B.Sc II (Hons.)
Organic Chemistry
Paper. III C.

Dr. Manju Kumari.

Aromatic Compounds.

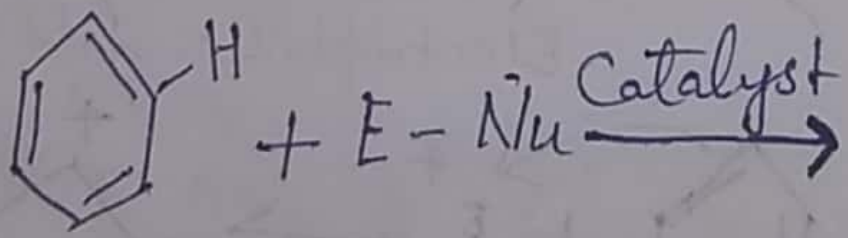
Benzene (C_6H_6):

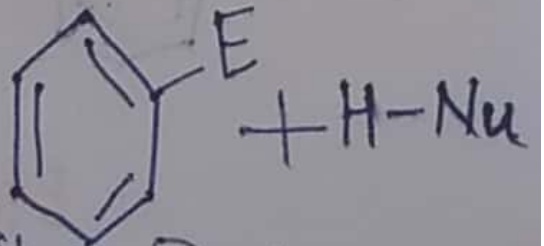
Chemical Properties:

Electrophilic Substitution Reactions:

Benzene undergoes electrophilic substitution reactions. The benzene ring with its delocalized π electrons is an electron-rich system. It is attacked by electrophiles, giving substitution products.

These reactions can be represented as;





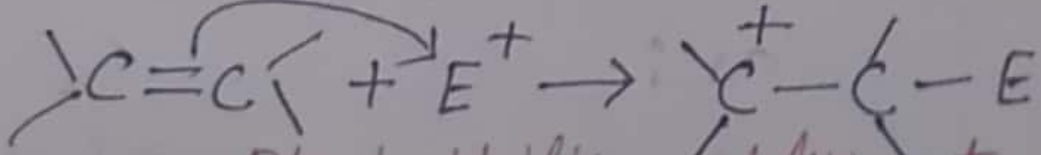
Substitution Product.

where E^+ is any electrophile and Nu^- is a Nucleophile.

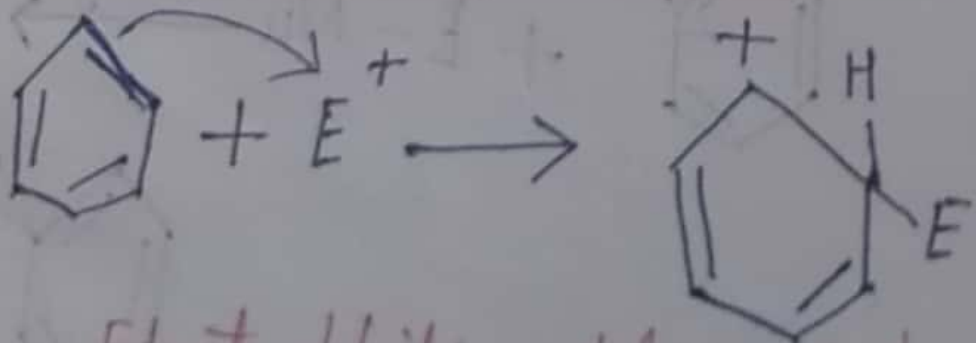
Such reactions in which hydrogen atom of the aromatic ring is replaced by an electrophile are called electrophilic aromatic substitution reactions.

Why benzene undergoes electrophilic substitution reactions whereas alkenes undergoes addition reactions ?

Both benzene and alkenes are susceptible to electrophilic attack because of their exposed π electrons. Both react with electrophiles to form stable carbonium ions.

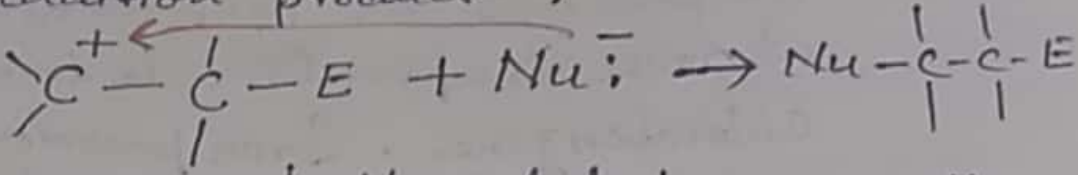


Electrophilic addition to an Alkene

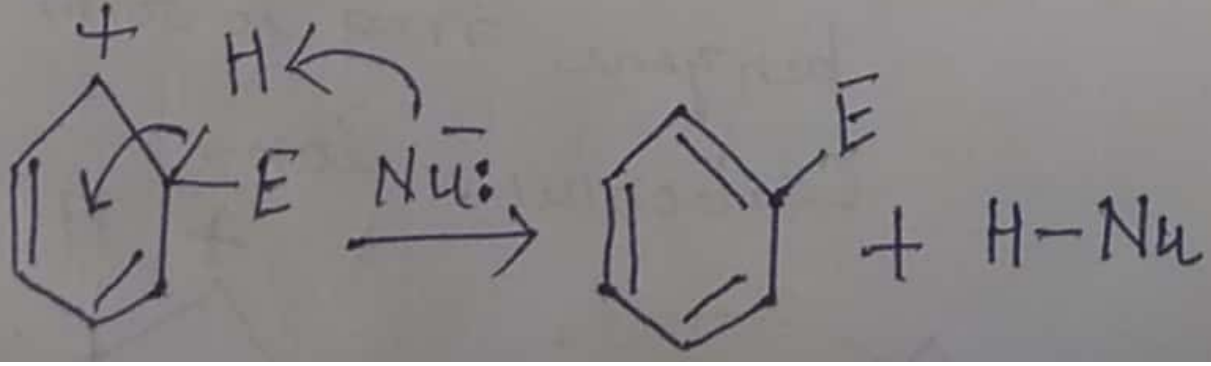


Electrophilic addition to benzene.

The carbonium ion produced from the alkene usually combines with a nucleophile to give the overall addition product :

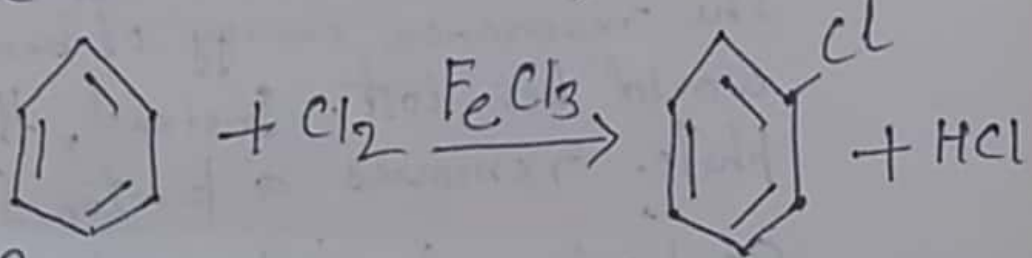


If this happened to benzene, the product would no longer be aromatic The resonance energy of benzene would be lost. Instead, the nucleophile removes a proton from the carbonium ion intermediate. The loss of proton allows the electrons from the C–H bond to go back into the ring and regenerate the aromatic π system. Net change in the replacement of a hydrogen atom by an electrophile :



(c) Halogenation :

Benzene reacts with chlorine in the presence of $FeCl_3$ or $AlCl_3$ at room temperature to form chlorobenzene. Iron powder can be used in place of ferric chloride ($2Fe + 3Cl_2 = 2FeCl_3$).

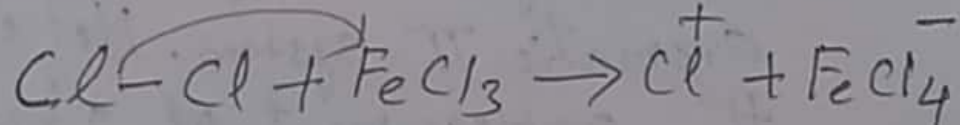


Benzene

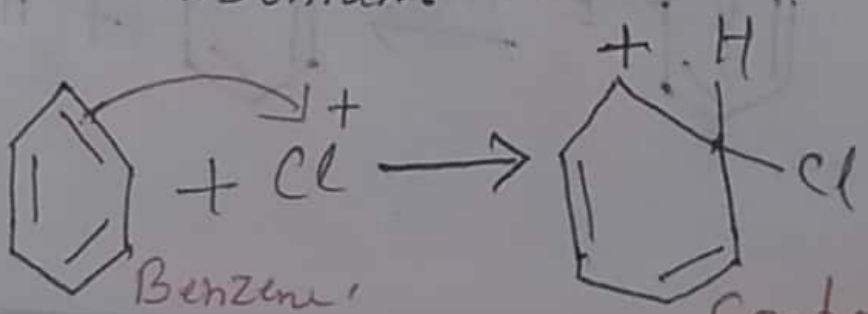
Chlorobenzene.

Mechanism :

Step I Formation of Electrophile



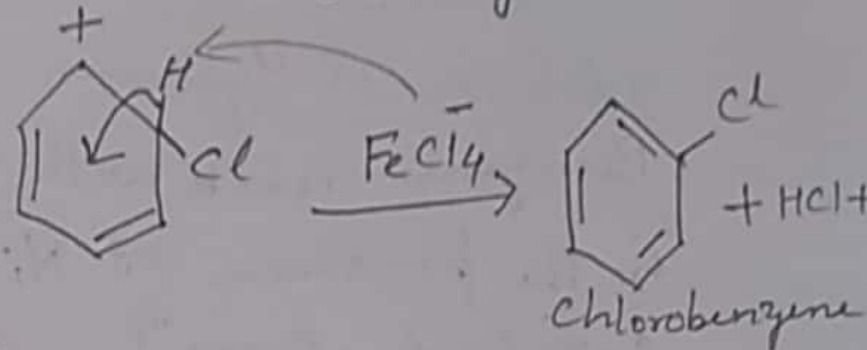
Step II Electrophile attacks the benzene ring to form a Carbonium ion.



Benzene.

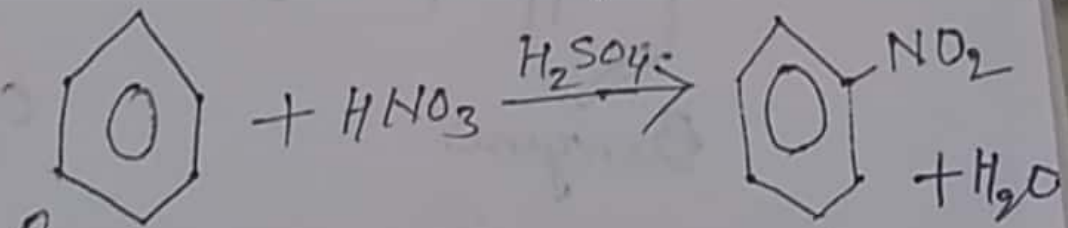
Carbonium ion

Step III. Loss of proton yields chlorobenzene.



Chlorobenzene

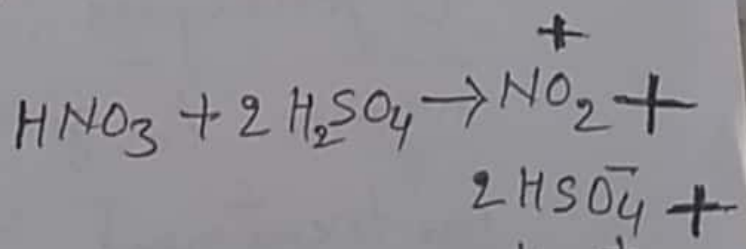
Nitration: Benzene reacts with concentrated nitric acid in the presence of conc. H_2SO_4 at 60°C to form nitrobenzene.



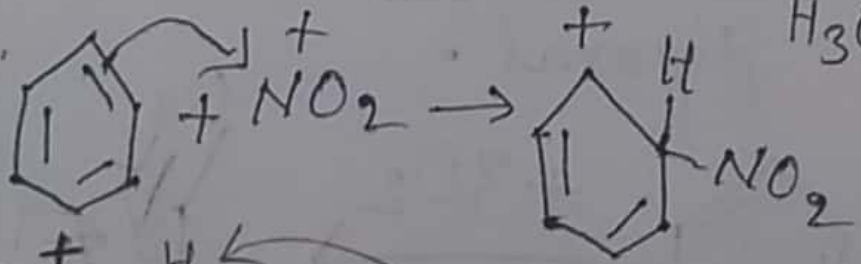
Benzene — Nitrobenzene

Mechanism:

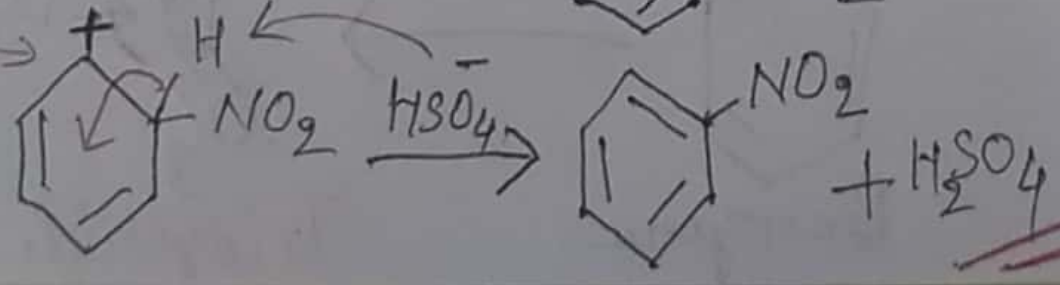
Step. I



Step II.



Step III →

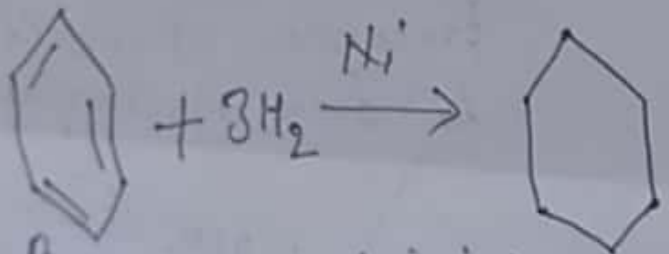


6.

ADDITION REACTIONS

Addition of Hydrogen:

Benzene reacts with hydrogen in the presence of Ni / Pt. catalyst at 150°C under pressure to form cyclohexane.



Benzene ... Cyclohexane

Oxidation Reactions:

Ozonolysis: Benzene reacts with ozone to give a triozonide which on treatment with Zn / H2O yields glyoxal.