: Radical: $\dot{C}H_3$; $\dot{O}H$; $\dot{Cl}$; $\dot{O}R$

[formed as homolytic cleavage].

⇒ Odd electron species.
⇒ Paramagnetic.
⇒ Very high temperature & light promotes radical formation.
⇒ Highly unstable; reactive.
⇒ Octet incomplete.
⇒ Has a tendency to undergo dimerisation.
⇒ Some alkyl radical has tendency to undergo disproportionation.
⇒ Intermediate.

: Radical formation:

: Photolysis:

⇒ $RO{-}Cl \xrightarrow{h\nu} R\dot{O} + \dot{Cl}$

alkyl hypochlorite

⇒ $RO{-}NO \xrightarrow{h\nu} R\dot{O} + NO$

⇒ $X_2 \xrightarrow{h\nu} 2\dot{X}$

⇒ $R{-}N{=}N{-}R \xrightarrow{h\nu} 2\dot{R} + N{\equiv}N\uparrow$

Azocompound

⇒ $R{-}\underset{O}{\underset{\|}{C}}{-}O{-}O{-}\underset{O}{\underset{\|}{C}}{-}R \xrightarrow{h\nu} 2R{-}\underset{O}{\underset{\|}{C}}{-}\dot{O}$

$\downarrow$

$CO_2\uparrow + 2\dot{R}$

Acyl Peroxide

: Thermolysis:

$HO{-}OH \xrightarrow{\Delta} 2H\dot{O}$

$RO{-}OR \xrightarrow{\Delta} 2\dot{O}R$

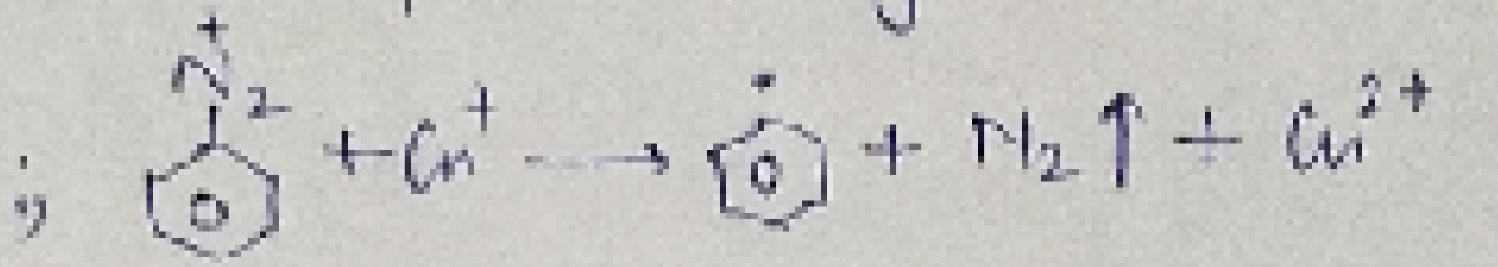
Dialkyl peroxide

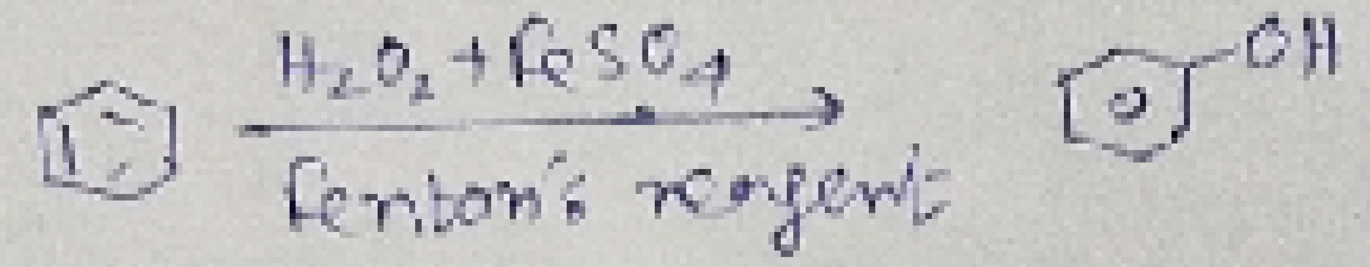
$R{-}\underset{O}{\underset{\|}{C}}{-}O{-}\underset{O}{\underset{\|}{C}}{-}R \xrightarrow{\Delta} 2\dot{R} + CO_2\uparrow$

$PbMe_4 \xrightarrow{\Delta} 4\dot{M}e + \cdot\dot{P}b\cdot$

Tetraalkyl lead

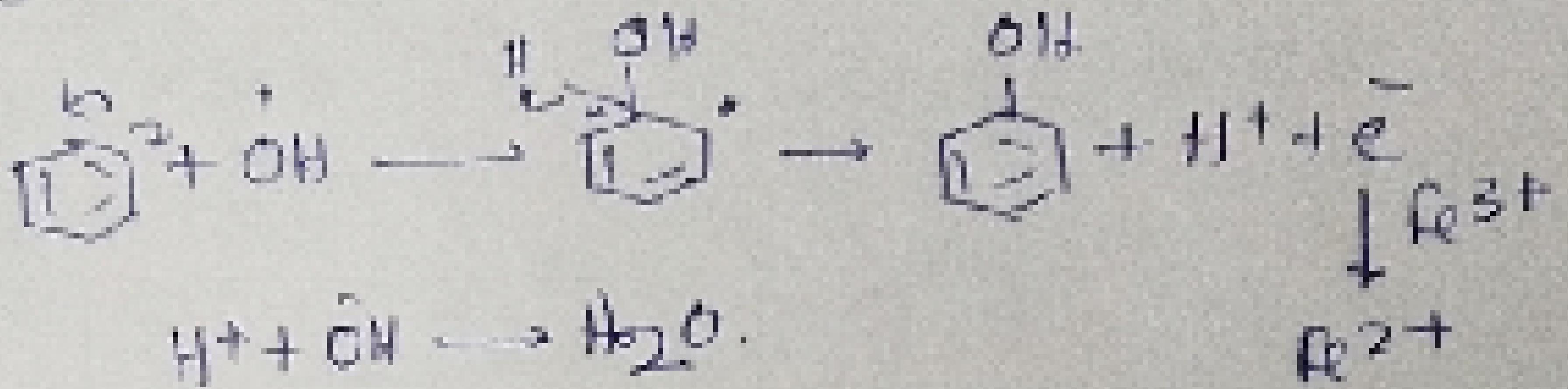
Radical formation by redox reaction.

i) 

ii) 

$Fe^{2+} \longrightarrow Fe^{3+} + \bar{e}$.

$HO-OH + \bar{e} \longrightarrow \bar{O}H + \dot{O}H$

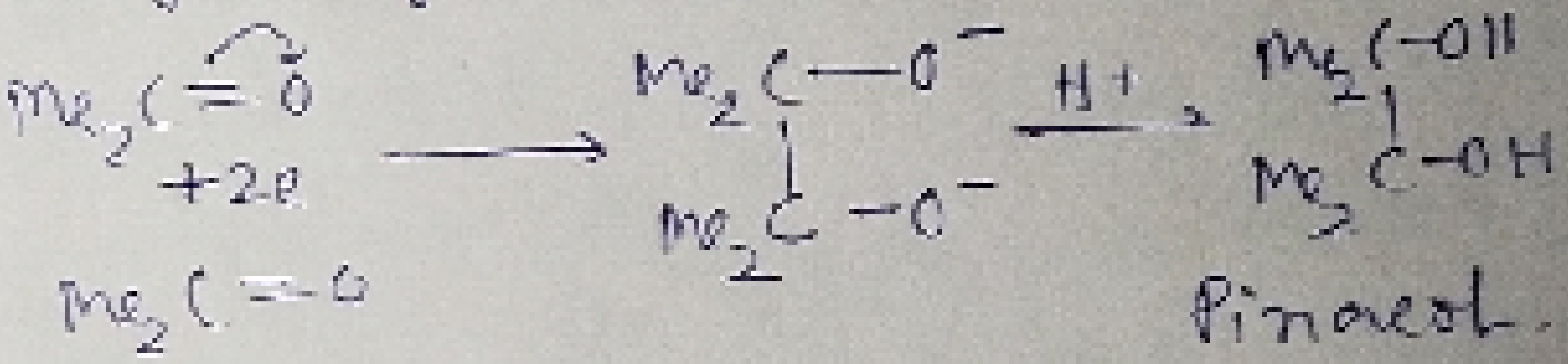


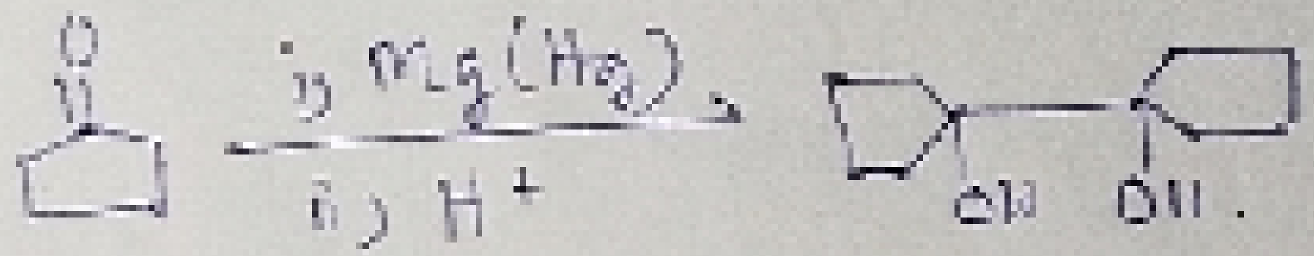
$H^+ + \bar{O}H \longrightarrow H_2O$.

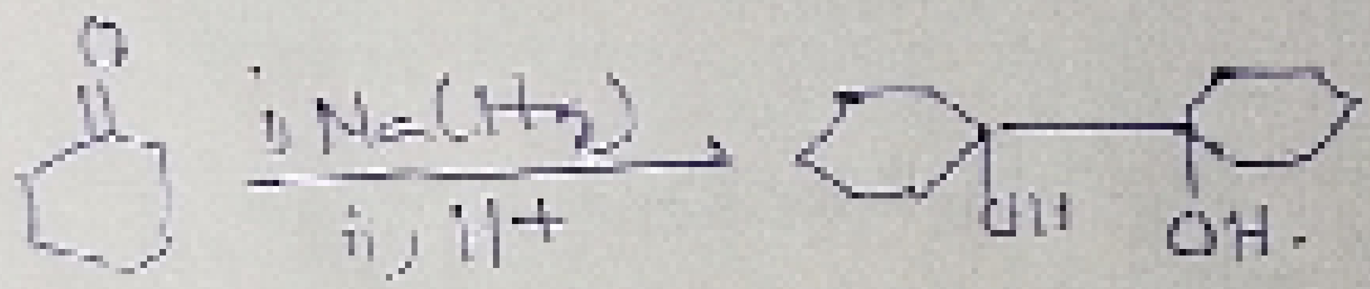
c) $Me_2C=O \xrightarrow[\text{2. } H^+]{\text{1. Mg } (\bar{e} \text{ donor})} Me_2\underset{OH}{C}-\underset{OH}{C}Me_2$

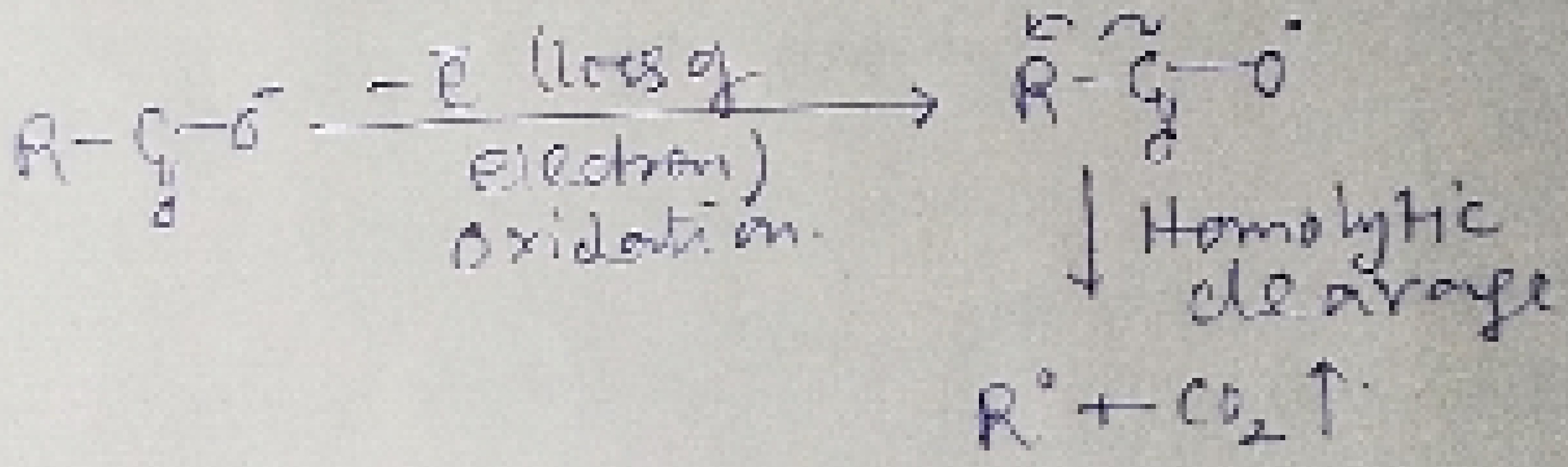
Acetone $\qquad\qquad\qquad$ Pinacol.

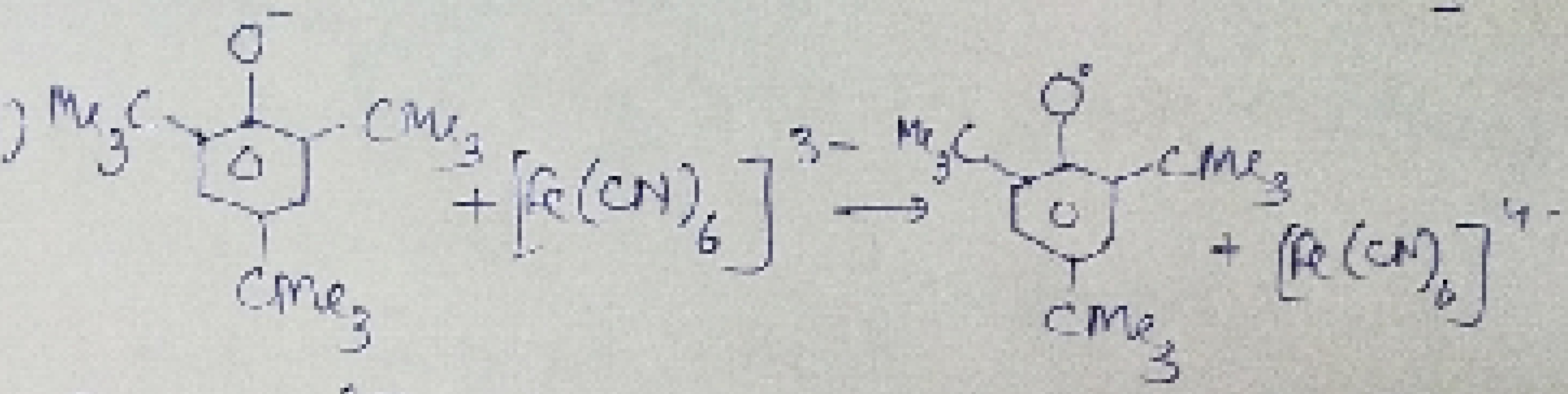
$Mg \longrightarrow Mg^{2+} + 2\bar{e}$



d) 

e) 

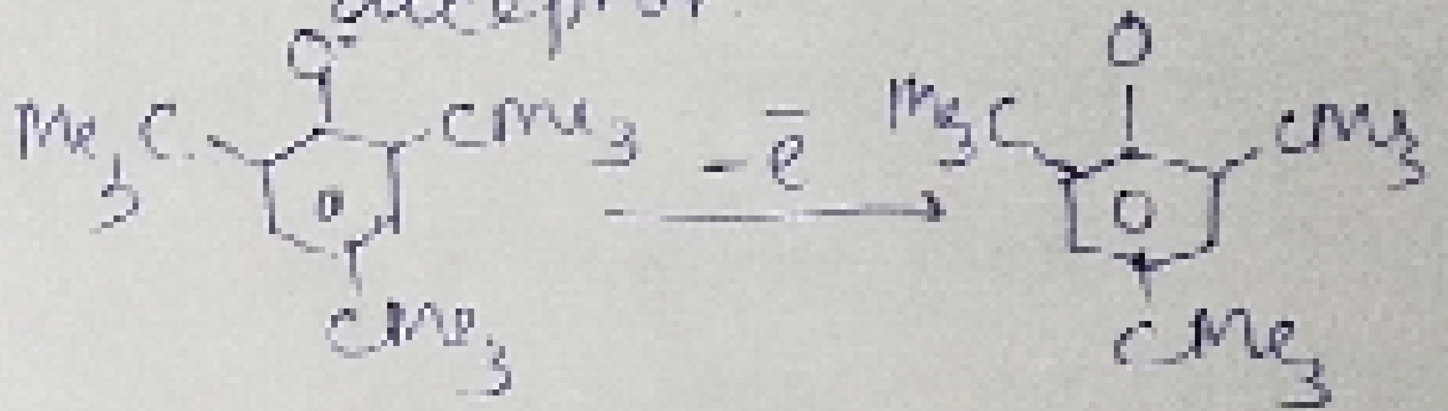
f) 

g) 

$[Fe(CN)_6]^{3-}$ ⇒ Ferricyanide ion $K_3[Fe(CN)_6]$

$$[Fe(CN)_6]^{3-} \xrightarrow{+\bar{e}} [Fe(CN)_6]^{4-} \text{ or } K_4[Fe(CN)_6]$$

one $\bar{e}$ ~~donor~~ acceptor   ferrocyanide.



Some miscellaneous examples.

$$R{-}X + Na \longrightarrow \dot{R} + NaX$$

$$Na \longrightarrow Na^+ + \bar{e}$$ Redox reaction.

$$R{-}X + \bar{e} \longrightarrow \dot{R}$$

$$Me_2\underset{CN}{C}{-}N{=}N{-}\underset{CN}{C}Me_2 \xrightarrow{\Delta} \underset{(2eq)}{Me_2\dot{C}{-}CN} + N{\equiv}N$$

Nonredox reaction,

: Radical shape:

$\dot{C}H_3$ ⇒ sp^2 hybridised; trigonal planar

$\dot{C}Me_3$ ⇒ sp^2 hybridised; trigonal planar

$\dot{C}F_3$ ⇒ sp^3; Pyramidal.

$\dot{C}H_2F$; $\dot{C}H_2OH$; $\dot{C}HF_2$ are predominantly pyramidal.

Stability of free radical.

i) $R_3\dot{C} > R_2\dot{C}H > R\dot{C}H_2 > \dot{C}H_3$ [+I effect; +H effect].

ii) $\dot{I} > \dot{Br} > \dot{Cl} > \dot{F}$ [size factor].

iii) $Te\dot{H} > Se\dot{H} > \dot{S}H > \dot{O}H$

iv) $Ph_3\dot{C} > Ph_2\dot{C}H > Ph\dot{C}H_2$ [Resonance effect].

v) $H_3C-\dot{C}H_2 > CH_2=\dot{C}H > HC\equiv\dot{C}$ [s-character].

Radical has tendency to undergo dimerisation.

a) $\dot{R} + \dot{R} \rightarrow R-R$.

b) $\dot{Ph} + \dot{Ph} \rightarrow Ph-Ph$.

c) $\dot{X} + \dot{X} \rightarrow X_2$

All steps are highly exothermic; $E_{act} \simeq 0$.
These are extremely spontaneous.

Following radical can not undergo dimerisation

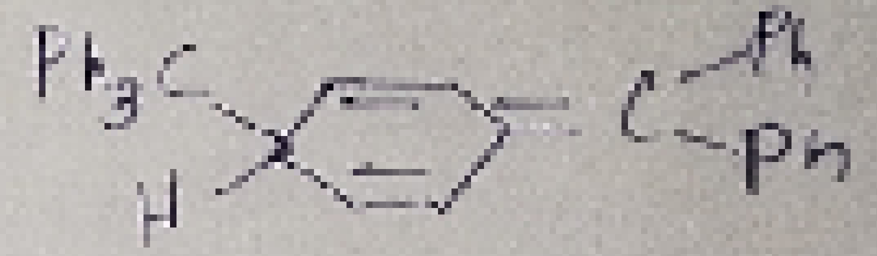
$H\dot{O} + \dot{O}H \not\rightarrow HO-OH$ (Peroxy linkage in

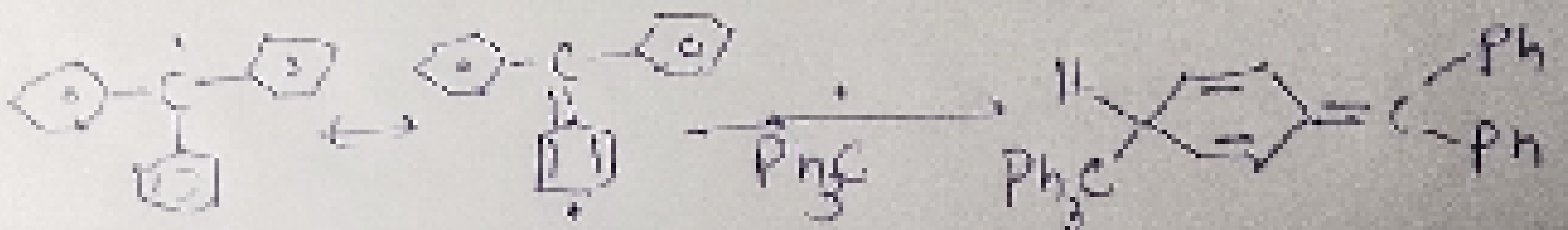
$R\dot{O} + \dot{O}R \not\rightarrow RO-OR$ pdt side unstable)

$R-\underset{O}{\overset{}{C}}-\dot{O} + \dot{O}-\underset{O}{C}-R \not\rightarrow R-\underset{O}{C}-O-O-\underset{O}{C}-R$

→ $Ph_3\dot{C}$ undergo dimerisation but can not form Ph_3C-CPh_3. [due to steric factor].

Its dimer structure





Reactions based on free radical.

i) Wurtz Reaction.

Alkyl halide in presence of Na in dry ether gives alkane as product

$2\,R\text{-}X + 2Na \xrightarrow{Et_2O} R\text{-}R + 2NaX$

$R\text{-}X + R'\text{-}X + 2Na \xrightarrow[D.E]{} R\text{-}R + R\text{-}R' + R'\text{-}R' + NaX$

Radical mechanism

$2(Na \longrightarrow Na^+ + \bar{e})$

$2(R\text{-}X + \bar{e} \longrightarrow R^\cdot + X^-)$

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

$2\,R\text{-}X + 2Na \longrightarrow R\text{-}R + 2NaX$

⇒ CH_4 can't be prepared.

⇒ Ether is used as solvent.

⇒ Dry ether should be used, otherwise in presence of H_2O, Na reacts violently

In presence of two different alkyl halide

$R\text{-}X + R'\text{-}X + n\bar{e} \xrightarrow[\text{(coming Na)}]{} R^\cdot + \dot{R}'$

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

$\dot{R}' + \dot{R}' \longrightarrow R'\text{-}R'$

$R^\cdot + \dot{R}' \longrightarrow R\text{-}R'$

[When 3 alkanes are formed % yield of one alkane will be low].

$EtX + EtX \xrightarrow[D.E]{Na} Et\text{-}Et$

$MeX + MeX \xrightarrow{\;"\;} Me\text{-}Me$

$PhCH_2X + Na \xrightarrow{\;"\;} PhCH_2\text{-}CH_2\text{-}Ph$

To get symmetrical alkane, we can use only one R-X. % yield will be more.

e.g CH_3-CH_3 ; Et-Et ; n-hexane ; $PhCH_2-CH_2-Ph$.

To get nonsymmetrical alkane we can use 2 different types of R-X.

i) $CH_3-X + Et-X \xrightarrow[(D.E)]{Na} CH_3-Et$.

ii) $Et-X + nPr-X \xrightarrow[(D.E)]{Na} Et-nPr$.

iii) $PhCH_2-X + CH_3-X \xrightarrow[D.E]{Na} PhCH_2-CH_3$.

But in (i) other alkane can be formed.

CH_3-CH_3 ; Et-Et : % yield of CH_3-Et is less.

In (ii), other alkane can be formed.

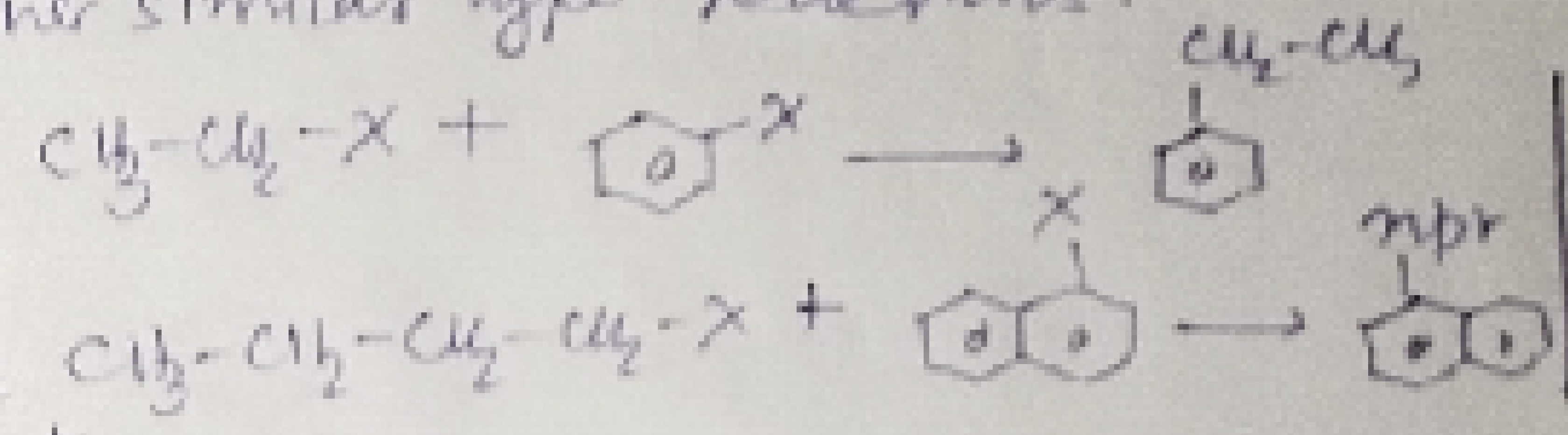
Et-Et ; Et-nPr ; nPr-nPr.

% yield of Et-nPr is less.

So it is not a convenient method to prepare all types of alkane.

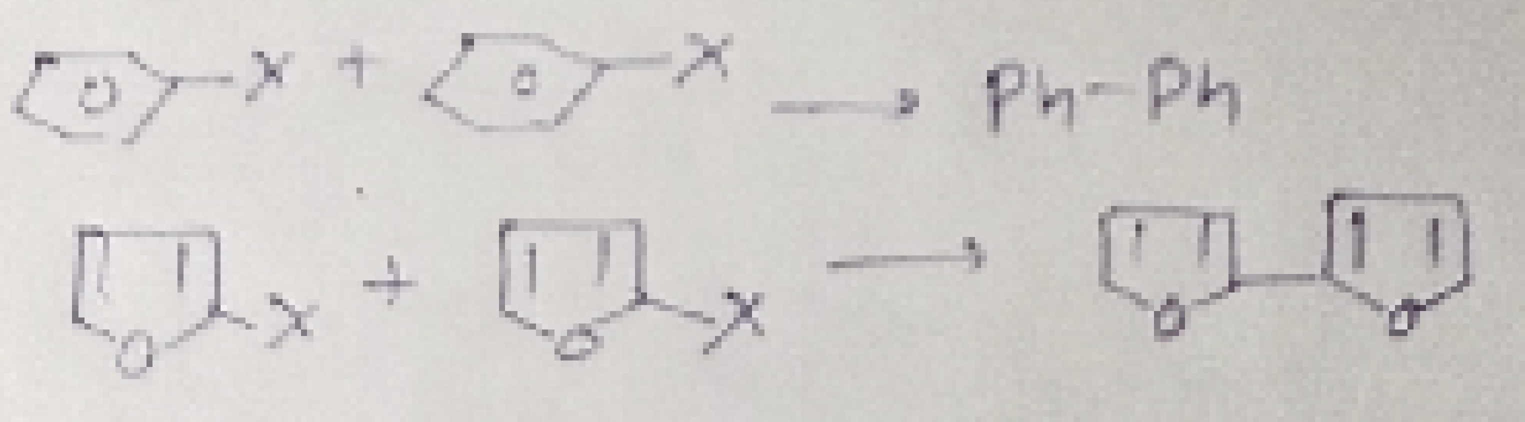
Other similar type reactions:

Alkyl + Aryl Halide



Wurtz Fittig Reaction.

Aryl Halide



Fittig reaction.

Another mechanism proposed also for Wurtz Reaction.

Ionic Mechanism:

$2Na \longrightarrow 2Na^+ + 2e^-$.

$R{-}X + 2e^- \longrightarrow R^- + X^-$

$R^- + R{-}X \xrightarrow[\text{mechanism}]{S_N2} R{-}R$.

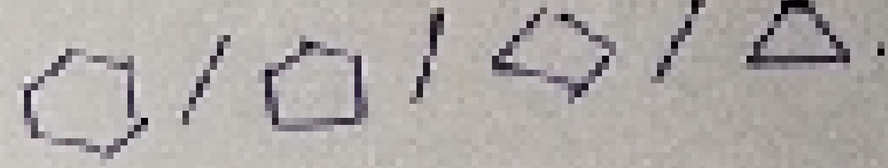
So in Wurtz reaction both free radical & carbanion formed as intermediate.

This is example of redox reaction.

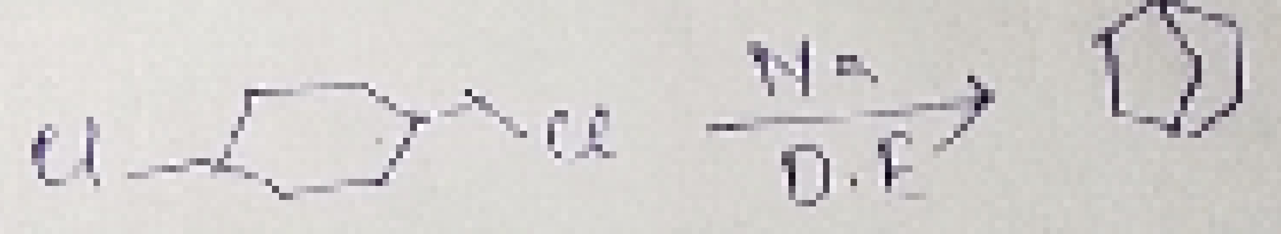
. Intramolecular Wurtz reaction:

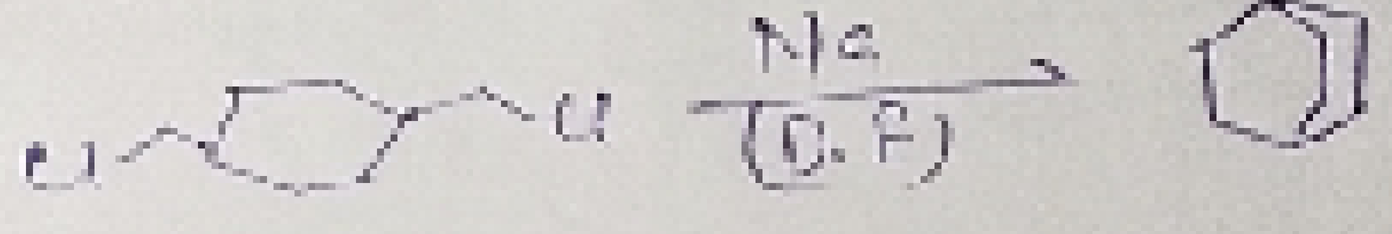
⇒ Applicable for dihalide/ Polyhalide.

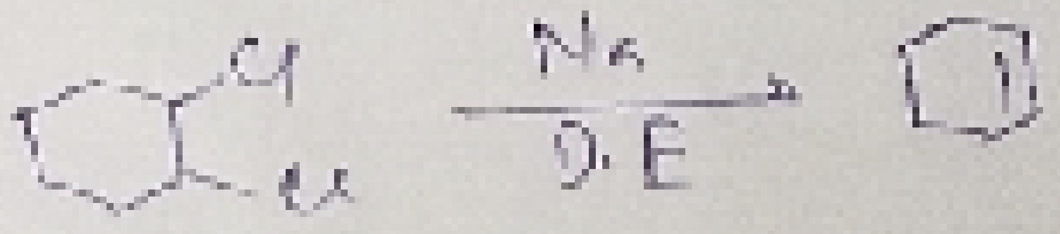
a) $\underset{Cl}{CH_2}-\underset{Cl}{CH_2} \xrightarrow[(D.E)]{Na} CH_2{=}CH_2$

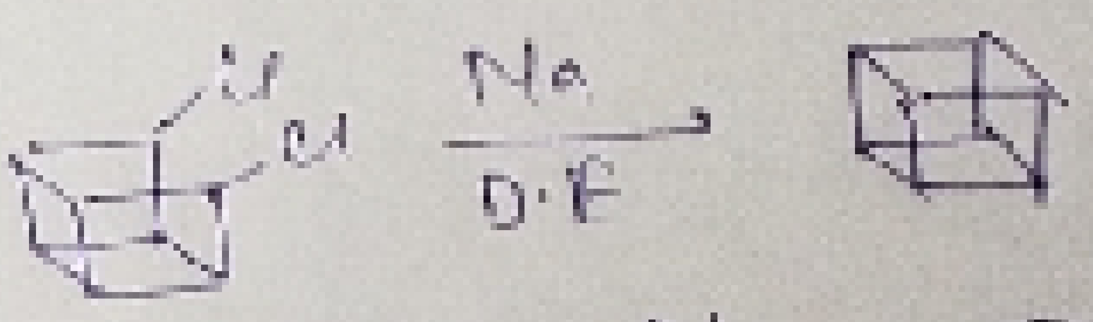
b) $Cl-(CH_2)_{3/4/5/6}-Cl \xrightarrow[D.E]{Na}$ 

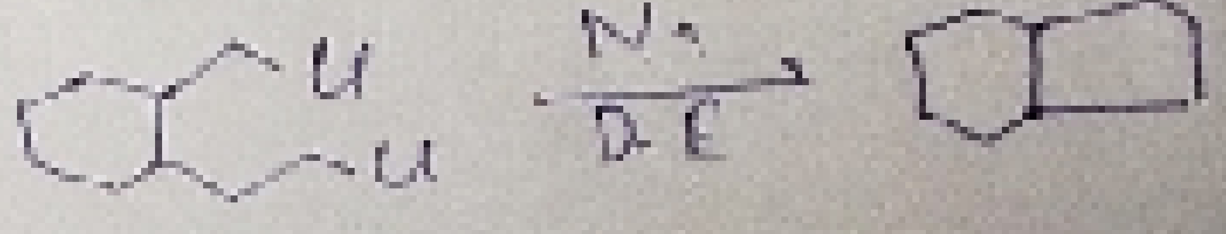
c) $Cl-(CH_2)_n-Cl \xrightarrow[D.E]{Na} -(CH_2)_n-$

d) 

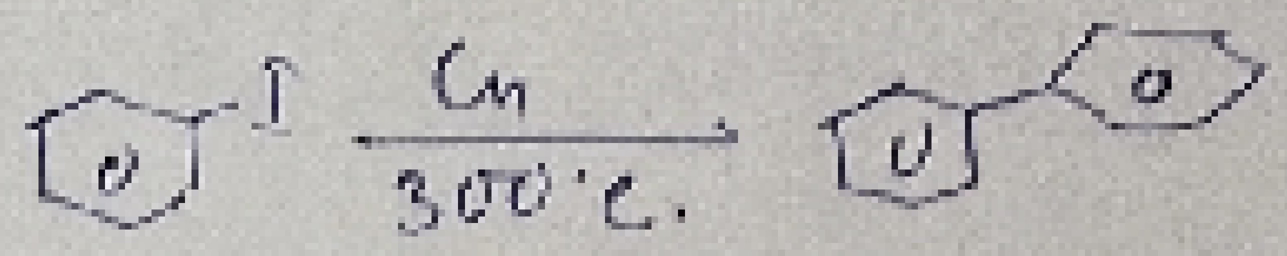
e) 

f) 

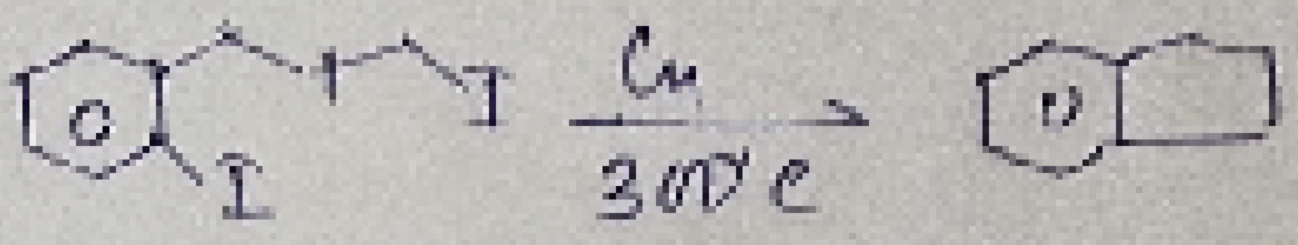
g) 

h) 

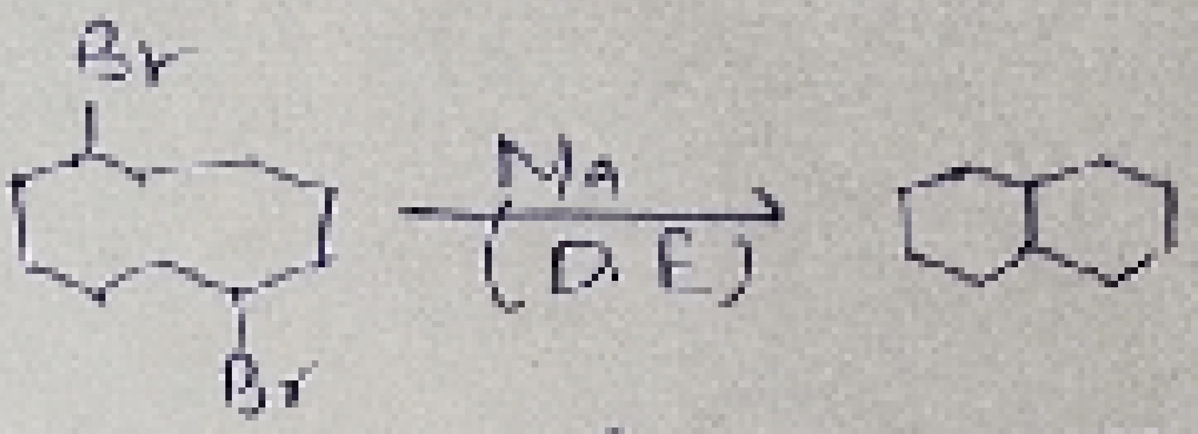
i) Ulman reaction



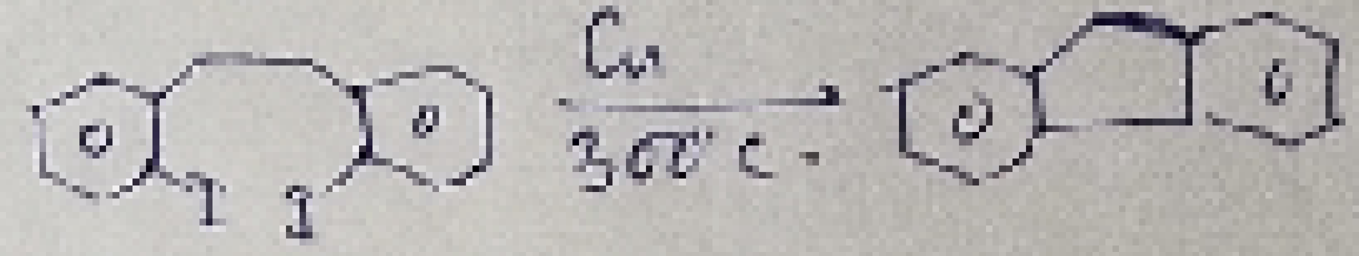
ii)



iii)



iv)



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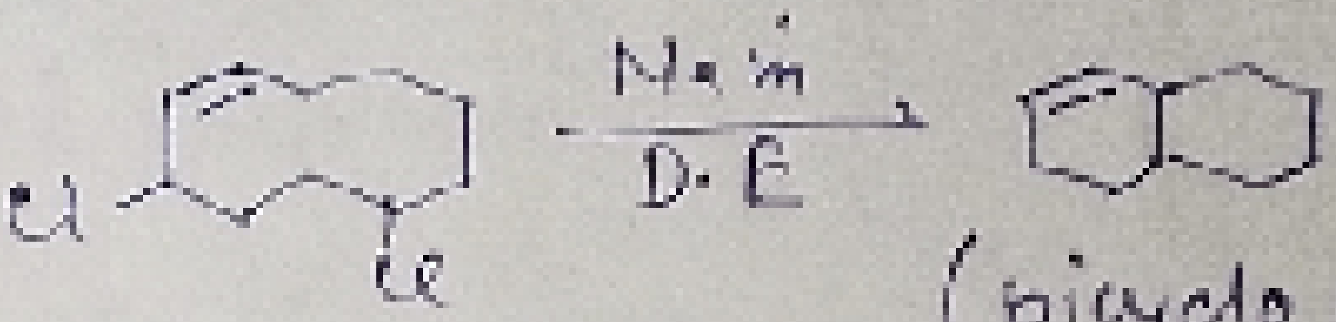
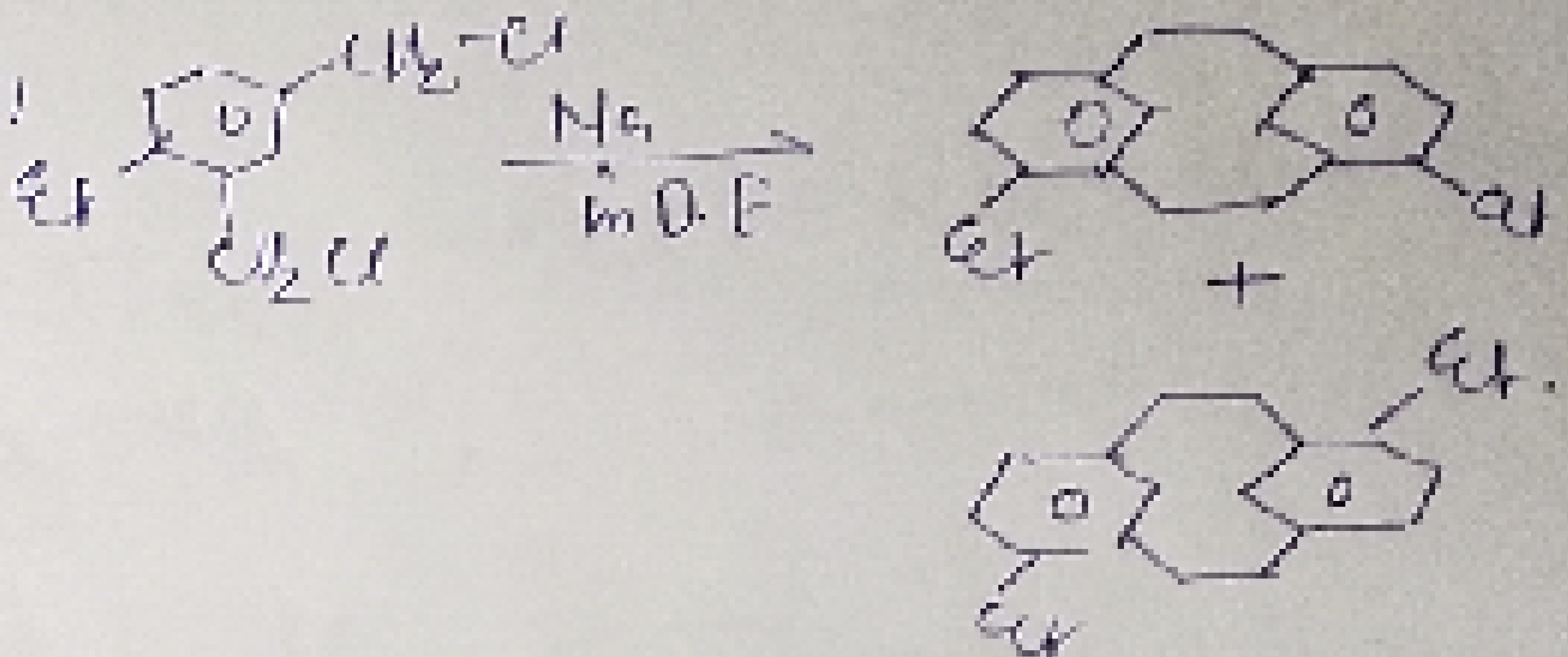


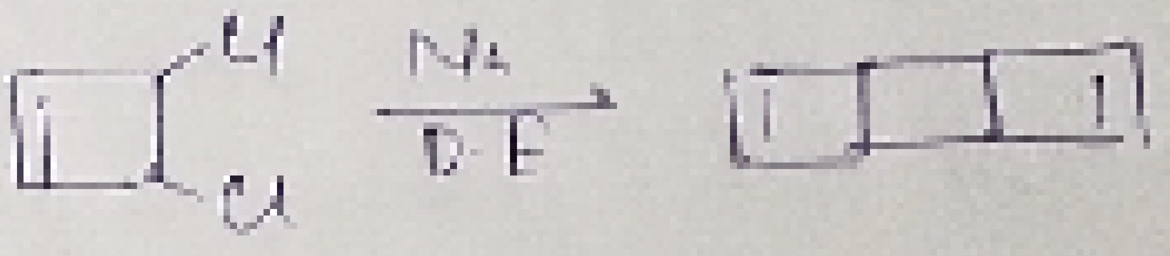
(odd no of DOU)

(bicyclo product)

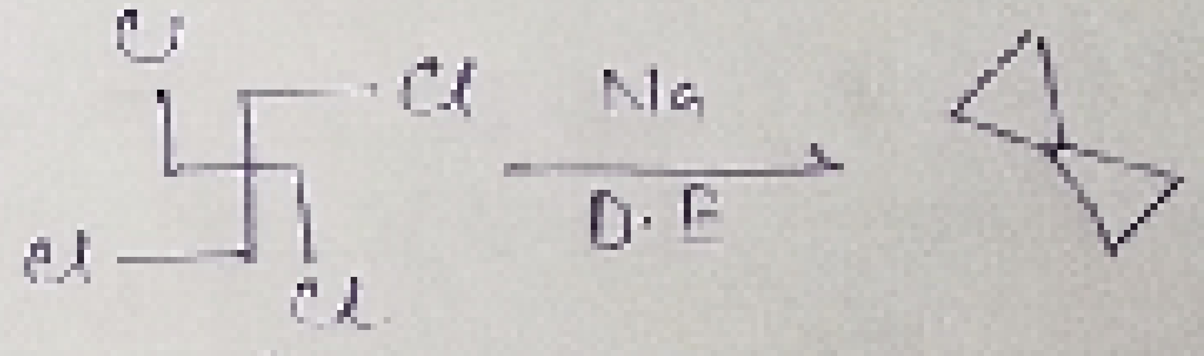
vi)



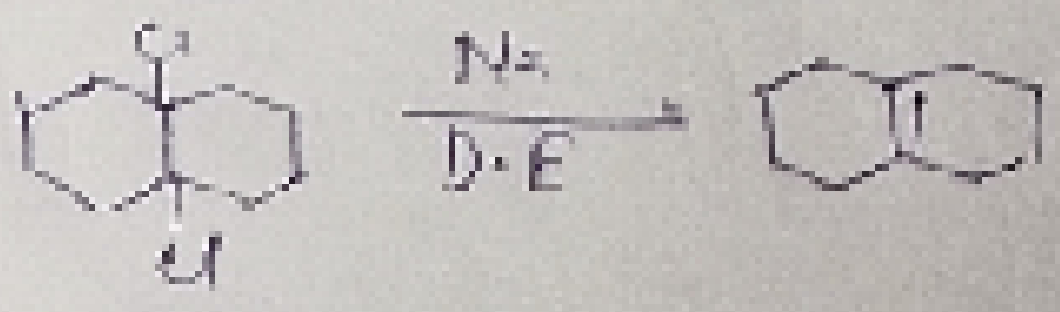
vii)



viii)



ix)



x

Q. Which compound can be prepared from Wurtz Reaction in good yield. 9

a) Et–Et.

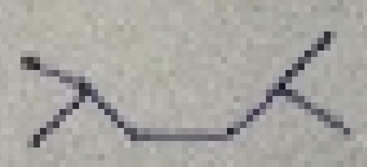
b) CH_4.

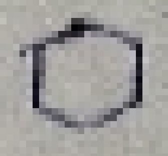
c) Et–nPr

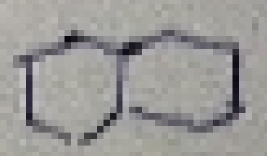
d) 

e) 

f) 

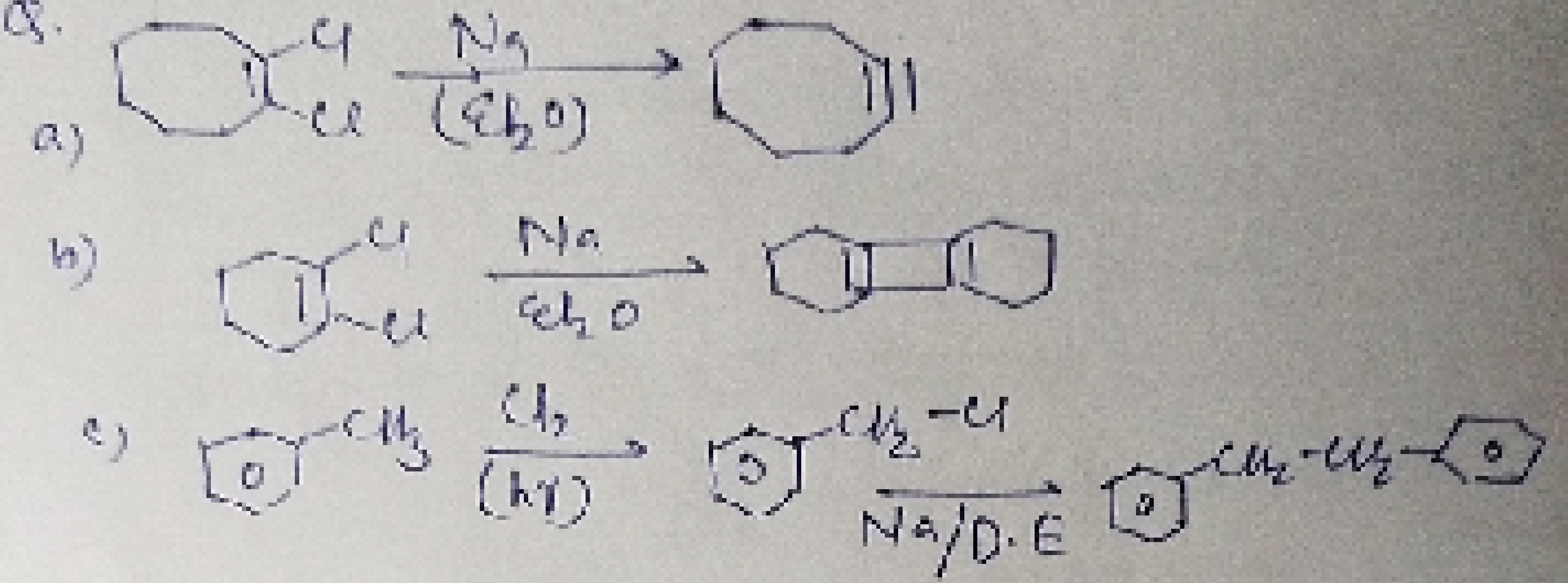
g) 

h) 

i) 

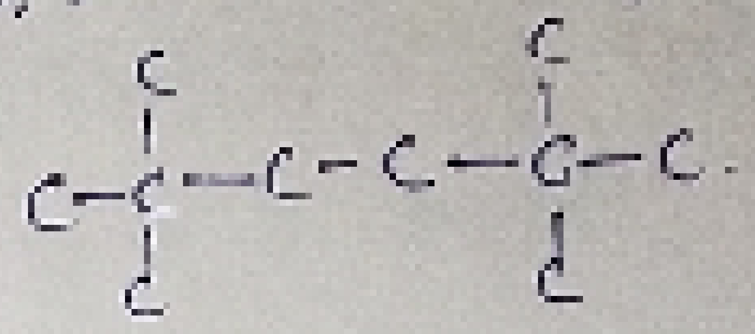
Ans: a, d, g, h, i.

Q.

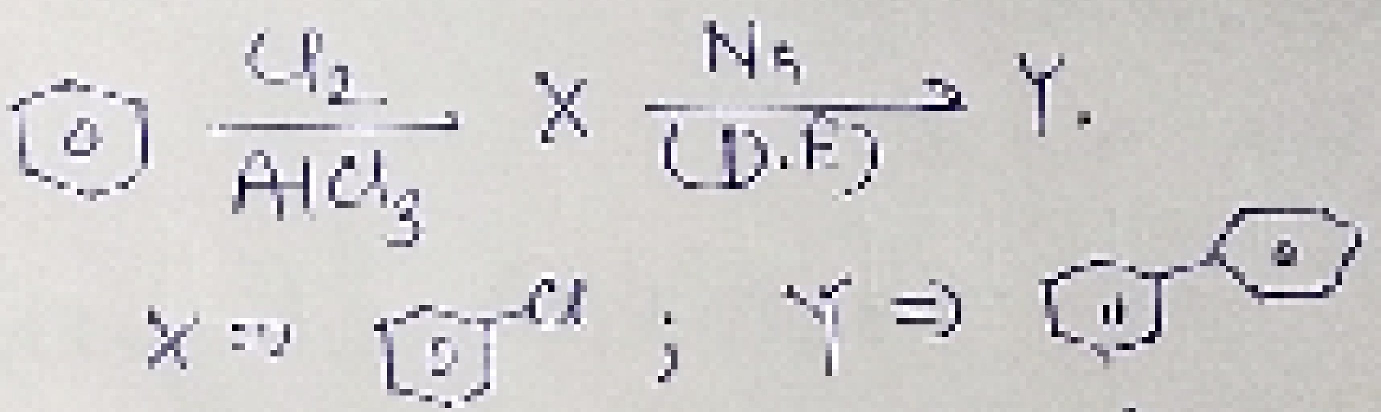


Q. $X \xrightarrow[(Et_2O)]{Na}$ 2,2,5,5 tetramethyl hexane.

[$X \Rightarrow Me_3C-CH_2-Cl$]



Q.



: Limitation of Wurtz Reaction:

Me_3C-CMe_3 ; Et_3C-CEt_3 can't be prepared

$Me_3C-X \xrightarrow[D.E]{Na} H_3C-\dot{C}(CH_3)-CH_3 + H_3C-\dot{C}(CH_3)-CH_3$

↓ disproportion

$H_3C-CH(CH_3)-CH_3 + H_2C=C(CH_3)-CH_3$

(reduced product) (oxidised pdt)

$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$; Me_3C-CMe_3 ; $H_3C-\underset{CH_3}{CH}-CH_3$.

Et_3C-CEt_3 ; Et_3C-Et can't be prepared by Wurtz Reaction.

$Me_3C-Cl \xrightarrow[(D.E)]{Na} Me_3C-CMe_3$ dimerised pdt (not formed)

$\longrightarrow Me_2C=CH_2 + HCMe_3$ disproportionation pdt (formed).

$H_3C-CH_2-Cl + CH_3-CH_2-CH_2-Cl$

$\xrightarrow[D.E]{Na}$ Et-Et + Et-npr + npr-npr [dimerised pdt]. (major)

$CH_2=CH_2 + CH_3-CH=CH_2$

EtH + nprH

[disproportionation pdt) minor pdt)

Tendency to dimerise:

$CH_3-\dot{C}H_2 > (CH_3)_2\dot{C}H > (H_3C)_3\dot{C}$

Tendency to disproportionation.

$(H_3C)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3-\dot{C}H_2$

$CH_3-CH=CH_2 \xrightarrow[+H_2O_2]{HBr} CH_3-CH_2-CH_2-Br$

$\downarrow$ Na / D.E

n-hexane.

: Kolbe Electrolysis :

Na salt of monocarboxylic acid when undergoes electrolysis, alkane is generated at anode.

$$R-\underset{\underset{O}{\parallel}}{C}-OH \xrightarrow{NaOH} R-\underset{\underset{O}{\parallel}}{C}-ONa$$

monocarboxylic acid → sodium salt of acid.

$$R-\underset{\underset{O}{\parallel}}{C}-O-Na \text{ (aq. solution)} \xrightarrow[\text{Electrolysis}]{} R-R\uparrow + CO_2\uparrow \text{ (Anode)} + H_2\uparrow \text{ (cathode)}.$$

Solution have NaOH.

pH of solution increases steadily & at a point when pH becomes constant indicates to completion of reaction.

$$R-\underset{\underset{O}{\parallel}}{C}-ONa \longrightarrow R-\underset{\underset{O}{\parallel}}{C}-O^- + Na^+$$

$$Na^+ + e^- \cdot H_2O \longrightarrow H^+ + \bar{O}H$$

$$H^+ + e^- \longrightarrow \tfrac{1}{2} H_2\uparrow \text{ (cathode)}$$

$$R-\underset{\underset{O}{\parallel}}{C}-O-\dot{O} \longrightarrow R-\underset{\underset{O}{\parallel}}{C}-\dot{O} \quad \text{[Anode]}.$$

$$R-\underset{\underset{O}{\parallel}}{C}-\dot{O} \longrightarrow R^\cdot + CO_2\uparrow$$

$$R^\cdot + R^\cdot \longrightarrow R-R.$$

Solution have NaOH.

$$R-\underset{\underset{O}{\parallel}}{C}-O^\cdot + R^\cdot \longrightarrow R-\underset{\underset{O}{\parallel}}{C}-OR \text{ (ester is formed as biproduct).}$$

Q. Aqueous solution of potassium propanoate is electrolysed. Possible organic products

a) n-butane b) $C_2H_5CO_2C_2H_5$ c) CH_3-CH_3 d) $CH_2=CH_2$

Solution: $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OK \longrightarrow CH_3-CH_2-\overset{O}{\overset{\|}{C}}-O^- + K^+$

$H_2O \longrightarrow H^+ + \bar{O}H$

$H^+ + \bar{e} \longrightarrow \frac{1}{2}H_2\uparrow$ (Cathode/Reduction)

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-O^- \xrightarrow[-\bar{e}]{} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-O^\bullet$

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-O^\bullet \longrightarrow CH_3-\dot{C}H_2$

$CH_3-\dot{C}H_2 + \dot{C}H_2-CH_3 \xrightarrow[\text{sation}]{\text{dimeri}} \text{n-butane}$

$CH_3-\dot{C}H_2 + \dot{C}H_2-CH_3 \xrightarrow[\text{tionation}]{\text{dispropor}} CH_2=CH_2 + CH_3-CH_3$.

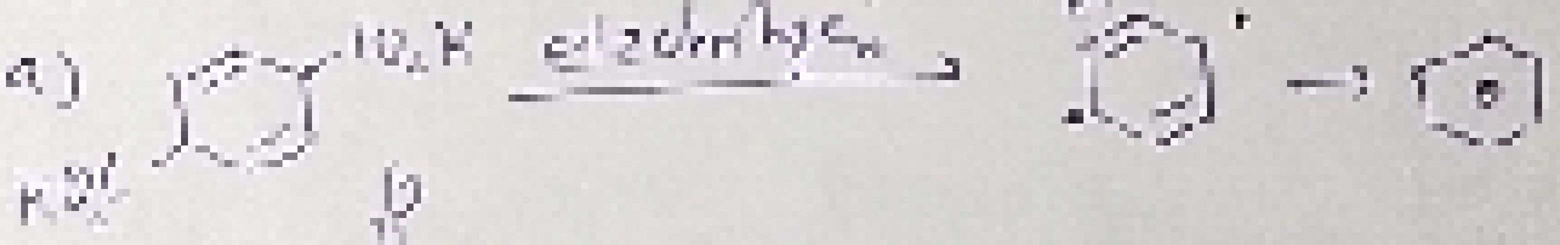
$CH_3-\dot{C}H_2 + CH_3-CH_2-\overset{O}{\overset{\|}{C}}-O^\bullet \longrightarrow CH_3-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$.

⇒ CH_4 can't be prepared.

⇒ yield of symmetrical alkane > yield of non-symmetrical alkane.

⇒ To get n-hexane, we should use $CH_3-CH_2-CH_2CO_2Na$.

⇒ To get n-butane, we should use $CH_3CH_2CO_2Na$.

a) 

b) $\begin{array}{l} CH_2-\overset{O}{\overset{\|}{C}}-OK/Na \\ | \\ CH_2-\underset{O}{\underset{\|}{C}}-OK/Na \end{array} \xrightarrow{\quad} CH_2=CH_2$ OMSGAPSA.

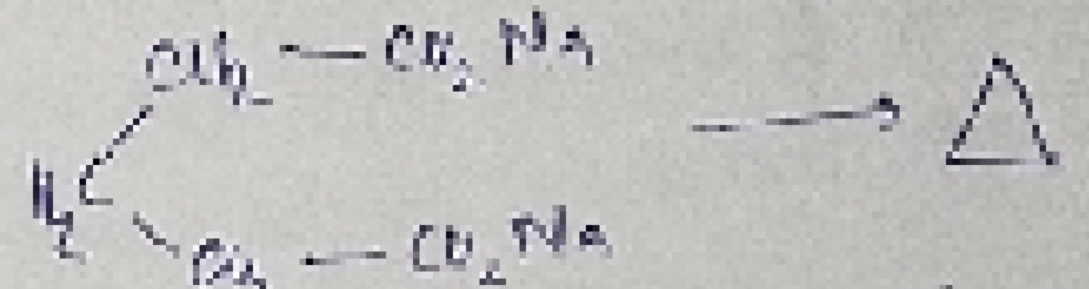
Na/K salt of ~~oxalic~~ succinic acid.

(c) $CH(CO_2Na)=CH(CO_2Na) \xrightarrow{\text{electrolysis}} HC\equiv CH$.

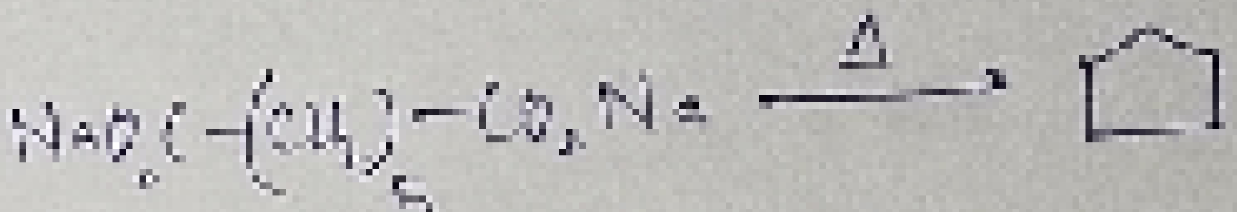
Na-salt of maleic acid

(d) $NaO_2C-CH=CH-CO_2Na \xrightarrow{\text{electrolysis}} HC\equiv CH$.

Na-salt of fumaric acid.

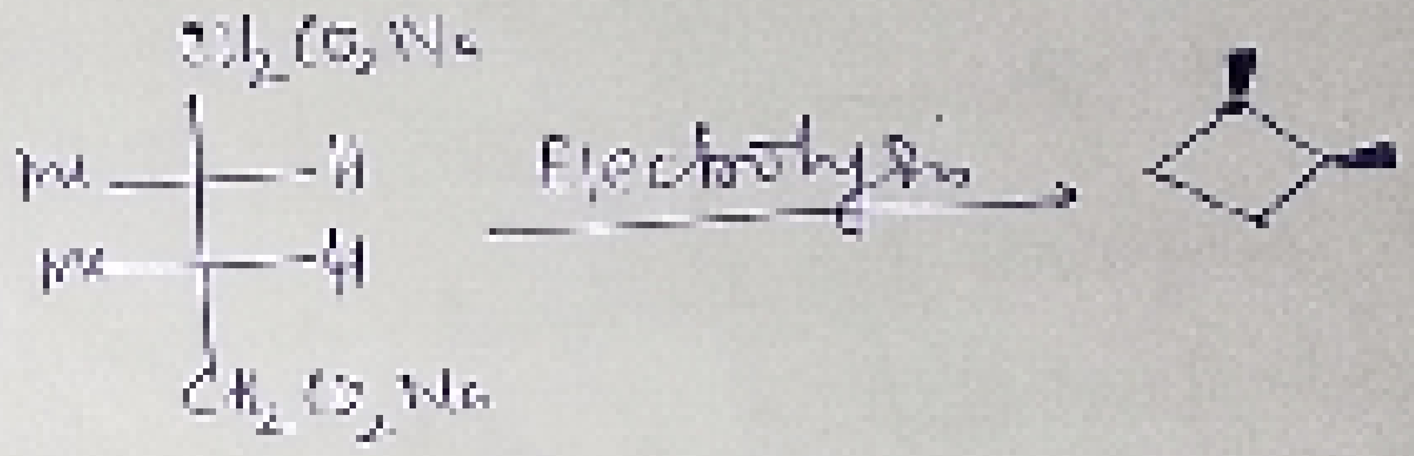
e) 

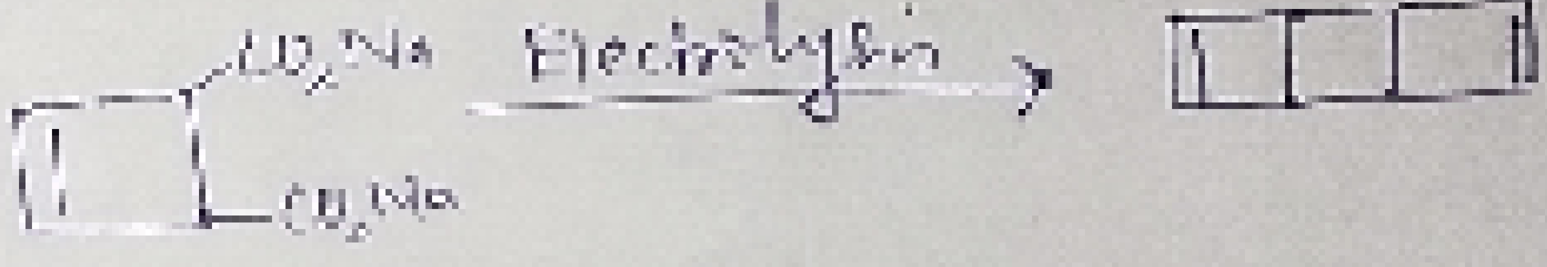
Na-salt of glutaric acid

f) 

Na-salt of pimelic acid

(e) to (f) are examples of intramolecular Kolbe Electrolysis.

g) 

h) 

i)