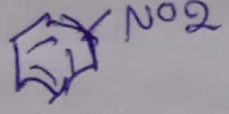
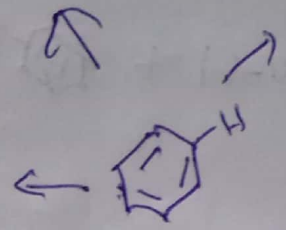
Electrophilic aromatic substitution replace a proton on benzene with another nucleophilic electrophilic Aromatic Substitution.

Halogenation.

Acylation.



Nitration.



Alkylation

Sulfonation.

Hydroxylation.

General electrophilic Aromatic substitution of Benzene

$$E-NO \rightarrow E^{+} + NO-H$$

$$+ E-NO \rightarrow$$

$$+ NO-H$$

Benzene

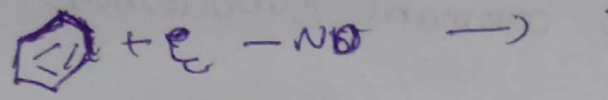
Electrophilic Aromatic substitution product

Mecanism.

Generation of electrophile.

$$E-NO \rightarrow E^{+} NO \rightarrow \text{Nucleophilic}$$

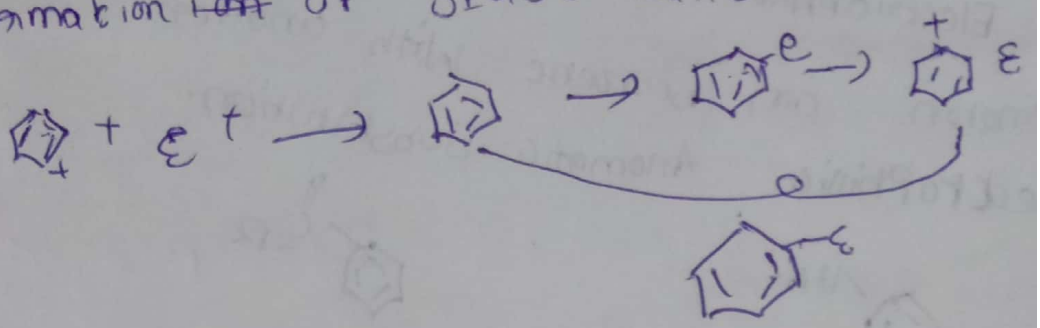
electrophile



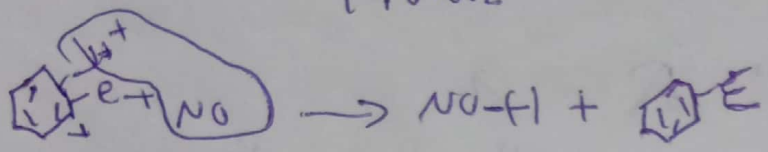
Benzene

electrophile.

(ii) formation of Stable Carbocation.

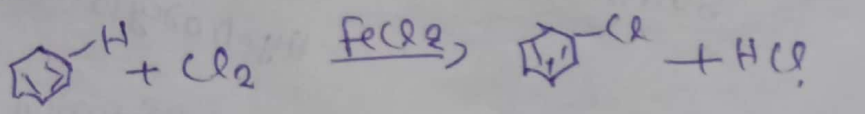


(iii) Removal of proton



Reactions of Benzene.

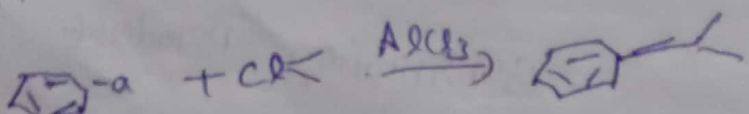
Halogenation.



Chloro Benzene.

Friedal Crafts Alkylation of Benzene.

⇒ It forms a new C-C bond between an aromatic ring and an alkyl group.

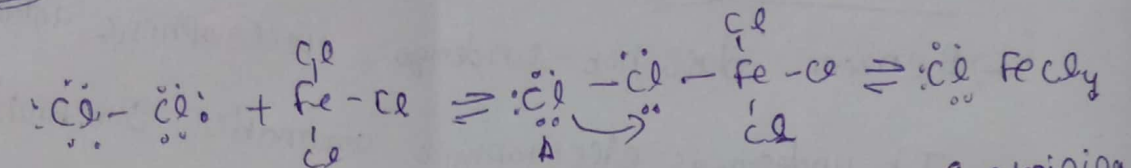


Benzene 2 chloro propane.

cumene

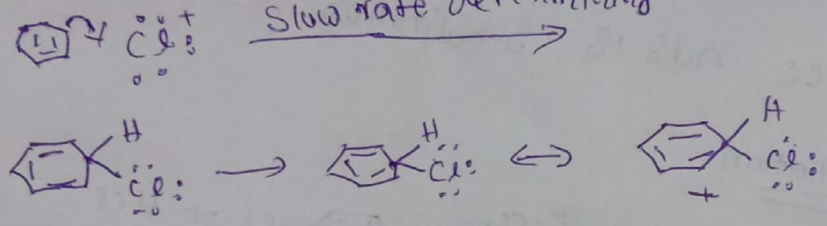
Chlorination:

Step 1: formation of a chloronium ion



Chlorine (Lewis) — Ferric chloride (a lewis acid) — A molecular complex with a +ve charge on chlorine — Containing a chloronium ion chlorine

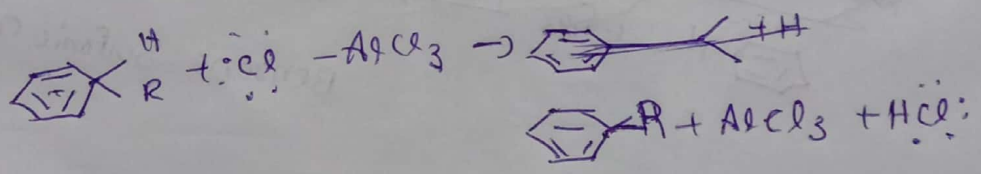
Step-2: Attack of the determining.



Slow rate determining

Resonace Solubilized cation intermediate The The charge is delocalized onto three atoms of the ring.

Step-3: Proton transfer regenerates aromatically

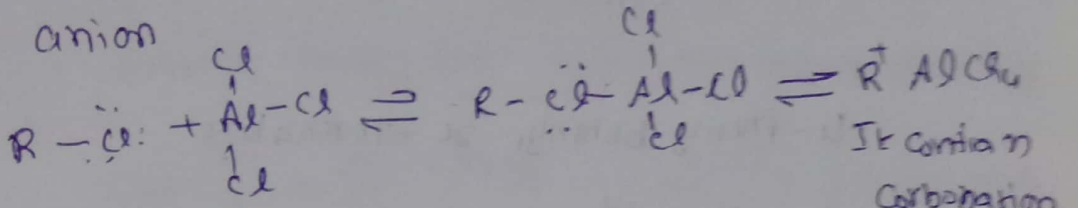


Aluminium chloride

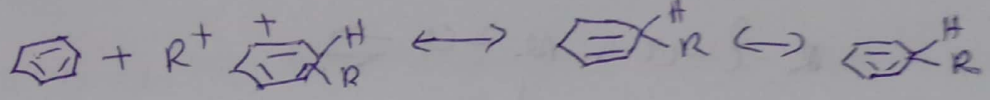
Nitration:

Friedal Crafts Alkylation of Benzene.

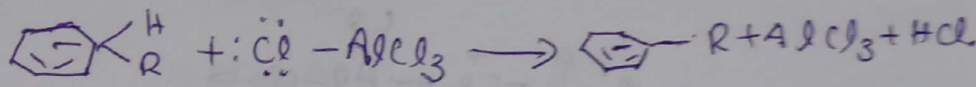
Step:1 formation of ~~liquid~~ alkyl cation as



Step:2 attack of alkyl cation on ring

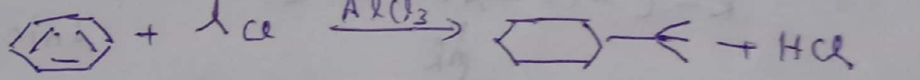


Step-3 :- proton transfer regenerates aromaticity



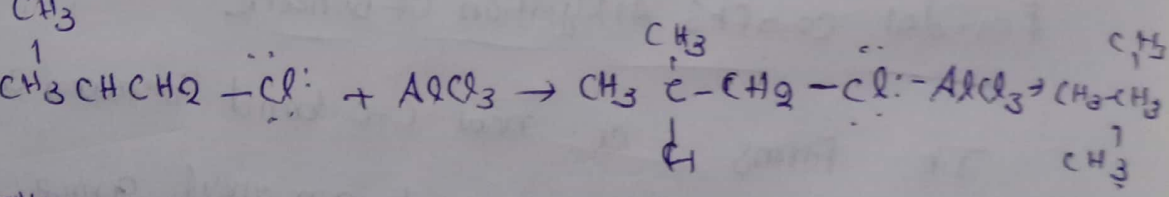
Limitations-

Carbocation rearrangements are common

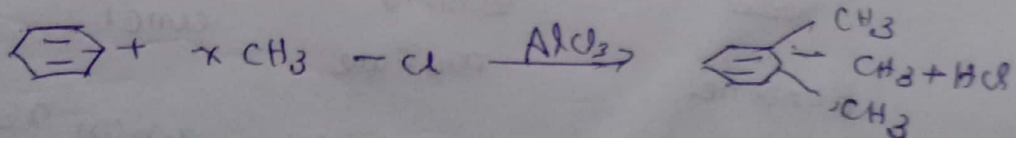


~~Isobenzene~~
Isobutyl
Chloride

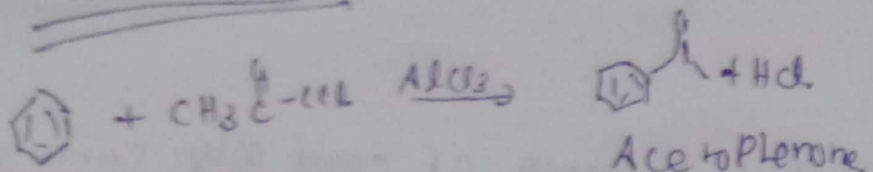
tert Butyl benzene



Polyalkylation an alkyl group added to ring activates the ring and further alkylation



Friedal Crafts Acylation:

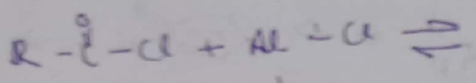


Acetophenone

Acetyl chloride

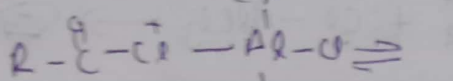
4-Phenyl butanoyl chloride

The electrophile is an acylium ion.

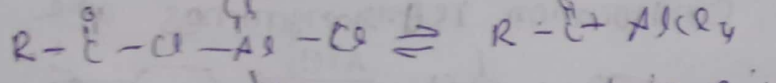


An acyl chloride

Aluminium Chloride



Aluminium chloride



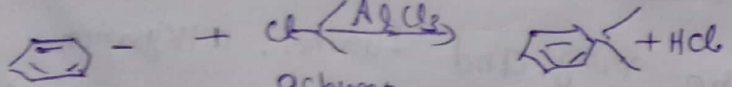
Amolecular Complex with the

Anion Pair

Carbocation

Friedal Crafts Alkylation of Benzene

It forms a new C-C bond between an aromatic ring and an alkyl group

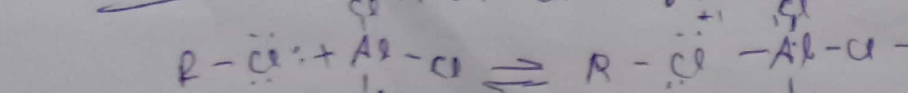


Benzene

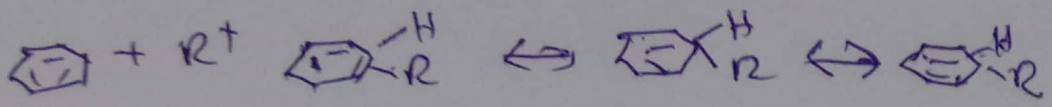
2-chloro propane

Cumene

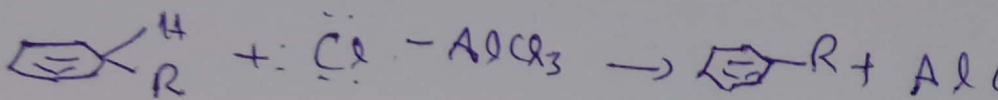
Step 1: formation of alkyl cation as anion pair



Step-2 attack of alkyl cation ring.

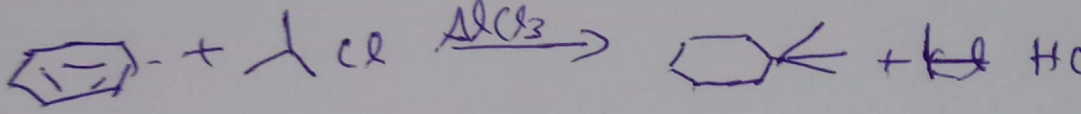


Step-3 proton transfer regenerates aromaticity.



Limitation.

Carbocation rearrangements are common



Isobutyl Chloride