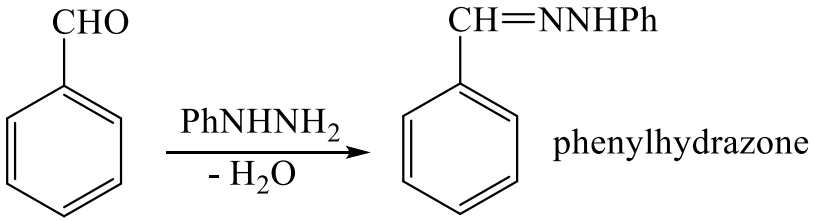
2- Cannizaro reaction



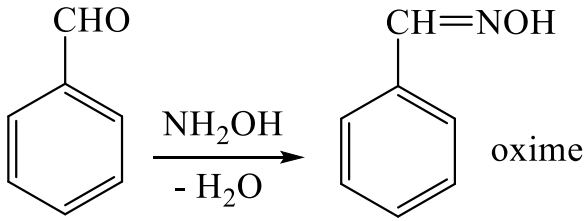
3- With hydrazine



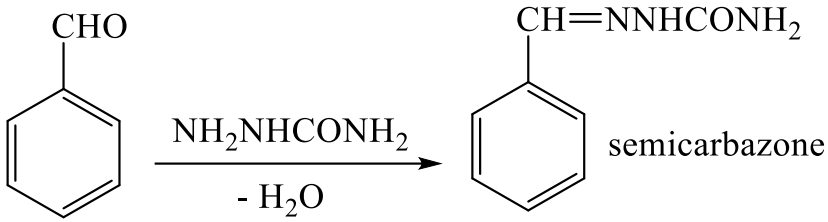
4- With phenylhydrazine



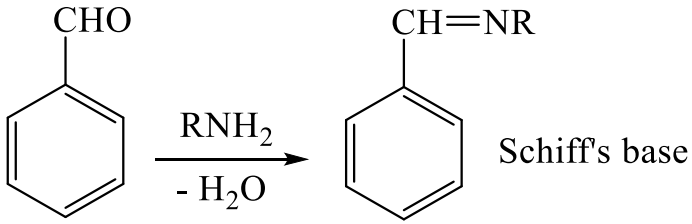
5- With hydroxyl amine



6- With semicarbazide



7- With amines

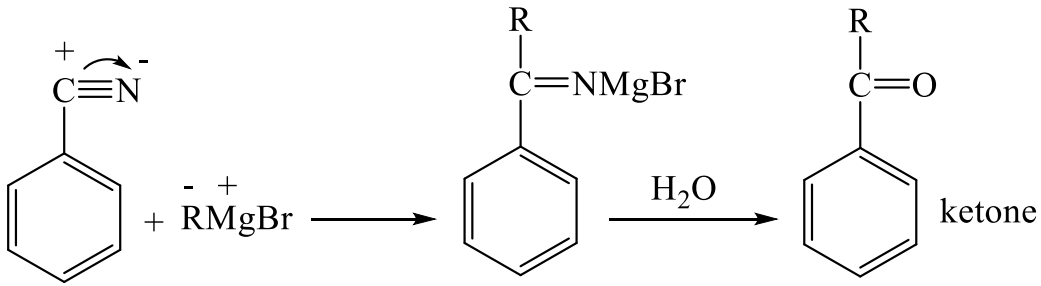


Aromatic ketones

Aromatic ketones

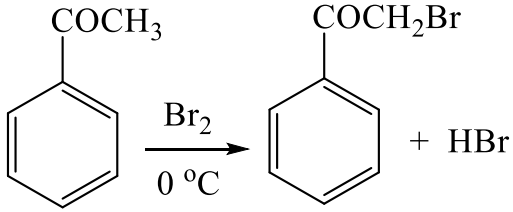
Synthesis

By the reaction of Grignar reagents benzonitrile

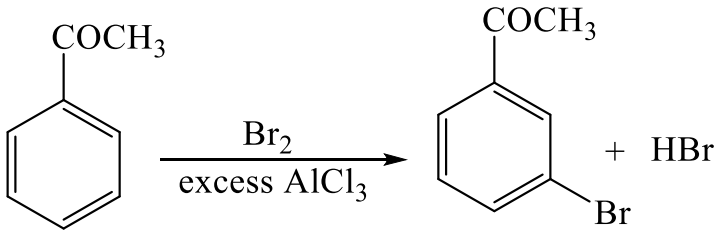


Reactions

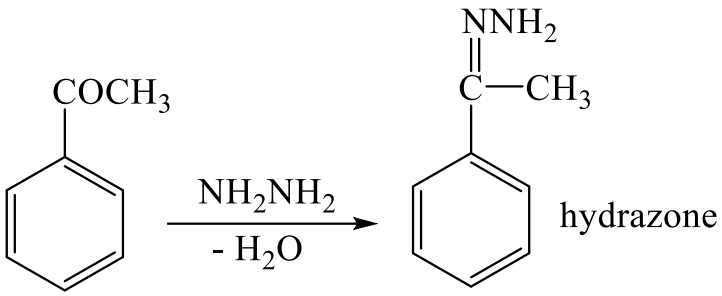
1- With bromine



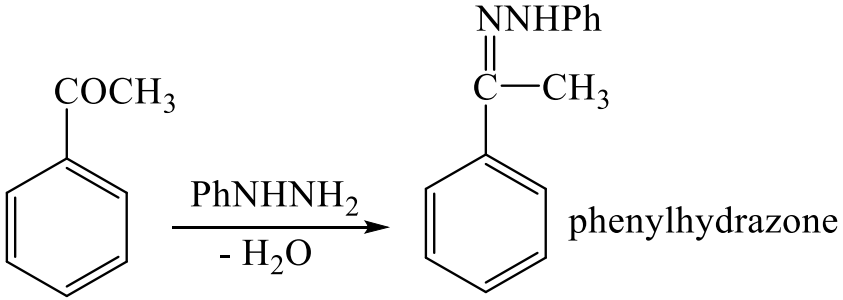
phenacyl bromide



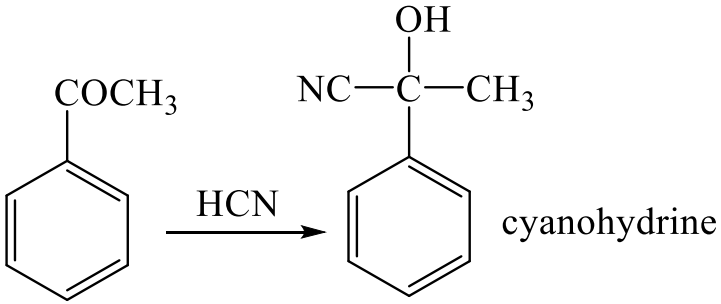
2- With hydrazine



3- With phenyl hydrazine



4- With hydrogen cyanide



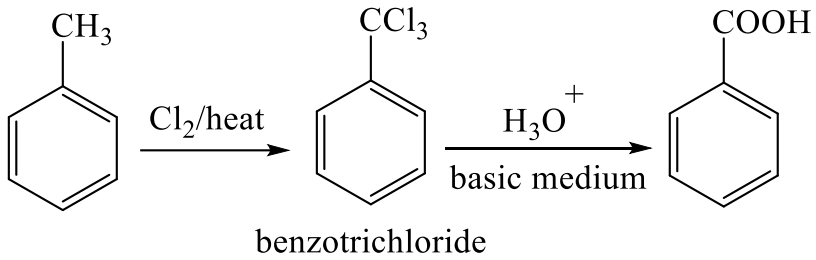
Aromatic carboxylic acids

ArCOOH

Aromatic carboxylic acids

Synthesis

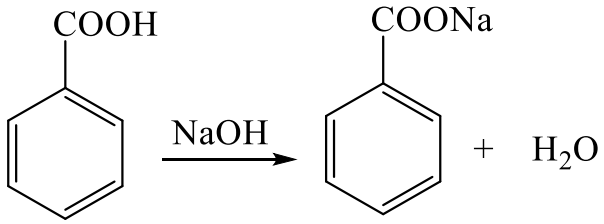
From toluene



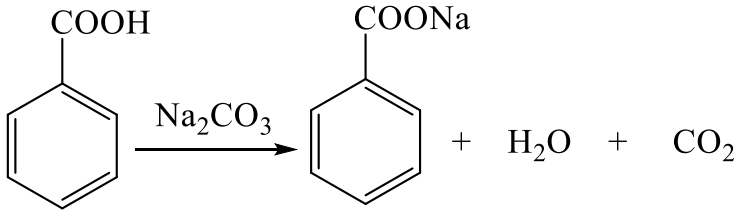
benzotrichloride

Reactions

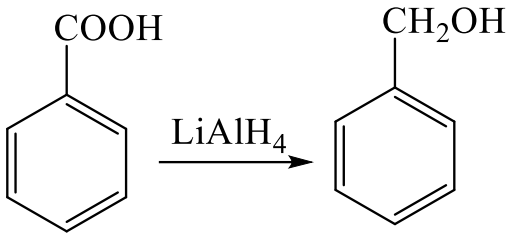
1- With NaOH



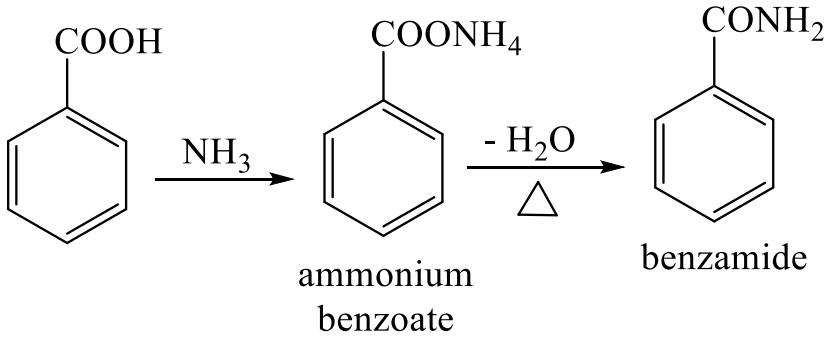
2- With Na_2CO_3



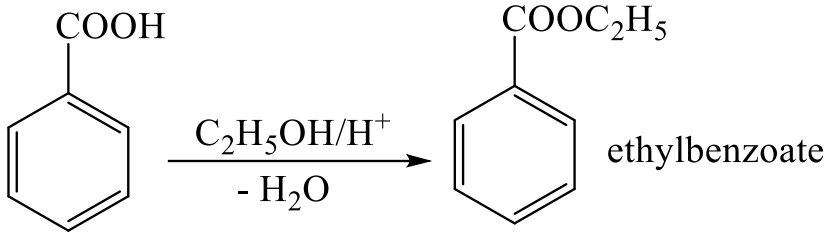
3- With lithium aluminium hydride



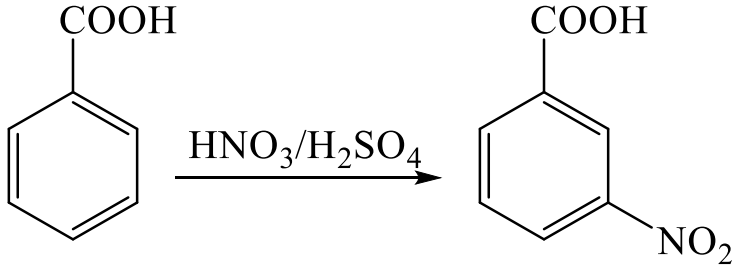
4- With ammonia



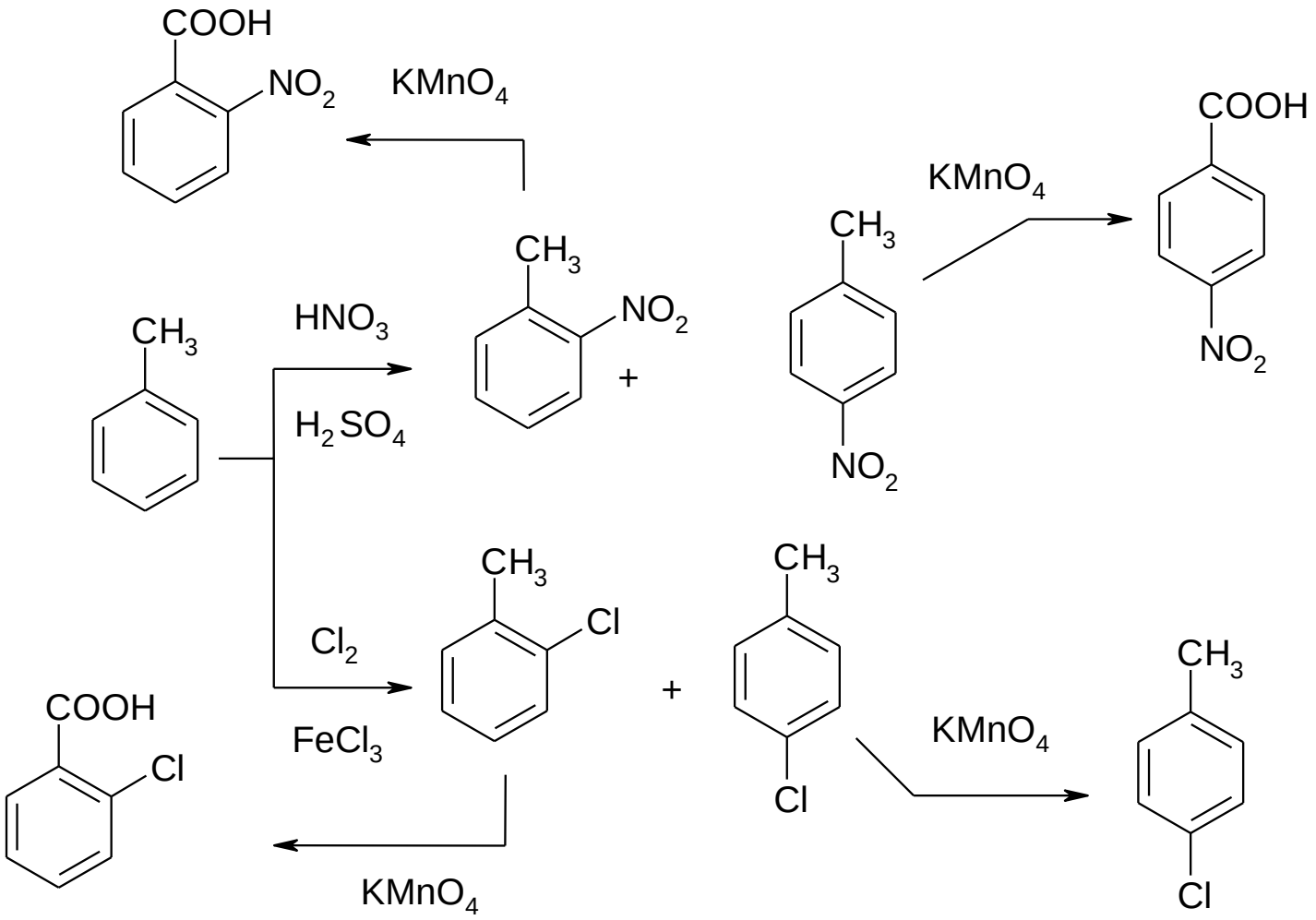
5- Ester formation



6- Nitration



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



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- Reaction of aromatic compound book
- Text book of organic chemistry