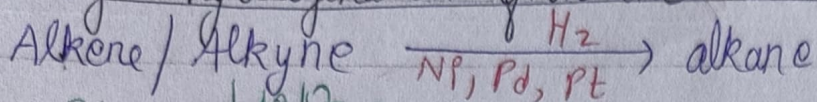


# Hydrocarbons

## Alkanes

### I GMP

#### 1. Catalytic hydrogenation of unsaturated compounds.



- syn addition

- Pd, Pt can react at room temp. But Ni requires high temp. 200 - 300 °C  $\Rightarrow$  Sabatcho Reaction. But by using (Ni-Al/NiAl) Raney Ni reaction can be completed at room temp.

- cis alkene + syn addition  $\longrightarrow$  meso compound  
trans alkene + syn addition  $\longrightarrow$  racemic mixture.

- case of hydrogenation  $\propto \pi$  e<sup>-</sup> density  $\propto$  steric hindrance

- when there are 2  $\pi$  bonds and H<sub>2</sub> (not in excess), then follow above rule to decide which bond gets reduced.

#### 2. Wurtz Reaction - $\text{R-X} \xrightarrow[\text{dry ether}]{\text{Na}} \text{R-R}$ (doubling of C)

- ionic mechanism

(SN<sub>2</sub>) reactivity of substrate  $\propto$  1/steric hindrance

- FR mechanism

- methane cannot be prepared from Wurtz rx<sup>n</sup>.

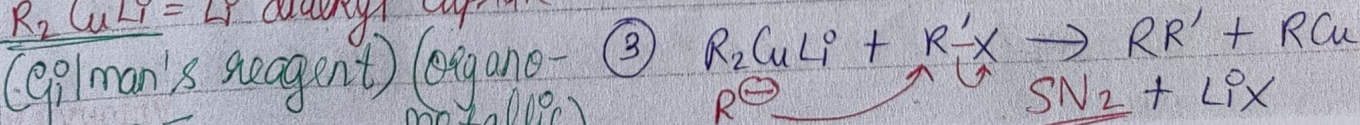
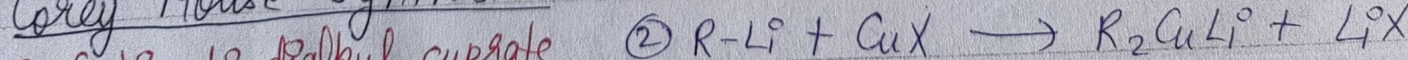
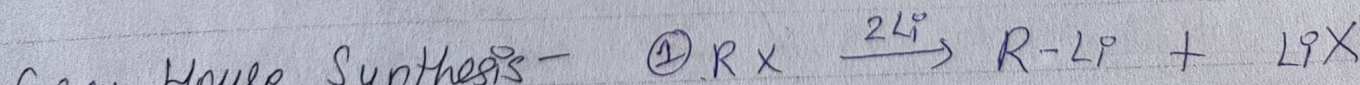
- ether should be dry (free from moisture) or else the product formed will be an alcohol.

- to get odd no. of C in product, mixture of alkyl halides must be used. But by using mixture of RX, even product is a mixture,  $\therefore$  yield  $\downarrow$  es.

#### 3. Frankland Reaction - $\text{RX} \xrightarrow[\text{dry ether}]{\text{Zn}} \text{R-R}$ (doubling)

- similar mechanism as Wurtz.

#### 4. Corey House Synthesis -



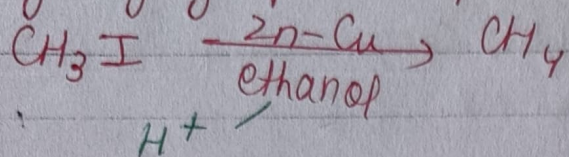
R<sub>2</sub>CuLi = Li dialkyl cuprate  
(Gilman's reagent) (organo-metallic)

SN<sub>2</sub> + LiX

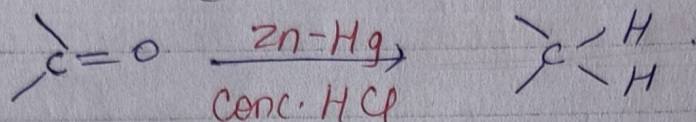
5. Reduction of RX  $RX \xrightarrow{Zn/HCl} R-H$

mechanism - (1)  $Zn \rightarrow Zn^{+2} + 2e^-$  (2)  $R-X \rightarrow R^+ + X^-$   
 (3)  $R^+ + 2e^- \rightarrow R^-$  (4)  $R^- + HCl \rightarrow R-H + Cl^-$

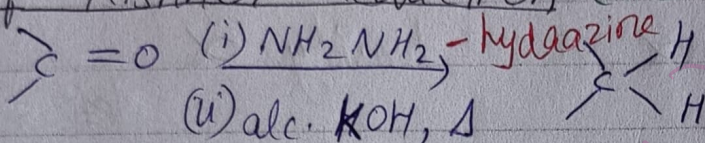
very highly pure  $CH_4$  can be prepared from -



6. Clemmenson Reduction (reactant = aldehyde/ketone)

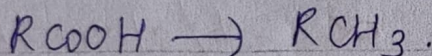
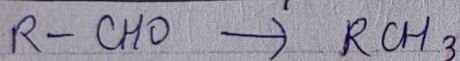


7. Wolff Kishner Reduction (reactant = ald. / ketone)

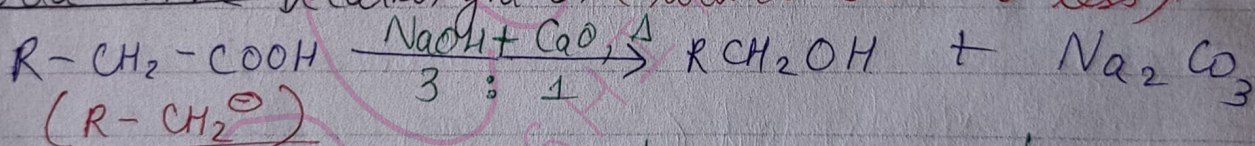


This is the more preferred method because there is formation of gaseous product ( $N_2$ )  $\therefore$  leads to more forward reaction.

8. Red P + HI /  $\Delta$   $R-OH \rightarrow RH$



9. Soda-Lime Decarboxylation (Product has 1C less)

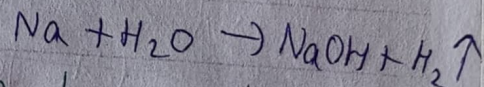
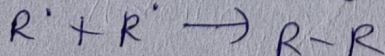
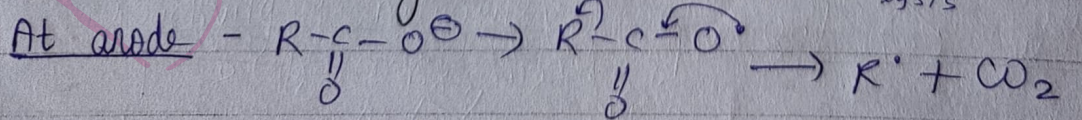


-  $CaO$  absorbs  $CO_2$  and thus facilitates the formation of carbanion.

- Reactivity of carboxylic acid & stability of  $C^-$  intermediate.

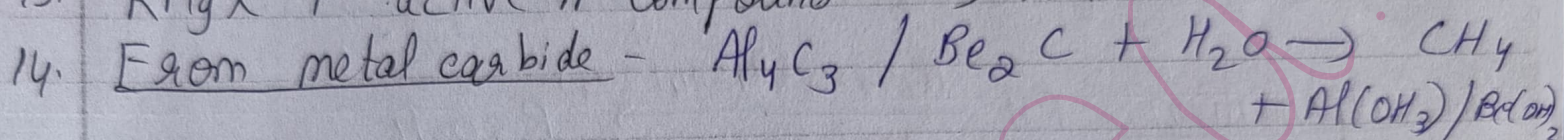
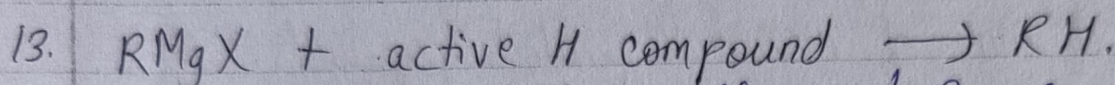
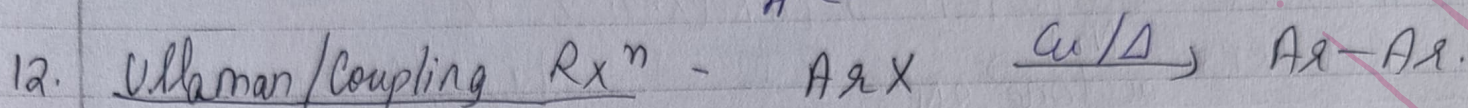
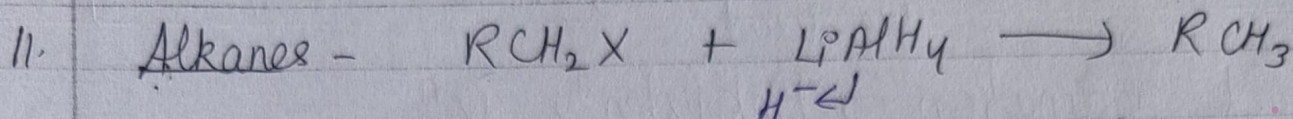
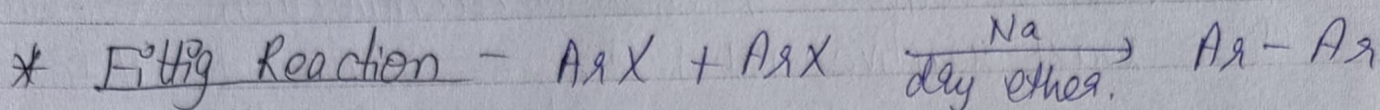
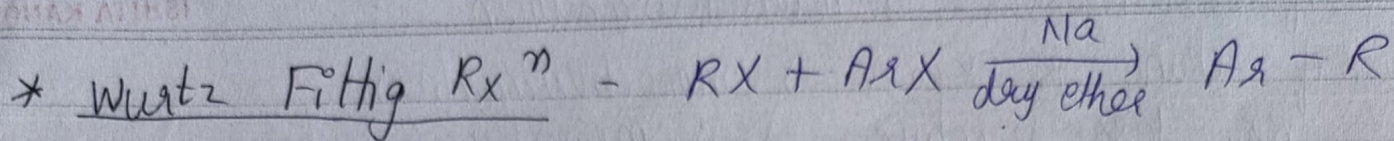
-  $\beta$ -keto acids undergo decarboxylation only on mild heating.

10. Kolbe's Electrolysis  $RCOO^- Na^+ / K^+ \xrightarrow{\text{electrolysis}} R-R$  (doubling, even no. C)



- with time, the soln. becomes alkaline due to by-product  $NaOH$ .

- for formation of alkane with odd C, use mixture of salts as reactants.



## II Physical Properties

- London forces exist

- as no. of C  $\uparrow \Rightarrow$  MP, BP  $\uparrow$

- BP =  $CH_4 < C_2H_6 < C_3H_8 < C_4H_{10} < C_5H_{12} \dots$

- MP = also depends on efficiency of packing

$\therefore$  even C  $>$  odd C.

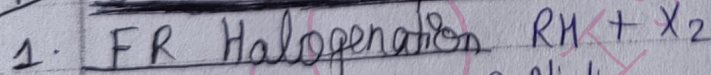
$\therefore CH_4 < C_2H_6 > C_3H_8 < C_4H_{10} > C_5H_{12} \dots$

- all alkanes are lighter than  $H_2O$ .

- density keep increasing with mass until a certain no. of C.

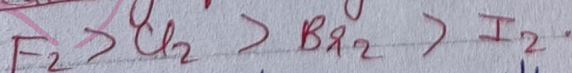
- not soluble in water.

## III Chemical Properties



- 3 steps = (i) chain initiation  
(ii) chain propagation  
(iii) chain termination.

- reactivity of halogens -



-  $F_2$  can react even in the dark.

- practically fluorination is done by halogen exchange reaction (Sawart's rx<sup>n</sup>).  $RCI / RBr \xrightarrow[HgF/COF_3]{AgF} RF$

-  $\therefore F_2$  is highly reactive, generally multi fluorination takes place

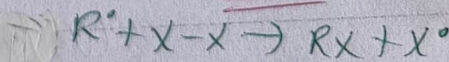
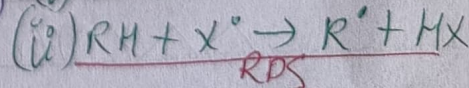
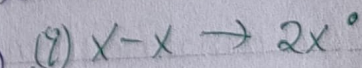
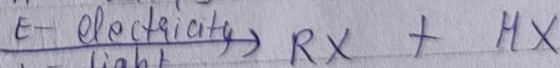
H - heat /  $\Delta$

E - electricity

L - light

P - peroxide

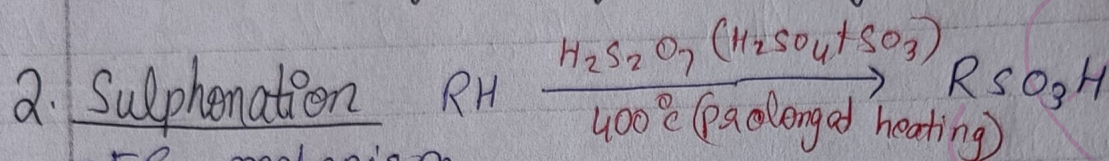
R - radiation (hr)



- if  $\text{Cl}_2$  is excess  $\Rightarrow$  multichlorination
- if alkane is excess  $\Rightarrow$  monochlorination.
- $\text{Br}_2$  = less reactive  $\Rightarrow \therefore$  monobromination
- $\text{I}_2$  = least reactive  $\text{RH} + \text{I}_2 \rightleftharpoons \text{RI} + \text{HI}$   $\therefore$  yield  $\downarrow$  less stable  
To increase yield, OA like  $\text{HNO}_3/\text{HIO}_3/\text{HIO}_4$  are used.

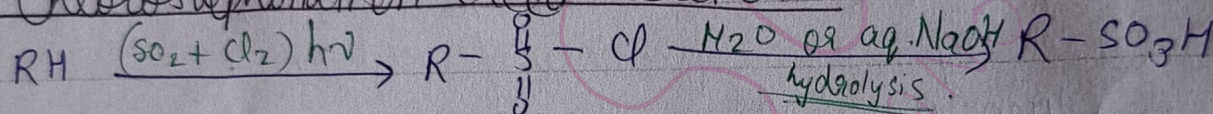
- Indirect iodination  $\Rightarrow$  Finkelstein's rxn  
 $\text{RCl}/\text{RBr} \xrightarrow[\text{acetone}]{\text{NaI}} \text{RI} + \text{NaCl}/\text{NaBr} \downarrow$   $\text{SN}^2$

- calculation of no. of monohalogenated products.

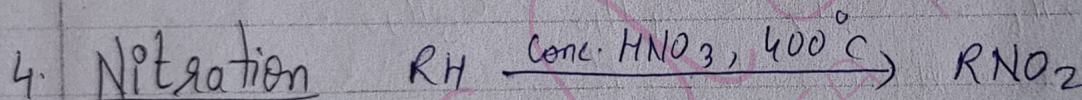


- FR mechanism
- reactivity  $\propto$  stability of  $\text{R}^\bullet$

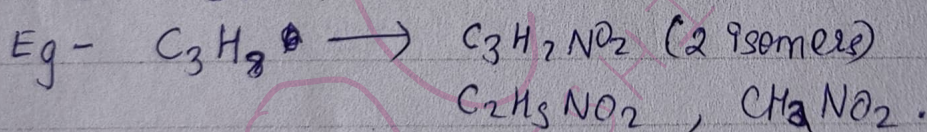
3. Chlorosulphonation (Reed Reaction)



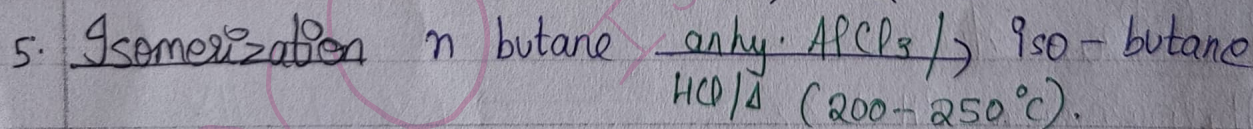
- FR mechanism



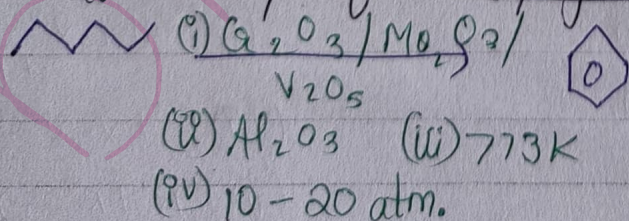
- FR mechanism



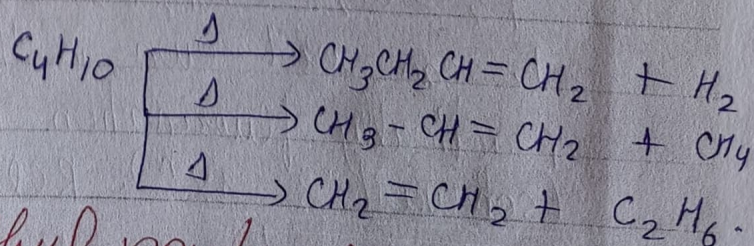
(mixture of diff. nitro alkanes formed due to thermal cracking).



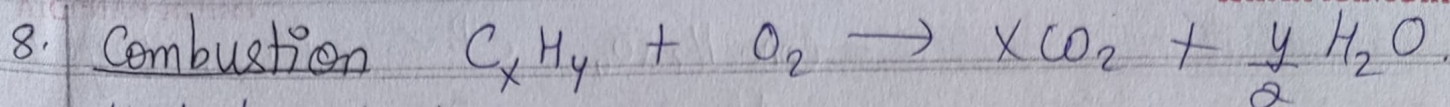
6. Aromatization/Reforming/Cyclization



7. Pyrolysis/Thermal Cracking

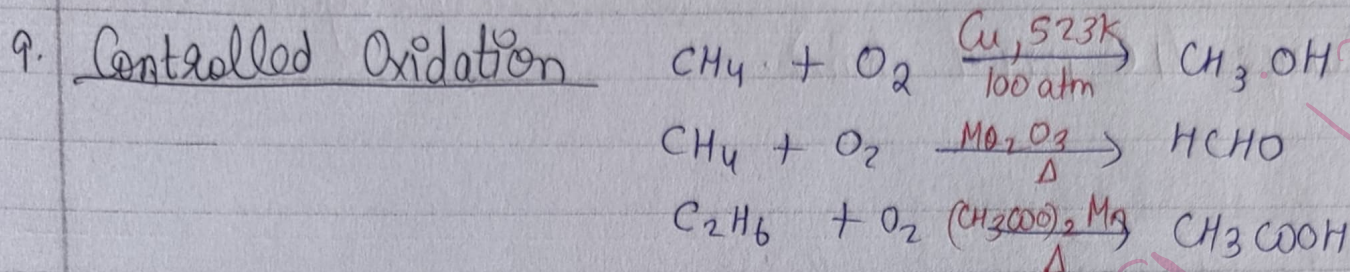


(Isooctane = 2,2,4-trimethyl pentane)



- Heat of Combustion (HOC)

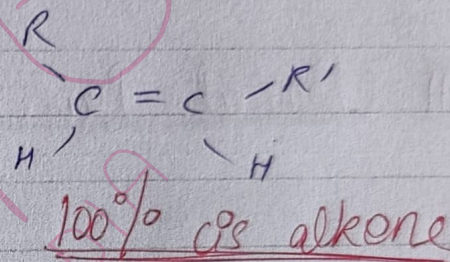
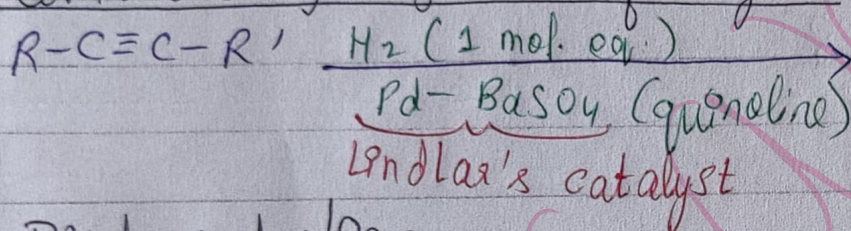
HOC  $\propto$  no. of C atoms  $\propto \frac{1}{\text{branching}} \propto \frac{1}{\text{stability}}$



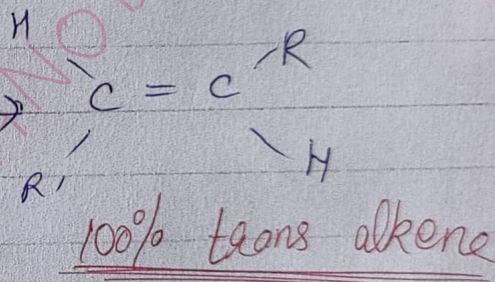
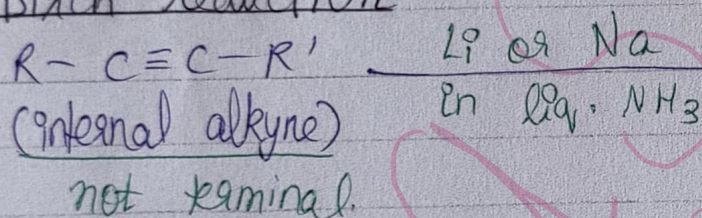
## Alkenes

### I GMP

#### 1. Controlled Hydrogenation of Alkynes

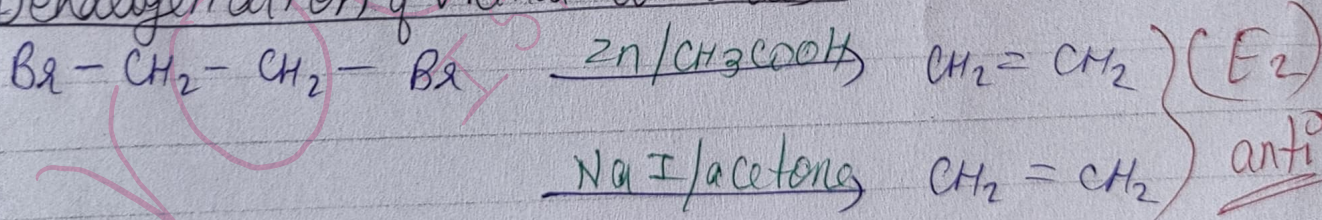


#### 2. Birch reduction

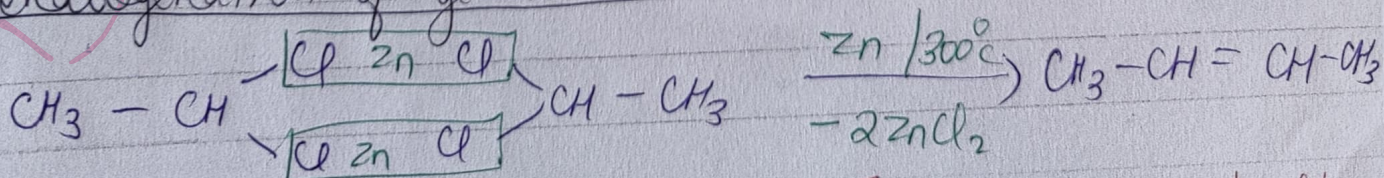


#### 3. Dehydrohalogenation of Alkyl halides - E<sub>1</sub>/E<sub>2</sub>.

#### 4. Dehalogenation of vicinal dihalides



#### 5. Dehalogenation of geminal dihalides



#### 6. Pyrolysis of Ester (Hofmann rule) [less substituted alkene = major product.]

#### 7. Hoffman Elimination of Tertiary alkyl ammonium salt

Remove  $\beta H$ , wherever  $\ominus$  is more stable  $\Rightarrow$  major product

8. Dehydration of Alcohols - conc.  $H_2SO_4$   $C^\oplus \checkmark$ ,  $E_1$ , saytzeff  
 $Al_2O_3$   $C^\oplus \times$ ,  $E_2$ , saytzeff  
 $ThO_2$   $C^\oplus \times$ ,  $E_2$ , hoffmann.
9. Kolbe's Electrolysis - (Reactant = Na/K salt of saturated dicarboxylic acid)

(Always 4 C parent chain).

## II Physical Properties

- MP, BP  $\uparrow$  with mass
- MP, BP  $\propto \downarrow$  branching (for same no. of C)
- insoluble in water, soluble in non-polar solvents.

## III Chemical Properties