Hydrocarbons

Alkanes

* Alkanes = Paraffins
  Para = Parum (Little)
  Affins = Affinity (Reactivity)

  so alkanes don't react with acids, bases and other reagents in ordinary conditions.

* General formula = C_nH_{2n+2}
  First member = CH_4 (methane or marsh gas)

* Bond length → C–C = 1.54 A°
  C–H = 1.12 A°

* Bond Energy → C–C = 84 Kcal./mol
  C–H = 97 K Cal./mol

* They show C.I., P.I., O.I., conf. Iso.

* Non Polar in nature.

Methods of preparation ⟶

(1) From alkenes/alkynes ⟶

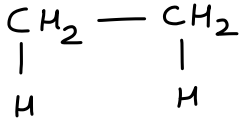
Reagents ⟶ Ni/H_2, Pd/H_2, Pt/H_2,

$Ni/200-300^{\circ}C/H_2$, Raney $-Ni/H_2$,

Sabatier Senderens reaction

(Alloy of Ni and Al digested with NaOH)

$Pd-C/H_2$

Ex. $CH_2=CH_2 \xrightarrow[H_2]{Ni}$ 

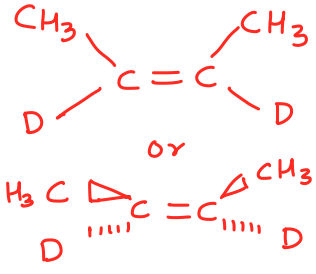
* Syn Addition of reagent.

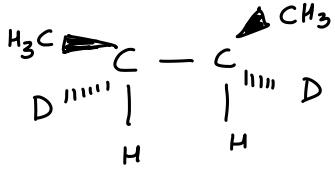
Cis + syn = Meso

Trans + syn = Racemic mix.

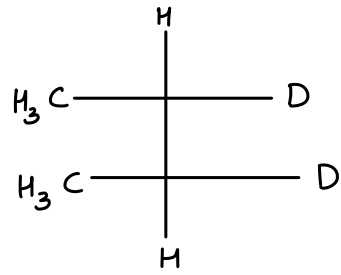
Cis + Anti = Racemic mix.

Trans + Anti = Meso

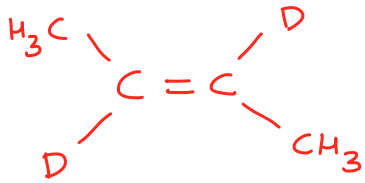
Ex. 

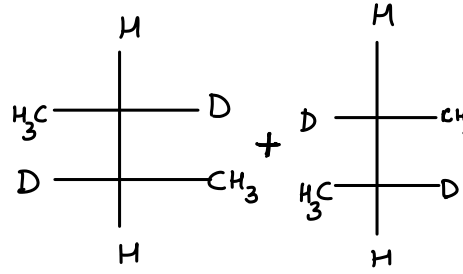


or

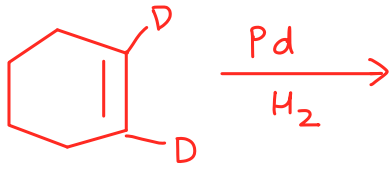


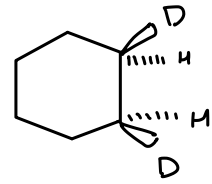
Ex.



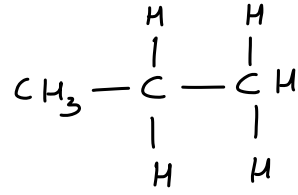


Ex.

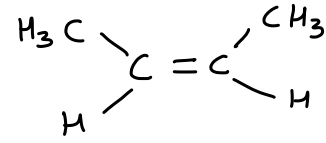




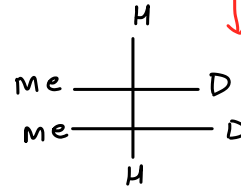
Ex. $CH_3-C\equiv CH \xrightarrow[2\,H_2]{Ni}$



Ex. $CH_3-C\equiv C-CH_3 \xrightarrow[1\,eq.\,H_2]{Ni}$

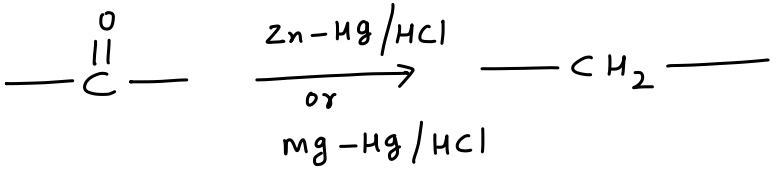


$\xrightarrow{Pt/D_2}$

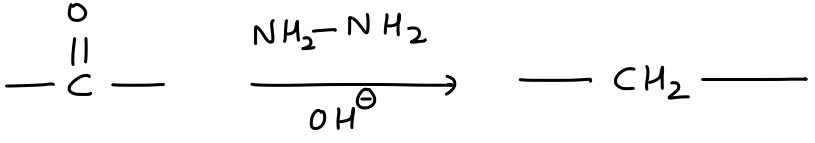


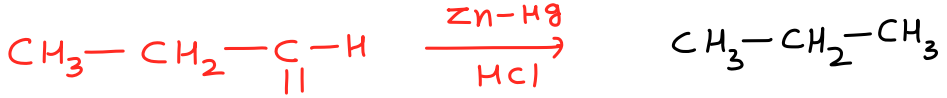
(2) From carbonyl comp. ⟶

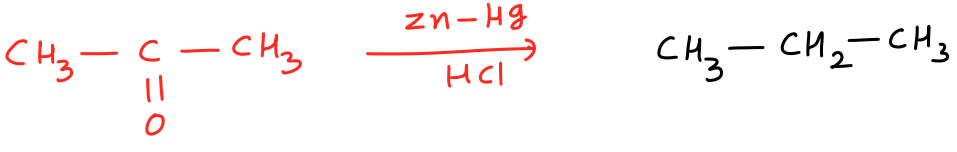
(i) clemmensen reduction ⟶

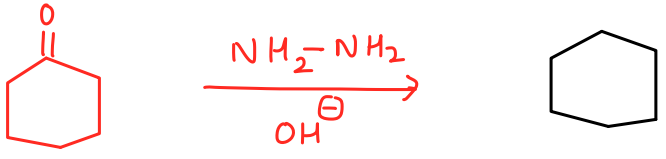


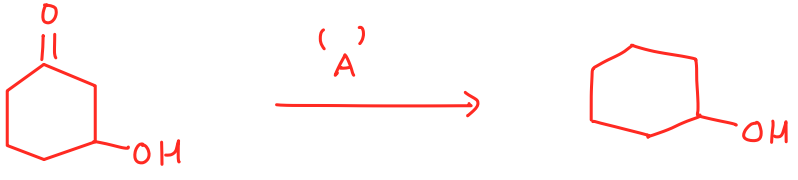
(ii) wolff Kishner reduction ⟶



Ex. 

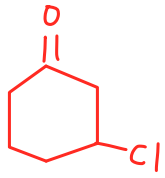
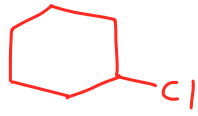
Ex. 

Ex. 

Ex. 

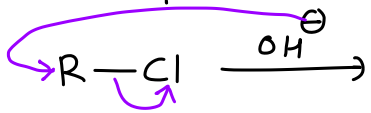
A = $NH_2-NH_2/OH^{\ominus}$ $\quad$ A ≠ Zn-Hg/HCl

Reason → $R-OH \xrightarrow{HCl} R-\overset{+}{O}(H)-H \; Cl^- \rightarrow R-Cl + H_2O$

Ex.   

A = Zn − Hg / HCl or Mg − Hg / HCl

A ≠ $NH_2-NH_2 \,/\, OH^{\ominus}$

Reason → 

(3) By Alcohol / carbonyl comp. / carboxylic acid →

* $R-OH \xrightarrow{Zn\text{-}dust} R-H + ZnO$ (Alkane)

Ex. $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{Zn\text{-}dust} CH_3-CH_2-CH_3 + ZnO$

 $\xrightarrow{Zn\text{-}dust}$  + ZnO

* $R-OH \xrightarrow[150-200^{\circ}C]{2\,eq.\ HI + Red\text{-}P} R-H$

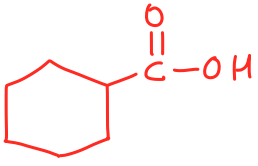
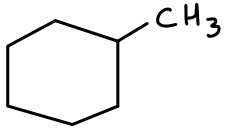
Mech. → $R-OH \xrightarrow{HI} R-I + H_2O$

$$R-I \xrightarrow{HI} R-H + I_2$$

$$6\,I_2 + P_4 \xrightarrow{(red)} 4\,PI_3$$

* $R-\underset{\underset{O}{\|}}{C}-R' \xrightarrow[\Delta]{4\,eq\ HI,\ Red-P} R-CH_2-R'$

* $R-\underset{\underset{O}{\|}}{C}-OH \xrightarrow[\Delta]{6\,eq.\ HI,\ Red-P} R-CH_2-H$

Ex.  $\xrightarrow[\Delta]{6\,eq.\ HI + Red-P}$ 

Ex. $CH_3-CH_2-OH \xrightarrow[\Delta]{2\,eq.\ HI + red-P} CH_3-CH_3$

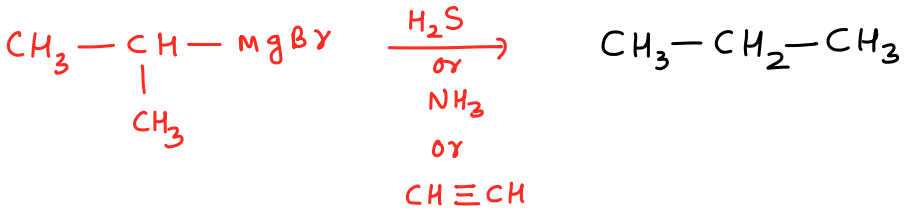
(4) By Rxn of Grignard reagent →

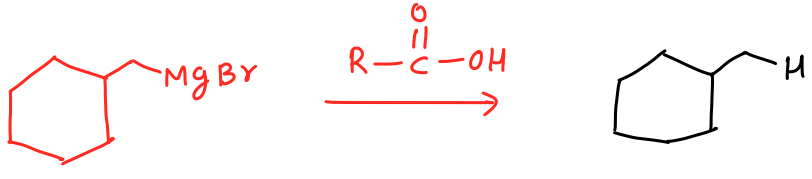
$\overset{\delta-}{R}-\overset{\delta+}{Mg}X$ + $\underset{\text{Acidic-H}}{\overset{\textcircled{H}}{}}-Y \longrightarrow R-H + Mg\begin{matrix}X\\Y\end{matrix}$

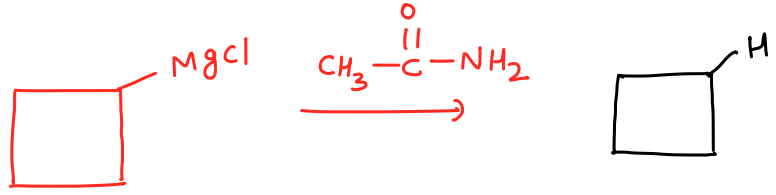
Grignard reagent — Alkane

It is K/a Zerewitinoff method and it used for quantitative analysis of Acidic-H.

Ex. $CH_3-CH_2-MgCl \xrightarrow[\text{or } CH_3-CH_2-OH]{H_2O} CH_3-CH_3$







(5) By Alkyl halides →

(a) Reduction (b) wurtz Rx^n

(c) Frankland Rx^n (d) Corey house synthesis

(a) Reduction of R–X →

$$R-X \xrightarrow{2H} R-H + HX$$

Reagents →

(i) $LiAlH_4$ (LAH)
↳ not for 3° halide (Alkene will form)

(ii) $NaBH_4$ (SBH)
↳ not for 1° halide (NO Rx^n)

(iii) Ph_3SnH (Triphenyl tin hydride, TPH)

(iv) $t\text{-}Bu_3SnH$ (trit-butyl tin hydride, BTH)

(v) $Zn + NaOH$

(vi) $Zn + HCl$

(vii) $Sn + HCl$

(viii) $Fe + HCl$

(ix) $HI + red\text{-}P$

(x) $Na + C_2H_5OH$

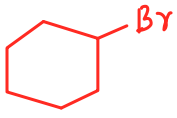
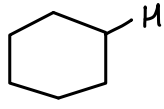
(xi) $Zn - Cu / C_2H_5OH$

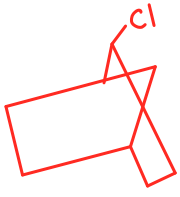
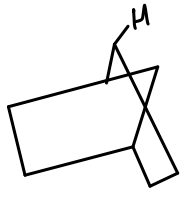
(xii) $Zn + CH_3COOH$

(xiii) $Al - Hg / NaOH$

(xiv) $Mg - Hg / H_2O$

Ex. $CH_3 - CH_2 - Br \xrightarrow{TPH} CH_3 - CH_2 - H$

Ex.  $\xrightarrow{NaBH_4}$ 

Ex.  $\xrightarrow{Zn/dil.HCl}$ 

(b) Wurtz $Rx^n \longrightarrow$

$$2R - X \xrightarrow[\text{dry-ether}]{2Na} R - R + 2NaX$$

i.e. Et_2O, THF

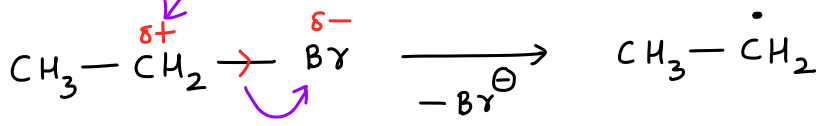
Mech. $\longrightarrow$ $Na \longrightarrow Na^+ + e^-$

(E.P. metal)

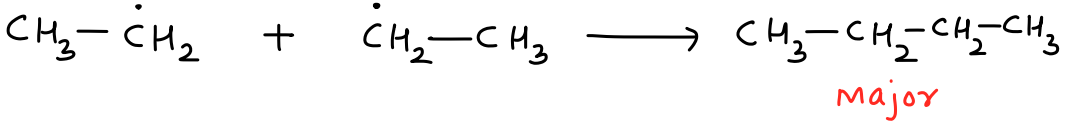
Mech. →

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

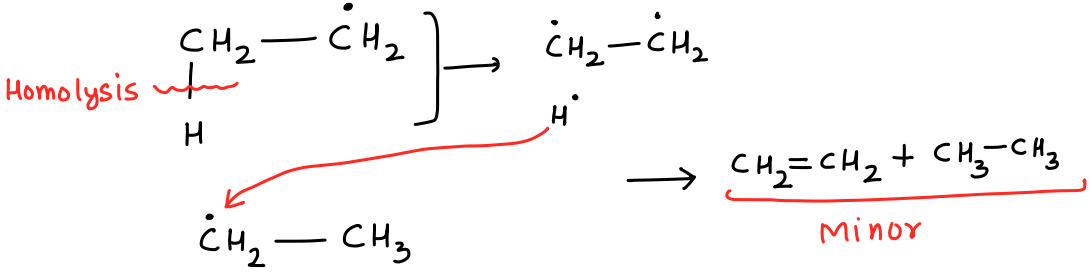
(E.P. metal)



Dimerisation →

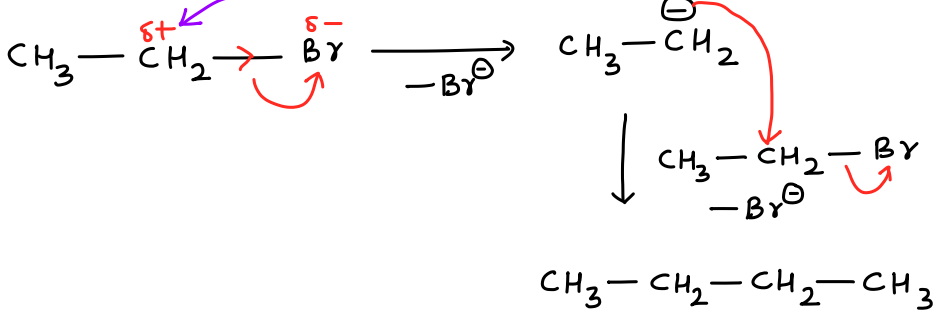


Disproportionation →



Another Mech. →

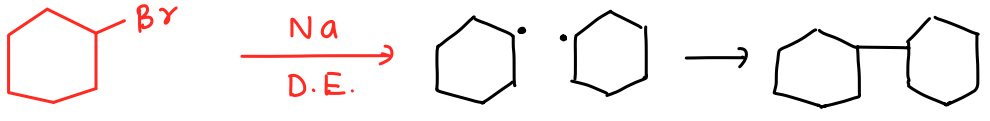
$2Na \longrightarrow 2Na^+ + 2e^-$

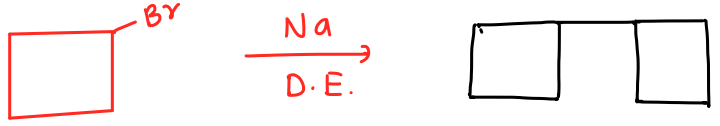


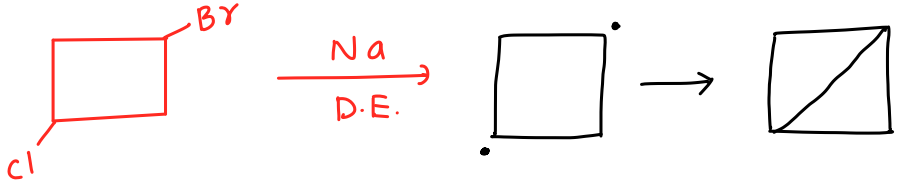
Reactivity order → 1° R–X > 2° R–X > 3° R–X

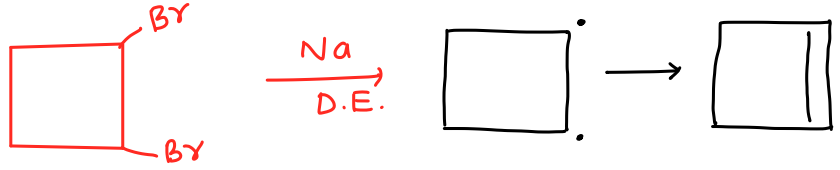
* This method is useful for preparation of alkanes of even no. of carbon atoms.
* CH_4 can't be prepared by this method.
* In the place of Na, finely divided Ag, Cu can also be used.
* Here we take dry ether as wet ether give rise to the formation of alcohols.
* Reactivity → R–I > R–Br > R–Cl > R–F

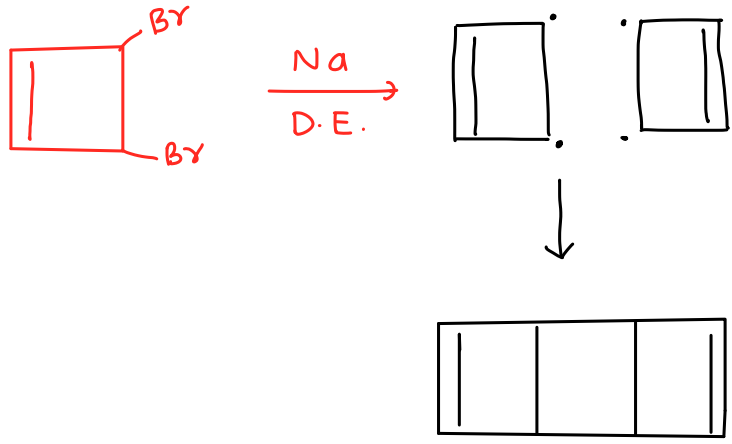
Ex.











CH_3-Br + CH_3-CH_2-Br $\xrightarrow[D.E.]{Na}$ $CH_3-CH_3 + CH_3-CH_2-CH_2-CH_3 + CH_3-CH_2-CH_3$

Mix. of Products

(c) Frankland Rx^n ⟶

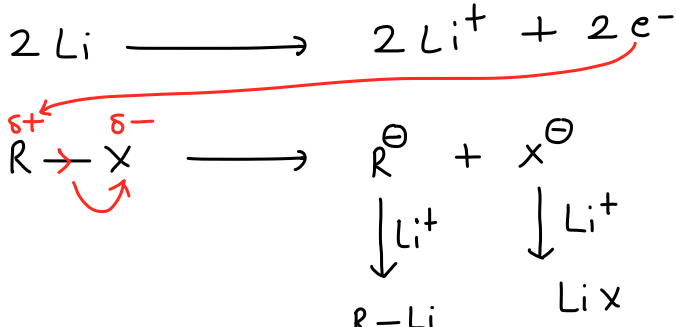
$$R-X + Zn + X-R \xrightarrow{C_2H_5OH} R-R + ZnX_2$$

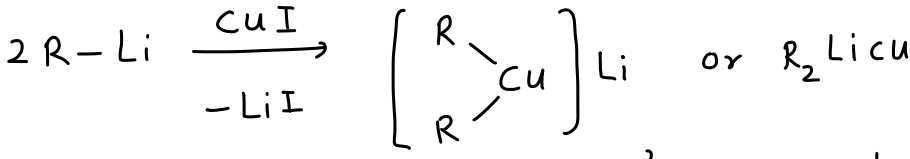
* Disproportionation Rx^n doesn't take place.

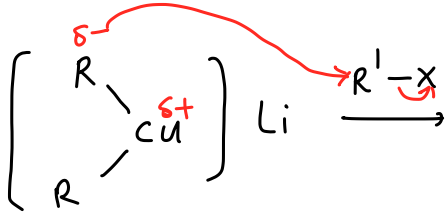
(d) corey house synthesis ⟶ This method is useful for preparation of alkanes of odd no. of carbon atoms.

$$R-X + R'-X \xrightarrow[(ii)\ CuI]{(i)\ Li/ether} R-R' + LiX + LiI + CuX$$

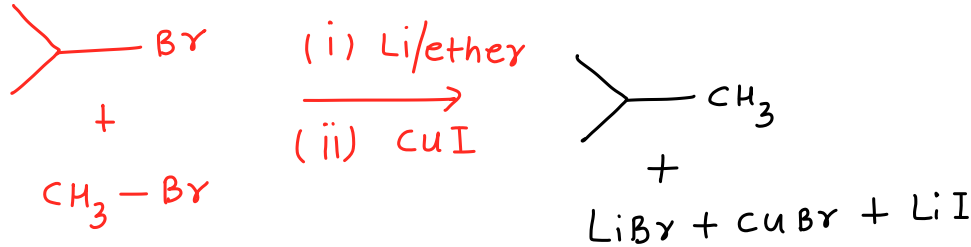
Mech. →


2 Li → 2 Li+ + 2 e−
δ+ δ−
R → X
R⊖ + X⊖
Li+
Li+
R–Li
organo Lithium
Li X


2 R–Li
CuI
–LiI
R
Cu
R
Li
or R2LiCu
Gilman's reagent


δ
R
Cu
δ+
R
Li
R'–X
R – R'

Ex.


Br
+
CH3 – Br
(i) Li/ether
(ii) CuI
CH3
+
LiBr + CuBr + LiI

Ex.


Br
[et2cu]Li
CH2–CH3

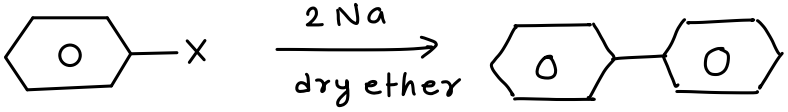
Ex. CH_3-CH_2-Br $\xrightarrow[(ii)\ CuBr]{(i)\ Li/ether}$ (A)

(iii) $CH_3-CH_2-\underset{\displaystyle Cl}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-H$

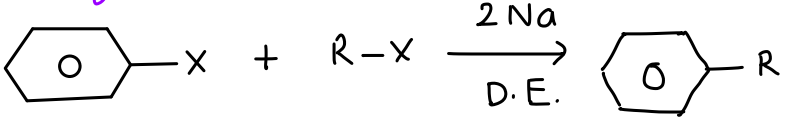
$$A = CH_3-CH_2-\underset{\displaystyle CH_2-CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-H$$

Note →

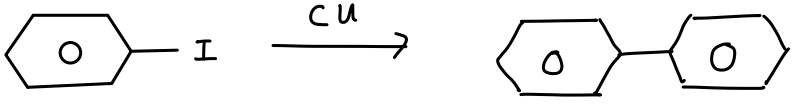
Fittig Rx^n ⟶



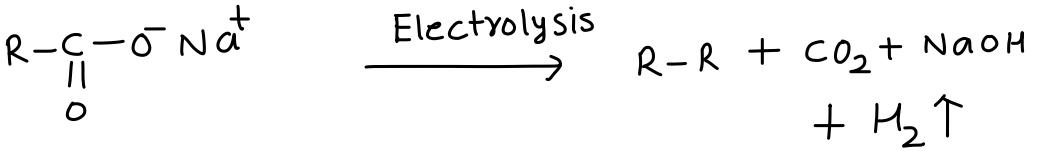
wurtz-fittig Rx^n ⟶



Ullamann Rx^n ⟶

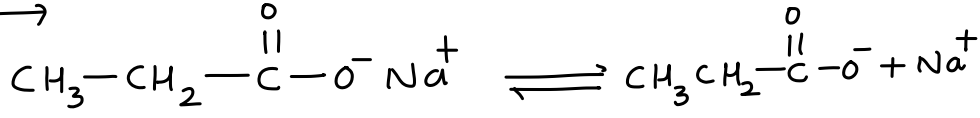


(6) Kolbe's electrolysis →

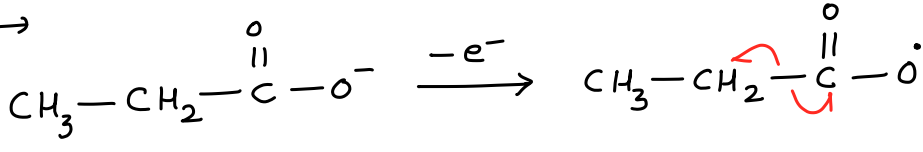


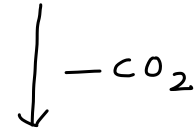
aq. soln of Sod. or Pott.
Salt of carboxylic acid

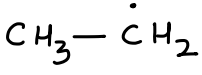
Mech. →

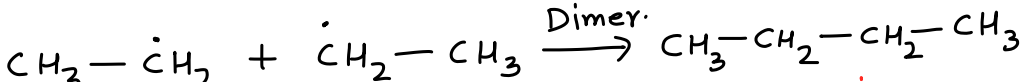


Anode →

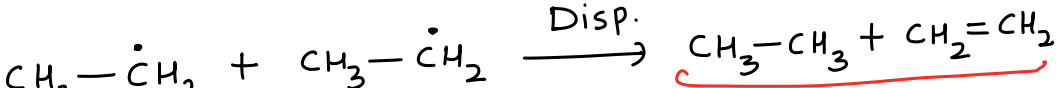




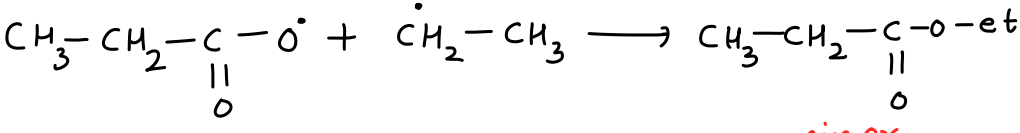




major



minor



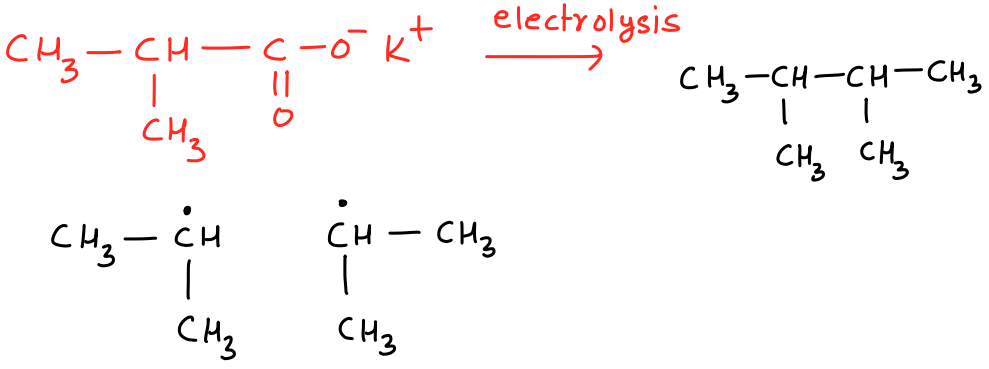
minor

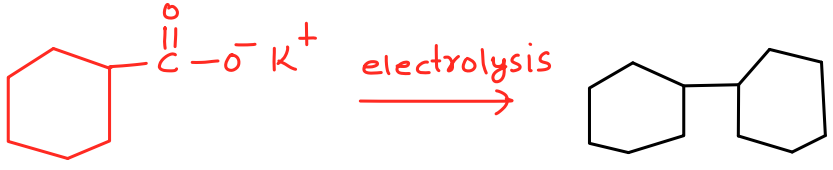
Cathode → SRP ⇒ H_2O > Na^+, K^+

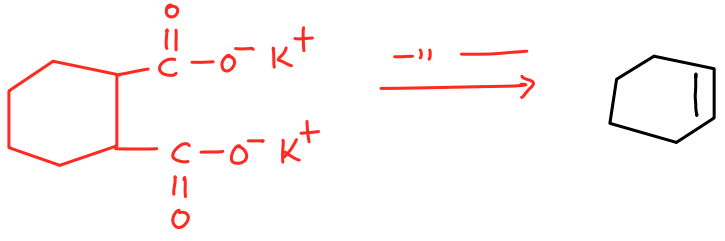
$2e^- + 2H_2O \longrightarrow H_2\uparrow + 2OH^-$

$Na^+ + OH^- \longrightarrow NaOH$

Resulting soln $\Rightarrow$ alkaline $(pH > 7)$

Ex. 

Ex. 

Ex. 

(7) From metal carbides →

$Be_2\overset{(-4)}{C} + H_2O \longrightarrow Be(OH)_2 + CH_4$

$Al_4\overset{(-4)}{C_3} + H_2O \longrightarrow Al(OH)_3 + CH_4$

Homework

Hydrocarbons workbook
DTS-1-11
Q.1,2,5,6,9,15,33,43,46,65,67-70,72,77,84,100,104, 106-111,115,126,128

JEE MAIN archive
Q.15,20

JEE ADVANCED ARCHIVE
Q.2,4,17,18,29,31,38,39,47,69,70,76,89,91,100,103