AROMATIC ELECTROPHILIC SUBSTITUTION

(PART-2)

and

Some Other Topics

Friedal Crafts Reaction

This can be described as a nucleophilic reaction in which the arene is the nucleophile. Alkyl halide form 1:1 adducts with Lewis acids.

$$RCl + AlCl_3 \rightleftharpoons R-\overset{+}{Cl}-\overline{AlCl_3}$$

$$ArH + R-\overset{+}{Cl}-\overline{AlCl_3} \longrightarrow \left[Ar\begin{matrix}H\\R\end{matrix}\right]^{+} AlCl_4^-$$

$$\left[Ar\begin{matrix}H\\R\end{matrix}\right]^{+} AlCl_4^- \downarrow$$

$$ArR + HCl + AlCl_3$$

Two types of catalyst:

① $AlCl_3 > BF_3 > SbCl_5 > FeCl_3 > SnCl_4 > ZnCl_2$

② HF, H_2SO_4, H_3PO_4

If the alkyl halide is S- or tertiary then the predominant speaies is carbonium ion.

$$R-\overset{+}{Cl}-\overline{AlCl_3} \rightleftharpoons AlCl_4^- + R^+ \xrightarrow{ArH} \left[Ar\begin{matrix}H\\R\end{matrix}\right]^{+} AlCl_4^-$$

This shows that n-alkyl groups can be introduced without rearrangement at low temp. since ionisation of the adduct is slow.

At higher temp eg

$$Me-CH_2CH_2-Cl + AlCl_3 \rightleftharpoons AlCl_4^- + Me-\overset{\oplus}{C}H_2CH_2$$

Hydride shift ↓

$$Me-\overset{\oplus}{C}H-CH_3$$

↓ PhH

$$PhCHMe_2$$

Similarly isobutyl chloride gives t-butyl benzene.

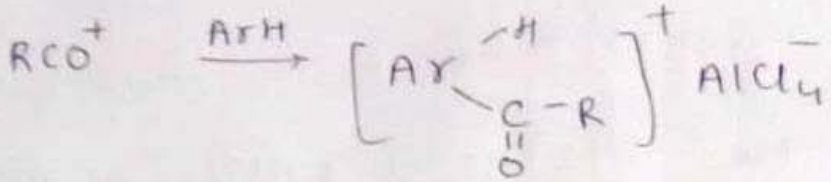
$$\Rightarrow \underset{\text{Alcohols}}{ROH} + BF_3 \rightleftharpoons \left[R-\overset{H}{\underset{\oplus}{O}}-BF_3\right] \rightleftharpoons R^+ + HOBF_3^-$$

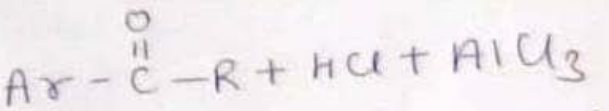
$$\Rightarrow \underset{\text{Alkenes}}{Me_2C=CH_2} + H^+ \xrightarrow{H_2SO_4} Me_3\overset{+}{C} \xrightarrow{PhH} PhCMe_3$$

Friedal Craft's acylation

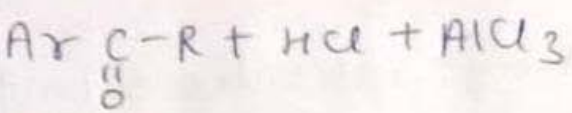
$$RCOCl + AlCl_3 \rightleftharpoons [RCO-\overset{+}{Cl}-\overset{-}{AlCl_3}]$$

$$\rightleftharpoons RCO^+ + AlCl_4^-$$

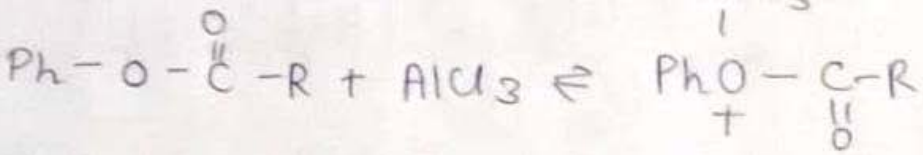


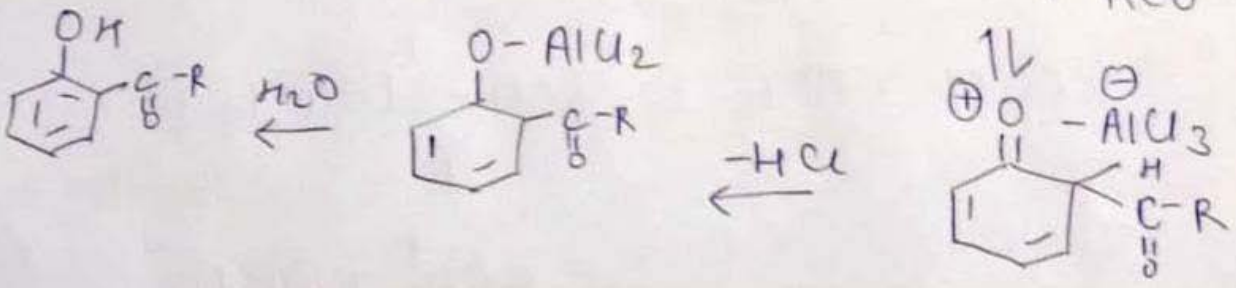


Evidence is also there for adduct of active species

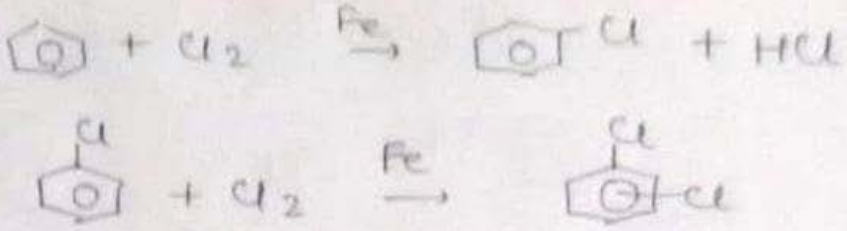


Fries rearrangement



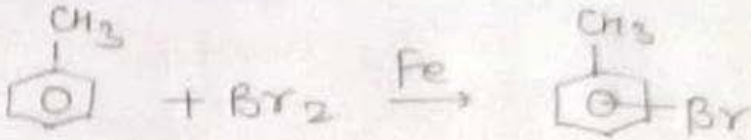


Halogenation



o-&-p-dichloro benzene

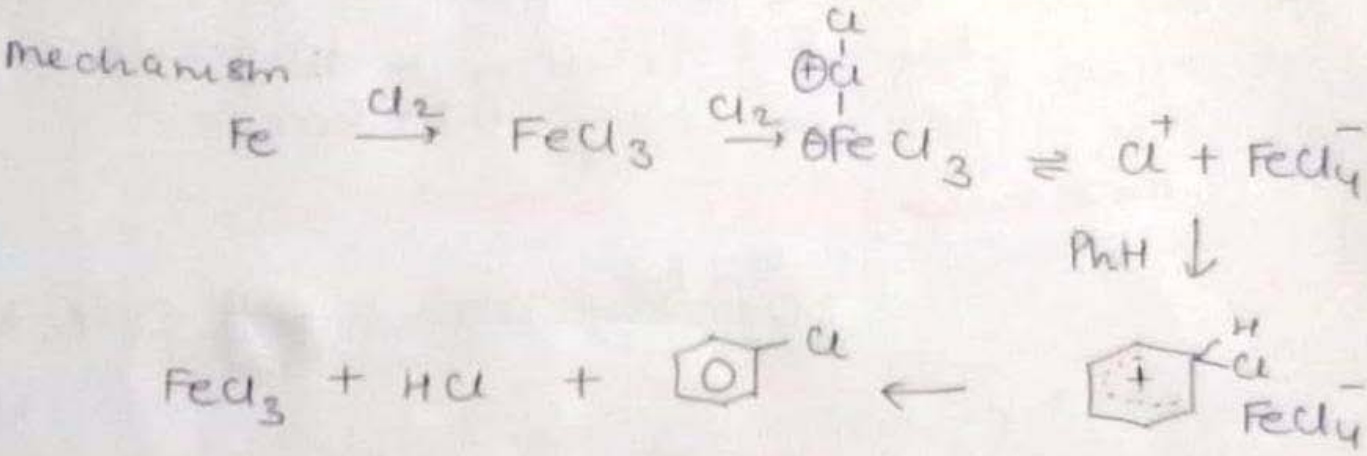
Similarly



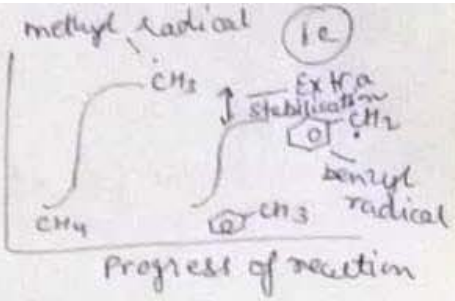
$$Rate = k[PhH][X_2][L.A]$$

L.A = Lewis acid

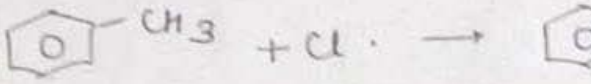
Mechanism



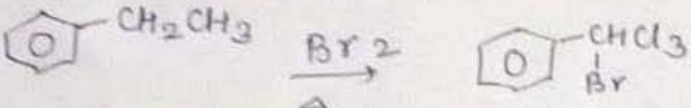
Side chain halogenation

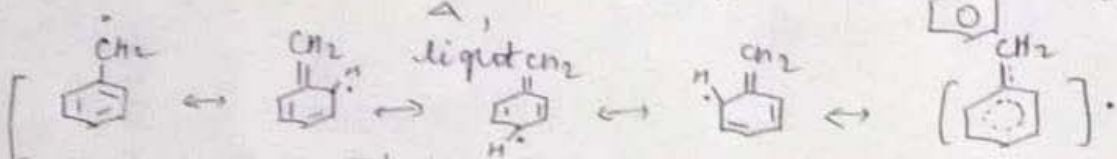


$$Cl_2 \xrightarrow{h\nu} 2Cl\cdot$$

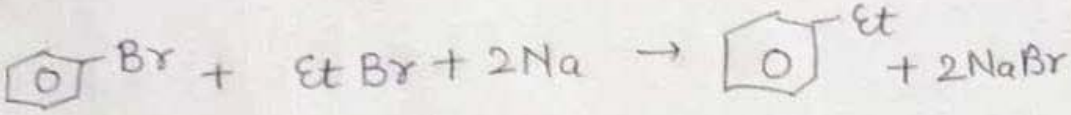


$\downarrow Cl_2$

eg 

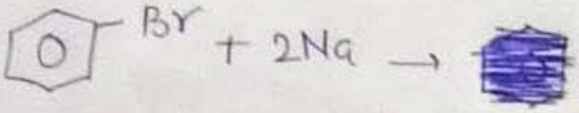


Wurtz Fittig Reaction



This method provides an alternative the F.C reaction & long side chains can be easily introduced.

Mechanism



$$C_6H_5^-Na^+ + EtBr \rightarrow C_6H_5\text{-}Et + NaBr$$

Other product are Et - Et

$$Et^- Na^+ + C_6H_6Br \longrightarrow C_6H_5-Et + NaBr$$

Fittig Reaction

$$2\,C_6H_5Br + 2\,Na \longrightarrow C_6H_5-C_6H_5 + 2NaBr$$

Wurtz Reaction — 2 mechanisms

(1) $C_2H_5-Br + 2Na^{\cdot} \rightarrow C_2H_5^- Na^+ + NaBr$

$C_2H_5^- Na^+ + C_2H_5Br \longrightarrow C_2H_5-C_2H_5 + NaBr$

(2) $C_2H_5-Br + Na^{\cdot} \longrightarrow C_2H_5^{\cdot} + NaBr$

$C_2H_5^{\cdot} + C_2H_5^{\cdot} \longrightarrow C_2H_5-C_2H_5$

Kolbé electrolytic method

$$RCO_2K + R'CO_2K + 2H_2O \longrightarrow R-R' + 2CO_2 + H_2 + 2KOH$$

mechanism $C_2H_5CO_2^- \longrightarrow C_2H_5CO_2^{\cdot}$

$\downarrow$

$C_2H_5^{\cdot} + CO_2$

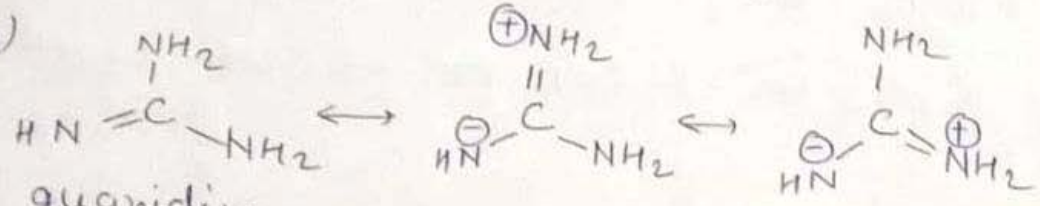
$2C_2H_5^{\cdot} \longrightarrow C_4H_{10}$

$2C_2H_5 \rightarrow$ Ethane + Ethene

$C_2H_5^{\cdot} + C_2H_5CO_2^{\cdot} \rightarrow C_2H_5CO_2C_2H_5$

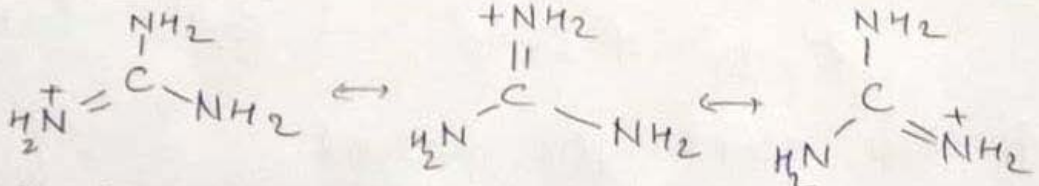
Q) Why guanidine is strong base?

A)



guanidine

In the cation



Both are resonance stabilised but in cation the charge is symmetrically distributed & 3 equivalent structures of equal energy. NO effective delocalisation in neutral molecule which involve charge separation. So cation is more resonance stabilised.

References and suggested further reading