B.Sc. I Paper-II (Organic Chemistry)

Lecture-1

Aromatic Hydrocarbons

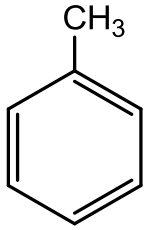
Dr A. K. Yadav
Assistant Professor-Chemistry
Maharana Pratap Government P. G. College, Hardoi, (U.P.)

Introduction

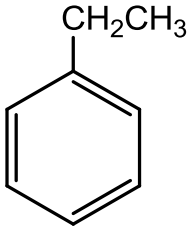
Benzene and its alkyl substituted homologues are known as aromatic hydrocarbons or arenes.

General Formula: C_nH_{2n-6}

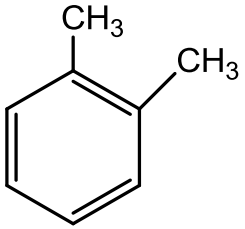
Benzene



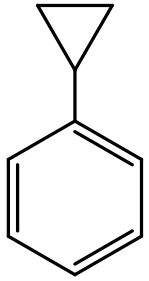
Toluene



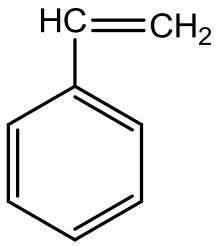
Ethyl benzene



o-Xylene



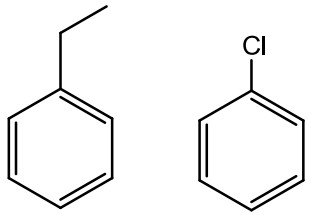
Cyclopropyl Benzene



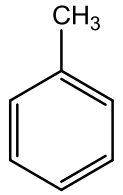
Vinyl Benzene

Nomenclature

- The root word for benzene derivative is Benzene in both IUPAC and common name
- When only one substituent is attached to benzene

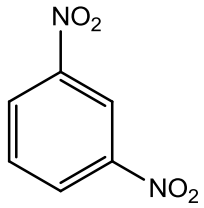


- Special name to monosubstituted benzene



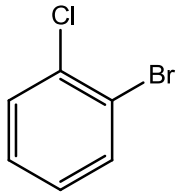
Toluene

- When two similar substituent attached



m-Dinitrobenzene

- When two dissimilar substituent attached

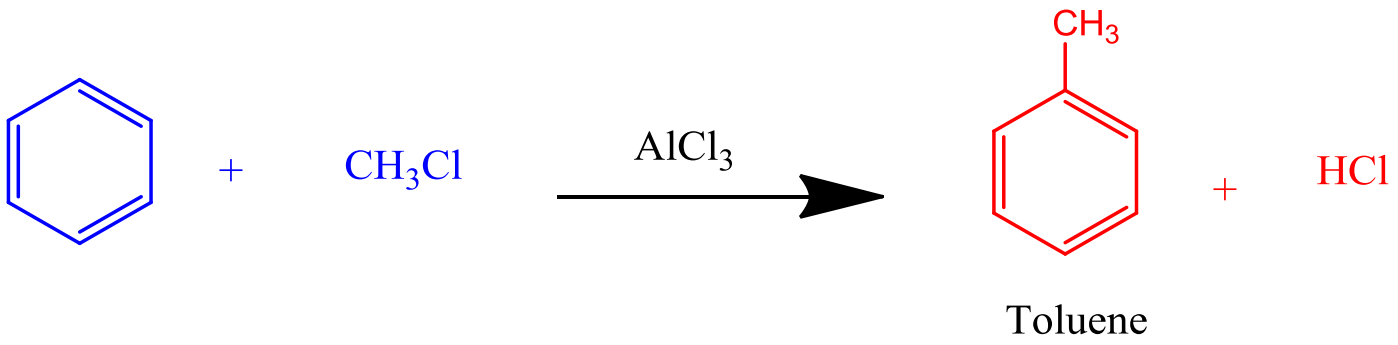


o-Bromochlorobenzene

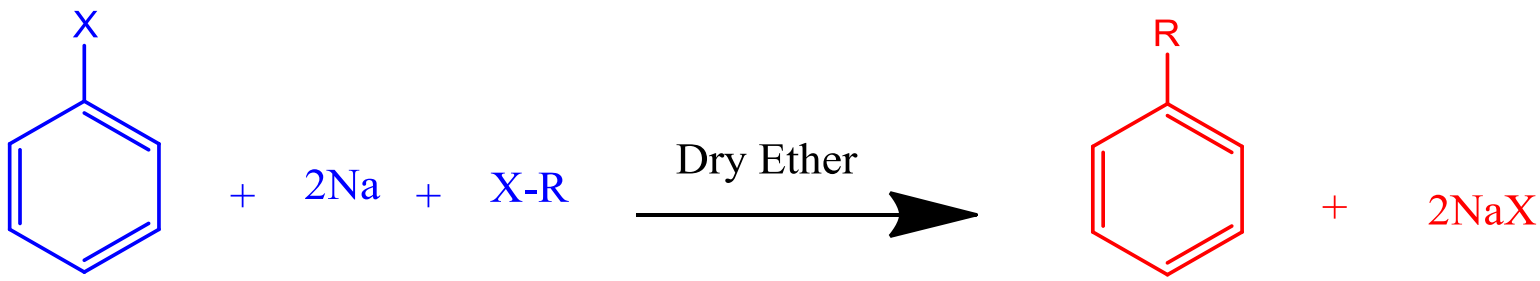
Preparation of Aromatic Hydrocarbons

- Friedel-Crafts Alkylation
- Wurtz-Fittig reaction
- Reduction of acylbenzenes
- Hydrogenation of alkenylbenzenes

Friedel-Crafts Alkylation

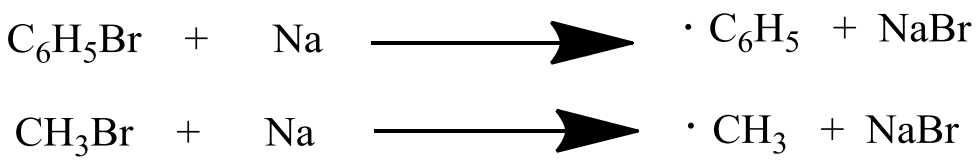


Wurtz-Fittig reaction

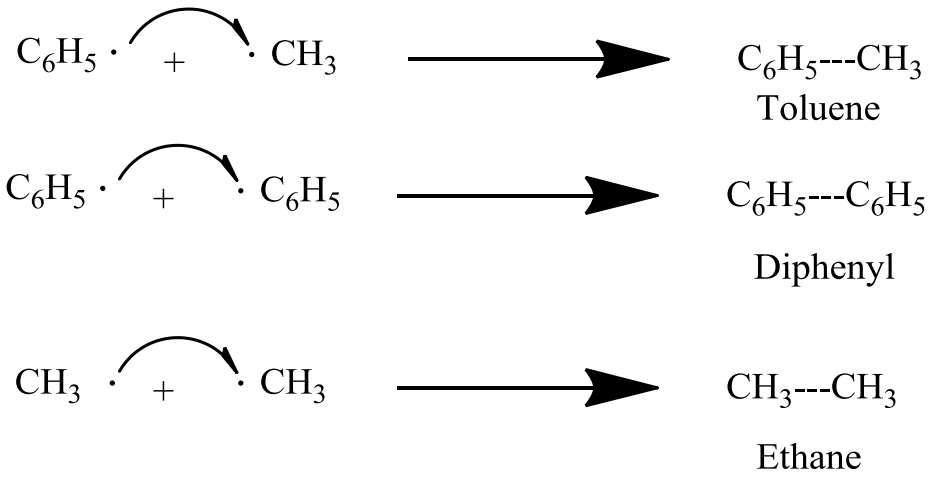


Mechanism :

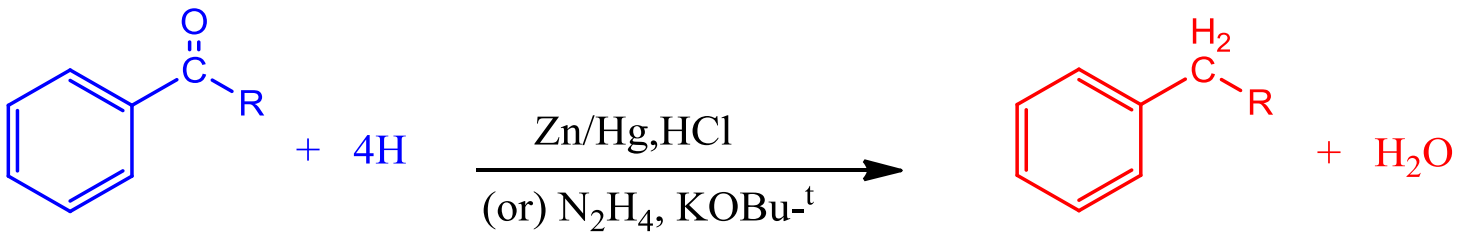
Step:1 Formation of free radicals:



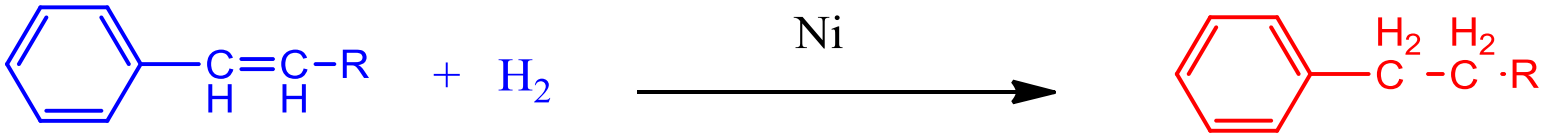
Step:2 Carbon-Carbon coupling of free radicals:



Reduction of acylbenzenes



Hydrogenation of alkenylbenzenes



General Physical Properties

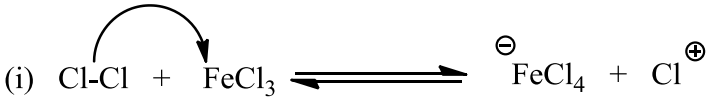
- Alkylbenzenes are all colourless liquids with a characteristic odour
- Lighter than water
- Non-polar
- Miscible with non-polar solvents like petroleum ether, CCl_4 etc.
- M.P. and B.P. show the usual regular gradation
- Inflammable and burns with sooty flame

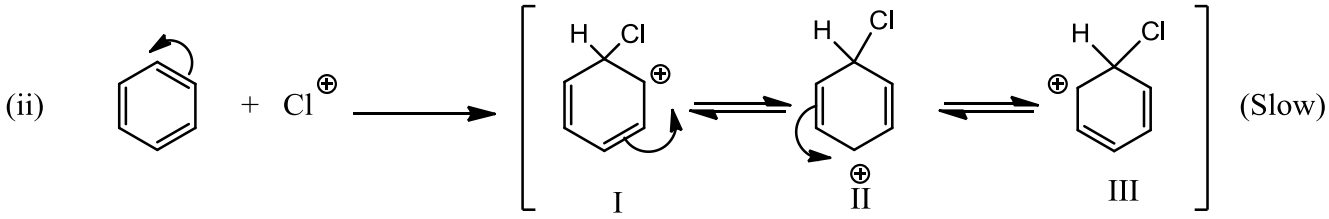
General Chemical Properties

A. Electrophilic aromatic substitution reactions

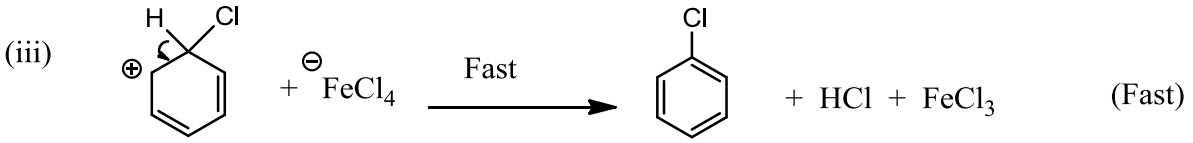
1. Halogenation:

Mechanism:



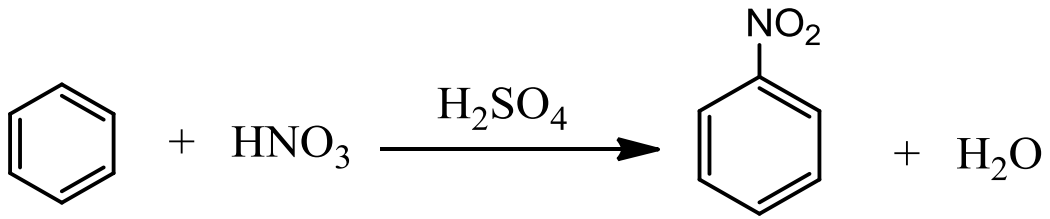


Resonance Stabilized Carbocation

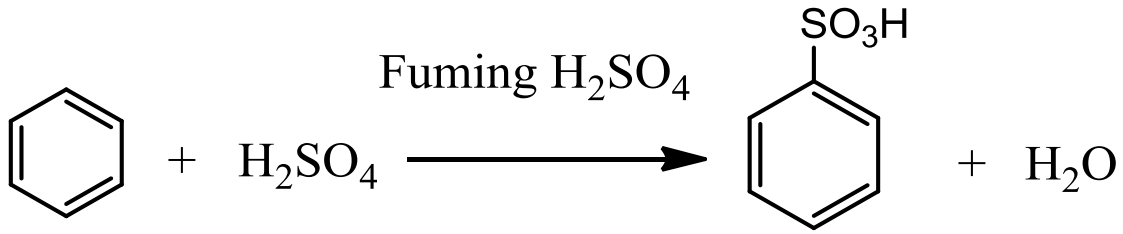


σ-complex

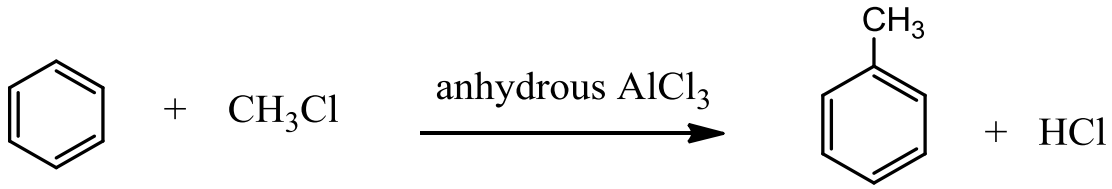
2. Nitration:



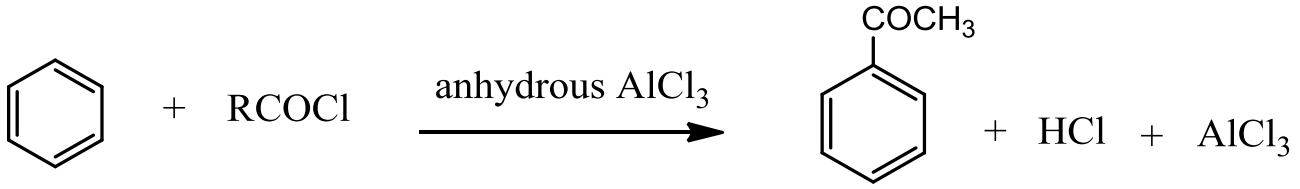
3. Sulphonation:



4. Friedel-Crafts Alkylation:

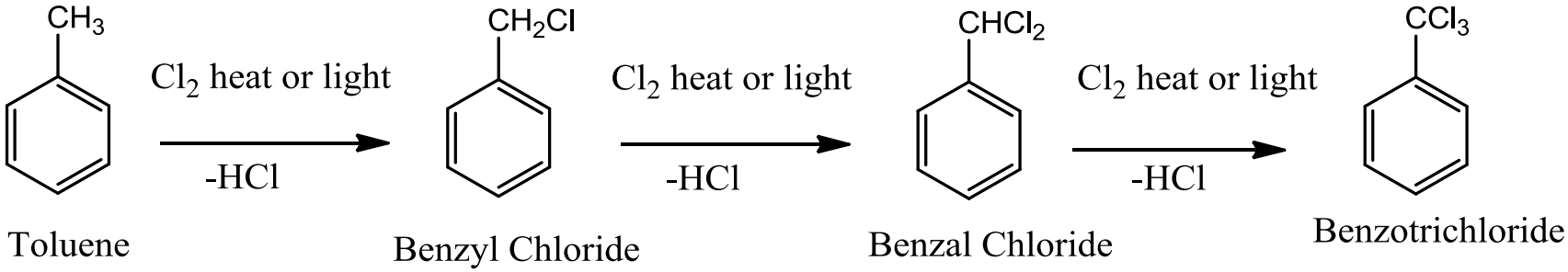


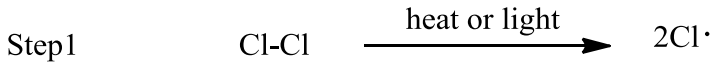
5. Friedel-Crafts Acylation:

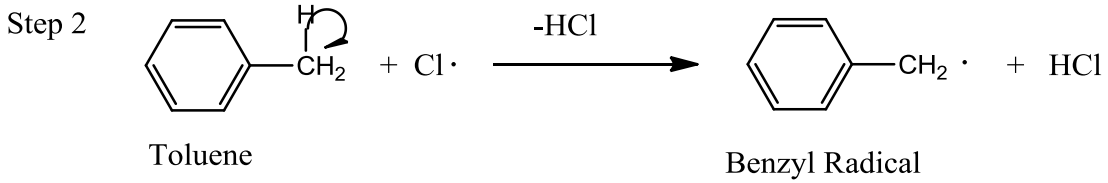


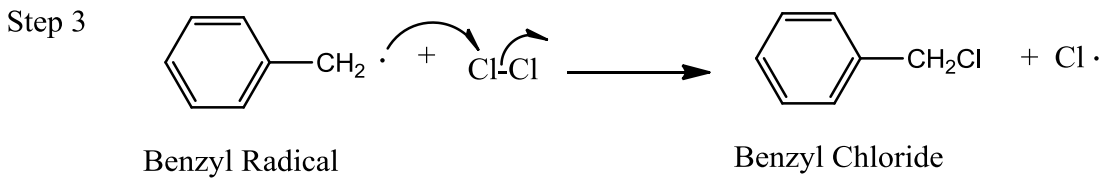
B. Free radical substitution and addition reactions:

1. Reactions of the side chain:



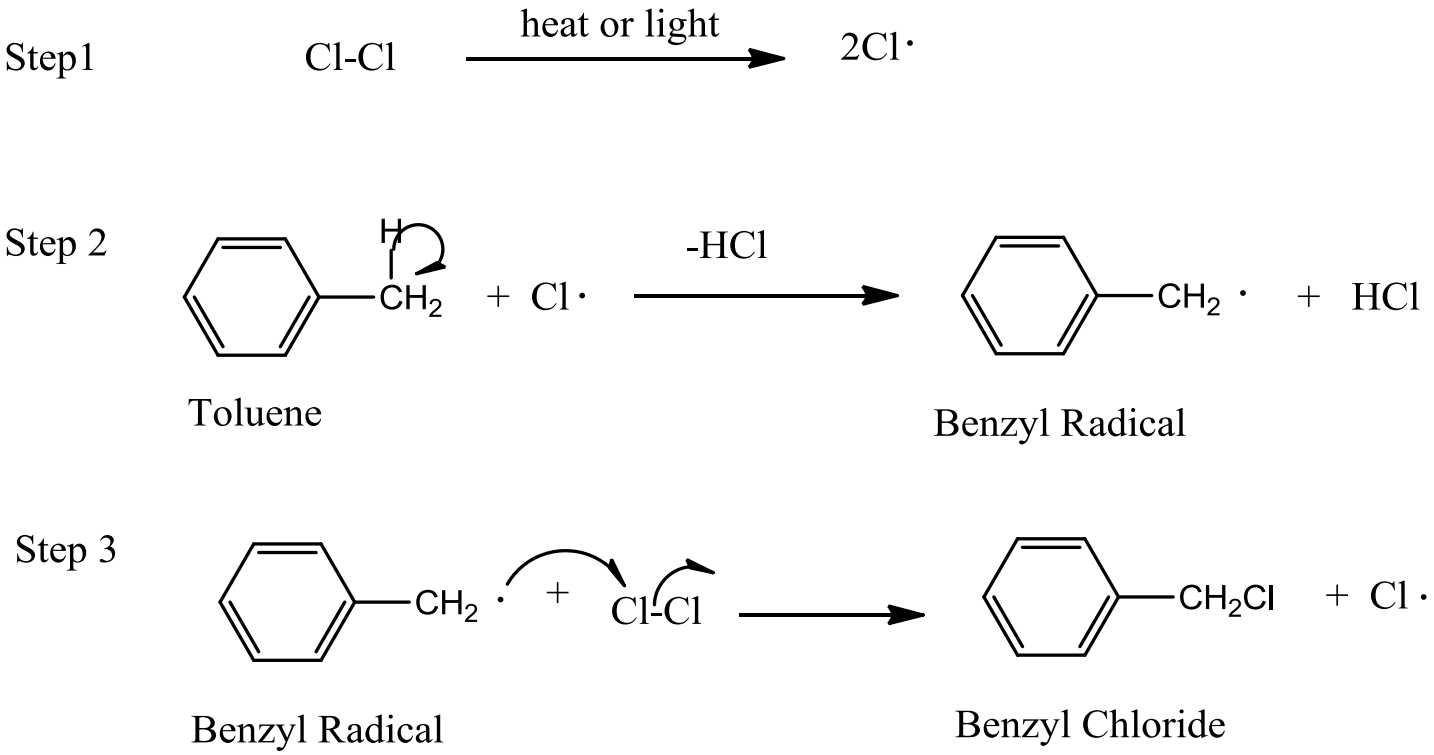






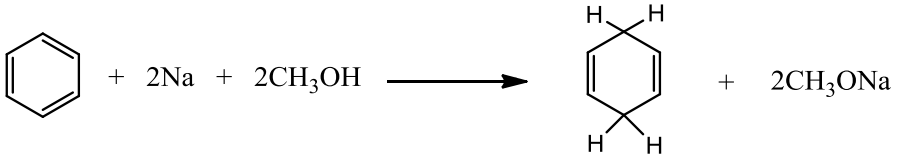
Mechanism:

Free radical substitution reaction, similar to that of halogenation of alkanes



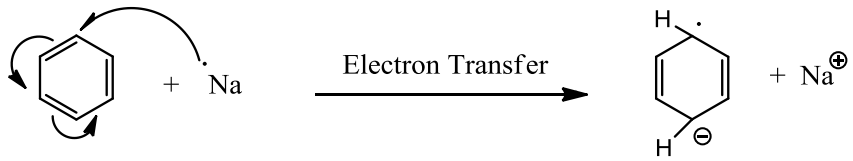
Step 2 and 3 are repeated, step-2 is the chain initiating step and step-3 is the chain propagating step

2. Birch Reduction:

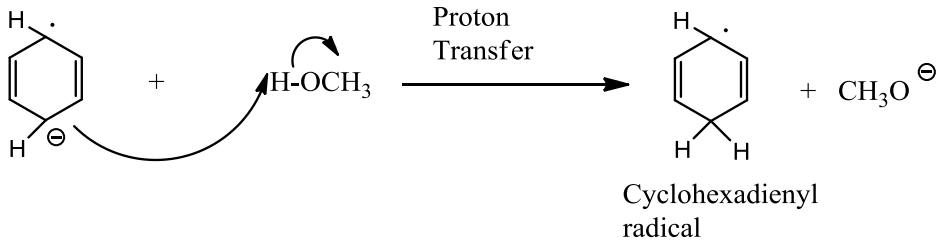


Mechanism:

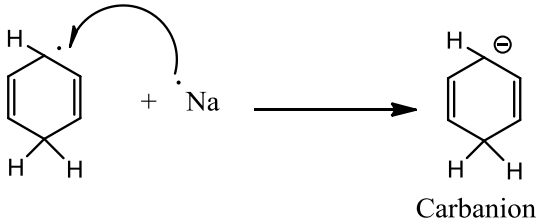
Step 1



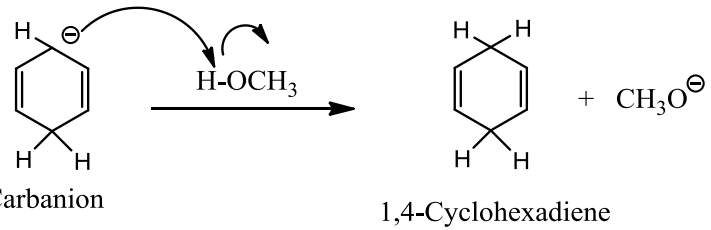
Step 2



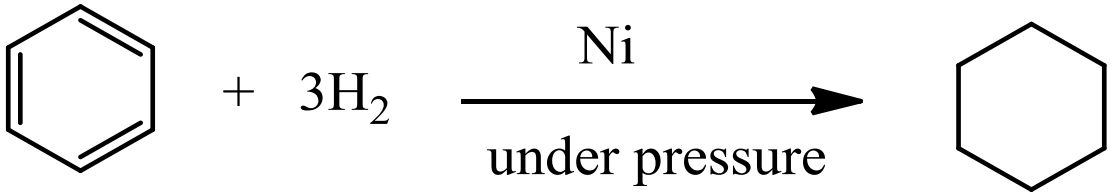
Step 3



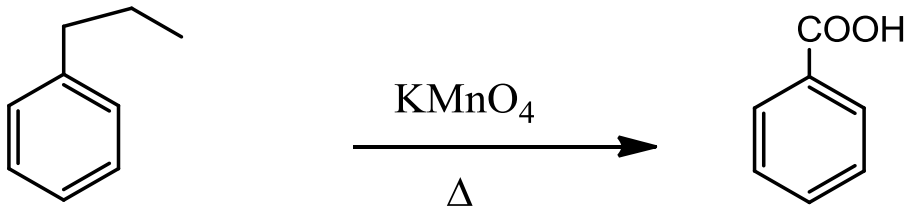
Step 4



3. Addition of hydrogen:



C. Oxidation



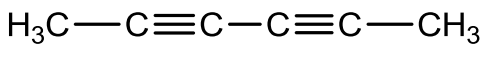
n-propylbenzene

Structure of Benzene

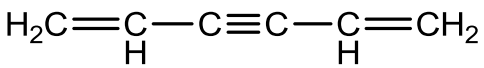
Molecular formula of Benzene- C_6H_6

It shows high degree of unsaturation

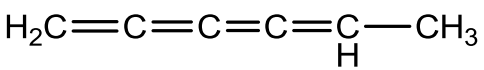
It should contain four double bonds or four double bond equivalents



(I)



(II)



(III)

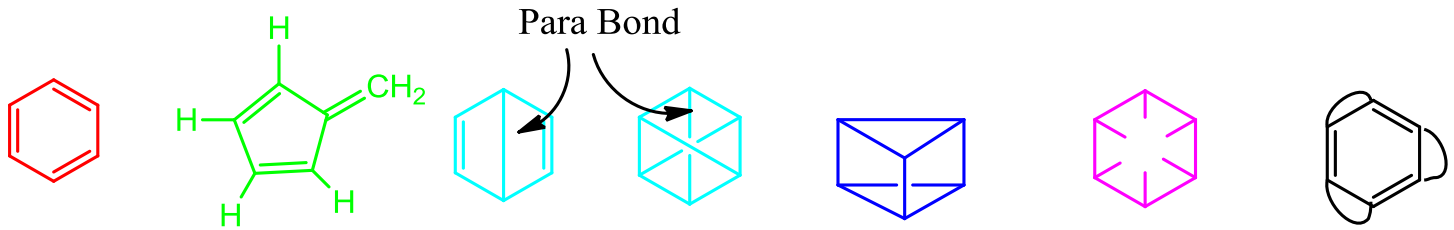
All these structures do not explain the behaviour of benzene

- ✓ Benzene is **stable to oxidising agents**, like $KMnO_4$
- ✓ Benzene adds **three and only three molecules of hydrogen and halogens** unlike the addition to aliphatic unsaturated hydrocarbons
- ✓ Benzene undergoes s**ubstitution** by **halogens** under conditions which are quite different from alkanes

- ✓ Benzene gives only **one** mono substitution and **three** disubstitution products
- ✓ Structures II and III would not give only **one** mono substitution product
- ✓ Structure I would not give **three** isomeric disubstitution products

Hence benzene contains three double bonds but these double bonds are remarkably different from aliphatic double bonds

Various ring structures were proposed for benzene (IV to X)



(IV) Kekule (1858)

(V)

(VI) Dewar (1867)

(VII) Claus (1867)

(VIII) Ladenberg (1868)

(IX) Armstrong & Baeyer (1888)

(X) Thiele's Formula (1899)

THANK YOU