(#) Peroxide Effect / Anti Markonicov's addn / Kharash effect :-

(1) $H_3C-CH=CH_2 + H-Br$

H: less stable; Br: most stable

$\xrightarrow{}$ $H_3C-\underset{Br}{CH}-CH_3$

(*) Electrophilic addn
(*) Ionic addn
(*) M. addn

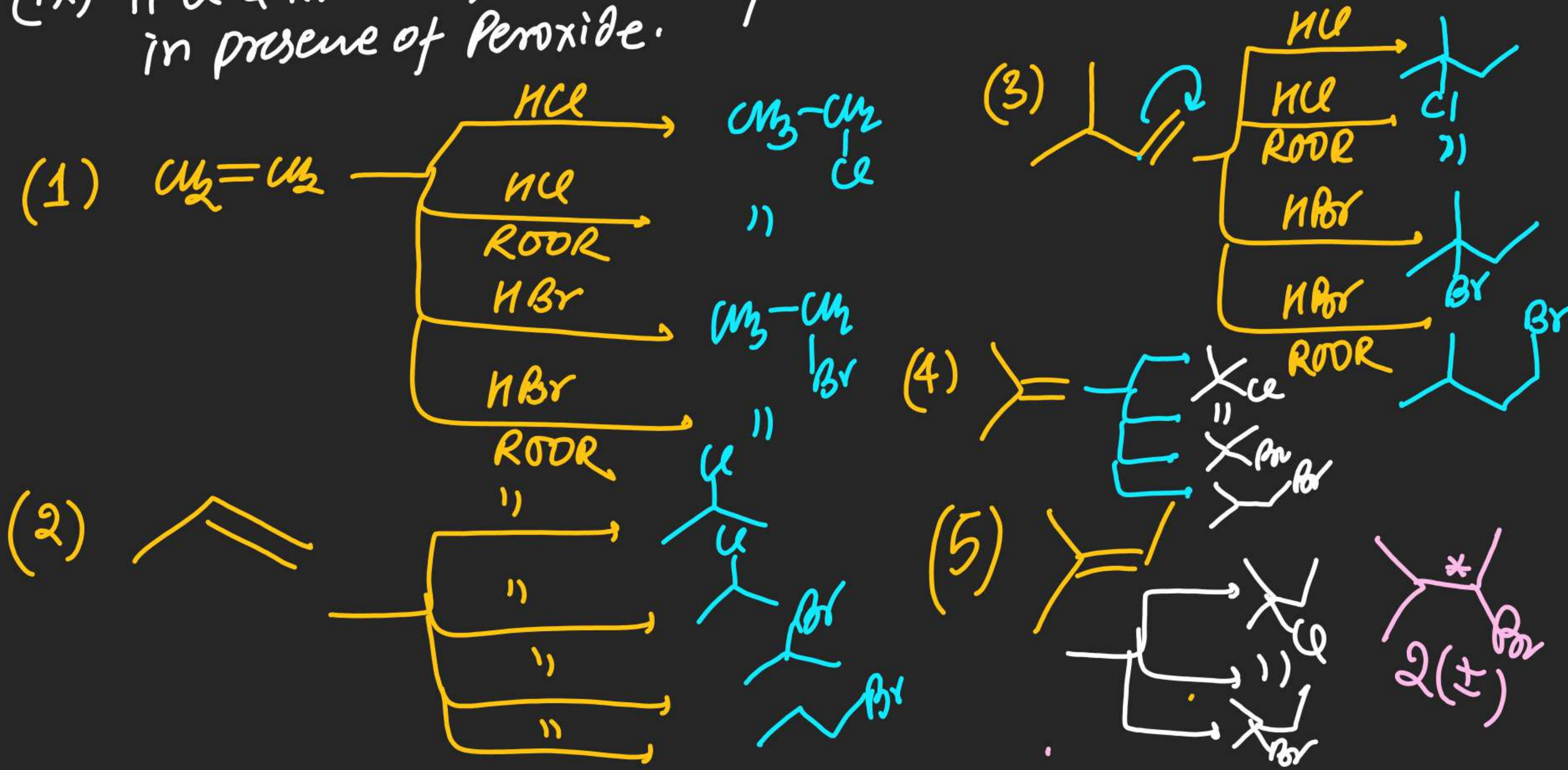
$\xrightarrow{R-O-O-R}$ $H_3C-CH_2-\underset{Br}{CH_2}$ most stable

(*) Anti M. addn
(*) Free Radical addn

$\Rightarrow$ On addn of HBr on alkene in presence of peroxide it gives Product formed By following Anti Markonicov's addn.

(2) $CH_3-CH=CH_2 + H-X \xrightarrow{R-O-O-R} CH_3-CH_2-\underset{X}{CH_2}$

(ix) H-Cl & HF shows ionic addn / M. addn even in presence of Peroxide.



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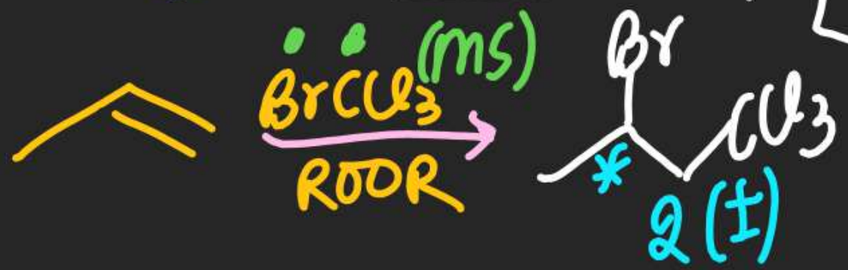
(6) 

(7)

(8) 

(9) 

(10) 

(11) 

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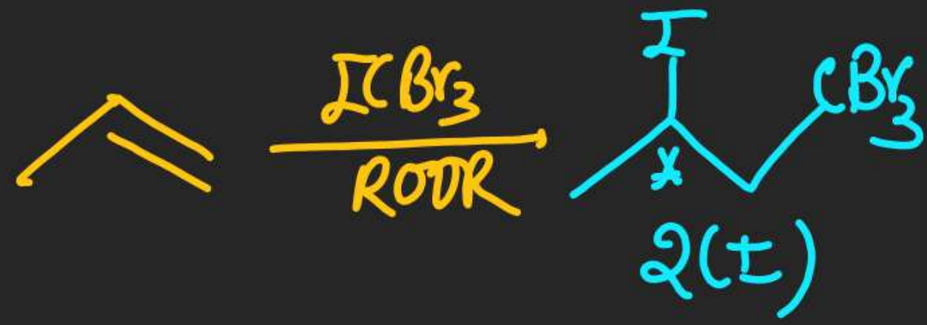
(13) 

(14) 

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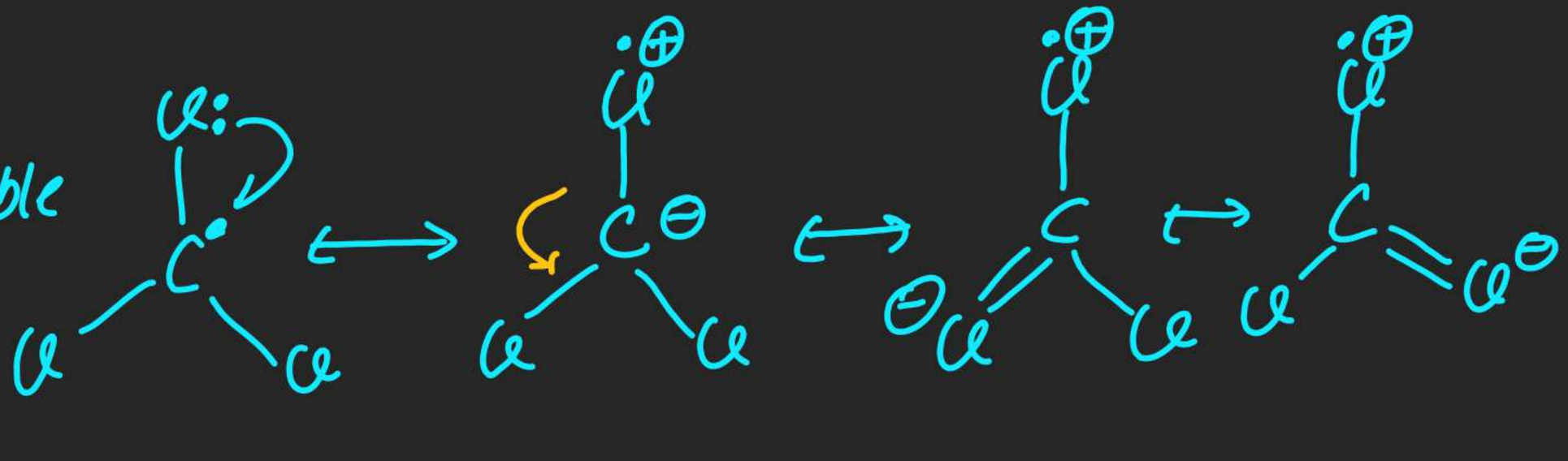
more stable due to Resonance



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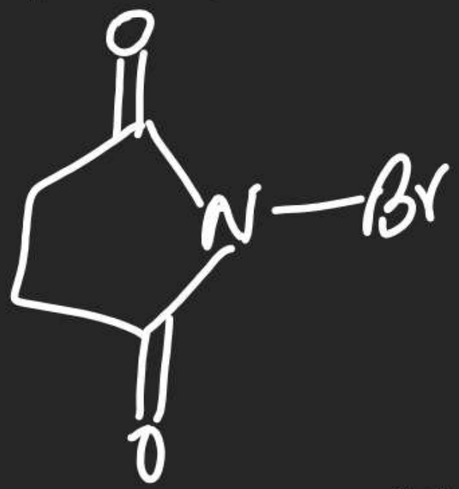
Free Radical Substitution Reaction :-

⇒ when a free Radical substitutes another Radical during a Reaction is known as free Radical Substitution Rxn

(1) NBS

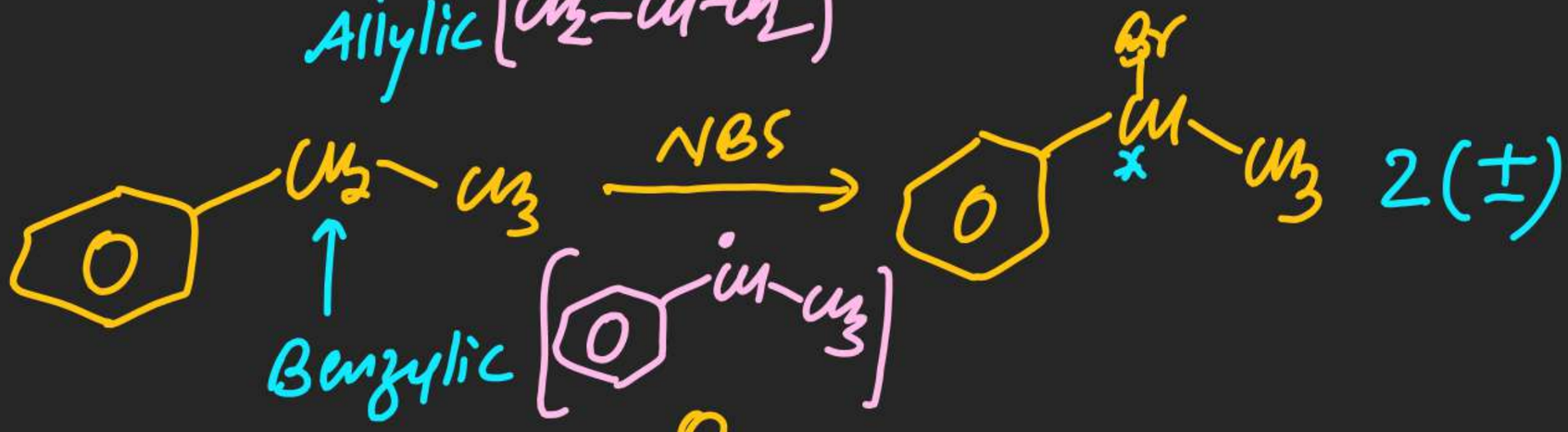
⇒ N-Bromo Succinimide

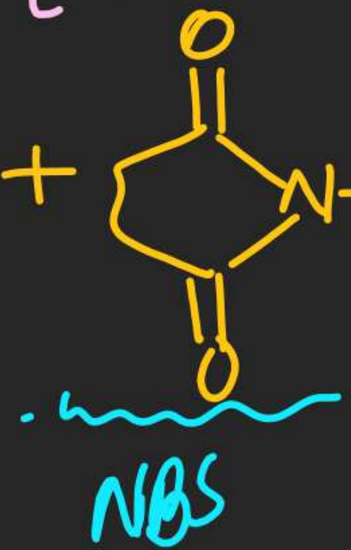
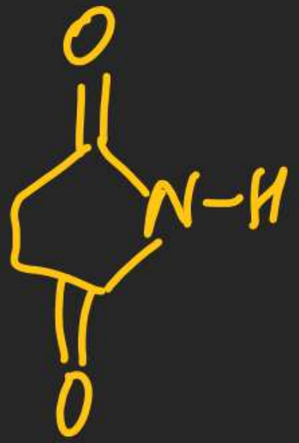
⇒ 

⇒ It oxidises Allylic & Benzylic position by Bromonating it.

(1) $CH_2=CH-CH_3 \xrightarrow{NBS} CH_2=CH-CH_2-Br$

Allylic $[CH_2=CH-\dot{C}H_2]$

(2) 

(3) $CH_2=CH-CH_3 +$  $\longrightarrow CH_2=CH-CH_2-Br +$ 

NBS

⟹ It also oxidizes 1° & 2° Alcohols.

(4) $R-CH_2-OH \xrightarrow{NBS} R-C(=O)-H$

$\hookrightarrow [R-\dot{C}H-OH] \longrightarrow [R-CH(Br)-\overset{\oplus}{O}H] \xrightarrow{-HBr} R-C(=O)-H$

(5) $\begin{matrix} R \\ R \end{matrix}\!\!>\!CH-OH \xrightarrow{NBS} \begin{matrix} R \\ R \end{matrix}\!\!>\!C=O$

⟹ NBS is a Source of Br_2

⟹ NBS Supply Br_2 in Small instalments during Reaction

⟹ Pure NBS is inert

⟹ Impure NBS is used having Impurity of Br_2 or HBr.

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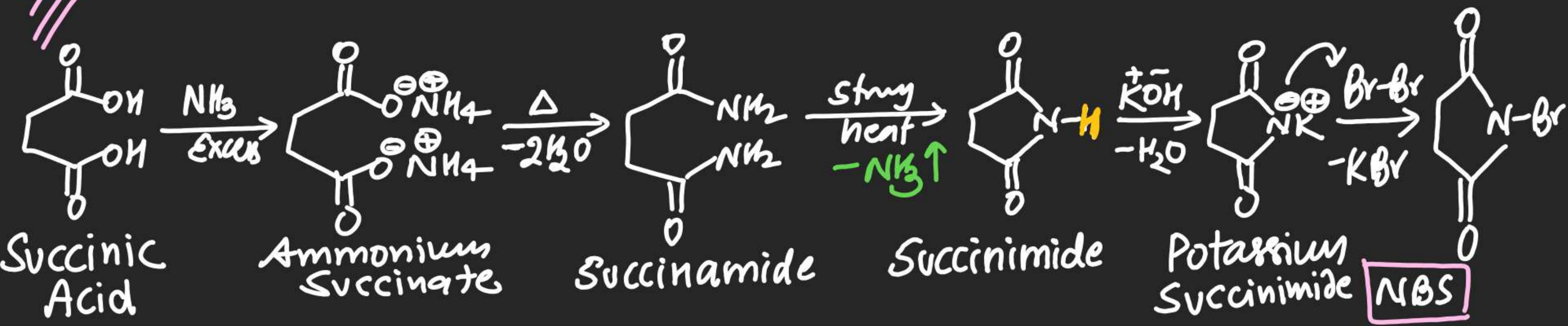
(#) Prepration of NBS :-

NBS can be prepared By using following Sequence of Rxn



(6) $CH_3-\overset{14}{C}H=CH_2 \xrightarrow{NBS}$

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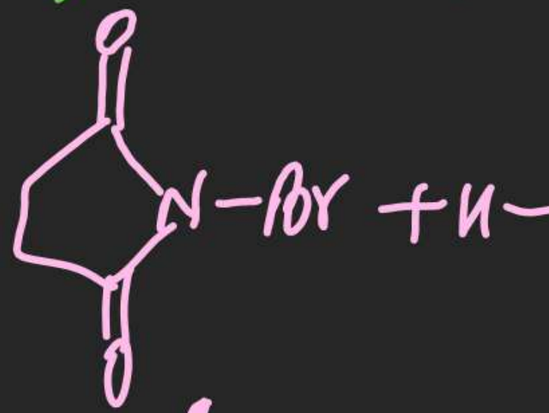
Mechⁿ: let us Consider Impurity is Br_2

$$Br-Br \xrightarrow{h\nu} 2Br^{\bullet}$$

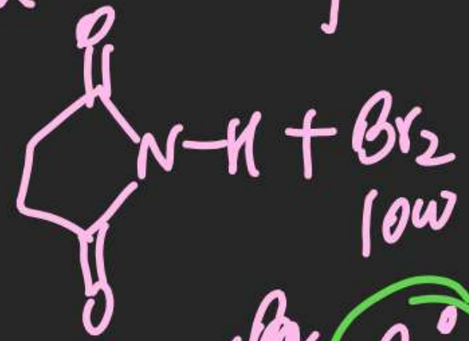
(Small in Conc.)

$$Br^{\bullet} + {}^{1}4CH_2=CH-CH_2-H \xrightarrow{r.d.s} \left[{}^{1}4CH_2=CH-\dot{C}H_2 \leftrightarrow {}^{1}4\dot{C}H_2-CH=CH_2 \right] + H-Br$$

(low Conc.)



$$+ H-Br \longrightarrow$$



$$+ Br_2$$

low

$${}^{1}4CH_2=CH-\dot{C}H_2 + Br-Br \longrightarrow {}^{1}4CH_2=CH-CH_2-Br + Br^{\bullet}$$

$$CH_2=CH-CH_2-Br$$

${}^{1}4$

Note (i) For Radical Intermidiate
(ii) Chain Reaction

(#) Find Total number of mono Brominated product Excluding & including Stereoisomerism.

(7) $CH_3-CH_2-CH=CH_2 \xrightarrow{NBS}$

Allylic

Soln:

Possible Radical: $CH_3-\dot{C}H-CH=CH_2 \leftrightarrow CH_3-CH=CH-\dot{C}H_2$

Possible Product

$CH_3-\underset{*}{CH}(Br)-CH=CH_2 + CH_3-CH=CH-CH_2(Br)$

$2(d+l)$ $\quad$ $2(Z+E)$

Exstero 2 $\quad$ Instero 4

(8) $CH_3-CH=CH-CH_3 \xrightarrow{NBS}$

(9) $CH_3-CH=CH-CH_2-CH_3 \xrightarrow{NBS}$

(10)  $\xrightarrow{NBS}$

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(11)  NBS →

(12)  NBS →

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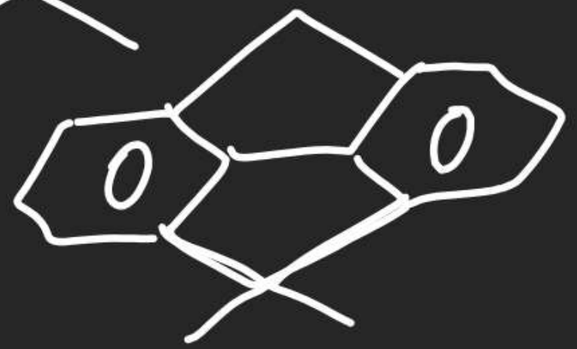
(13)  NBS →

(#) Write major Product

(14)  $\xrightarrow{NBS}$

(15)  $\xrightarrow{NBS}$

(16)  $\xrightarrow[(1eq)]{NBS}$ P $\xrightarrow[(1eq)]{NCS}$ Q

(17)  $\xrightarrow{NBS}$

(18)  $\xrightarrow{NBS}$

(19)  $\xrightarrow{NBS}$

(20)  $\xrightarrow{NBS}$

(21)  $\xrightarrow{NBS}$

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(#) Reed'ff Reaction:-

⇒ alkane on Reaction with SO_2Cl_2 gives alkyl halide as a Product

(1) $R-H + SO_2Cl_2 \xrightarrow{h\nu} R-Cl + H-Cl + SO_2$

mechⁿ:

Initiation: $SO_2Cl_2 \xrightarrow{h\nu} SO_2 + 2Cl^{\cdot}$

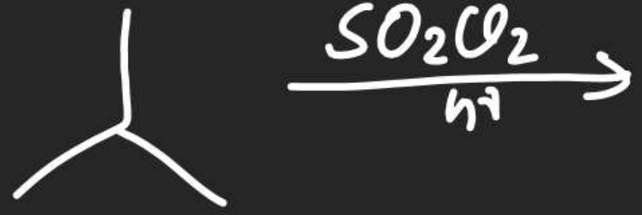
Propagation: $Cl^{\cdot} + R-H \longrightarrow R^{\cdot} + HCl$

$R^{\cdot} + SO_2Cl_2 \longrightarrow R-Cl + SO_2 + Cl^{\cdot}$

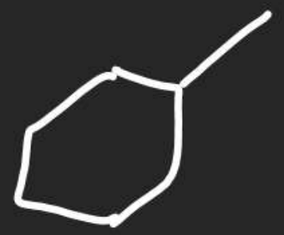
Termination: $Cl^{\cdot} + Cl^{\cdot} \longrightarrow Cl_2$

Note

(i) Free Radical intermidiate
(ii) Chain Rxn
(iii) Oxidation of alkane

(2)  $\xrightarrow[h\nu]{SO_2Cl_2}$

(3)  $\xrightarrow[h\nu]{SO_2Cl_2}$

(4)  $\xrightarrow[h\nu]{}$ 

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(#) Photohalogenation :-

$\Rightarrow$ halogenation of Alkane By using X_2 & photon's Energy of UV rays.

(1) $R-H + X_2 \xrightarrow{h\nu} R-X + H-X$

mechanism :-

Initiation: $X-X \xrightarrow{h\nu} 2X^{\bullet}$

Propagation: $X^{\bullet} + R-H \xrightarrow{\text{Y.d.b}} R^{\bullet} + H-X$

$R^{\bullet} + X-X \longrightarrow R-X + X^{\bullet}$

Termination: $X^{\bullet} + X^{\bullet} \longrightarrow X_2$

$\therefore$

Note

(i) Free Radical intermidiate

(ii) Chain Reaction

(iii) Oxidation of Alkene

(iv) Formation of $R^{\bullet}$ is r.d.s

(v) order of rate of reaction for $\geq C-H$

$3^{\circ} \geq C-H > 2^{\circ} \geq C-H > 1^{\circ} \geq C-H$

(vi) order of rate of rxn for X_2

$F_2 >> Cl_2 > Br_2 >> I_2$

Flvorination:- Flvorination is highly Exothermic & Explosive phenomenon & it gives Carbon Black.

(2) $CH_4 + 2F_2 \longrightarrow C_{Black} + 4HF$

Chlorination:- Chlorination is highly Exothermic & Explosive phenomenon & it gives Carbon Black in B.S.L

(3) $CH_4 + 2Cl_2 \xrightarrow{BSL} C_{Black} + 4HCl$

(*) Chlorination can be carried out in D.S.L (diffused sunlight)

(4) $CH_4 + Cl_2 \xrightarrow{h\nu} CH_3-Cl$