

MOP :-

Alkanes

(I) from alkynes, alkenes :

i) Catalytic hydrogenation> 5

→ wilkinson> 9

(II) from alkyl halides :

i) Wurtz rxn> 11

ii) Franckland rxn> 17

iii) Corey-house synthesis> 17

iv) Reduction> 19

v) Grignard's reagent> 20

(III) from Carboxylic acids

i) Sodalime decarboxylation> 22

ii) Kolbe's Electrolysis> 25

(IV) from Carbonyl Compounds

i) Clemmensen's reduction> 27

ii) Wolf-Kishner's reduc.> 28

iii) Mozingo's reduction> 29

iv) By using HI & red phosphorous> 29

(V) from Carbides> 30

(I) from alkynes, alkenes :

i) Catalytic hydrogenation

$H_2 + Pt/Pd/Ni$, Raney Ni> 5

* Wilkinson's cat

$Rh(PPh_3)Cl$ > 9

(II) from alkyl halides :

i) Wurtz rxn

$Na + Dry\ ether$ > 11

ii) Frankland rxn

$Zn + Dry\ ether$ > 17

iii) Corey-house synthesis

1) Li 2) $CuCl$ 3) $R'-X$ > 17

iv) Reduction

$LiAlH_4$, $NaBH_4$, TBH> 19

v) Grignard's reagent

$RMgX + H\ source$ > 20

(III) from Carboxylic acids

i) sodalime decarboxylation

$NaOH + CaO$ > 22

ii) Kolbe's Electrolysis

Electrolysis> 25

④ from Carbonyl Compounds

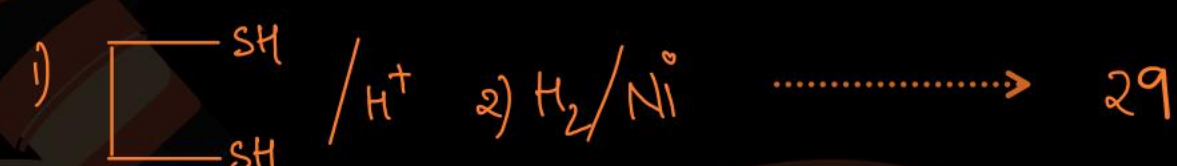
i) Clemmensen's reduction



ii) Wolf-Kishner's reduction



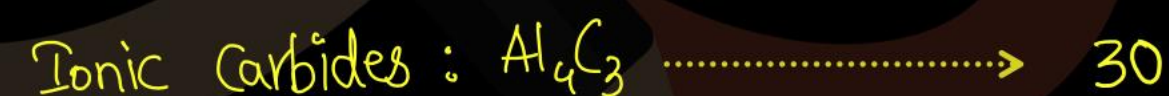
iii) Mozingo's reduction



iv) By using HI
& red phosphorous



⑤ from Carbides



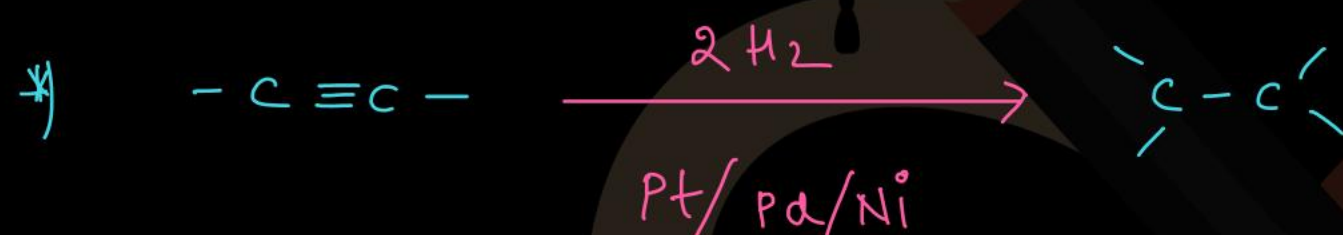
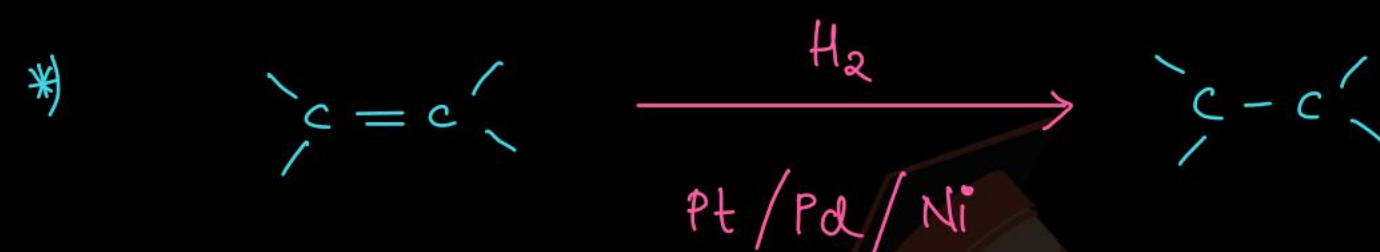
Properties :-

- ① Halogenation> 30
 - chlorination> 37
 - Bromination> 38
 - Iodination> 41
- ② Nitration> 42
- ③ Sulphonation> 43
- ④ Isomerisation> 44
- ⑤ Aromatisation> 44
- ⑥ Pyrolysis> 45
- ⑦ Combustion> 45
- ⑧ Controlled oxidation> 46
- ⑨ Rxn with steam> 47
- ⑩ Physical properties> 47

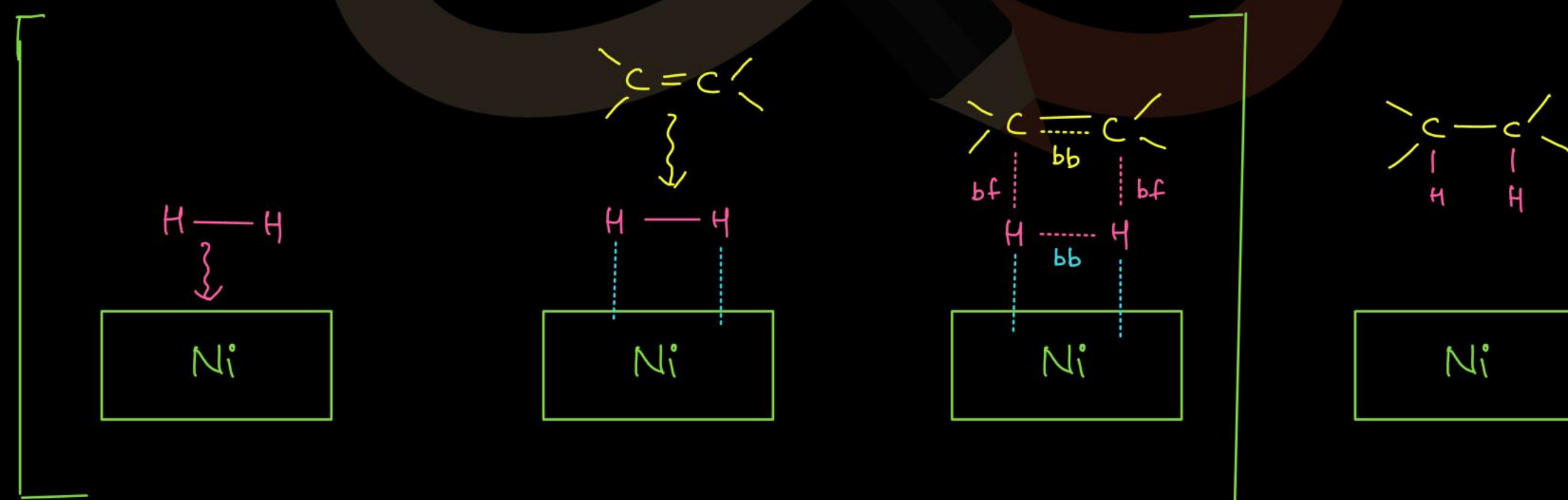
(I) from alkynes, alkenes

i) Hydrogenation of alkenes & alkynes :-

↓ Addition of H



Mechanism :-



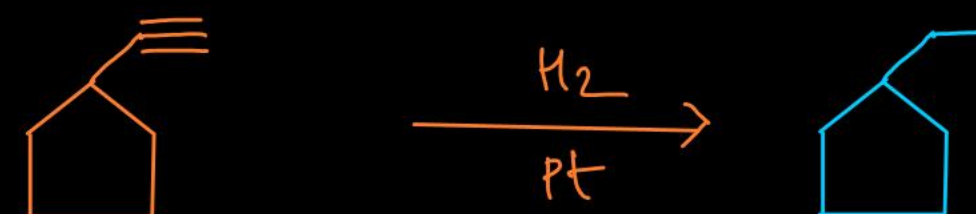
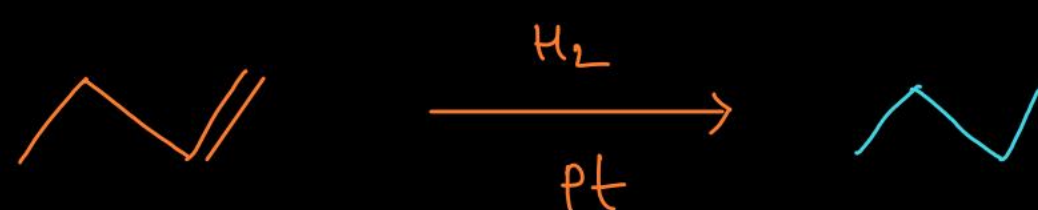
Transition state

Imp points:-

- 1) There is no formation of Intermediate
- 2) 4 membered cyclic transition state is formed
- 3) Adsorption process (Surface phenomenon)
- 4) Exothermic process ($\Delta H < 0$)
- 5) rate $\propto \frac{1}{\text{steric hindrance}}$
- 6) rate (Alkynes > Alkenes)
linear > trigonal planar
- 7) Syn addition

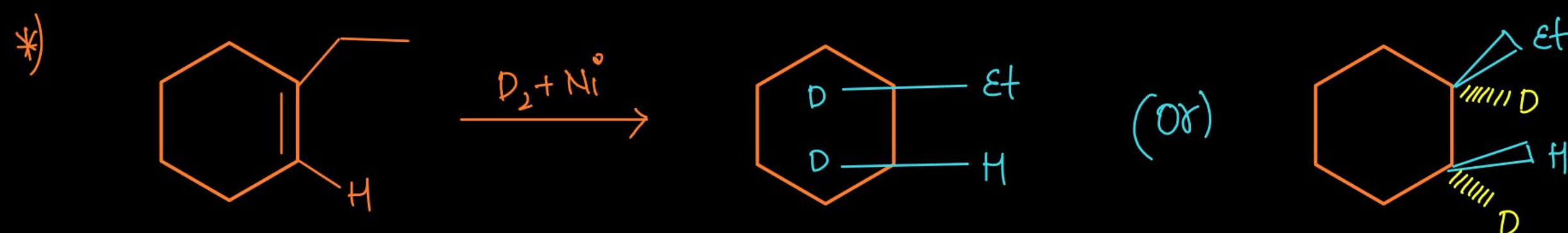


Ex:-

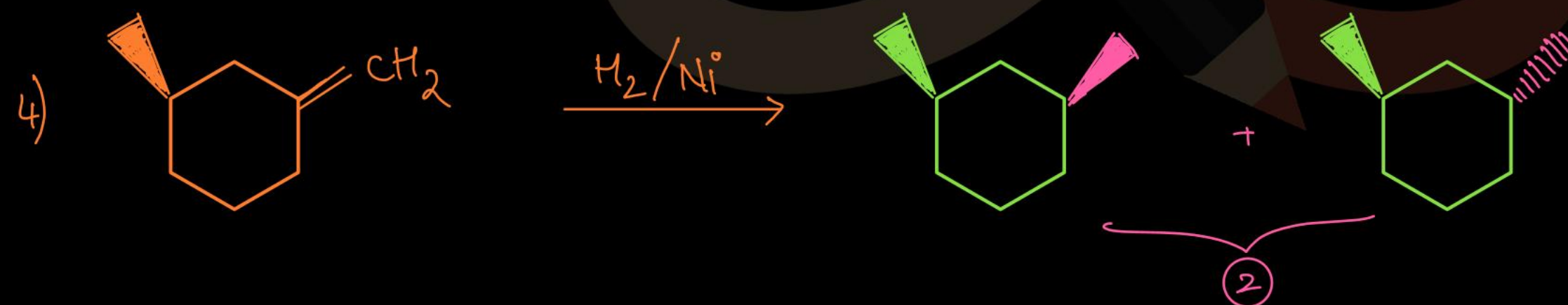
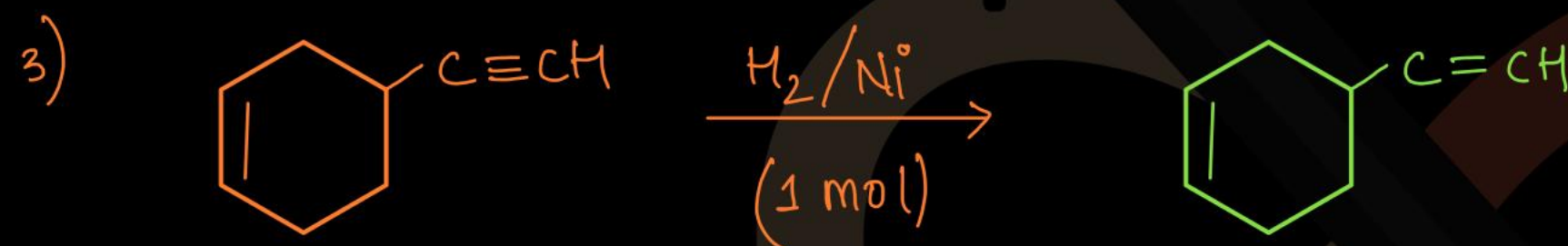
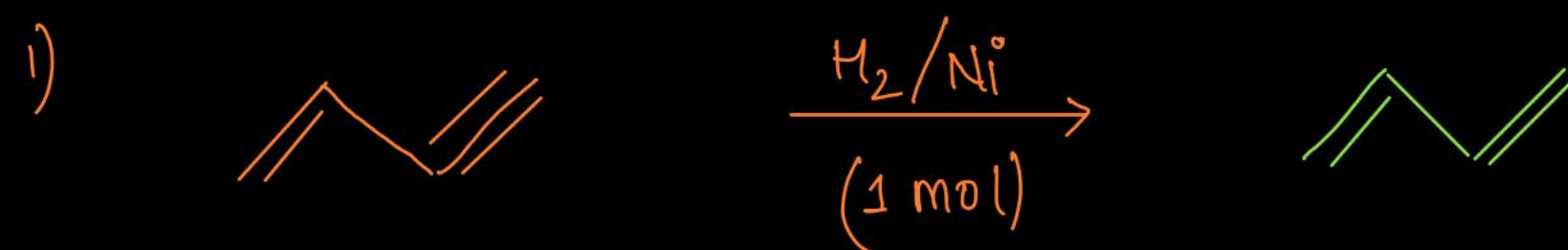


Stereochemistry of rxn :-

cis-alkene	$\xrightarrow{\text{Syn}}$	Erythro
trans-alkene	$\xrightarrow{\text{Anti}}$	Erythro
trans-alkene	$\xrightarrow{\text{Syn}}$	Threo
cis-alkene	$\xrightarrow{\text{Anti}}$	Threo



Practice :-

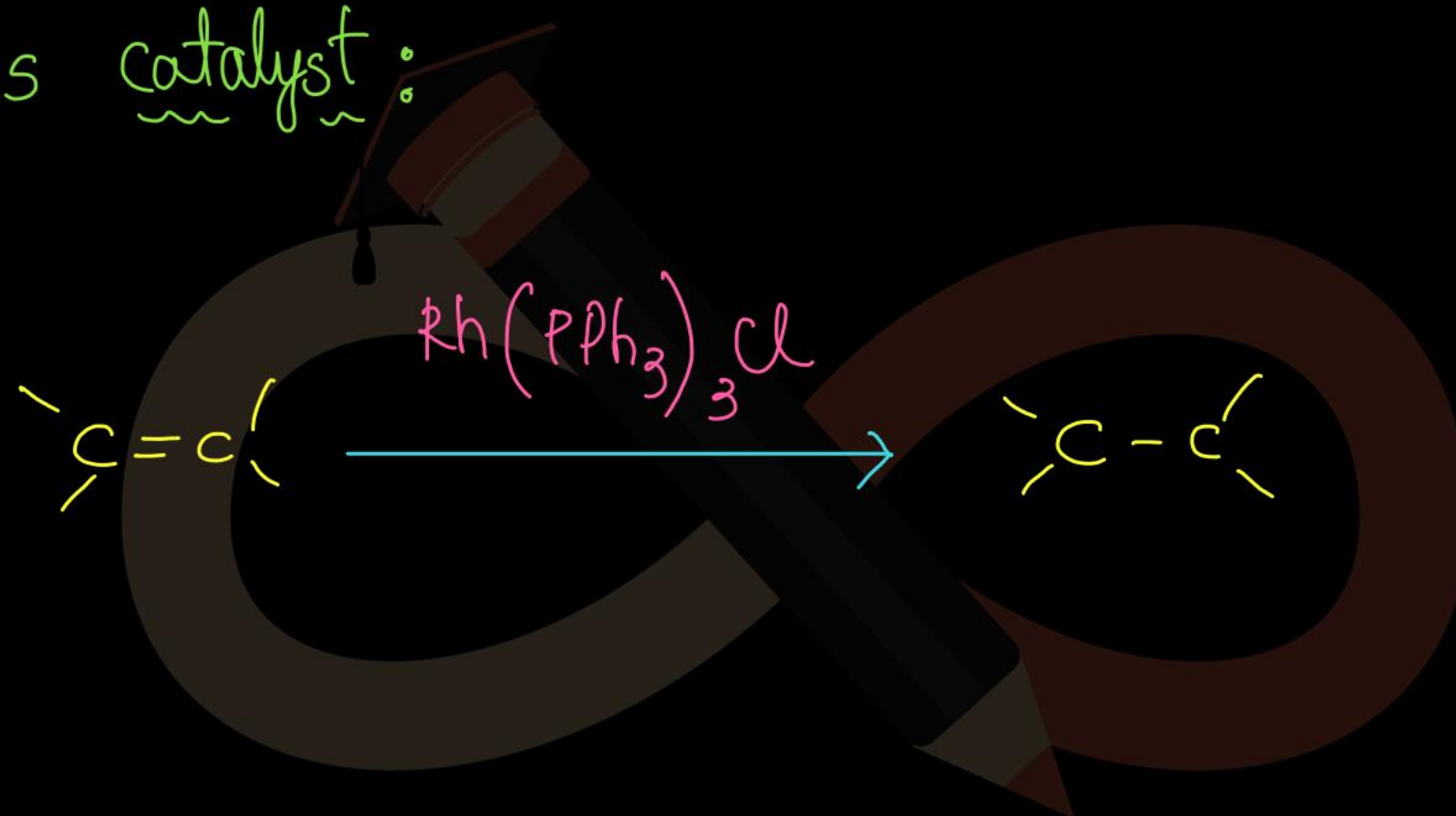


Note:-

1) Raney Nickel (Alloy of Ni, Al in NaOH)

2) Raney Nickel is better than Nickel

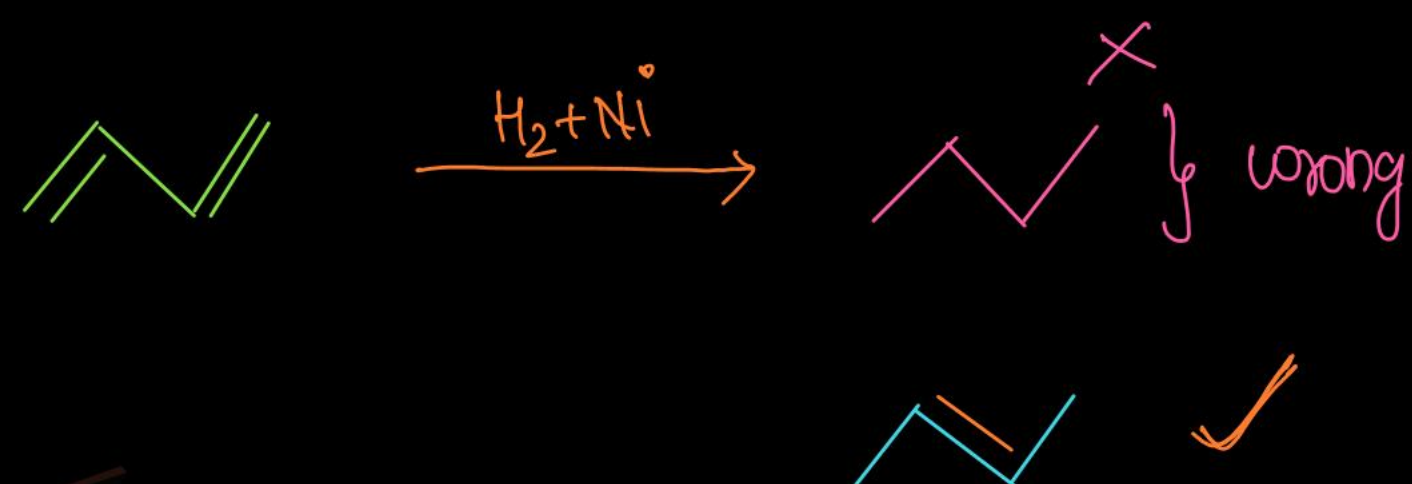
*) Using Wilkinson's catalyst:



Note:-

*) 1,4-addition

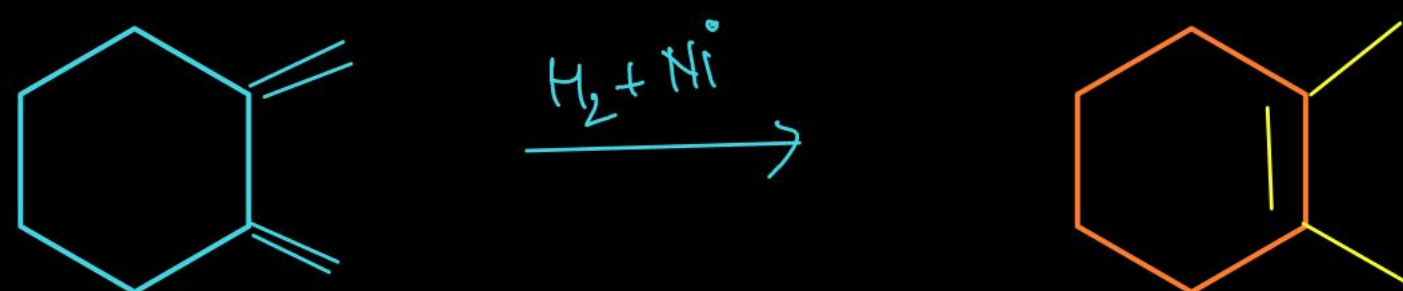
⇒ In conjugated alkenes (di-enes)



Mechanism

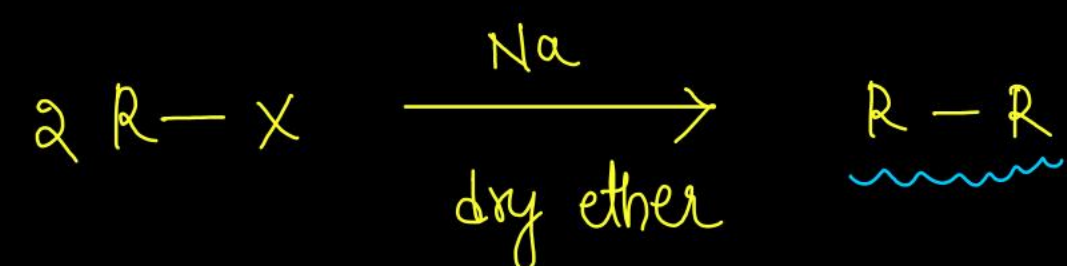


Ex:-



② from alkyl halides :

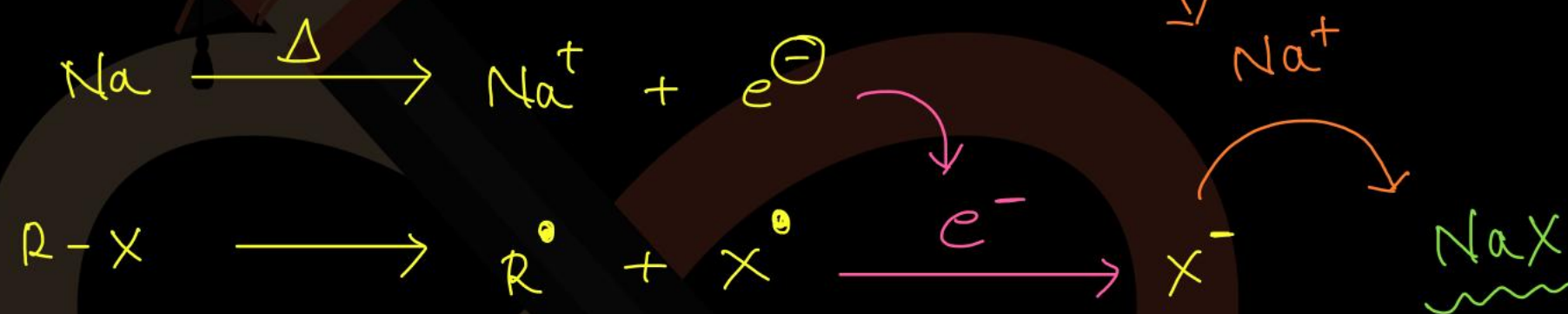
i) Wurtz Reaction



*) Useful for the preparation of symmetrical alkanes.

Mechanism :-

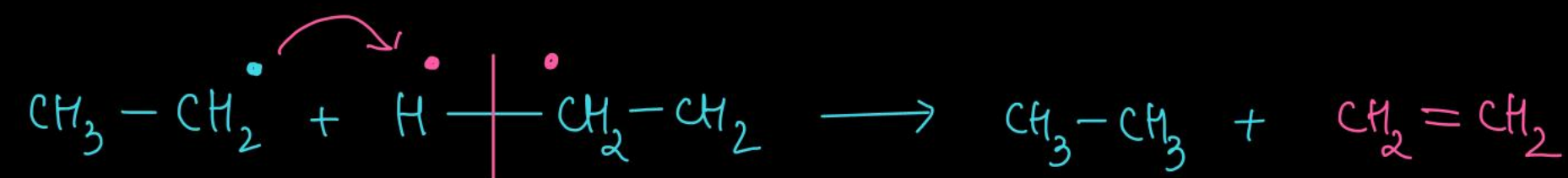
i) free radical :



Combination



Disproportionation



Note:-

① reactivity $\propto \frac{1}{S.H}$ ($1^\circ R-X > 2^\circ R-X > 3^\circ R-X$)

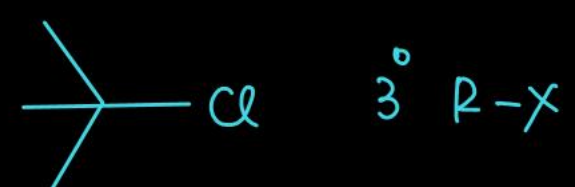
② reactivity (Intra > Inter)

③ $R-F < R-Cl < R-Br < R-I$

Imp (*)



→ Combination (major) ⇒



→ Disproportionation (major)

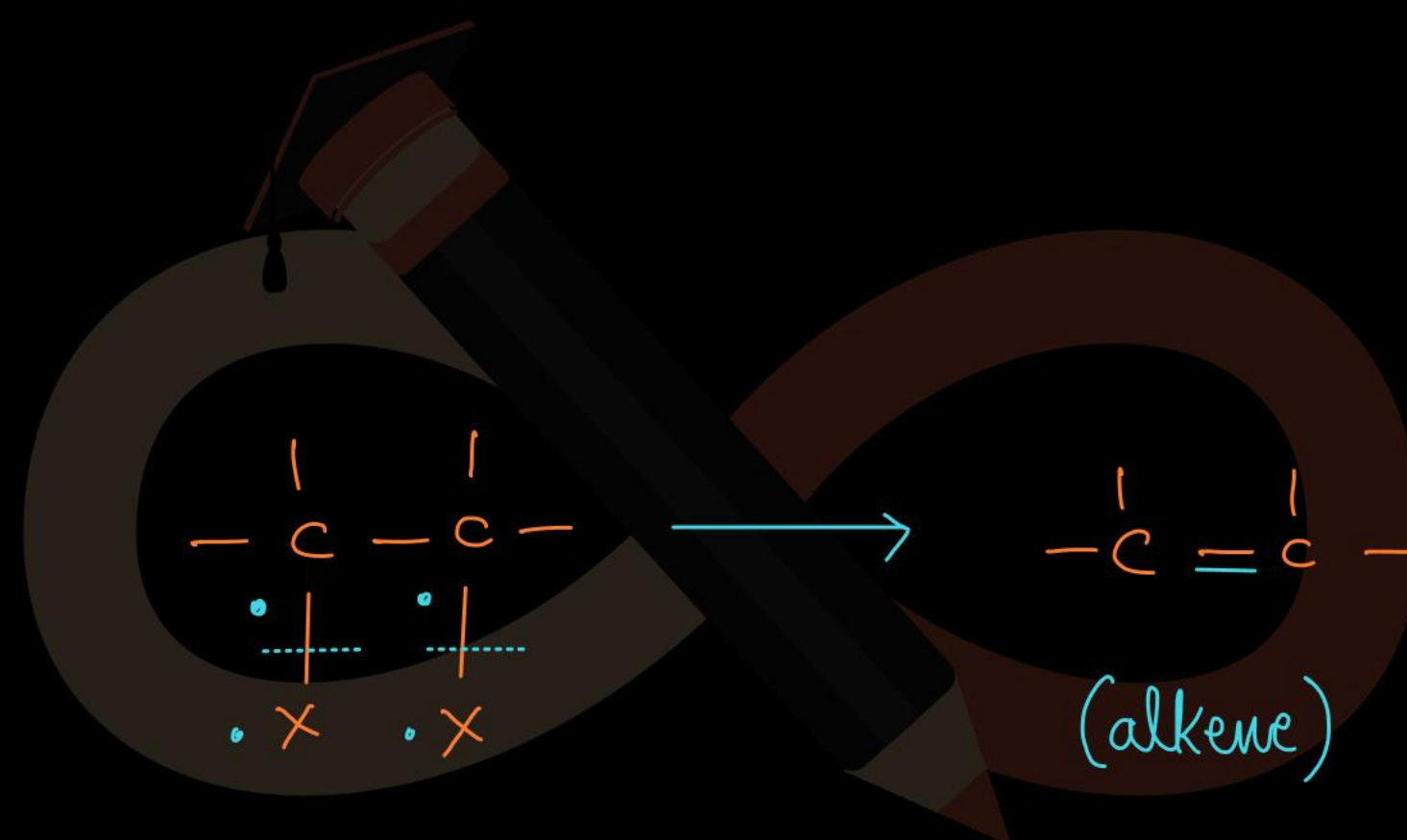


Mixed halide wurtz rxn



Intramolecular wurtz rxn

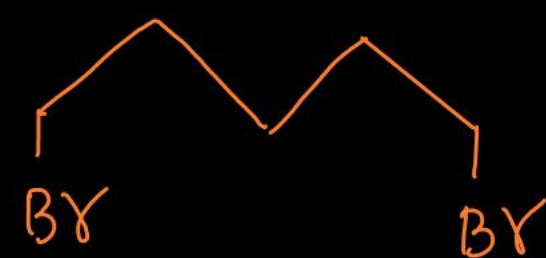
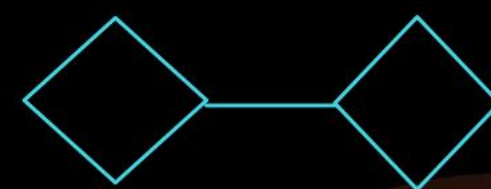
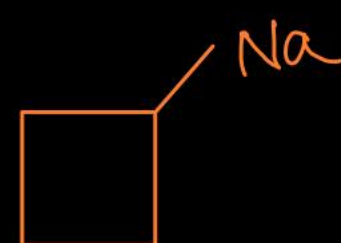
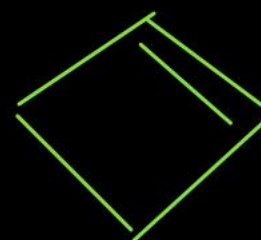
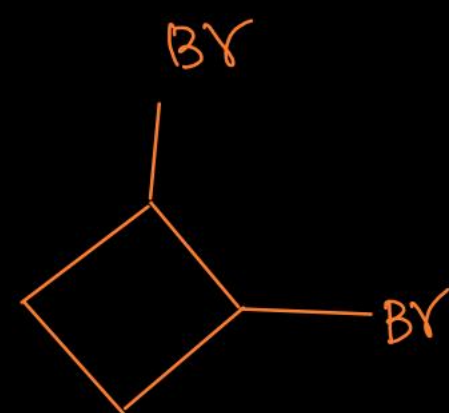
1,2 dihalide



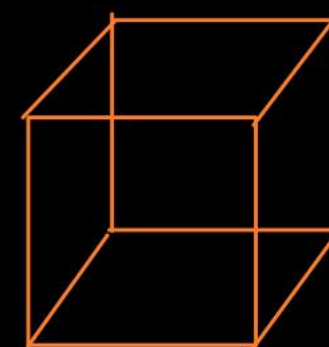
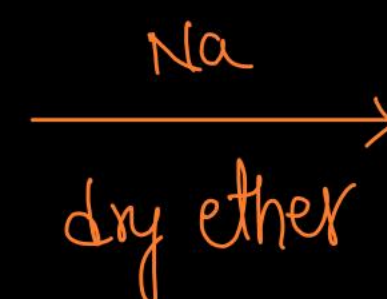
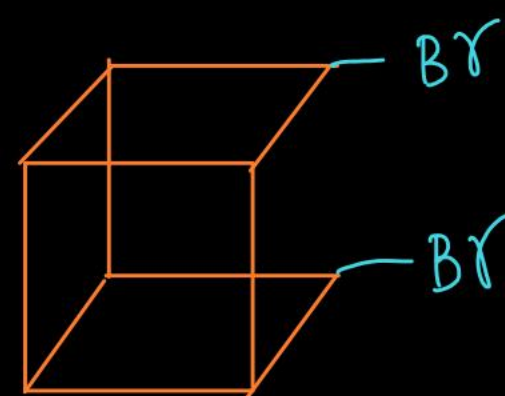
(1,3), (1,4) -----

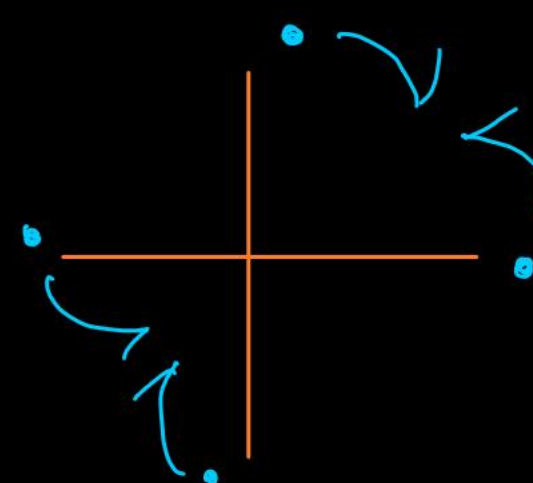
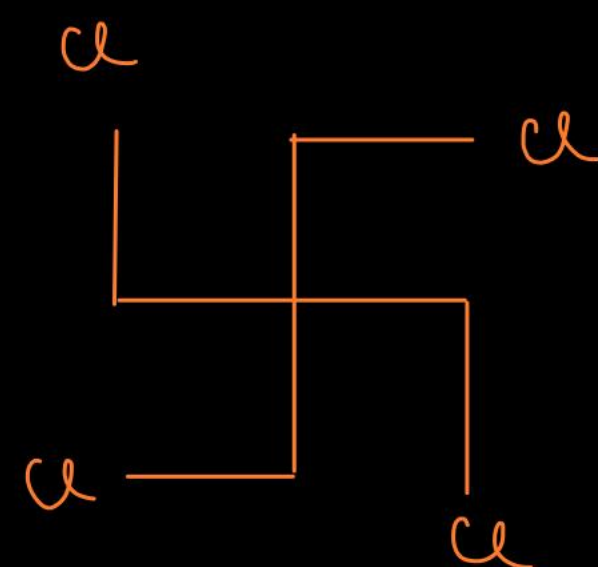
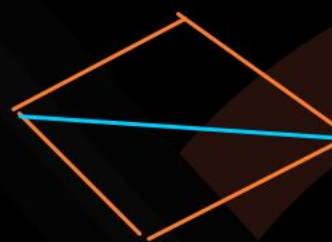
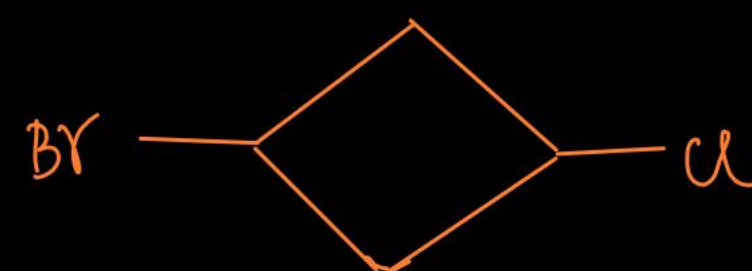
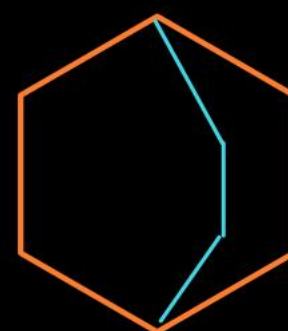


Practice :-

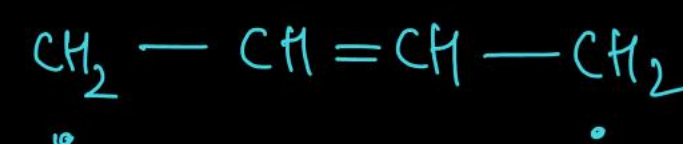
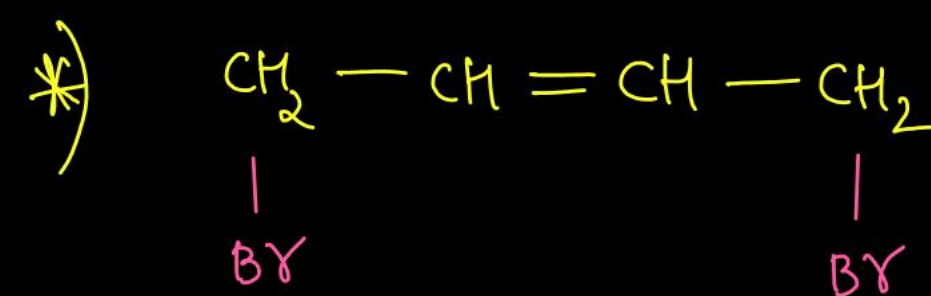


(Intra)

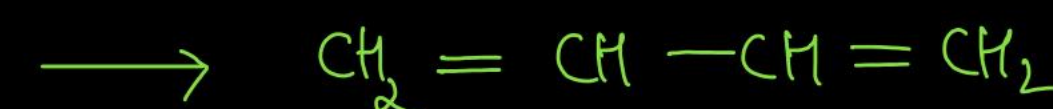
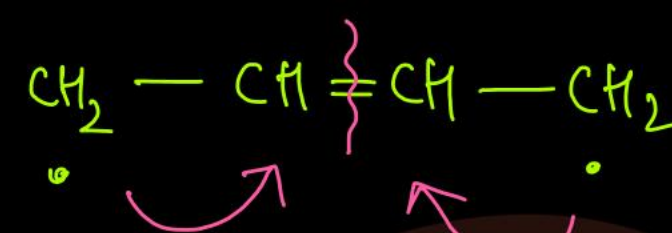




Imp:-

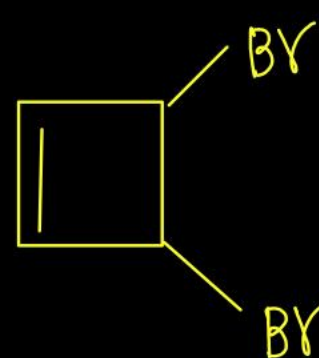


(but this is not major)



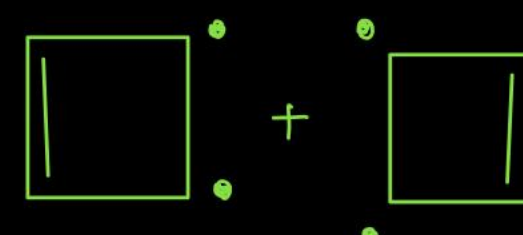
(conjugated) [$\therefore$ Major]

*)



Intra - but still minor

$\therefore$ Anti-aromatic is highly unstable



=



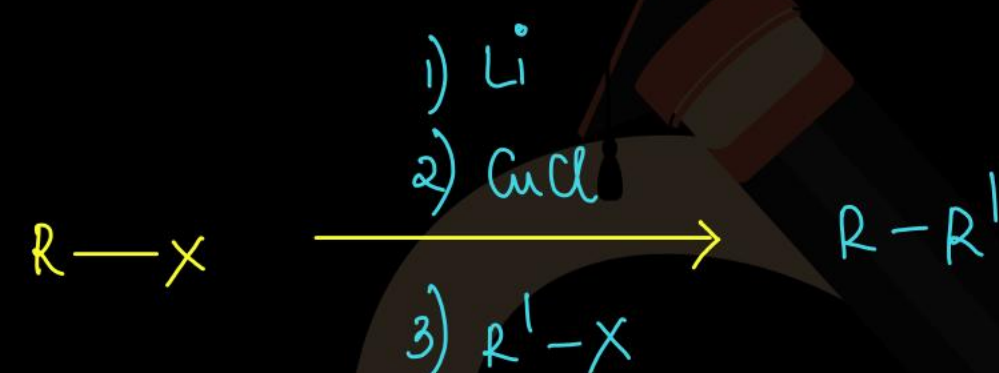
(Major)

Non-aromatic

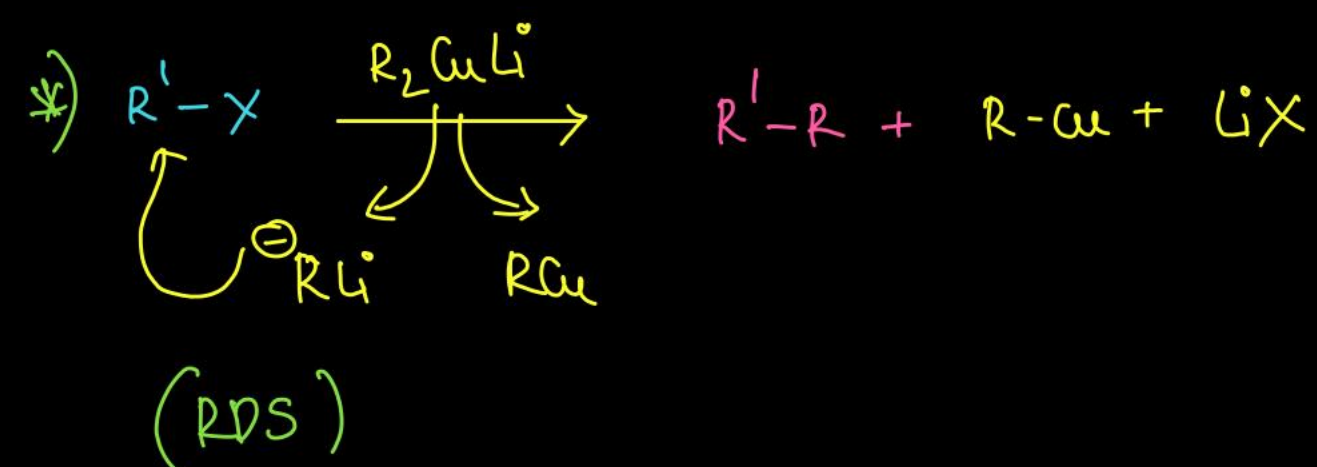
ii) Frankland rxn :-



iii) Corey-house synthesis



Mechanism :-



Note:

1) Attack of $R^{\ominus}$ is RDS

2) $\text{rate} \propto \frac{1}{\text{S.H. of R-X}}$ ($1^{\circ} > 2^{\circ} > 3^{\circ}$)

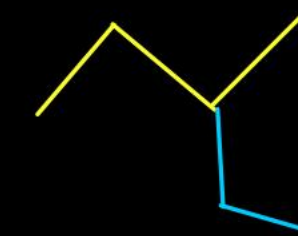
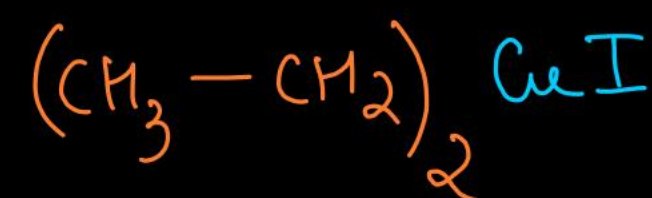
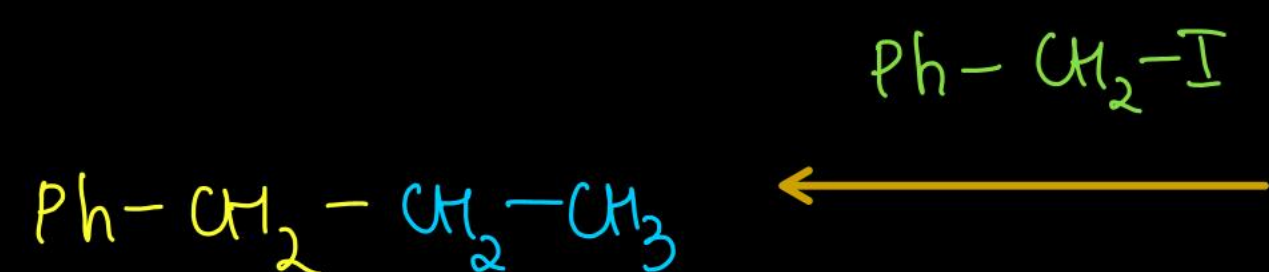
3) If R' is same, then ($R-F < R-Cl < R-Br < R-I$)

4) Useful for the prep of unsymmetrical alkanes

Ex:-



CuI



iv) Hydrogenation :-

Case i) Zn/H^+



Case ii) By using complex metal hydrides

(LiAlH_4 , NaBH_4 , Ph_3SnH , Bu_3SnH)

	LAH	SBH	TPTH / TBH
1° R-X	Alkane	-	Alkane
2° R-X	Alkane	Alkane	Alkane
3° R-X	Alkene	Alkane	Alkane

LAH = Lithium Aluminium Hydride

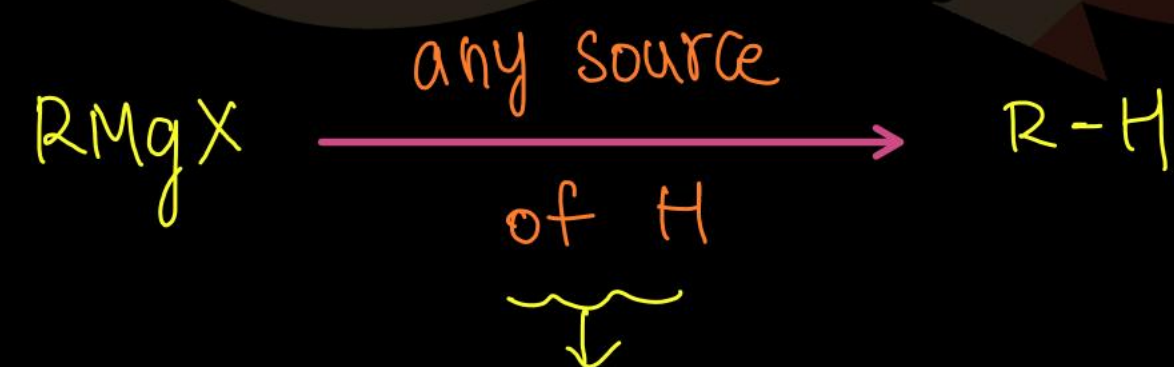
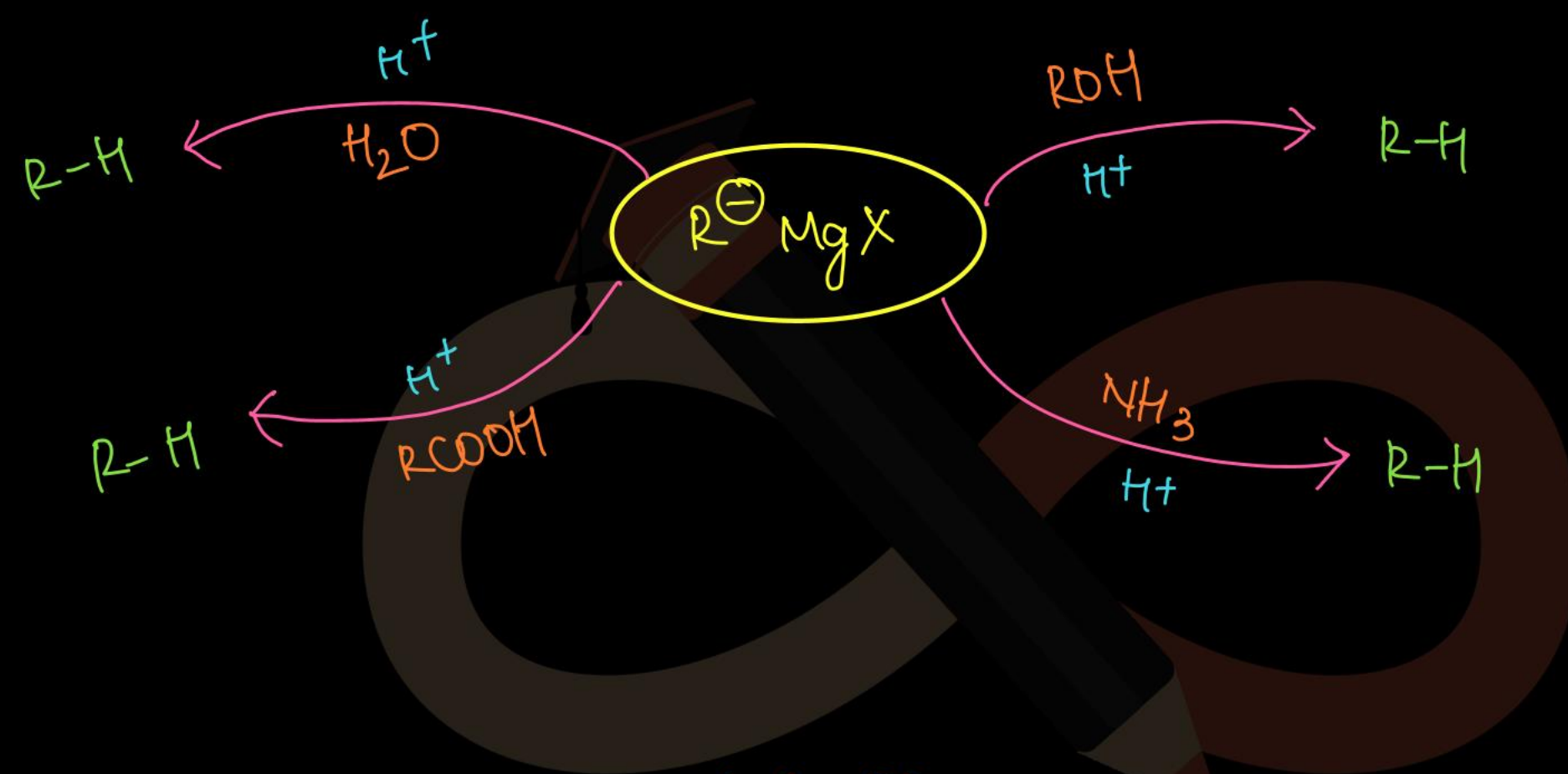
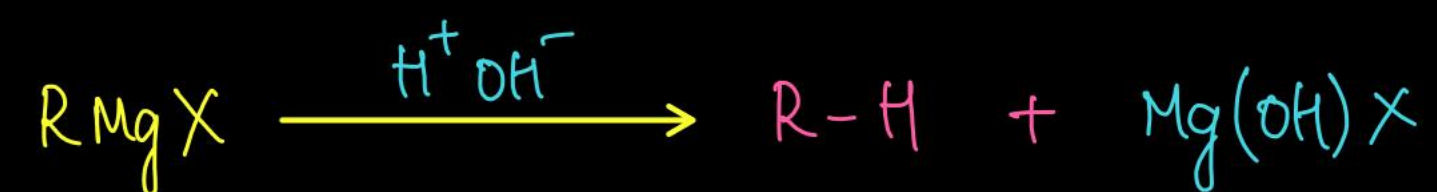
SBH = Sodium Borohydride

TPTH = Triphenyl tin hydride

TBH = Tributyl tin hydride

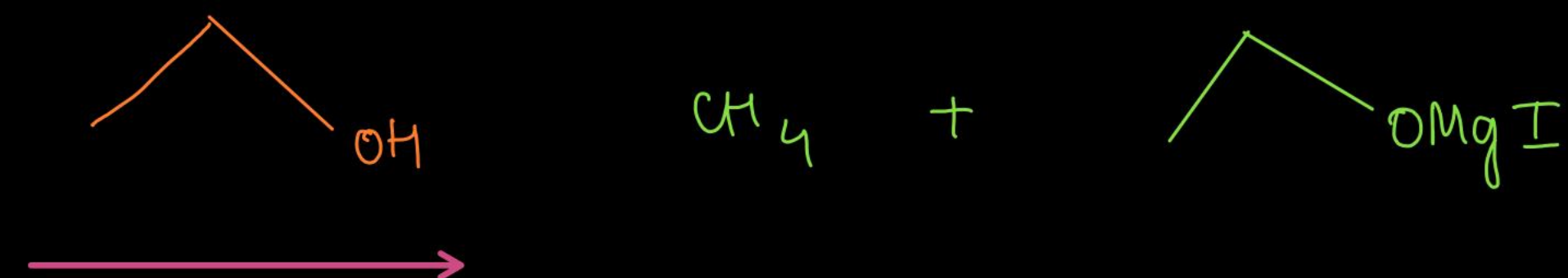
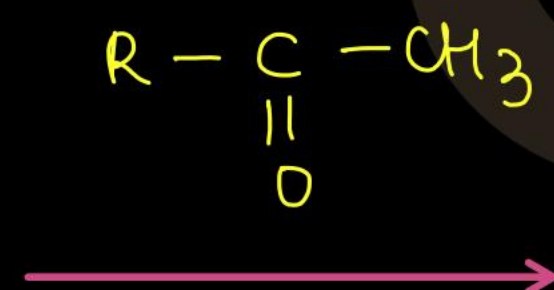
) Same result.

v) Grignard's reagent :-



(but not simple aldehydes, ketones, esters having $\alpha\text{-H}$, kinetically not possible)

Ex:-



III) from Carboxylic acids.

i) Sodalime decarboxylation :-

(1:3 mixture of NaOH + CaO)

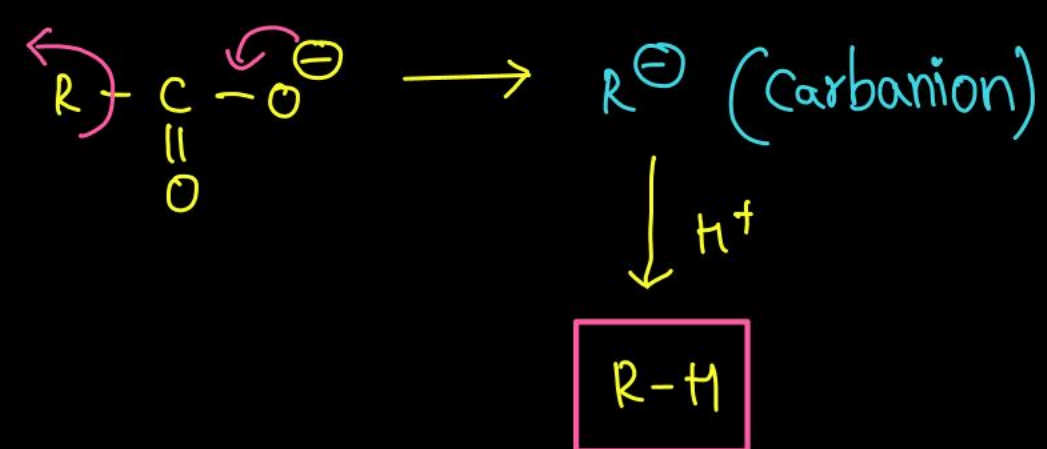
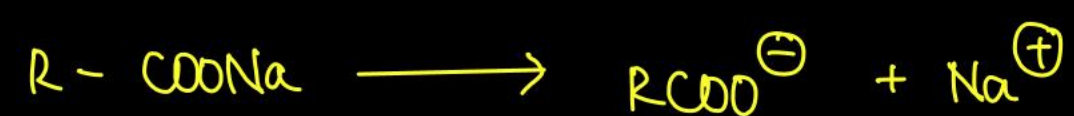
*) Carboxylic acid $\xrightarrow[\text{CaO}]{\text{NaOH}}$ Alkane



*) Salt of Carboxylic acid $\xrightarrow[\text{CaO}]{\text{NaOH}}$ Alkane



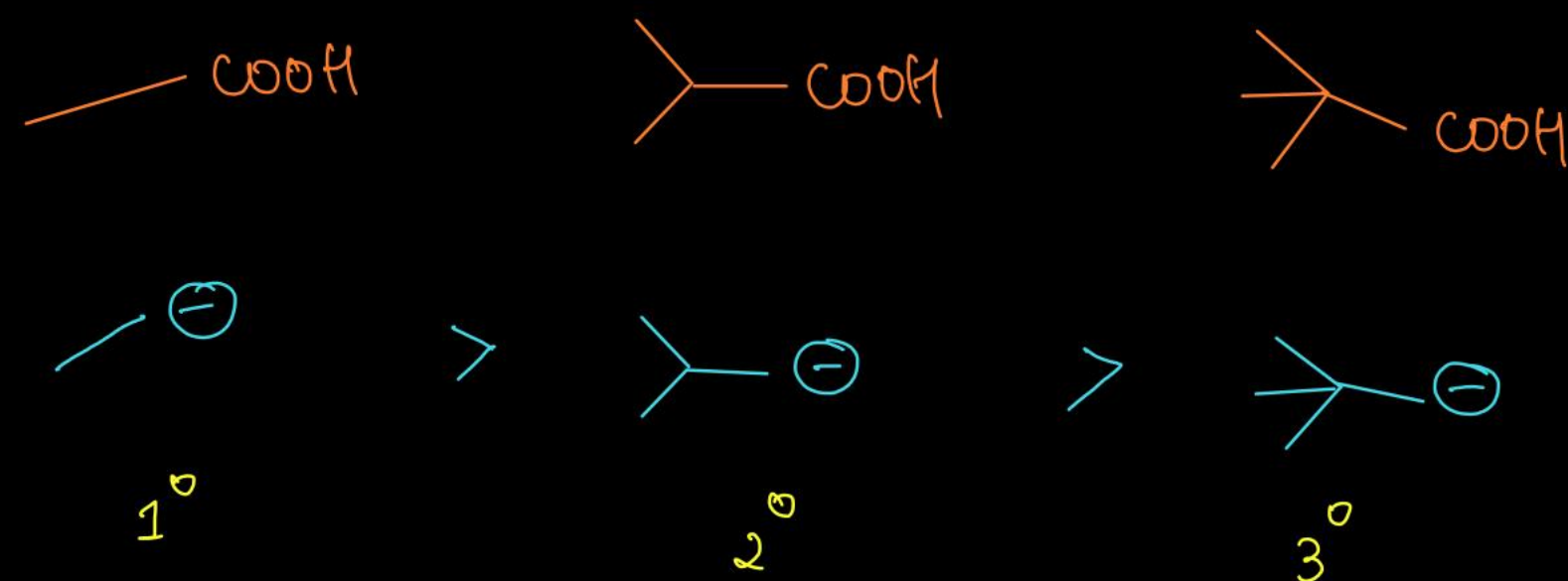
Mechanism



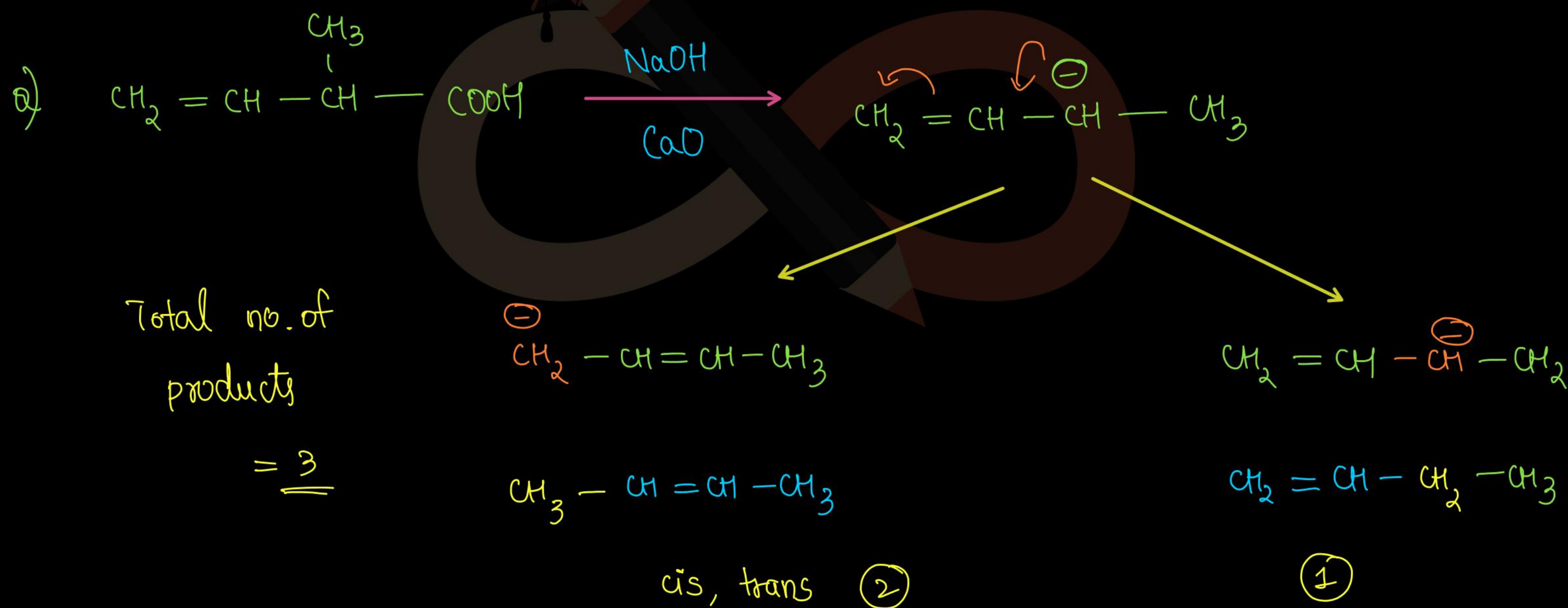
Imp:-

1) formation of $R^\ominus$ is RDS

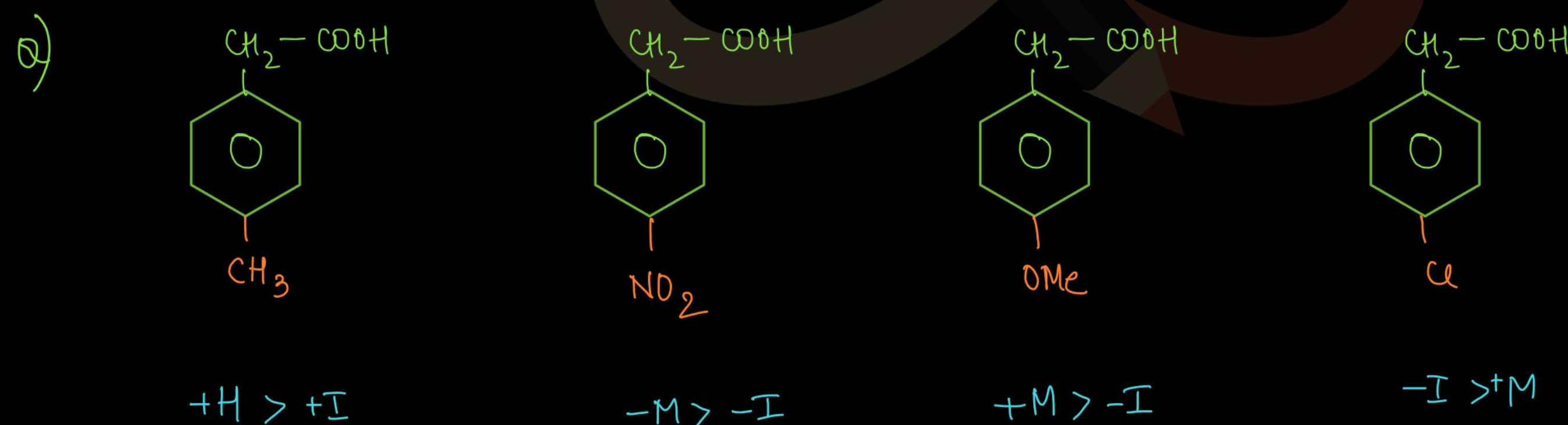
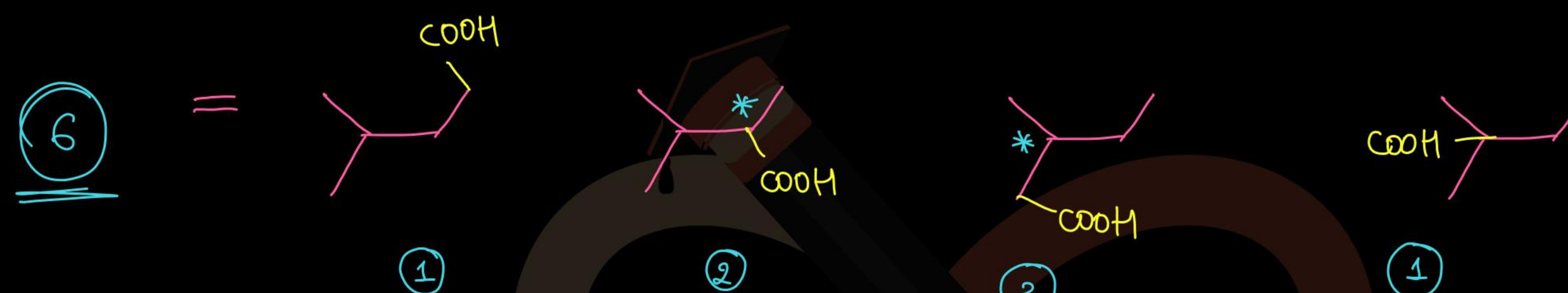
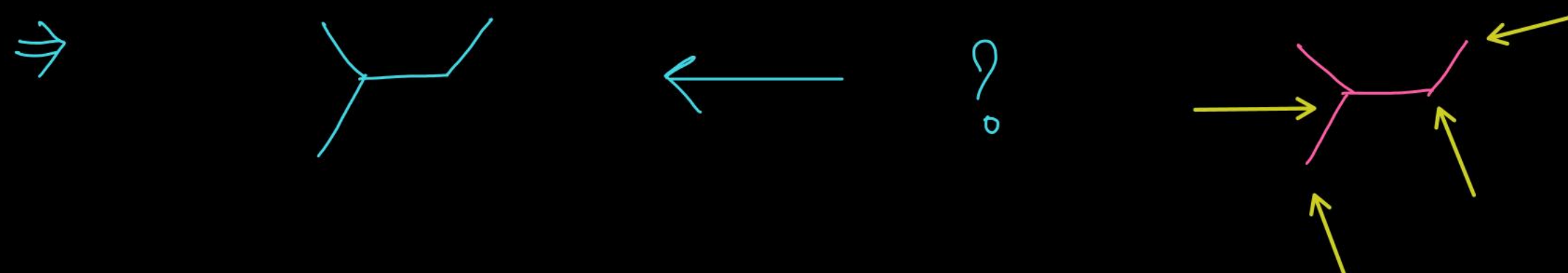
* 2) rate $\propto R^\ominus$ stability



Practice :



Q) How many mono Carboxylic acids on Sodalime decarboxylation gives pentane?



ii) Kolbe's Electrolysis :- (same as wurtz)

Salt of Carboxylic acid $\longrightarrow$ Alkane



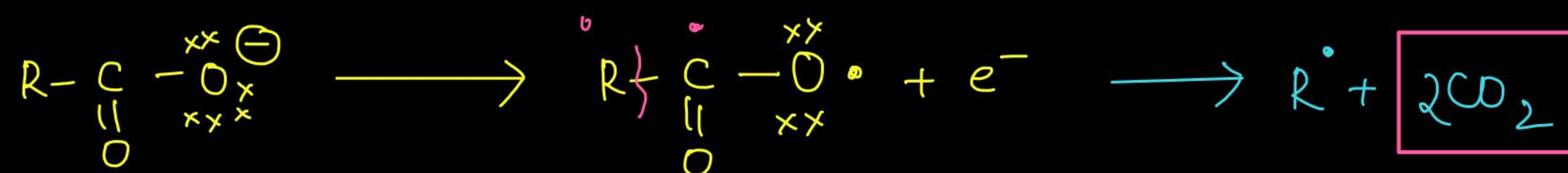
Ex^{e-}



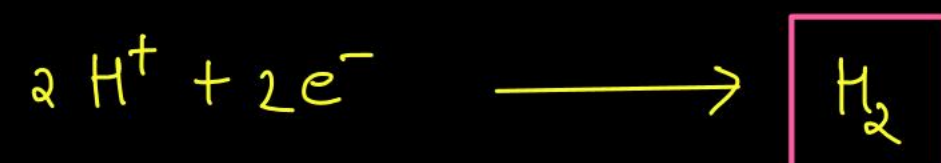
Mechanism :-



at Anode,



at Cathode,



Imp points:

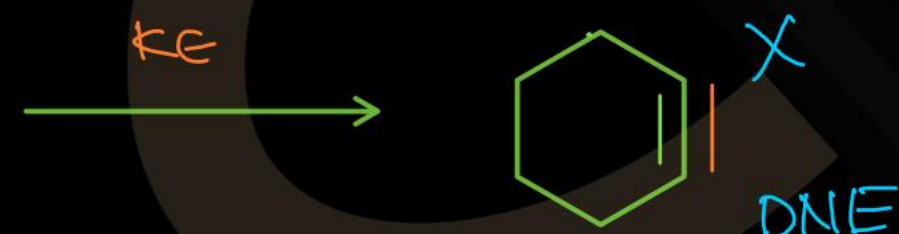
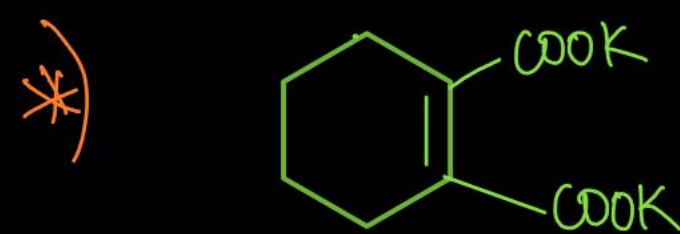
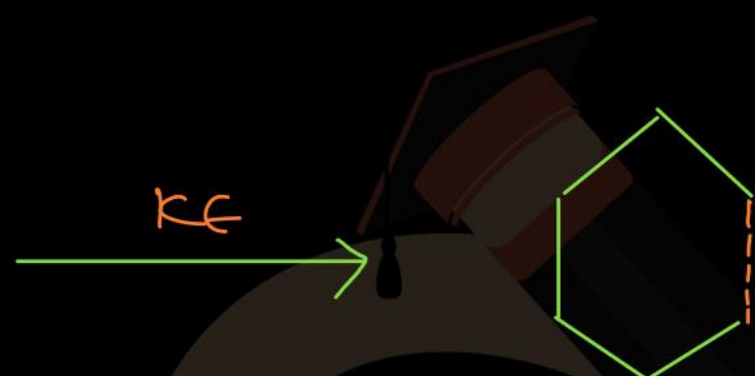
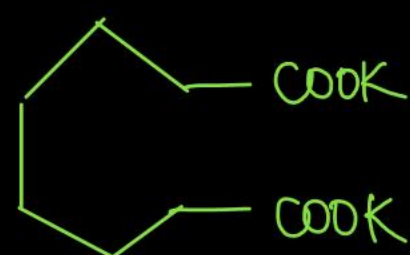
1) Cathode : reduction $\Rightarrow H_2$

2) Anode : Oxidation $\Rightarrow CO_2 + R-R$

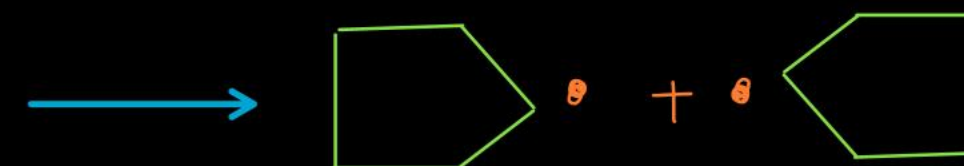
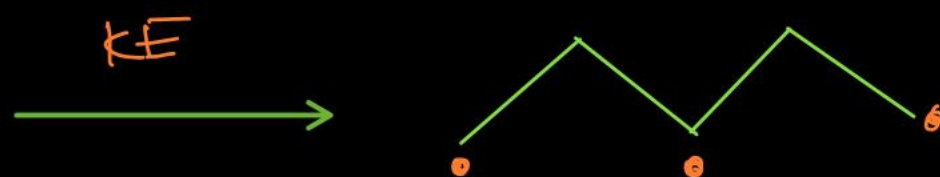
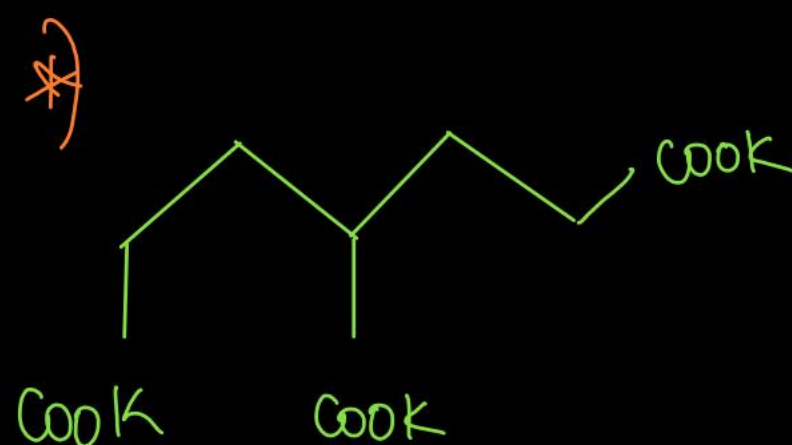
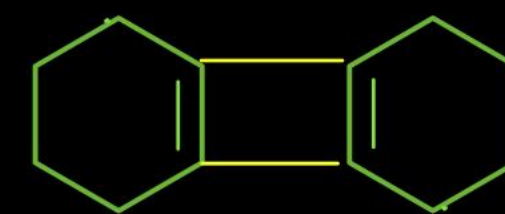
* 3) Nature of sol after electrolysis $\rightarrow KOH$

$\Rightarrow$ basic nature

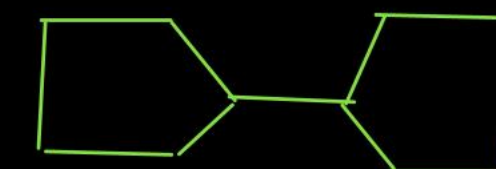
Practice:-



instead, we get



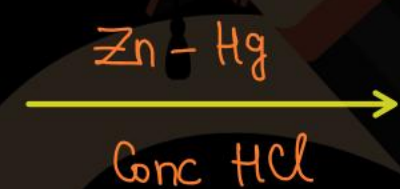
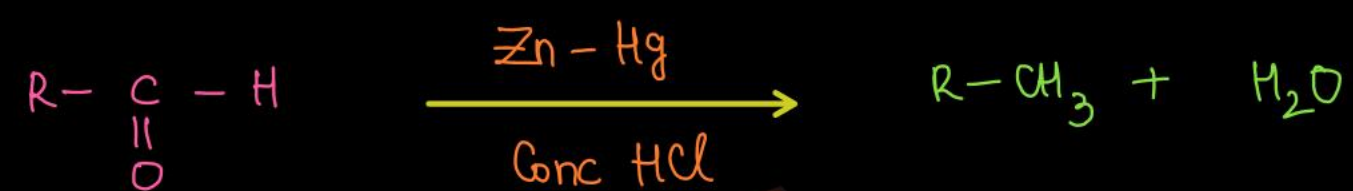
(5 mem > 3 mem)



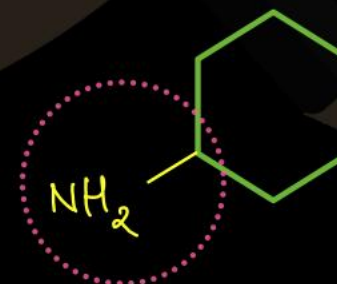
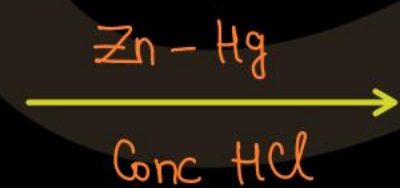
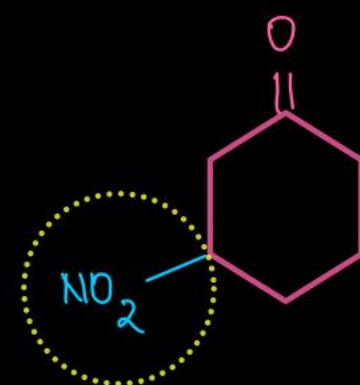
(4) from Carbonyl Compounds :

i) Clemmensen's reduction

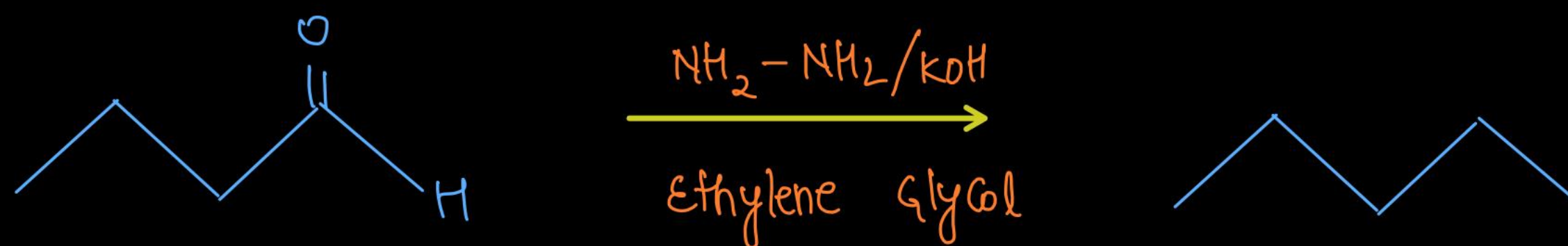
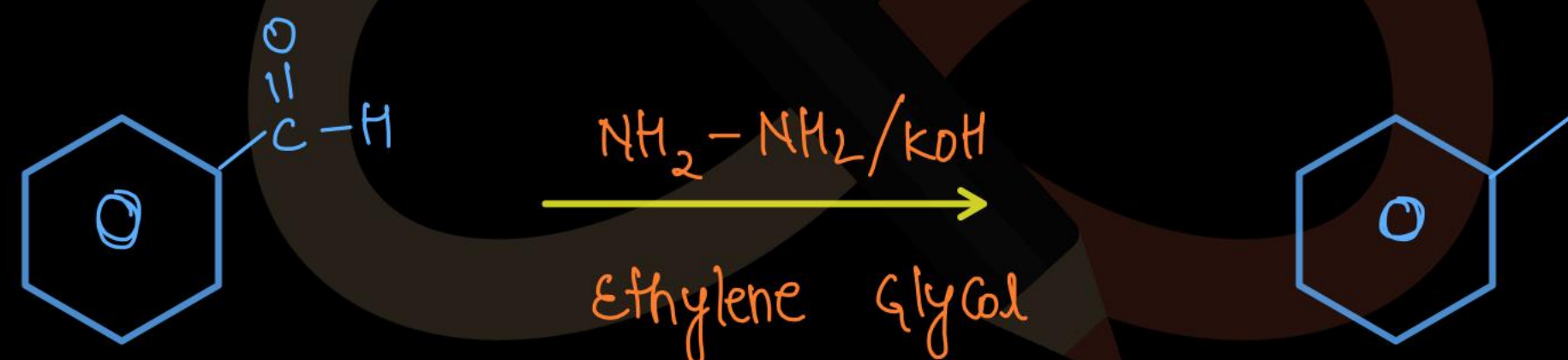
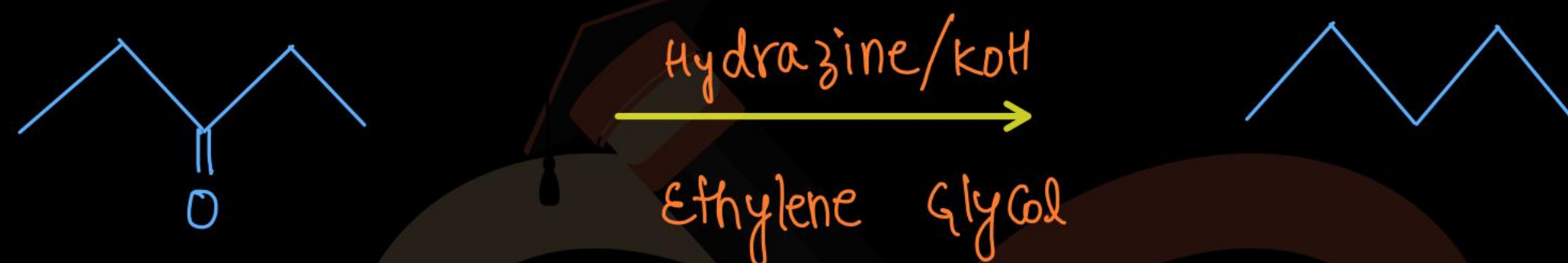
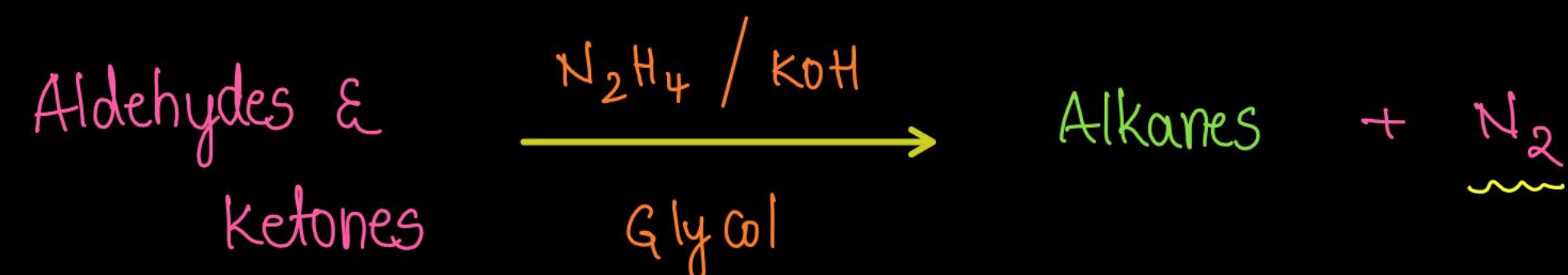
Aldehydes & Ketones $\xrightarrow[\text{Conc HCl}]{\text{Zn-Hg}}$ Alkanes



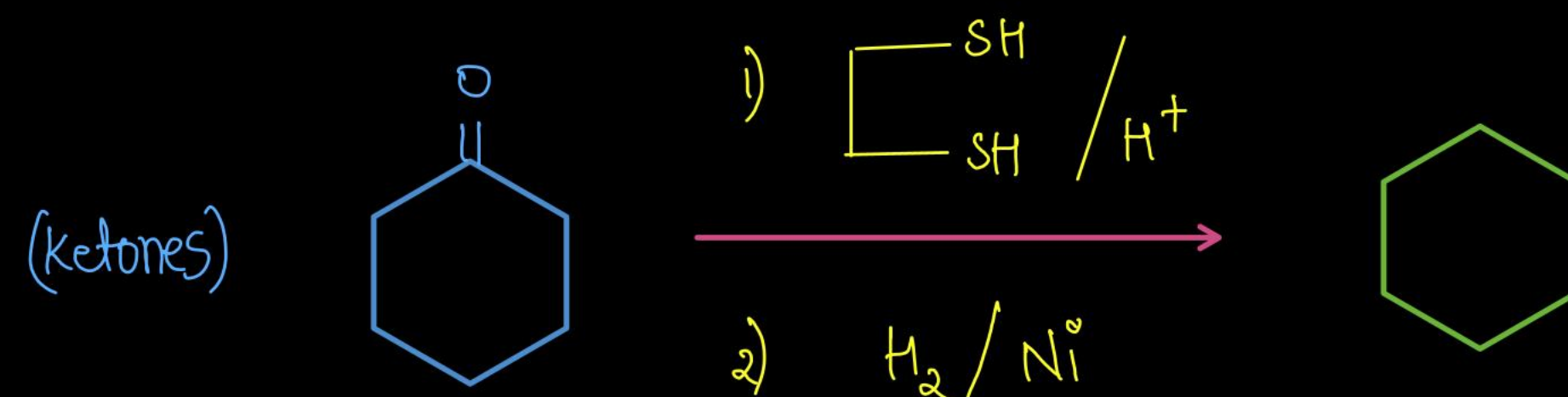
*)



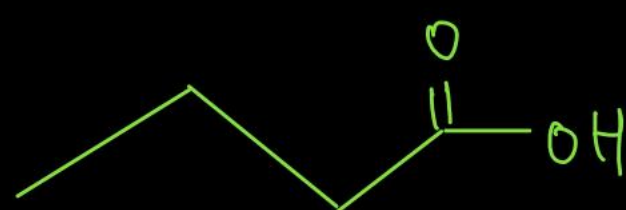
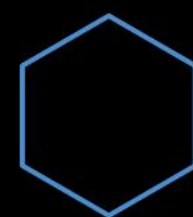
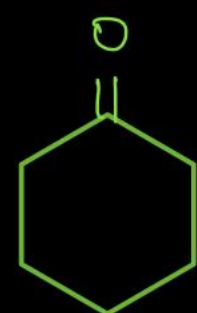
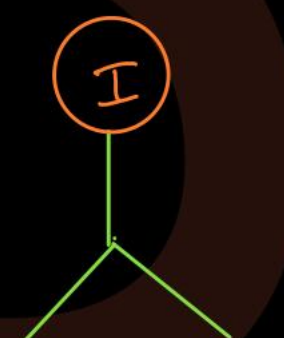
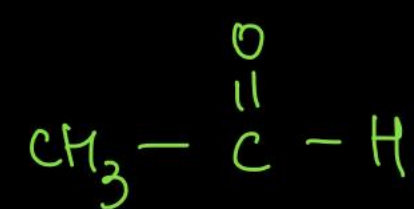
ii) Wolff Kishner Reduction



iii) Mozingo's reduction

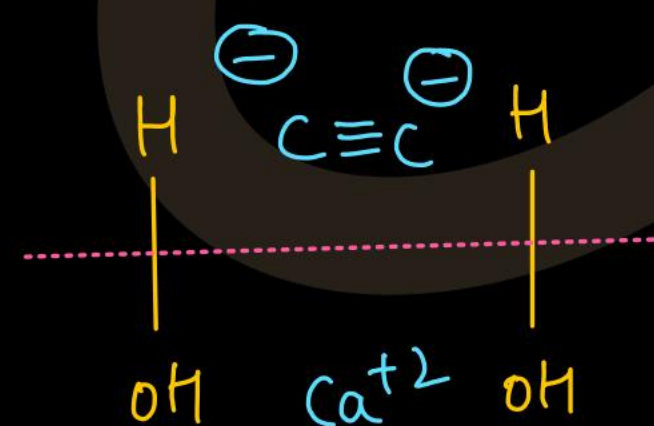
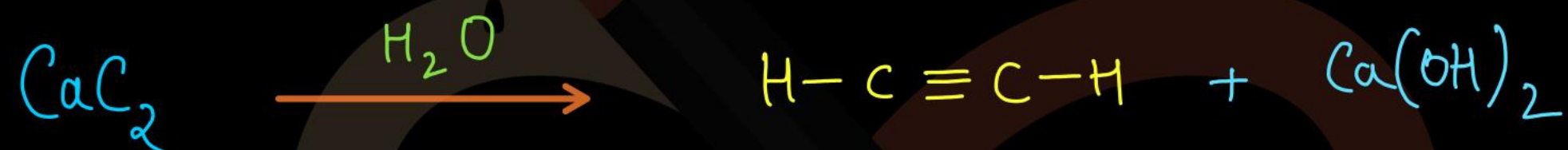


iv) By using HI and red phosphorous:

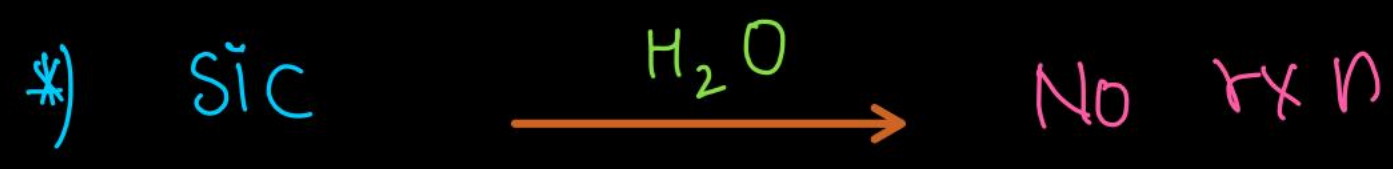
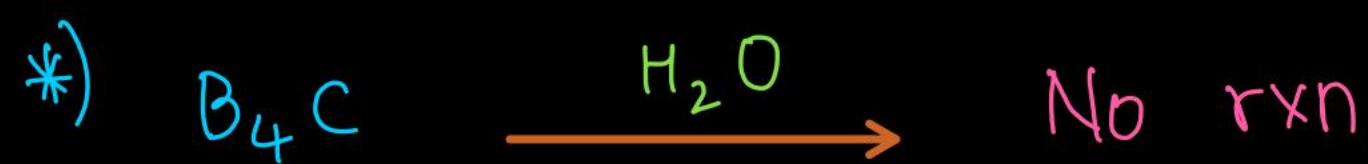


⑤ from Carbides

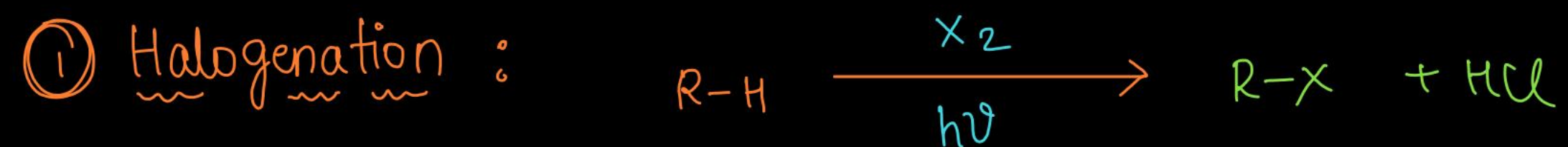
Ionic



Covalent



Properties of alkanes :-



Mechanism :

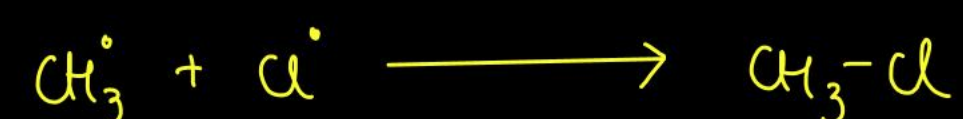
i) Chain initiation



ii) Chain propagation :-



iii) Chain termination

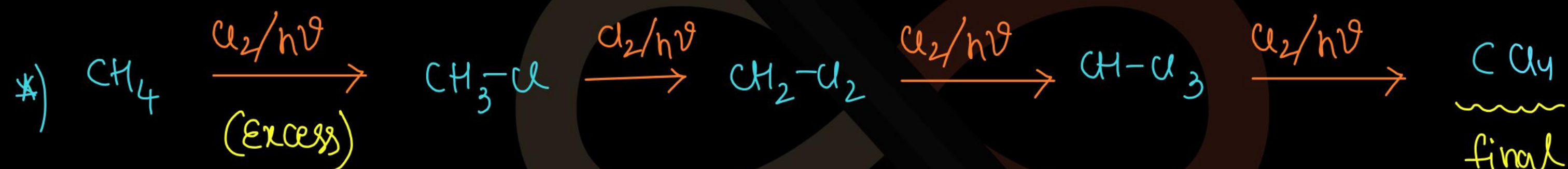


Imp points :-

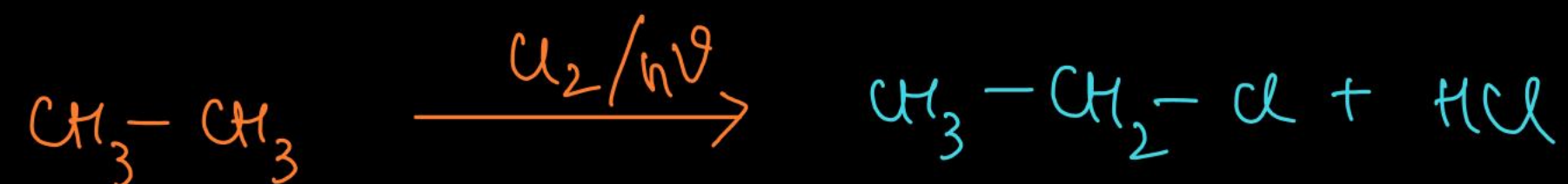
1) Free radical Subs Rxn

2) Rate of Rxn : $F_2 \gg \text{Cl}_2 > \text{Br}_2 > \text{I}_2$ (slow & reversible)
 highly exothermic
 (uncontrollable)

Note:-



*) for better yield of Ethyl chloride ;



↳ ethane should be excess

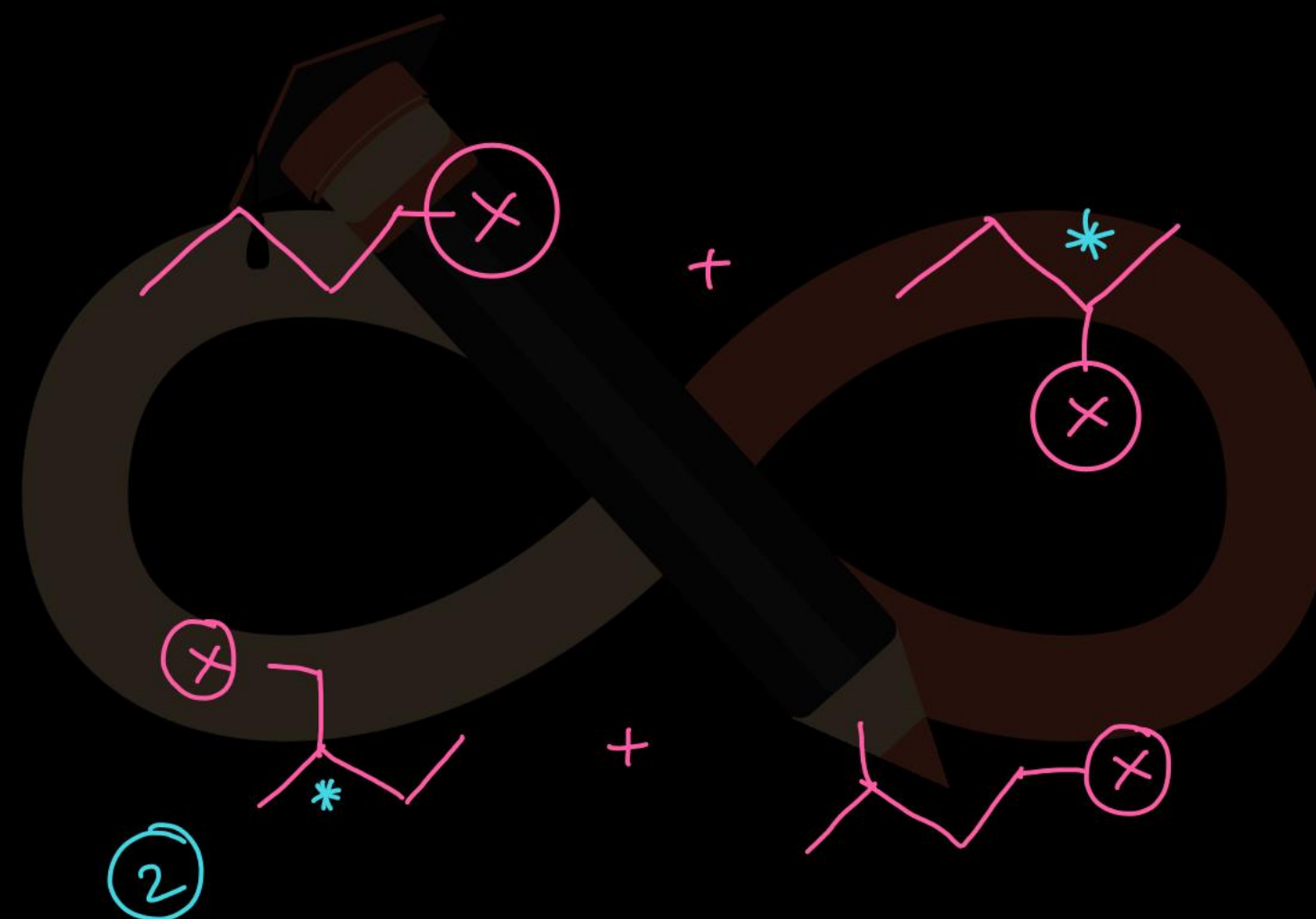
Q) Find total no. of structural products = x

total no. of products (inc stereo) = y

total no. of resolvable products = z (optically pure)

total no. of fractional products = w

i)



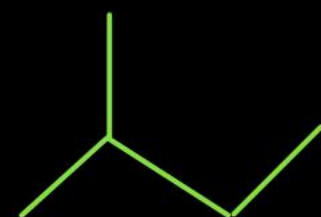
$x = 2$

$y = 3$

$z = 2$

$w = 2$

ii)



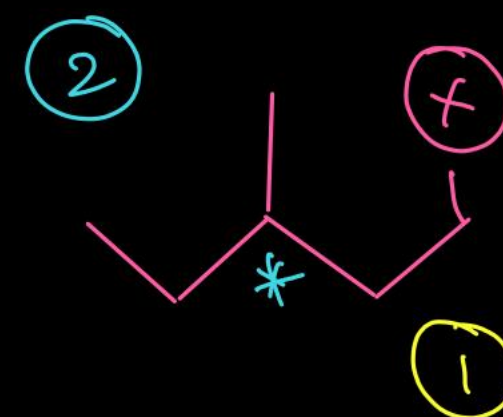
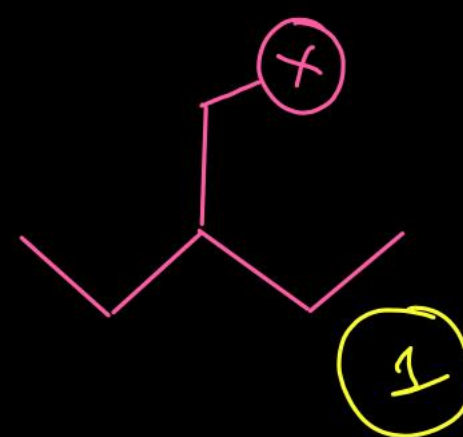
$x = 4$

$y = 6$

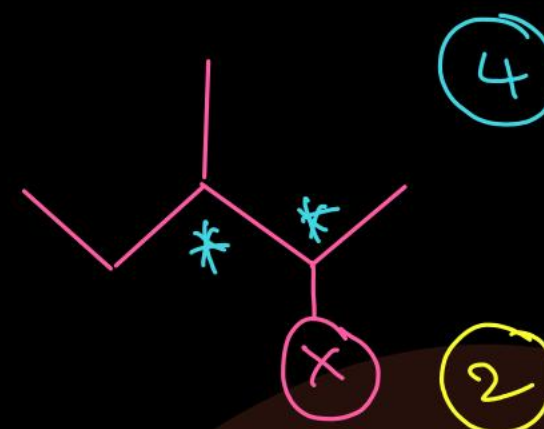
$z = 4$

$w = 4$

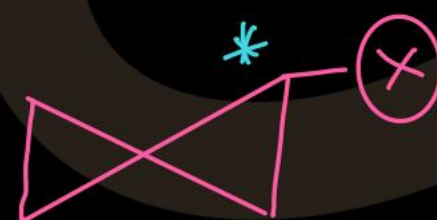
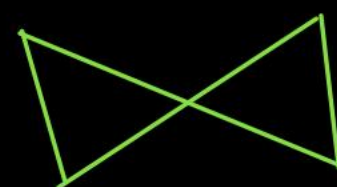
iii)



$$\begin{array}{ll} x = 4 & z = 6 \\ y = 8 & w = 5 \end{array}$$

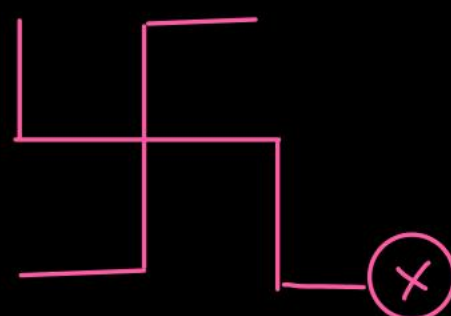
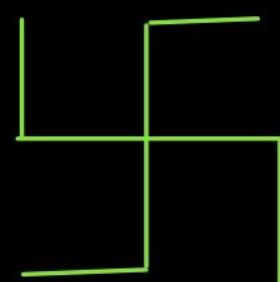


iv)

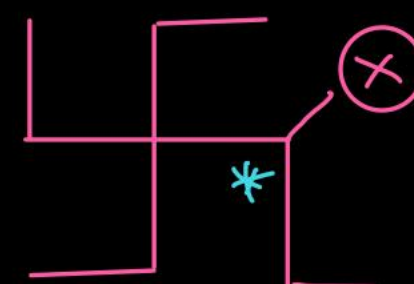


$$\begin{array}{ll} x = 1 & z = 2 \\ y = 2 & w = 1 \end{array}$$

v)

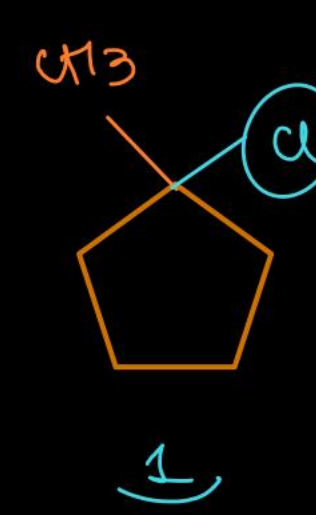
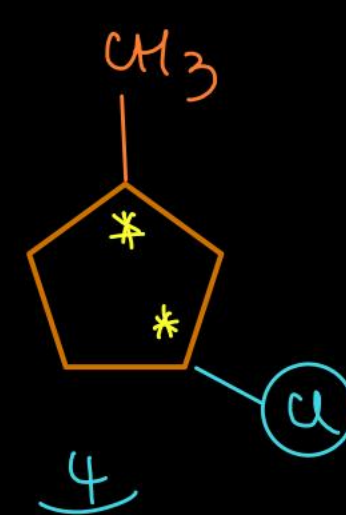
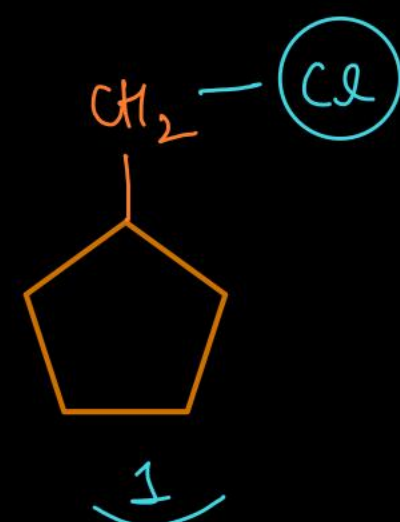
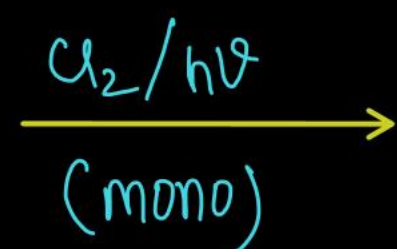
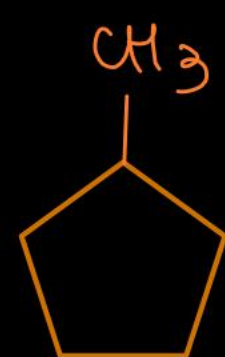


+



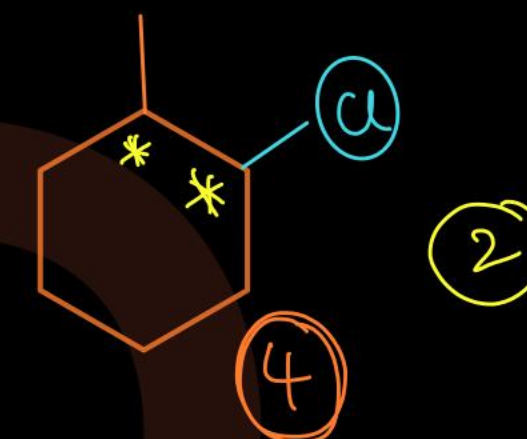
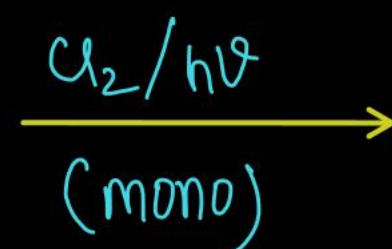
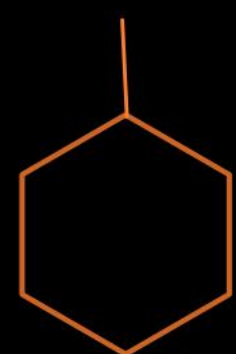
$$\begin{array}{ll} x = 2 & z = 2 \\ y = 3 & w = 2 \end{array}$$

vii)



$$\begin{aligned} x &= 4 \\ y &= 6 \\ z &= 6 \\ w &= 6 \end{aligned}$$

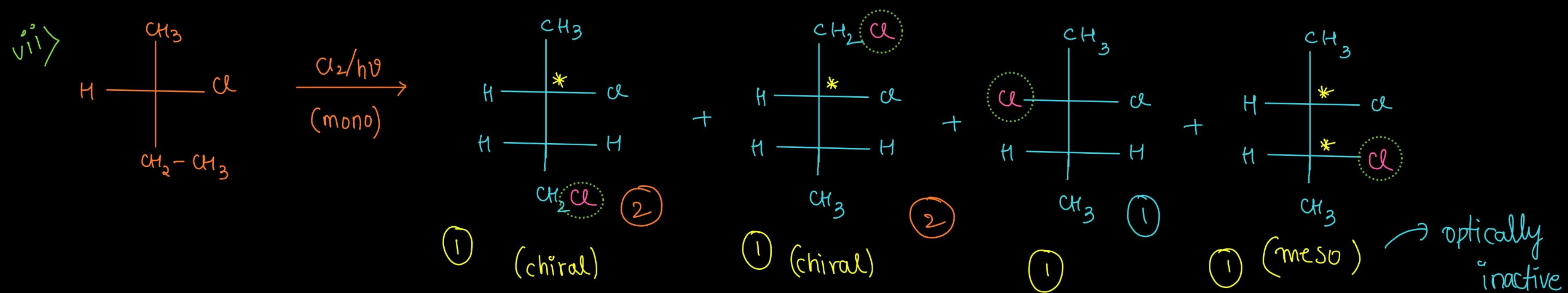
viii)



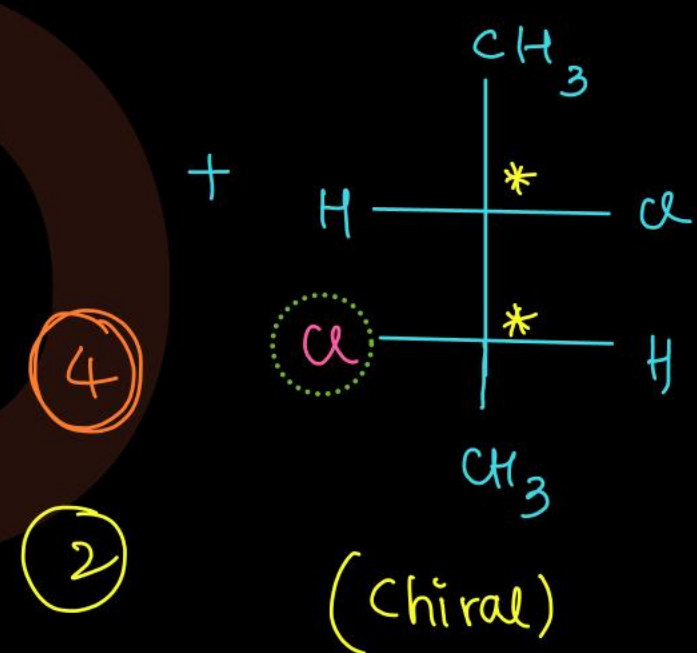
→ cis / trans
(2)

2 fractions

$$\begin{aligned} x &= 5 \\ y &= 12 \\ z &= 8 \quad \text{only (c, d)} \\ w &= 8 \end{aligned}$$



total no. of structural products = 5
 total no. of products (inc stereo) = 10
 total no. of resolvable products = 8 (optically pure)
 total no. of fractional products = 6



How to find Major Product ? (Relative Selectivity Order)

Case 1 > for chlorination

$$\% 1^\circ \text{ product} = \frac{n_1 r_1}{n_1 r_1 + n_2 r_2 + n_3 r_3} \times 100$$

$$\% 2^\circ \text{ product} = \frac{n_2 r_2}{n_1 r_1 + n_2 r_2 + n_3 r_3} \times 100$$

$n_1 \rightarrow$ no. of 1° H

$n_2 \rightarrow$ no. of 2° H

$n_3 \rightarrow$ no. of 3° H

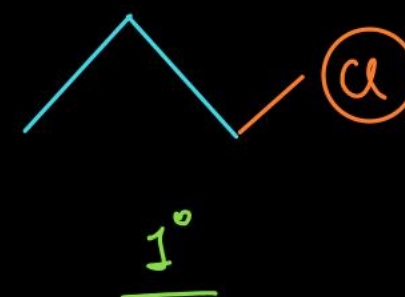
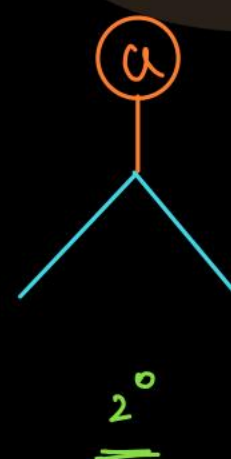
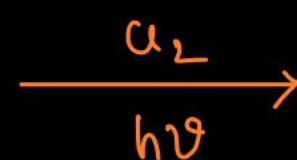
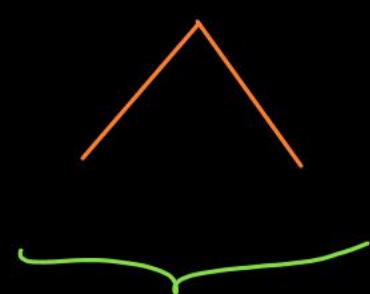
$r_1 : r_2 : r_3$

1 : 3.8 : 5

$r_1 \rightarrow$ r.o.r at 1° C

Ex:

i)



$$n_1 r_1 = 6 \times 1$$

$$n_2 r_2 = 2 \times 3.8$$

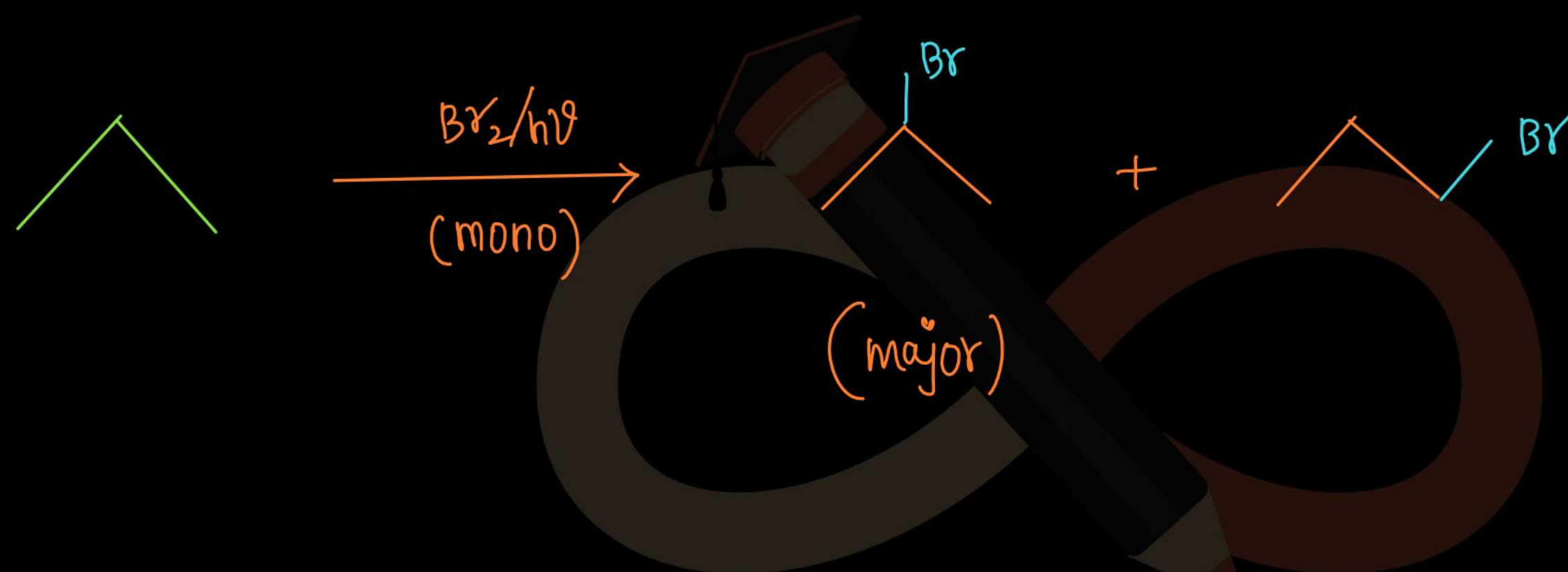
$$\Rightarrow n_2 r_2 > n_1 r_1 \quad \Rightarrow 2^\circ \text{ is major}$$

Case-2 for Bromination

$$r_1 : r_2 : r_3 = 1 : 82 : 160$$

$$\Rightarrow 3^\circ > 2^\circ > 1^\circ$$

Ex:-



Note:-

chlorination

(vs)

Bromination

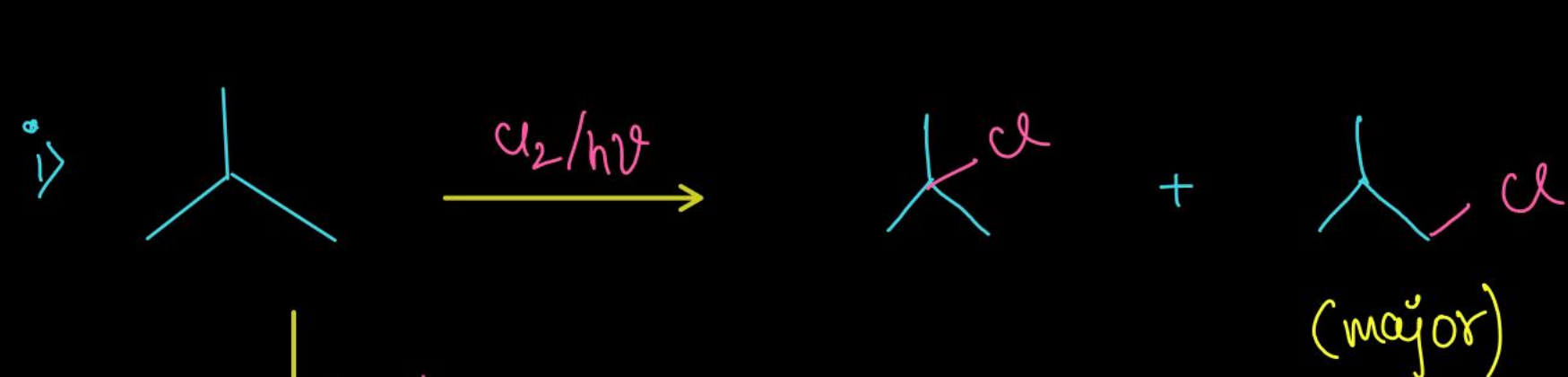
$\Rightarrow$ more reactive

less reactive

$\Rightarrow$ less selective

more selective

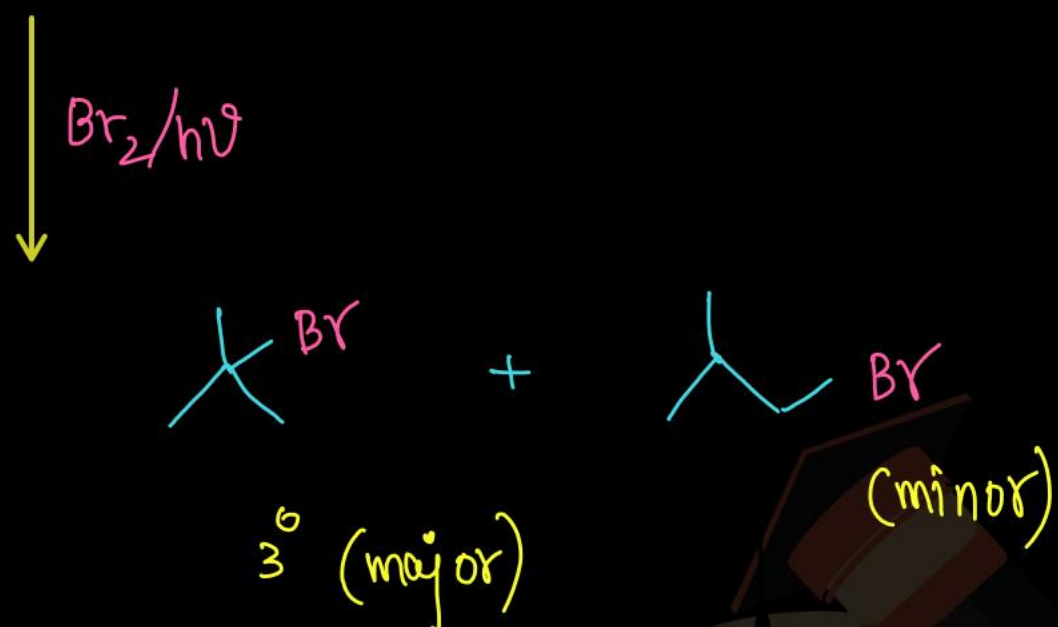
Practice:



$$n_1 r_1 = 9 \times 1 = 9 \quad \checkmark$$

$$n_2 r_2 = 0$$

$$n_3 r_3 = 1 \times 5 = 5$$



* ii)



$$n_1 r_1 = 9 \times 1 = 9 \quad (\times)$$

$$n_2 r_2 = 2 \times 3.8 = 7.6$$

$$n_3 r_3 = 1 \times 5 = 5$$

both are 1° ,
but not similar

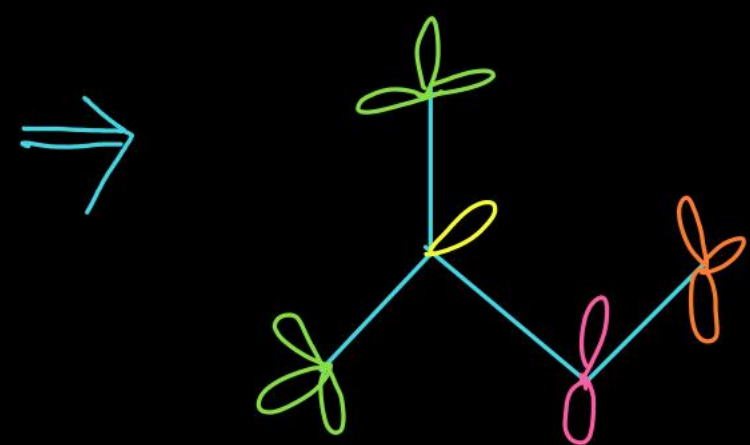


$$n'_1 = 6$$

$$n'_1 r_1 = 6$$

$$n_1 = 3$$

$$n_1 r_1 = 3$$



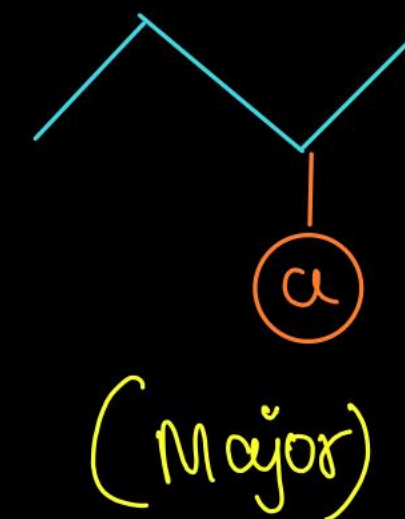
$$n_p = 6 \times 1 = 6$$

$$n_p' = 3 \times 1 = 3$$

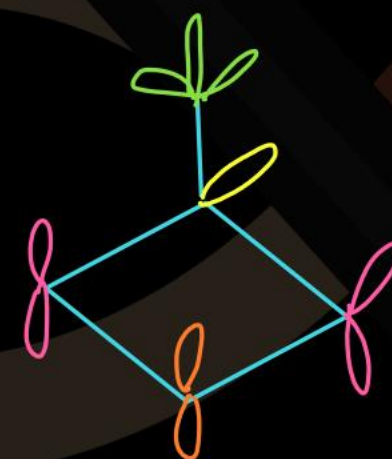
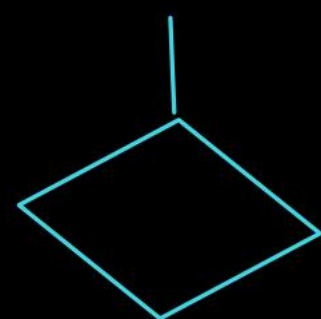
$$n_s = 2 \times 3.8 = 7.6 \quad \checkmark$$

$$n_t = 1 \times 5 = 5$$

⇒ 2° is major



iii)

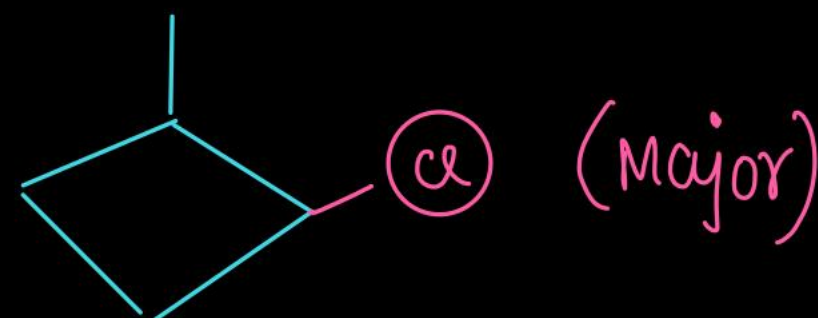
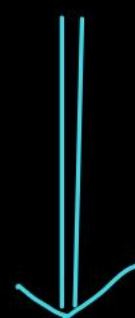


$$n_p = 3 \times 1 = 3$$

$$n_s = 4 \times 3.8 = 15.2 \quad \checkmark$$

$$n_s' = 2 \times 3.8 = 7.6$$

$$n_t = 1 \times 5 = 5$$



* Iodination :-

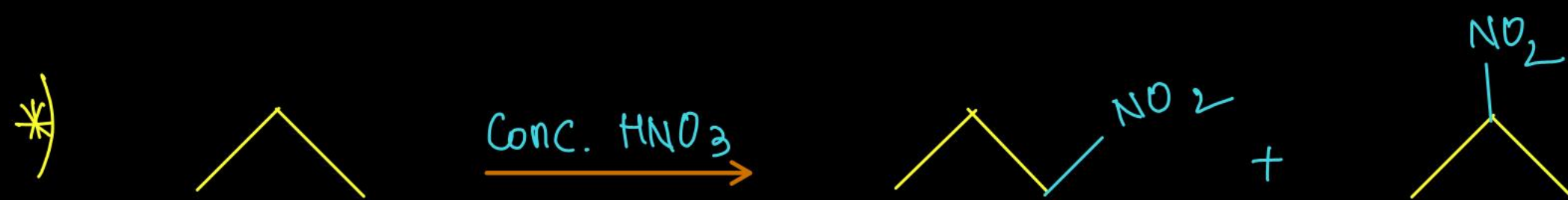
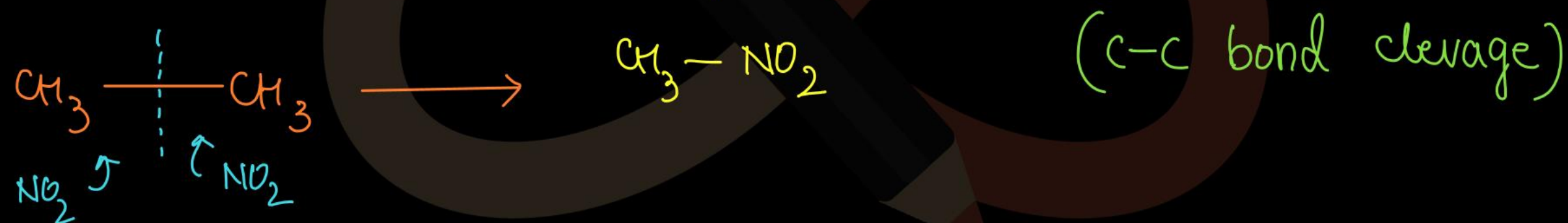
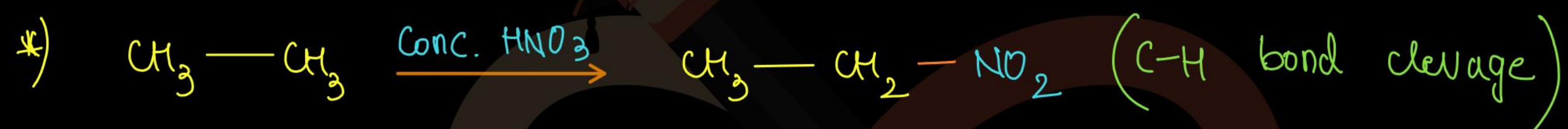
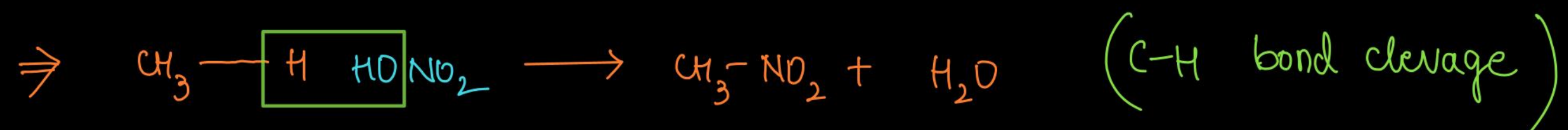
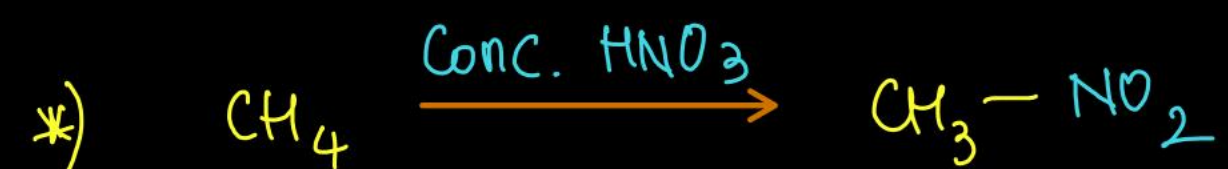


but HI is Good RA

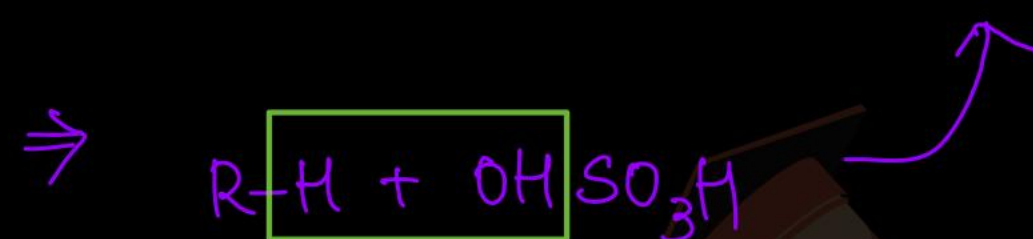
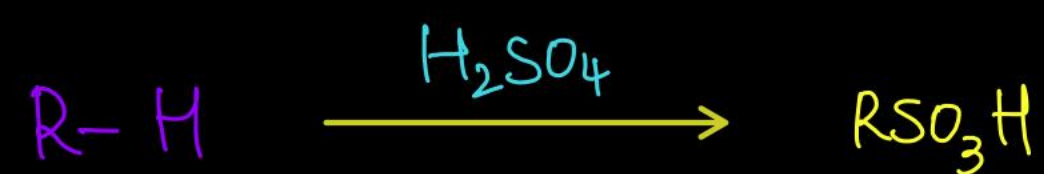
Hence, we use O.A



② Nitration (vapour phase) :-



③ Sulphonation :- Conc H_2SO_4 / fuming H_2SO_4 / oleum $\text{H}_2\text{S}_2\text{O}_7$

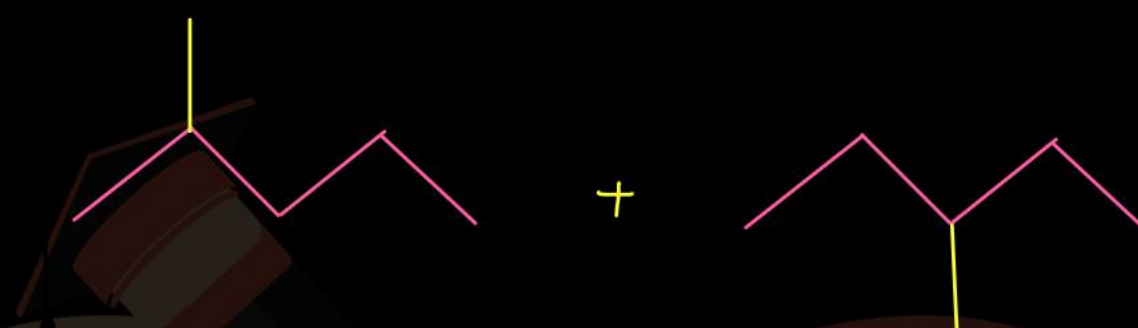
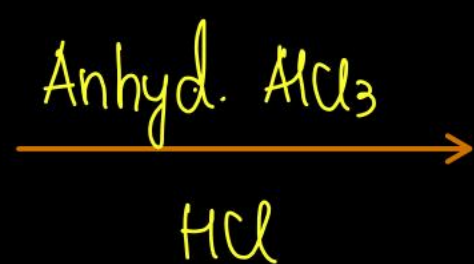
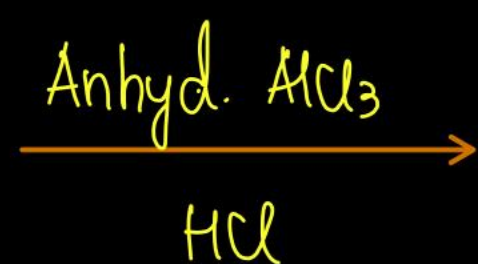


Imp points :-

- 1) rate of rxn $\propto$ Stability of Free Radical
- 2) rxn is feasible when alkane has ≥ 6 Carbons
- 3) In case of lower alkanes, it is feasible only when 3°H is present



④ Isomerisation :-



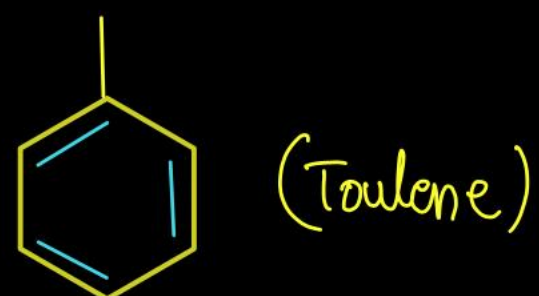
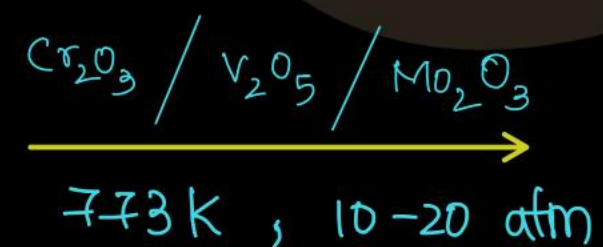
*) Branching ↑

⇒ octane no. ↑

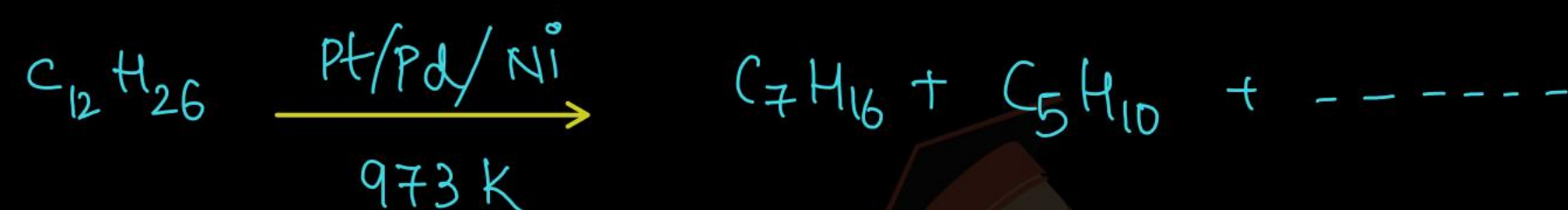
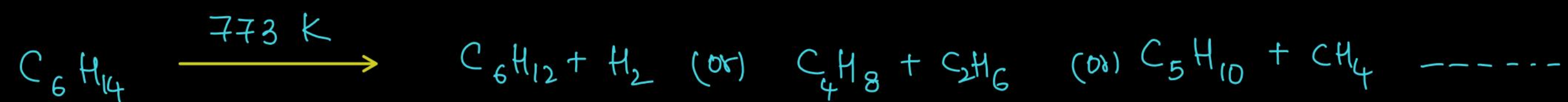
⇒ fuel eff ↑

⇒ knocking ↓

⑤ Aromatisation



⑥ Pyrolysis (cracking) :- (Heating in absence of air)

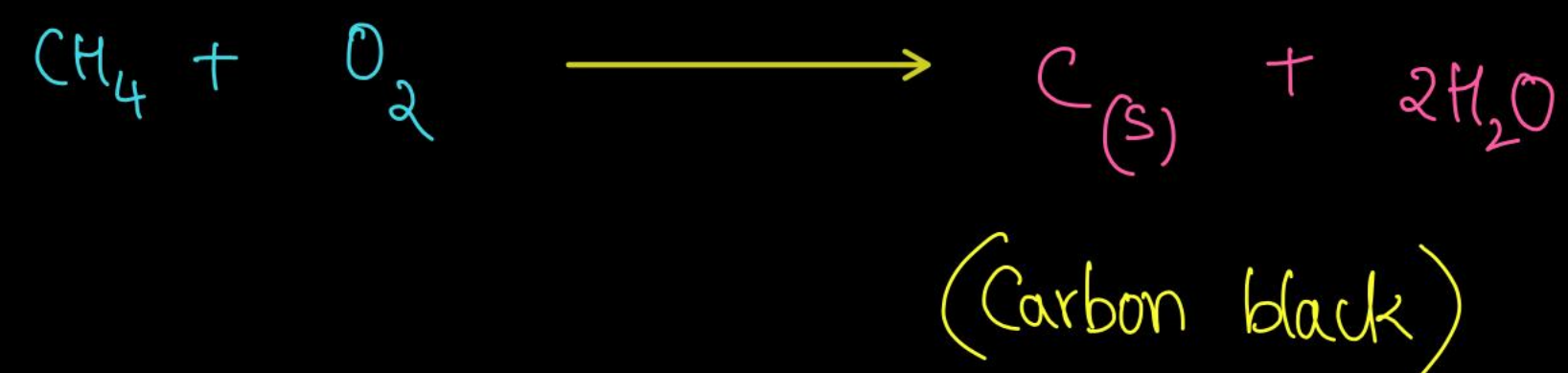


⑦ Combustion :-

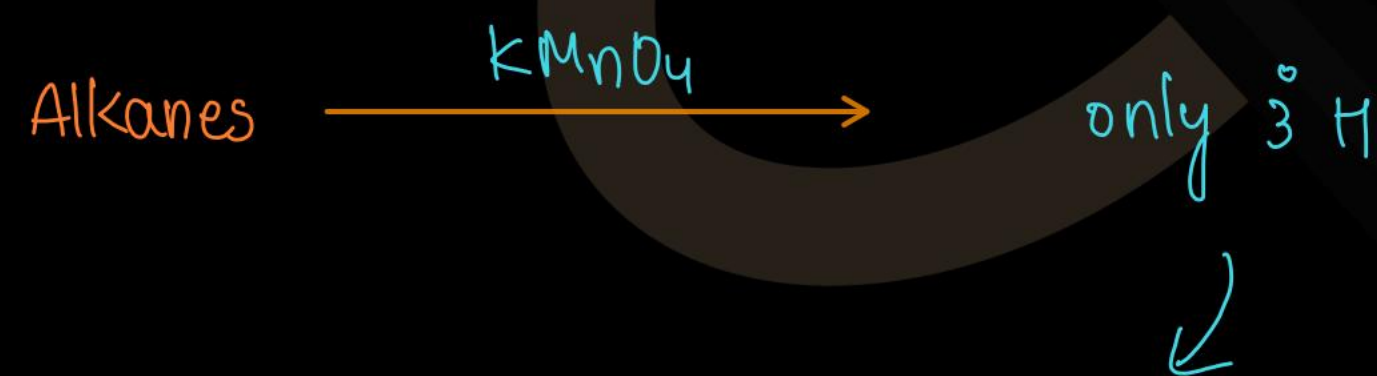
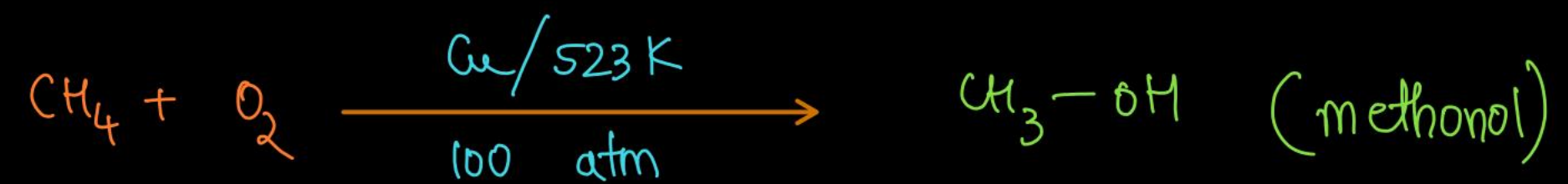
a) Complete Combustion



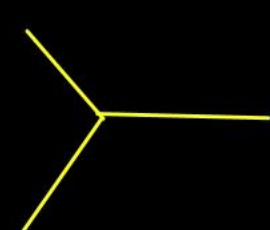
b) Incomplete Combustion



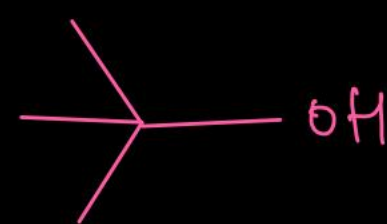
⑧ Controlled Oxidation



Imp *)



isobutane



(tertiary butyl alcohol)

⑨ Rxn with Steam :-



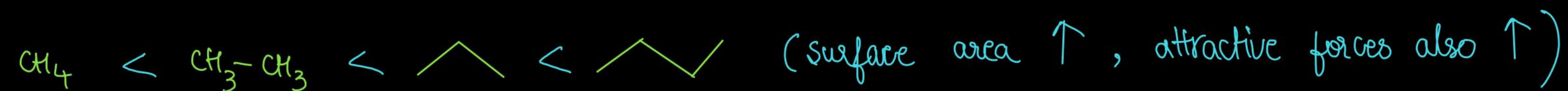
CO + H₂
→ water gas / syn gas

Physical properties :-

- ① Alkanes are mostly non-polar
- ② They possess weak van der Waals forces
- ③ $\text{C}_1 - \text{C}_4$ } gases
 $\text{C}_5 - \text{C}_{17}$ } liq
 $\text{C}_{18} \geq$ } solids
- ④ Colourless, odourless
- ⑤ Hydrophobic in nature (water repellent)

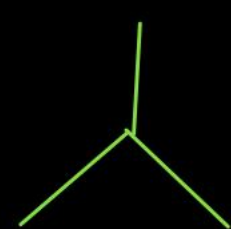
⑥ Boiling point

a) As no. of C $\uparrow$, BP $\uparrow$



b) In isomeric alkanes,

as branching increases $\uparrow$, BP $\downarrow$



$<$



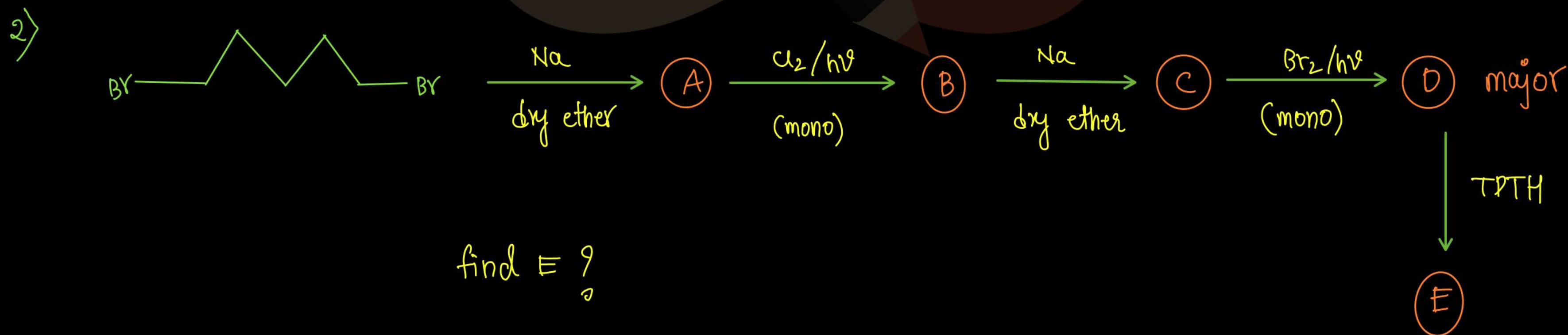
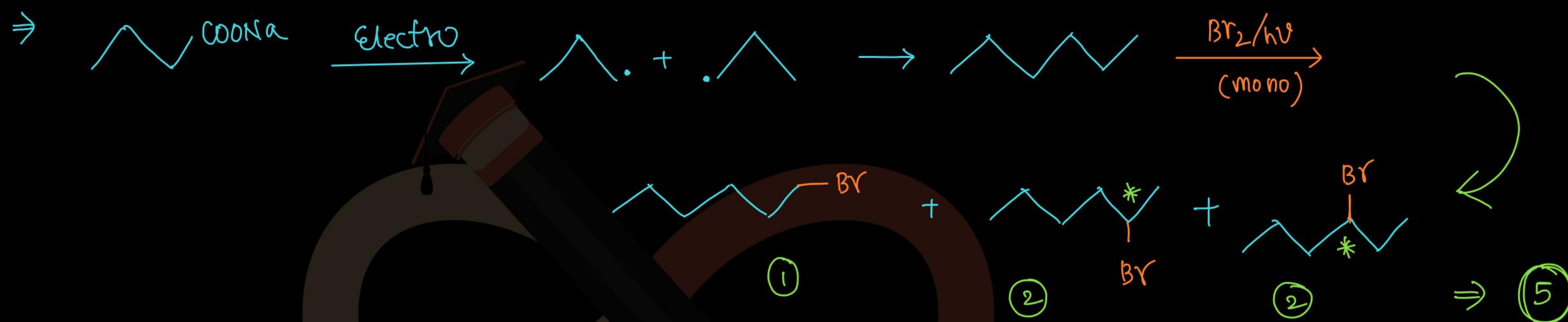
(surface area $\downarrow \therefore$ BP $\downarrow$)

⑦ MP $\rightarrow$ irregular

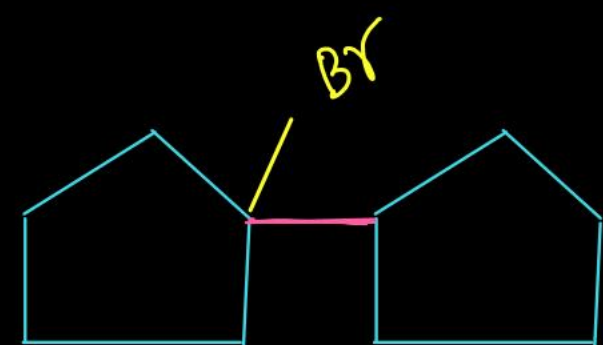
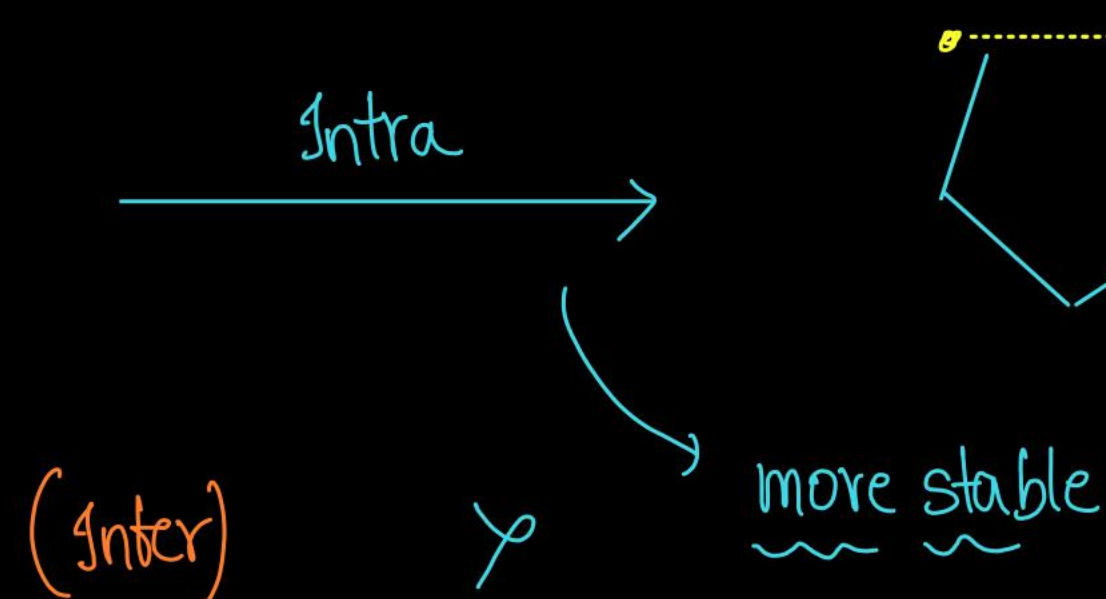
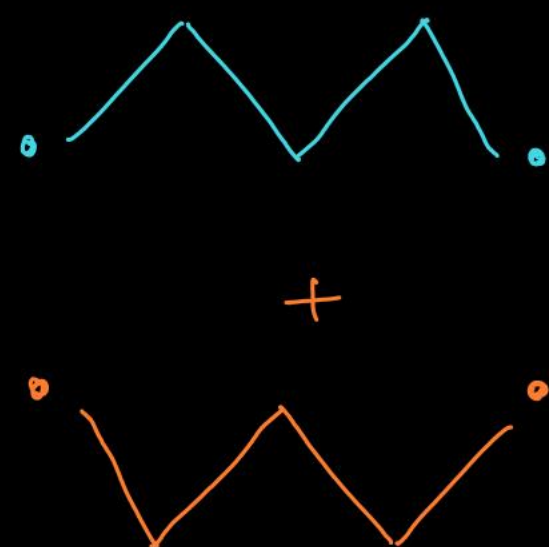
⑧ Heat of Combustion $\propto$ No. of C-atoms $\propto \frac{1}{\text{branching}}$

⑨ Calorific value $\propto \frac{\text{No. of H-atoms}}{\text{No. of C-atoms}}$

Practice:



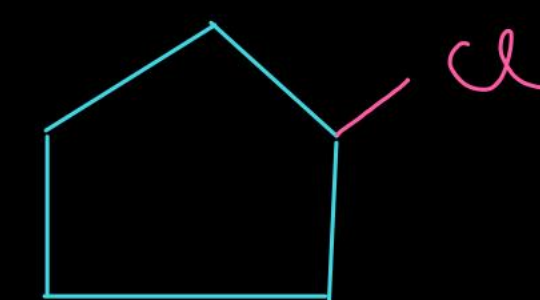
⇒



(D) 3° (major)

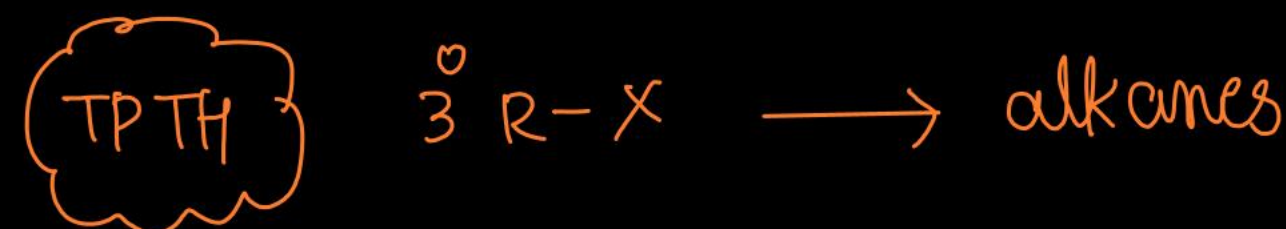


(C)

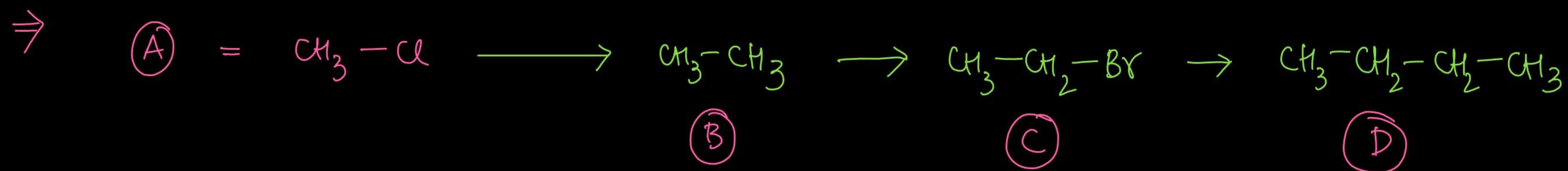
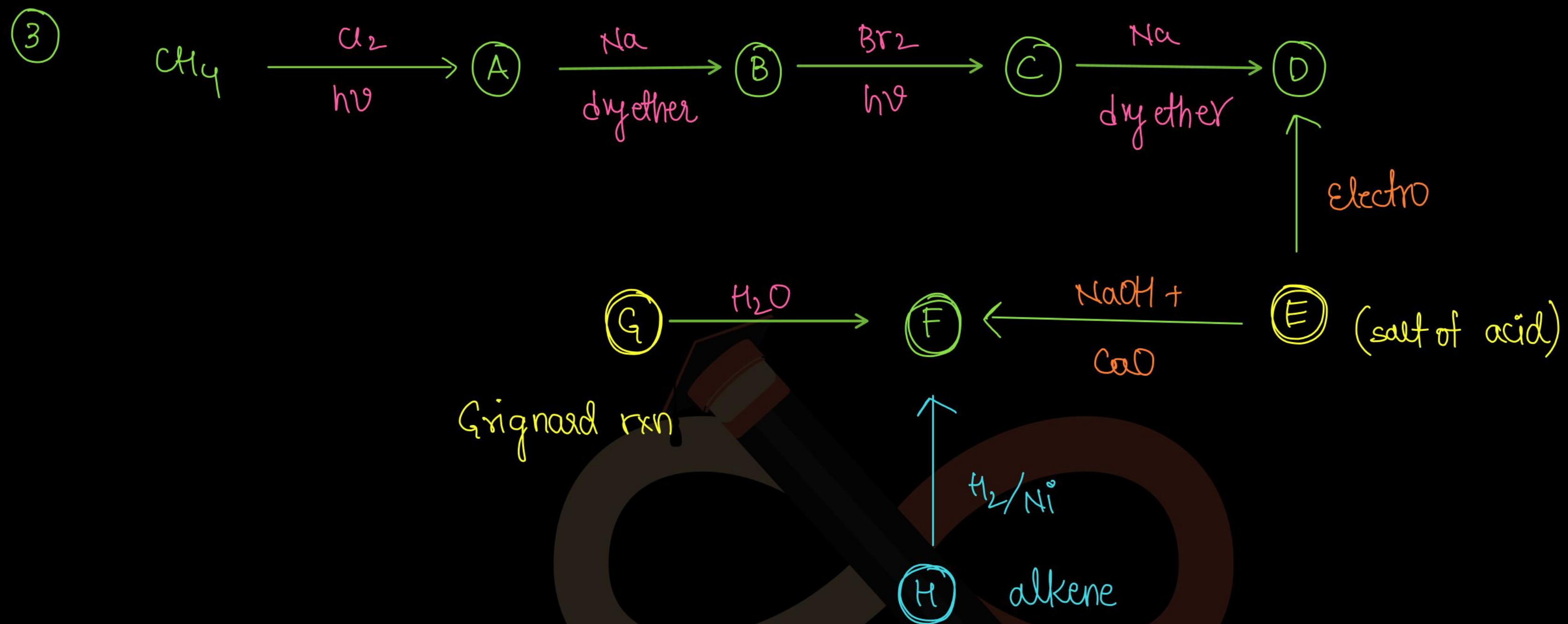


(B)

TPTH

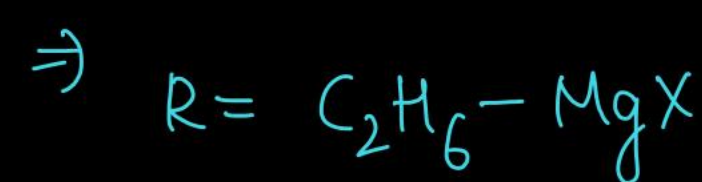


(E)





$\text{NaOH} + \text{CaO}$



$\textcircled{G}$

$\textcircled{F}$

H_2/Ni

