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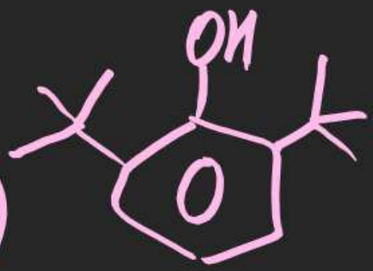
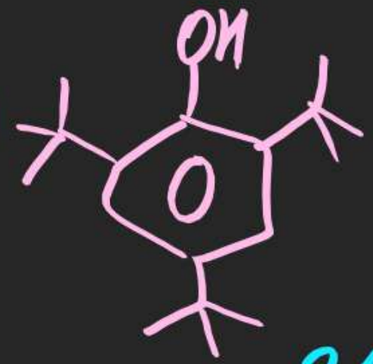
(13) 

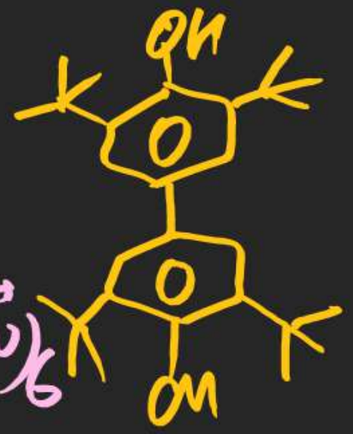
(14) 

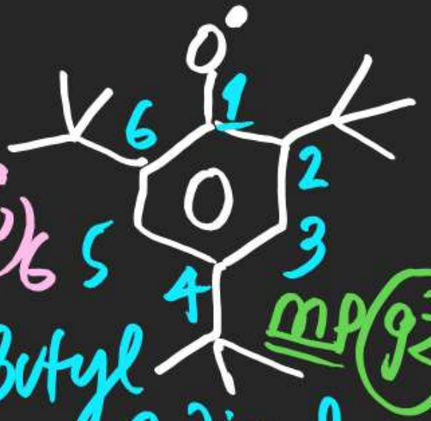
(15) 

(16) 

(17) 

(i) NaOH
(ii) $K_3Fe(CN)_6$

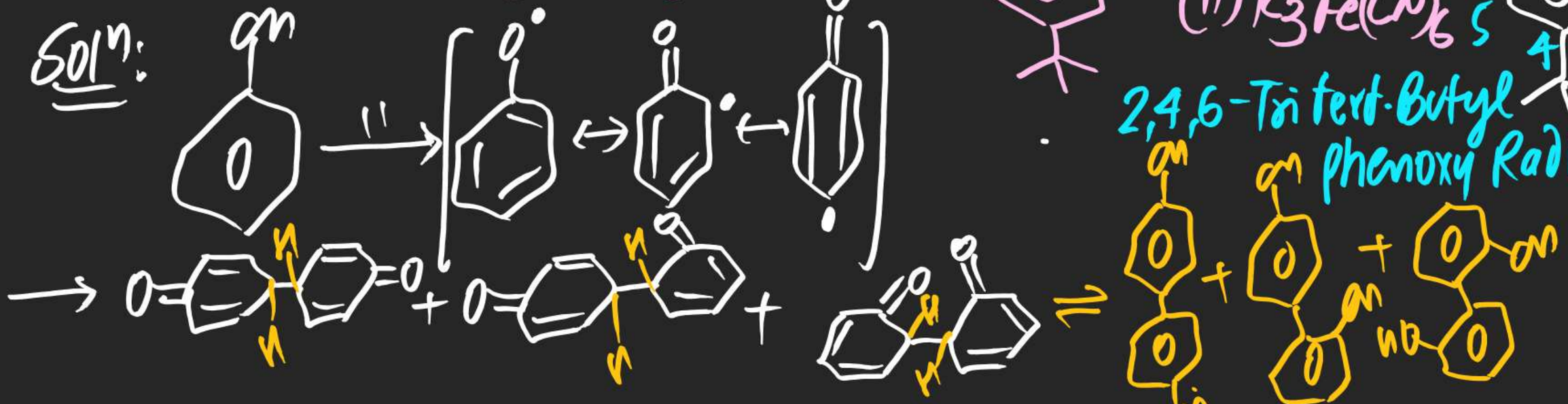




mp (92°)

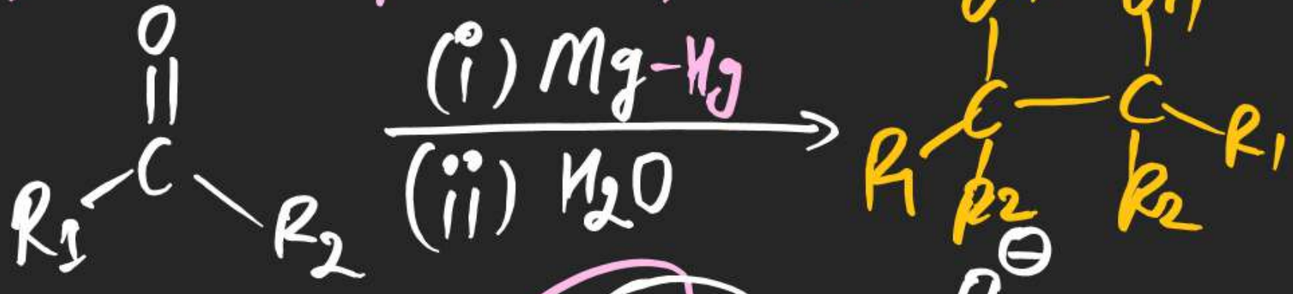
2,4,6-Tri tert-Butyl phenoxy Radical

Soln:



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

(1)

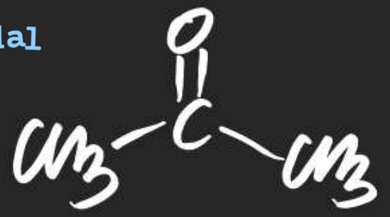


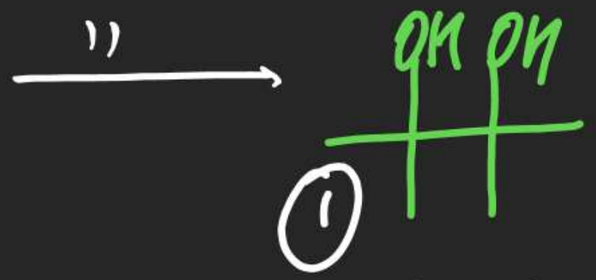
Mechⁿ:

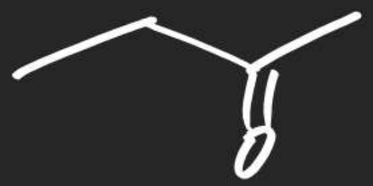
Note (i) Anion-Radical intermidiate

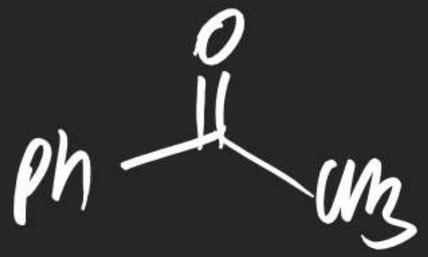
(ii) Total No. of pinacole = 3 [$R_1 \neq R_2$]

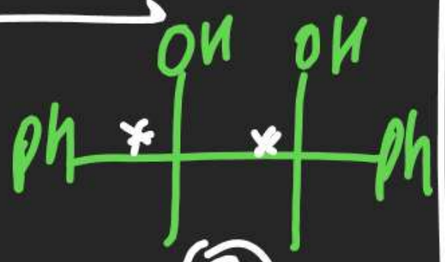
(iii) Total No. of pinacole = 1 [$R_1 = R_2$]

(2) 



(3) 

(4) 



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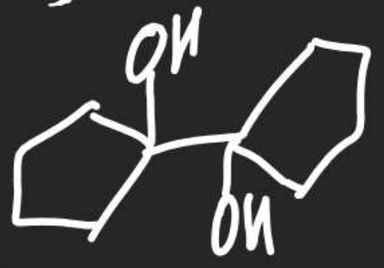
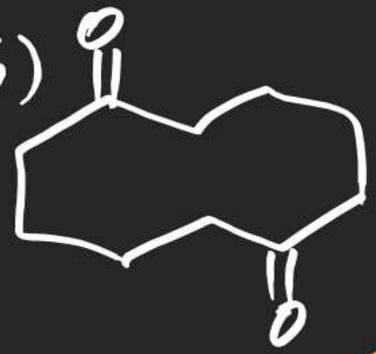
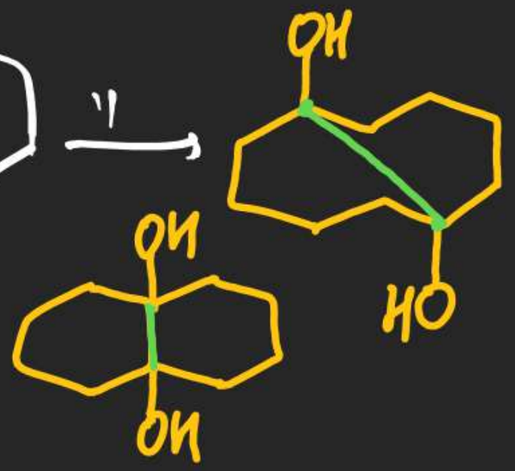
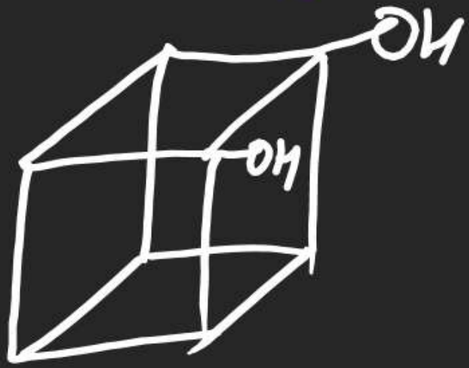


(6) 



(7) 

(8) 



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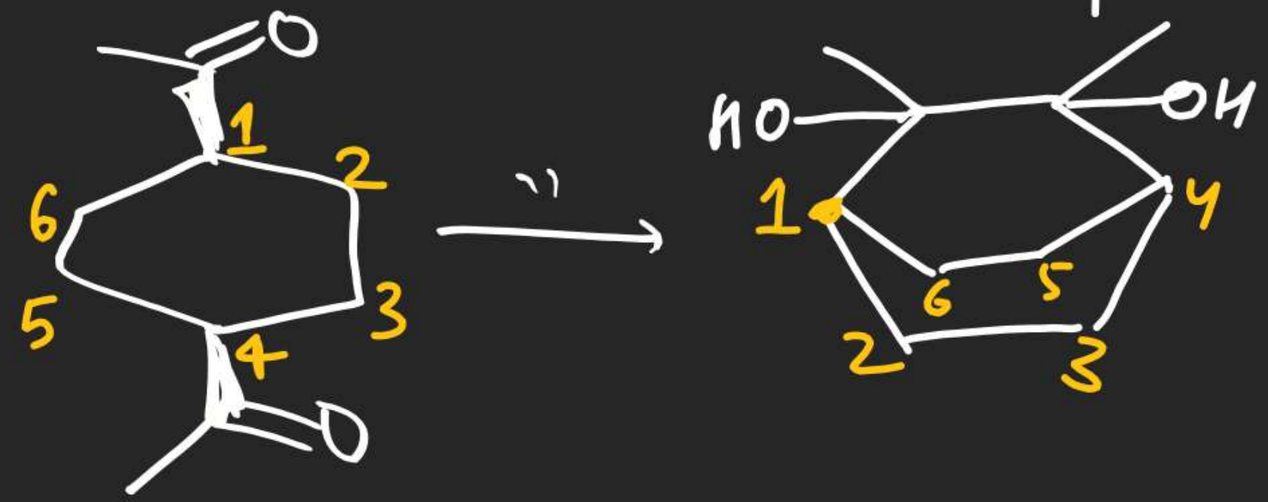
(9)

3

(10)



Acyloin Formation:

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

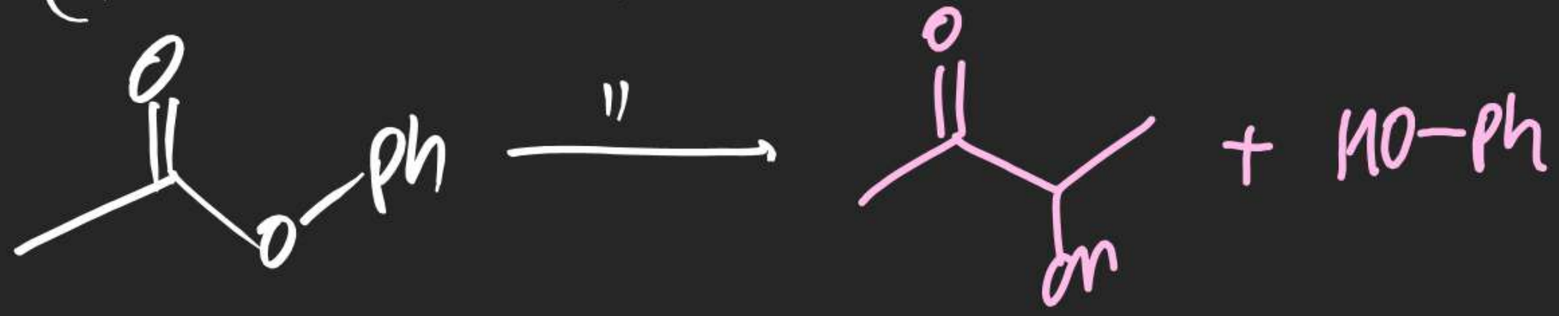
(1) $R_1-C(=O)-OR_2$ (Esters) $\xrightarrow[(ii)\ H_2O]{(i)\ Na\text{-}Hg}$ $R_1-CH(OH)-C(=O)-R_1$ (Acyloin) $+\ R_2-OH$

Mechanism:

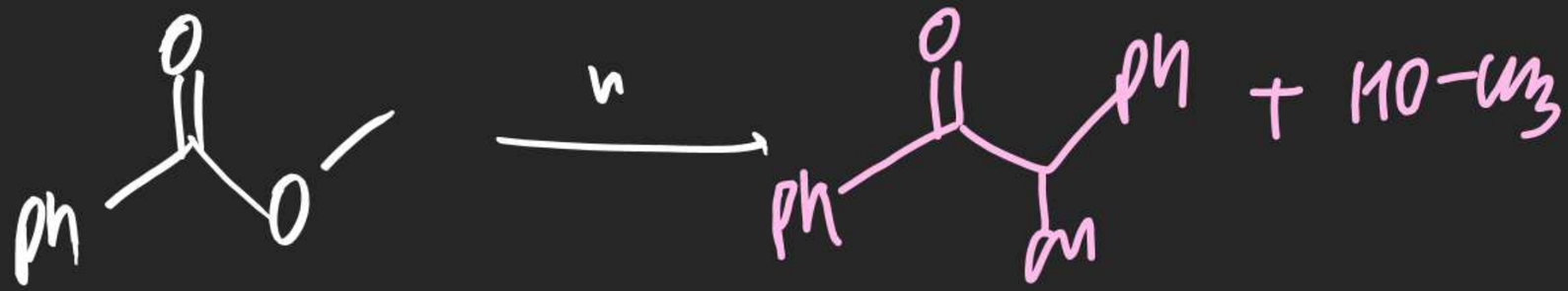
$2\ R_1-C(=O)-OR_2 \xrightarrow{2\ Na} R_1-C(O^{\ominus})(\cdot)-OR_2 \longrightarrow R_1-C(OR_2)-C(OR_2)-R_1 \longrightarrow$

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

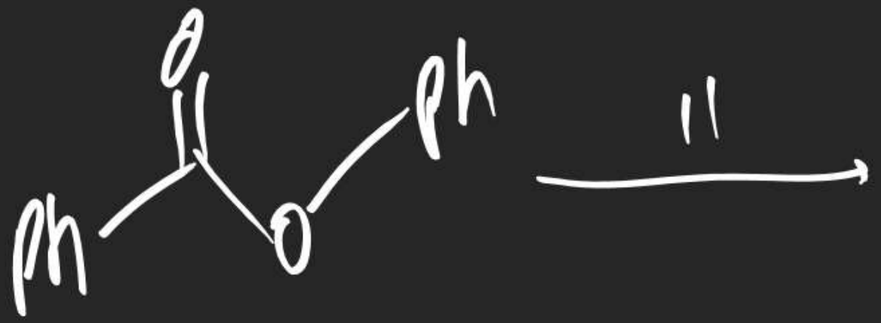
Note (i) Anion Radical intermidiate
(ii) Reduction of esters

(2) 

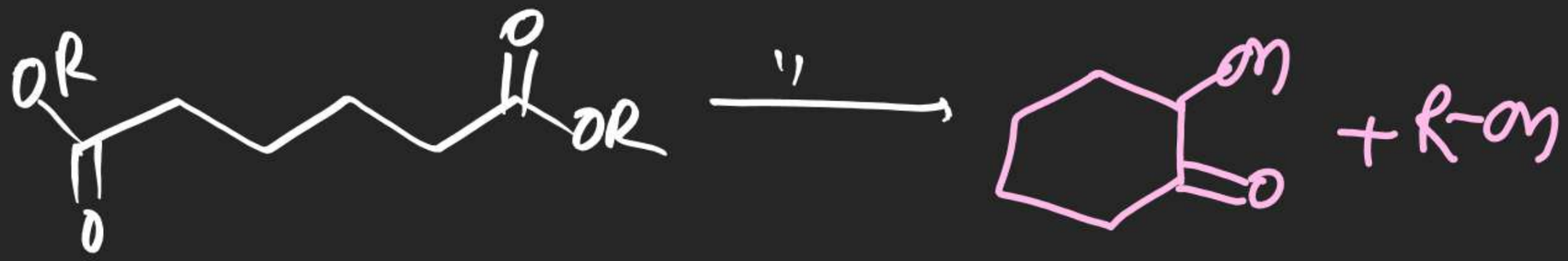
+ HO–Ph

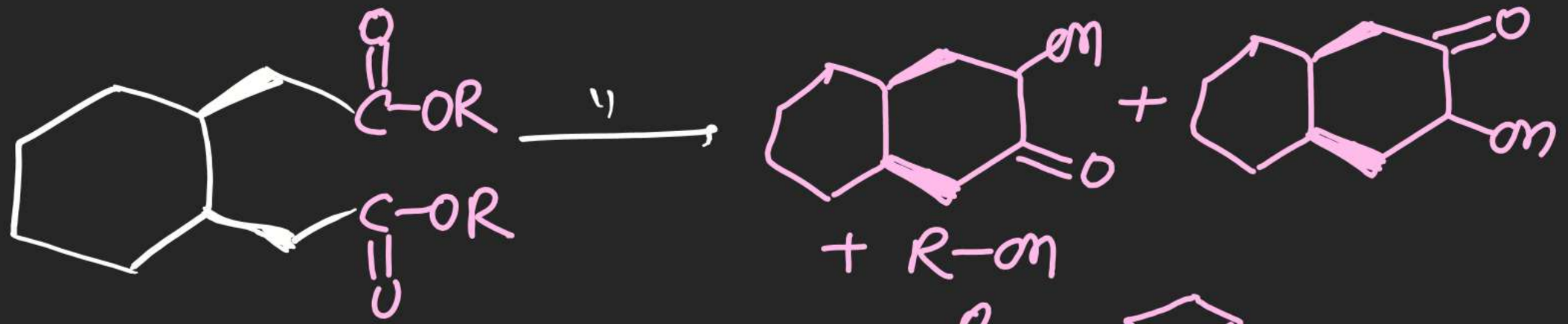
(3) 

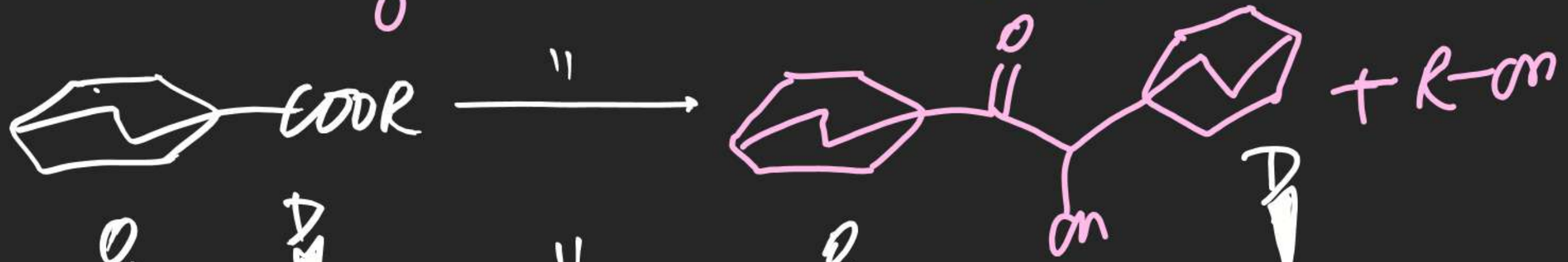
+ HO–CH3

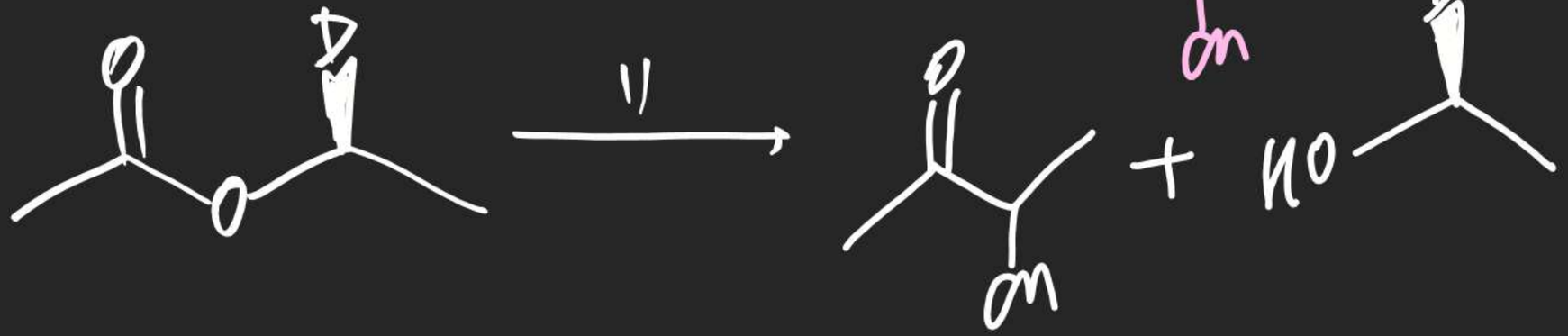
(4) 


+ HO–Ph

(5) 

(6) 

(7) 

(8) 

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(#) Wurtz Reaction:

⇒ In this Reaction alkyl halide is treated with Sodium metal in dry ether so that hydrocabon is obtained as a Product.

(1) $R-X + 2Na + X-R \longrightarrow R-R + NaX$

Mechanism: Radical mechanism

$$2Na + 2R-X \xrightarrow{\text{Y.D.R}} 2R^{\bullet} + 2NaX$$

$$2R^{\bullet} \longrightarrow R-R$$

Ionic Mechanism:

$$2Na + R-X \xrightarrow{\text{Y.D.R}} R^{\ominus}\overset{\oplus}{Na} + NaX$$

$$R^{\ominus}\overset{\oplus}{Na} + R-X \longrightarrow R-R + NaX$$

Note (i) Free Radical & Carbanion intermidiate

(ii) Breaking of $>C-X$ Bond is r.d.s

(iii) order of rate of ox^n for R–X

$$R-I > R-Br > R-Cl > R-F$$

(iv) It's Reduction of alkyl halide

(v) Na is highly Reactive metal with moisture hence used in dry conditions

$$H-O-H + Na \longrightarrow NaOH + \frac{1}{2}H_2\uparrow$$

(moisture)

(vi) Formation of Symmetrical & Even no of Hydrocarbon alkane takes place in good yeild By Wurtz Reaction

(a) $2CH_3-Cl \xrightarrow[\text{Dry ether}]{Na} CH_3-CH_3$ (good yeild)

(b) $2CH_3-CH_2-Br \xrightarrow[CH_3-CH_3]{Na} CH_3-CH_3 + CH_3-CH_2-CH_3$ (good yeild)

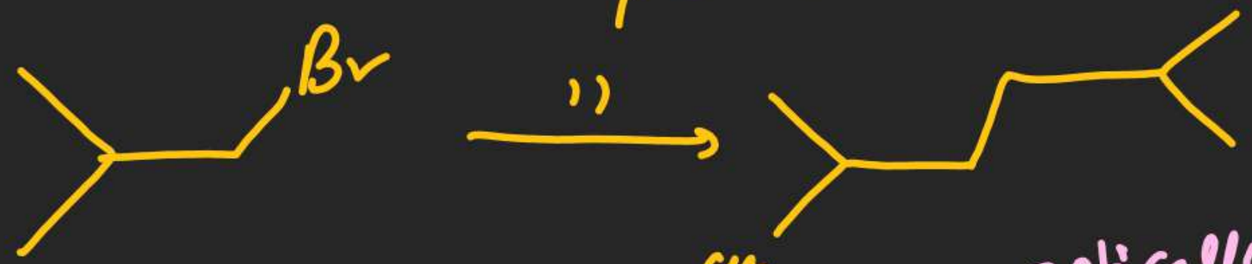
(vii) Formation of unsymmetrical & odd no of Hydrocarbon alkane takes plane in poor yeild By Wurtz Reaction

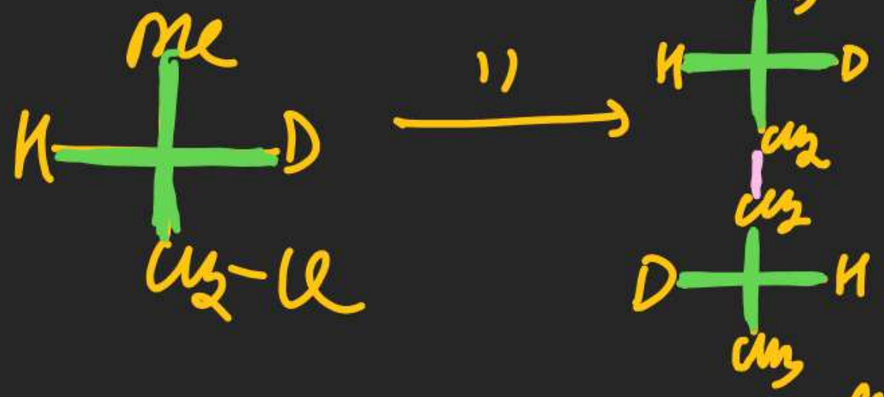
(c) $H_3C-Cl + H_3C-CH_2-Cl \xrightarrow[CH_3-CH_2]{Na} \underbrace{H_3C-CH_2-CH_3 + CH_3-CH_2-CH_2-CH_3 + CH_3-CH_3}_{\text{(Poor yeild)}}$

. . .

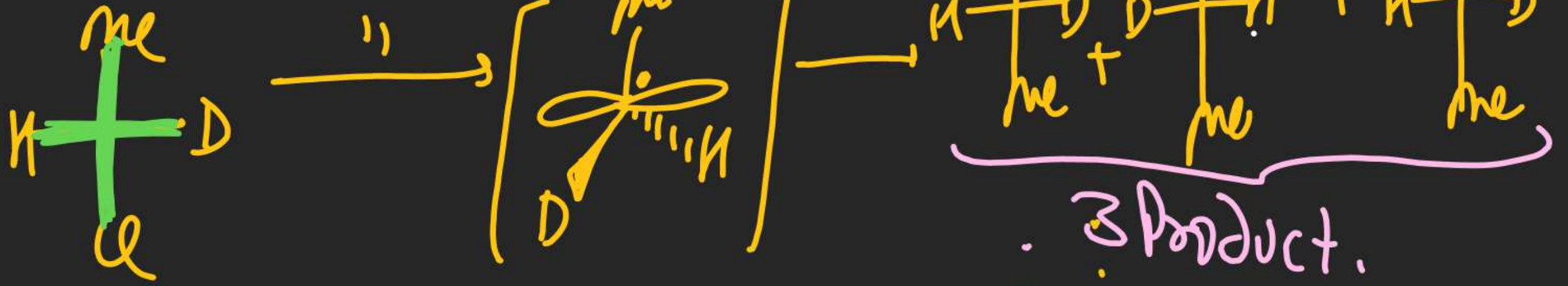
(viii) CH_4 never can be obtained By wurtz Rxn

(1) $CH_3-CH_2-CH_2-Cl \xrightarrow[\text{Dry Ether}]{Na} CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

(2) 

(3) 

Optically Active
(1 Product)

(4) 

∴ 3 Product.

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(5) 

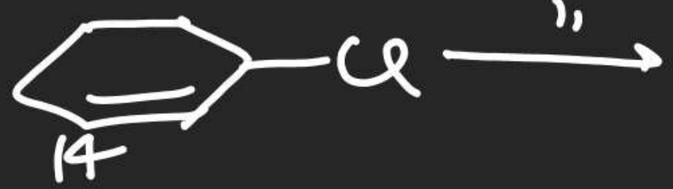
(6) 

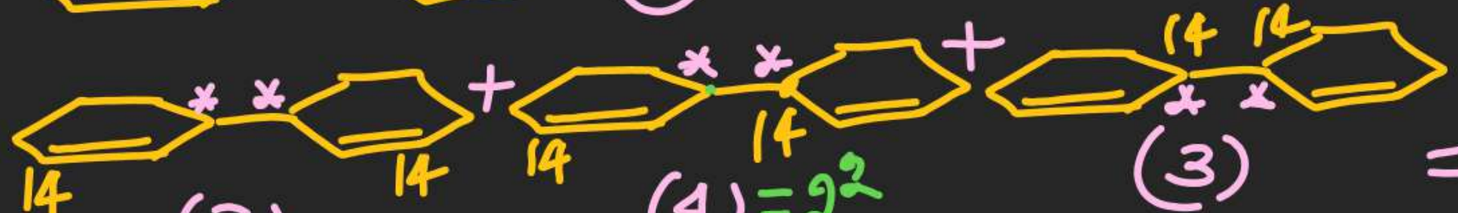
Soln: 

P–P P–Q Q–Q

(7) 

③

(8) 



(3) (4) $= 2^2$ (3) $= 10$

(9) 

(10) 

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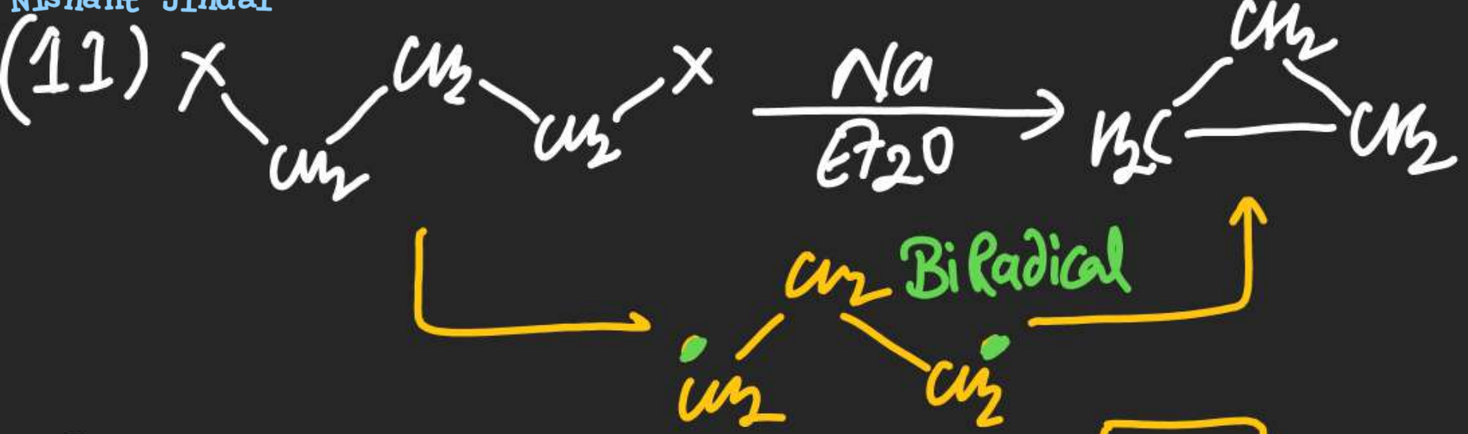
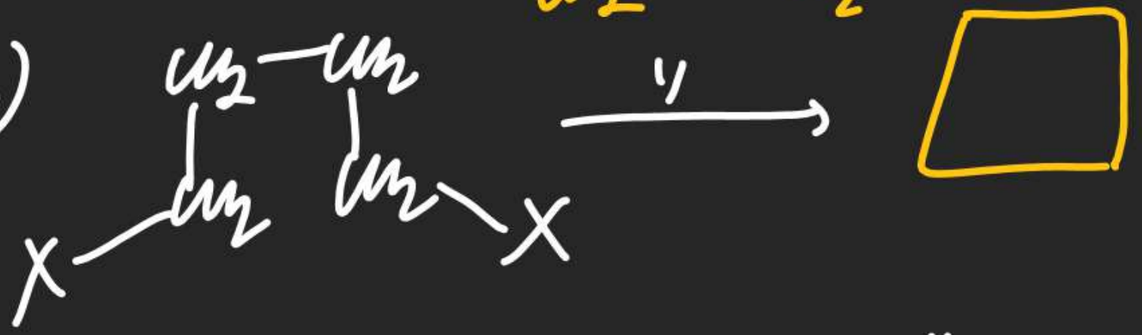
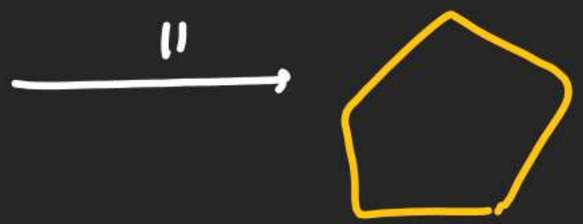
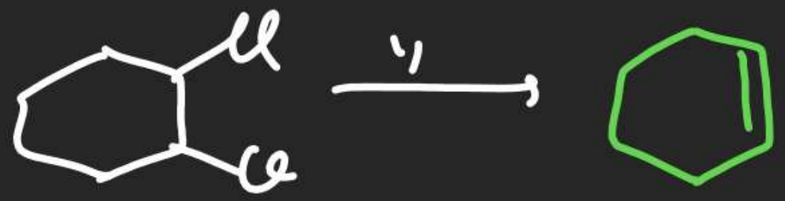
(11) 

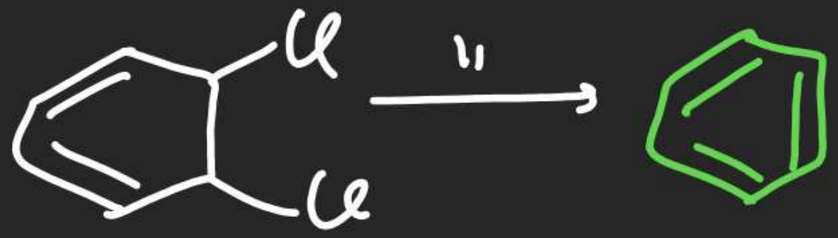
(12) 

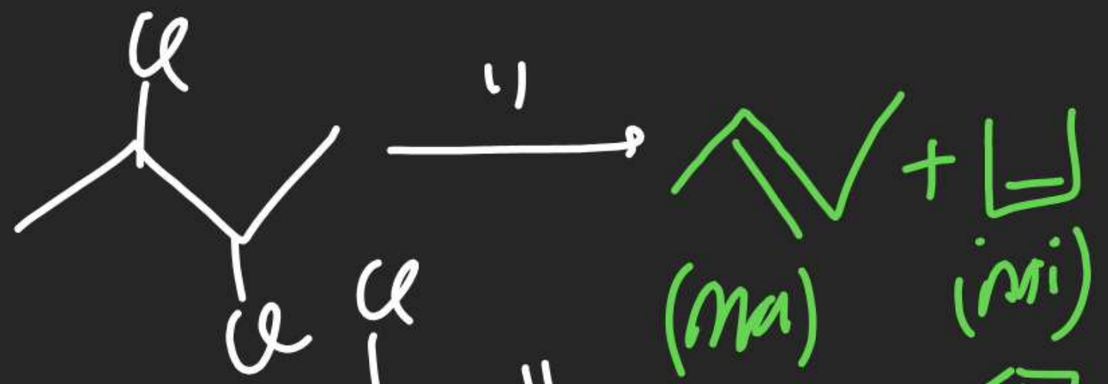
(13) $X-CH_2-(CH_2)_3-CH_2-X$ 

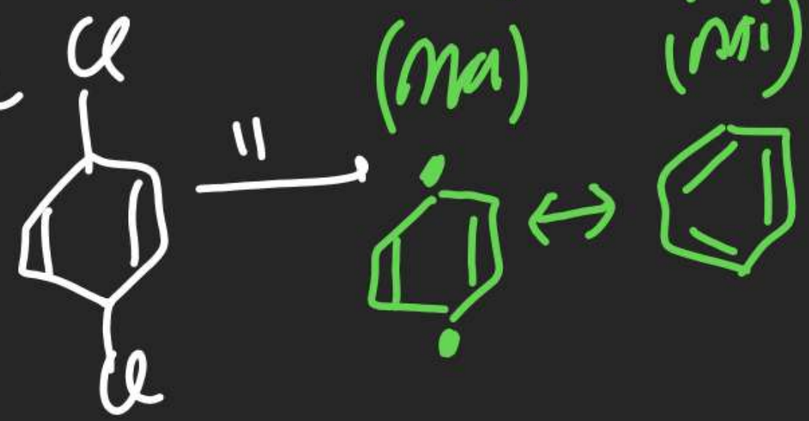
(14) $X-CH_2-(CH_2)_4-CH_2-X$ 

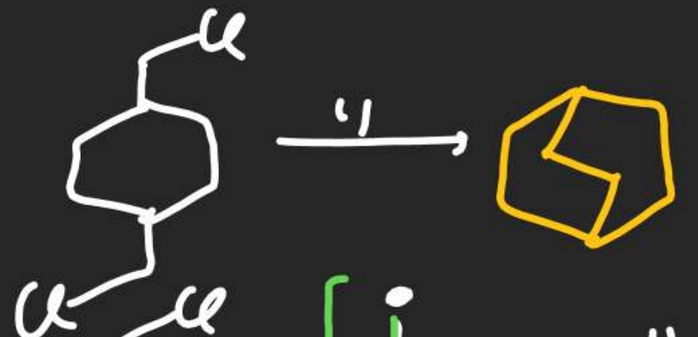
(15) $X-CH_2-(CH_2)_5-CH_2-X \xrightarrow{Na} +(CH_2)+_n$ polymer

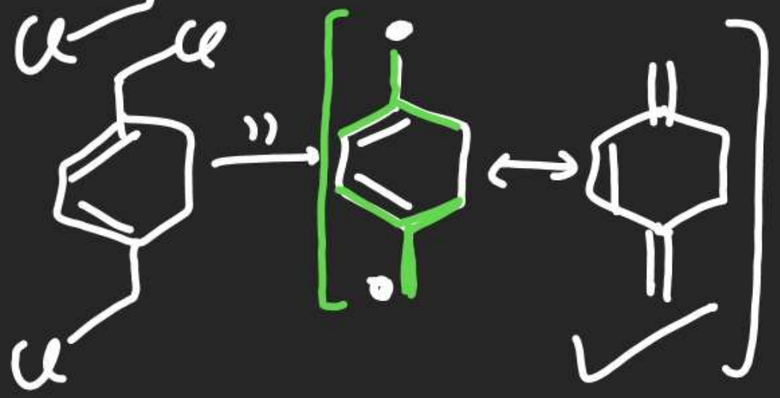
(16) 

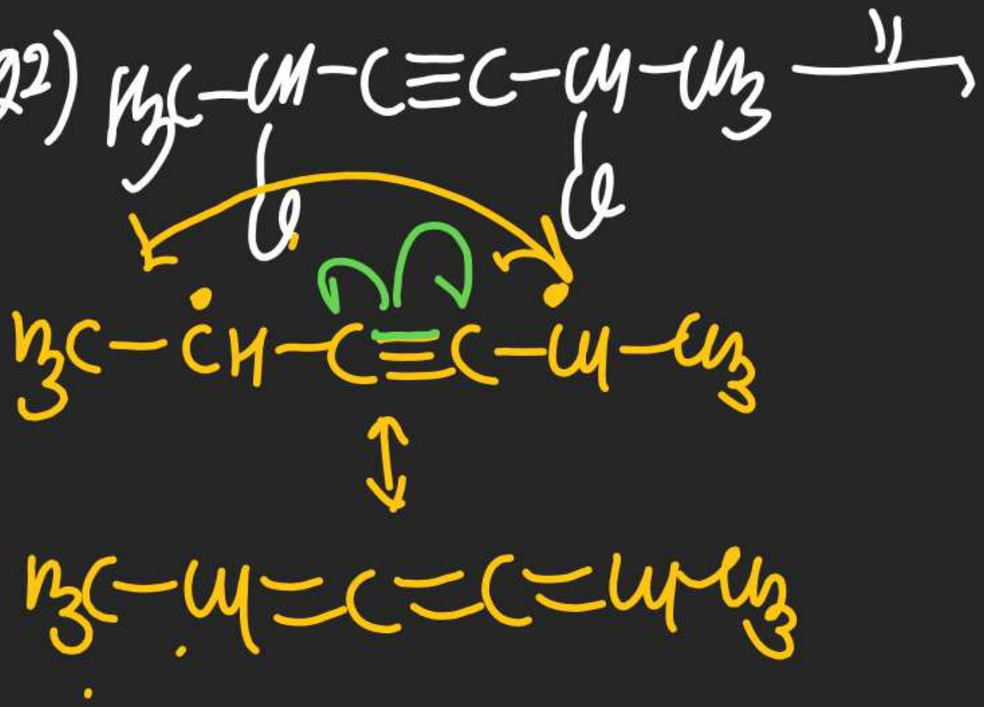
(17) 

(18) 

(19) 

(20) 

(21) 

(22) 

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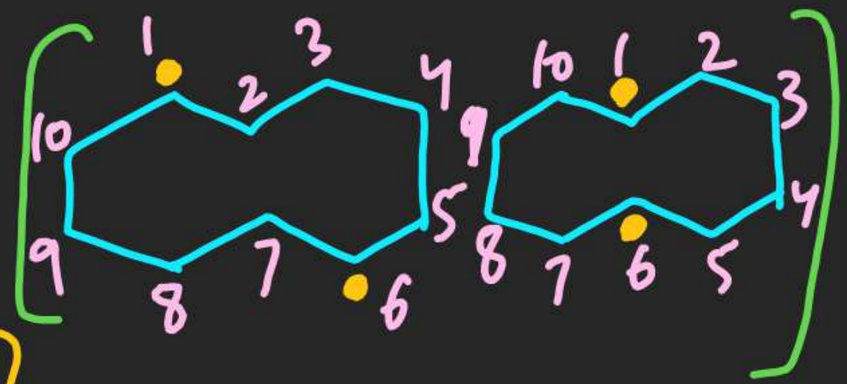
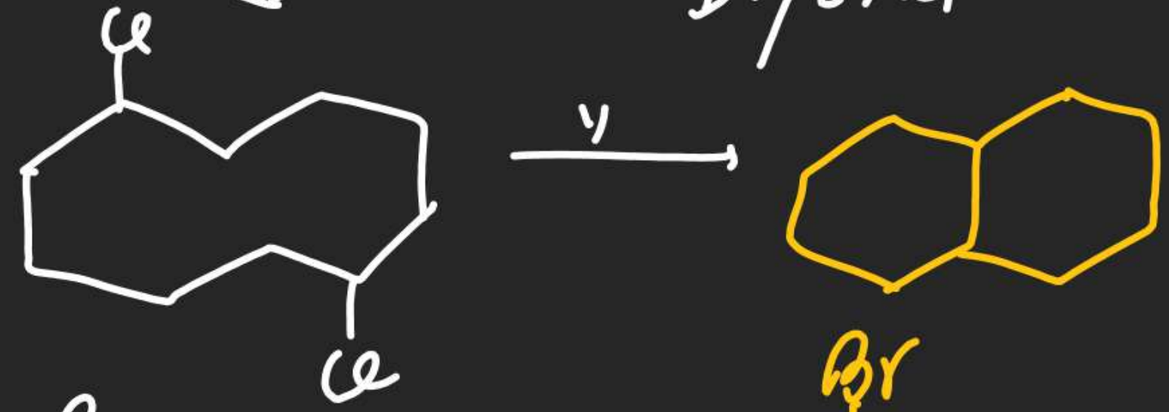
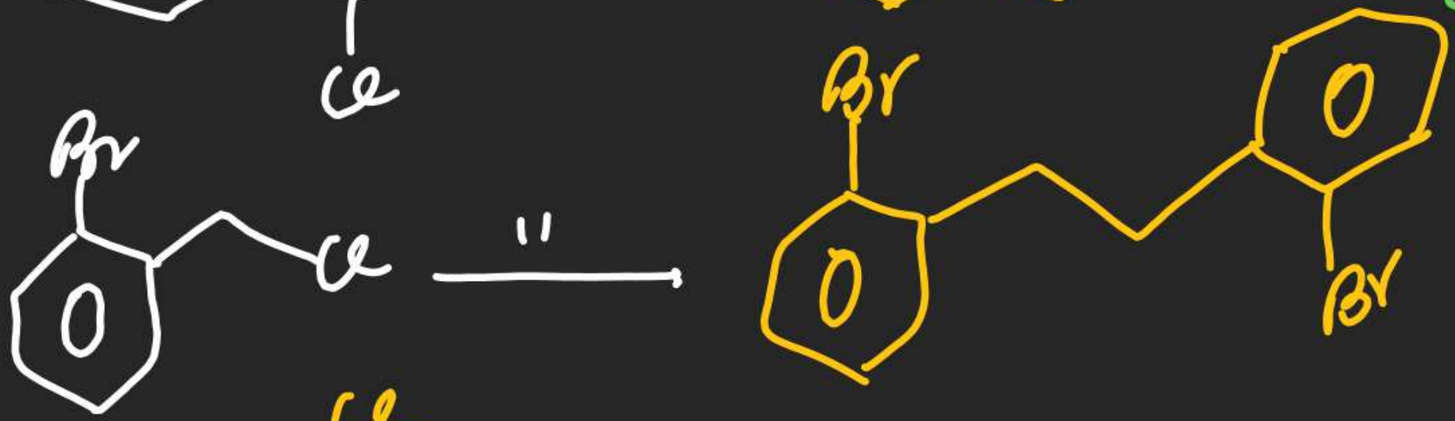
(23) 



(24) 

(25) 

(26) 

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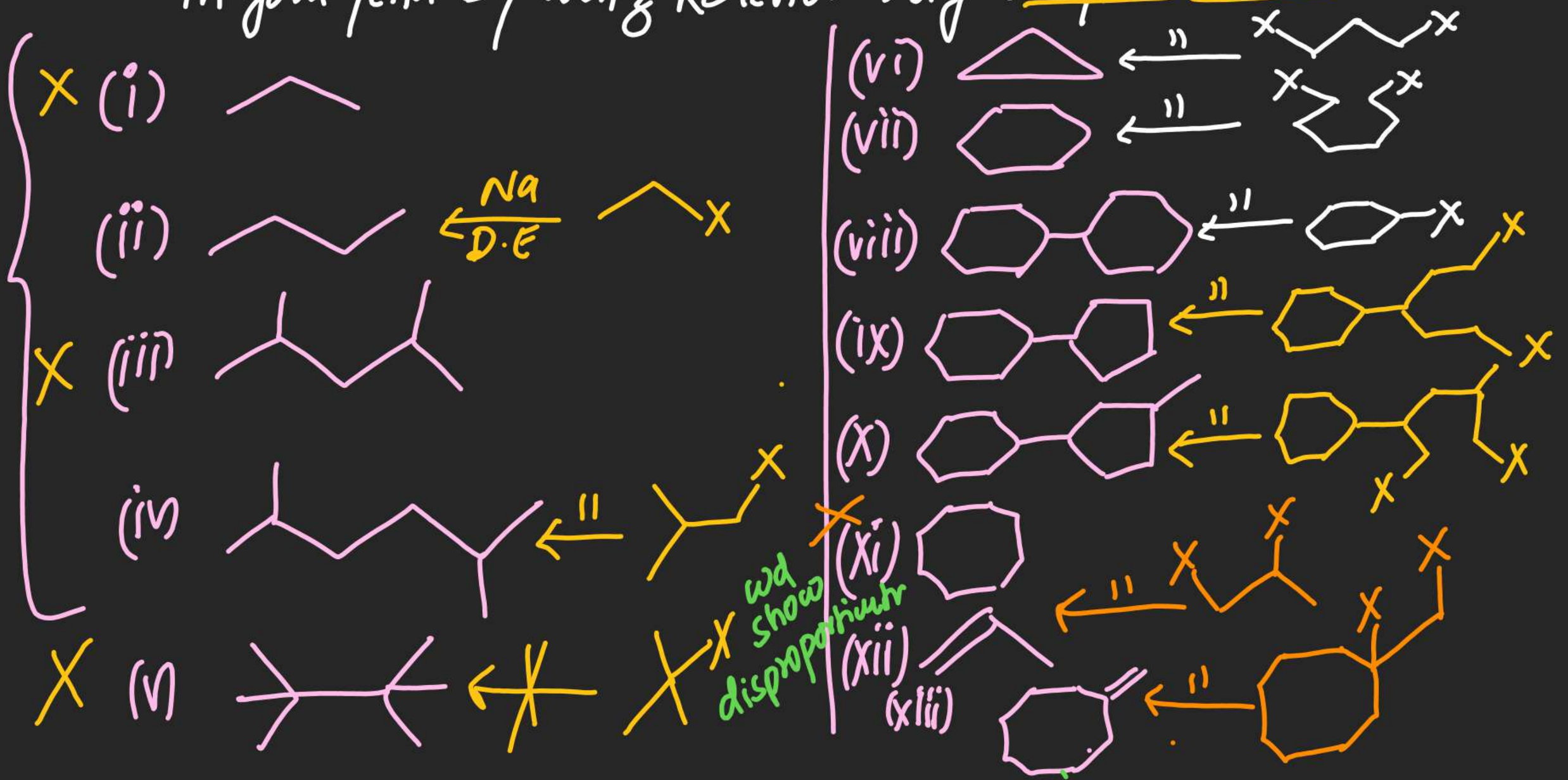
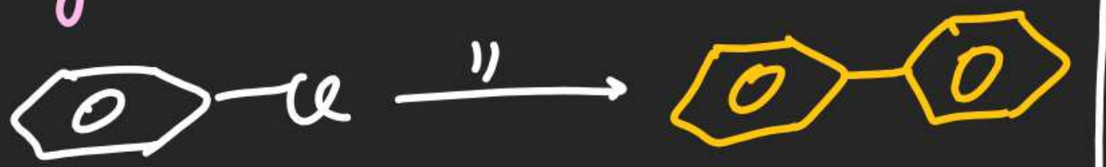
(27) which of the following Never Can be obtained in good yeild By Wurtz Reaction using a Single Reactant.



(#) Fitting Reaction:-

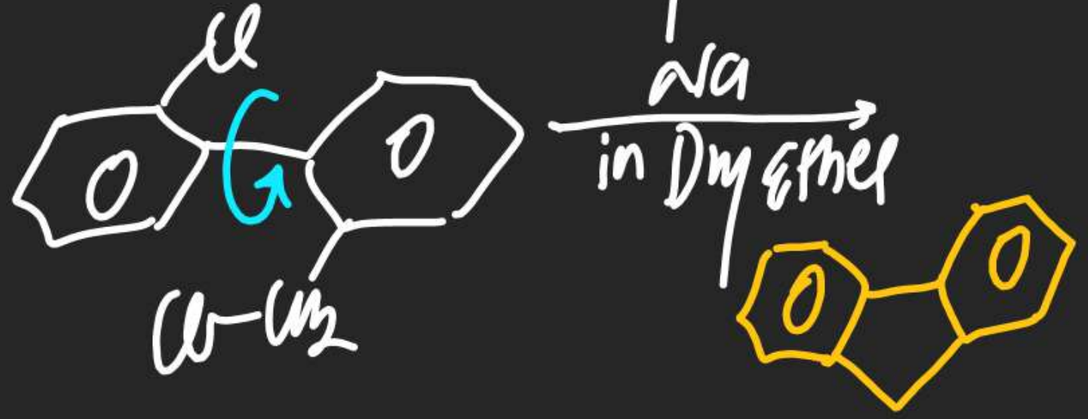
(28) $Ar-X \xrightarrow[\text{in Dry Ether}]{Na} Ar-Ar$

Aryl halide

(29) 

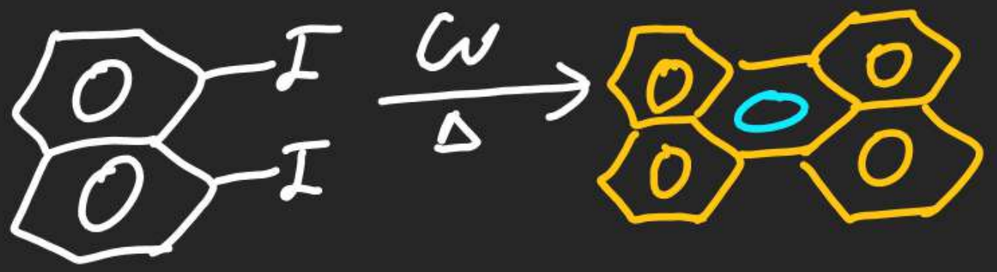
(#) Wurtz-Fitting Reaction:-

(30) $R-X + Ar-X \xrightarrow[\text{in Dry ether}]{Na} R-Ar$

(31) 

(#) Ullmann Reaction:-

(32) $Ar-I \xrightarrow[\Delta]{Cu} Ar-Ar$

(33) 

(#) Frankland Reaction:-

(34) $2R-X \xrightarrow{Zn} R-R + ZnX_2$

(35) $CH_3-CH_2-Br \xrightarrow{Zn}$ 

M.I.T.

(36) $2\,H\text{-}CCl_3 + 6Ag \longrightarrow H\text{-}C\equiv C\text{-}H + 6AgCl$

"Ethyne"

(37) $2\,H_3C\text{-}CCl_3 \xrightarrow{6Ag} H_3C\text{-}C\equiv C\text{-}CH_3$

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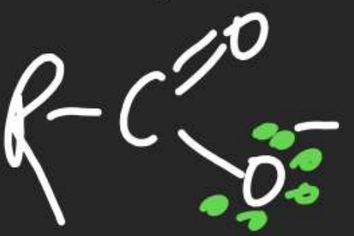
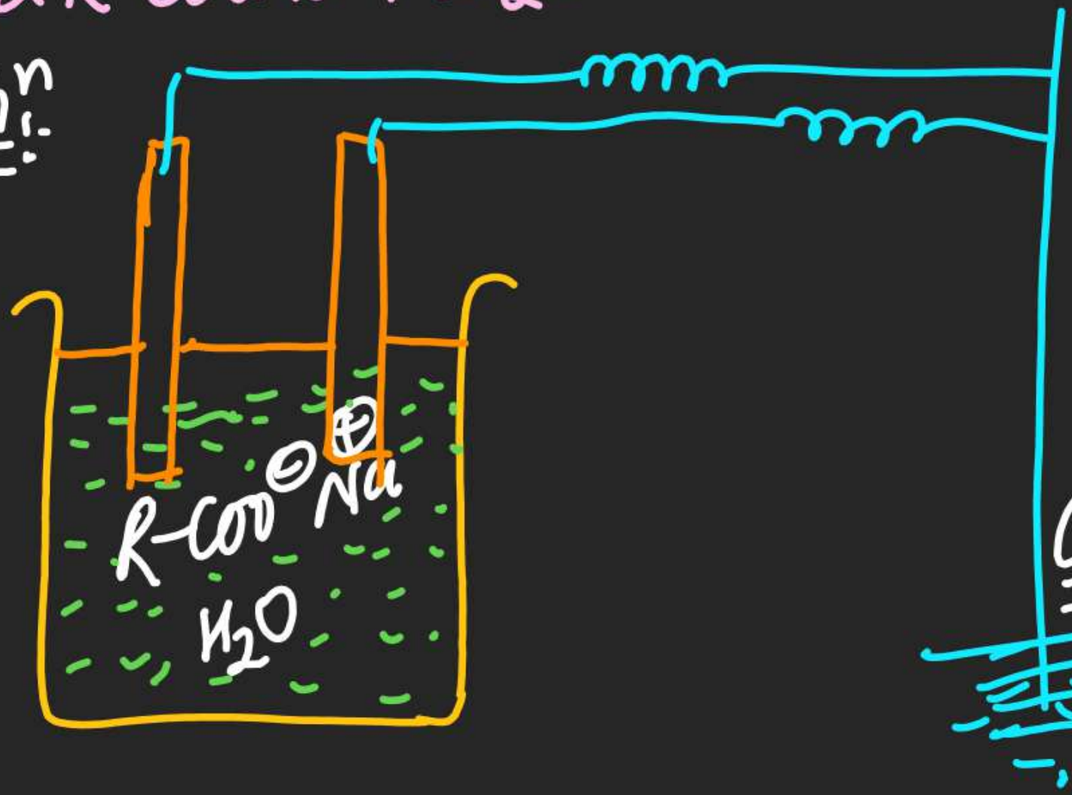
(#) Kolbey's Electrolysis :-

⇒ On Electrolysis of Aq. Solution of Sodium Salt of Carboxylic Acid gives HydroCarbon as a Product.



(1) $2R\text{-}COONa + 2H_2O \longrightarrow R\text{-}R + 2CO_2 + \boxed{2NaOH} + H_2\uparrow$

Mechⁿ :-



Anode :- (Oxidation)

$R\text{-}C(=O)\text{-}O^{\ominus} \longrightarrow R\text{-}C(=O)\text{-}O^{\bullet} + e^{\ominus}$

$R\text{-}C(=O)\text{-}O^{\bullet} \longrightarrow R^{\bullet} + CO_2$

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

Cathode (Reduction)

$H\text{-}O\text{-}H + e^{\ominus} \longrightarrow H\text{-}O^{\ominus} + \frac{1}{2}H_2\uparrow$

Note (i) Free Radical intermidiate

(ii) CO_2 is evolved at Anode

(iii) H_2 ——— Cathode

(iv) pH of Rxn ↑ as Reaction Proceeds.

(v) CH_4 never can be obtained.

(2) $CH_3-COONa + H_2O \xrightarrow{KE} CH_3-CH_3$

Sodium Acetate

(3) $CH_3-CH_2-COONa + H \xrightarrow{''} CH_3-CH_2-CH_2-CH_3$

Sodium Propionate

(4) $CH_2-COONa$ / $CH_2-COONa$ $+H_2O$ ⟶ CH_2 ‖ CH_2

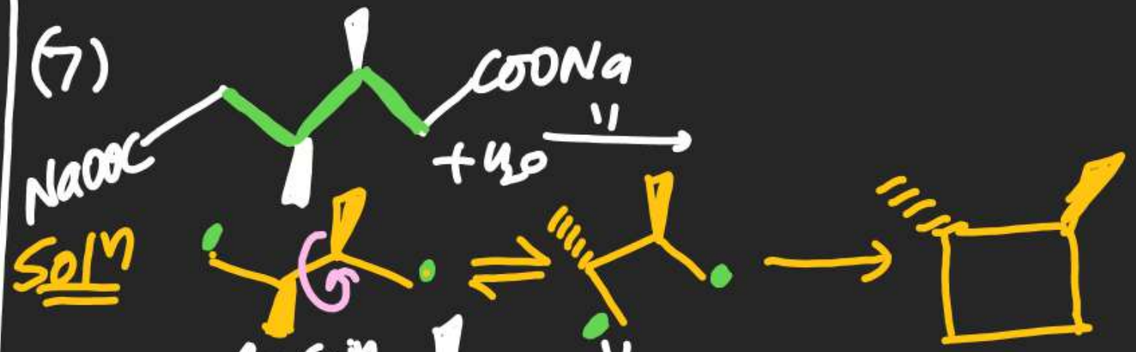
Sodium succinate

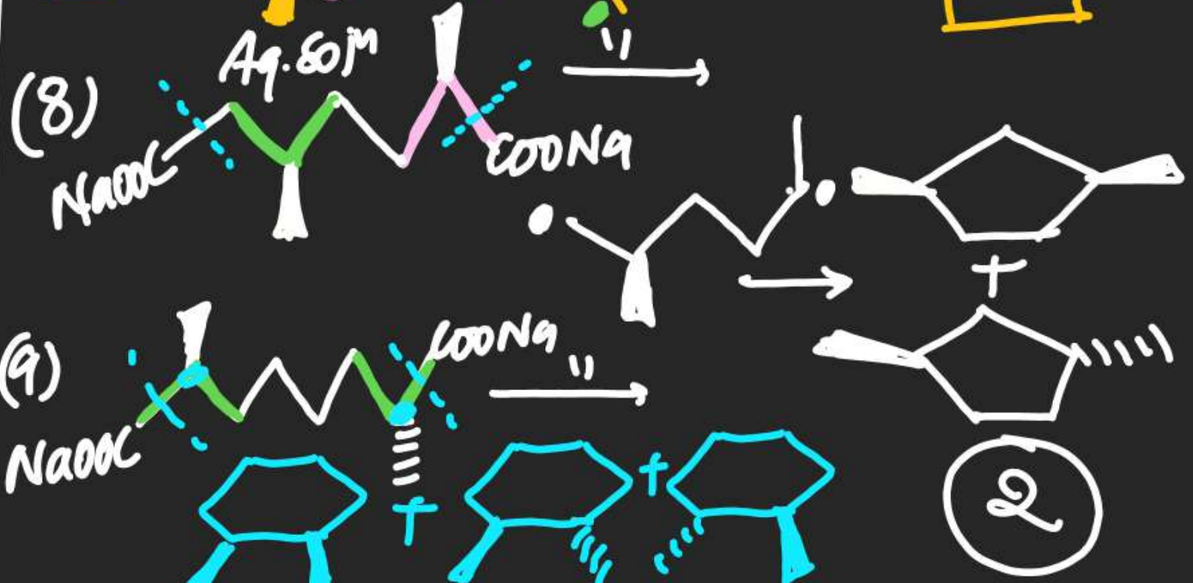
(5) $CH-COONa$ ‖ $CH-COONa$ $+H_2O$ ⟶ HC ||| HC

Sodium maleate

(6) $CH-COONa$ ‖ $NaOOC-CH$ $+H_2O$ ⟶ HC ||| HC

Sodium Fumarate

(7) 

(8) 

(9)

(10) 

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(11) 

Soln:

(12) 

Soln:

(13) 

Soln

$2H\text{-}COONa + 2H_2O \rightarrow \underbrace{H_2 + 2CO_2}_{\text{Anode}} + 2NaOH + \underbrace{H_2}_{\text{Cathode}}$

1eq

At Anode: $\frac{1}{2}$ eq. H_2 & 1eq CO_2

At Cathode: $\frac{1}{2}$ eq H_2

(15) $D\text{-}COONa + H_2O \xrightarrow{\Delta} \frac{1}{2}D_2\uparrow + CO_2 + NaOH + \frac{1}{2}H_2$

(1eq)

(16) $CH_2\text{-}CO_2Na$
$CH_2\text{-}SO_3Na$ $+ H_2O \xrightarrow{\Delta}$

(1eq) $\underset{CH_2}{\overset{CH}{\|}} + \underbrace{CO_2}_{1eq} + \underbrace{SO_3}_{1eq} + \underbrace{\frac{1}{2}H_2}_{1eq} + Na$

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

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

- → $H_3C-\underset{Br}{CH}-CH_3$
  - (*) Electrophilic addⁿ
  - (*) Ionic addⁿ
  - (*) M. addⁿ
- R-O-O-R → $H_3C-CH_2-CH_2-Br$
  - (*) Anti M. addⁿ
  - (*) Free Radical addⁿ

⇒ On addⁿ of HBr on alkene in Presence of peroxide it gives Product formed By following Anti Markonicov's addⁿ.

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

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Mechanism:

Initiation step:

$$R-O-O-R \xrightarrow{\Delta} 2\,R-O^{\bullet}$$

$$R-O^{\bullet} + H-X \longrightarrow R-OH + X^{\bullet}$$

Propagation step:

(P1)

$$X^{\bullet} + CH_3-CH=CH_2 \xrightarrow{(\text{r.d.s})} CH_3-\underset{X}{\overset{\bullet}{C}}H-CH_2$$

X = F	$\Delta H < 0$
X = Cl	$\Delta H < 0$
X = Br	$\Delta H < 0$
X = I	$\Delta H > 0$

(P2)

$$CH_3-\underset{X}{\overset{\bullet}{C}}H-CH_2 + H-X \longrightarrow CH_3-CH_2-\underset{X}{CH_2} + X^{\bullet}$$

X = F	$\Delta H > 0$
X = Cl	$\Delta H > 0$
X = Br	$\Delta H < 0$
X = I	$\Delta H < 0$

Termination step:

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

or

Note (i) Free Radical intermidiate

(ii) Each Radical Rxn Involves following steps

(a) Initiation
(b) Propagation
(c) Termination

(iii) Chain Reaction

(iv) Free Radical addition Rxn

(v) Radical Reaction takes place only when its ALL propagation steps are Exothermic:

(Rxn wd be feasible) P_1 $\Delta H < 0$

P_2 $\Delta H < 0$

(vi) Bond strength order of

$\geq C-X$: $\geq C-F > \geq C-Cl > \geq C-Br > \geq C-I$

$H-X$: $H-F > H-Cl > H-Br > H-I$

(vii) Free Radical Reactions can be slow down By adding O_2, S_2 known as free Radical Scavengers.

$$R^{\bullet} \xrightarrow{O_2} R-O-O^{\bullet}$$

M.Imp

(viii) only H-Br out of all H-X shows Antimarkonicovs addn because its Both Propagation steps are Exothermic

	H-Cl	H-Br	H-I
P_1	$\Delta H<0$	$\Delta H<0$	$\Delta H>0$
P_2	$\Delta H>0$	$\Delta H<0$	$\Delta H<0$

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

(1) $CH_2=CH_2$

HCl

HCl
ROOR

HBr

HBr
ROOR

(2)

"

"

"

"

(3)

HCl

HCl
ROOR

HBr

HBr
ROOR

(4)

(5)

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(6) 

(7) 

(8) 

(9) 

(10)  $\xrightarrow[ROOR]{BrCl_3}$

(11)  $\xrightarrow[ROOR]{H_2S}$

(12)  $\xrightarrow[ROOR]{CCl_4}$

(13)  $\xrightarrow[ROOR]{ICBr_3}$

(14)  $\xrightarrow[ROOR]{HBr}$