Free-radical reaction organic chemistry Unit-IV

* Intermediate species is an Free-radical.
* Free radical is a neutral species, containg a one or more unpaired electron, and so very reactive species. eg. methyl radical $\cdot CH_3$ — Paramagnetic in nature
* In Free-radical rea^M, consist of at least two step :
  (i) Initiation - Formation of Free-radicals.
  (ii) Termination - destruction of free radicals.

$$A-B \longrightarrow A^\cdot + B^\cdot \quad -(i)$$

$$A^\cdot + B^\cdot \longrightarrow A-B \quad -(ii)$$

⇒ ProPagation step → generation of one molecule and one free radical

$$R^\cdot + R'H \longrightarrow RH + R'^\cdot$$

* also known as chain rea^M.
* ~~There mon~~ Some general Characteristics of free-radical rea^{M}s

① rea^{M}s are fairly similar whether they are occuring in the vapour or liquid Phase.
② They are largely unaffected by the Pr. of acids or bases or by changes in the Polarity of solvents.
③ Their rates are decreased by "inhibitors" — (substance that scavenge free radicals e.g. nitric oxide, molecular oxygen or benzoquinone.
④ They are initiated by free-radical sources.

* ~~The~~ First organic Free-radical discovered — Triarylmethyl $Ph_3C^\cdot$ by Gomberg

Free-radical substitution Mechanism:-

Three steps – O.P. agrawal Page 389

$$R\text{-}X \longrightarrow R\text{-}y$$

Production of $R^{\cdot}$ by cleavage of R-X

$R^{\cdot}$ by cleavage of R-X $\xrightarrow{\text{cleavage}}$ $R^{\cdot} + X^{\cdot}$ — SH1

$R^{\cdot}$ by abstraction (no cleavage) $\leftarrow R\text{-}X + \omega\cdot \xrightarrow{\text{abstraction}} R^{\cdot} + \omega\text{-}X$ — SH2

$\omega\cdot$ is produced by adding a comp. – Peroxides, Hydroperoxide } initiator

⇒ once $R^{\cdot}$ is formed, it can go to product in two ways –

⇒ by abstraction

In the case of long chain referred ← $R^{\cdot} + y\text{-}\omega \longrightarrow R\text{-}y + \omega^{\cdot}$

⇒ by coupling with another radical.

$R^{\cdot} + y^{\cdot} \longrightarrow R\text{-}y$

⇒ In abstraction rxn transition state formed, in some cases this transition state have Polar Character.

Ex. abstraction of hydrogen from methyl gp. of toluene by bromine → because Br is more electronegative than Carbon.

$$\left[Ph\overset{\delta+}{C}H_2 - H \cdots Br^{\delta-}\right]$$

Polar transition state.

Evidence in favour of:- electron-withdrawing gp. in the para position of toluene (destabilized the positive charge) decrease the rate of hydrogen abstraction by bromine.

$Ar^{\cdot} - Ar \rightarrow [Ar\text{-}Ar]$

$Ar^{\cdot}$ —

Mechanism at an aromatic substrate :-

⇒ When R is aromatic –

$$R-X \longrightarrow R-Y$$

⇒ the simple abstraction mechanism cannot account for all reactions of aromatic substrate.

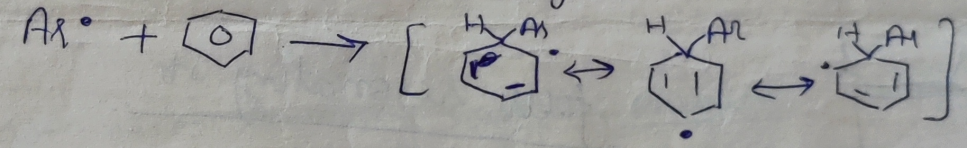
For eg. $Ar^{\bullet} + Ar-H \rightarrow Ar-Ar$.

On solvn → Coupling of two rings cannot be explained on the basis of a simple abstraction.

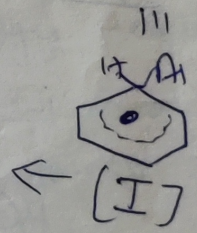
$$Ar^{\bullet} + Ar-H \rightarrow Ar-Ar + H^{\bullet}$$

⇒ Abstraction of Phenyl gp. can be explained ~~on~~ by a mechanism similar to that of electrophilic and nucleophilic aromatic substitution.

First step ⇒ radical attacks on the ring

$Ar^{\bullet}$ + 

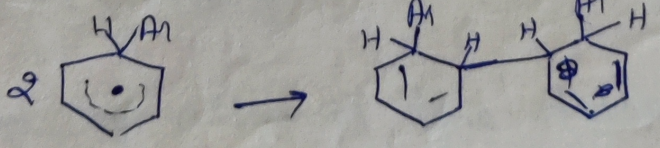
* Intermediate [I] is relatively stable because of resonance.



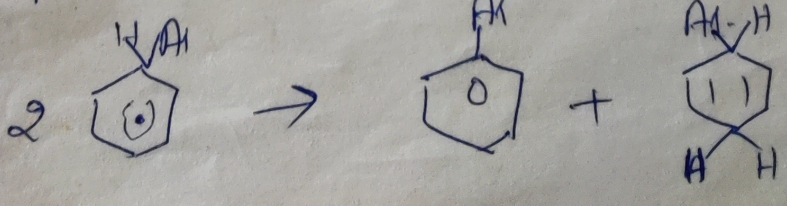
Second step → Termination -

⇒ The reaction can be terminate in three ways -

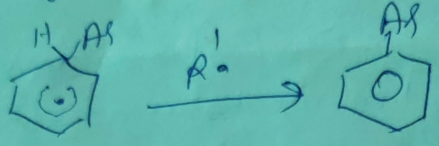
⇒ by simple coupling



⇒ by disproportionation -



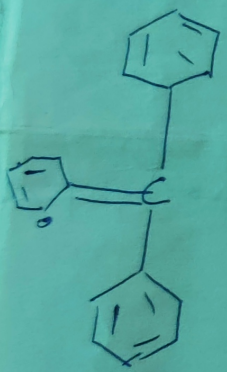
③ ⇒ If a species ($R^{1}\cdot$) is present which abstract hydrogen, by abstraction.



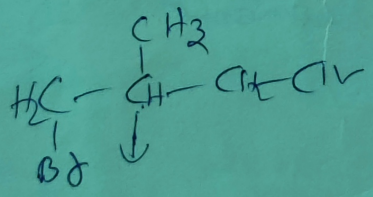
hexamethyl ethane ⟶ dissociate into radicals

hexaPhenyl ethane → triphenyl methyl radical.

$Ph_3\dot{C}$



four resonating Str.



(A)

Relative stability of free-radicals:-

benzyl > allyl > 3° > 2° > 1° > CH_3, vinyl.

(A) (B)

(B) Reactivity for Aliphatic substrate:-

⇒ In chain reaⁿ or free radical reaⁿ, abstraction step determines what product will be formed.

⇒ (a) Nearly always univalent atom is abstracted by free-radical [Hydrogen or halogen]

$CH_3CH_3 + Cl^\circ$ → $H-Cl + CH_3-\dot{C}H_2$; $\Delta H = -2$ Kcal/mol.

$CH_3CH_3 + Cl^\circ$ → $CH_3-CH_2-Cl + H^\circ$; $\Delta H = +18$ Kcal/mol.

* Here, Cl° abstract H from ethane and form H-Cl

* The principal reason for this is steric. the univalent atom is much more exposed to attack by the incoming radical.

* Another reason is — in many cases is energetic

(a) In above case- energy required for breaking of bond C_2H_5-H is = 100 Kcal/mol

⇒ energy liberate during H-Cl bond formed is = 103 Kcal/mol.

C_2H_5-Cl = 82 Kcal/mol.

Note:- * The steric reason is more important, because in many cases where ΔH is not very different for two comps, the univalent atom is chosen.

[Bredt's rule]

* (1) In case of alkenes, the decreasing order of the ease of abstraction of different

140
120
20
100
160 - 20