SENIOR FIVE TERM 3

TOPIC 1/2: Organic Chemistry I PART 2

Topic competency: The learner analyses the structures, functional groups, and reactivity of organic compounds, and applies knowledge of organic reactions and organic reaction mechanisms to synthesise organic molecules.

Alkylhalides (R-X, X = Cl, Br, I)

These are compounds with atleast one halogen atom attached to the parent chain.

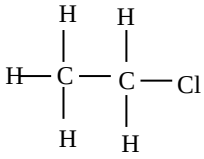
Classification of mono substutued alkylhalide

As seen earlier, they are classified like alcohols.

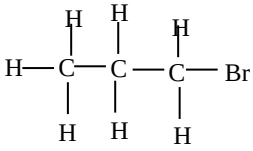
They are **three** classes of alkylhalide depending on the number of alkyl groups attached to a carbon atom that carry a halide.

(a) Primary alkylhalide have one alkyl group on the carbon atom that carries a halide.

Examples



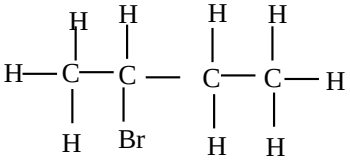
Chloroethane



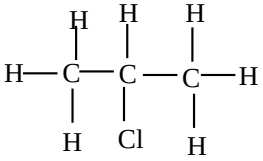
1-Bromopropane

(b) Secondary alkylhalide have two alkyl groups attached to a carbon atom that carry a halide

Examples



2-Bromobutane

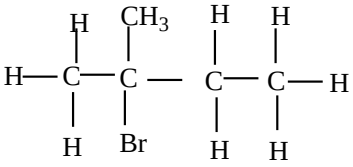


2-chloropropane

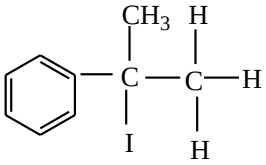
(c) Tertiary alkylhalide

Tertiary alkylhalide have three alkylgroups attached to the carbon atoms that carry OH group

Examples



2-bromo-2-methylbutanane

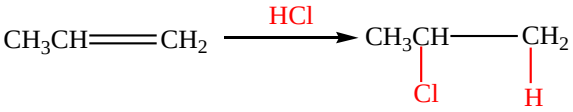


2-iodo-2-phenylpropane

Preparation of alkylhalide

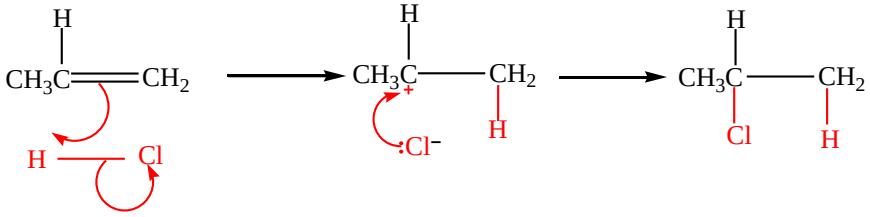
1. By reacting alkenes with halogenhalide

Example



Mechanism

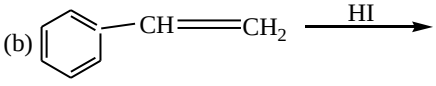
Remember: the reaction occurs at the double bond and hydrogen atom goes to a carbon that carries highest number of hydrogen atoms.



Trial 1

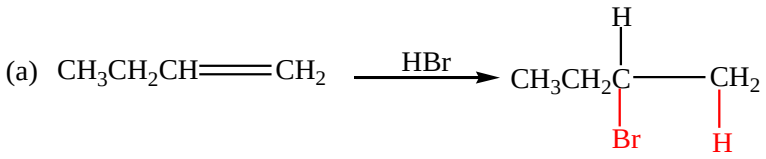
Complete and write a mechanism for the following reactions (mark yourself after)

(a) $CH_3CH_2CH{=}CH_2 \xrightarrow{HBr}$

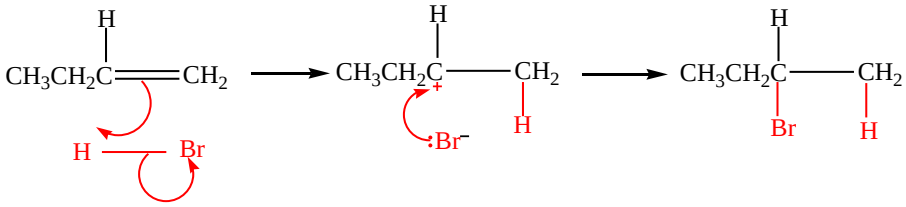
(b) 

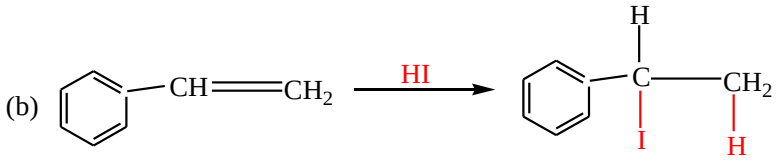
Solution to Trial 1

In these reactions, the double bond breaks and hydrogen halide adds itself a cross the carbon atoms that were forming the double bond. Hydrogen atom adds to a carbon atom the carries the highest number of hydrogen atom of those that form a double bond. Make sure you account for the charges.

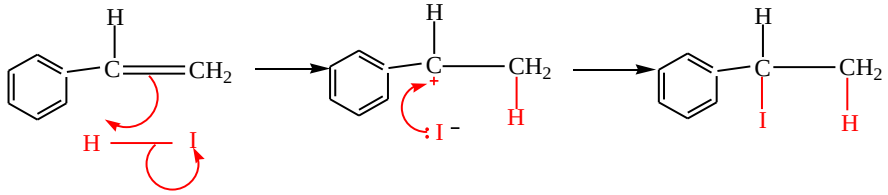


Mechanism





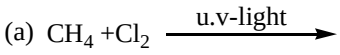
Mechanism

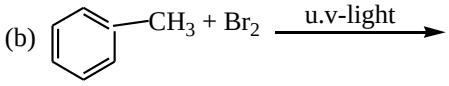


2. By reacting chlorine gas or bromine with alkanes. The reaction occurs in the presence of u.v light. This was dealt with when dealing with reactions of alkanes.

Trial 2

Complete the following equation and write a mechanism





Solution to Trial 2

These reactions follow a free radical mechanism, be keen to observe the initiation and formation of free radicals as the reaction proceeds. Every dot (un paired electron) must be accounted for.

(a) $CH_4 + Cl_2 \xrightarrow{\text{u.v-light}} CH_3Cl$

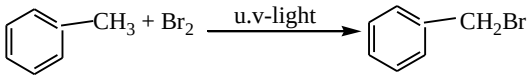
Methane — chloromethane

Mechanism

$Cl_2 \xrightarrow{\text{u.v-light}} 2\dot{Cl}$ chlorine radical

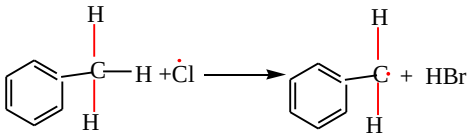
$H_3C{-}H + \dot{Cl} \longrightarrow H_3\dot{C} + HCl$ methyl radical

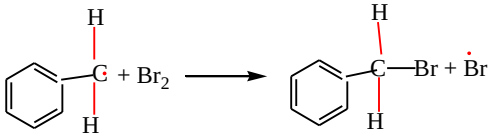
$H_3\dot{C} + Cl_2 \longrightarrow H_3C{-}Cl + \dot{Cl}$

(b) 

Mechanism

$Br_2 \xrightarrow{\text{u.v-light}} 2\dot{Br}$ Bromine radical





3. By reacting alcohols with

(a) Phosphorus halide

Examples 1

(i) $CH_3CH_2OH \xrightarrow{PCl_5} CH_3CH_2Cl$

(ii) $CH_3\underset{\underset{OH}{|}}{CH}CH_3 \xrightarrow{PBr_3} CH_3\underset{\underset{Br}{|}}{CH}CH_3$

(b) With HX (X= Cl, Br, I)

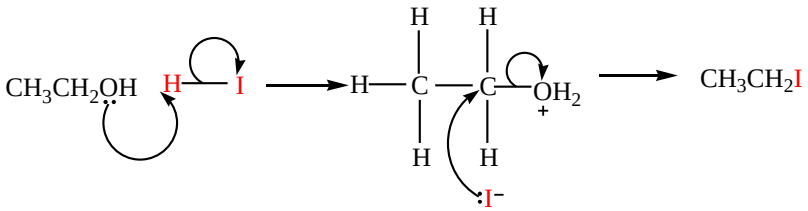
HI and HBr react readily with alcohols but the reaction of HCl is catalyzed with anhydrous zinc chloride. The mechanism of the reaction depends on the class of alcohol. Though secondary alcohols react like either primary or tertiary alcohols.

Example 2

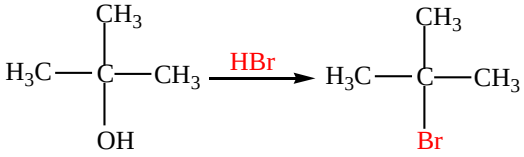
Primary alcohol

$CH_3CH_2OH + HI \longrightarrow CH_3CH_2I + H_2O$

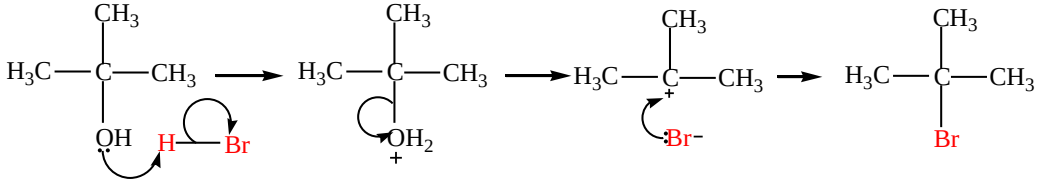
Mechanism



Tertiary alcohol

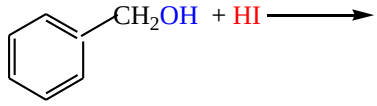


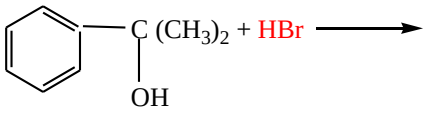
Mechanism



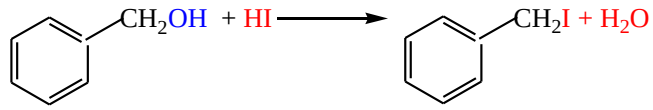
Trial 3

Complete and write a mechanism, thereafter mark yourself

(i) 

(ii) 

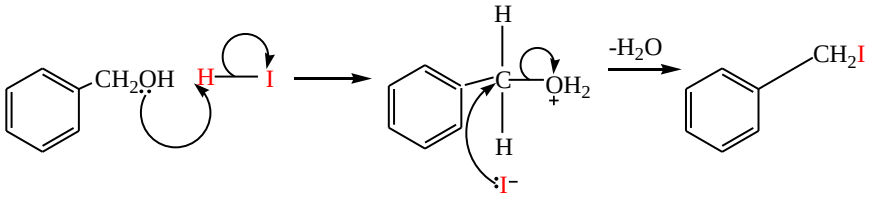
Solution to trial 3

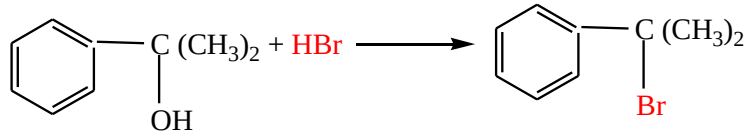
(i) 

Phenylmethanol Iodophenylmethane

Mechanism

Note that phenylmethanol is a primary alcohol

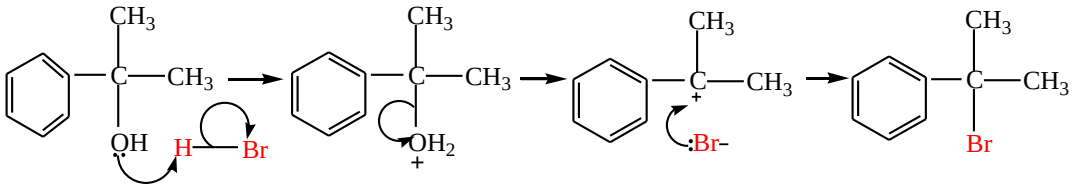


(ii) 

2-Phenylpropan-2-ol

Mechanism

Please note that 2-phenylpropan-2-ol is a tertiary alcohol

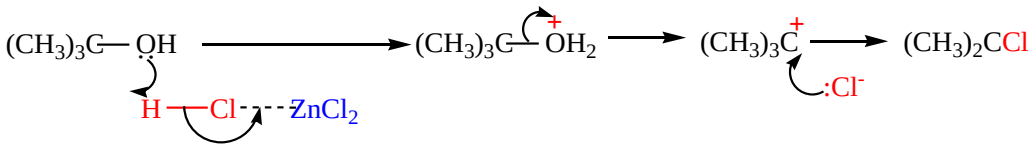


(c) Reaction of HCl with alcohols is catalyzed by anhydrous zinc chloride because HCl bond is strong. Primary alcohol does not react, secondary alcohol reacts slowly, and tertiary alcohol reacts faster.

Example 3

$(CH_3)_3COH \xrightarrow{HCl/ZnCl_2} (CH_3)_3CCl$

Mechanism



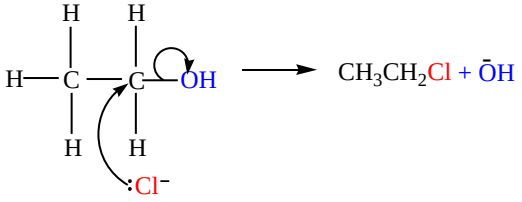
(d) Reaction of alcohol with KX (X= Cl, Br, I)

The mechanisms depend on the class of alcohols. The mechanism of secondary alcohols is either similar to those of primary or tertiary alcohols

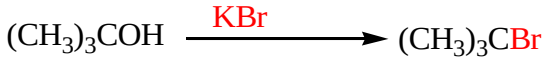
Primary alcohol

$CH_3CH_2OH + KCl \longrightarrow CH_3CH_2Cl + \bar{O}H$

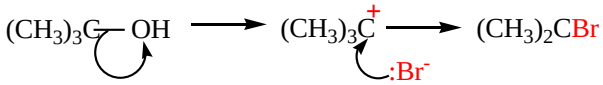
Mechanism



Tertiary alcohol



Mechanism

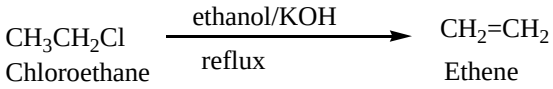


Chemical properties

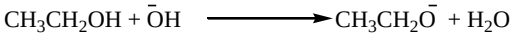
(a) Formation of alkenes

Alkylhalides react with hot alcoholic potassium hydroxide to form alkenes. The mechanism depends on the class of alkylhalide but mechanism of reaction for secondary alkylhalide is similar to that of the primary or tertiary alkylalide. These reactions were also considered when we dealt with preparation of alkene

Example 4

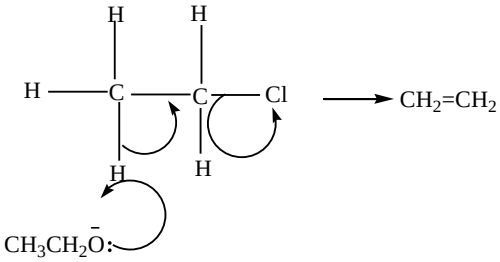


Mechanism

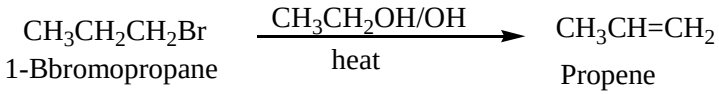


Ethanol

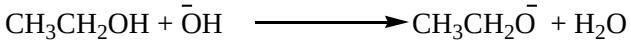
Then



Example 5

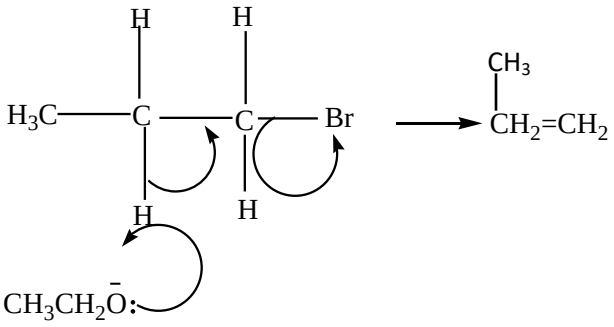


Mechanism



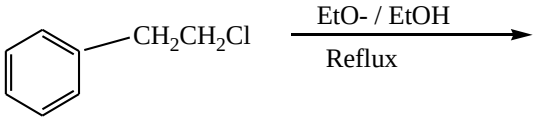
Ethanol

Then

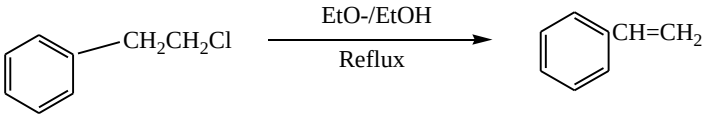


Trial 4

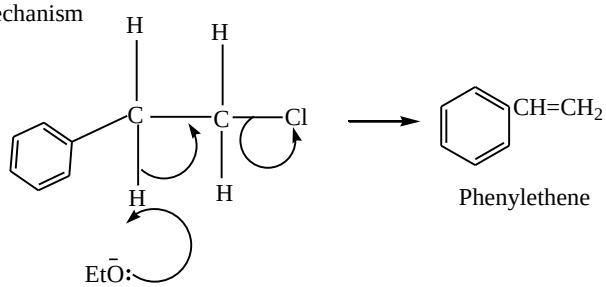
Complete and write a mechanism



Solution to trial 4



Mechanism

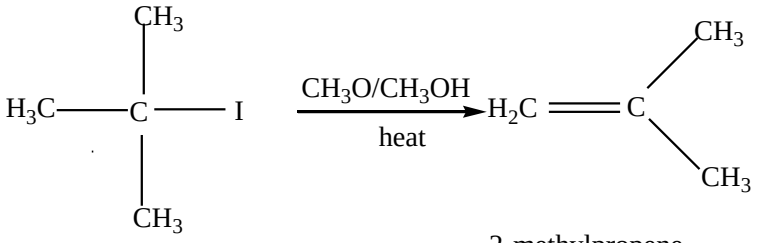


Phenylethene

(i) Secondary alkyl halides undergo the same mechanism as primary alkyl halides or that of tertiary alkyl halides

(ii) Tertiary alkyl halides undergo a mechanism called E1 or elimination unimolecular because a water molecule is eliminated and the slowest step involves one molecule only.

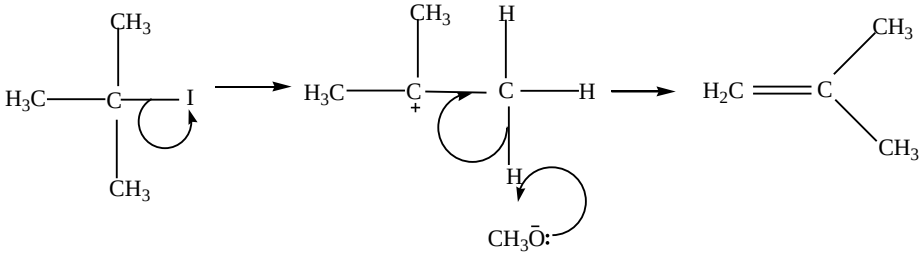
Example



2-Iodo-2-methylpropane

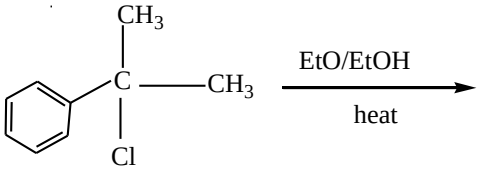
2-methylpropene

Mechanism

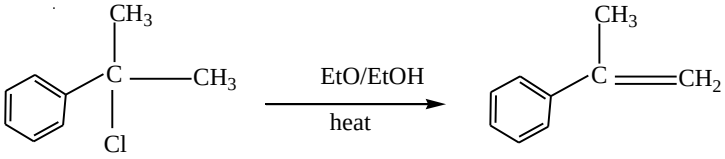


Trial 5

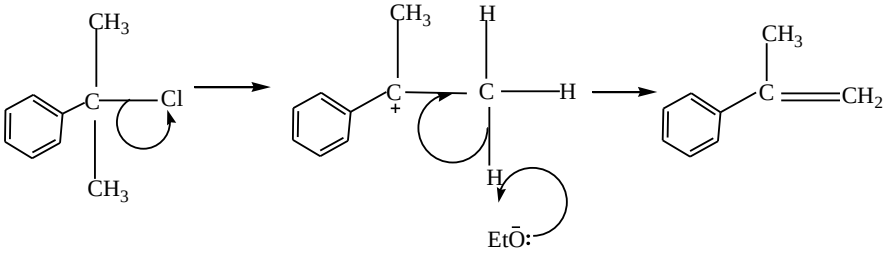
Complete and write a mechanism



Solution to trial 5



Mechanism



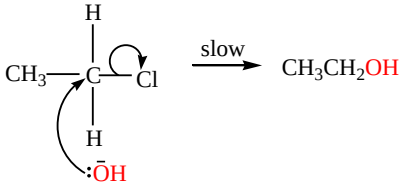
(b) Reaction of alkyl halide with alkalis (NaOH or KOH)

Alkyl halides react with hot alkalis to form alcohols. The secondary alkyl halides react by either mechanism of primary or tertiary alkyl halides.

Primary alkyl halide

$$CH_3CH_2Cl + KOH \longrightarrow CH_3CH_2OH + Cl^-$$

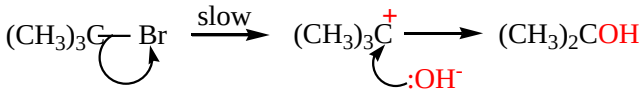
Mechanisms



The mechanism is described as SN^2 (substitution nucleophilic bimolecular) because a nucleophile (-OH) substitutes a halide atom and the slow step in the reaction involved two species i.e. –OH and alkylhalide.

$$(CH_3)_3CBr \xrightarrow{KOH} (CH_3)_3COH$$

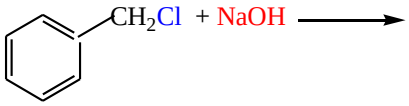
Mechanism



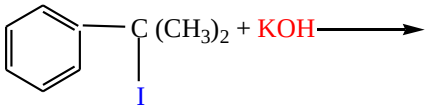
Trial 7

Complete and write a mechanism, thereafter mark yourself

(i)

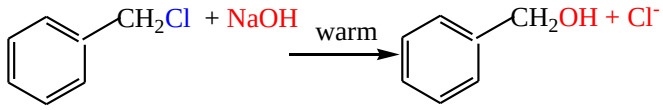


(ii)



Solution to trial 7

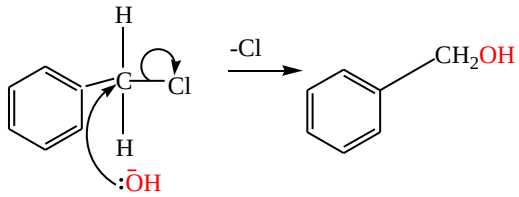
(i)



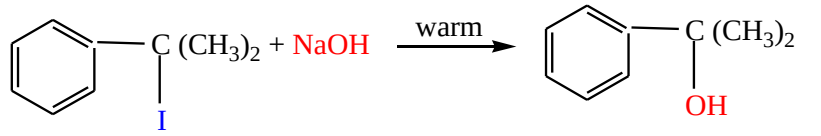
Chlorophenylmethane Phenylmethanol

Mechanism

Note that chlorophenylmethane is a primary alkyl halide



(ii)

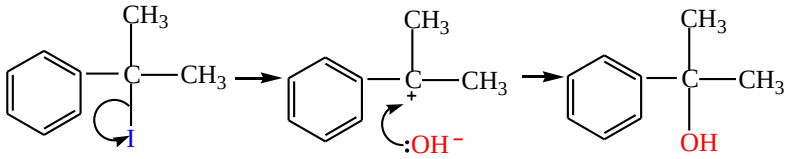


2-Iodo-2-phenylpropane

2-phenylpropan-2-ol

Mechanism

Note that 2-iodo-2-phenylpropane is a tertiary alkyl halide



(c) Reaction alkylhalides with potassium cyanide

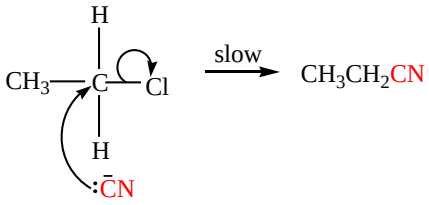
Alkyl halides react with potassium cyanide to form nitrile. This reaction is important because it increases the carbon chain by one carbon atom. Primary alkyl halides undergo SN^2 while tertiary alkyl halides undergo SN^1 mechanism whereas secondary alkyl halides undergo either mechanism.

Examples 7

(i) $CH_3CH_2Cl + KCN \longrightarrow CH_3CH_2CN + Cl^-$

chloroethane

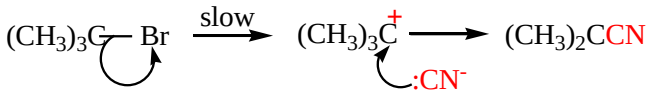
Mechanism (note that chloroethane is a primary alkyl halide)



(ii) $(CH_3)_3CBr \xrightarrow{KCN} (CH_3)_3CCN$

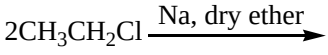
2-bromo-2-methylpropane

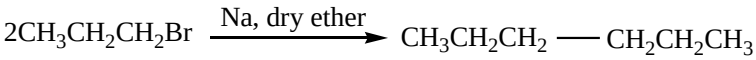
Mechanism (2-bromo-2-methylpropane is tertiary alkyl halide)



(d) Coupling reaction

Two alkyl halides couple in presence of sodium and dry ether or zinc-copper couple to form alkane of twice the number of carbon atoms as the parent alkyl halide.

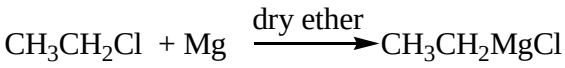




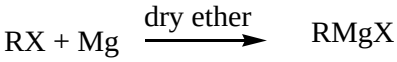
(e) Formation of Gridnard's reagent

Alkyl halides react with magnesium in presence of dry ether to form compound called Gridnard's reagent.

Example 8

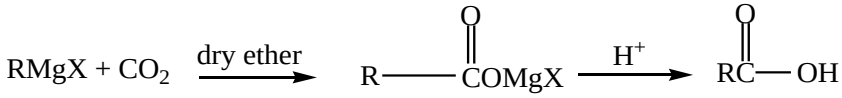


Generally

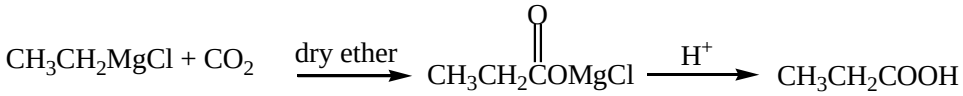


Gridnard's reagents are important synthetic molecules that enable us to increase the parent carbon chain by unlimited number of carbon atoms in synthesis.

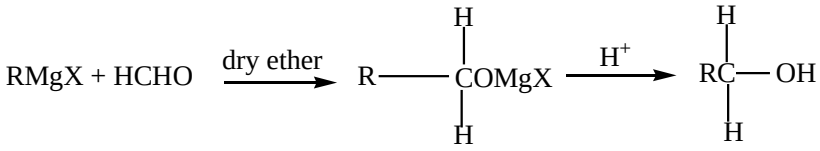
(i) Gridnard's reagent reacts with carbon dioxide to produce carboxylic acid. The parent chain increase by one carbon atom.



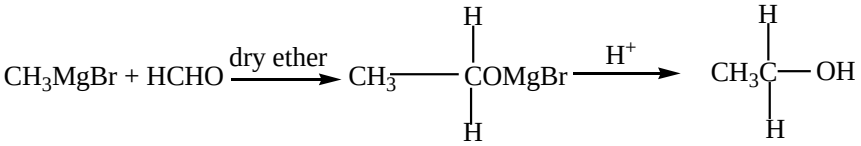
Example



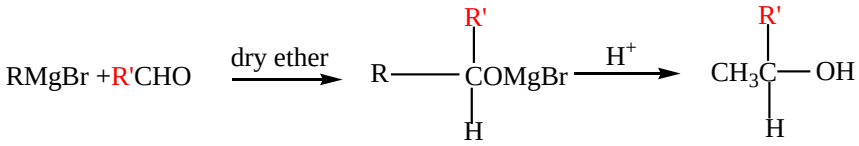
(ii) Gridnard's reagent reacts with methanal to produce primary alcohols. The parent chain increase by one carbon atom.



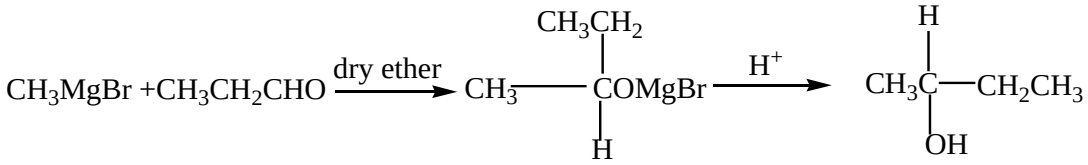
Example 9



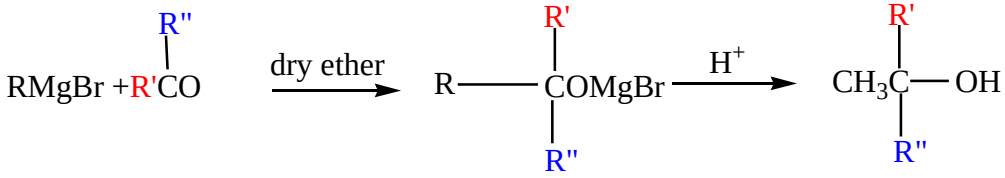
(iii) Gridnard's reagent reacts with aldehydes to produce secondary alcohols.



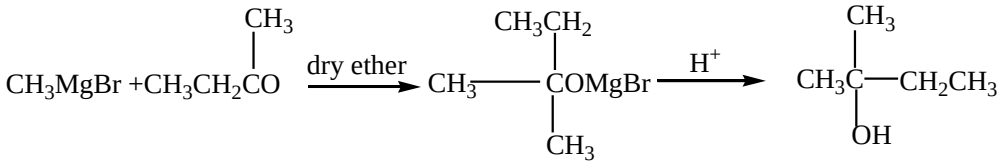
Example 10



(iv) Gridnard's reagent reacts with ketones to produce secondary alcohols.



Example



Uses alkyl halides in industrial processes

(i) **Solvents:** They are used as solvents in chemical reactions and for cleaning and degreasing, especially for non-polar compounds.

(ii) **Refrigerants and propellants:** Some alkyl halides, like CFCs, were historically used as refrigerants and aerosol propellants.

(iii) **Chemical synthesis:** They are crucial intermediates in the production of a vast number of other compounds, including pharmaceuticals, pesticides, and polymers like polyvinyl chloride and Teflon.

(iv) **Flame retardants:** Certain alkyl halides, particularly those containing bromine and fluorine, are used in fire retardants and fire extinguishers.

(v) **Cleaning agents and other products:** They are used in commercial cleaning agents, paint removers, and other specialty chemicals.

Environmental damage caused by alkylhalides:

- **Ozone depletion:** Chlorofluorocarbons (CFCs), a type of alkyl halide, are responsible for destroying the ozone layer.
- **Global warming:** Some volatile alkyl halides act as greenhouse gases with a high global warming potential.
- **Pollution:** Many halocarbons are serious pollutants that can persist in the environment. For example, DDT, an aryl halide, is not biodegradable and can harm the ecosystem.

Human health risks due to alkylhalides:

- Some alkyl halides can be toxic, and their use requires careful handling and risk mitigation.

Benefits of alkylhalides in medicine:

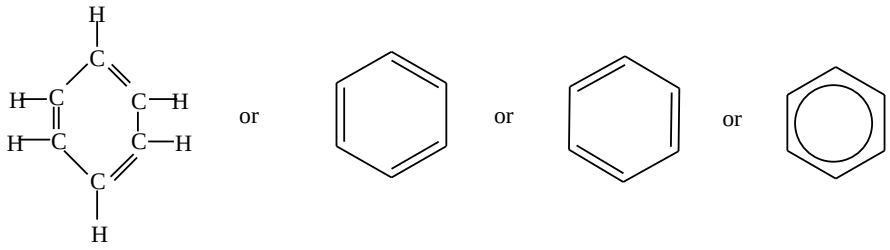
- The pharmaceutical industry uses alkyl halides to synthesize medicines. Approximately 20% of small molecule pharmaceuticals and 30% of all chemicals contain a halogen.
- Some alkyl halides are used as anesthetics.

Benzene

Chemical formula: C_6H_6.

Structure

Benzene is a cyclic compound with delocalized conjugated double bonds, i.e. the double bond is free to shift from one place to another through the whole molecule.



Effect of delocalization of double bond in to the structure of benzene.

(i) Benzene ring is very stable that it is preserved in most chemical reaction, that is, it's is generally unreactive towards electrophilic reagents.

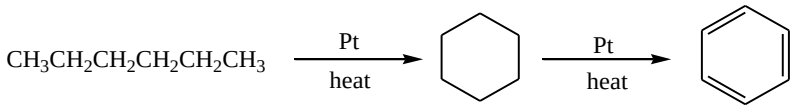
(ii) The six carbon-carbon bonds in the benzene are equal in length (i.e. 1.39Å) intermediate between the carbon-carbon double bond (1.34 Å) and carbon-carbon single bond (1.54 Å)

Physical properties

a. It is a colorless with a characteristic aromatic smell.
b. It is insoluble in water but soluble in organic solvents and its self is a good solvent.
c. It burns with a smoky and luminous flame

Industiral preparation

Benzene is obtained by catalytic dehydration of hexane (from petroleum)



Chemical properties

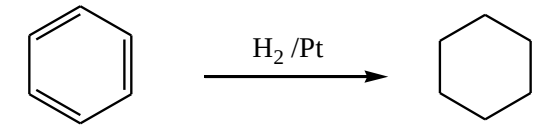
Benzene is not easily attacked by electrophilic reagents. In its reactions, benzene undergoes mostly electrophilic substitution reaction in which an electrophile substitutes a hydrogen atom, rather than addition reactions in which the benzene ring system would be destroyed.

Reactions

1. **Combustion**
   Benzene reacts with oxygen to form carbon dioxide and water only.
   $2C_6H_6 + 15O_2 \longrightarrow 12CO_2 + 6H_2O$
   In insufficient oxygen benzene is oxidized to water and carbon producing a smoky flame (test for aromaticity)
   $2C_6H_6 + 3O_2 \rightarrow 6C(s) + 6H_2O$

2. Catalytic hydrogenation

Benzene undergoes catalytic hydrogenation to cyclohexane



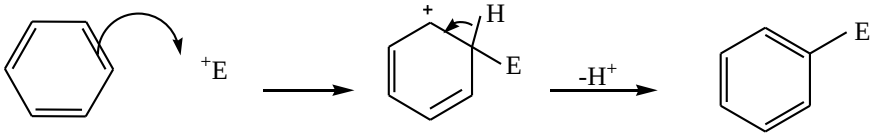
Benzene Cylohexane

The heats of hydrogenation and combustion of benzene are lower (by 36kcal/mole) than expected. In other words, benzene is more stable by 30kCal than we would expect cyclohexatriene to be. The 36kCal is the benzene stabilization energy or resonance energy.

3. Aromatic electrophilic substitution reaction

Here an electrophile substitutes a hydrogen atom on a benzene ring.

General mechanism

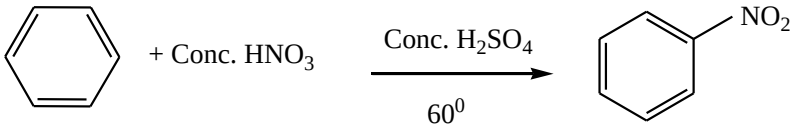


Benzene

a. Nitration

This is the introduction of the nitro group on the benzene ring using a hot mixture of concentrated sulphuric acid and concentrated nitric acid.

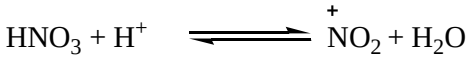
Example 11



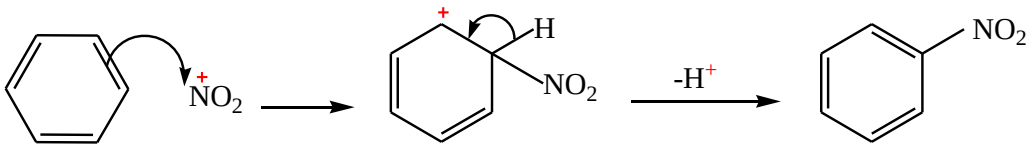
Benzene Nitrobenzene, yellow liquid

The formation of a yellow liquid of nitrobenzene when benzene is reacted with a mixture of concentrated nitric acid and concentrated sulphuric acid distinguishes benzene from cyclohexane,

Mechanism



then,



Uses

Approximately 95% of nitrobenzene is consumed in the production of aniline, which is a precursor to rubber chemicals, pesticides, dyes (particularly azo dyes), explosives, and pharmaceuticals.

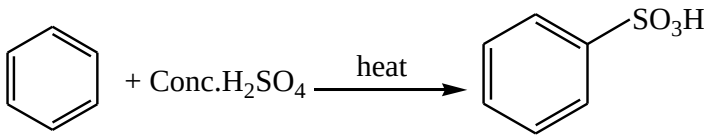
Specialized applications

Nitrobenzene is also used to mask unpleasant odors in shoe and floor polishes, leather dressings, paint solvents, and other materials. Redistilled, as oil of mirbane, nitrobenzene has been used as an inexpensive perfume for soaps. A significant merchant market for nitrobenzene is its use in the production of the analgesic paracetamol (also known as acetaminophen) . Nitrobenzene is also used in Kerr cells, as it has an unusually large Kerr constant.

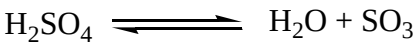
b. Sulphonation

This is the introduction of the sulphonic group ($-SO_3H$) on to the benzene ring. It's done by heating benzene with concentrated suphuric acid. A process for the sulphonation of benzene comprises passing benzene vapor into sulphuric acid, the initial temperature of which is between about 95 and about 110^0C.

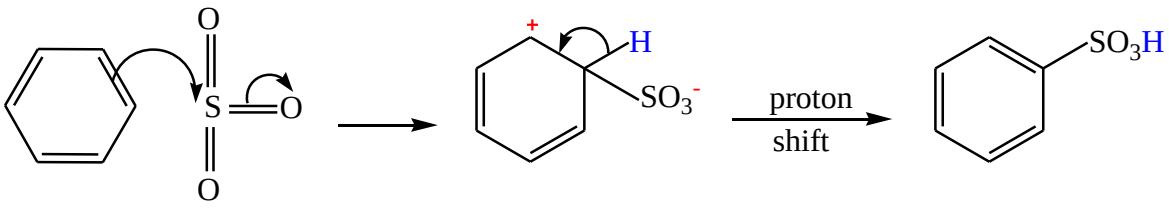
Example 12



Mechanism



then,



Benzene sulphonic acid is a coloress crystalline compound that is soluble in water.

Uses of benzene sulphonic

Benzensulfonic acid is commonly used as the active ingredient in laundry detergent used in clothes washing machines.

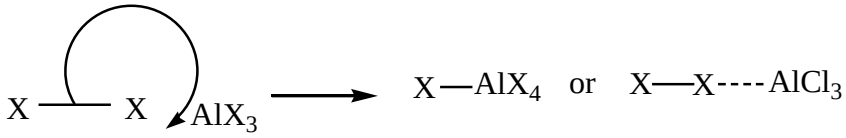
A variety of pharmaceutical drugs are prepared as benzenesulfonate salts and are known as besilates (INN) or besylates(USAN).

In a diluted form, it is also used as a polymer remover /stripping agent.

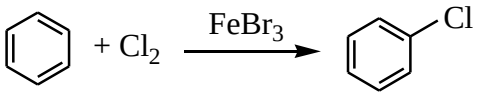
Benzenesulfonic acid and related compounds undergo desulfonation when heated in water near 200 °C. The temperature of desulfonation correlates with the ease of the sulfonation:
$C_6H_5SO_3H + H_2O \rightarrow C_6H_6 + H_2SO_4$

c. Halogenation

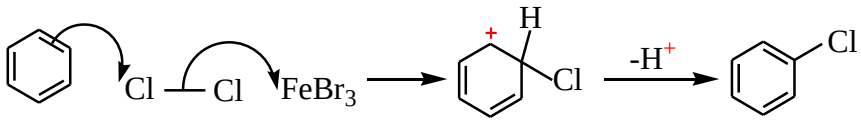
This requires the use of electron carriers ($AlCl_3$, FCl_3) as catalysts. The electron carrier is usually a halide of iron or aluminium, the electron carriers' function is to polarize the halogen molecule by withdrawing the electrons from the bond between the two halogen atoms.



Example 12



Mechanism

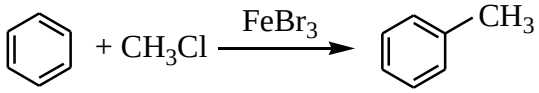


Chlorobenzene was historically important in the manufacture of chlorinated pesticides, especially DDT, and in the production of phenol and aniline. Monochlorobenzene's principal current use is as a chemical intermediate in the production of chemicals such as nitrochlorobenzenes and diphenyl oxide. These chemicals are subsequently used in the production of herbicides, dyestuffs, and rubber chemicals. Additionally, monochlorobenzene is used as a solvent in degreasing processes (e.g., in metal cleaning operations), paints, adhesives,waxes and polishes.

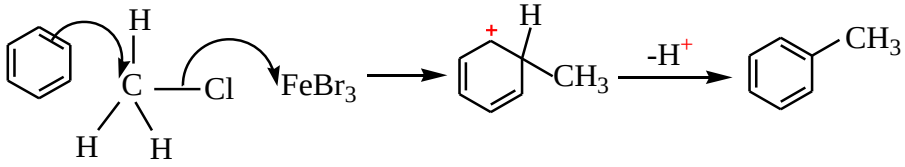
d. Friedel –Craft alkylation

This is a reaction of benzene with an alkyl halide to give an alkyl benzene

Example 13



mechanism

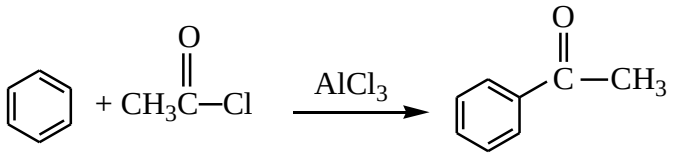


The majority of toluene/methylbenzene is used as a component of petrol. It is also used in paints, lacquers, inks, adhesives, rubber, and cleaning agents. It is used to manufacture benzene, urethane raw materials, and other organic chemicals. It is used in the production of pharmaceuticals, dyes, and cosmetic nail products.

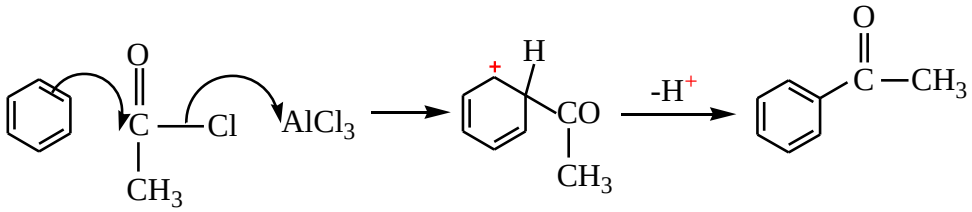
e. Friedel –Craft acylation

This is the introduction of an acylo group (-OCR) to the benzene ring. The reaction is carried out by reacting benzene with an acid halide in presence of an electron carrier.

Example 14



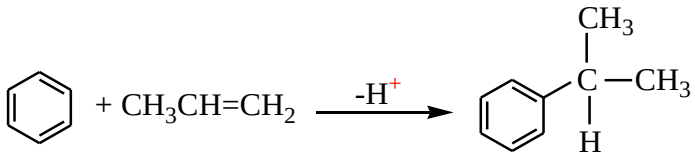
Mechanism



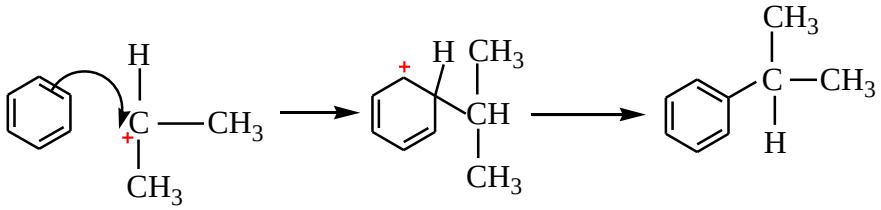
f. Reaction with alkene

In the presence of an acid benzene react with alkenes to form alkylbenzene.

Example 15



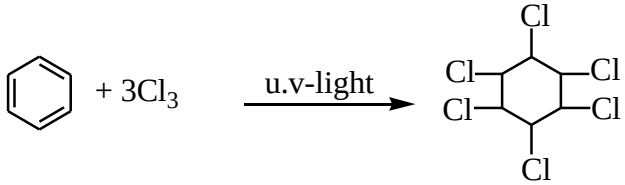
MECHANISM



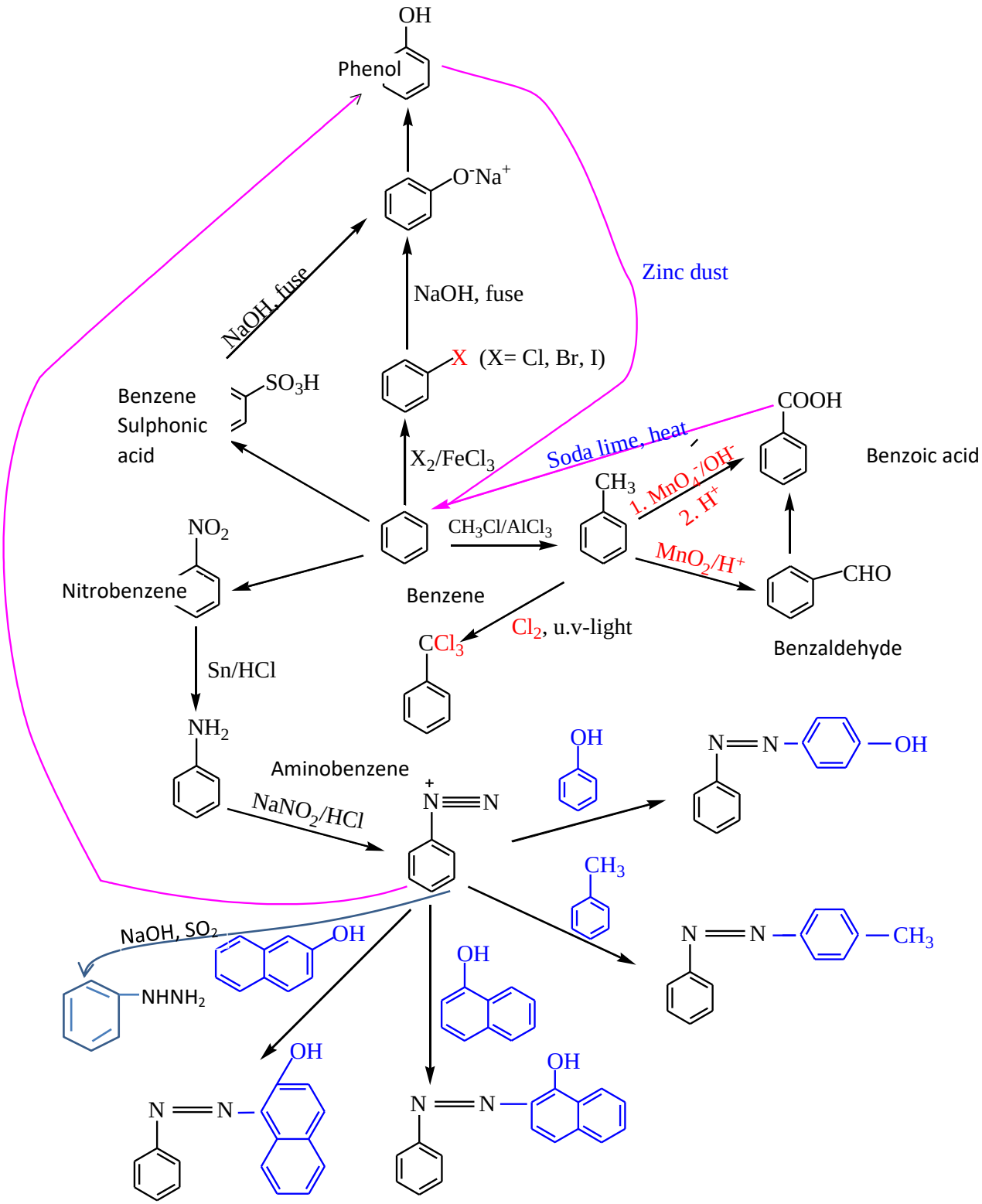
4. Other reactions

a. Halogenation in the presence of u.v-light

Benzene reacts with chlorine by addition reaction to form saturated product; 1,2,3,4,5,6-hexachlorohexane



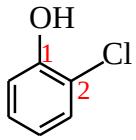
Derivatives of benzene



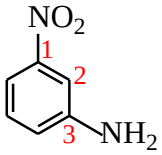
Nomenclature of derivatives of benzene with more than one substituent.

Number the carbon atoms on the ring and include the position(s) of the groups in the name.

Example 16



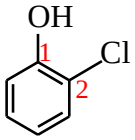
2-Chlorophenol



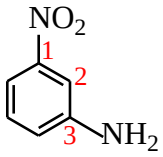
3-aminonitrobenzene

The prefixes; ortho, meta and para- usually abbreviated as o-, m-, and p- may be used for describing the relative positions of substituents in a di-substituted benzene.

Example 17



2-Chlorophenol
Or o-chlorophenol



3-aminonitrobenzene
Or m-aminonitrobenzene

Effects of substituent group on the reactivity of the ring

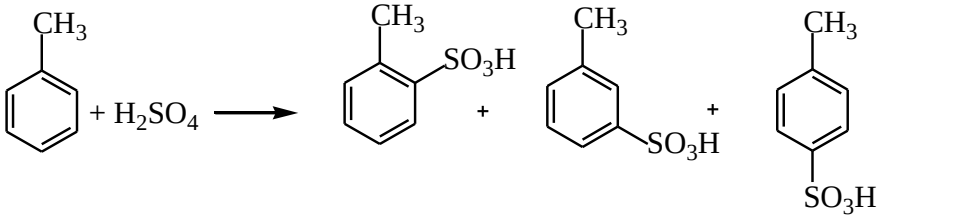
A group attached to the benzene ring may have either of the two effects:

(i) Groups (such alkyl groups) that donate electrons to the benzene ring make the ring more reactive towards electrophilic substitution reaction

(ii) Groups that donate electrons to the benzene ring like alkyl group that those with at least one lone pair of electron (-NH_2, -OH, Cl, Br) direct the incoming groups to position 2 or postion 4. For this reason they are described as 2, 4-directiong grousps

Example 18

e.g. sulphonation of methylbenzene.

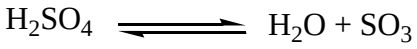


o-toluene sulphonic acid 32%

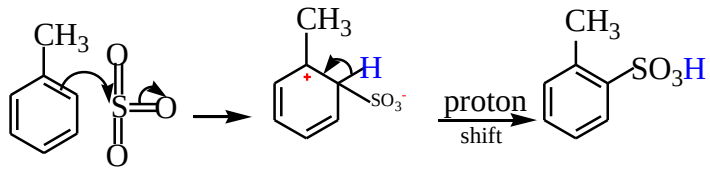
m-toluene sulphonic acid 6%

p-toluene sulphonic acid 62%

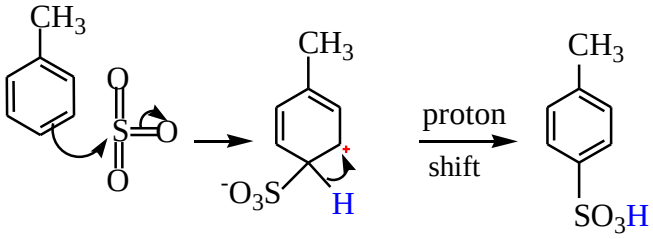
Mechanism



Then,

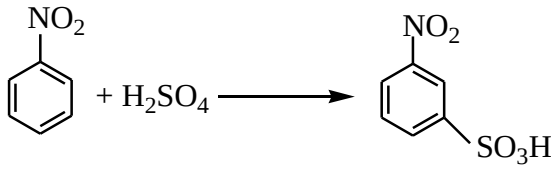


Or

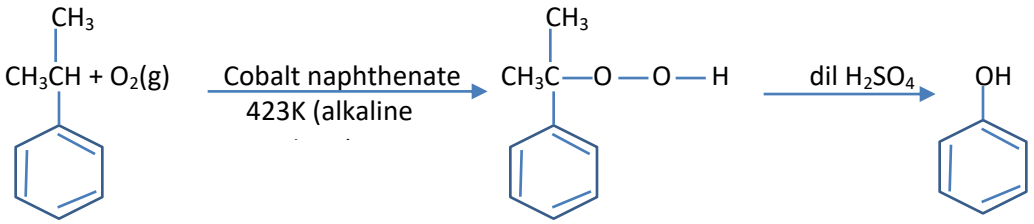


(iii) Groups that withdraw electron from benzene ring such as nitro or carboxylic groups, make the ring less reactive torwards electrophilic reagent. They the direct the incoming group to position 3 and are called meta directing groups.

Example 19



Preparation of phenol form cumene or 2-phenylpropane



The environmental and health impacts of benzene derivatives

Environmental impacts

(i) **Air pollution:** Benzene can react with other chemicals to form smog in the atmosphere.

(ii) **Water and soil contamination:** Benzene can contaminate water and soil through spills, leaks, or atmospheric deposition via rain and snow.

(iii) **Ecological damage:** Benzene and other hydrocarbons can directly harm aquatic organisms, damage habitats, and persist in sediments, leading to bioaccumulation in the food chain.

Health impacts

(i) **Acute effects:** Short-term exposure to high levels can cause headaches, dizziness, confusion, a rapid heart rate, and even death. It can also cause skin and eye irritation.

(ii) **Chronic effects:** Long-term exposure can lead to serious health problems, including:

- **Blood disorders:** A reduction in red and white blood cells, leading to conditions like aplastic anemia, anemia, and thrombocytopenia.
- **Cancer:** Benzene is a known human carcinogen, and chronic exposure is linked to leukemia and other blood-related cancers.
- **Immune system damage:** Exposure can weaken the immune system, making the body more susceptible to infection.

(iii) **Reproductive and developmental effects:** Studies in pregnant animals have shown that benzene can cause low birth weight, delayed bone formation, and bone marrow damage. The effects on human reproduction are not fully understood but are a concern.

Thank you
Dr. Bbosa Science