

# EXAMS ROAD

"Bringing Excellence to Students"



EXAMSROADOFFICIAL



EXAMSROAD



EXAMSROAD



EXAMSROAD

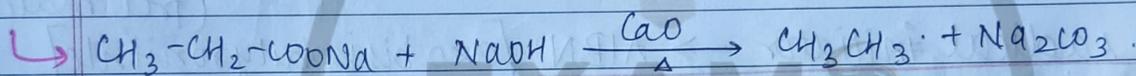
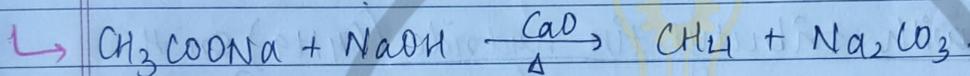
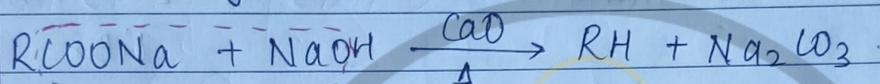
# ALKANES

Date   
Page

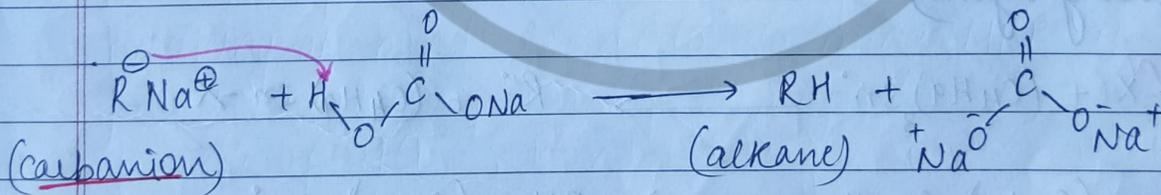
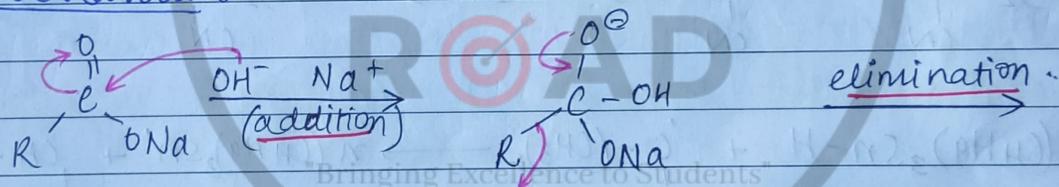
- Paraffins ;  $C_nH_{2n+2}$  ; petroleum & natural gas, marsh gas. (non-reactive)
- Can exhibit chain, optical & conformational isomerism

## → Preparation of Alkanes

### ① Decarboxylation of salt of alkanic acid:



### Mechanism:-

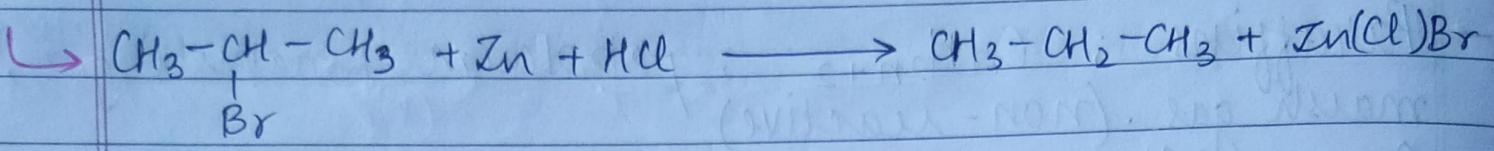


Carbanion is reaction intermediate. Presence of EWG in acid ↑ rate of reaction.

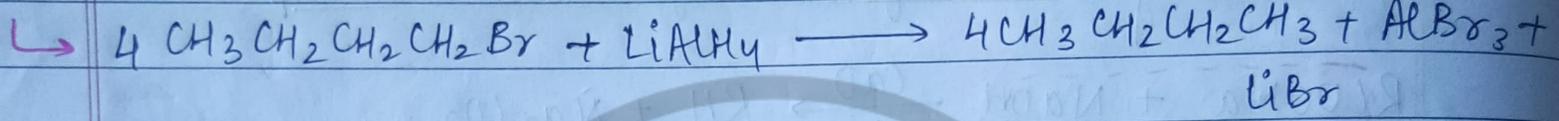
### ② Reduction of alkyl halides

(a) Reduction with metals & acid.

$\text{Zn}$  &  $\text{CH}_3\text{COOH}$ ,  $\text{Zn}$  &  $\text{HCl}$ ,  $\text{Zn}-\text{Cl}$  couple & (alcohol) ethanol  $\Rightarrow$  Good reducing agents

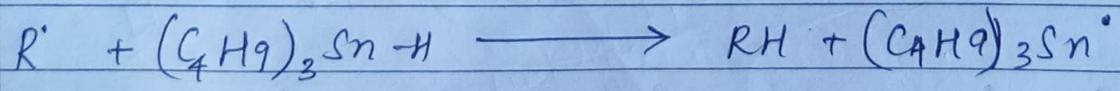
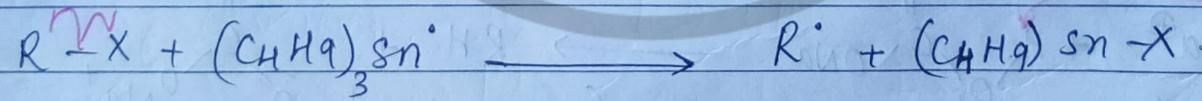
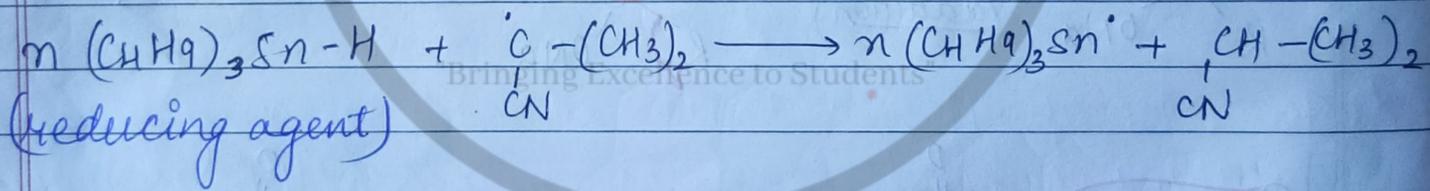
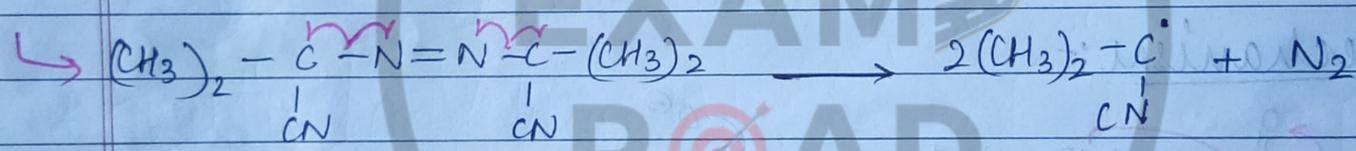


(b) Reduction with LiAlH<sub>4</sub>, NaBH<sub>4</sub> (hydride transfer reagents)  
 (S<sub>N</sub><sup>1</sup>/S<sub>N</sub><sup>2</sup>)



(c) Reduction with tributyl tin hydride (C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>Sn-H  
 (free radical)

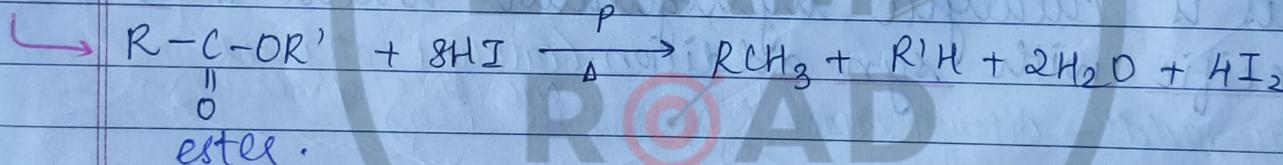
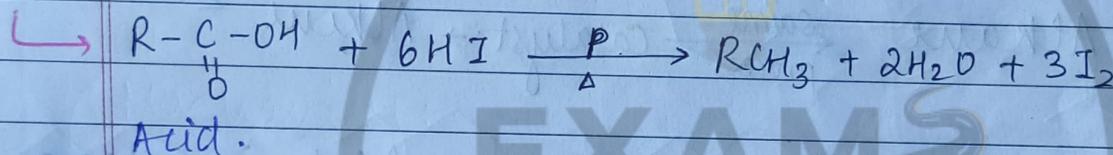
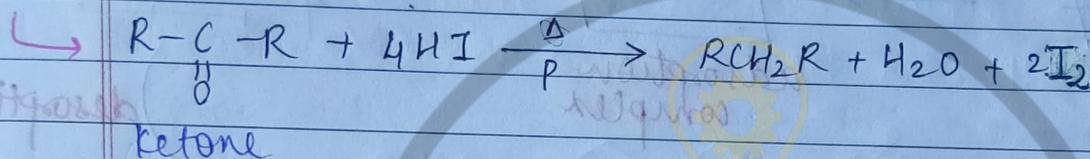
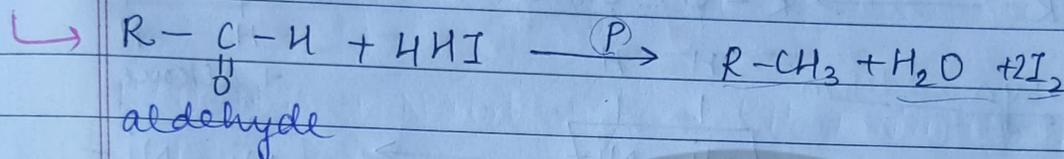
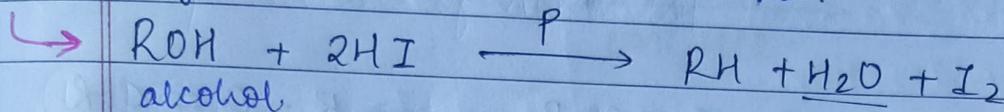
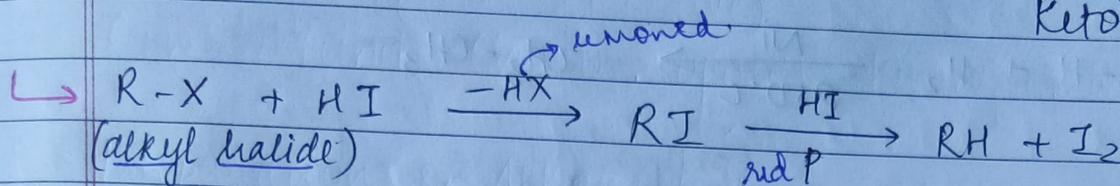
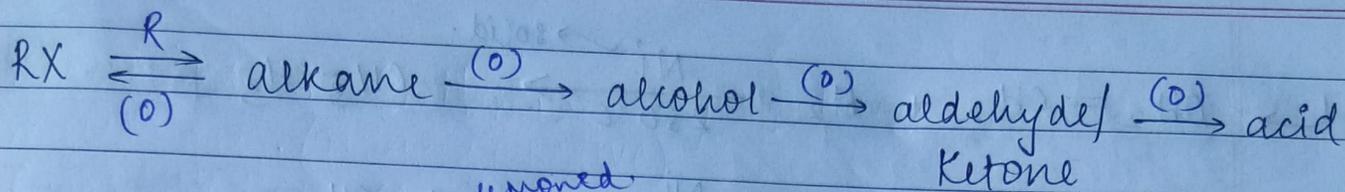
Free radical initiator  $\Rightarrow$  AIBN [azo bis isobutyronitrile]



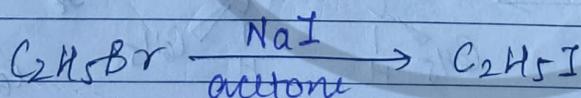
(d) Reduction with red P & HI

RX  $\rightarrow$  alkane  $\hookrightarrow$  strong RA.  
 Alcohol  $\rightarrow$  Alkane

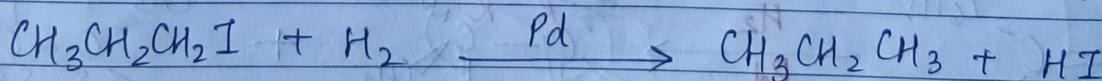
aldehyde, ketones, carboxylic acids  $\rightarrow$  alkane



✓ Halide exchange: [Finkelstein react<sup>n</sup>]

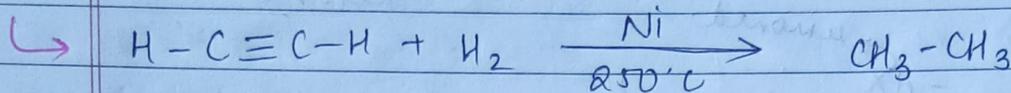
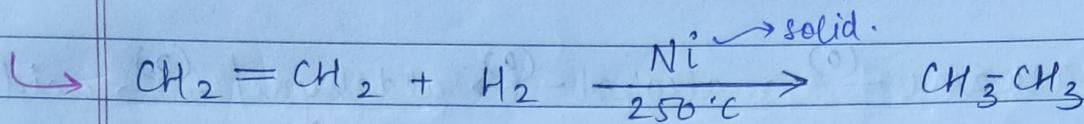


(e) Reduction with hydrogen gas. (catalyst - Palladium)

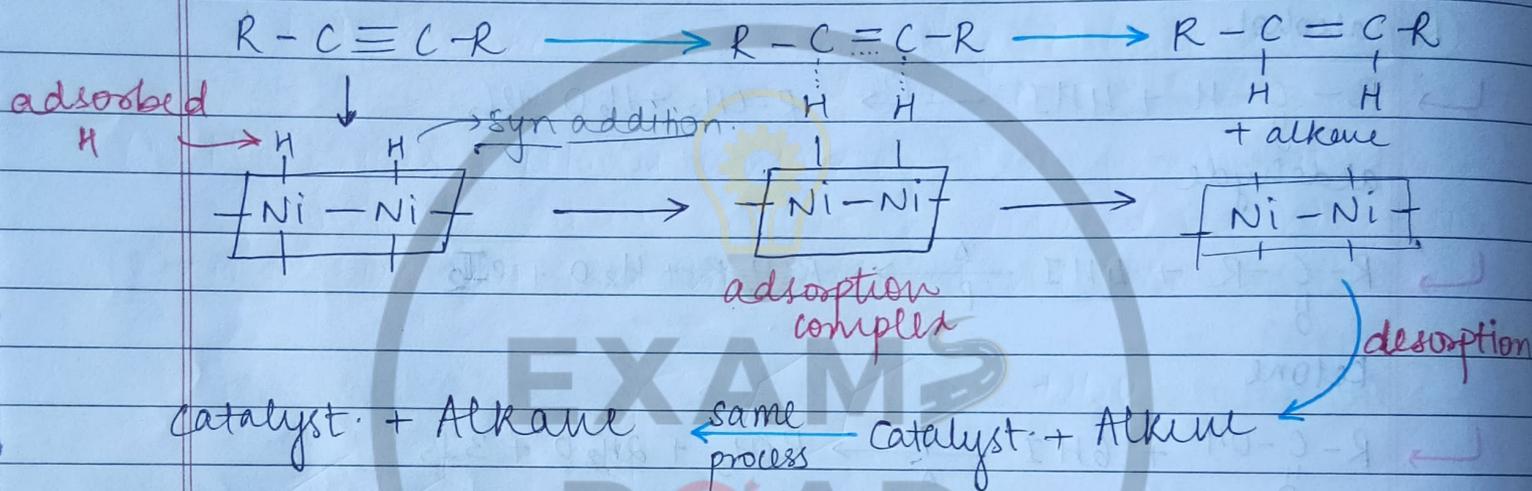


③ Hydrogenation of alkenes & alkynes.

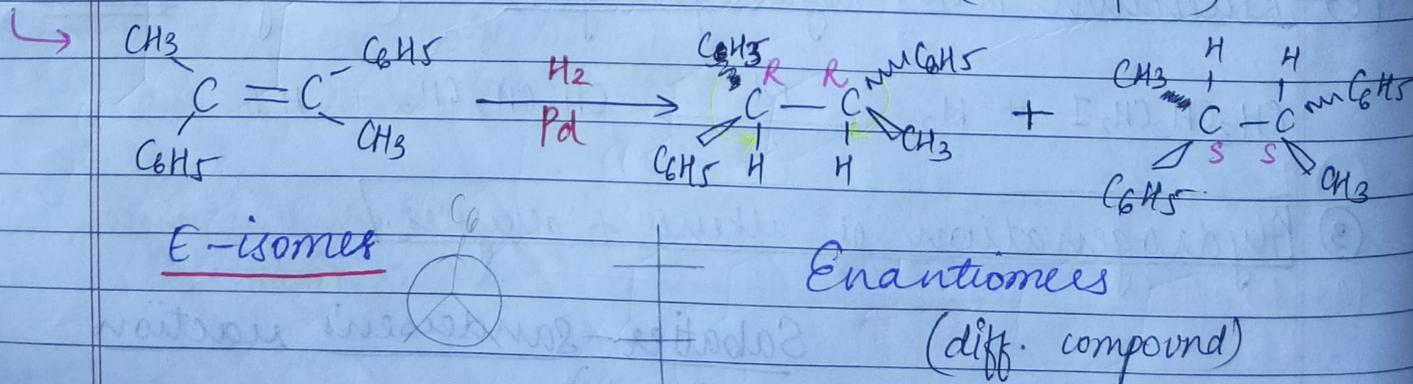
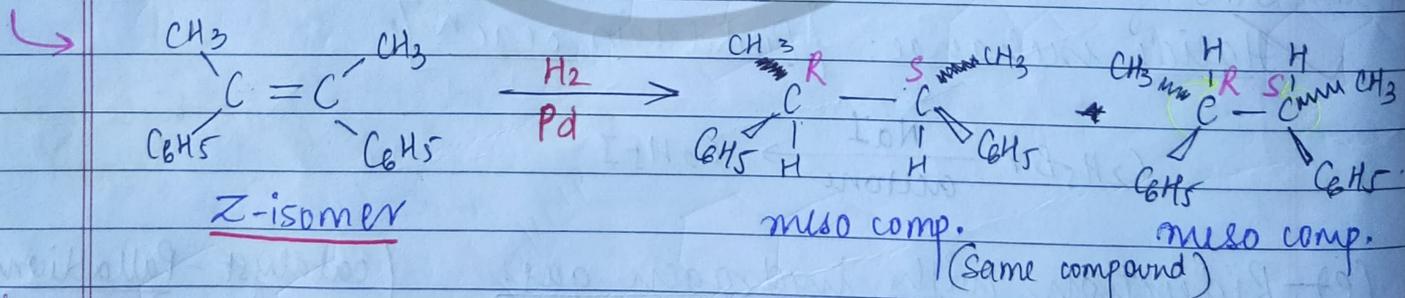
Sabatier-Gandensen's reaction  
(heterogeneous react<sup>n</sup>.)



Mechanism:-

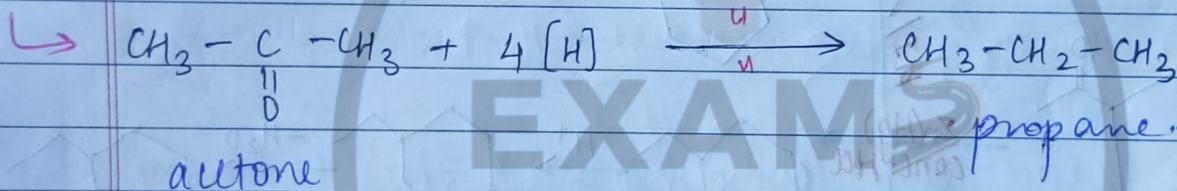
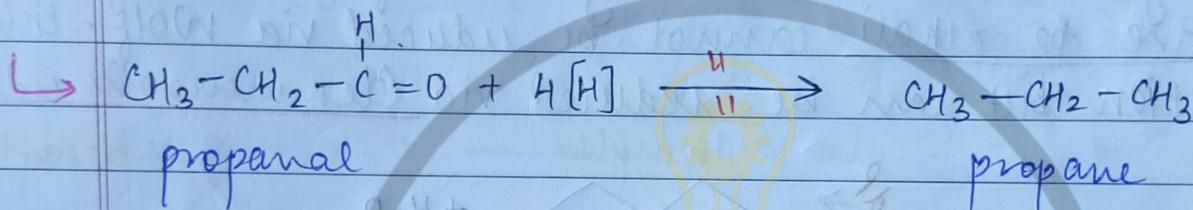
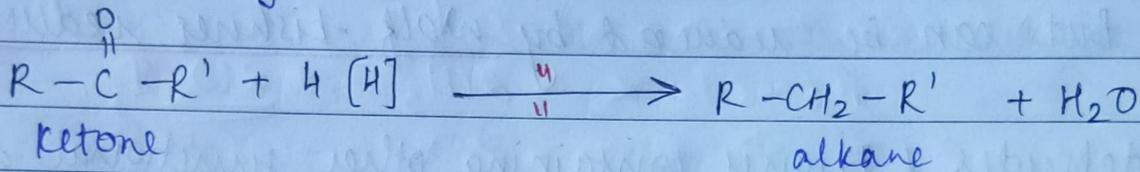
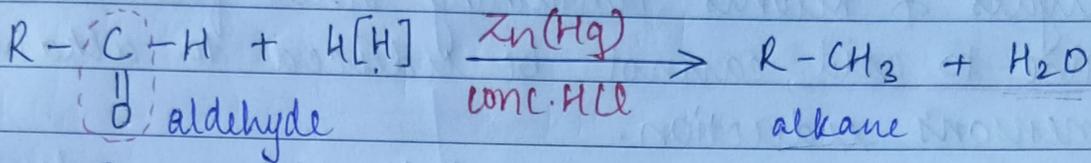


\* This is catalytic hydrogenation which is stereo-specific with syn addition. (catalyst attaches only from one side of alkene) (anti-add<sup>n</sup> - catalyst attaches from both sides.)

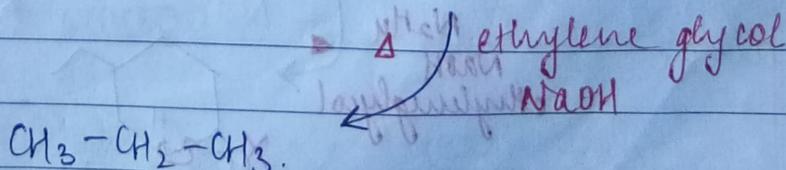
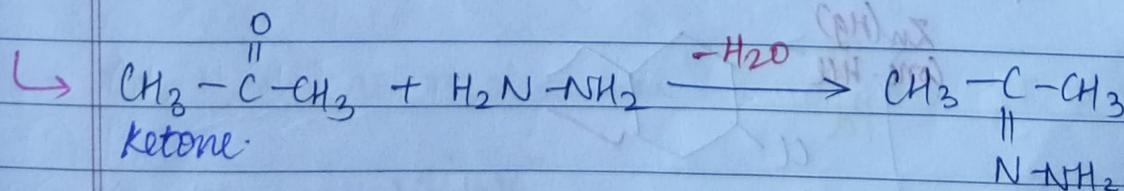
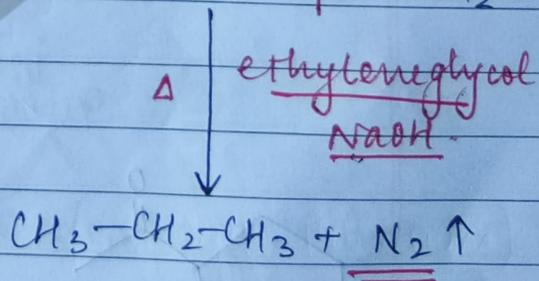
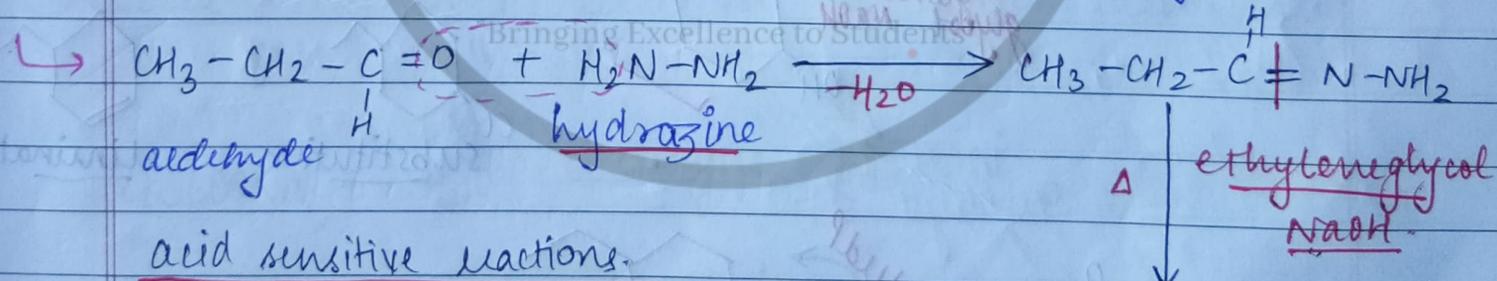


④ Clemmensen's reduction (reduction of aldehydes & ketones)

$Zn(Hg) \Rightarrow Zn$  amalgam & conc. HCl. (metal + acid reducing agent)



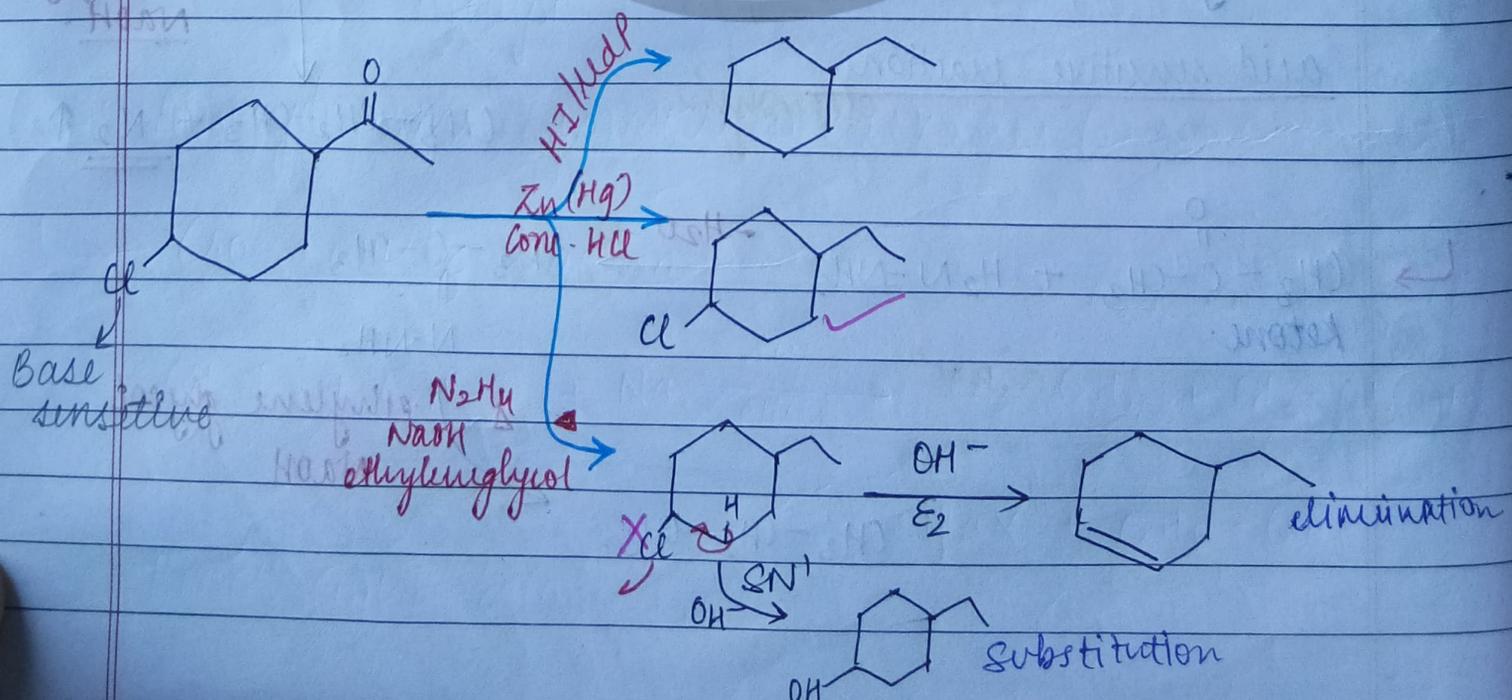
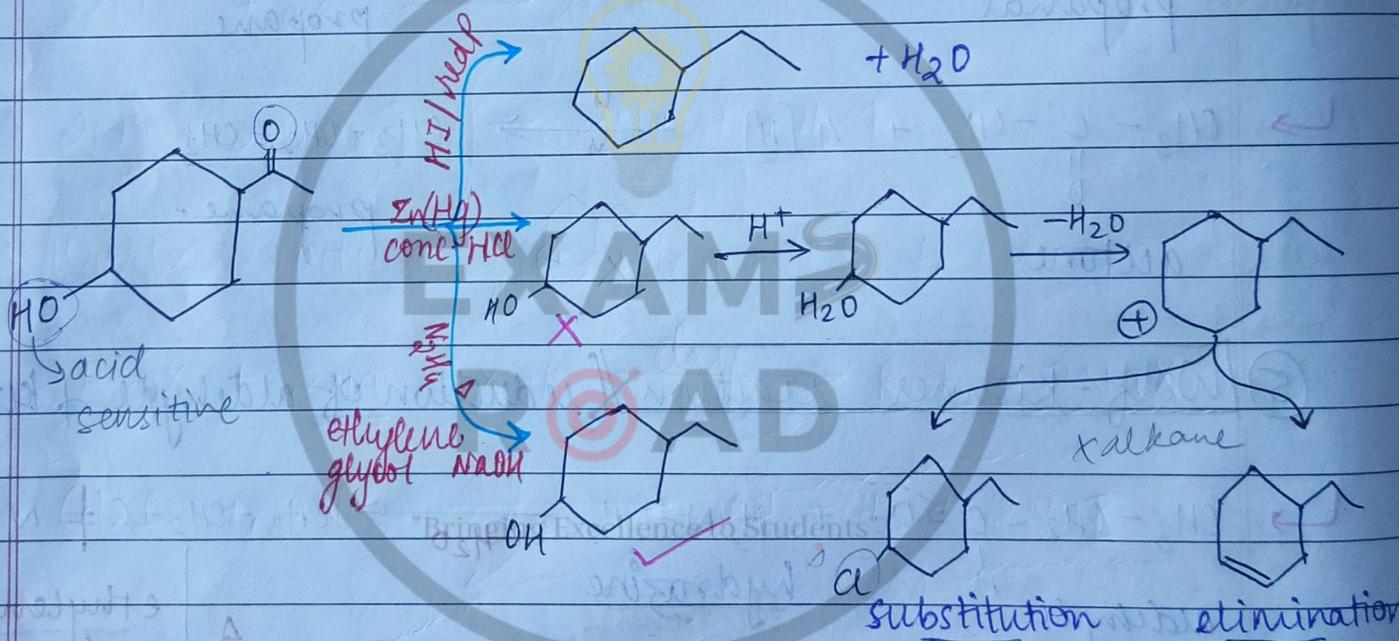
⑤ Wolf-Kishner reaction (reduction of aldehyde & ketones)



Comparison b/w Clemmensen & Wolf Kishner's reduction reactions.

(i) Aldehydes & ketones containing other functional groups sensitive to acid, cannot be reduced to alkane by Clemmensen's reduction. But can be reduced by Wolf Kishner reduction.

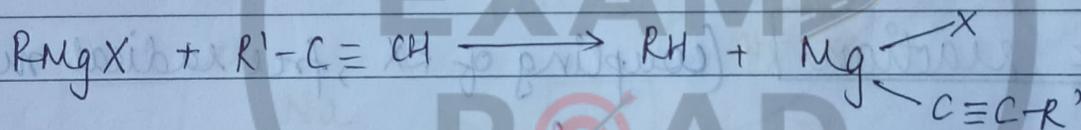
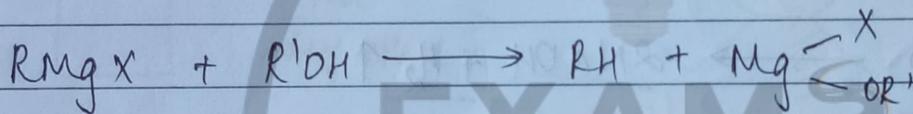
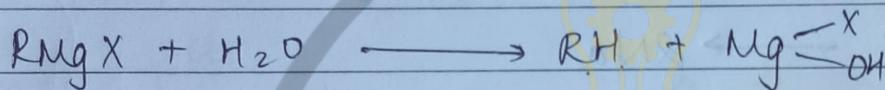
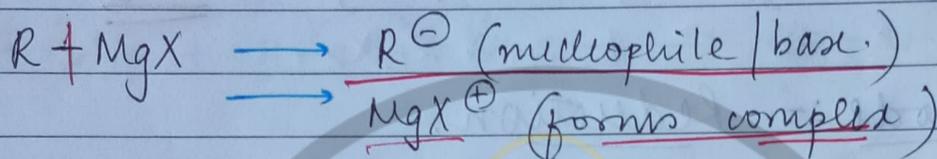
(ii) Aldehydes & ketones containing other functional groups sensitive to alkali cannot be reduced via Wolf-Kishner reduction but can be reduced via Clemmensen's reduction.



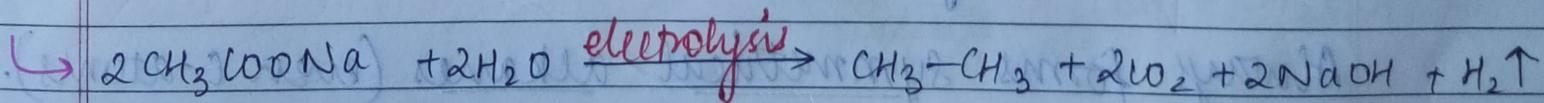
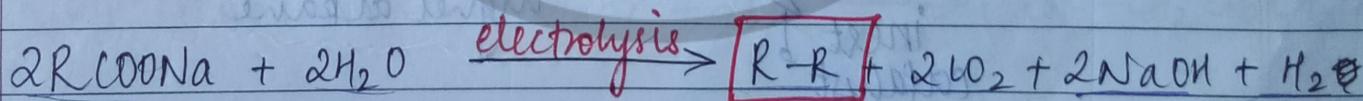
⑥ Grignard's Reagent /  $[R-MgX]$  (alkyl magnesium halide)

It is an organo-metallic reagent, a strong base & strong nucleophile.

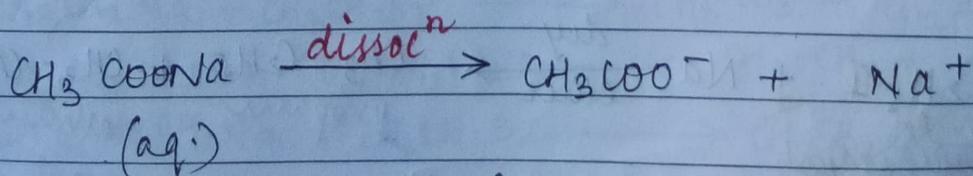
It can easily react with weakly acidic substances such as water, alcohol, ammonia,  $R-NH_2$ ,  $R_2-NH$ ,  $R-C \equiv CH$ , phenols,  $R-COOH$ , etc to give alkane.



⑦ Kolbe's reaction (electrolysis of sodium carboxylate)



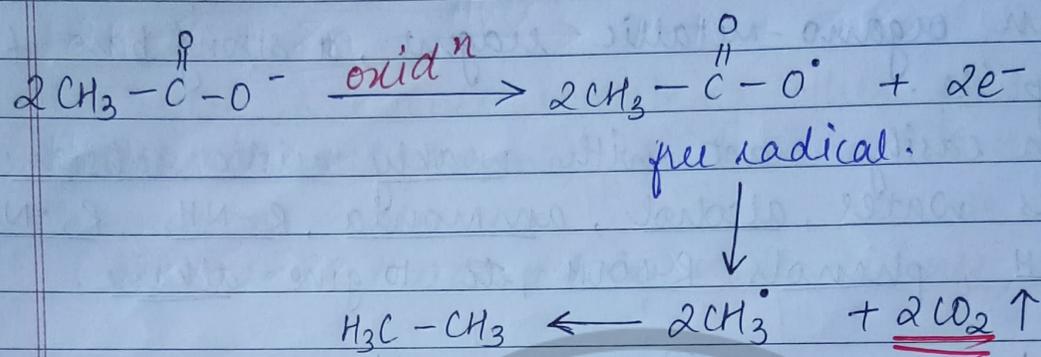
free radical mechanism



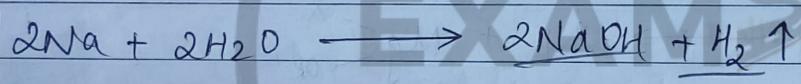
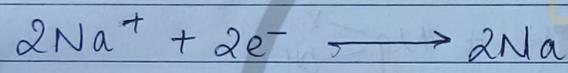
(anode)

(cathode)

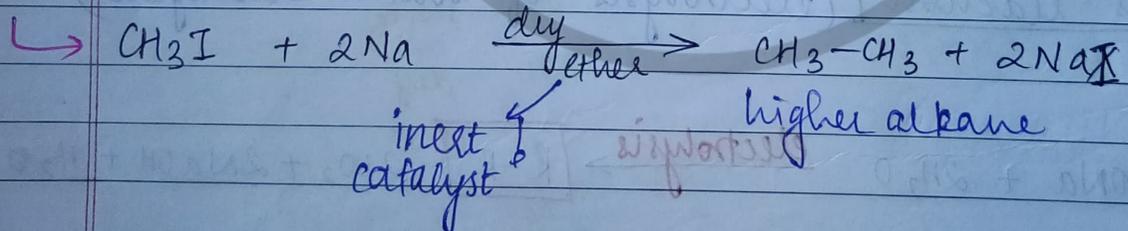
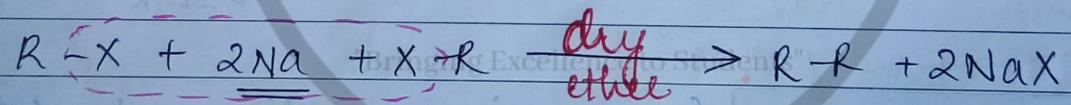
@ Anode :- oxidation.



@ Cathode :- Reduction.

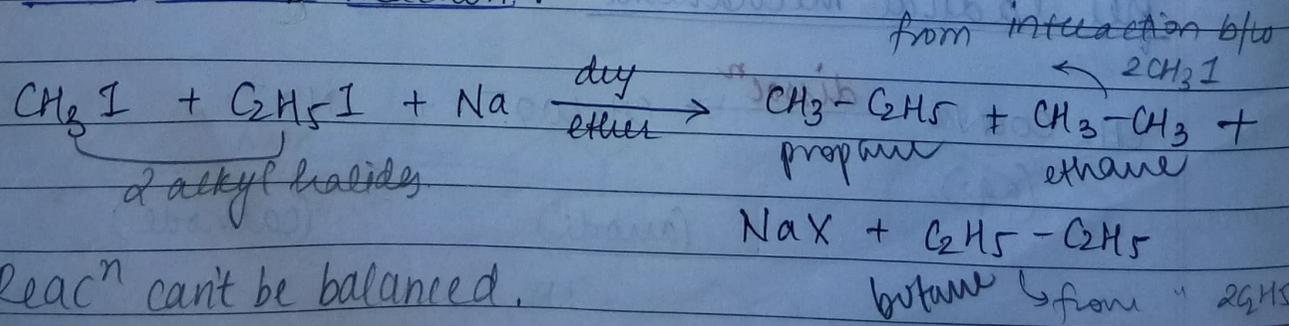


\* ⑧ Wurtz reaction (coupling of RX, free radical mech.)



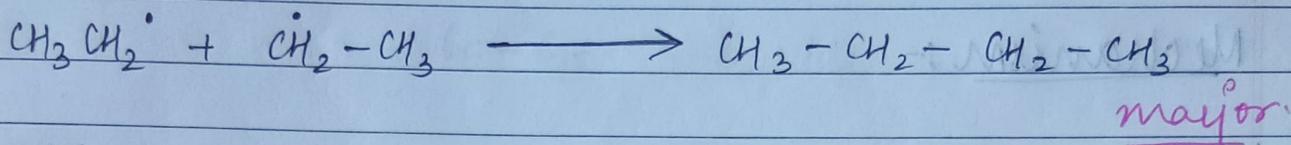
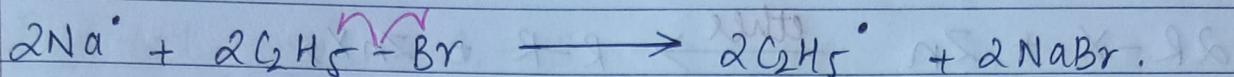
Always forms symmetrical alkanes (even C-atoms).

- Cross-wurtz reaction :-

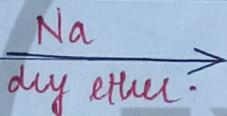
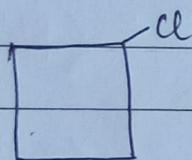
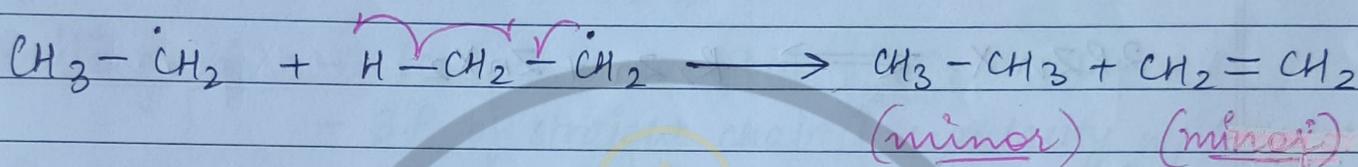


Reac<sup>n</sup> can't be balanced.

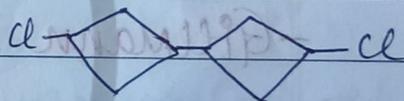
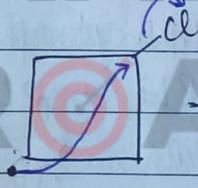
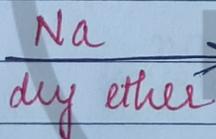
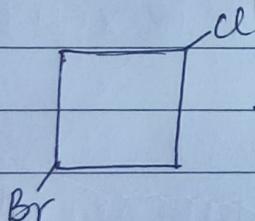
## Free radical mechanism :-



## side reaction :

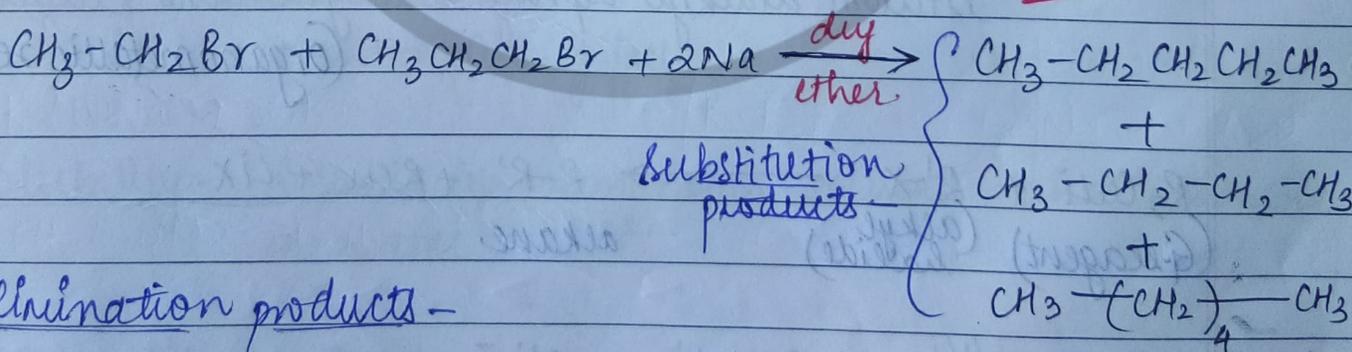


\*

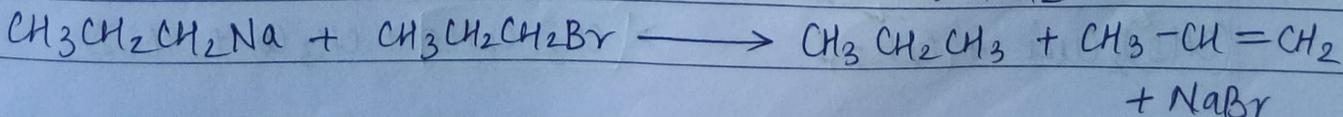
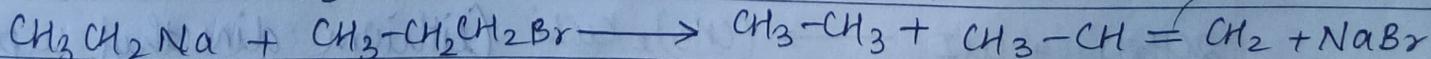
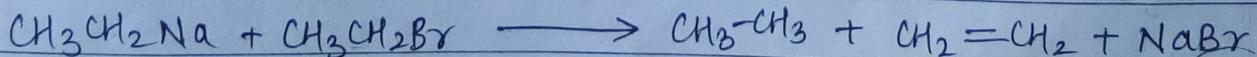


major

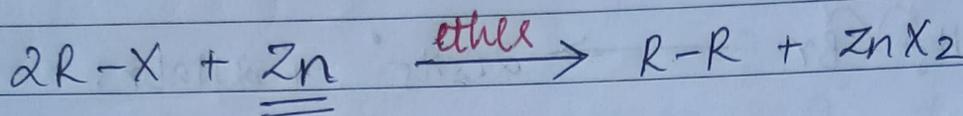
internal nucleophilic attack is faster.



## Elimination products -



## ⑨ Frankland reaction

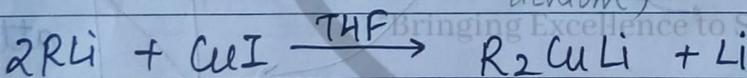
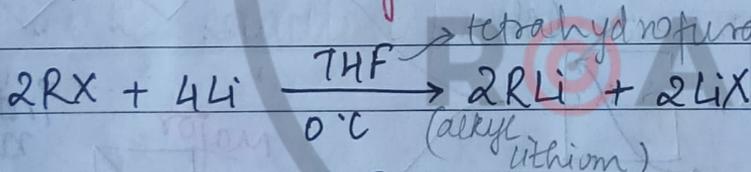


Mechanism:-

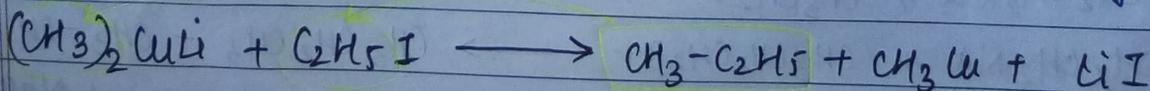
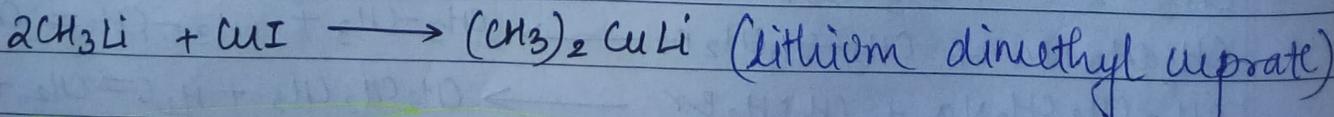
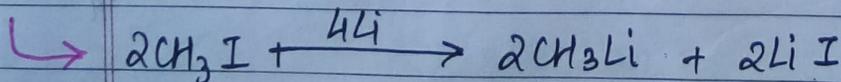
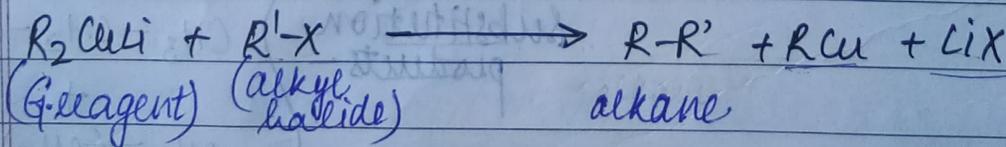


## ⑩ Corey House Synthesis

- Gillmann reagent:  $[R_2CuLi]$



lithium dialkyl cuprate  $\Rightarrow$  gillman's reagent.  
(organometallic reagent)



## → Physical Properties.

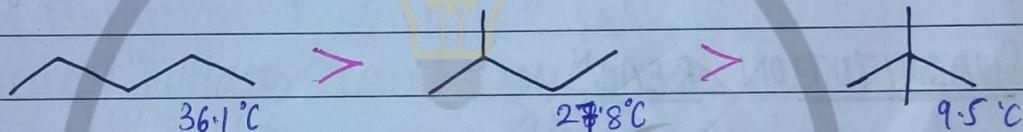
(1) Physical state -  $C_1 - C_4 \Rightarrow$  gases

$C_5 - C_{17} \Rightarrow$  liquids

$C_{18} - \Rightarrow$  solids

(2) Boiling point - Low [B.P.  $\uparrow$  -  $C \uparrow$  - Branching  $\downarrow$ ]

- B.P. of straight chain  $\uparrow$  regularity w/  $\uparrow$  mol. mass.
- Branched alkane has  $\downarrow$  b.p.



(3) Melting point - M.p.  $\uparrow$  w/  $\uparrow$  mol. mass ( $\uparrow C$ )

- n-alkanes w/ even no. of carbons  $>$  n-alkanes w/ odd no. of carbons  
(compact packing in crystal lattice)

(4) Density - low density  
- max  $\Rightarrow$  0.8 g/ml.

(5) Solubility - soluble in non polar solvents and insoluble in water

\* for melting point;  $C_{18} > C_{19}$  (adjacent even)

$C_{18} < C_{20}$  (even +  $\uparrow$  carbon atoms)

$C_{19} < C_{20}$  (even no. of carbons)

## → Chemical Properties

(1) less reactive - no reaction w/ acids, bases, ~~organic acids~~, oxidising & reducing agents, electrophiles & nucleophiles.

(2) C-C + C-H - strong  $\sigma$  bonds.

(3) Non-polar, ~~non~~ functional group or lone pair.

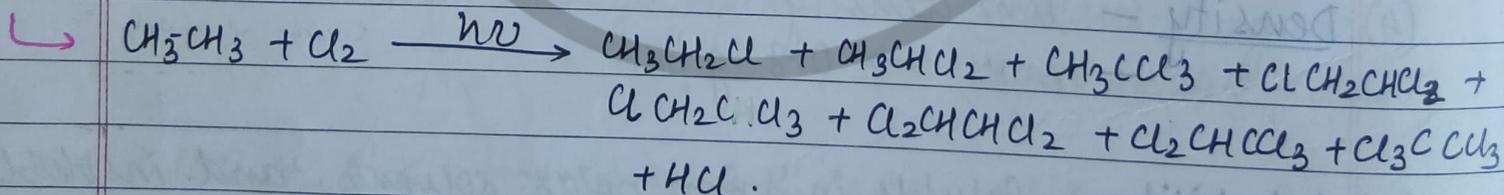
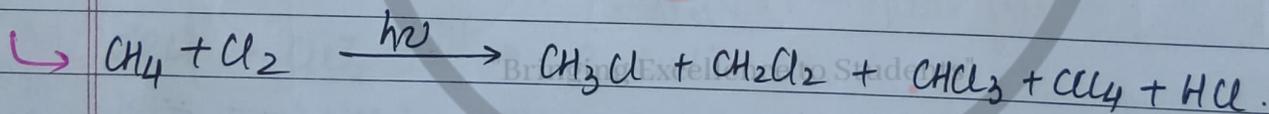
\* Only possible reaction are substitution by <sup>free</sup> radical pathway

• SUBSTITUTION REAC<sup>N</sup>:

(1) Halogenation of alkanes (Chlorination & Bromination)

[sunlight / v.v / heat 250-400°C]

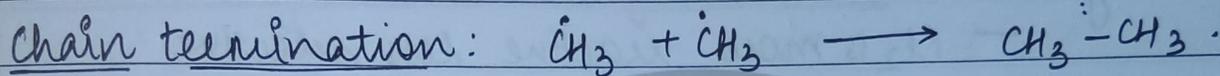
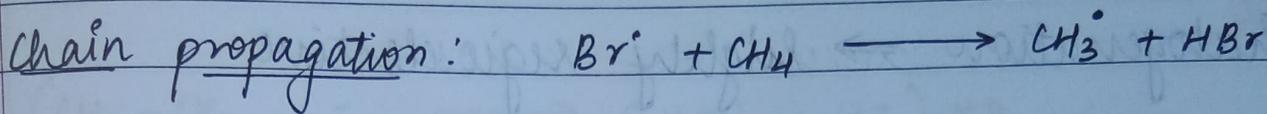
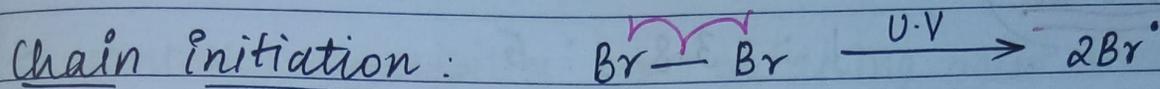
Many products are formed:



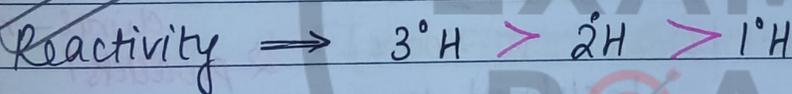
Reactivity of  $\text{X}_2 \Rightarrow \text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

\* Fluorination  $\Rightarrow$  highly exothermic (explosion) [uncontrollable]  
Iodination  $\Rightarrow$  endothermic & reversible  $\rightarrow$  ( $\downarrow$  products due to backward reaction)

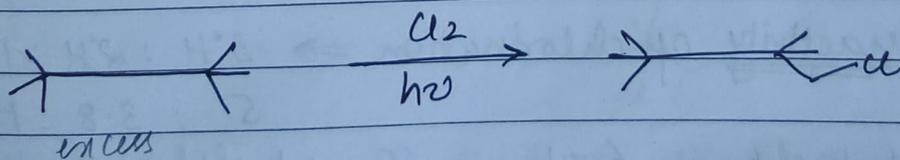
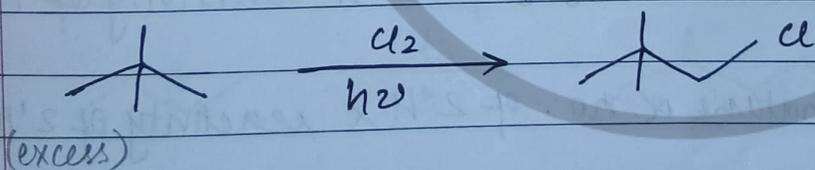
# - Free radical mechanism for halogenation:



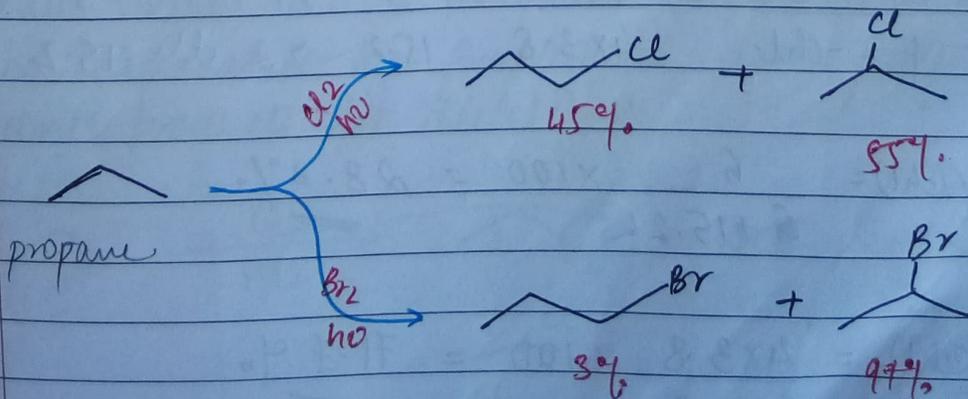
\* Free radical initiator can be used  $\Rightarrow$  AIBN, dibenzyl peroxide, dialcyl butyl peroxide.

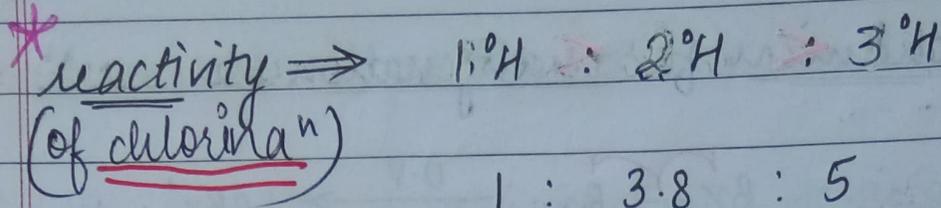


## - Monochlorination



(taking substrate in excess ensures only mono-chloromolecules & inhibits formation of di, tri & tetra-chloro products)

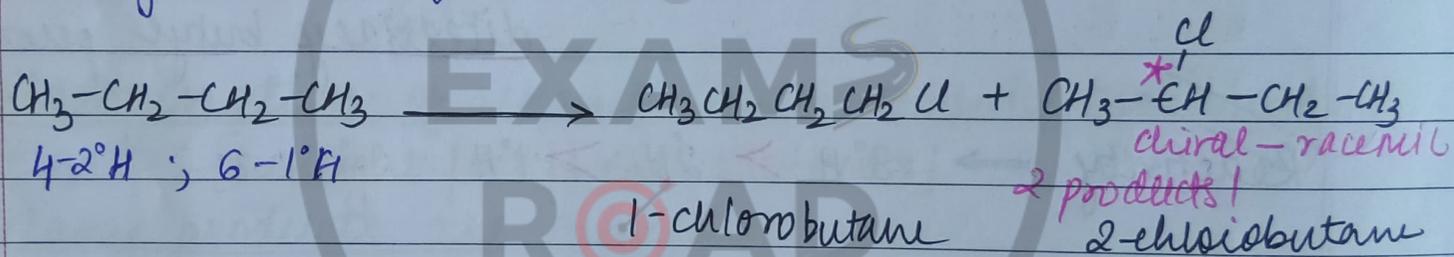




\* halogenation  $\Rightarrow$  highly regioselective

Bromination is more regioselective than chlorination although —  $\text{Br}_2$  less reactive  $\text{Cl}_2$   
 —  $\text{Cl}_2$  is more reactive less selective  
 —  $\text{Br}_2$  is less reactive more selective

\* Calculation of expected product distribution of mono-halogenation of alkane:



Amount of 1-chlorobutane  $\propto$  no. of  $1^\circ\text{H} \times$  reactivity of  $1^\circ\text{H}$

Amount of 2-chlorobutane  $\propto$  no. of  $2^\circ\text{H} \times$  reactivity of  $2^\circ\text{H}$

\* The relative reactivity of chlorination  $\Rightarrow 3^\circ\text{H} : 2^\circ\text{H} : 1^\circ\text{H}$   
 $5 : 3.8 : 1$

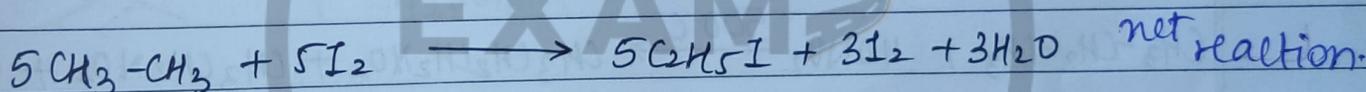
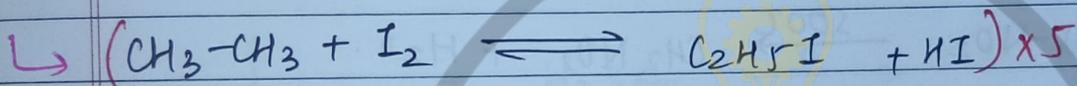
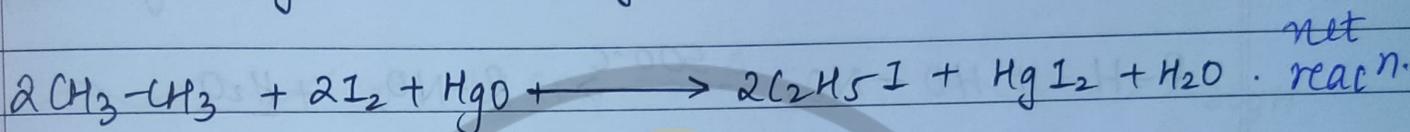
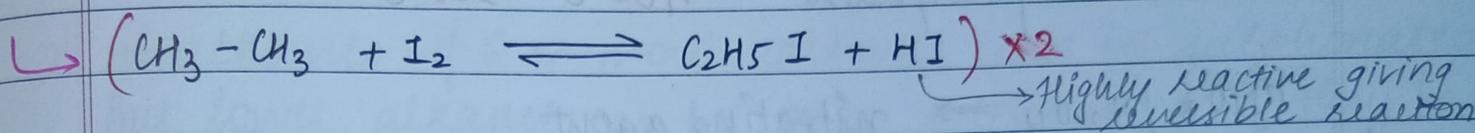
$\therefore$  Amount of 1-chl. =  $\frac{6 \times 1}{4 \times 3.8} = \frac{6}{15.2} \rightarrow 1\text{-chl.} = 6$   
 Amt of 2-chl.       $4 \times 3.8$        $15.2 \rightarrow 2\text{-chl.} = 15.2$  } + total

% yield (1chl) =  $\frac{6}{6 + 15.2} \times 100 = 28.3\%$

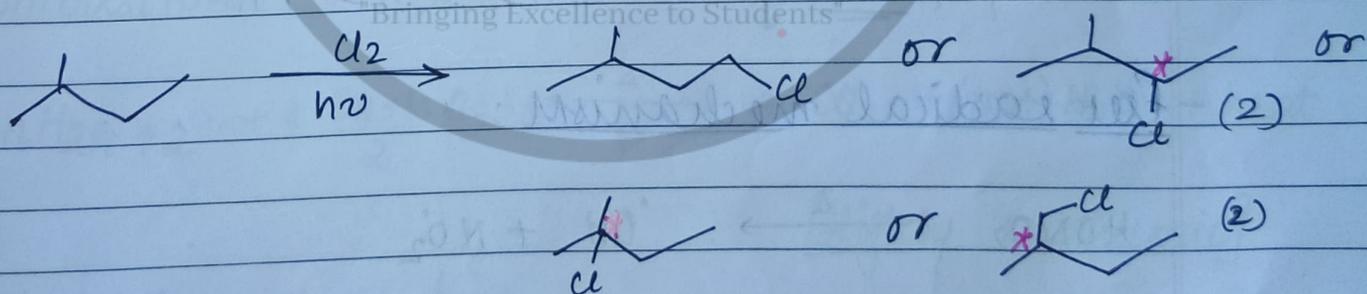
% yield (2chl) =  $\frac{4 \times 3.8}{6 + 15.2} \times 100 = 71.7\%$

- Iodination (highly endothermic reversible reaction)

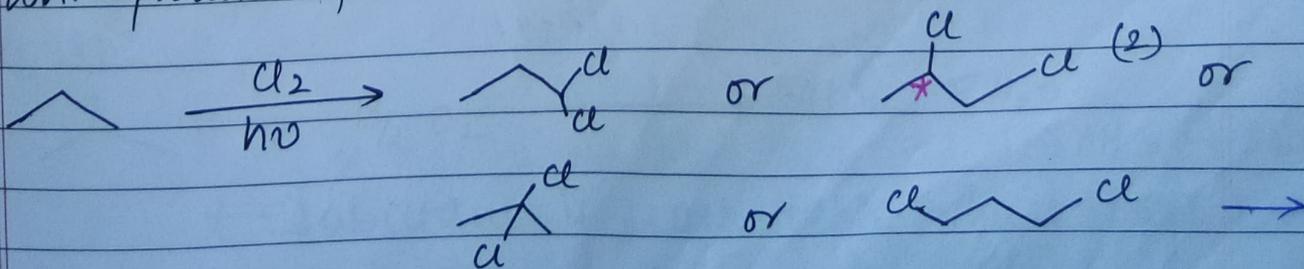
to control reversibility  $\Rightarrow$  oxidising agent is added like  $\text{HIO}_3, \text{HgO}, \text{HNO}_3$



Q Write products for monochl<sup>n</sup>:



thus these are 6 products formed out of which 4 can be separated by fractional distillation.  
 Write products for dichl<sup>n</sup>:



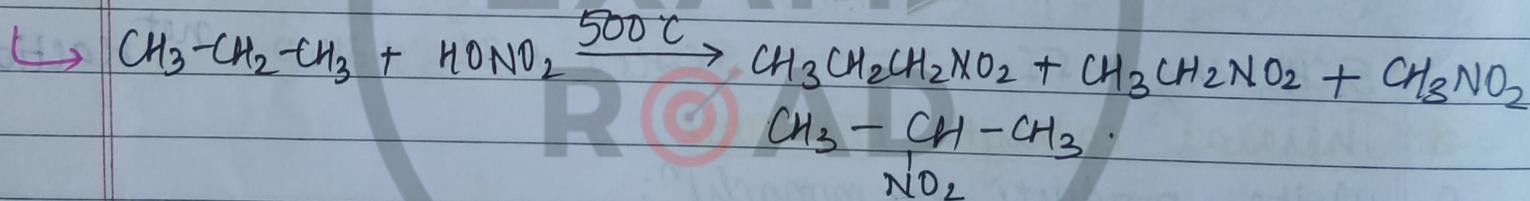
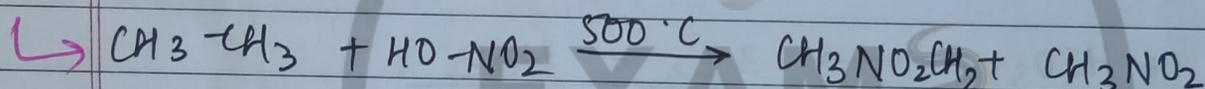
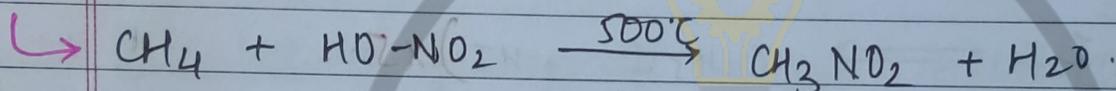
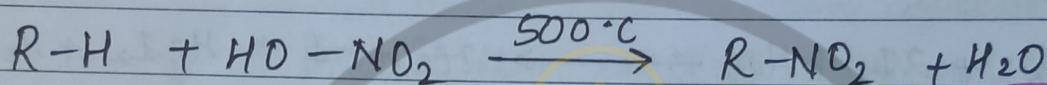
← Here, there are 5 products out of which 4 can be separated via fractional distillation

## (2) Nitration

Vapour phase  $\Rightarrow 400^\circ\text{C} - 500^\circ\text{C}$

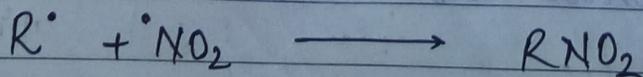
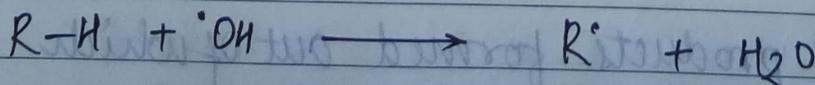
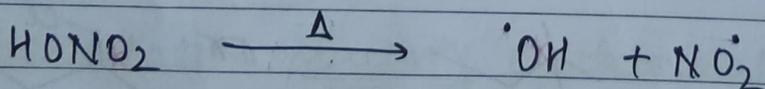
$\text{HNO}_3 / \text{N}_2\text{O}_4 \Rightarrow$  nitrating agent.

\* C-H & C-C bonds can be broken due to high temp.



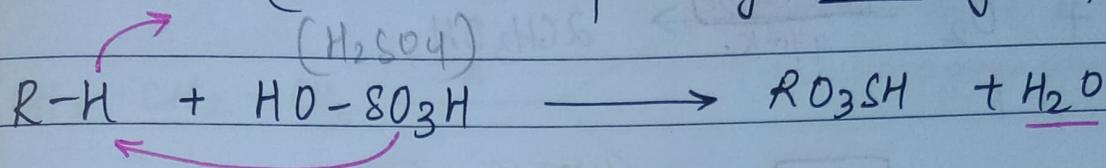
order of reactivity  $\Rightarrow 3^\circ\text{H} > 2^\circ\text{H} > 1^\circ\text{H}$

- free radical mechanism:

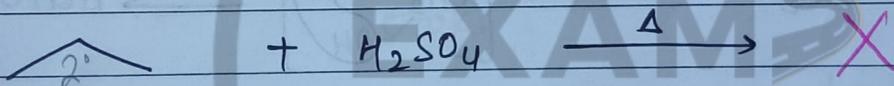
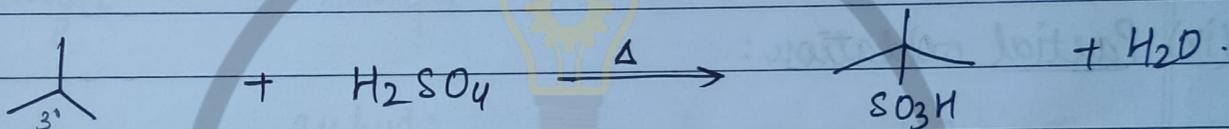


### (3) Sulphonation

(Substitution of  $-H$  by  $-SO_3H$  group)

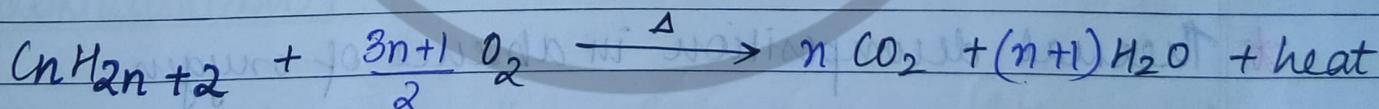


\* n-alkanes w/ 6 or more carbons can be sulphonated. But lower alkanes can be only sulphonated if they have  $3^\circ H$ .



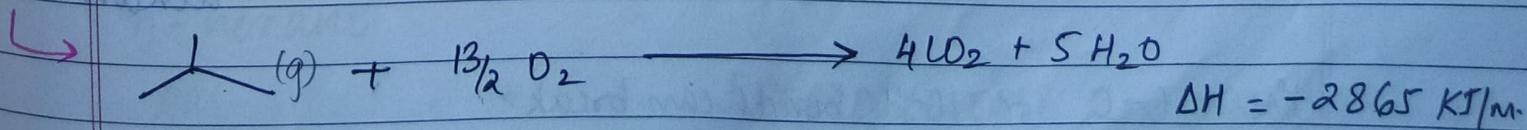
\* Thermal catalytic Reactions :-

### (4) Combustion



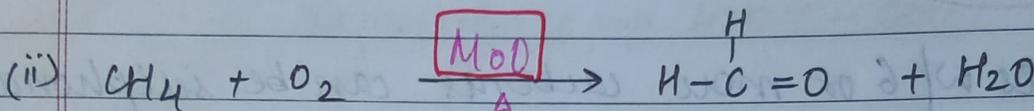
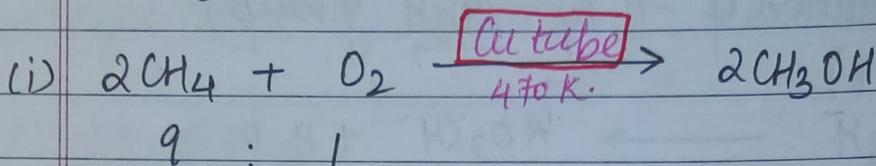
[Highly exothermic]

$$\Delta H_c \propto \frac{1}{\text{stability of alkane}}$$

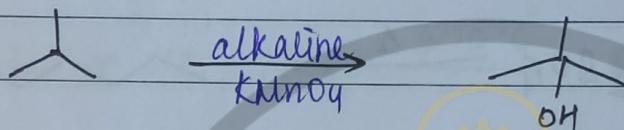


\* Isobutane is more stable than n-butane

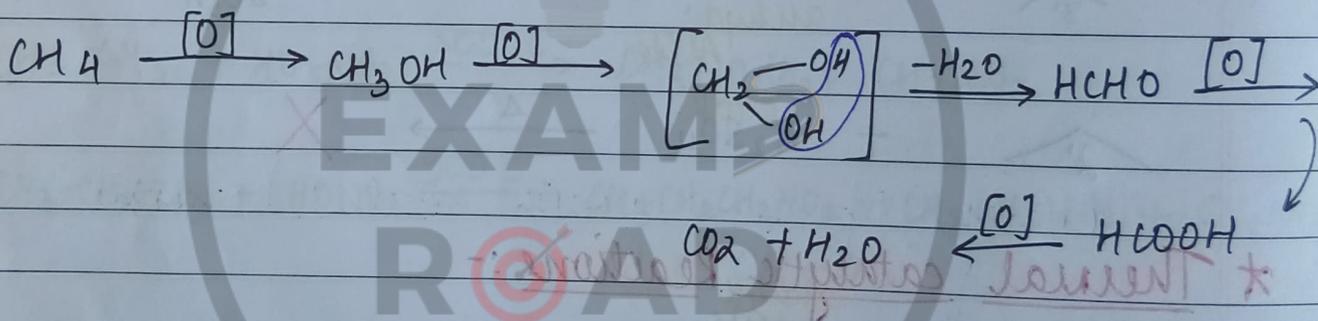
## (5) Catalytic oxidation



(iii) alkaline KMnO<sub>4</sub> : 3°H atom is oxidised to -OH group.



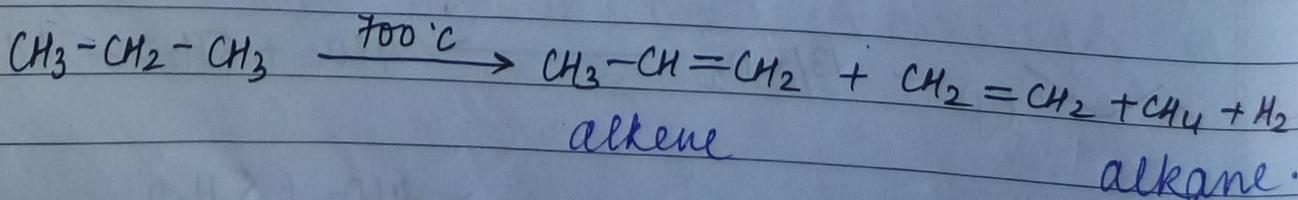
(iv) Partial oxidation :



## (6) Cracking of alkane (for fuels)

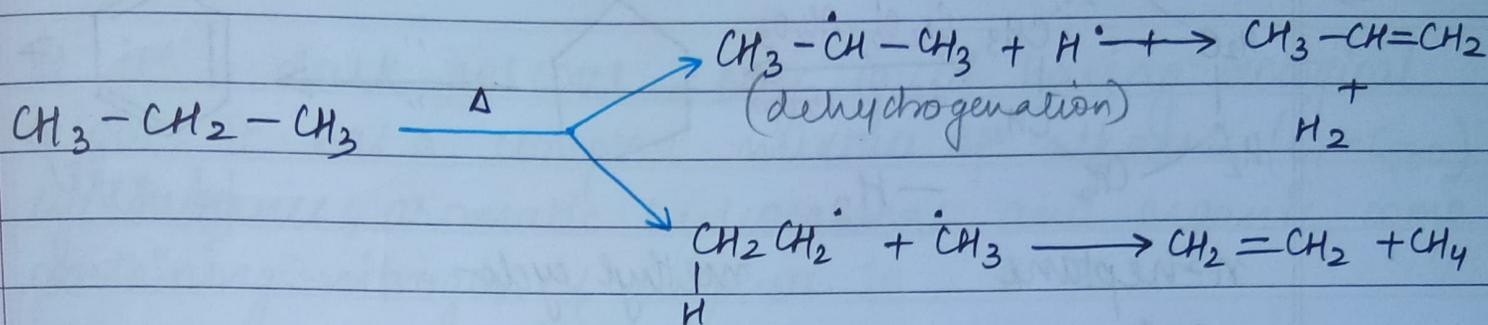
\* Thermal decomposition in absence of oxygen.

cracking  $\left\{ \begin{array}{l} \text{Thermal (only heat)} \\ \text{Catalytic (SiO}_2, \text{Al}_2\text{O}_3, \text{zeolite)} \end{array} \right.$



thus C-C or C-H bonds can break.

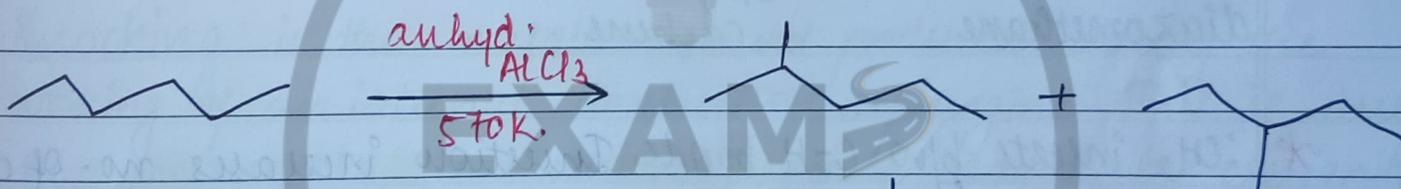
## Free radical mechanism:



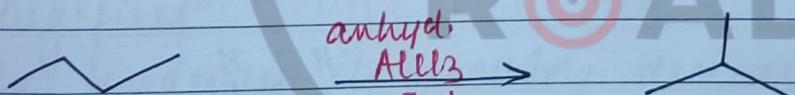
## (7) Isomerisation of alkane

n-alkanes to branched alkanes.

\* catalyst  $\rightarrow$  Anhyd.  $\text{AlCl}_3$  @ 570K.

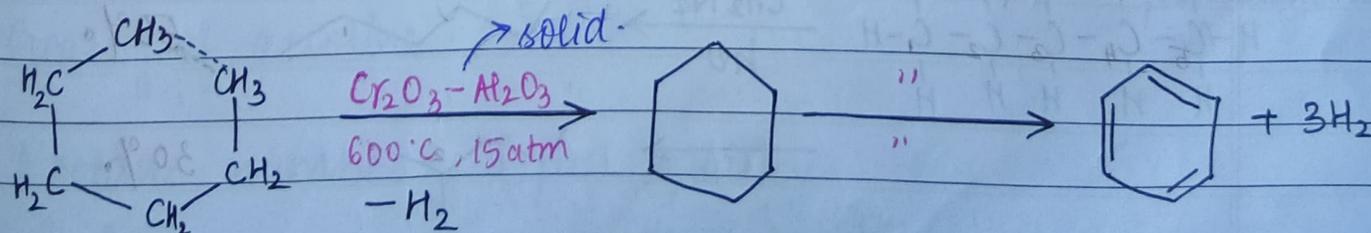


mechanism via 1,2-hydride shift / 1,2-methyl shift



## (8) Aromatisation

\* Alkanes w/ 6 or more than 6 carbons.  $[\uparrow \text{temp.}; \uparrow \text{pressure}]$

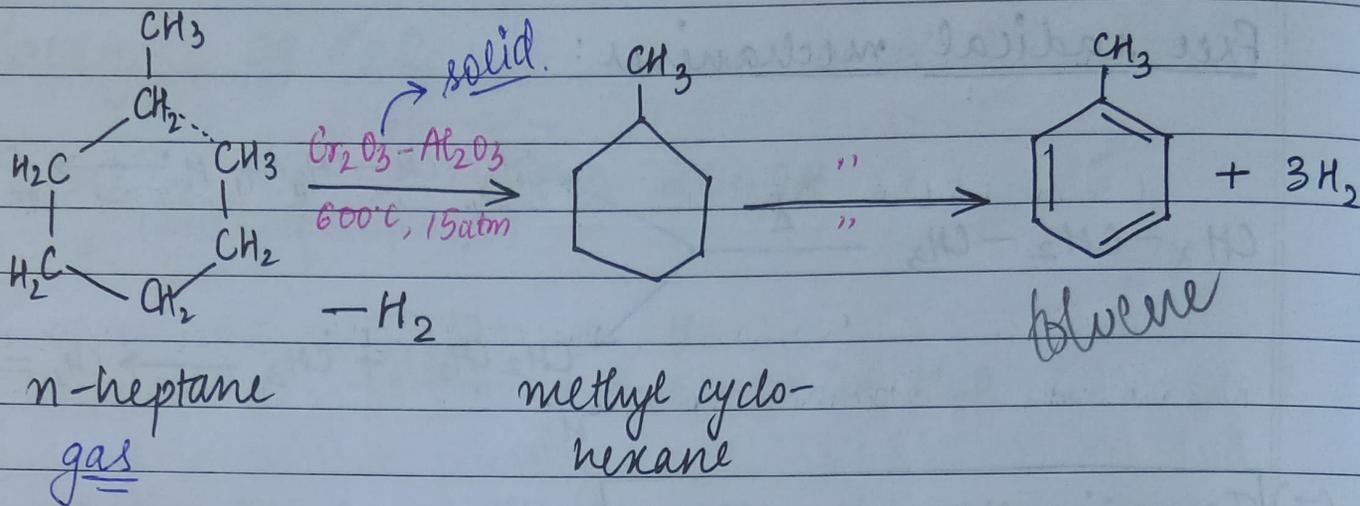


n-hexane

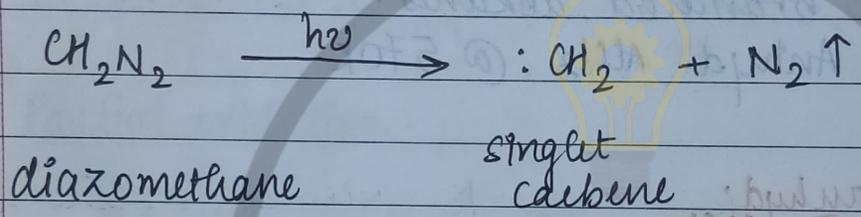
cyclohexane

gas

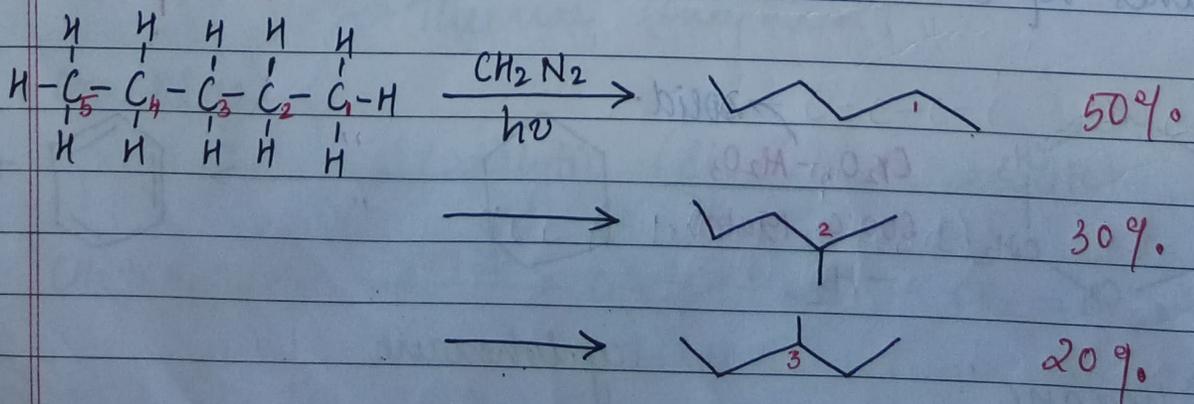
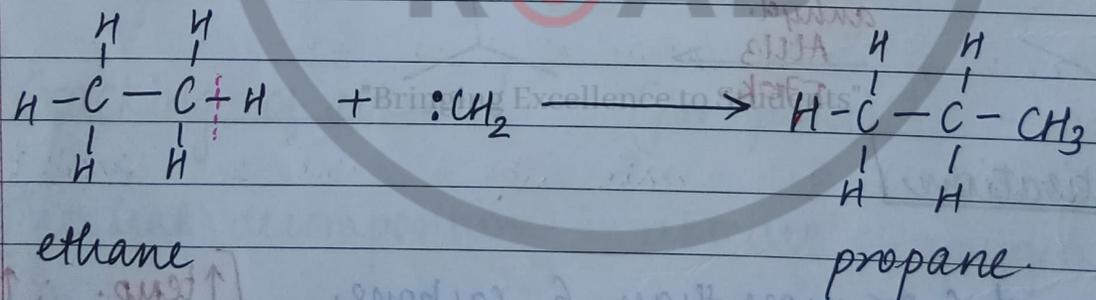
Heterogeneous Reaction  
(many phases)



(9) Singlet methylene insertion b/w C-H bonds



\*  $\text{:CH}_2$  inserts b/w C-H bonds. Insertion increases no. of carbons of alkane. (Terminal insertion is easy /  $1^\circ$  insertion)



insertion at  $\text{C}_1$  is more possible as primary carbon is less crowded and easy to attach to.

## → Petroleum / Crude oil

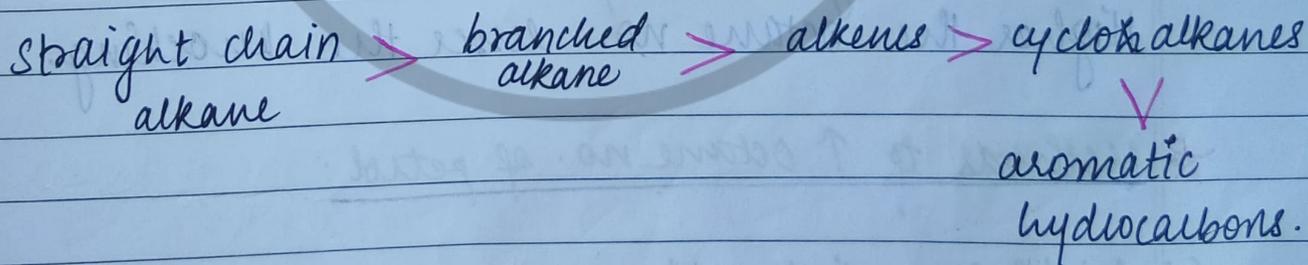
It is a dark, viscous & oily liquid having biological origin. It has a complex mixture of alkanes ( $C_1 - C_{30}$ ), cycloalkanes, aromatic hydrocarbons and organic comp. containing nitrogen & sulphur.

### • Refining of Crude oil:

Crude oil is subjected to fractional distillation to separate different fractions.

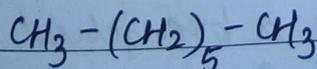
\* Knocking is the metallic sound produced during the working of an internal combustion of engine. This is due to uncontrolled combustion of fuel caused by pre-ignition initiated by hot surface of the cylinder before the spark plug fires.

The tendency of knocking decreases as:



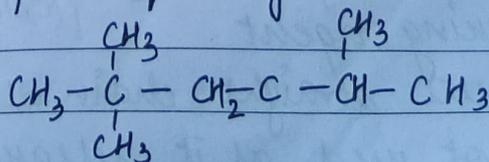
### \* Quality of gasoline

↑ octane number, ↑ fuel quality



n-heptane

Octane no. - 0



2,2,4-trimethyl pentane (iso-octane)

Octane no. - 100

\* A fuel of good quality produces minimum knocking. The anti-knock property of a fuel or its quality is expressed in terms of octane no. of a fuel.

A scale has been set up to express octane no. of a fuel for which n-heptane & 2,2,4-trimethyl pentane (iso-octane) are selected as standards.

N-heptane (high knocking fuel) is arbitrarily assigned an octane no. 0 while iso-octane is given an octane no. 100. (low knocking fuel)

The octane no. given to a fuel is simply the % of iso-octane in a mixture of n-heptane & iso-octane that has same knocking performance as that of the fuel.

Ex → A fuel performance is as good as a mixture containing 45% iso-octane and remaining n-heptane, then, octane no. 45 is given to fuel.

Higher the octane no. lesser the knocking.

\* Methods to ↑ octane no. of petrol:

(i) Add<sup>n</sup> of anti-knocking compound:

A small amt. of TEL (tetra-ethyl lead) is added as an anti-knocking agent.  $[(C_2H_5)_4Pb.]$

This converts straight chain alkane to a branched one.

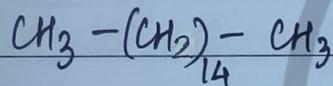
This is not used as it releases lead & ↑ pollution. Thus its use has been discontinued.

(2) Reforming:

A straight chain gasoline is first subjected to isomerisation & then aromatisation which results in ↑ branched chain & aromatic hydrocarbons.

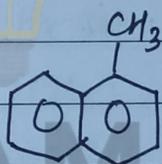
• Diesel oil

Determined by Cetane number.



n-Hexadecane

Cetane no. - 100



α-methyl naphthalene

Cetane no. - 0