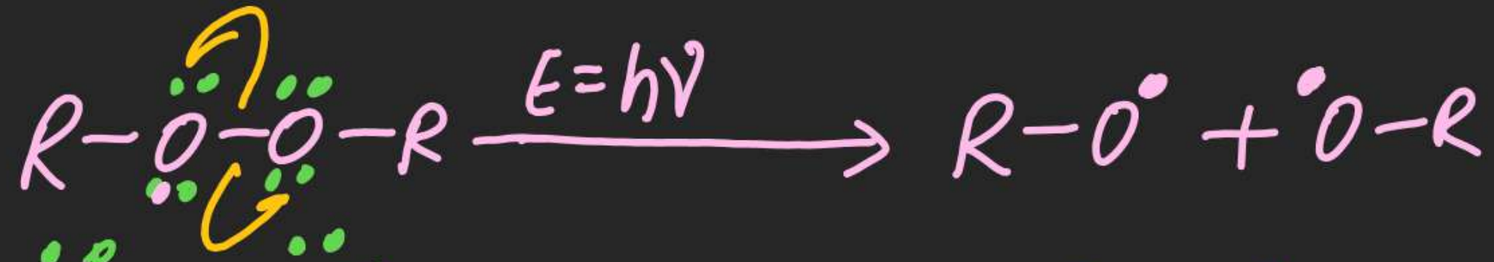
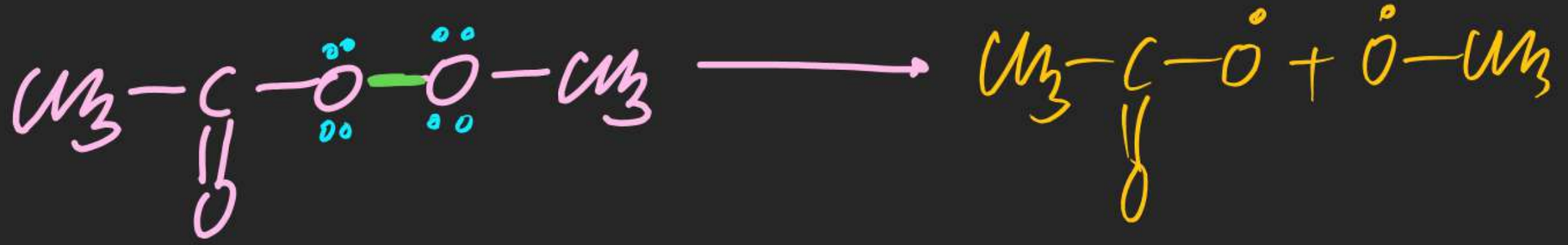
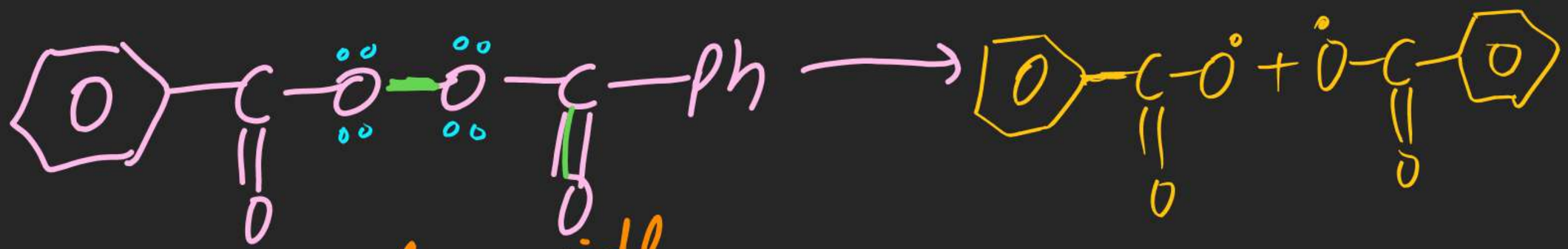
(1) 

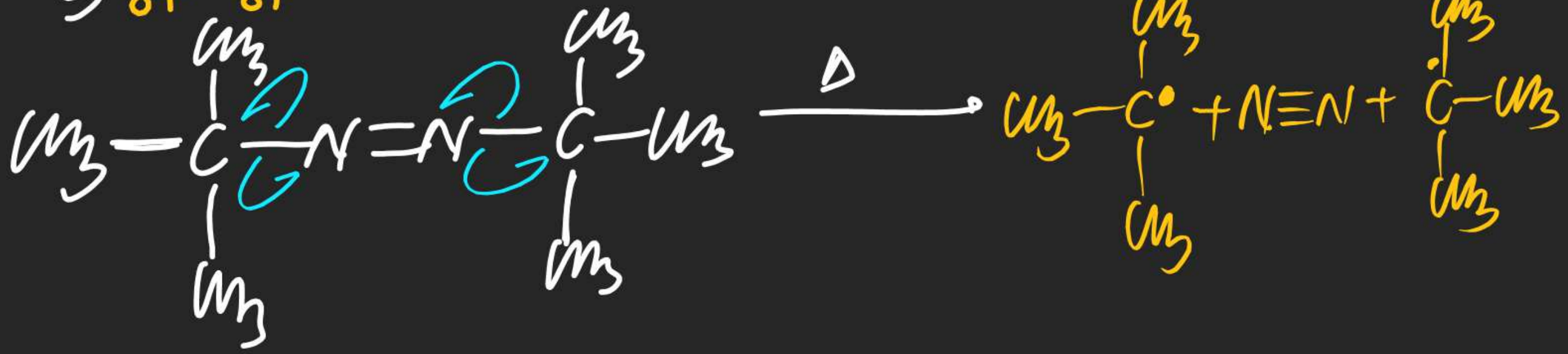
(2) 

(3) 

(4) 

(2) Thermolysis (Pyrolysis) :- By heating homolytic fission is carried out.

(5) 

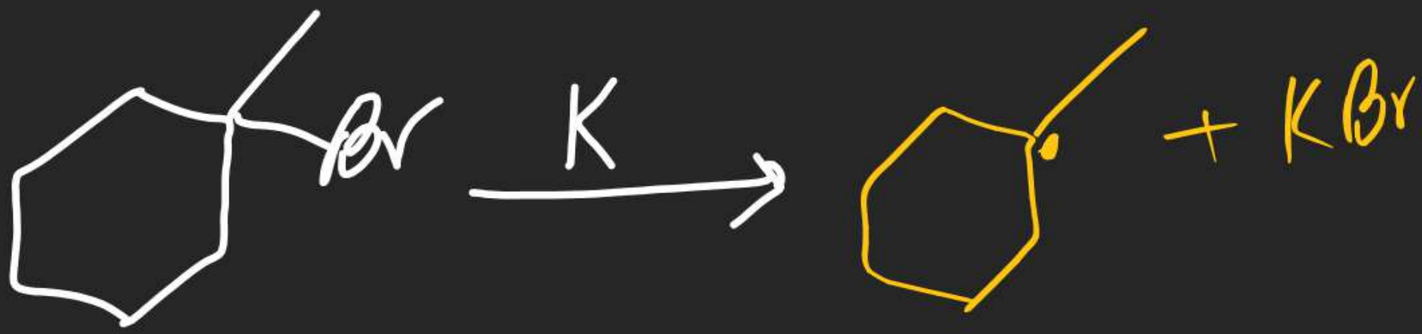
(6) 

(7) 

(3) By Use of metal & metal ion:-

(8) $Na + R\overset{\delta+}{-}X\overset{\delta-}{} \longrightarrow R^{\bullet} + Na^{+}X^{-}$

(9) 

(10) 

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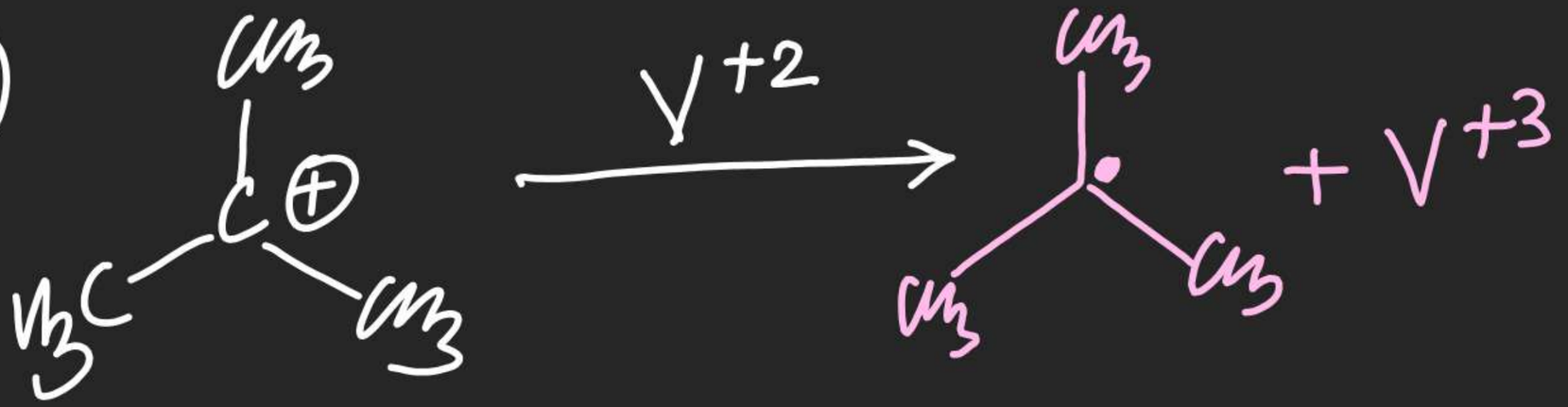
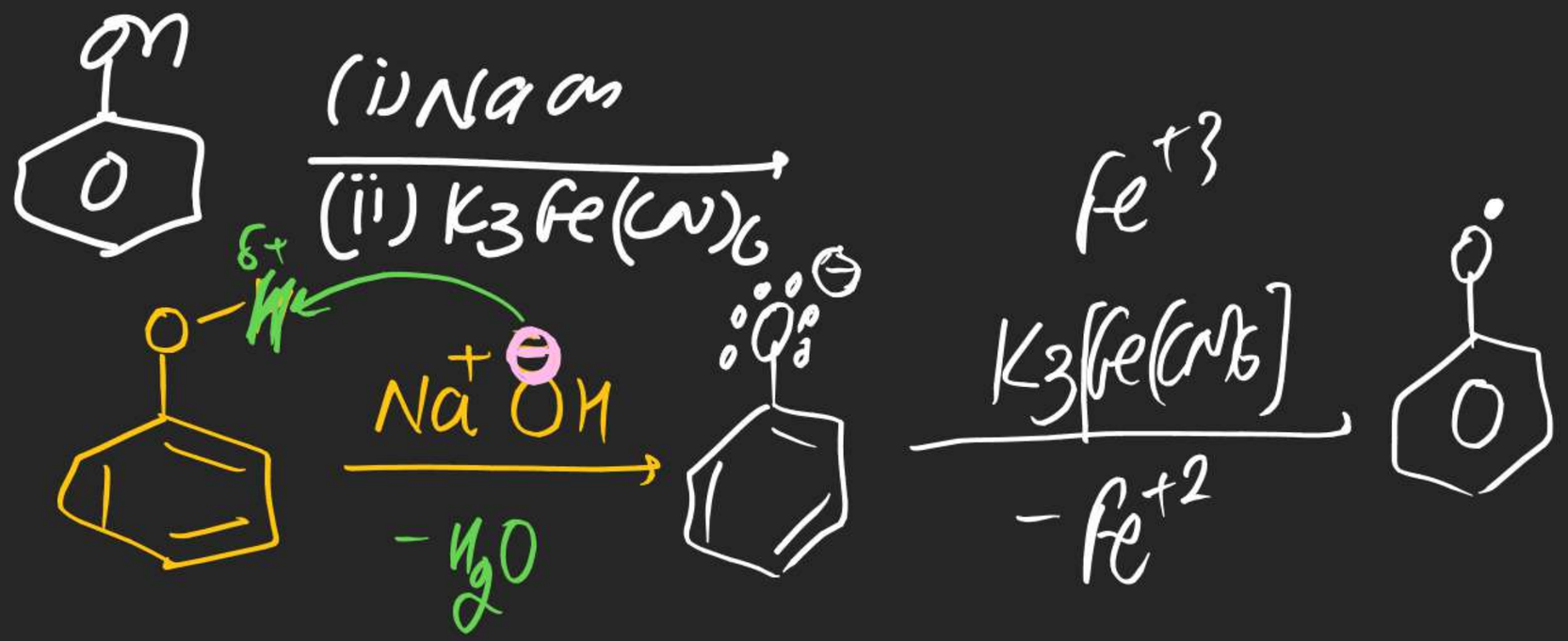
(11)



(12)



(4) By Radical itself :-

(13) $R^{\bullet} + X-X \longrightarrow R-X + X^{\bullet}$

(14) $X^{\bullet} + R-H \longrightarrow R^{\bullet} + HX$

(15) $X^{\bullet} + CH_2=CH_2 \longrightarrow CH_2(X)-\dot{C}H_2$

(16) $X^{\bullet} + CH_3-CH=CH_2 \rightleftharpoons CH_3-\dot{C}H-CH_2(X)$ [Antimarkonicoff's addn]
Reversible Rxn

(high)

Explanation

(17) $X^{\bullet} + CH_2-CH=CH_2 \longrightarrow \dot{C}H_2-CH=CH_2 + HX$ [NBS]

(low)

Explan :-

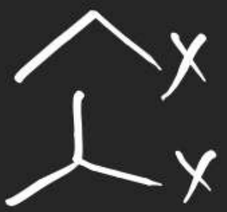
Reactions shown By Free Radical :-

(i) Rearrangement :- Free Radicals usually not show Rearrangement.

(ii) Combination / Disproportionation :-

⟹ Radicals usually Prefer Combination

(1) $CH_3^{\bullet} + X-X \longrightarrow CH_3-X$

(2) $CH_3-CH_2^{\bullet} + X-X \longrightarrow$ 

(3) $CH_3-CH^{\bullet}(CH_3) + X-X \longrightarrow$

(4) $(CH_3)_3C^{\bullet} + X-X \longrightarrow$ 

$\Rightarrow$ Rate of Combination $\propto \frac{1}{\text{Steric Crowdiy}}$

$\Rightarrow$ In inert medium Radicals get dimerised.

(5) $2\dot{C}H_3 \longrightarrow CH_3-CH_3$

(6) $2CH_3-\dot{C}H_2 \longrightarrow$ 

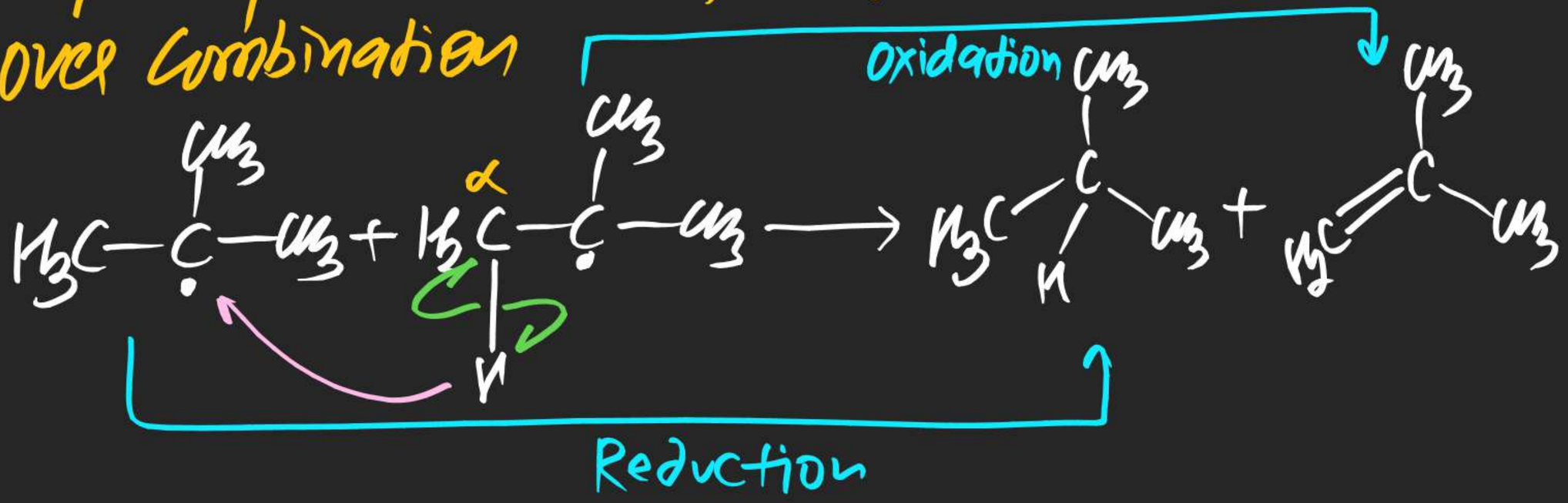
(7) $2CH_3-\dot{C}H-CH_3 \longrightarrow$ 

(8) $2H_3C-\dot{C}(CH_3)_2 \longrightarrow$ 

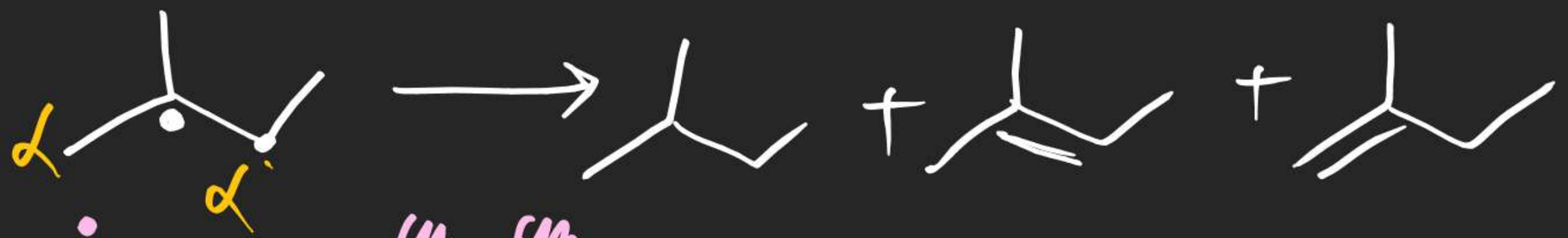
VPY (Very Poor yeild)

Note: higher degree radicals prefer disproportionation over combination

(9)



(10)



(11) $\dot{C}H_3 \longrightarrow CH_3-CH_3$

(12) $Ph-\dot{C}H_2 \longrightarrow Ph-CH_2-CH_2-Ph$

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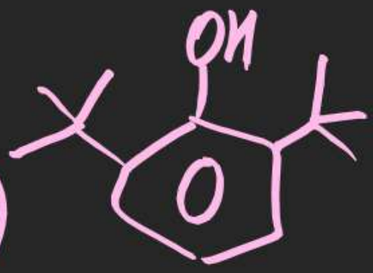
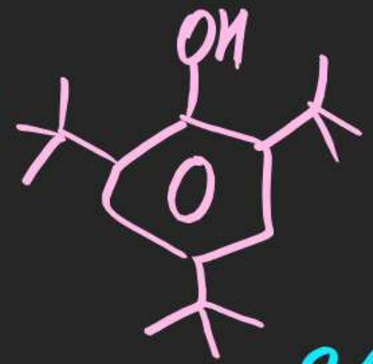
(13) 

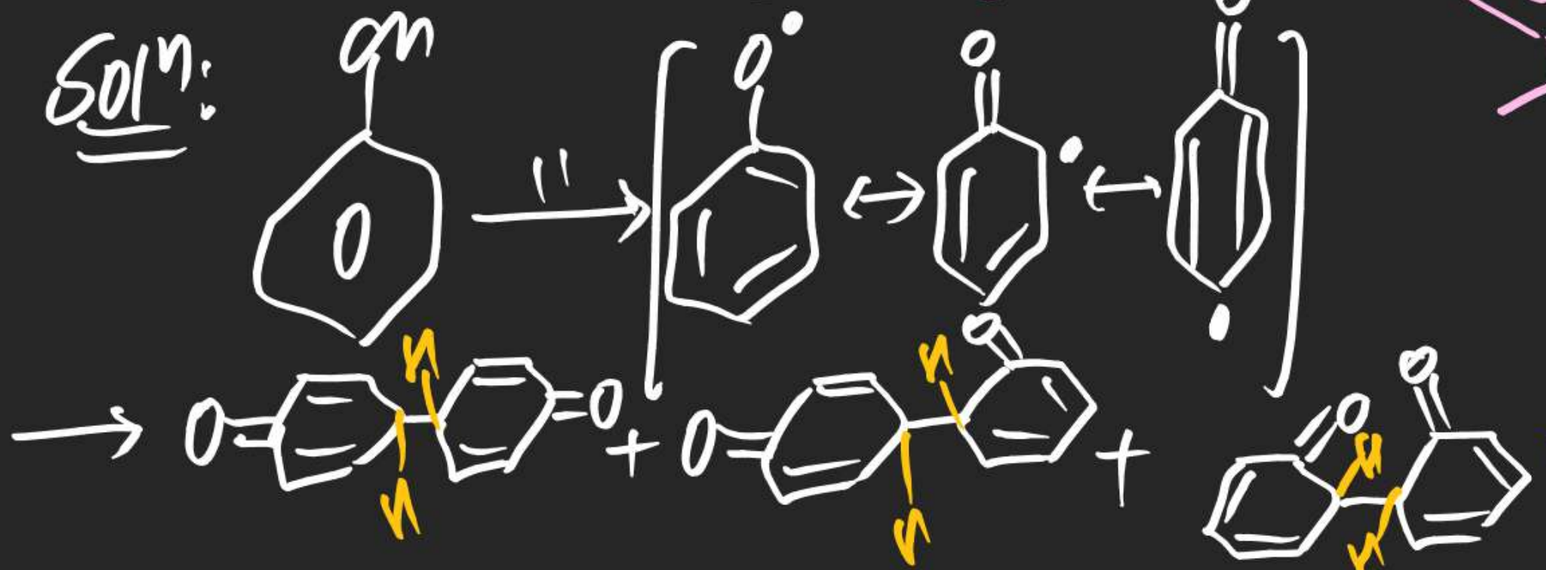
(14) 

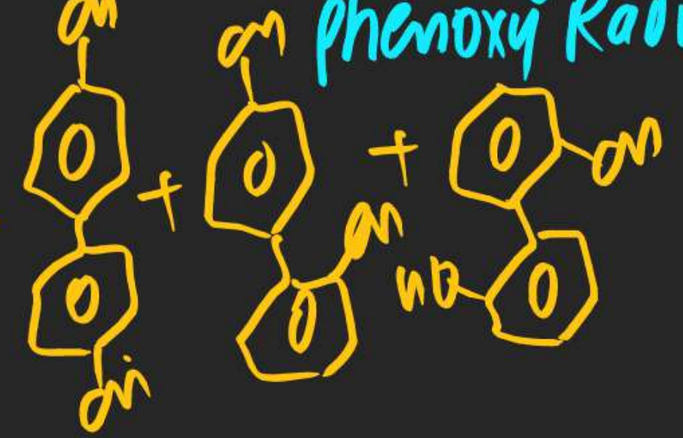
(15) 

(16) 

(17) 

Soln:

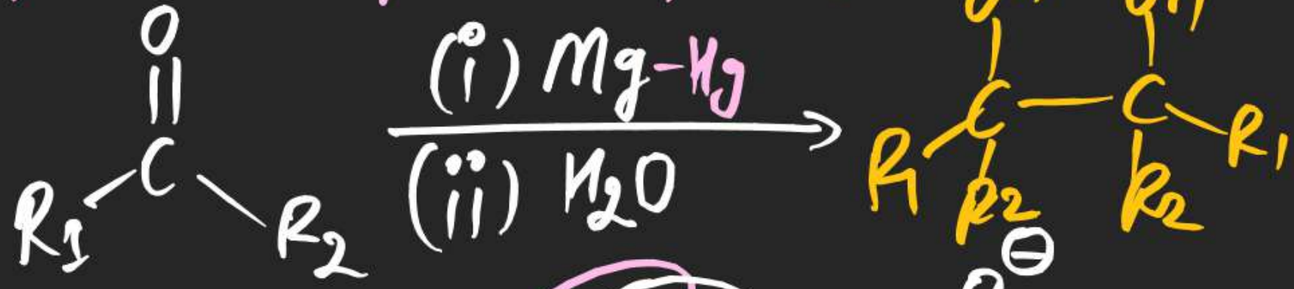




2,4,6-Tri tert-Butyl phenoxy Radical

m.p. (92°)

(#) Pinacole formation :- Carbonyl compound on Reduction By Mg-Hg followed By hydrolysis gives vic-diol / Glycol / Pinacole.

(1) 

Mechⁿ: 

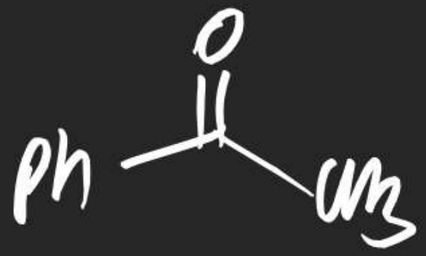
Note (i) Anion-Radical intermidiate

(ii) Total No. of pinacole = 3 $[R_1 \neq R_2]$

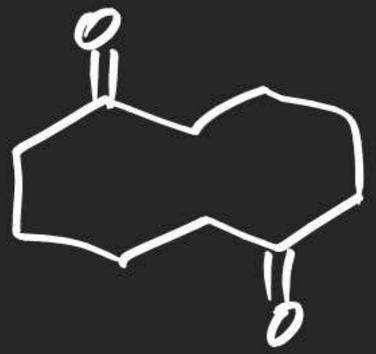
(iii) Total No. of pinacole = 1 $[R_1 = R_2]$

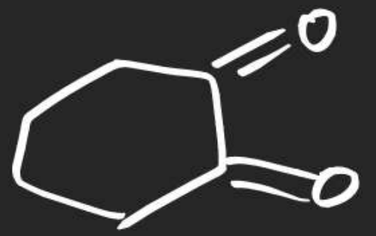
(2)  $\xrightarrow{H^+}$

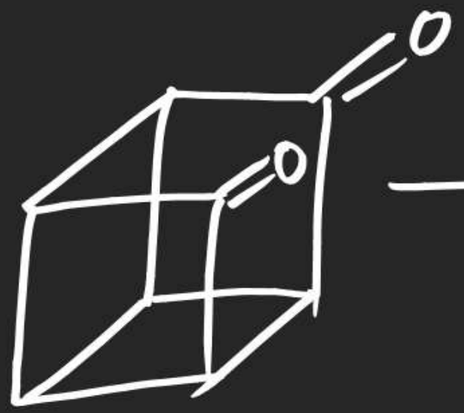
(3)  $\xrightarrow{H^+}$

(4)  $\xrightarrow{H^+}$

(5)  $\xrightarrow{H^+}$

(6)  $\xrightarrow{H^+}$

(7)  $\xrightarrow{H^+}$

(8)  $\xrightarrow{H^+}$

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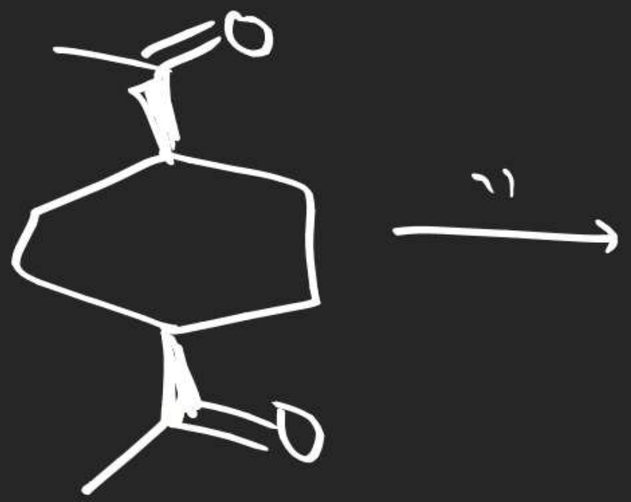
(9) 

(10) 

Acyloin Formation:

In this Rxn Esters gets Reduced By Na-Hg So that α-Hydroxy Carbonyl (Acyloin) is obtained.

(1) $R_1-C(=O)-OR_2$ (Esters) $\xrightarrow[(ii)\ H_2O]{(i)\ Na\text{-}Hg}$ $R_1-CH(OH)-C(=O)-R_1$ (Acyloin) $+\ R_2-OH$

Mechanism:

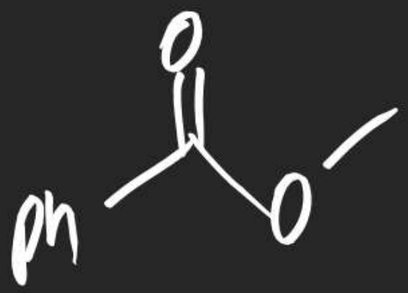
$2\ R_1-C(=O)-OR_2 \xrightarrow{2\ Na} 2\ R_1-\dot{C}(O^{\ominus})-OR_2 \longrightarrow R_1-C(O^{\ominus})(OR_2)-C(O^{\ominus})(OR_2)-R_1 \longrightarrow -(OR_2)$

$R_1-C(=O)-C(=O)-R_1 \xrightarrow{Na\text{-}Hg} R_1-C(O^{\ominus}Na^{\oplus})=C(O^{\ominus}Na^{\oplus})-R_1 \xrightarrow{H_2O} R_1-C(OH)=C(OH)-R_1 \rightleftharpoons R_1-CH(OH)-C(=O)-R_1$

Note (i) Anion Radical intermidiate
(ii) Reduction of esters

(2) 

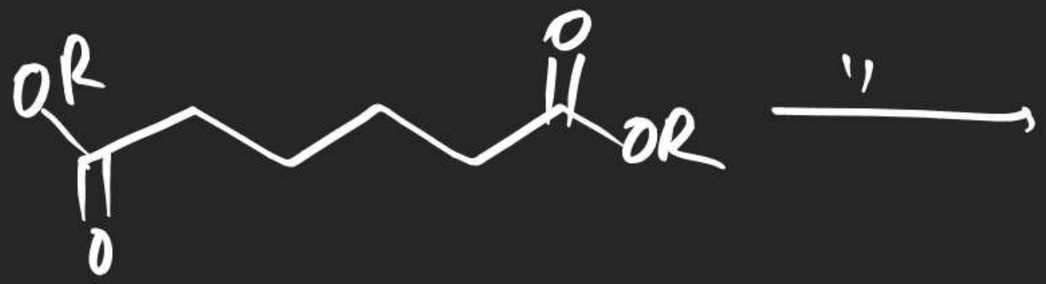
⟶ ||

(3) 

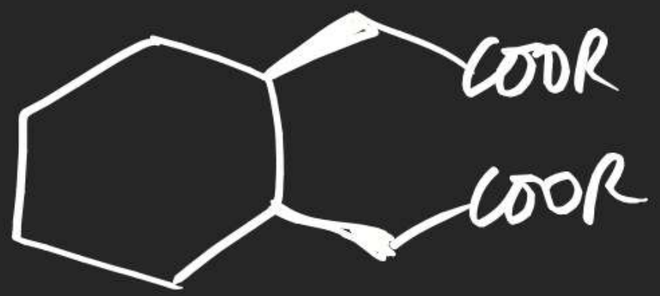
⟶ n

(4) 

⟶ ||

(5) 

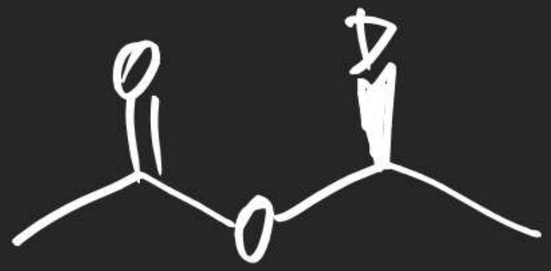
$\xrightarrow{h\nu}$

(6) 

$\xrightarrow{h\nu}$

(7) 

$\xrightarrow{h\nu}$

(8) 

$\xrightarrow{h\nu}$