Free radical Reaction ①

Hunsdiecker Reaction

$RCOOAg + Br_2 \rightarrow RBr + CO_2 + AgBr$

$RCOOAg \rightarrow RBr$

Mech →

① $RCOOAg + X_2 \rightarrow R-\overset{O}{\overset{\|}{C}}-OX + AgX$

② $R-\overset{O}{\overset{\|}{C}}-O-X \rightarrow R-\overset{O}{\overset{\|}{C}}-O^{\cdot} + X^{\cdot}$ (Initiation step)

Propagation

③ $R-\overset{O}{\overset{\|}{C}}-O^{\cdot} \rightarrow R^{\cdot} + CO_2$

④ $R^{\cdot} + R-\overset{O}{\overset{\|}{C}}-OX \rightarrow R-X + RCOO^{\cdot}$ etc

Allylic Halogenation → ex of Free radical Substitution

→ catalysed by peroxide, heat or light

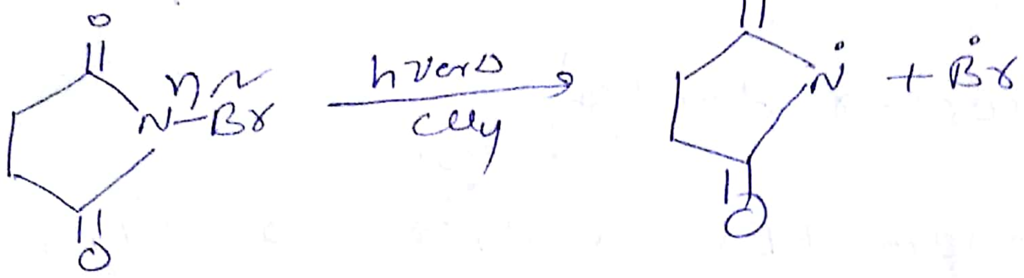
alkenes can be halogenated in the allylic position by NBS, NCS etc (Cl atom)

- Regioselection Reaction
- Halogenation at allylic position
- Reaction takes place in nonpolar solvent (most often CCl_4 is used).
- NBS is only slightly soluble in CCl_4, this ensures the low conc of Br_2 necessary.

$CH_3-CH=CH_2 \xrightarrow[h\nu / CCl_4]{NBS} Br-CH_2-CH=CH_2$

Mech. → (2) [Br_2 dangerous है so इसे Indirectly]

(I)



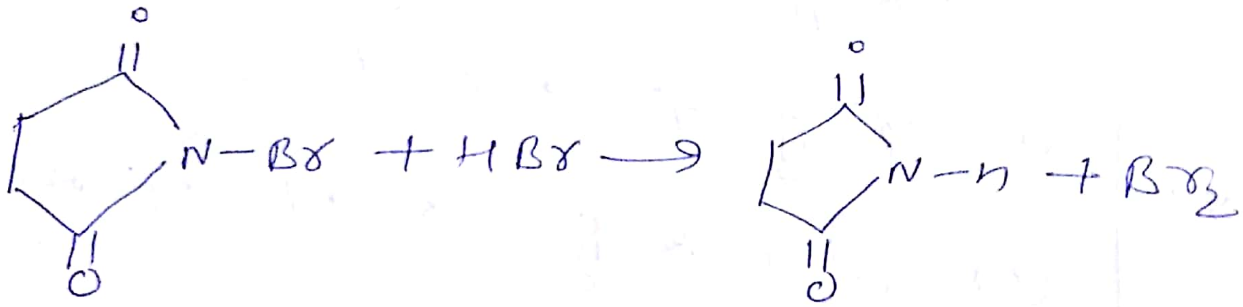
NBS

(II) $CH_3-CH=CH_2 + \dot{B}r \rightarrow CH_2=CH-\dot{C}H_2 + HBr$

or

$CH_2=CH-CH_2-H$

(III)



(IV) $CH_2=CH-\dot{C}H_2 + Br_2 \rightarrow Br-CH_2-CH=CH_2 + \dot{B}r$

⇒ Free radical Substitution

↳ Halogenation of alkanes →

$$R-H + X_2 \xrightarrow[\text{or } 250-400^\circ C]{h\nu} R-X + HBr$$

Mech →

$$X_2 \xrightarrow[\text{or } \Delta]{h\nu} 2X^\cdot \quad \text{] Initiation}$$

$$R-H + X^\cdot \rightarrow R^\cdot + HX$$
$$R^\cdot + X_2 \rightarrow R-X + X^\cdot \quad \text{] Propagation}$$

$$R^\cdot + X^\cdot \rightarrow R-X$$
$$X^\cdot + X^\cdot \rightarrow X_2$$
$$R^\cdot + R^\cdot \rightarrow R-R \quad \text{] Termination}$$

↳ Reactivity order, $F_2 > Cl_2 > Br_2 > I_2$

(X) Alkylation of aromatic compounds by Diazonium salts

$$Ar'H + ArN_2^+ X^- \xrightarrow{OH^-} Ar-Ar'$$

↳ Gomberg reaction

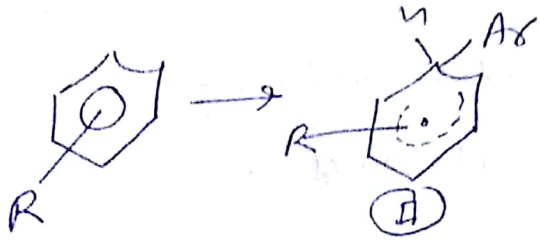
Mech →

(i) $ArN_2^{\oplus} X^- \xrightarrow{OH^-} ArN_2^+ OH^-$ or $Ar-N=N-OH$

(ii) $Ar-N=N-OH \xrightarrow[-H_2O]{Ar-N=N-OH} Ar-N=N-O-N=N-Ar$ Anhydride.

(iii) $Ar-\overset{\eta}{N}=\overset{\eta}{N}-\overset{\eta}{O}-N=N-Ar \rightarrow Ar^\cdot + N_2 +$ $Ar-N=N-O^\cdot$ (A)

(4)

(IV) $Ar^{\cdot}$ + 

(V)  + $Ar-N=N-\dot{O}$ (A) →  + $ON-N=N-Br$

Sandmeyer reaction

$$ArN_2^+X^- \xrightarrow{CuX} ArX + N_2$$

Mech → 2 step

(1) $ArN_2^+X^-$ ~~[illegible]~~

or

$Ar-N=N-X$ + CuX (+1) → $Ar^{\cdot}$ + N_2 + CuX_2 (+2)

(2) $Ar^{\cdot} + CuX_2 \rightarrow Ar-X + CuX$

Free radical reaction (5)

(A) Halogenation of alkanes → as-

$$CH_4 + X_2 \xrightarrow[\text{or } \Delta]{h\nu} CH_3X + HX$$

↳ It is a chain reaction

(A) Chlorination →

Initiation → $Cl-Cl \xrightarrow[\text{or } \Delta]{h\nu} 2Cl^{\cdot}$

58

$\Delta H = +58$ Kcal/mol or 243.6 KJ/mol

For this required energy (+58 or 243.6) is supplied by heating the reaction mixture up to 250°C or irradiating it at 487.5 nm

(B) Chain-propagation step →

(i) $Cl^{\cdot} + H-CH_3 \rightarrow HCl + CH_3^{\cdot}$

1.02 1.03

abstraction of H atom

$\Delta H = -1$ Kcal/mol or 4.2 KJ/mol

(ii) $Cl-Cl + CH_3^{\cdot} \rightarrow CH_3Cl + Cl^{\cdot}$

58

$\Delta H = -23$ Kcal/mol or 96.6 KJ/mol

Both step are exothermic & proceed readily

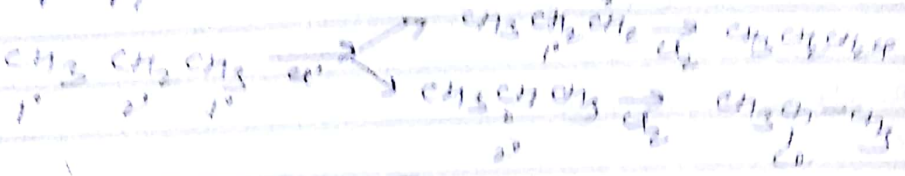
(C) Termination → by the union of two radical.

$Cl^{\cdot} + Cl^{\cdot} \rightarrow Cl_2$

$CH_3^{\cdot} + CH_3^{\cdot} \rightarrow CH_3-CH_3$

$CH_3^{\cdot} + Cl^{\cdot} \rightarrow CH_3Cl$

(X) The Hydrogen atoms in an alkane are substituted in the general order
$1^\circ < 2^\circ < 3^\circ$
So chlorination of propane give n-propyl & isopropyl chlorides in the ratio of 1:1



1° H = 6 ratio = $\frac{6}{2}$ = (3:1) But chlorination of 2° radical is 3.5 times faster than 1° so ratio is (1:1)

(XI) → **Bromination**

Similar to chlorination but reaction is slower

(a) Initiation → ΔH = +46 Kcal/mole = 193.2 KJ/mole

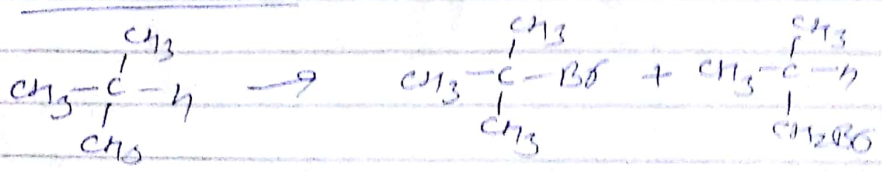
(b) Propagation → (i) ΔH = +15 Kcal/mol or 63 KJ/mol

(ii) −21 Kcal/mol or 88.2 KJ/mol

It is exothermic so occurs readily.

But Ist step is endothermic so it is somewhat difficult for a Bromine atom to acquire the activation energy required to abstract a H atom in competition with the chain-terminating steps.

→ But low reactivity of bromine atom is its high selectivity for 3° & 2° position than to a chlorine atom → यही कारण है कि Isobutane में gaseous bromination give mainly the 3° bromide.



3° 99% 1%

(X) Iodination → Since iodine atom is also very stable, kinetic chain in iodination is much shorter. The heat of reactions for the initiation & propagation steps in the iodination of CH_4 are as-

(a) Initiation → $\Delta H = +36$ Kcal/mol or 151.2 KJ/mol

(b) Propagation → +31 Kcal/mol or 130.2 KJ/mol

→ $\Delta h = -17$ Kcal/mol or 71.4 KJ/mol

↳ It is clear from above data that the hydrogen abstraction by iodine atom is appreciable endothermic & so the energy of activation for this step must be higher than 31 Kcal/mol or 130.2 KJ/mol.). To gain this energy an iodine atom must collide with a large no of alkane molecules & during this process, the chances of its getting combined with a IInd Iodine atom are quite high. So it is a very slow process.

(X) Fluorination → extremely rapid & exothermic process. Its rapidity के कारण, fluorination reactions are usually carried out in the gas phase by diluting the fluorine with N_2 or other inert gases.

Propagation → $\Delta h = -33$ Kcal/mol or 38.6 KJ/mol

$\Delta h = -71$ Kcal/mol or 298.2 "

Since fluorination proceeds in the dark even at -80° & in the absence of chemical chain initiation. So initial dissociation of a F_2 molecule is not an essential requirement for the success of a reaction.

(8)

$F-F \longrightarrow 2F^{\cdot}$ $\Delta H = 37$ Kcal/mol or 155.4 KJ/mol

Instead, chain initiation proceeds by the reaction of F_2 molecule with an alk give a F atom along with an $CH_3^{\cdot}$ $CR^{\cdot}$ which requires only 5 kcal/mole or 21K of energy & so takes place at low temp.

$$F-F + H-CH_3 \longrightarrow H-F + F^{\cdot} + \dot{C}H_3$$

37 102

($\Delta H = +5$ Kcal/mol 21 KJ