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Aromatic compounds

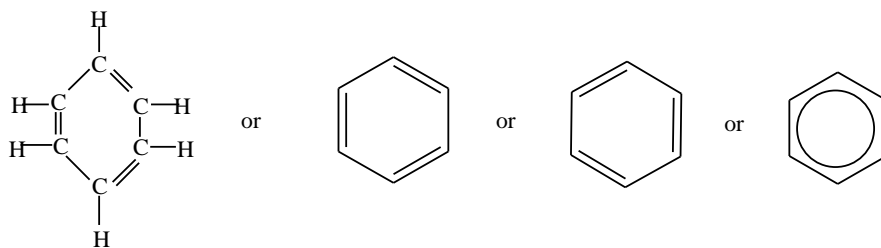
These include benzene and compounds that resemble benzene in chemical behavior.

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.

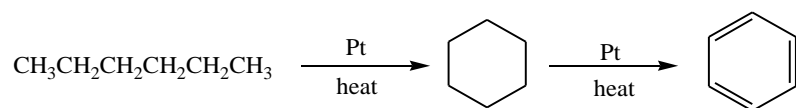
- Benzene ring is very stable that it is preserved in most chemical reaction, that is, it's is generally unreactive towards electrophilic reagents.
- The six carbon-carbon bonds in the benzene are equal in length (i.e. 1.39\AA) intermediate between the carbon-carbon double bond (1.34\AA) and carbon-carbon single bond (1.54\AA)

Physical properties

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

Industrial 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.

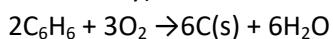
Reactions

1. Combustion

Benzene reacts with oxygen to form carbon dioxide and water only.

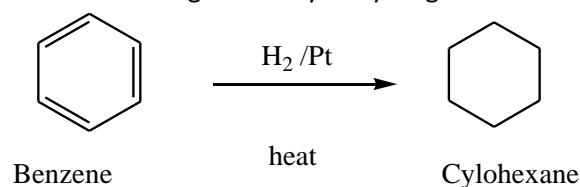


In insufficient oxygen benzene is oxidized to water and carbon producing a smoky flame (test for aromaticity)



2. Catalytic hydrogenation

Benzene undergoes catalytic hydrogenation to cyclohexane

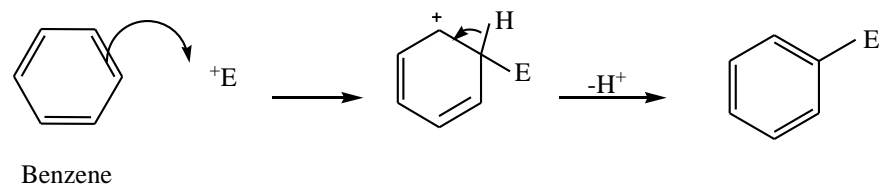


The heats of hydrogenation and combustion of benzene are lower (by 36kcal/mole) than expected. In other words, benzene is more stable by 30kCal than we would expect cyclohexatriene to be. The 36kCal is the benzene stabilization energy or resonance energy.

3. Aromatic electrophilic substitution reaction

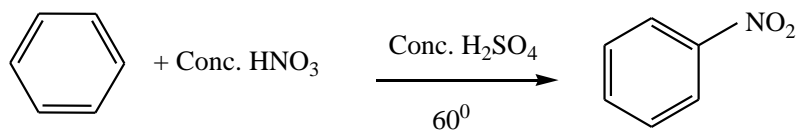
Here an electrophile substitutes a hydrogen atom on a benzene ring.

General mechanism



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.

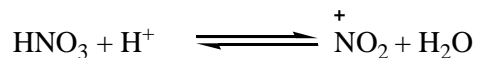


Benzene

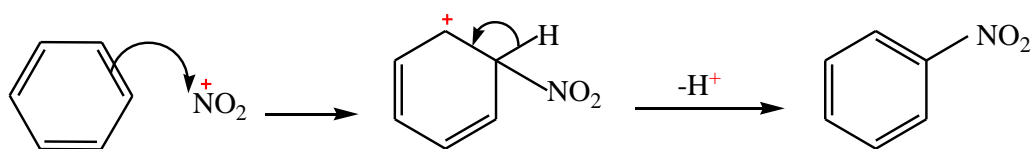
Nitrobenzene, yellow liquid

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

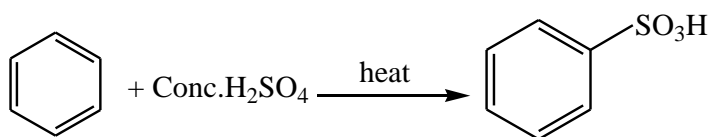
Approximately 95% of nitrobenzene is consumed in the production of aniline, which is a precursor to rubber chemicals, pesticides, dyes (particularly azo dyes), explosives, and pharmaceuticals.

Specialized applications

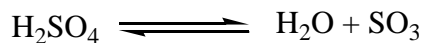
Nitrobenzene is also used to mask unpleasant odors in shoe and floor polishes, leather dressings, paint solvents, and other materials. Redistilled, as oil of mirbane, nitrobenzene has been used as an inexpensive perfume for soaps. A significant merchant market for nitrobenzene is its use in the production 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

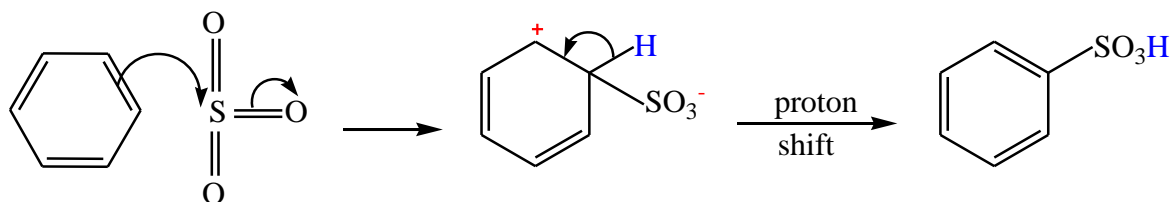
This is the introduction of the sulphonic group (-SO₃H) on to the benzene ring. It's done by heating benzene with concentrated sulphuric acid. A process for the sulphonation of benzene comprises passing benzene vapor into sulphuric acid, the initial temperature of which is between about 95 and about 110°C.



Mechanism



then,



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

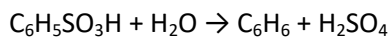
Uses

Benzenesulfonic 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).

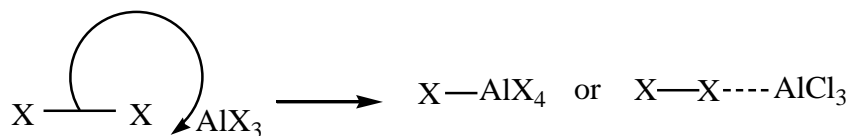
In a diluted form, it is also used as a polymer remover /stripping agent.

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:

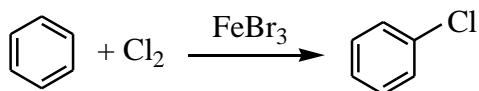


c. Halogenation

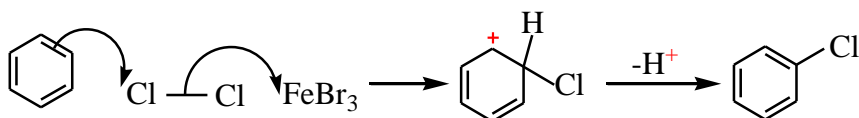
This requires the use of electron carriers (AlCl₃, FeCl₃) as catalysts. The electron carrier is usually a halide of iron or aluminium, the electron carriers' function is to polarize the halogen molecule by withdrawing the electrons from the bond between the two halogen atoms.



Example



Mechanism

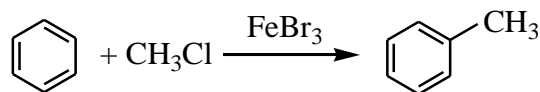


Chlorobenzene was historically important in the manufacture of chlorinated pesticides, especially DDT, and in the production of phenol and aniline. Monochlorobenzene's principal current use is as a chemical intermediate in the production of chemicals such as nitrochlorobenzenes and diphenyl oxide. These 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.

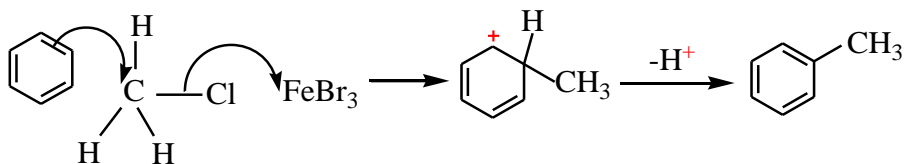
d. Friedel –Craft alkylation

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

Example



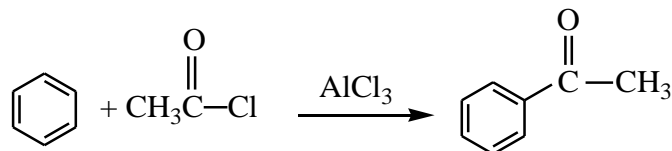
mechanism



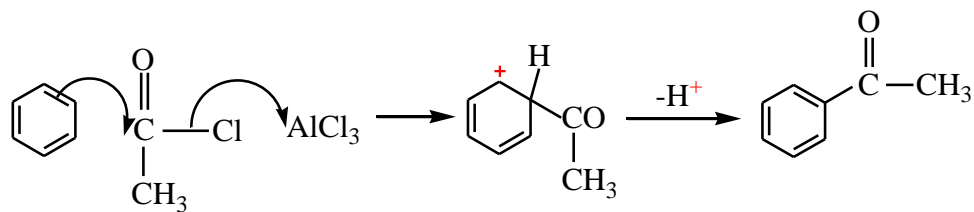
The majority of toluene/methylbenzene is used as a component of petrol. It is also used in paints, lacquers, inks, adhesives, rubber, and cleaning agents. It is used to manufacture benzene, urethane raw materials, and other organic chemicals. It is used in the production of pharmaceuticals, dyes, and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

e. 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 a halogen carrier.

Example

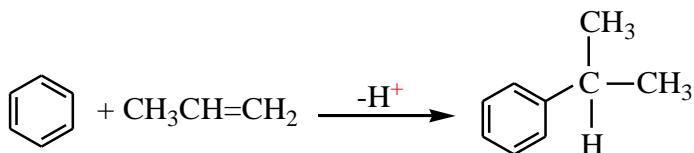


Mechanism

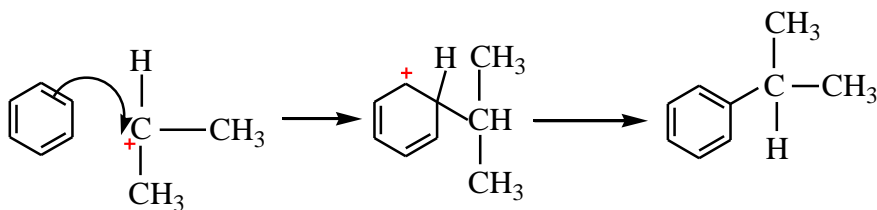


f. Reaction with alkene

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



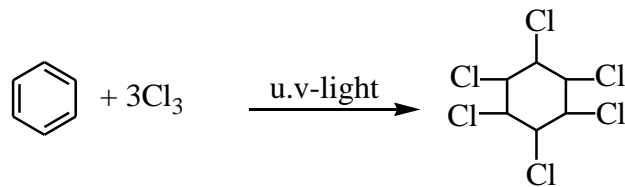
MECHANISM



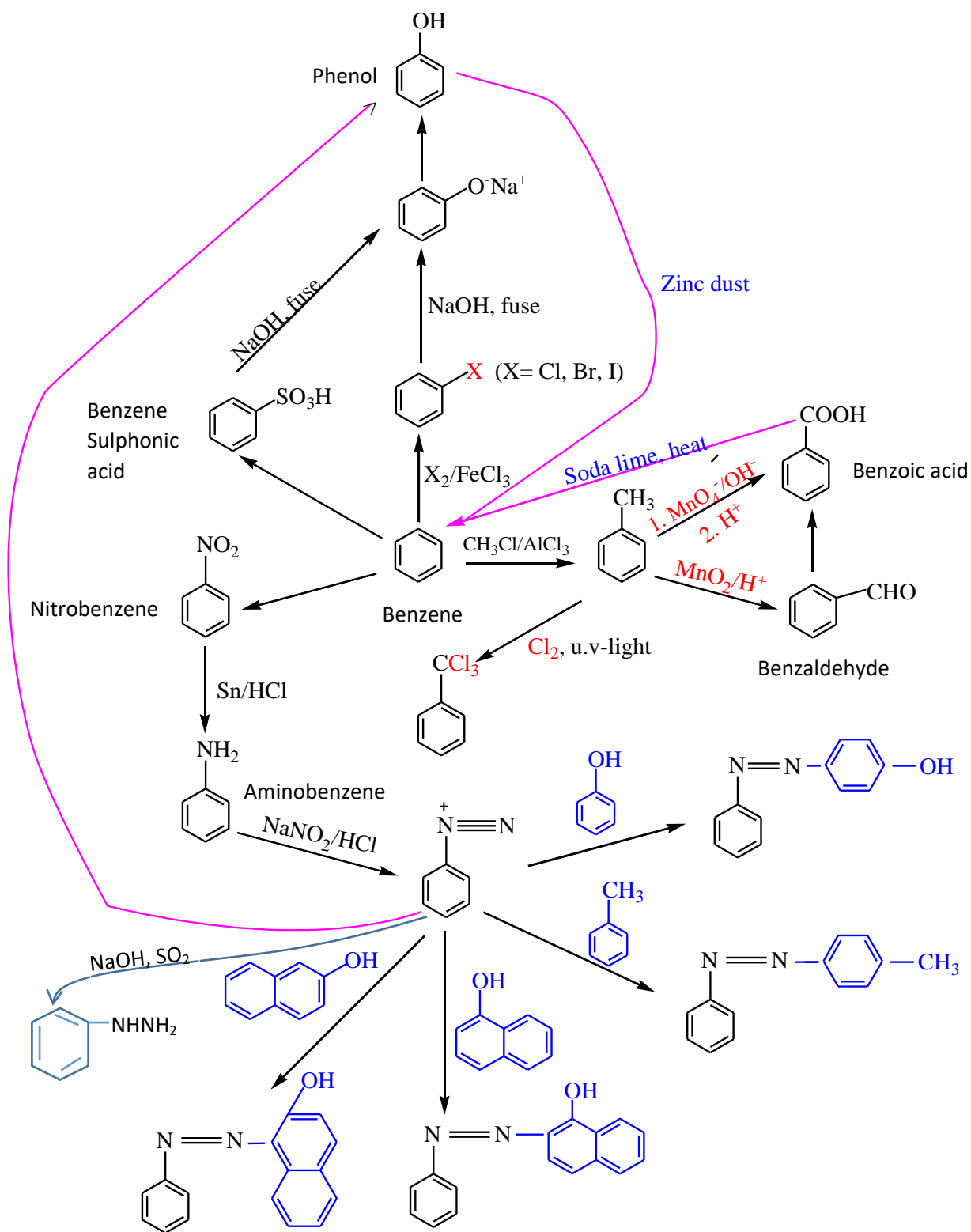
4. Other reactions

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

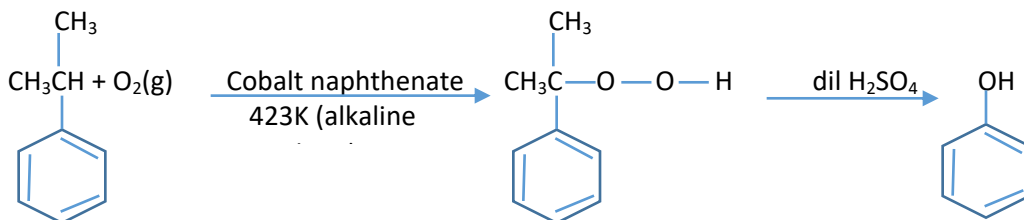
Benzene reacts with chlorine by addition reaction to form saturated product;
1,2,3,4,5,6-hexachlorohexane



Derivatives of benzene



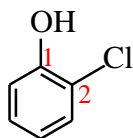
Preparation of phenol from cumene or 2-phenylpropane



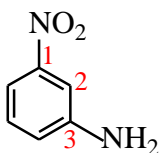
Nomenclature of derivatives of benzene with more than one substituent.

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

Examples



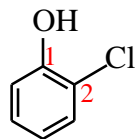
2-Chlorophenol



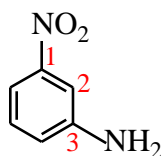
3-aminonitrobenzene

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



2-Chlorophenol
Or o-chlorophenol



3-aminonitrobenzene
Or m-aminonitrobenzene

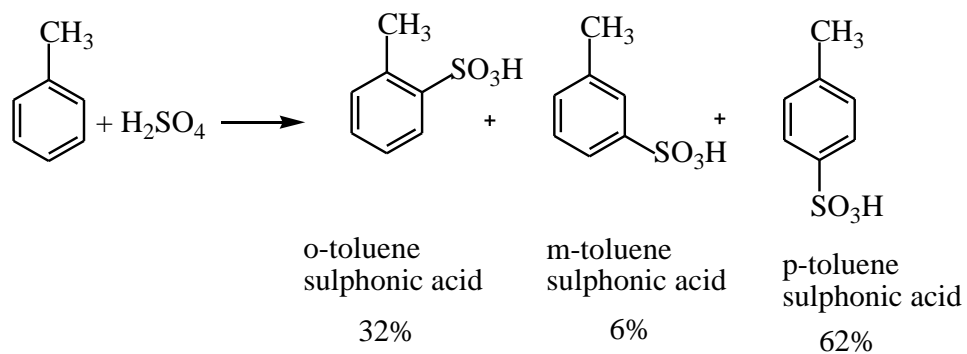
Effects of substituent group on the reactivity of the ring

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

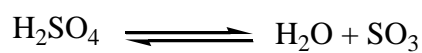
- Groups (such alkyl groups) that donate electrons to the benzene ring make the ring more reactive towards electrophilic substitution reaction
- Groups that donate electrons to the benzene ring like alkyl group that those with at least one lone pair of electron (-NH₂, -OH, Cl, Br) direct the incoming groups to position 2 or position 4. For this reason they are described as 2, 4-directioning groups

Example

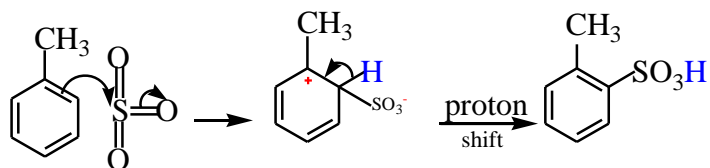
e.g. sulphonation of methylbenzene.



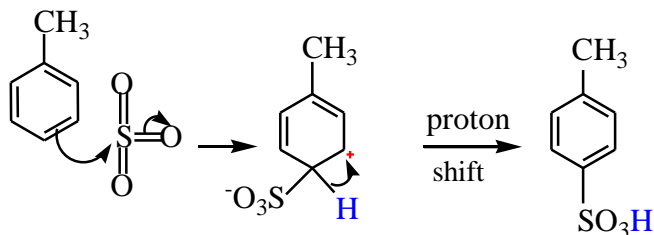
Mechanism



Then,

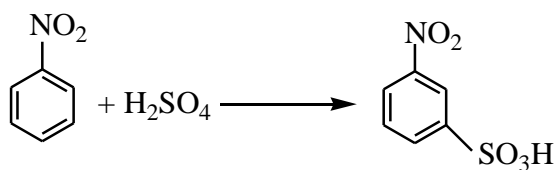


Or



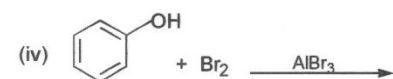
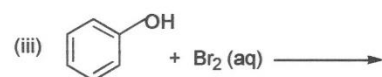
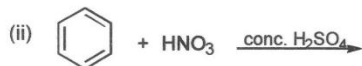
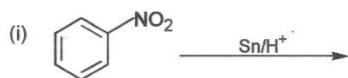
- (iii) Groups that withdraw electron from benzene ring such as nitro or carboxylic groups, make the ring less reactive towards electrophilic reagent. They direct the incoming group to position 3 and are called meta directing groups.

Example



Exercise

- (a) What property of benzene and its derivatives are classified as "aromatic".
- (b) Write a formula of benzene suggested by F.A Kekulé. what advantage and disadvantage of this formula.
- (c) Give explanation to "aromatic" properties of benzene in light of modern concepts of its structure.
- (d) Complete the following equations and give the mechanisms for the reactions.



2. (a) Compare the mechanism of electrophilic addition to alkenes with that of electrophilic substitution in the aromatic series, using the reaction of ethene and benzene with bromine. At what stages do the differences show and why?

(b) Explain why the groups $-\text{NO}_2$ and $-\text{CHO}$ should be meta-directors and have deactivating properties.

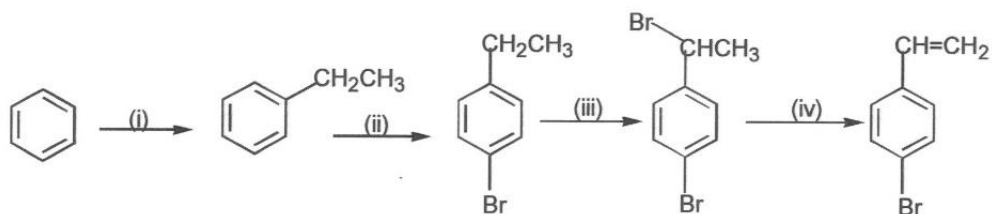
© Why are ortho and para isomers formed in the ratio of 7:9 in chlorination of chlorobenzene and 1:2 in bromination of chlorobenzene.

Answers

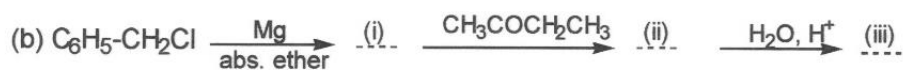
2a) The first stage, consisting in the action of electrophilic reagent Br^+ is similar to ethene and benzene. The corresponding carbonium ion is formed in each case. The main difference between aromatic substitution and electrophilic addition to alkenes consist in the cause of the second stage. σ -complex is stabilized by ejection of H^+ since an aromatic compound is thus formed, which is advantageous from the energy view point. The carbonium ion formed from ethene reacts with the nucleophilic reagent since this evolves deprotonization-the process that is less advantageous from the energy point of view.

2 (c) The ratio of ortho to para isomers depends on the volume of the entering substituent. the bulky bromine atom makes the ortho substitution difficult.

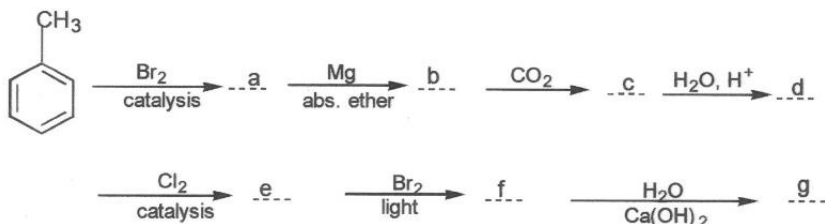
3. What reagents can be used to accomplish the following conversions.



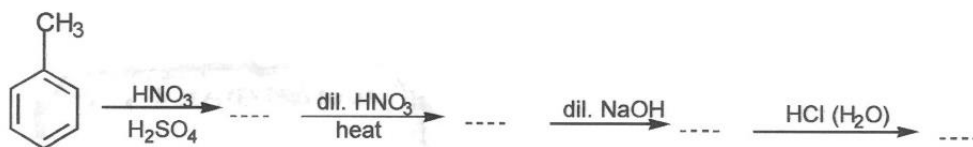
4. Complete the following:



5. What compounds are formed by the following conversion.



6. Complete the following.



7. Write structural formulas of the intermediate and products in the following



8. Name one reagent that can be used to distinguish between each of the following pair of compounds. In each case state what would be observed if each member of the pair is treated with the reagent and write the equation for the reaction.



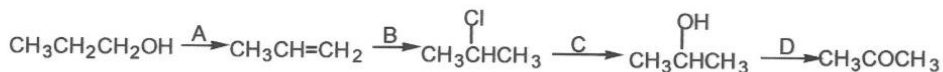
9. A compound P, $\text{C}_4\text{H}_8\text{Br}_2$ can be converted to Q, $\text{HC}\equiv\text{C}-\text{CH}_2\text{CH}_3$.

(a) write the structural formula and the IUPAC name of P.

(b) (i) State the reagent(s) and conditions that can be used to convert P to Q.

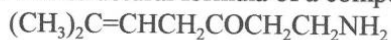
(ii) Write a mechanism for the reaction in b(i) above.

10. Propanone can be prepared from propan-1-ol according to the following scheme:



Identify the reagents A, B, C, and D and state the conditions and write the mechanism for each stage of reaction.

11. The structural formula of a compound Q is shown below:



a. Name the functional groups present in Q.

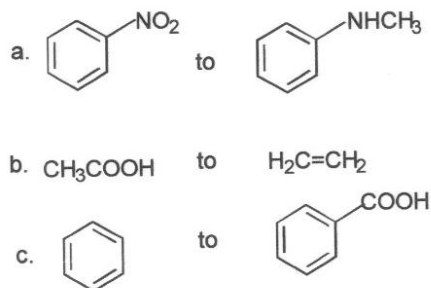
b(i). State what would be observed and write an equation for the reaction between Q and

* bromine water.

** Nitrous acid

*** Brady's reagent (2,4-dinitrophenylhydrazine).

12.(a) Write equations to show how the following conversion can be carried out, indicate the reagents and the conditions for the reaction.



(b) write equations, state the conditions and indicate a mechanism for a reaction in which ethanol react differently from phenol.

(c) Write equations to show how phenol can be prepared from benzene and chlorine on industrial scale.

13. Write equations to show how sulfuric acid reacts with each of the following compounds. In each case indicate the conditions for the reaction.

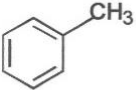
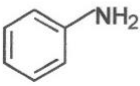
- Ethene
- Benzene
- Ethane-1,2-dioic acid.

14. A compound X, $\text{C}_4\text{H}_{10}\text{O}$, forms two layers after 5 minutes when reacted with Conc. HCl in presence of anhydrous ZnCl_2 . X changes the color of acidified potassium dichromate (vi) from orange to green.

- write the structural formula and the IUPAC name of X
- Write equation for the reaction between X and acidified potassium dichromate (vi) solution.
- Write equations to show how you would prepare X using an alkene as one of the starting material. Indicate the conditions for the reaction.

15. Propanone was used as one of the starting materials in manufacture of polypropene.

- write equation to show how propanone can be converted to propene and indicate the conditions for the reactions.
- Outline a mechanism for the reaction that lead to the formation of propene in (a)
- Write an equation for conversion of propene to polypropene.
- Name the type of polymerization in (c)
- State one structural feature that is essential for a molecule to undergo polymerization you have named in (d).

16. Both ethanol and phenol(hydroxybenzene) contain a common functional group.
- (i) Name one reagent that can be used to distinguish the two compound.
(ii) state what would be observed if each of the compounds is treated with the reagent you have named.
 - An aqueous solution of phenol is acidic to litmus whereas that of ethanol is neutral. Explain the observation.
 - Phenol and ethanol react with ethanoyl chloride to give a similar product.
 - Write equation for the reaction and name the organic product in each case.
 - outline the mechanism for the reaction between phenol and ethanoyl chloride .
17. Write equations to show how each of the following compounds, can be synthesized from the reagents on the left. Indicate the reagents and conditions for the reactions.
- $\text{CH}_3\text{C}\equiv\text{CH}$ from $\text{CH}_3\text{CH}=\text{CH}_2$
 - CH_3COOH from $\text{H}_2\text{C}=\text{CH}_2$
 - 
 from Benzoic acid
 - 
 from Benzoic acid
 - $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ from Chloroethane
- 18 (a) A compound Y contains carbon, 66.7% and hydrogen, 11.1%, the rest being oxygen. Determine the empirical formula of Y.
- The vapor density of Y is 36, determine the molecular formula. (Hint. Molecular mass is twice the vapor density)
 - Y reacts with 2,4-dinitrophenylhydrazine to form a yellow precipitate. Write the formulae and systematic names of all isomers of Y.
 - When Y is reacted with iodine in the presence of NaOH, a yellow precipitate is formed.
 - which one of the structures you gave in (c) is the structure of Y
 - Name the yellow precipitate formed.
 - write the equation for the reaction.

