PRACHAND NEET

ONE SHOT

Organic Chemistry

Hydrocarbon

By – Sudhanshu Sir

Topics *to be covered*

1. Alkanes
2. Alkenes
3. Alkynes
4. Benzene

PRACHAND SERIES

TELEGRAM CHANNEL

@PW_YAKEENDROPPER

Basics of Organic chemistry

1. Nomenclature.
2. Isomerism.
3. G.O.C

15. Practical organic chemistry

Reactions →

1. Alkane
2. Alkene
3. Alkyne
4. Benzene

} Hydrocarbon

5. R–X
6. 

} Haloalkanes & Haloarenes

7. R–OH
8. 
9. R–O–R

} alcohol, phenol & ether

10. $R-\overset{O}{\overset{\|}{C}}-H$
11. $R-\overset{O}{\overset{\|}{C}}-R$
12. $R-\overset{O}{\overset{\|}{C}}-OH$

} Aldehyde, ketone & Carboxylic acid.

13. Amines → Amines
14. Biomolecules.

Introduction

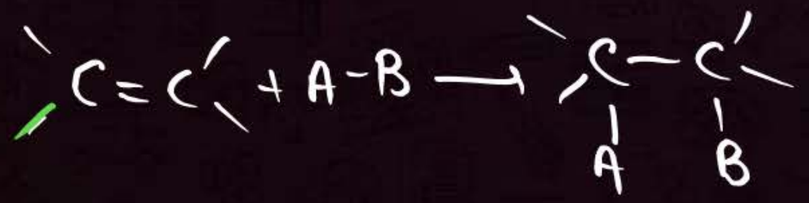
$$\underbrace{CH_4}_{\text{Reactant}} + \underbrace{Cl_2}_{\text{Reagent}} \xrightarrow{\text{UV light}} \underbrace{CH_3Cl}_{\text{Product}} + \underbrace{HCl}_{\text{byproduct}}$$

UV light → Catalyst / Medium

Types of Reactions

① Addition Reaction → Alkane ✗ → unsaturated compounds (D.O.U > 0)

- → D.O.U decreases
- → weak bond dissociates
- → Strong bond formation
- → entropy decrease



(2) Substitution Reaction

$$R-H + X_2 \longrightarrow R-X + HX$$

→ D.O.U = same

Substitution → ESR, NSR

Addition → EAR, NAR

elimination → E^1, E^2, E^{1CB}

(3) Elimination Rxn

$$CH_2(H)-CH_2(X) \xrightarrow[KOH]{alcoholic} CH_2=CH_2 + HX$$

→ D.O.U ↑

→ entropy ↑

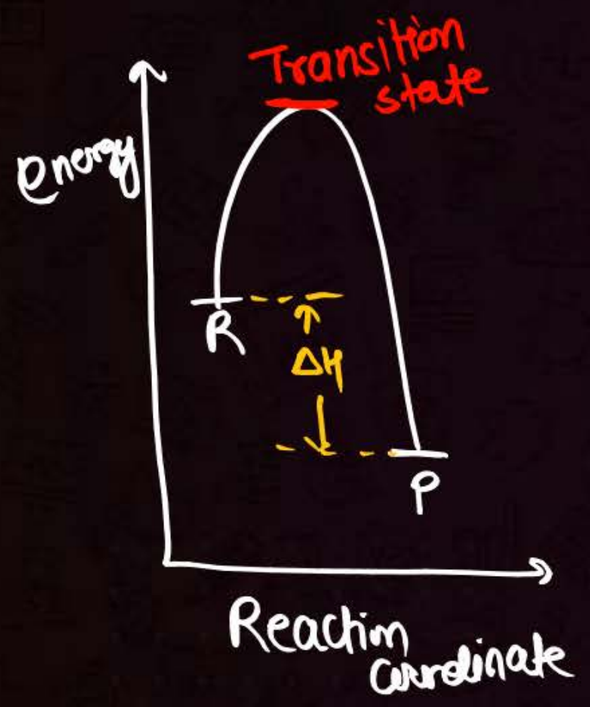
(4) Rearrangement Reaction

$$ABC \longrightarrow BAC$$

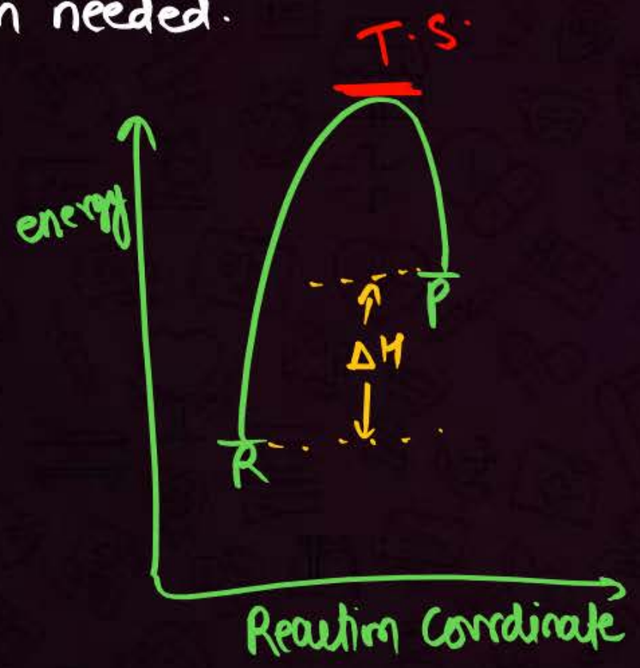
Another Classification

Elementary/Single step Reaction

- rxn occurs in one step.
- no mechanism needed.



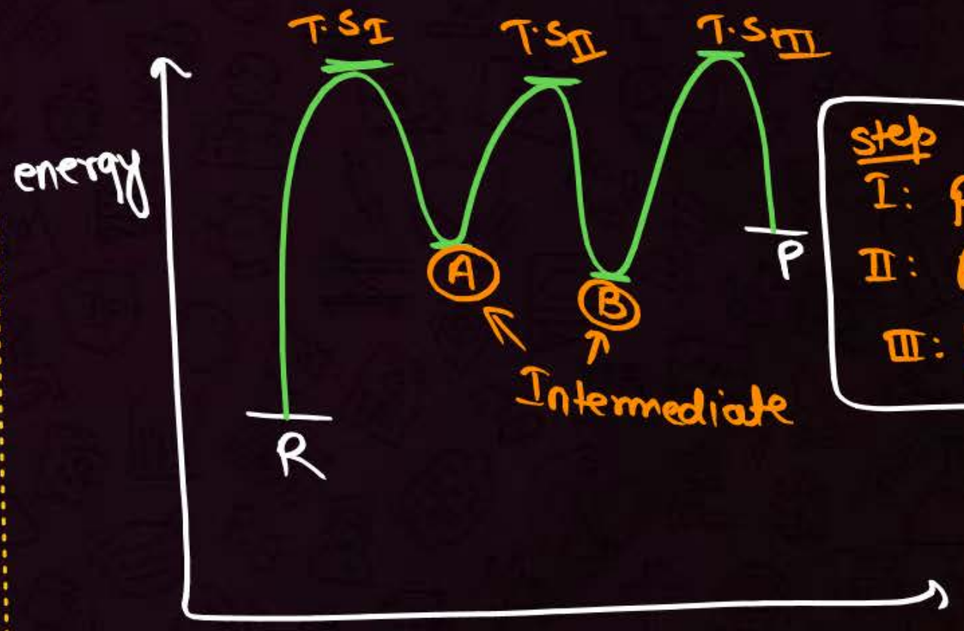
$\Delta H = H_P - H_R < 0$ (exothermic)



$\Delta H = H_P - H_R > 0$ (endothermic)

Complex/Multi-step Reaction

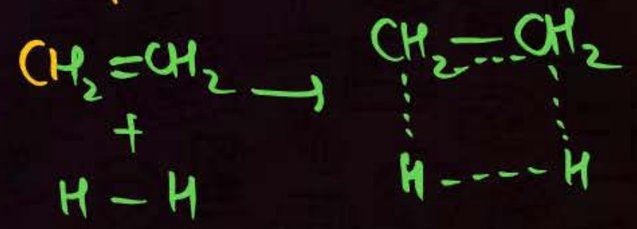
- rxn occurs in more than one step.
- mechanism needed.
- slowest step / High E_a step = Rate determining step.



step	
I:	$R \longrightarrow A$
II:	$A \longrightarrow B$
III:	$B \longrightarrow P$

For 'n' step
- Transition state = n
- Intermediate = (n-1)

Intermediate	Transition State
⇒ For 'n' step rxn ⇒ Intermediate = (n-1)	⇒ For 'n' step rxn, T.S = n
⇒ less energy	⇒ More energy
⇒ more stability	⇒ less stability.
⇒ separable from reaction mixture or Rearrangement can be possible	⇒ Cannot be separated from reaction mixture or Cannot undergo rearrangement.
⇒ obeys rules of chemical bonding.	⇒ donot obey rules of chemical bonding
⇒ formed after first step and consumed till last step.	⇒ formed in each step and consumed.



Intermediates

① Carbocation — $-\overset{|}{\underset{|}{C}}\oplus$

② Carbanion — $-\overset{|}{\underset{|}{C}}\ominus$

→ charged
→ Diamagnetic

③ Carbon free radical — $-\overset{|}{\underset{|}{C}}\cdot$

→ odd $e^{\ominus}$
→ paramagnetic
→ neutral

④ Benzyne 

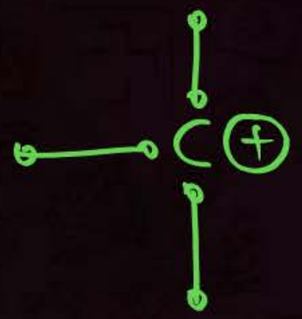
⑤ Nitrene $:\ddot{N}-$

⑥ Carbene $\ddot{C}<$

neutral

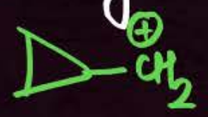
NOTE → out of 6 intermediates, only one intermediate $C^{\oplus}$ undergoes rearrangement for gain of stability.

Carbocation



Stability of $C^{\oplus}$

↳ Dancing Resonance > Aromaticity > α-effect > +M > +H > +I



antiaromaticity < −M < −H < −I

→ Hybridisation = sp^2

→ 3σ bond

→ Zero lone pair

→ $e^{\ominus}$ deficient species

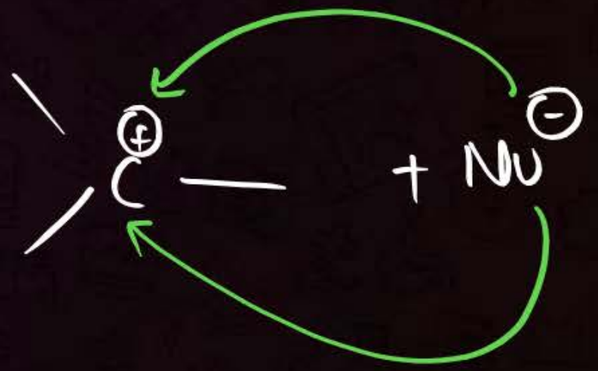
→ electrophile → when attack

→ Diamagnetic

→ vacant 2p orbital

→ trigonal planar

→ sterochemistry → if it has chiral centre, then it will give equal mixture of (d) & (l)



Rearrangement of Carbocation

→ Rearrangement is possible when stability increases.

→ stability remains same
stability decreases } No rearrangement of $C^{\oplus}$

$C^{\oplus}$ Rearrangement

1. Hydride shift
2. phenyl shift
3. Alkyl shift
4. Ring contraction
5. Ring expansion

Hydride Shift

$C-H > C-D > C-T$

$CH_3-CH_2-\overset{\oplus}{C}H_2 \longrightarrow CH_3-\overset{\oplus}{C}H-CH_3$

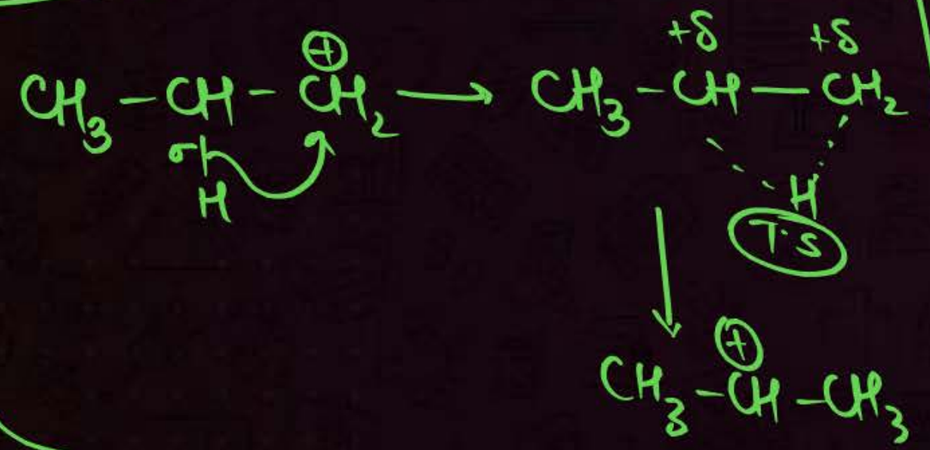
(2α-H) (6α-H)

- stability increases.
- Rearrangement possible

$\overset{\oplus}{C}H_2-CH_2-CH_3$

(2α-H)

Mechanism



C—H
C—D
C—T

Bond length decrease
Bond energy increase.

$CH_3-CH(CH_3)-CH_2-CH_2-\overset{\oplus}{C}H_2$ (2α-H)

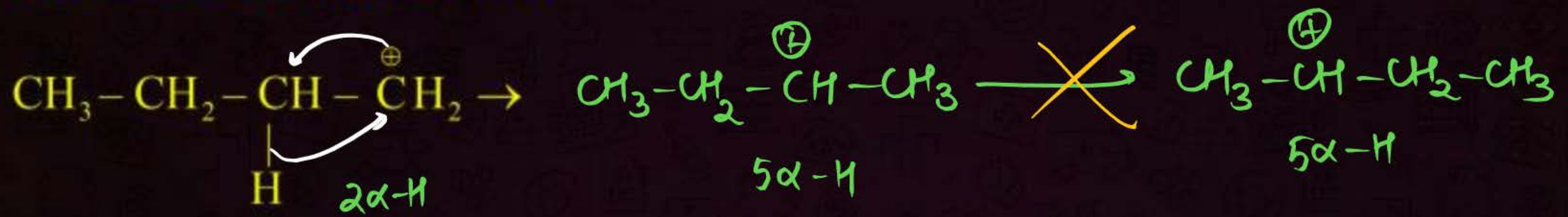
↓

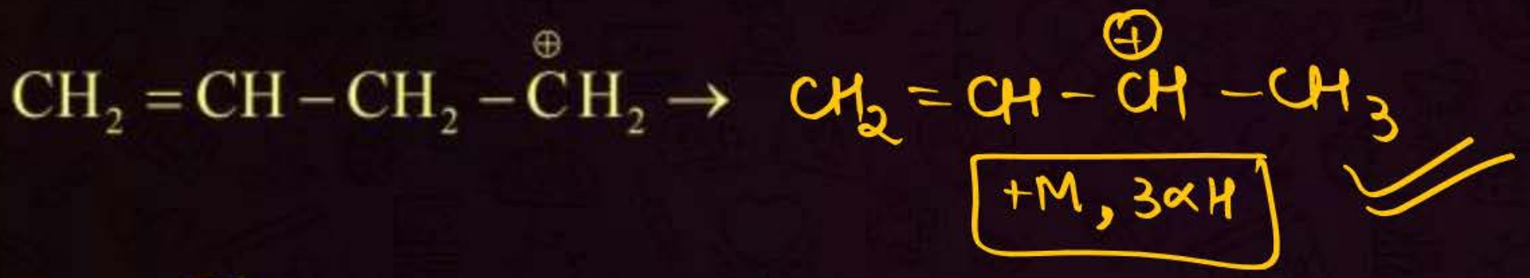
$CH_3-CH(CH_3)-CH_2-\overset{\oplus}{C}H-CH_3$ (5α-H)

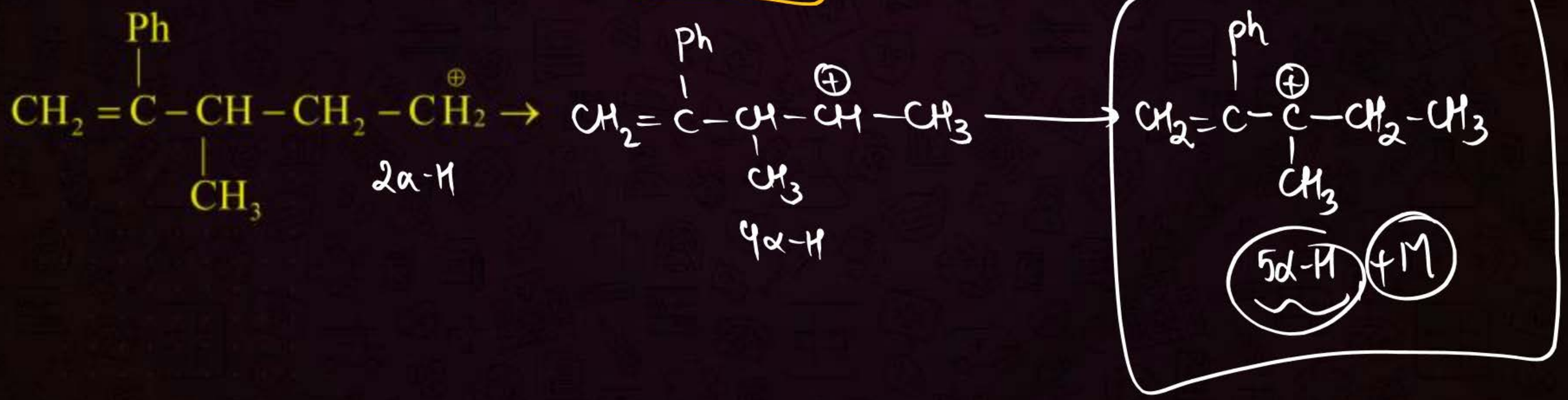
↓

$CH_3-CH(CH_3)-\overset{\oplus}{C}H-CH_2-CH_3$ (3α-H)

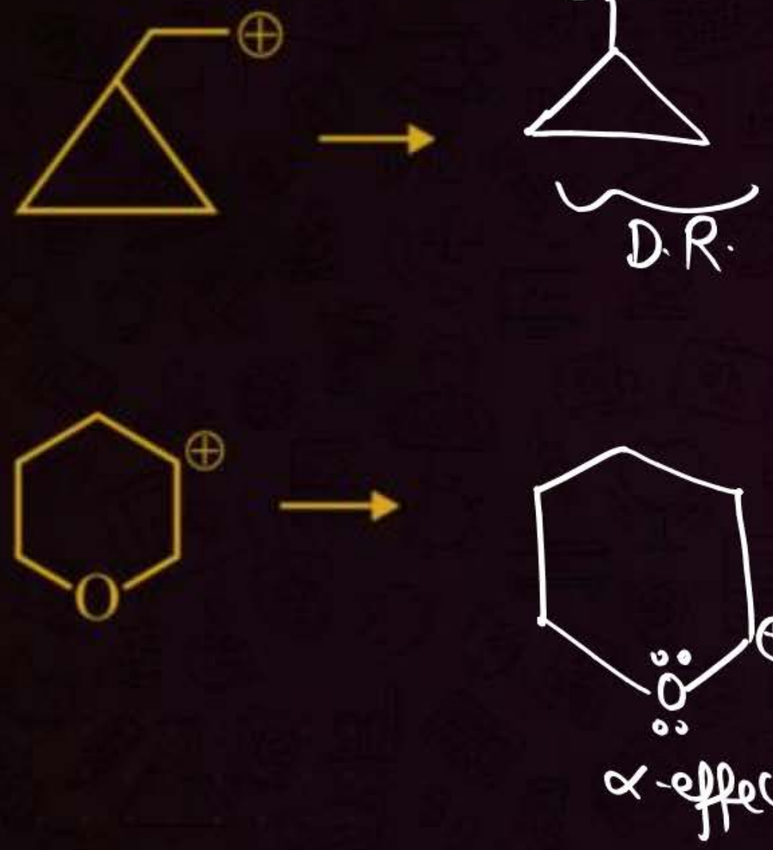
Questions of Hydride Shift

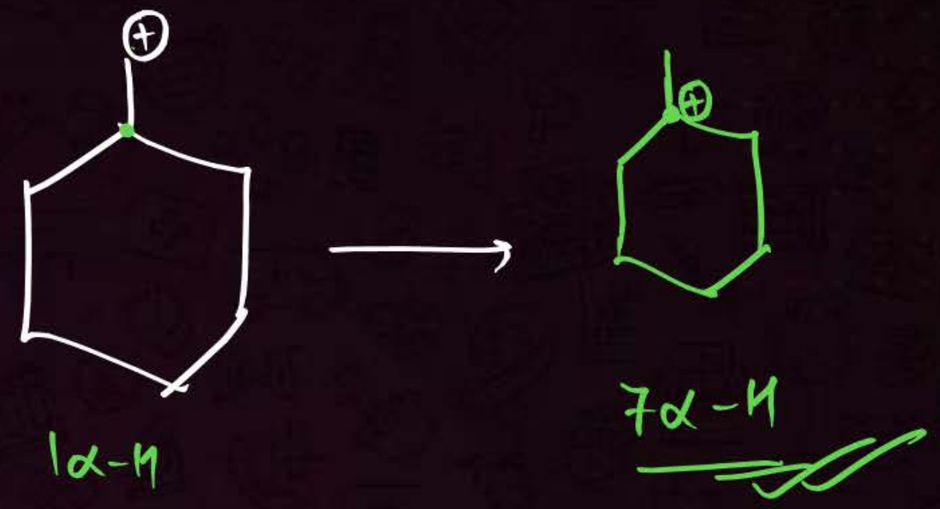




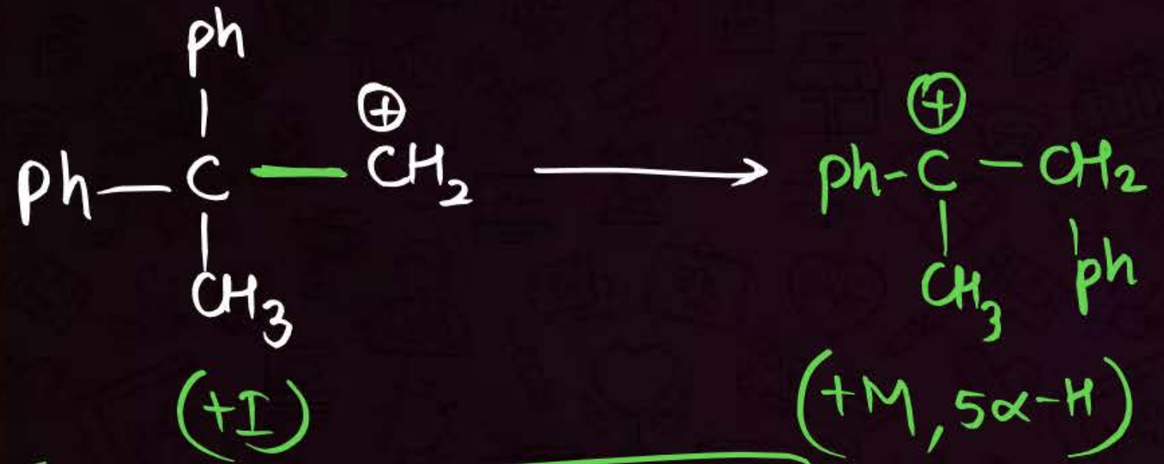


QUESTION



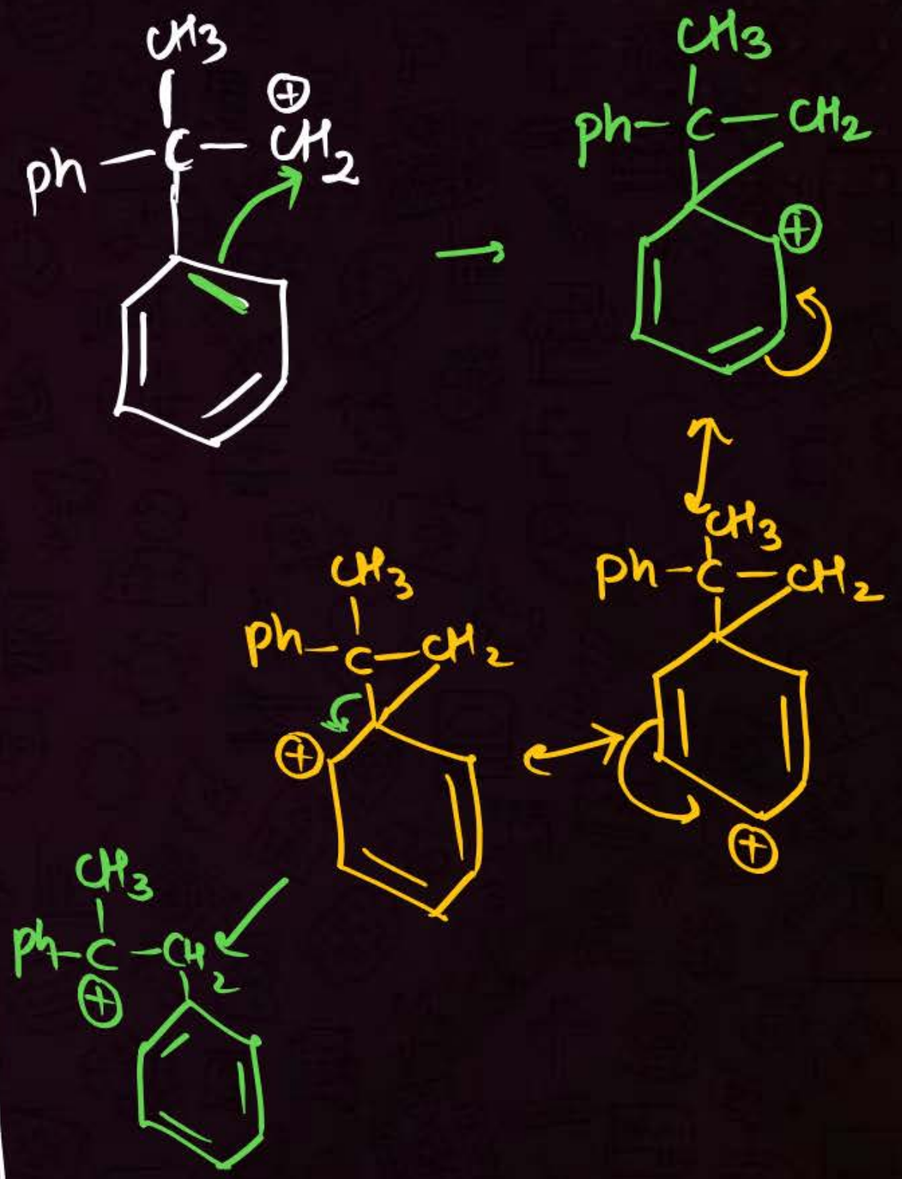


Phenyl Shift

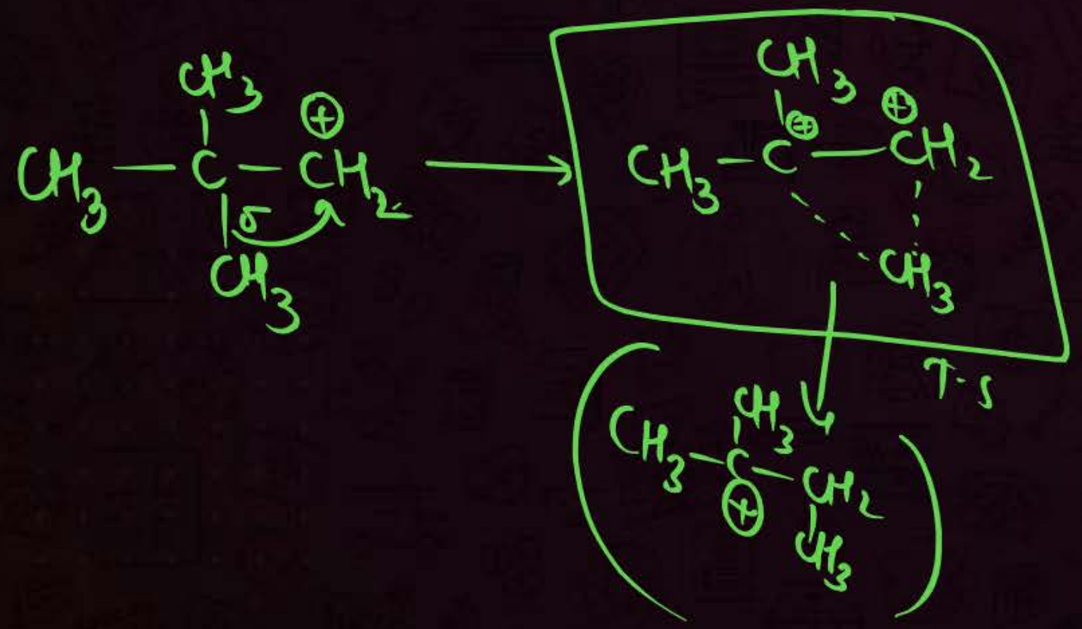


⇒ phenyl shift > alkyl shift

1. π-bond breaking up
2. Resonance stabilised
3. No partial double in T.S



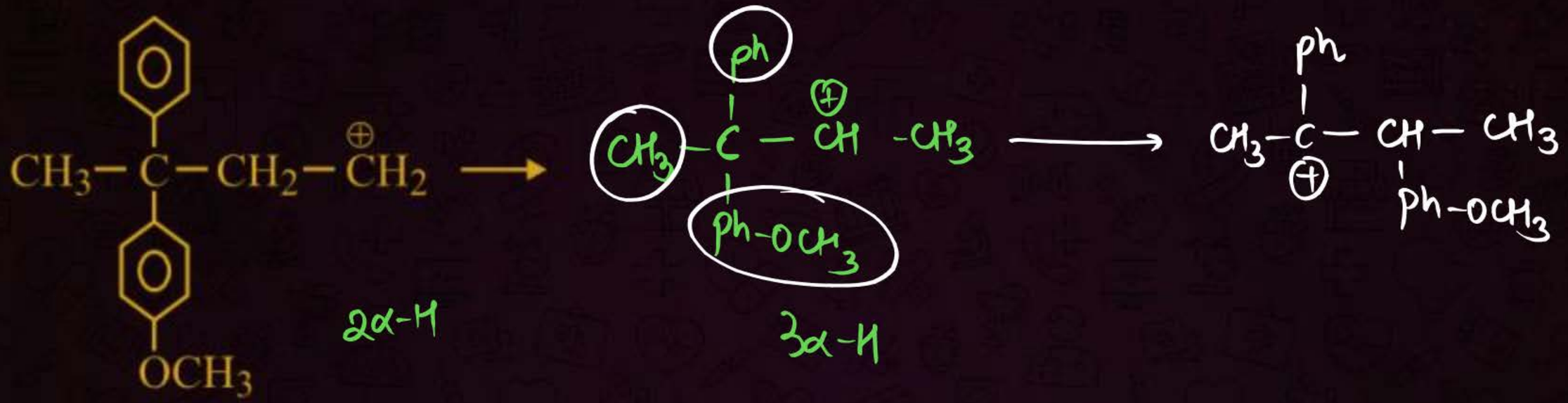
Alkyl Shift

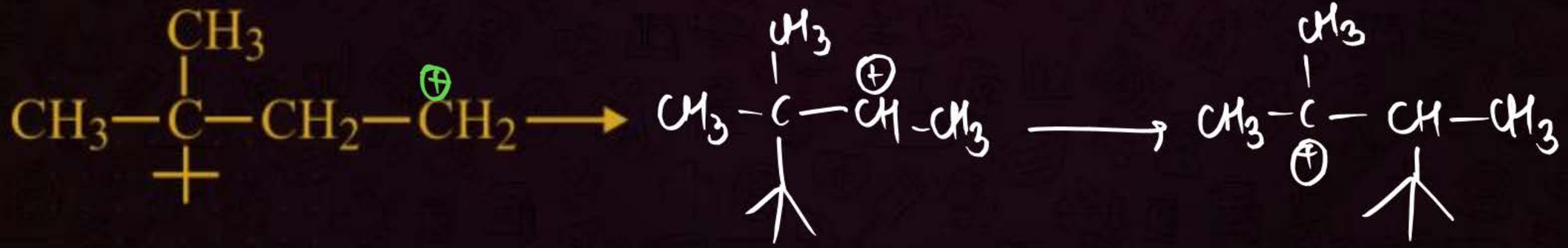


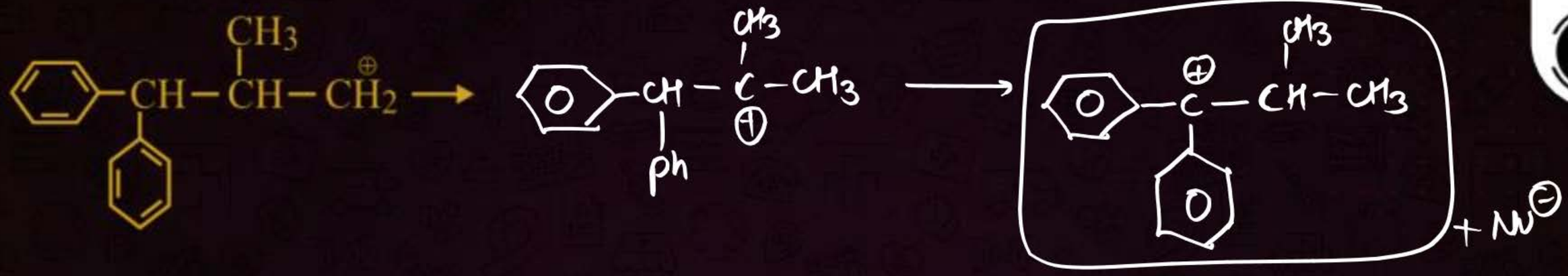
Rearrangement of $C^{\oplus}$

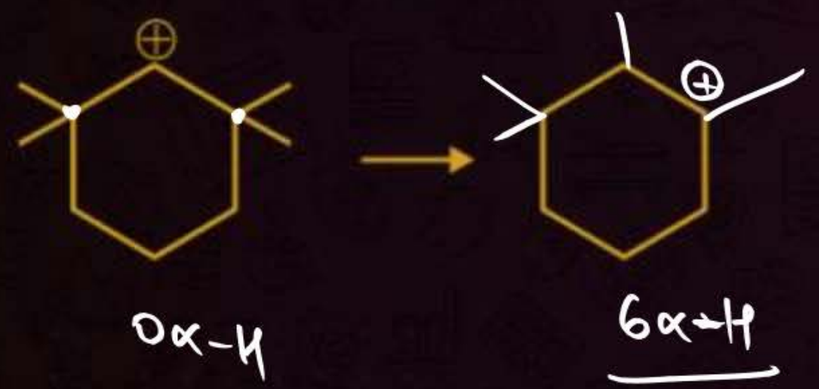
1. H > D > T
2. ph-EDG > ph > ph-EWG
3. 3° > 2° > 1° alkyl shift

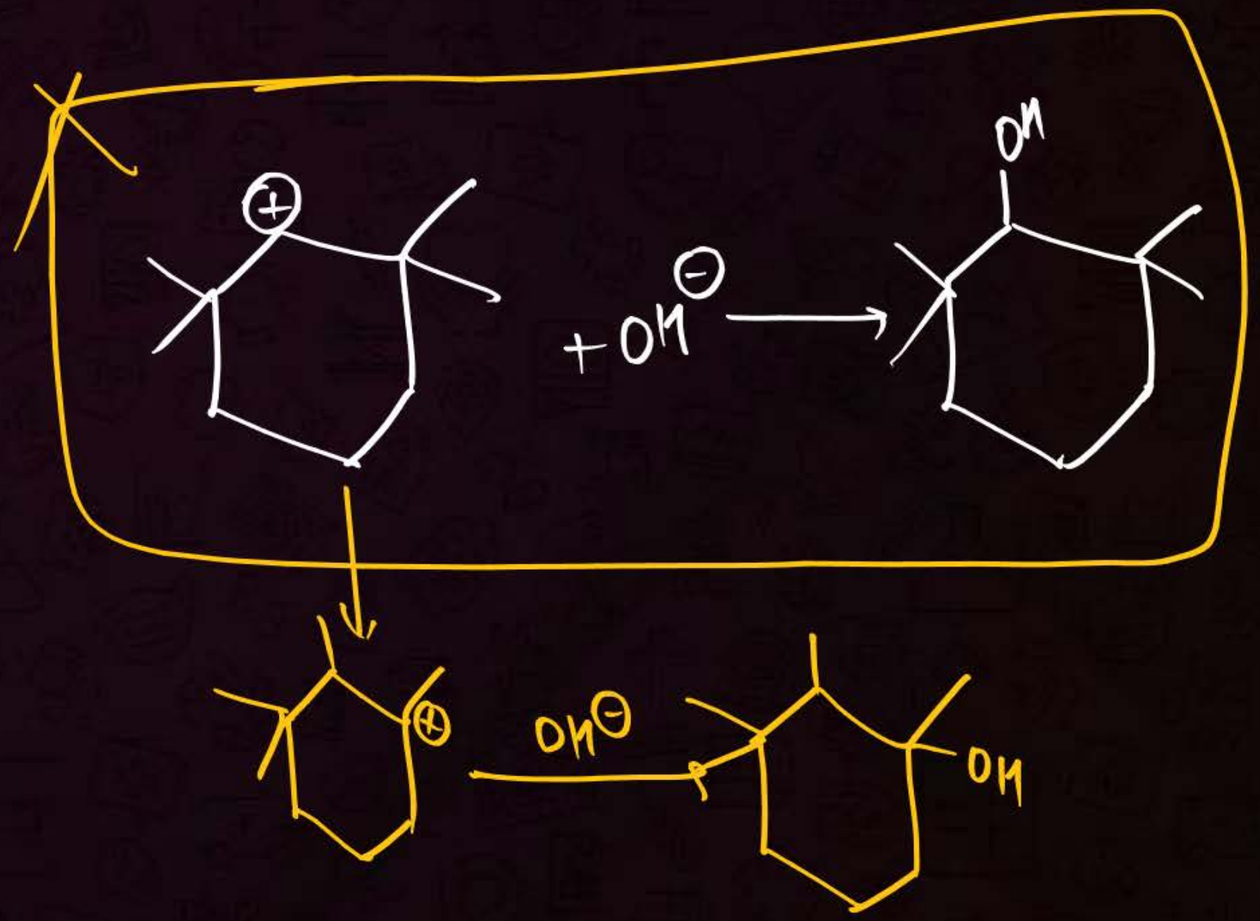
Questions on Rearrangement:



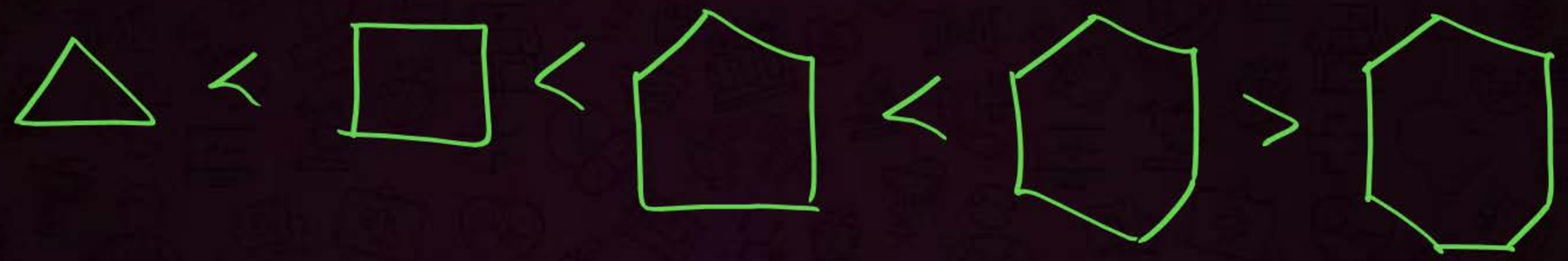



CH3
CH–CH–CH2
CH3
CH–C–CH3
Ph
CH3
C–CH–CH3
+ Nu⊖


0α-H
6α-H


+ OH⊖
OH
OH⊖
OH

Ring expansion and Ring Contraction



Stability order (Bayer's strain theory)

Steps to do in Ring expansion / Ring contraction

Step-I → Do numbering from the 'c' having (+ve) charge as (1).

Step-II → Join 1st & 3rd c bond

Step-III → Break 2nd & 3rd c bond.

Step-IV → (+ve) Charge on 2nd c.

⊕ Rearrangement order

R.E / R.C > H > D > T > ph

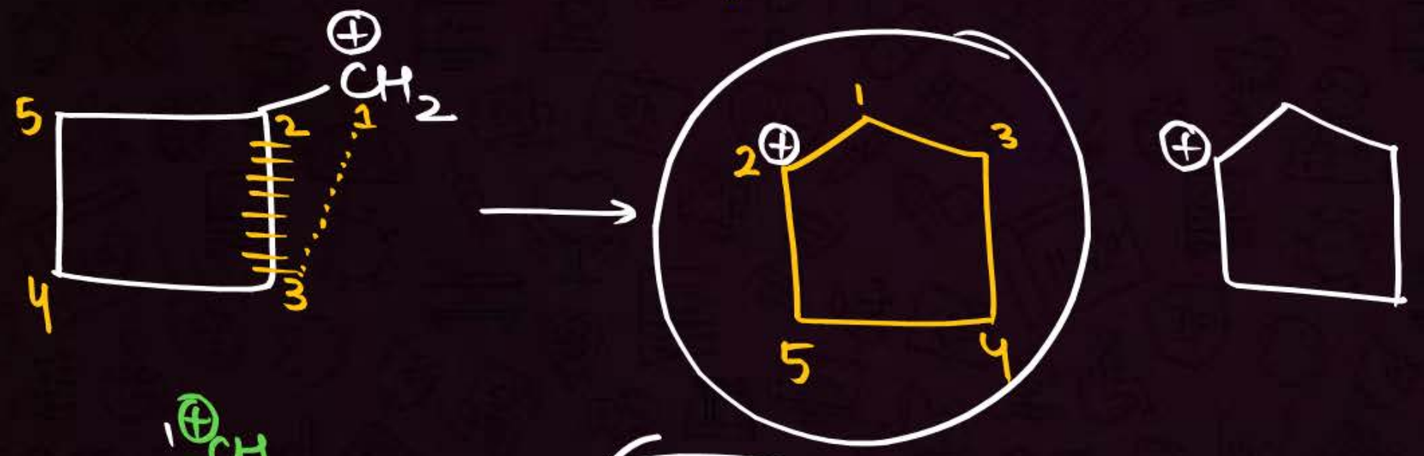
V

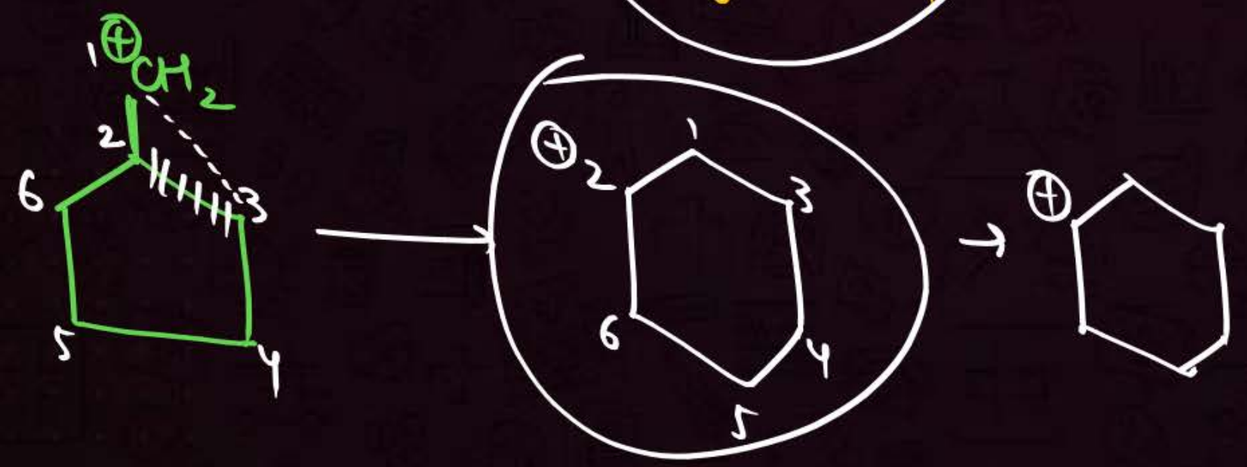
3° > 2° > 1°

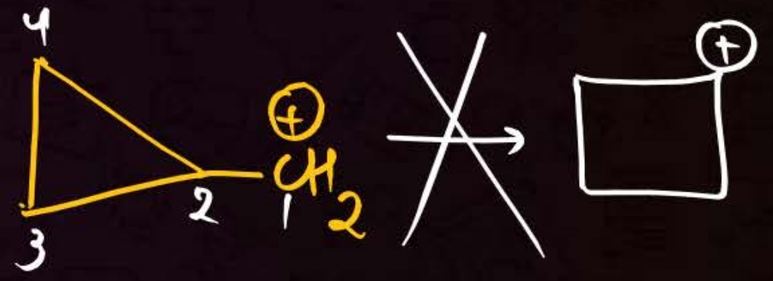
(4) Ring Expansion

- 4 membered ring → 5
- 5 membered ring → 6

Condition ⇒ +ve charge must be outside the ring.



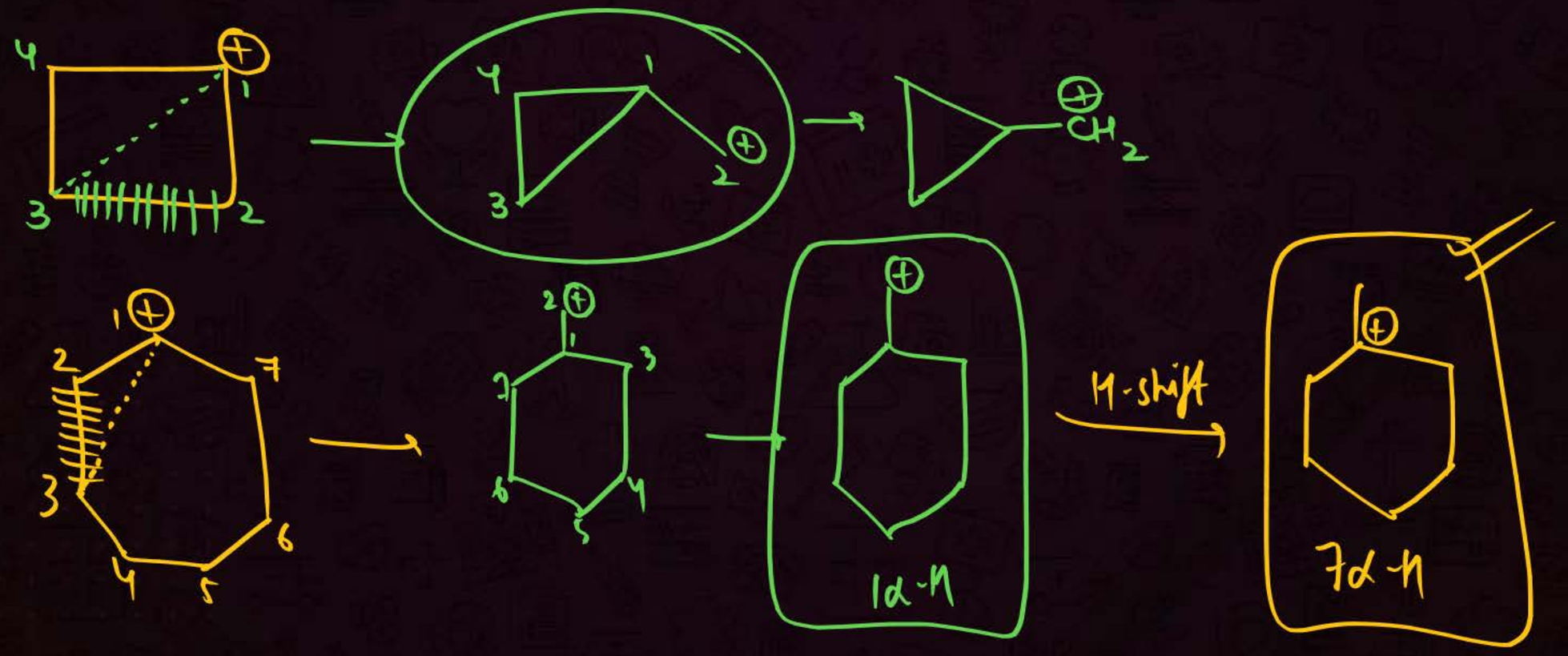




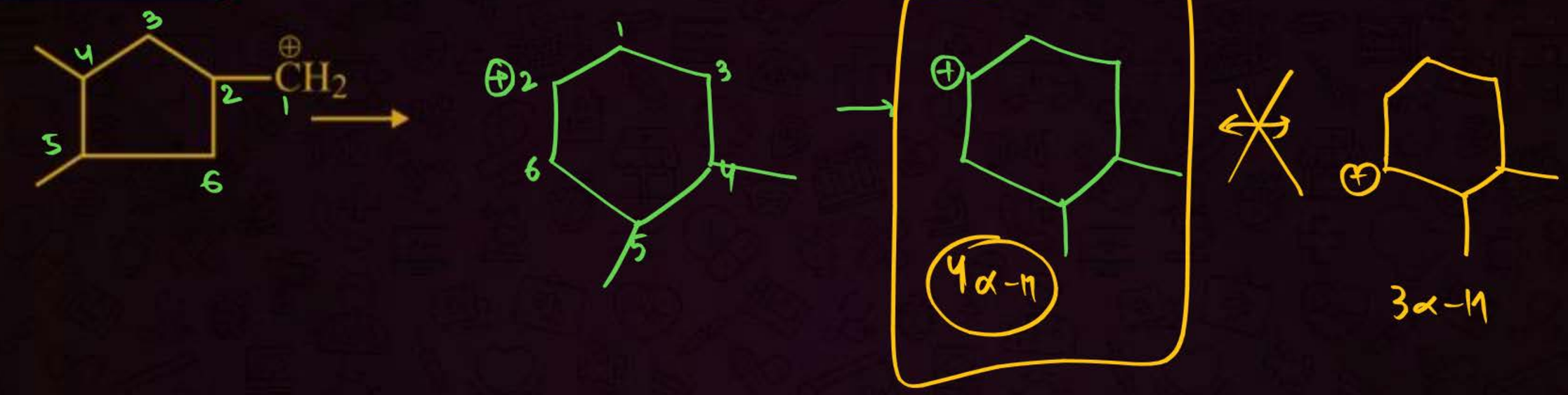
Dancing Resonance

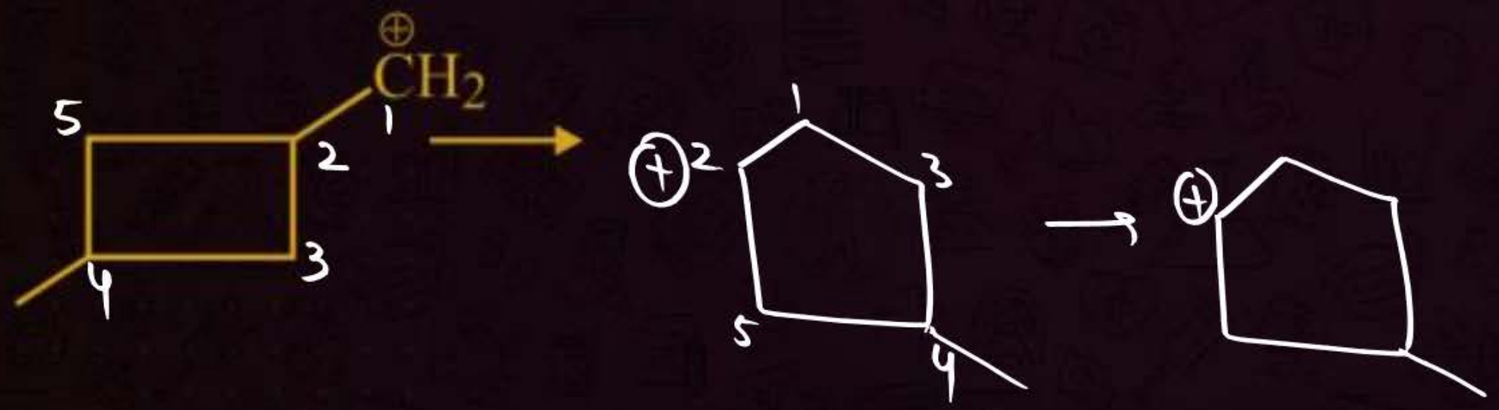
(5) Ring Contraction

- 4 membered ring → 3
- 7 membered ring → 6
- Condition ⇒ charge (+ve) on the ring.

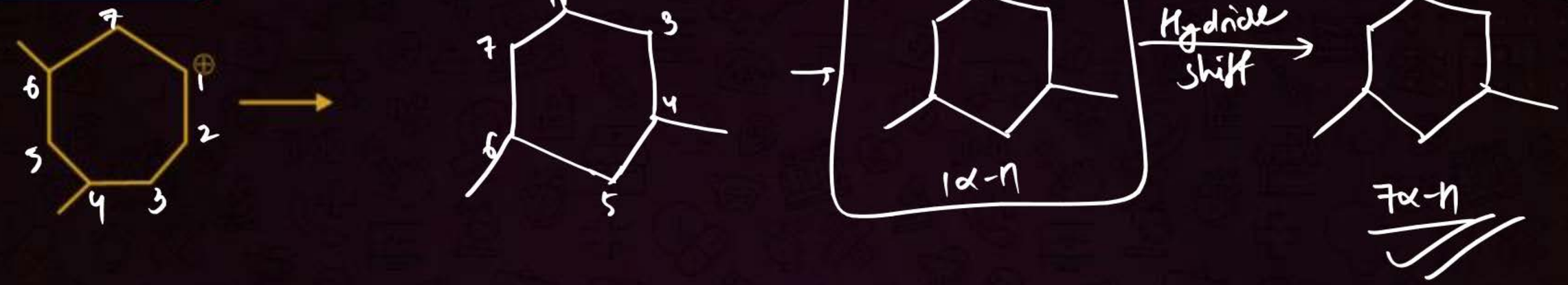


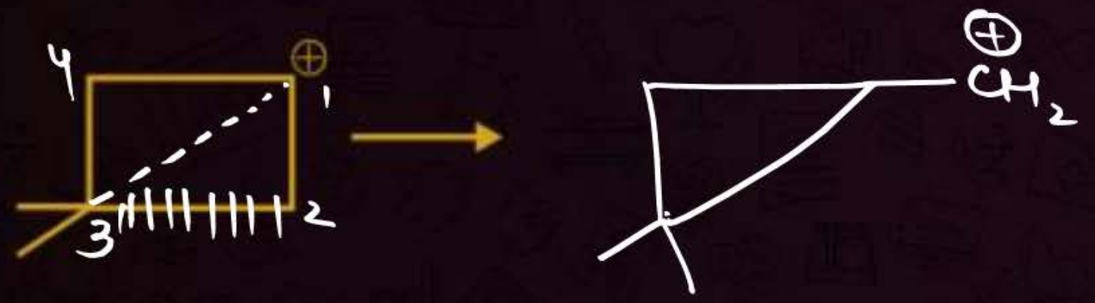
QUESTION





QUESTION





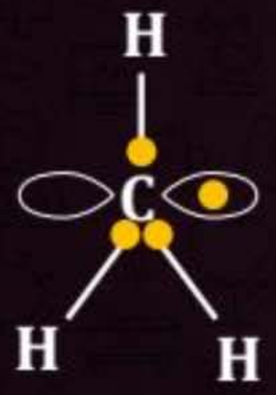
Free Radical

sunlight or hν
T > 500°C or 773K
peroxide catalyst

Formation (Homolytic Fission)

$$A - B \xrightarrow[T > 500°C,\ Peroxide]{h\nu\ or} A^{\circ} + B^{\circ}$$

$CH_3 \longrightarrow$



- 3 σ bonds, Neutral
- Zero lone pair
- Odd e^- molecule

- $e^- \rightarrow$ p-orbital
- Highly unstable
- Highly reactive
- sp^2 hybridized → Trigonal Planar
- Paramagnetic, $\mu \neq 0$
- $E^{\oplus}$, e^- deficient, 7 e^-)

Natural Tendencies of F.R.

Free radical → odd $e^{\ominus}$

→ highly unstable.

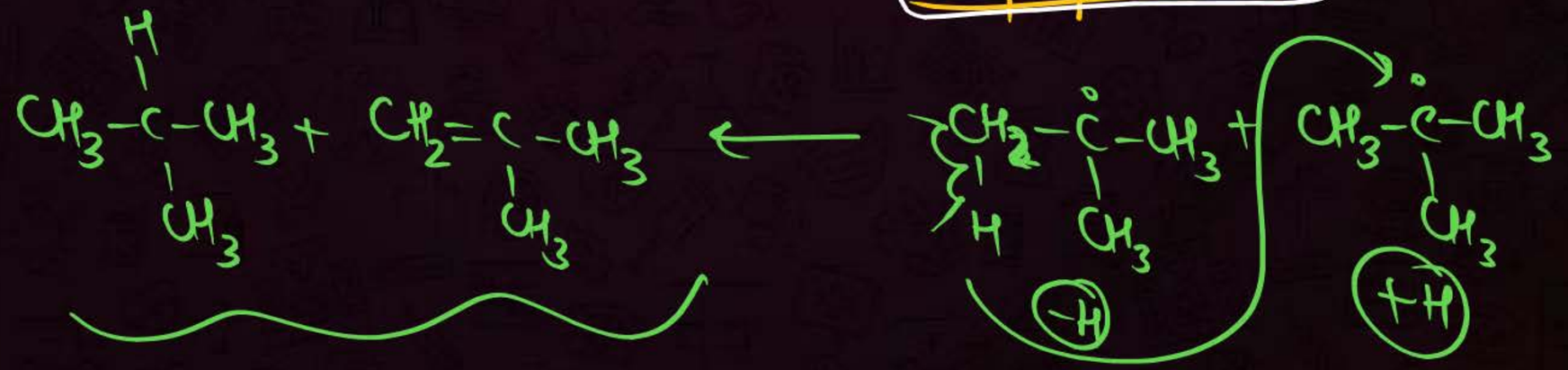
→ unpaired $e^{\ominus}$

→ high tendency to pair up

→ Combination

$$A^{\circ} + A^{\circ} \longrightarrow A-A$$

→ Disproportionation

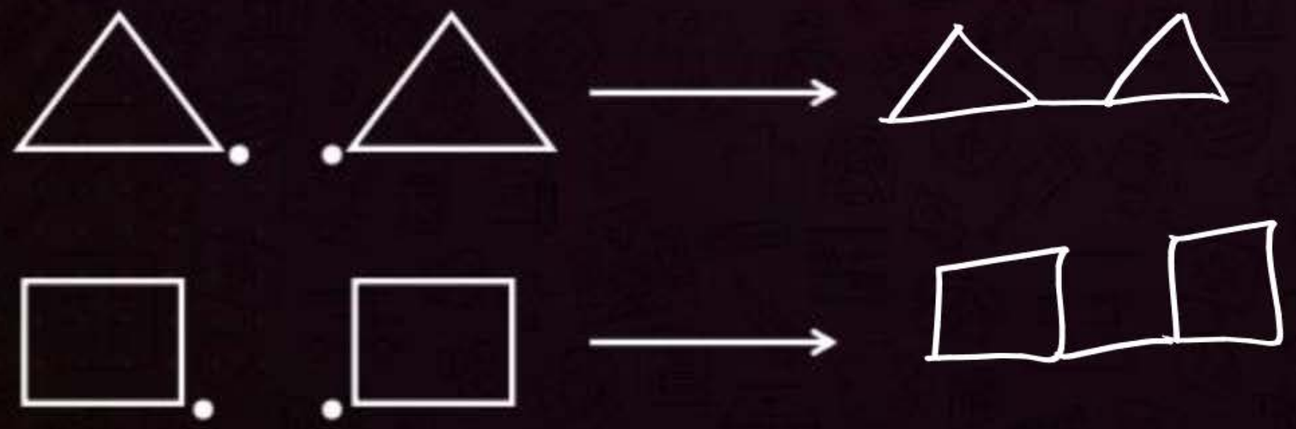


1. Combination:

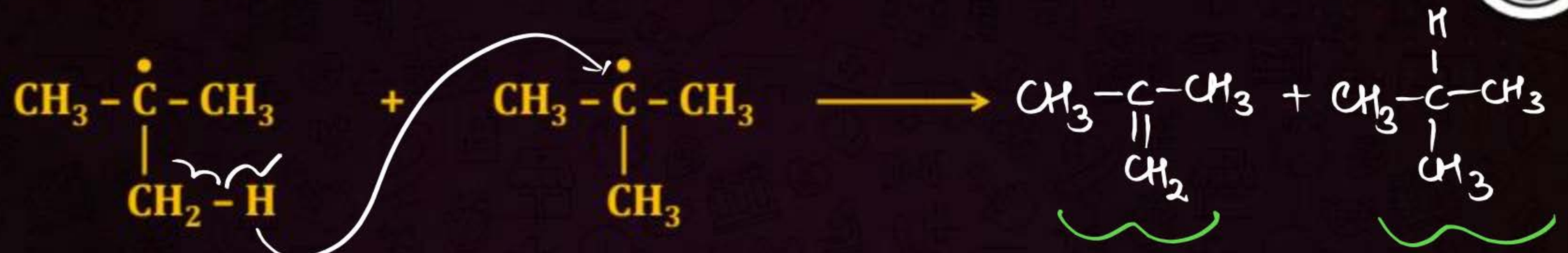
$$\dot{H} + \dot{H} \longrightarrow H-H$$

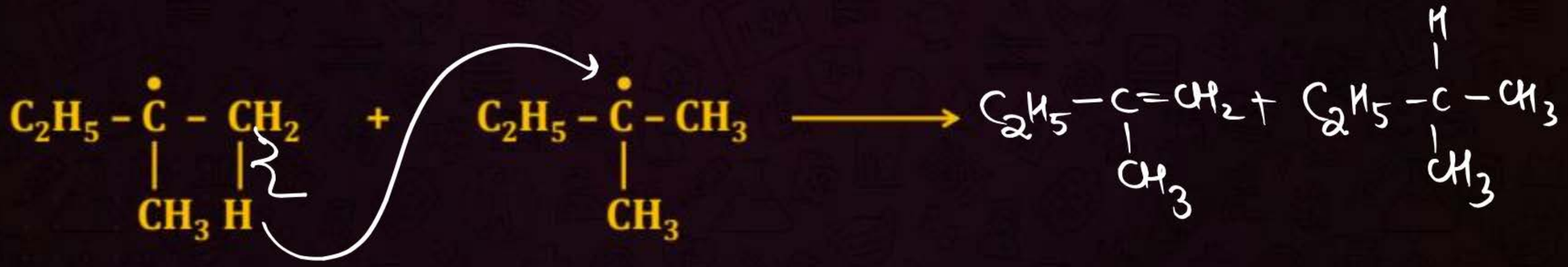
$$\dot{CH_3} + \dot{CH_3} \longrightarrow CH_3-CH_3$$

$$\dot{CH_3} + \dot{H} \longrightarrow CH_3-H$$



2. Disproportionation:





Note:

Degree

1° F.R → always Combination.

2° F.R → can show (C) + (D)

3° F.R → only shows (D)

if there is no option of disproportionation, consider combination product of all F.R

Temperature

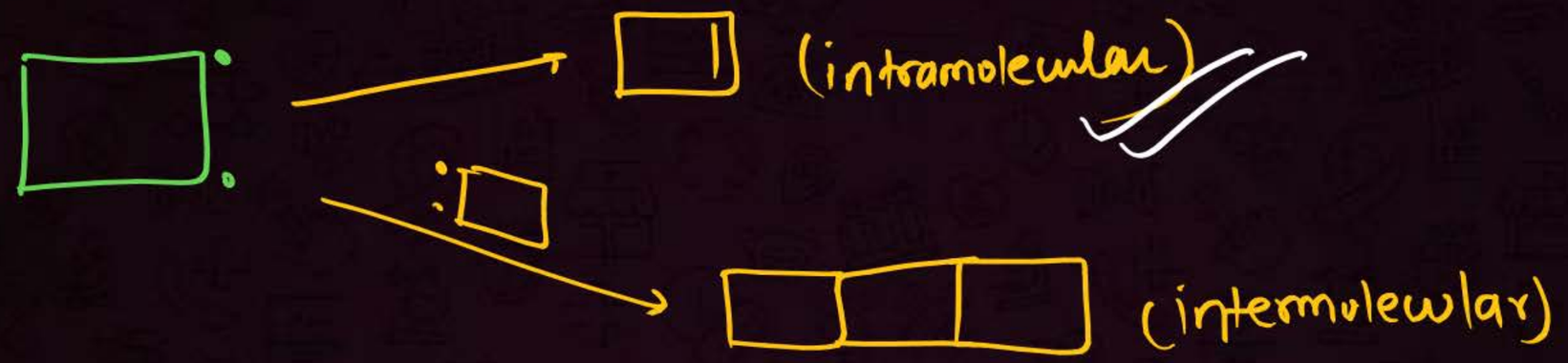
1° → (C)

2° → (C) low temp.

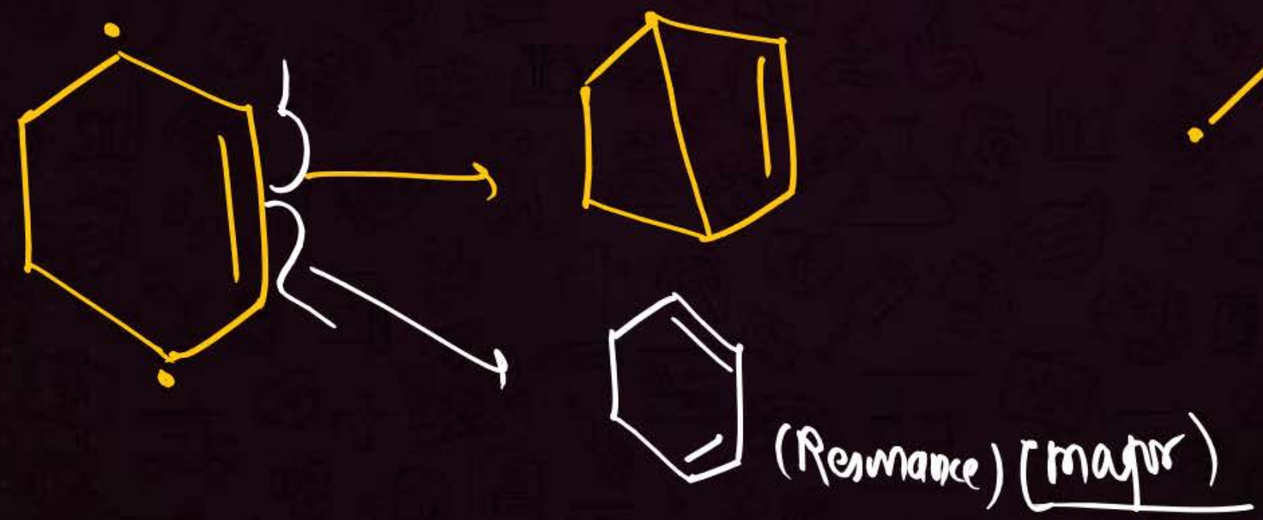
2° → (D) High temp.

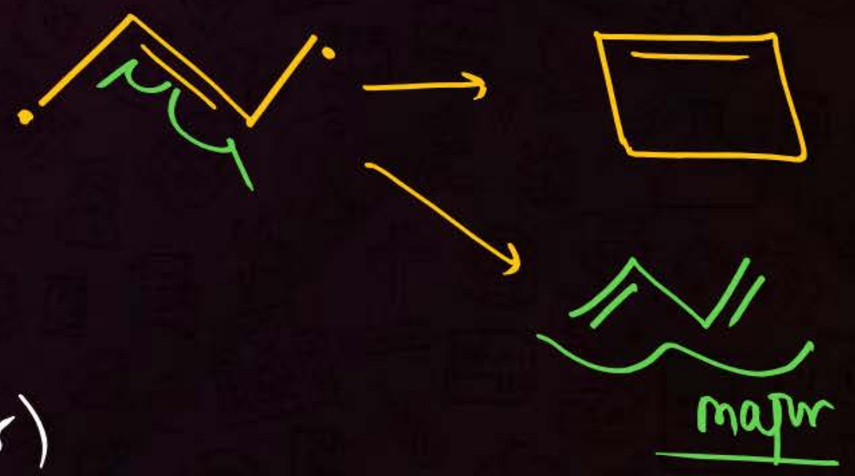
3° → (D) High temp.

Kinetics ⇒ Intermolecular < Intramolecular

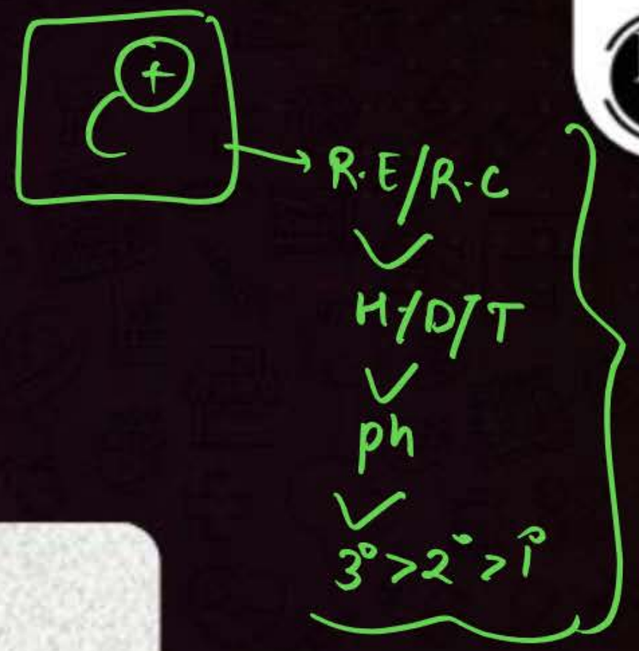


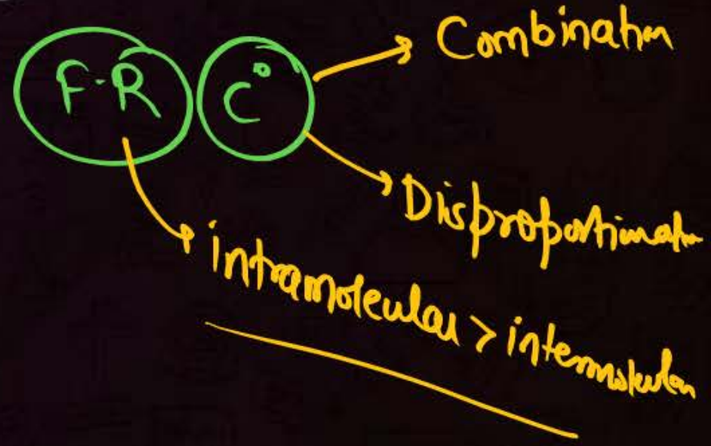
Stability ⇒ (Resonance stability) ↑ more preferred.





Hydrocarbon





Introduction

Alkane →	C_nH_{2n+2}	D.O.U = 0	Saturated compounds.
Alkene →	C_nH_{2n}	D.O.U = 1	Unsaturated compounds.
Alkyne →	C_nH_{2n-2}	D.O.U = 2	" "
Alkadiene/ Dialkene →	C_nH_{2n-2}	D.O.U = 2	" "
Benzene →	C_6H_6	D.O.U = 4	" "

Alkanes

- Known as Paraffins (little reactivity)
- sp^3 hybridised.
- Cannot show addition rxn.
- shows Free radical substitution.
  - ① Sunlight / hν
  - ② T > 500°C
  - ③ Peroxide catalyst

Alkanes
- Preparation
- physical properties
- Chemical properties

Preparations of Alkanes

(a) From Alkyl Halide (R–X)

1. Wurtz Reaction

R = aliphatic

Ar = Aromatic

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

Mechanism → Free radical mechanism

→ Reactivity order ⇒ R–I > R–Br > R–Cl > R–F

→ dry ether is used → ether → non-polar solvent

→ dry condition ⇒ to avoid moisture.

Intermediate = R°

$$Na + H_2O \longrightarrow NaOH + \frac{1}{2}H_2$$ → explosive

⇒ Product = symmetrical alkane

⇒ methane (CH_4) X

⇒ $CH_3-Cl + 2Na + Cl-CH_2-CH_3$

↓

$CH_3-CH_3 + CH_3-CH_2-CH_2-CH_3$

$+ CH_3-CH_2-CH_3$

⇒ not preferred for unsymmetrical alkane as it gives mixture of products.

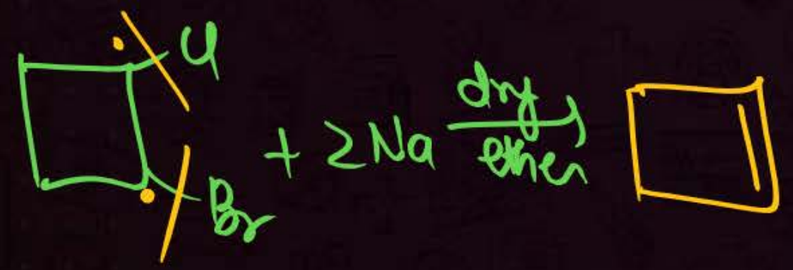
Mechanism:

Step-I $\quad Na \longrightarrow Na^{\oplus} + e^{\ominus}$

Step-II $\quad R-X \xrightarrow{e^{\ominus}} R^{\bullet} + X^{\ominus}$

Step-III $\quad R^{\bullet} + R^{\bullet} \longrightarrow R-R$

$$2\,CH_3-CH_2-Cl \xrightarrow[\text{dry ether}]{2Na} \underset{\text{butane}}{CH_3-CH_2-CH_2-CH_3}$$



→ partial double bond character b/w C–X due to delocalisation

→ not easy to break and form free radical.

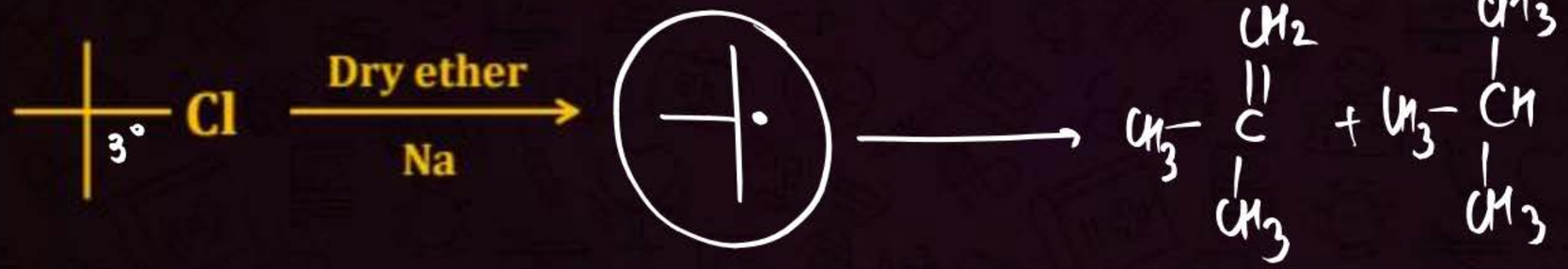
→ High temp. is needed.

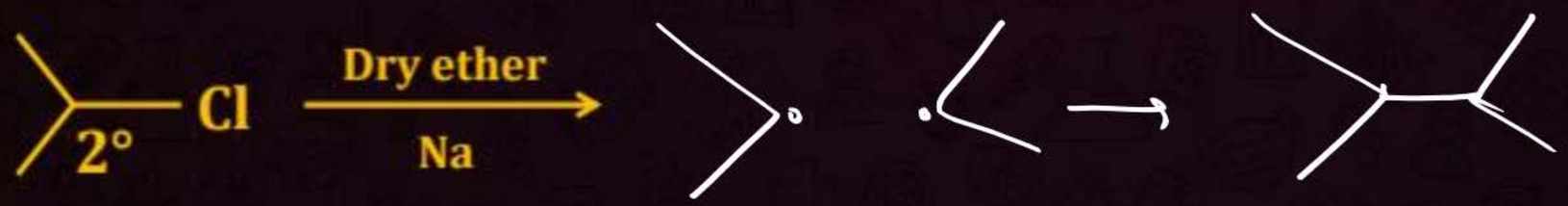
→ Solvent used ⇒ Tetrahydrofuran (THF)

for fittig rxn

QUESTION

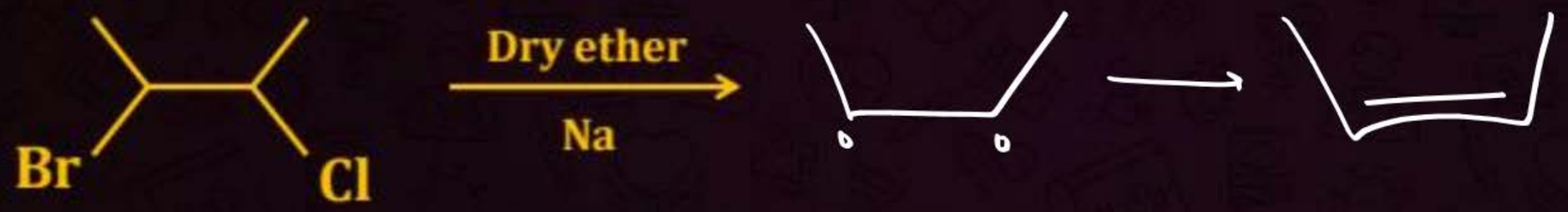
$$\overset{1^\circ}{CH_3CH_2Cl} \xrightarrow[\text{Na}]{\text{Dry ether}} CH_3-\dot{C}H_2 \quad \dot{C}H_2CH_3 \longrightarrow CH_3-CH_2-CH_2-CH_3$$

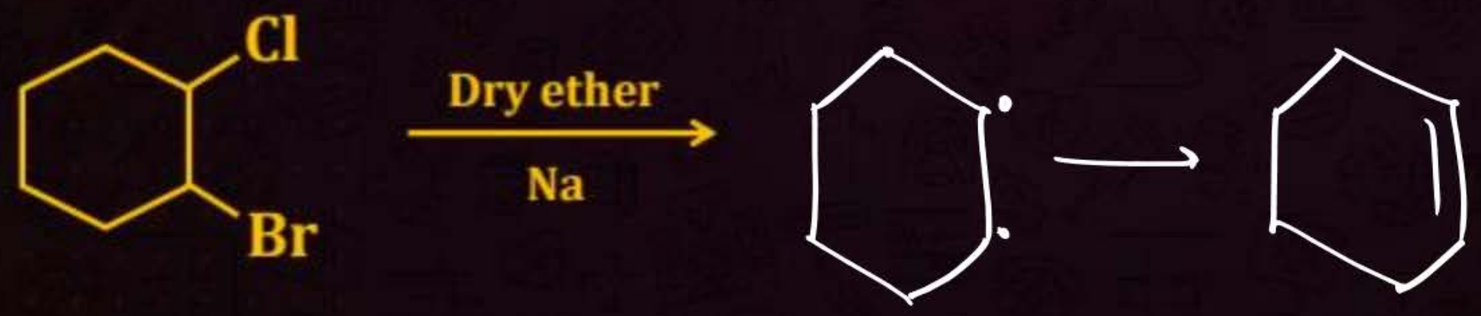


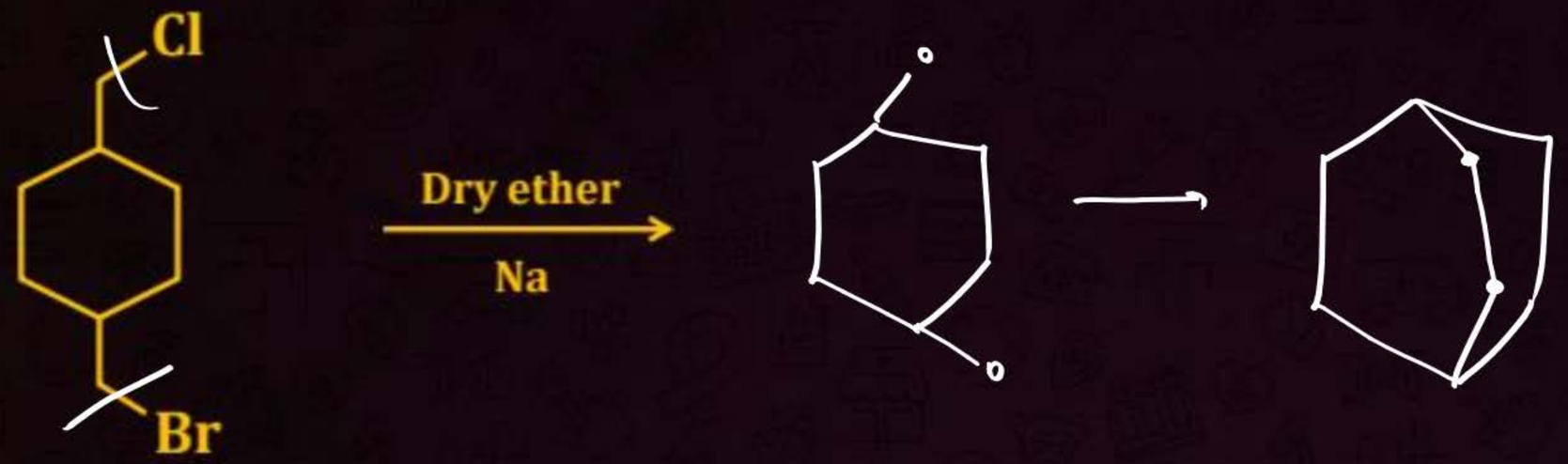


QUESTION

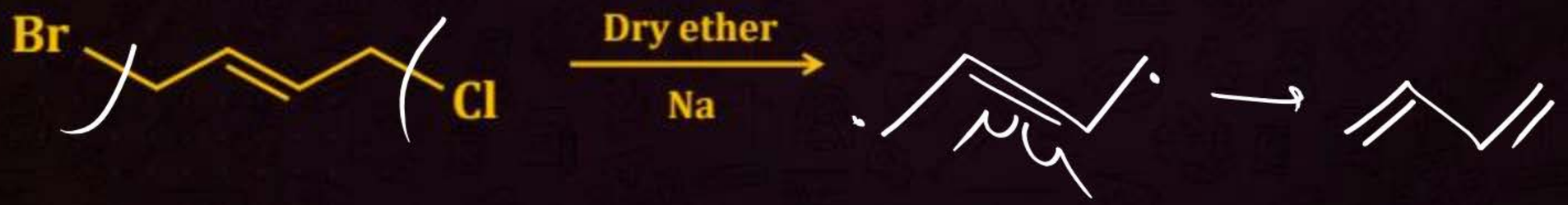
$$Ph-\overset{1^\circ}{C}H_2-Cl \xrightarrow[Na]{\text{Dry ether}} ph-CH_2-CH_2-ph$$



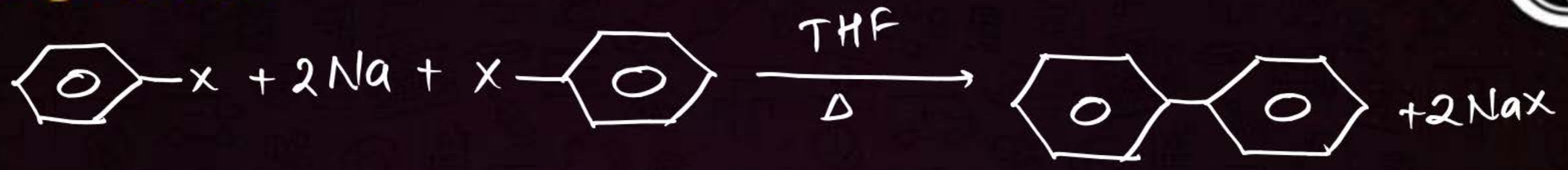



Cl
Br
Dry ether
Na


Cl
Br
Dry ether
Na


Br
Cl
Dry ether
Na

2. Fitting Reaction

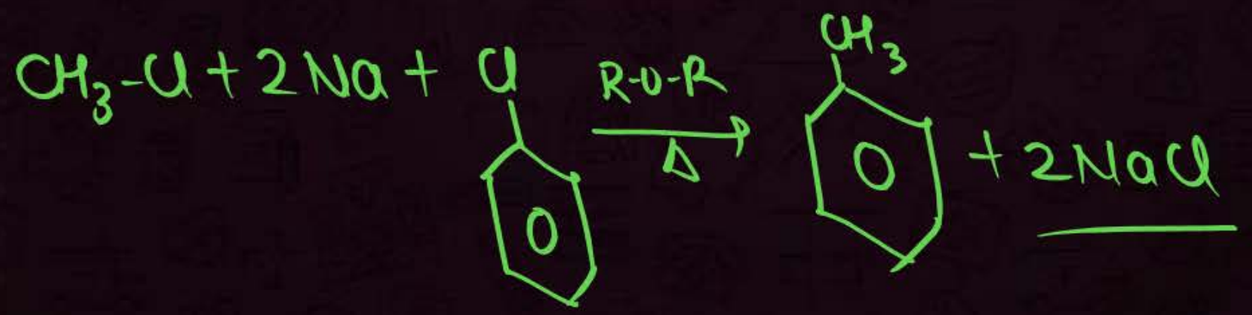


Biphenyl

$$Ar-X + 2Na + X-Ar \xrightarrow[\Delta]{THF} Ar-Ar + 2NaX$$

3. Wurtz fitting Reaction

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



4. Frankland Reaction

$$R-X + Zn + X-R \xrightarrow{D.E} R-R + ZnX_2$$

$$Ar-X + Zn + X-Ar \xrightarrow{D.E} Ar-Ar + ZnX_2$$

(Frankland Reagent = R_2Zn)

5. Ullmann's Reaction

$$R-X + Cu + X-R \xrightarrow{D.E} R-R + CuX_2$$

$$Ar-X + Cu + X-Ar \xrightarrow{D.E} Ar-Ar + CuX_2$$

6. Corey-house Synthesis → methane ✗

↳ used for preparation of unsymmetrical alkanes. $(R-R')$

$$\underbrace{R_2CuLi}_{\text{gilman's Reagent}} + \underbrace{R'-X}_{\text{should not be } 3^\circ \to \text{prefer elimination.}} \longrightarrow \underbrace{R-R'}_{} + R-Cu + LiX$$

$$\Rightarrow (CH_3)_2CuLi + C_2H_5-Br \longrightarrow CH_3-CH_2-CH_3 + CH_3-Cu + LiBr.$$

$$\Rightarrow \left(CH_3-\underset{\underset{CH_3}{|}}{CH}-\right)_2CuLi + CH_3-CH_2-Cl \longrightarrow \underset{\text{2-methyl butane}}{CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3} + CH_3-\underset{\underset{CH_3}{|}}{CH}-Cu + LiCl$$

Preparation of Gilman's Reagent

$$R-X + Li \longrightarrow RR-Li \xrightarrow{Cu} R_2CuLi$$

7. Using Grignard Reagent

methane preparation

$(R-MgX) \rightarrow$ organometallic compound.

$R^{\ominus}$ $\overset{\oplus}{Mg}X$

Preparation of Grignard reagent

$$R-X + Mg \xrightarrow{D.E} R-MgX$$

$$R-MgX + H-OH \longrightarrow R-H + Mg^{-X}-OH$$

$$R-MgX + H-NH_3 \longrightarrow R-H + Mg^{-X}-NH_2$$

$$R-MgX + H-C\equiv CH \longrightarrow R-H + Mg^{-X}-C\equiv CH$$

$$R-MgX + H-O-R' \longrightarrow R-H + Mg^{-X}-O-R'$$

$$\boxed{CH_3-MgBr + H_2O \longrightarrow \underbrace{CH_3-H}_{\text{methane}} + Mg^{-X}-OH}$$

⇒ Grignard reagent is kept anhydrous or prepared in lab at the time of rxn.

very reactive to form alkane by taking acidic (H).

8. Reduction

$$R-X \xrightarrow[\text{Zn-Cu couple}]{\text{Zn/CH}_3\text{COOH}} R-H$$

Zn/HCl

Al-Hg amalgam

Zn-NaOH

$$CH_3-Cl \xrightarrow{Zn/H^{\oplus}} CH_4$$

9. Red P/HI

↳ Best Reducing agent

↳ BAAP Reagent

$$\boxed{R-X \xrightarrow{\text{Red P} + HI} R-H}$$

- $R-X \xrightarrow{\text{Red P + HI}} R-H$
- $R-OH \xrightarrow{\text{Red P + HI}} R-H$
- $R-\overset{\overset{O}{\|}}{C}-H \xrightarrow{\text{Red P + HI}} R-CH_3$
- $R-\overset{\overset{O}{\|}}{C}-R' \xrightarrow{\text{Red P + HI}} R-CH_2-R'$
- $R-\overset{\overset{O}{\|}}{C}-X \xrightarrow{\text{Red P + HI}} R-CH_3$
- $R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{\text{Red P + HI}} R-CH_3$
- $R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{\text{Red P + HI}} R-CH_3$

$\boxed{R-X}$ →
1. wurtz
2. Fittig
3. wurtz-fittig
4. Frankland
5. Ullmann
6. Grignard reagent
7. Corey house synthesis
8. Reduction
9. Red P + HI

(b) From Carboxylic Acids

1. Kolbe's Electrolysis

$$R-\overset{O}{\overset{\|}{C}}-OH + Na \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^{\ominus}Na^{\oplus} + \frac{1}{2}H_2$$

$$2R-\overset{O}{\overset{\|}{C}}-OH + Mg \longrightarrow \left(R-\overset{O}{\overset{\|}{C}}-O\right)_2Mg + H_2\uparrow$$

$$3R-\overset{O}{\overset{\|}{C}}-OH + Al \longrightarrow \left(R-\overset{O}{\overset{\|}{C}}-O\right)_3Al + \frac{3}{2}H_2\uparrow$$

- → Free radical mechanism
- → methane X
- → anode → $R-R + CO_{2(g)}$
- → cathode → $H_2\uparrow + NaOH$
- → pH increase
- → symmetrical alkane

$$R-\overset{O}{\overset{\|}{C}}-O^{\ominus}Na^{\oplus} \Big/ R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\text{electrolysis}]{Na,\ H_2O} \underbrace{\boxed{R-R + 2CO_2}}_{\text{anode}} + \underbrace{\boxed{H_2 + NaOH}}_{\text{cathode}}$$

$$R-\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}-OH \xrightarrow[\text{electrolysis.}]{Na,\ H_2O} \underbrace{R-R + 2SO_3}_{\text{anode}} + \underbrace{H_2 + NaOH}_{\text{cathode.}}$$

Reaction Mechanism

At anode

$$R-\overset{O}{\overset{\|}{C}}-O^{\ominus} \xrightarrow{2e^{\ominus}} R-\overset{O}{\overset{\|}{C}}-O \longrightarrow R^{\circ} + CO_{2(g)}\uparrow$$

$$R^{\circ} + R^{\circ} \longrightarrow R-R \text{ (major)}$$

$$R^{\circ} + O^{\circ}-\overset{O}{\overset{\|}{C}}-R \longrightarrow R-O-\overset{O}{\overset{\|}{C}}-R \text{ (minor)}$$

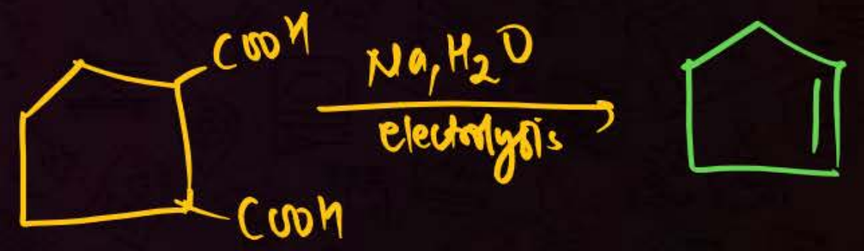
$$H-\overset{O}{\overset{\|}{C}}-O^{\ominus}Na^{\oplus} \xrightarrow[\text{electrolysis}]{H_2O} \underbrace{H_2 + CO_2}_{\text{anode}} + \underbrace{H_2 + NaOH}_{\text{Cathode}}$$

At Cathode

$$H_2O \longrightarrow 2H^{\oplus} + OH^{\ominus}$$

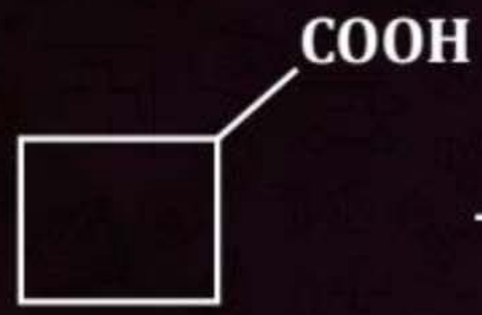
$$2H^{\oplus} + 2e^{\ominus} \longrightarrow 2H^{\circ}$$

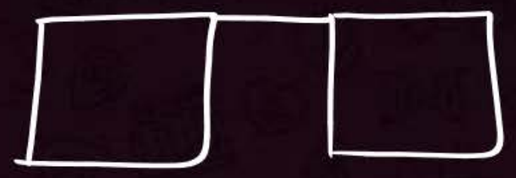
$$H^{\circ} + H^{\circ} \longrightarrow H_2(g)$$

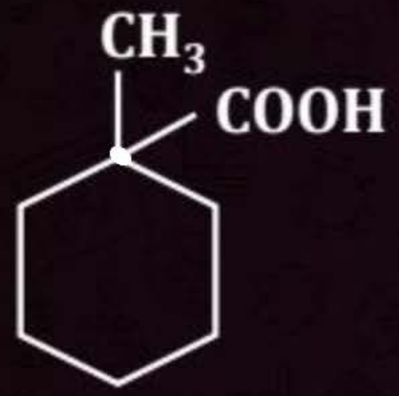


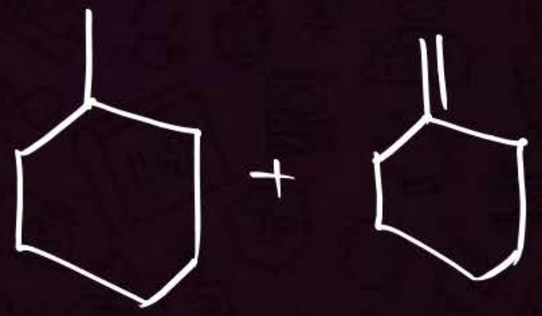
$$\underset{\text{propanoic acid}}{CH_3-CH_2-COOH} \xrightarrow[\text{electrolysis}]{Na/H_2O} CH_3-CH_2-CH_2-CH_3$$

Kolbe's Electrolysis:

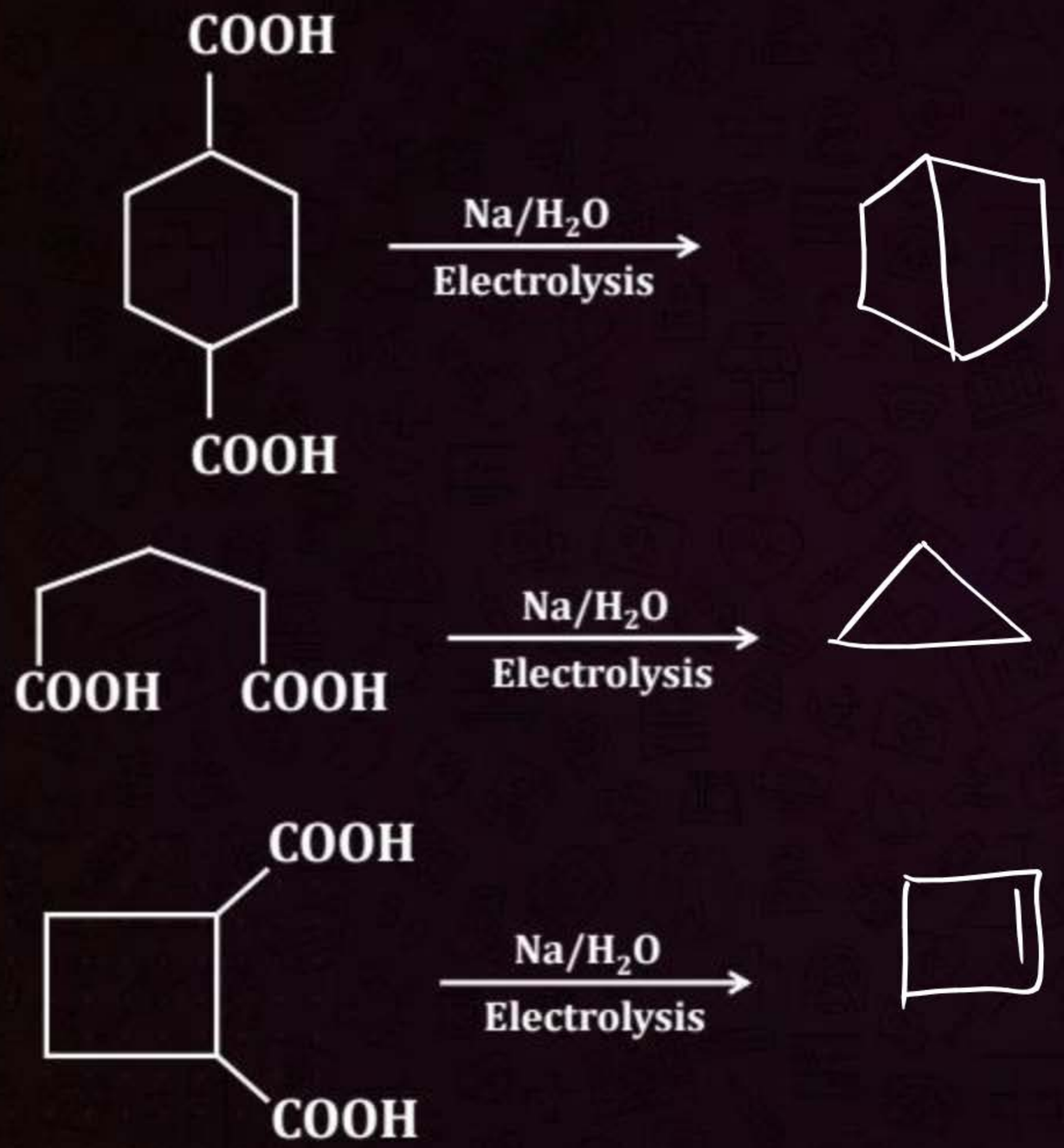
1. 

$\xrightarrow[\text{Electrolysis}]{Na/H_2O}$  $+ 2CO_2 + H_2 + NaOH$

2. 

$\xrightarrow[\text{Electrolysis}]{Na/H_2O}$ 

3. $CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2 - COOH \xrightarrow[\text{Electrolysis}]{Na/H_2O}$ $CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2 - CH_2 - \underset{\underset{CH_3}{|}}{CH} - CH_3$


COOH
COOH
Na/H2O
Electrolysis
COOH
COOH
Na/H2O
Electrolysis
COOH
COOH
Na/H2O
Electrolysis

2. Decarboxylation: (Removal of CO_2)

↳ prefix meaning for Removal

$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[(3:1)]{NaOH + CaO} R-H + Na_2CO_3$$

Mechanism

$$R-\overset{O}{\overset{\|}{C}}-O^{\ominus} \xrightarrow[\text{slow}]{rds} R^{\ominus} + CO_2\uparrow \xrightarrow{NaOH} Na_2CO_3$$

$$R^{\ominus} + H_2O \longrightarrow R-H$$

⇒ Rate of decarboxylation rxn ∝ stability of carbanion

→ Intermediate = Carbanion $R^{\ominus}$

↳ no Rearrangement.

↳ Stability order of $C^{\ominus}$

Aromaticity > Back Bonding

$\vee$ $-M$ $\vee$ $-H$ $\vee$ $-I$

antiaromaticity

$< +M < +H < +I <$

QUESTION

Which of the following is correct order for the ease of decarboxylation of these carboxylic acids?

CH_3COOH, CF_3COOH, CCl_3COOH

(a) (b) (c)

(A) a > b > c

(B) c > b > a

(C) b > c > a

(D) b > a > c

$\overset{\ominus}{C}H_3 < \overset{\ominus}{C}F_3 < \underbrace{\overset{\ominus}{C}Cl_3}_{\text{Back bonding}}$

3. Red P + HI

$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\text{Red P + HI}} R-CH_3$$

$$\boxed{R-\overset{O}{\overset{\|}{C}}-OH} \longrightarrow$$

- $\xrightarrow[\text{electrolysis}]{Na/H_2O} R-R + 2CO_2 + H_2 + NaOH$ (R°)
- $\xrightarrow[3:1]{NaOH + CaO} R-H + Na_2CO_3$ ($R^{\ominus}$)
- $\xrightarrow{\text{Red P + HI}} R-CH_3$

(C) From Aldehyde & Ketone

1. **Red R + HI**

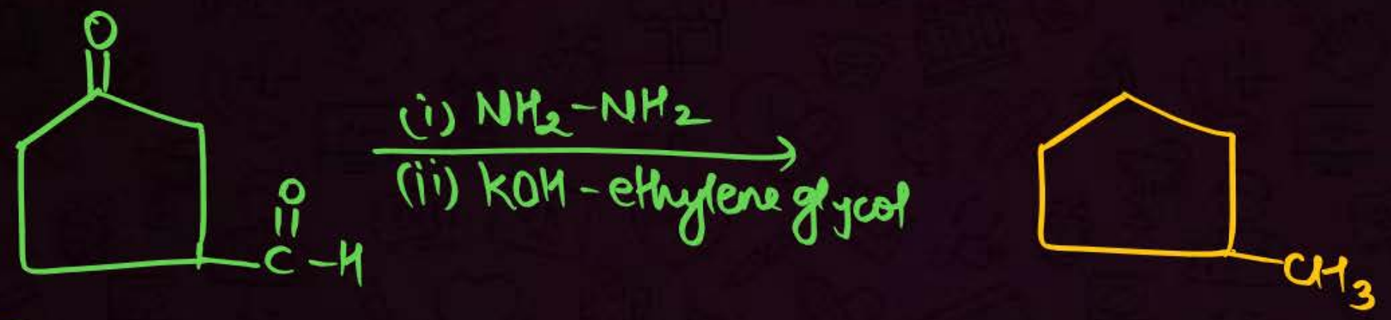
$$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\text{Red P + HI}} R-CH_3$$

$$R-\overset{O}{\overset{\|}{C}}-R' \xrightarrow{\text{Red P + HI}} R-CH_2-R'$$

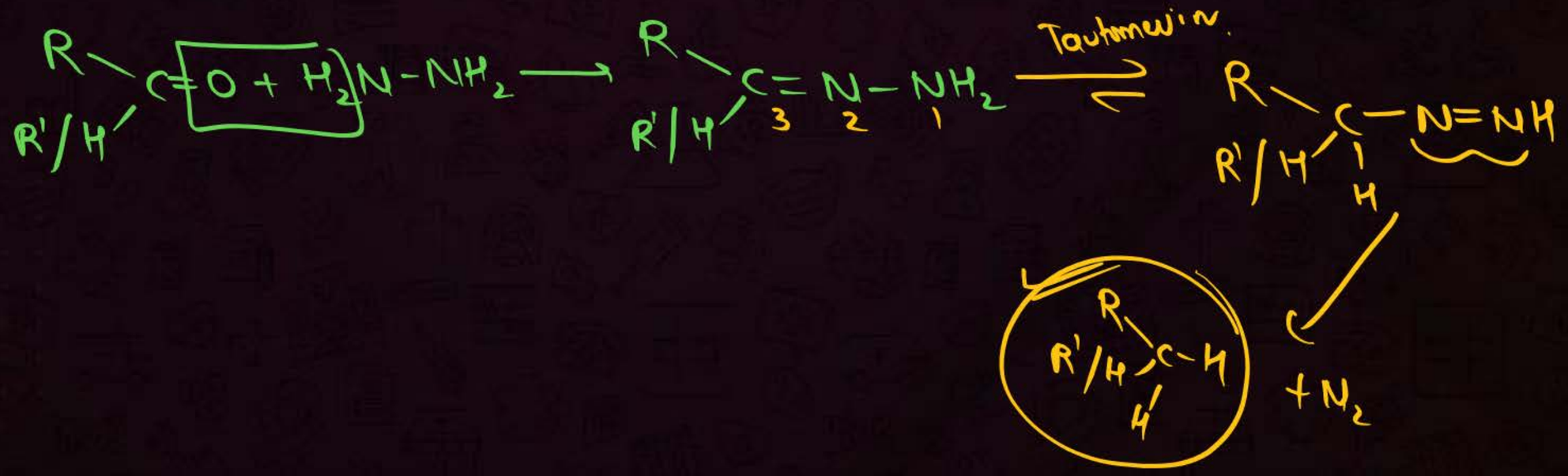
2. Wolff Kishner Reduction

$$R-\overset{O}{\overset{\|}{C}}-H/R' \xrightarrow[\text{(ii) ethylene glycol/KOH}]{\text{(i) } NH_2-NH_2 \text{ (hydrazine)}} R-CH_2-H/R'$$

→ Alert ⇒ avoid Base sensitive group.



Mechanism



3. Clemmensen's Reduction

$$R-\overset{O}{\overset{\|}{C}}-H/R' \xrightarrow[HCl]{Zn-Hg} R-CH_2-H/R'$$

Alert: avoid Acid sensitive group.

$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow[HCl]{Zn-Hg} CH_3-CH_2-CH_3$$

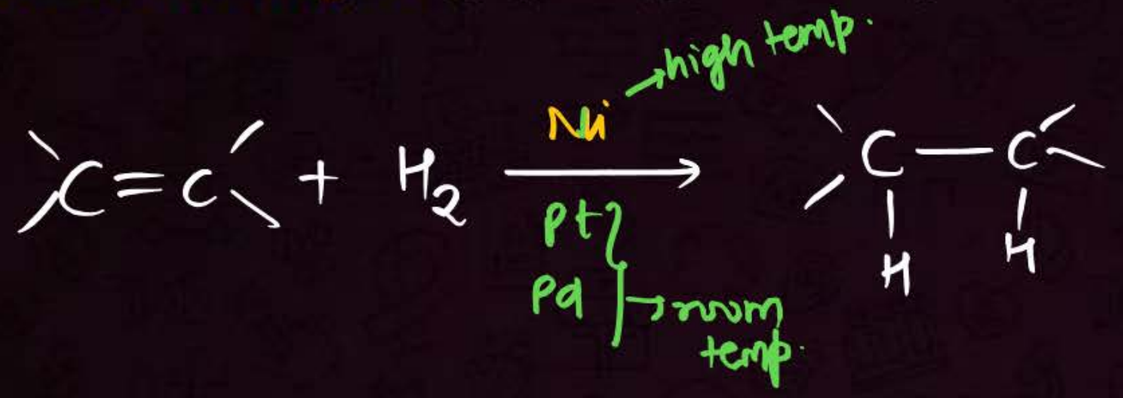
$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow[HCl]{Zn-Hg} CH_3-CH_2-CH_2-CH_3$$

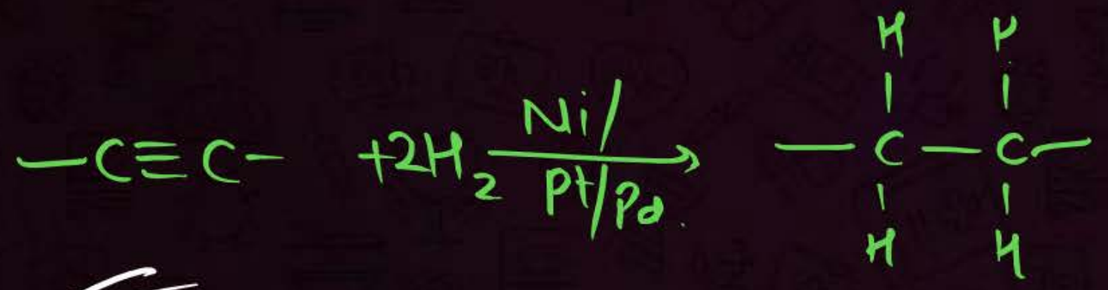
(d) From Aluminium & Beryllium Carbide

$$Al_4C_3 + H_2O \longrightarrow \boxed{CH_4} + Al(OH)_3$$

$$Be_4C_2 + H_2O \longrightarrow \boxed{CH_4} + Be(OH)_2$$

(e) From Alkene & Alkyne (Hydrogenation)





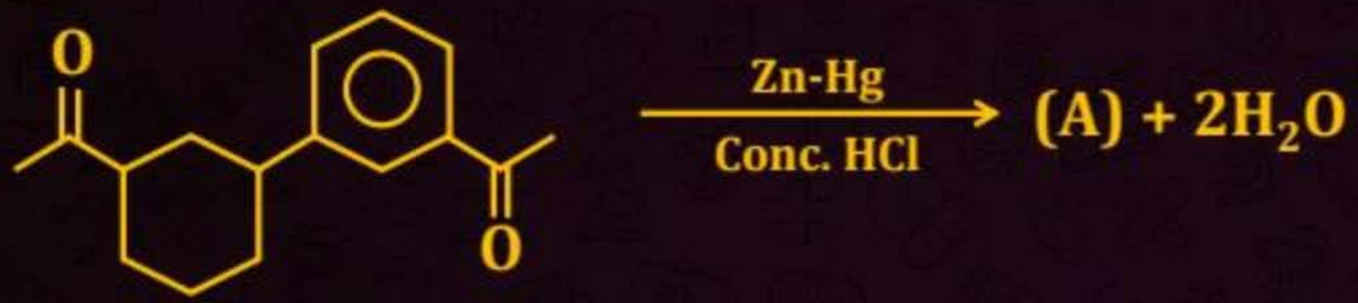
$\Delta H_{hydrogenation} \propto$ no. of π-bonds $\propto \frac{1}{\text{stability}}$

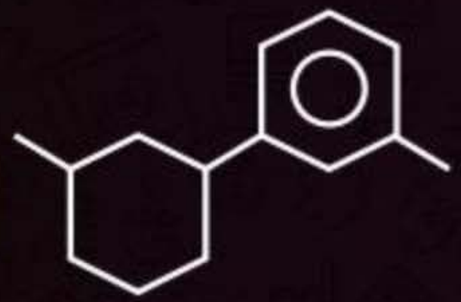
always exothermic

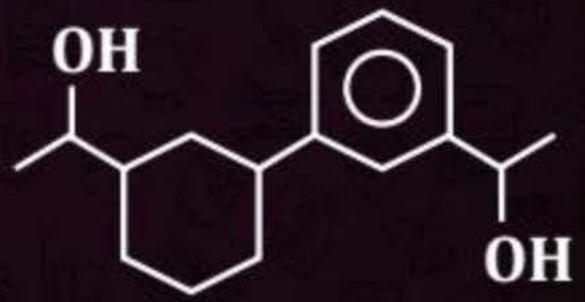
1. R–X → 9
2. R–C(=O)–OH → 3
3. R–C(=O)–H/R' → 3
4. Be/Al carbide → 1
5. alkene/alkyne → 1

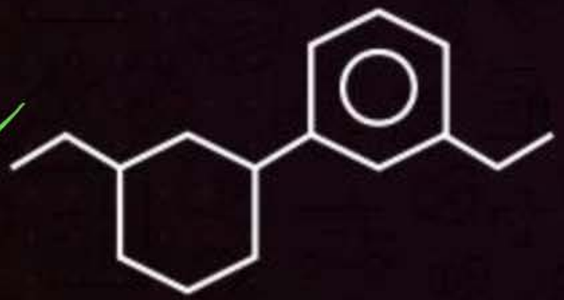
QUESTION

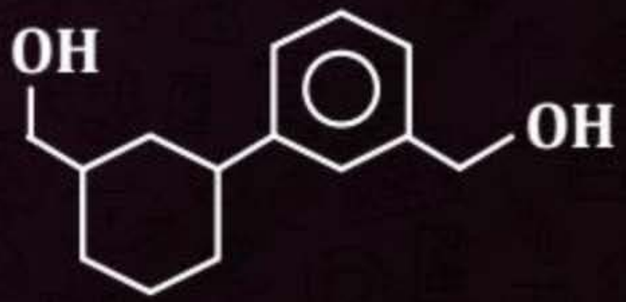
Identify product (A) in the following reaction:



A


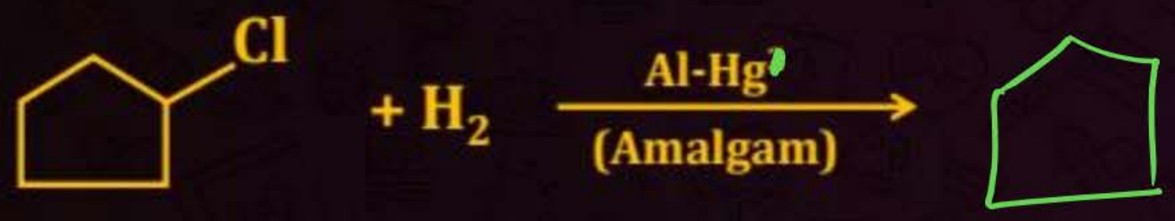
B


C


D


QUESTION

$$CH_3 - Cl + H_2 \xrightarrow{Zn + HCl} CH_4$$



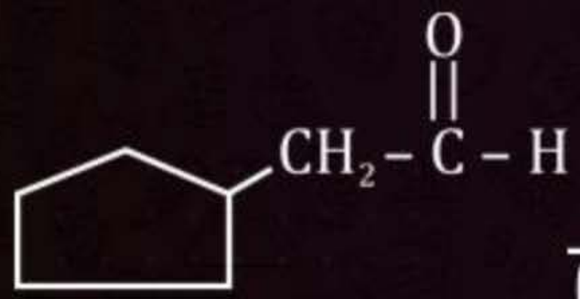
$$2CH_3 - I + Zn \longrightarrow CH_3 - CH_3 + ZnI_2$$

QUESTION

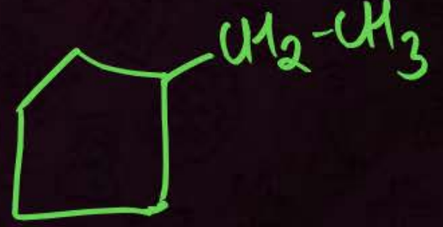
$$(CH_3)_2CuLi + C_2H_5Cl \longrightarrow C_2H_5-CH_3 + CH_3-Cu + LiCl$$

$$CH_3-\overset{\overset{O}{||}}{C}-OH \xrightarrow[CaO/\Delta]{NaOH^+} CH_4 + Na_2CO_3$$

Decarboxylation



$$\xrightarrow[\text{(ii) KOH/Ethylene glycol}/\Delta]{\text{(i) } NH_2-NH_2}$$



QUESTION

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH$

- $\xrightarrow[H_2O \text{ Electrolysis}]{Na}$ $CH_3-CH_2-CH_2-CH_3$ (A)
- $\xrightarrow[CaO,\ \Delta]{NaOH\ +}$ CH_3-CH_3 (B)
- $\xrightarrow[+\ HI]{Red\ P}$ $CH_3-CH_2-CH_3$ (C)

Relation between a, b, c $\longrightarrow$ Homologues

Physical Properties

1. Heat of Combustion

$\Delta H_{combustion} \propto$ no. of 'c'

$\propto \frac{1}{\text{Stability}}$

aliphatic ⇒ stability ∝ Branching

Alicyclic ⇒ stability ∝ Bayer's strain theory.

2. Physical State

$C_1 - C_4 \longrightarrow$ gases

$C_4 - C_{17} \longrightarrow$ liquid

$\geq C_{18} \longrightarrow$ solid

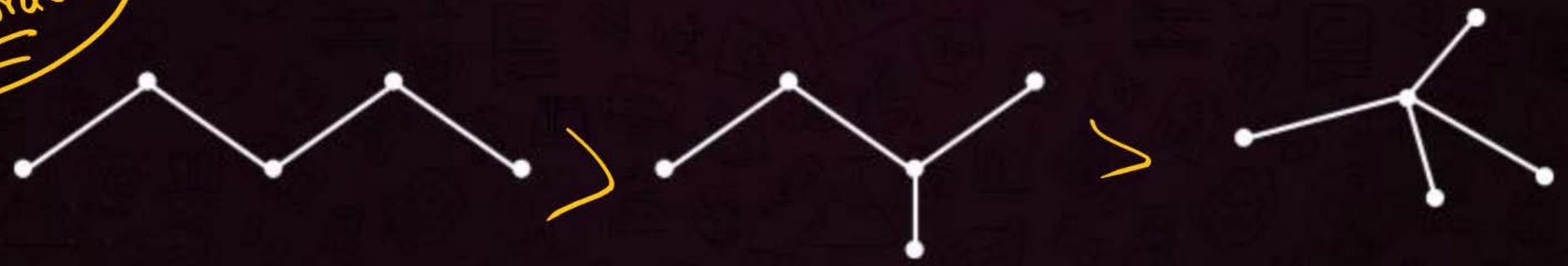
⇒ no. of C ↑ surface area ↑ vandewaal force ↑ IMF ↑

3. Boiling Point

B.pt $\propto$ no. of 'C' atoms. (for every $-CH_2$ increases, 20-30°C increase in B.pt)

$\propto \frac{1}{\text{Stability}}$ $\propto \frac{1}{\text{Branching}}$

B.pt order



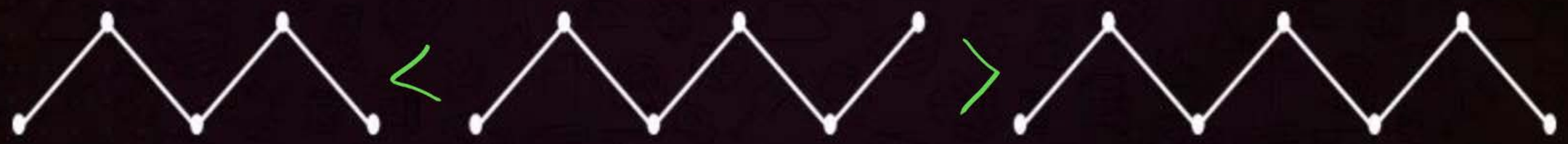
4. Melting Point

M.pt $\propto$ no. of 'c' atoms.

$\propto$ stability $\propto$ Branching

$\propto$ symmetry.

$\Rightarrow$ For every consecutive alkanes, M.pt of even no. 'c' alkanes > M.pt of odd no. of 'c' containing alkanes



5. Density

→ alkanes are lighter than water.

→ density ↑ mass ↑

↳ max. density upto 0.8 g/cm3.

6. Solubility

↳ alkanes = non-polar in nature

↳ soluble in non-polar solvent

Uses of Alkane:

- LPG (liquified Petroleum gas) - Cooking - Contains Propane, Butane
- LNG (liquified Natural gas) - fuel (Gasoline)
- Branching increased - Good Fuel - Example: isooctane
- CNG (Compressed Natural gas) -Vehicles fuel- contain (80-90)% Methane & traces of Ethane.
- Petrol - Vehicles fuel
- Grease (higher alkanes, hydrophobic) - used as Lubricant
- Natural gas - Methane Mainly (electricity,heat)
- Petroleum + Petrol - Dry Cleaning agent
- Kerosene oil, diesel - Fuel
- Higher Hydrocarbon - Solvent for paints

Chemical Properties of Alkanes

1. Photohalogenation of Alkanes

→ Free radical substitution

$$CH_4 + X_2 \xrightarrow[\text{or sunlight}]{h\nu} CH_3-X + HX$$

$$CH_4 + X_2\,(\text{excess}) \longrightarrow CH_3-X \xrightarrow{X_2} CH_2X_2 \xrightarrow{X_2} CHX_3 \xrightarrow{X_2} CX_4$$

CHX_3 → Haloform

CCl_4 → named as pyrene → used in fire extinguisher

$CHCl_3$ → chloroform

$CHBr_3$ → Bromoform

Mechanism

$$X-X \xrightarrow{h\nu} X^{\bullet} + X^{\bullet}$$

$$CH_3-H + X^{\bullet} \longrightarrow {}^{\bullet}CH_3 + HX$$

$${}^{\bullet}CH_3 + X^{\bullet} \longrightarrow CH_3-X$$

Types of Questions → **Monohalogenation**

↓

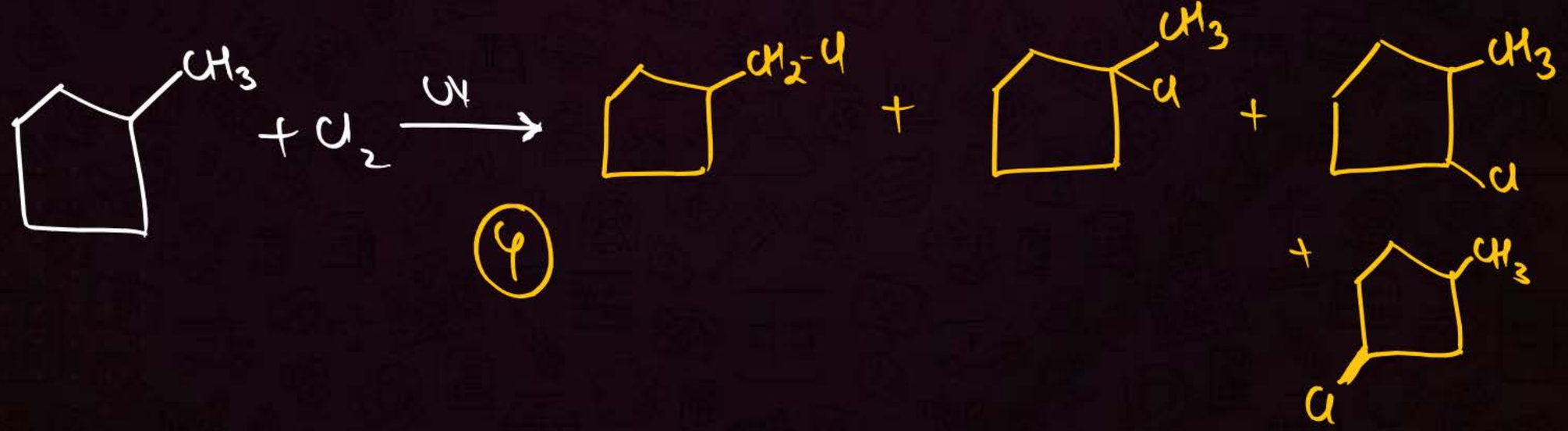
one (H) is substituted by one (X)

→ ① no. of different type of products.

→ ② Major | Minor.

$$CH_3-CH_2-CH_3 + Cl_2 \xrightarrow{UV} CH_3-CH_2-\underset{\underset{Cl}{|}}{CH_2} + CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3$$

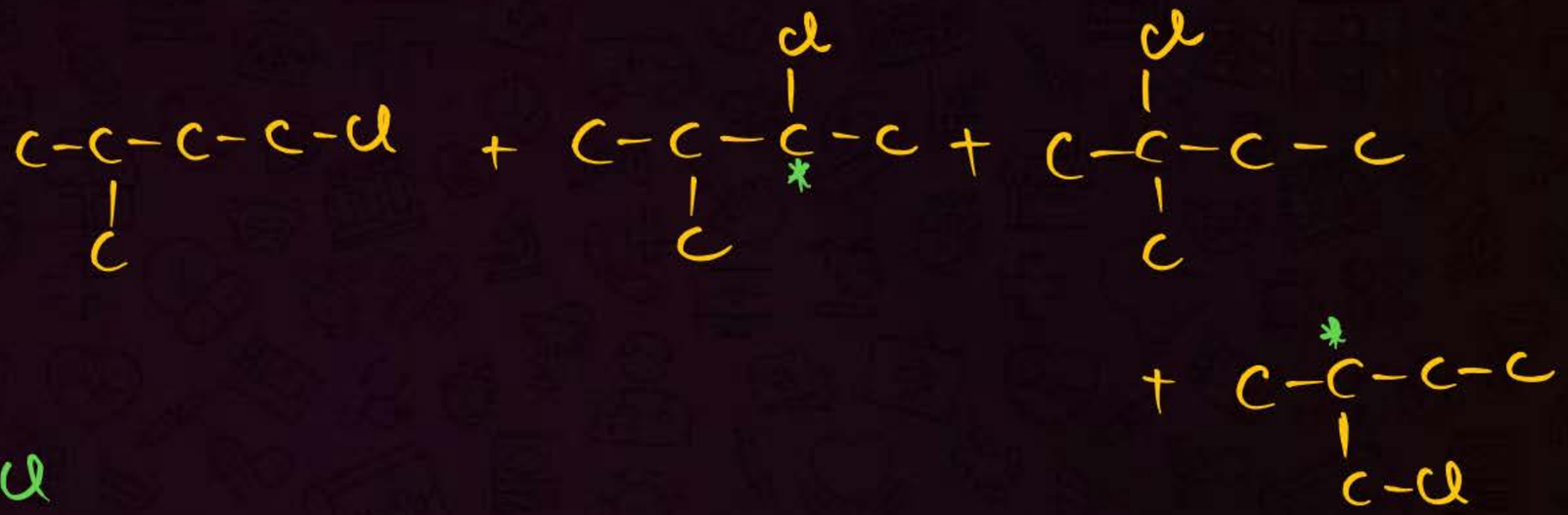
no. of products = no. of isomers possible

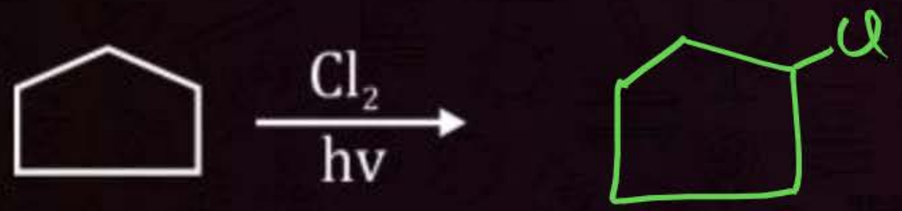


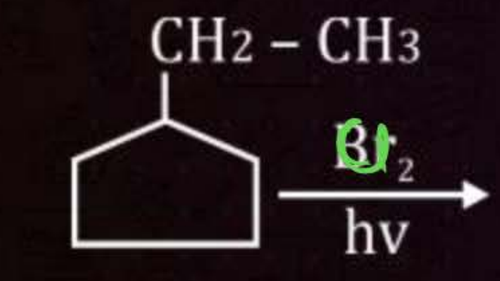
$$CH_3-CH_2-CH_3 \xrightarrow[h\nu]{Cl_2}$$

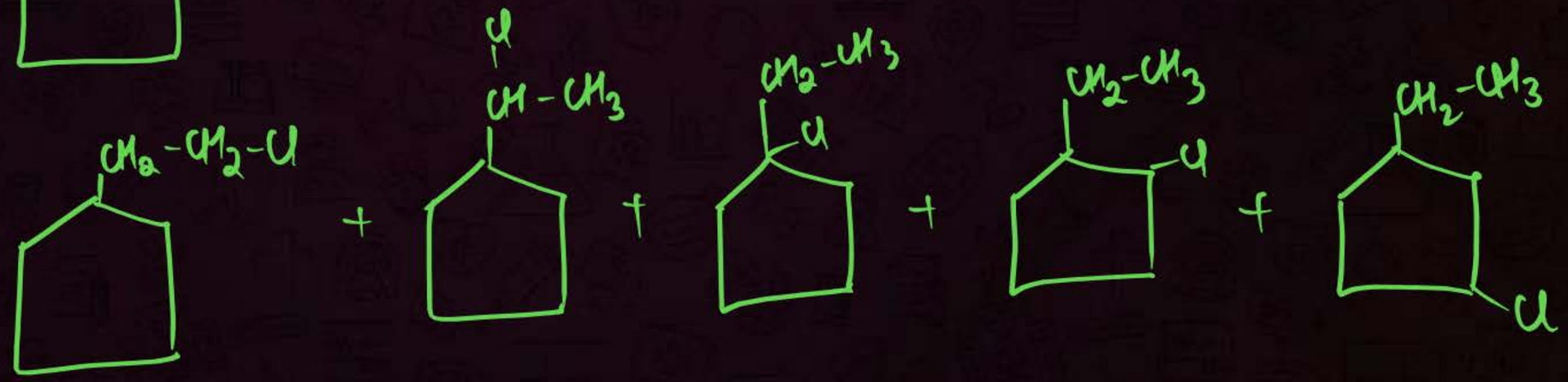
$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3 \xrightarrow[h\nu]{Cl_2}$$

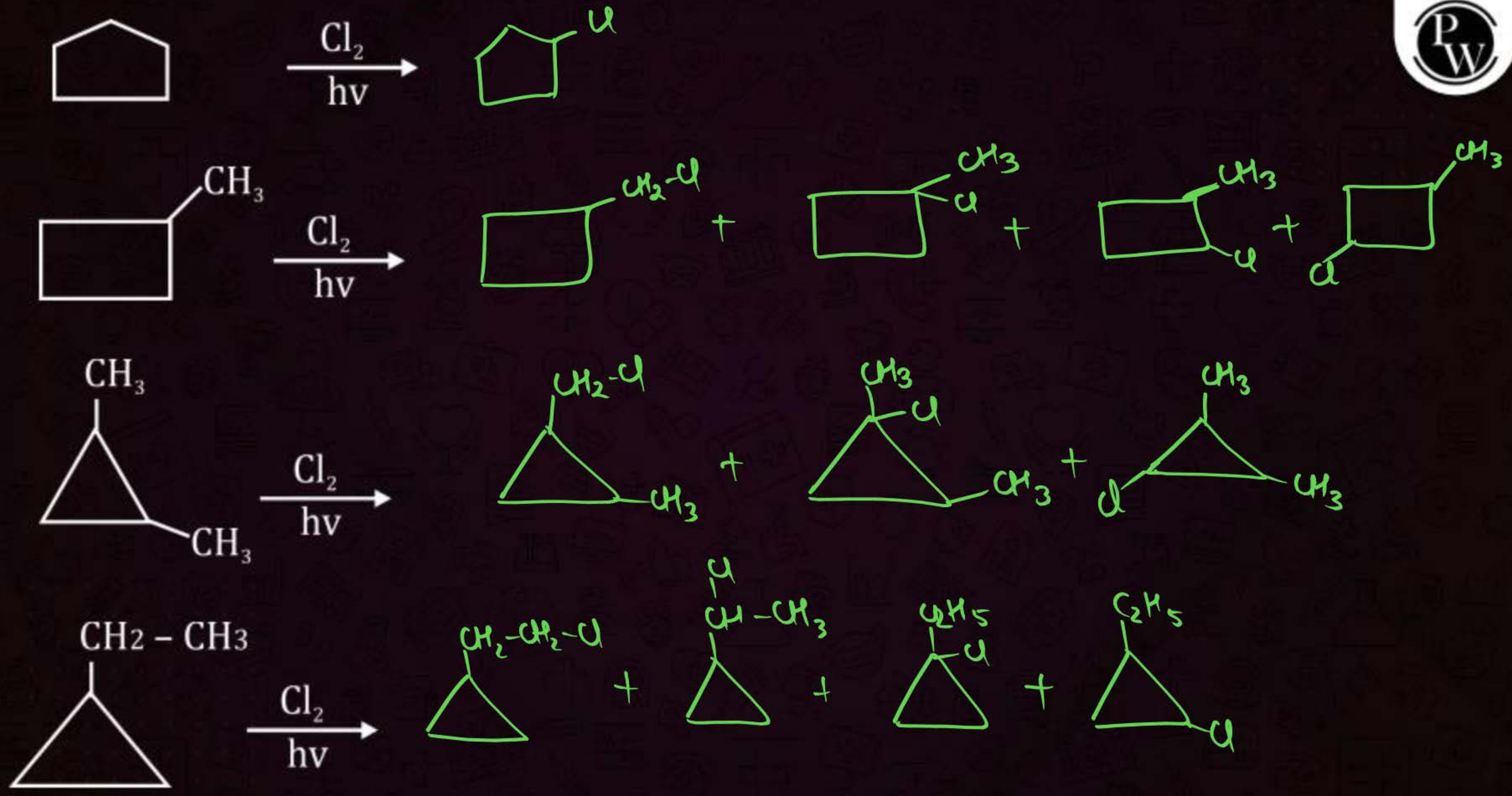
4





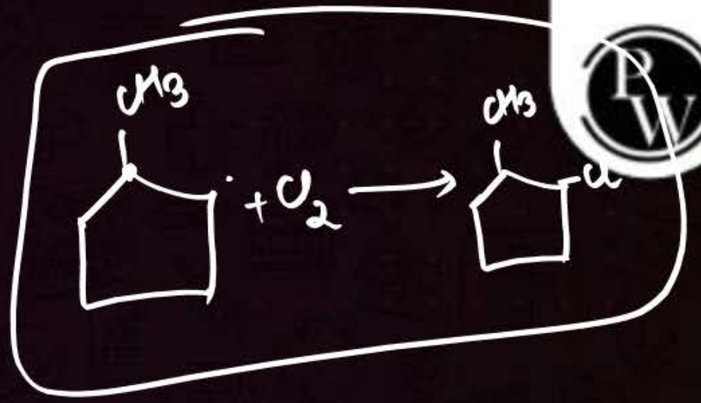





Cl2
hv
CH3
CH2-Cl
CH3
CH2-Cl
CH3
CH3
CH2 – CH3
CH2-CH2-Cl
C2H5

Note: → Stability of F·R ⇒ $3^\circ > 2^\circ > 1^\circ$

→ Reactivity order ⇒ $F_2 > Cl_2 > Br_2 > I_2$



Fluorination

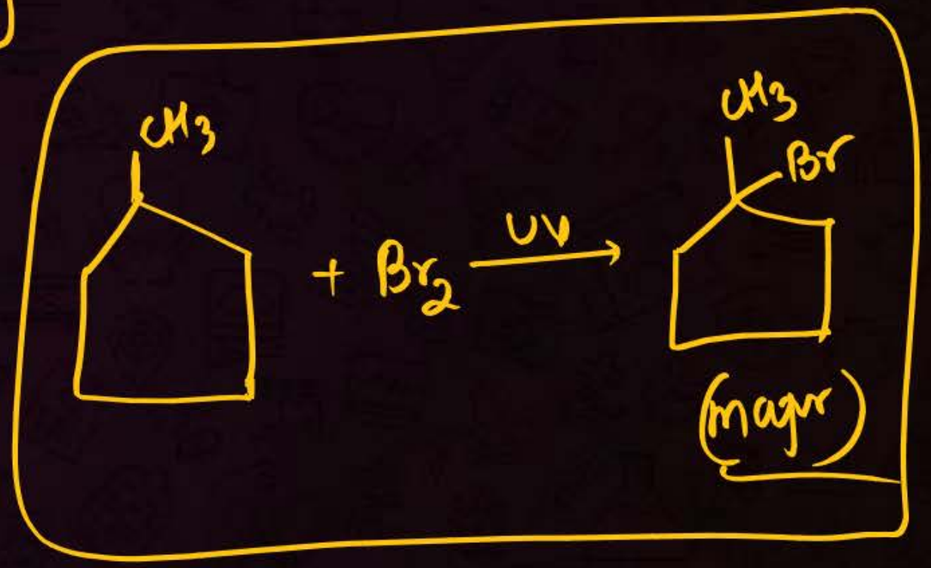
$$CH_4 + 2F_2 \xrightarrow{UV} C + 4HF$$ (explosive)

Chlorination ⇒ reactivity more, selectivity less

1° :	2° :	3°
1 :	3.8 :	5

Bromination ⇒ reactivity less, selectivity more

1° :	2° :	3°
1 :	82 :	1600



Iodination

$$CH_4 + I_2 \rightleftharpoons CH_3-I + HI$$

→ HI → Good reducing agent

→ for iodination, use oxidizing agent like HNO_3 to make the rxn irreversible

Calculation of Percentage of 1°, 2° & 3°

n_1 = No. of 1° - H-atom

n_2 = No. of 2° - H- atom

n_3 = No. of 3° - H-atom

$$\% \text{ of } 1^o = \frac{n_1^o R_1^o}{n_1^o R_1^o + n_2 R_2^o + n_3 R_3^o} \times 100$$

$$\% \text{ of } 2^o = \frac{n_2^o R_2^o}{n_1^o R_1^o + n_2 R_2^o + n_3 R_3^o} \times 100$$

$$\% \text{ of } 3^o = \frac{n_3^o R_3^o}{n_1^o R_1^o + n_2 R_2^o + n_3 R_3^o} \times 100$$

Questions:

$$CH_3-CH_2-CH_3 + Cl_2 \xrightarrow{h\nu} CH_3-CH_2-\underset{Cl}{CH_2} + CH_3-\underset{Cl}{CH}-CH_3$$

(major)

$$CH_3-CH_2-CH_3 + Br_2 \xrightarrow{h\nu} CH_3-\underset{Br}{CH}-CH_3$$

(major)

$$CH_3-\underset{CH_3}{CH}-CH_3 + Cl_2 \xrightarrow{h\nu} CH_3-\underset{CH_3}{CH}-CH_2-Cl$$

(major)

$$CH_3-\underset{CH_3}{CH}-CH_3 + Br_2 \xrightarrow{h\nu} CH_3-\overset{Br}{\underset{CH_3}{C}}-CH_3$$

Combustion

a. Complete Combustion:

$$\text{alkane} \xrightarrow[\text{(excess)}]{O_2} CO_2 + H_2O$$

$$C_4H_{10} + \frac{13}{2}O_2 \longrightarrow 4CO_2 + 5H_2O$$

b. Incomplete Combustion:

$$\text{alkane} \xrightarrow[\text{limited}]{O_2} \underset{\text{(Black)}}{C} + H_2O$$

4. Reaction with Steam

$$CH_4 + H_2O_{(g)} \xrightarrow[H.T]{1273} \underbrace{CO + H_2}$$

water gas or Blue gas | synthesis gas or syn-gas.

5. Pyrolysis/Cracking :- at high Temp / high (P), higher alkanes breaks into smaller molecules - alkane, alkene, H_2.

Si Al Z → break (C-C) bond.

Silicon, Aluminium, Zinc

V M C → break (C-H) bond.

Vanadium, Molybdenum, Chromium

$$CH_3-CH_2-CH_2-CH_2-CH_3 \xrightarrow[H.T\ H.P]{MO_2O_3} C_5H_{10} + H_2$$

(C_5H_{12})

$$\xrightarrow[H.T\ H.P]{Al_2O_3} C_3H_6 + C_2H_6$$

5. Nitration

$$CH_3-\boxed{H_{(g)} + HO}-NO_{2\,(g)} \xrightarrow{H.T} CH_3-NO_2$$

→ free radical mechanism

→ no. of product = no. of different isomers of NO_2

→ $\boxed{\text{'C' in alkane} < 6}$ → Reactivity less.

→ Reaction is done in vapour phase

→ $C \geq 6$ → Rxn at normal phase

$$CH_3-CH_2-CH_3 \xrightarrow{\text{Conc } HNO_3} CH_3-CH_2-CH_2-NO_2$$

$$+$$

$$CH_3-\underset{\underset{NO_2}{|}}{CH}-CH_3$$

6. Sulphonation

$$CH_3-\boxed{H_{(g)} + HO}-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH \longrightarrow CH_3-SO_3H$$

Reagent → oleum ($H_2S_2O_7$)

→ forming H_2SO_4 $\boxed{(H_2SO_4\,(SO_3))}$

→ all remaining points are same as nitration.

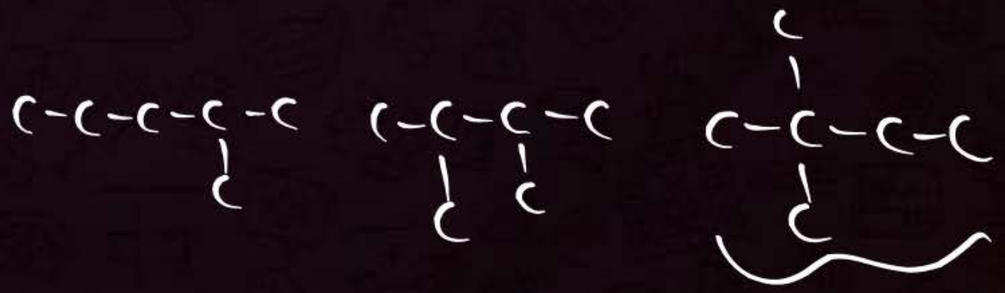
7. Isomerismation

- **Catalyst** → Anhy $AlCl_3$ / HCl, Δ

- $CH_3-CH_2-CH_2-CH_3$ or  $\xrightarrow[/HCl;\Delta]{\text{Anh. } AlCl_3}$ $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3$

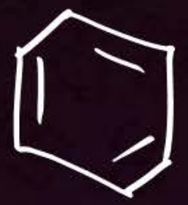
-  $\xrightarrow[/HCl;\Delta]{\text{Anh. } AlCl_3}$ 

Branching ↑
stability ↑

-  $\xrightarrow[/HCl;\Delta]{\text{Anh. } AlCl_3}$ 

8. Aromatisation

↳ Reagent ⇒ Cr_2O_3 / Mo_2O_3 , 15 atm.

C_6H_{14} (n-hexane) $\xrightarrow[15\ atm]{Mo_2O_3}$ 

Benzene.

C_7H_{16} (n-heptane) $\xrightarrow[15\ atm]{Mo_2O_3}$ 

Toluene

C_8H_{18} (n-Octane) $\xrightarrow{''}$ 

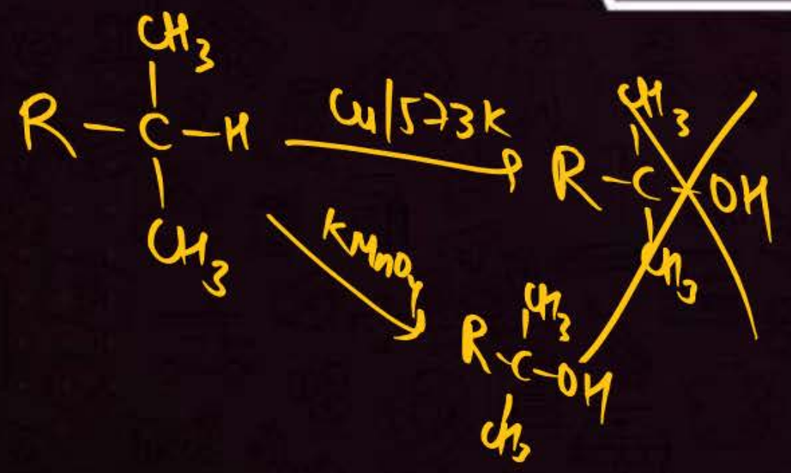
xylene

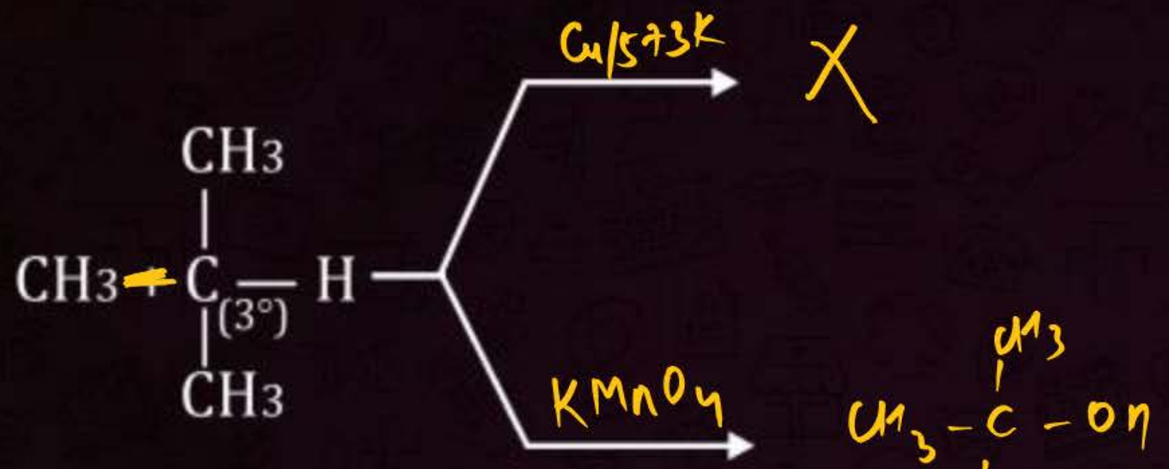
9. Catalytic Oxidation

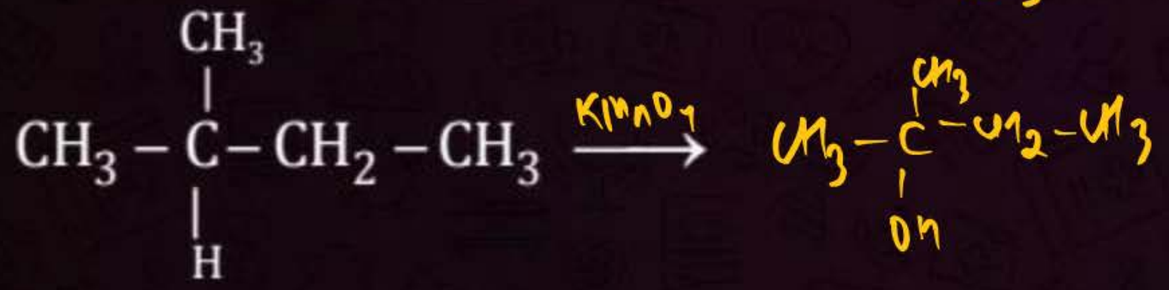
$$RCH_3 + O_2 \xrightarrow{Cu/573K} R-CH_2-OH$$

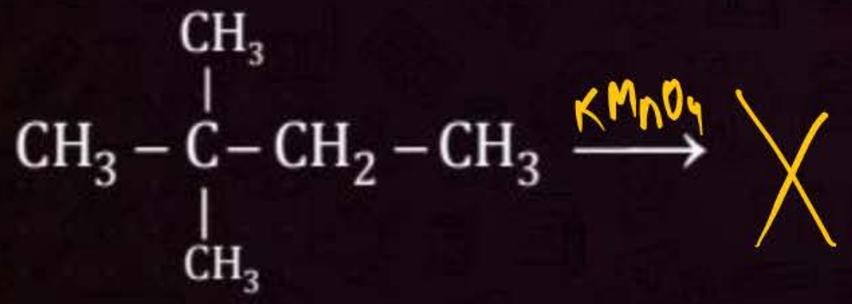
$$RCH_3 + O_2 \xrightarrow{Mo_2O_3} R-\overset{O}{\overset{\|}{C}}-H$$

$$RCH_3 + O_2 \xrightarrow{Mn(CH_3COO)_2} R-\overset{O}{\overset{\|}{C}}-OH$$




CH3
CH3 – C – H
(3°)
CH3
Cu/573K
X
KMnO4


CH3
CH3 – C – CH2 – CH3
H
KMnO4


CH3
CH3 – C – CH2 – CH3
CH3
KMnO4
X

QUESTION

Consider the above reaction and identify the missing reagent/chemical.

[NEET-2021]

$$CH_3CH_2COO^-Na^+ \xrightarrow[\text{Heat}]{NaOH^+} CH_3CH_3 + Na_2CO_3$$

(A) B_2H_6

(B) Red phosphorus

(C) CaO

(D) DIBAL-H

QUESTION

Which of the following alkane cannot be made in good yield by Wurtz reaction?

[NEET 2020]

(A) 2, 3-dimethylbutane

(B) n-heptane

(C) n-butane

(D) n-hexane

QUESTION

Hydrocarbon (A) reacts with bromine by substitution to form an alkyl bromide which by Wurtz reaction is converted to gaseous hydrocarbon containing less than four carbon atoms. A is [NEET 2018]

(A) $CH_3 - CH_3$

(B) $CH_2 = CH_2$

(C) $CH \equiv CH$

(D) CH_4

$$CH_4 + Br_2 \longrightarrow CH_3-Br \xrightarrow{2Na} CH_3-CH_3$$

QUESTION

Which of the following reactions is expected to readily give a hydrocarbon product in good yields? [CBSE AIPMT 1997]

(A) $RCOOK \xrightarrow[\text{oxidation}]{\text{Electrolysis}}$

(B) $RCOOAg \xrightarrow{I_2}$

(C) $CH_3CH_3 \xrightarrow[hv]{Cl_2}$

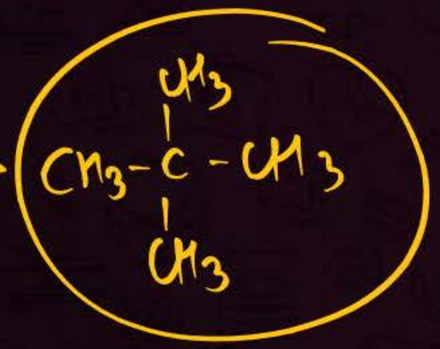
(D) $(CH_3)_2CCl \xrightarrow{C_2H_5OH}$

QUESTION

The alkane that gives only one mono-chloro product on chlorination with Cl_2 in presence of diffused sunlight is **[NEET (Odisha) 2019]**

(A) 2, 2-dimethylbutane

(B) neopentane



(C) n-pentane

(D) isopentane

QUESTION

The compound that will react most readily with gaseous bromine has the formula

[NEET 2016, Phase II]

(A) C_3H_6

(B) C_2H_2

(C) C_4H_{10}

(D) C_2H_4

QUESTION

Liquid hydrocarbons can be converted to a mixture of gaseous hydrocarbons by

[CBSE AIPMT 2010]

(A) oxidation

(B) cracking

(C) distillation under reduced pressure

(D) hydrolysis

QUESTION

In the commercial gasolines, the type of hydrocarbons which is more desirable, is

[CBSE AIPMT 1997]

(A) branched hydrocarbon

(B) straight chain hydrocarbon

(C) linear, unsaturated hydrocarbon

(D) toluene

QUESTION

In the free radical chlorination of methane, the chain initiating step involves the formation of [CBSE AIPMT 1994]

(A) chlorine free radical

(B) hydrogen chloride

(C) methyl radical

(D) chloromethyl radical

QUESTION

Reactivity of hydrogen atoms attached to different carbon atoms in alkanes has the order **[CBSE AIPMT 1993]**

(A) tertiary> primary > secondary

(B) Primary > secondary > tertiary

(C) Both (A) and (B)

(D) tertiary > secondary > primary

QUESTION

Which of the following compounds has the lowest boiling point?

[CBSE AIPMT 1994]

(A) $CH_3CH_2CH_2CH_2CH_3$

(B) $CH_3CH{=}CH{-}CH_2CH_3$

(C) $CH_3CH{=}CH{-}CH = CH_2$

(D) $CH_3CH_2CH_2CH_3$

Alkenes

Preparation:

1. Dehydration of Alcohol:

$$CH_2-CH_2 \xrightarrow[\Delta]{H^{\oplus}} CH_2=CH_2 + H_2O$$

(H, OH)

Mechanism

(Protonation of alcohol)

Step-I

$$CH_2-CH_2 + H^{\oplus} \longrightarrow CH_3-CH_2$$

(H, :O–H) → (H, ⊕O–H)

Step-II (Dehydration)

$$CH_3-CH_2 \xrightarrow[rds]{slow} CH_3-\overset{\oplus}{C}H_2 + H_2O$$

(⊕O–H, H)

Rate = K [$CH_3-CH_2-\overset{+}{O}-H$]

order = 1 = Molecularity

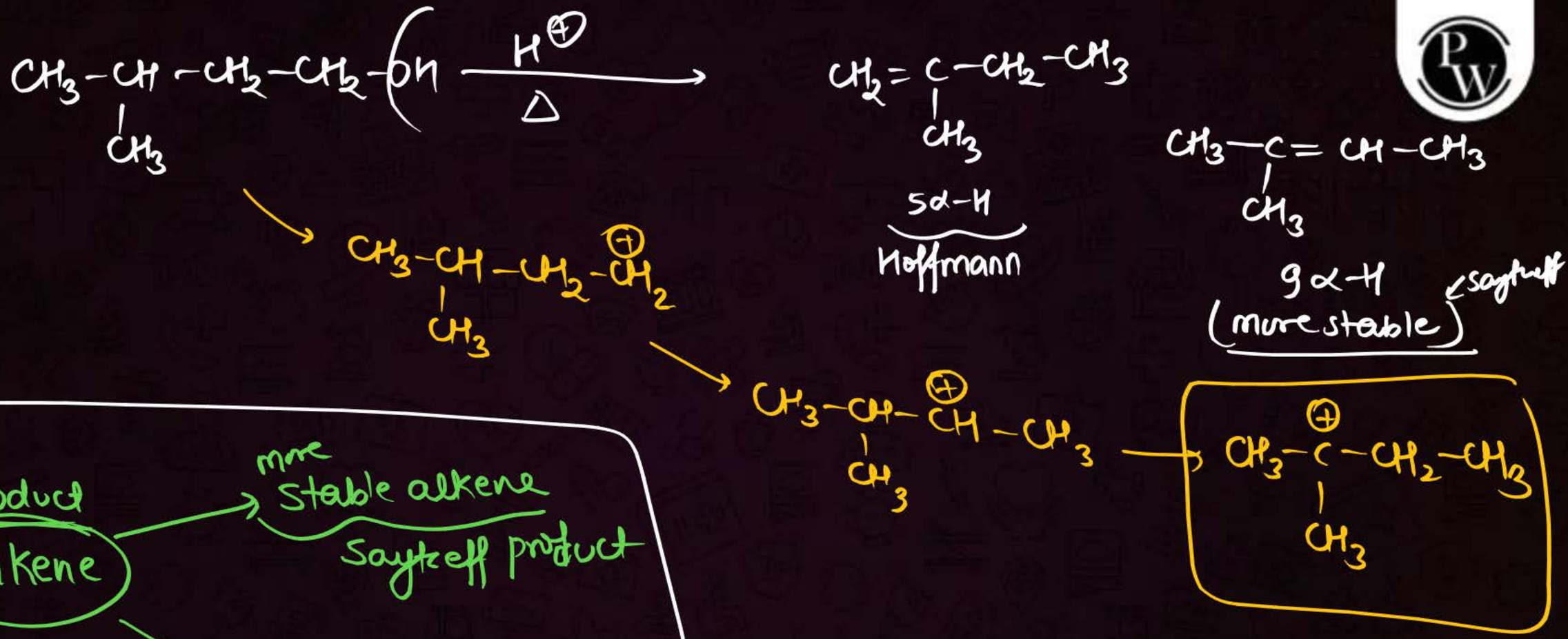
Step-III → Deprotonation

$$CH_2-\overset{\oplus}{C}H_2 \longrightarrow CH_2=CH_2 + H^{\oplus}$$

(H)

→ Rate of rxn ∝ Stability of ⊕

Trick → जहाँ OH है वहाँ ⊕ बनाओ, rearrange करो फिर alkene बना दो।

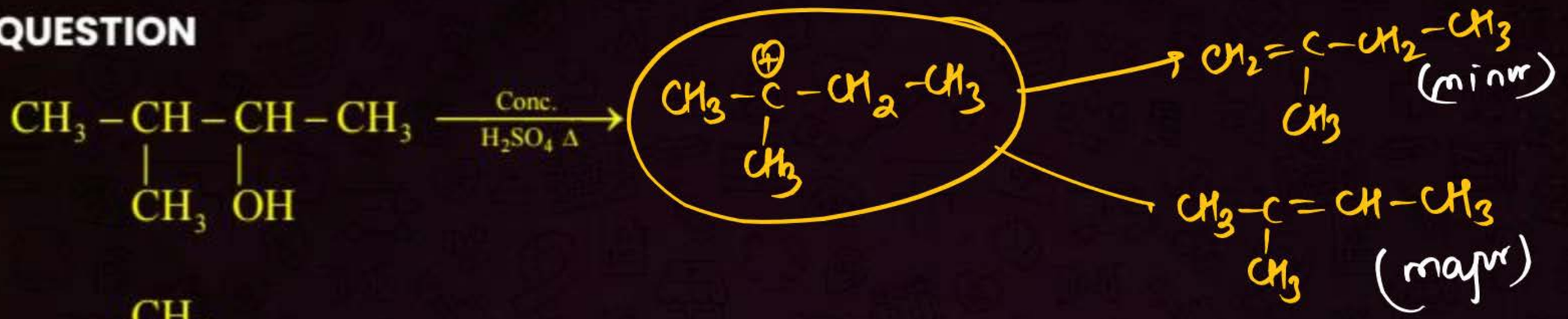


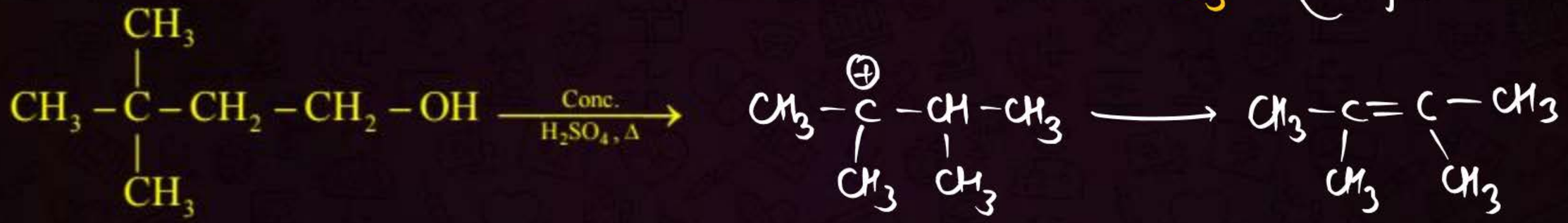
Product

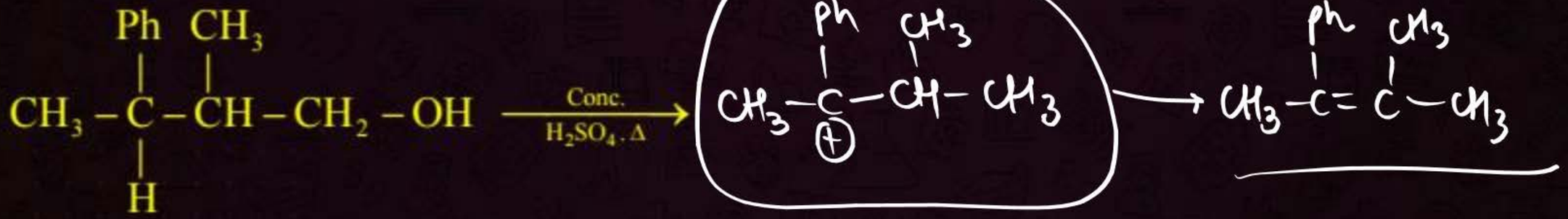
Alkene → more stable alkene — Saytzeff product

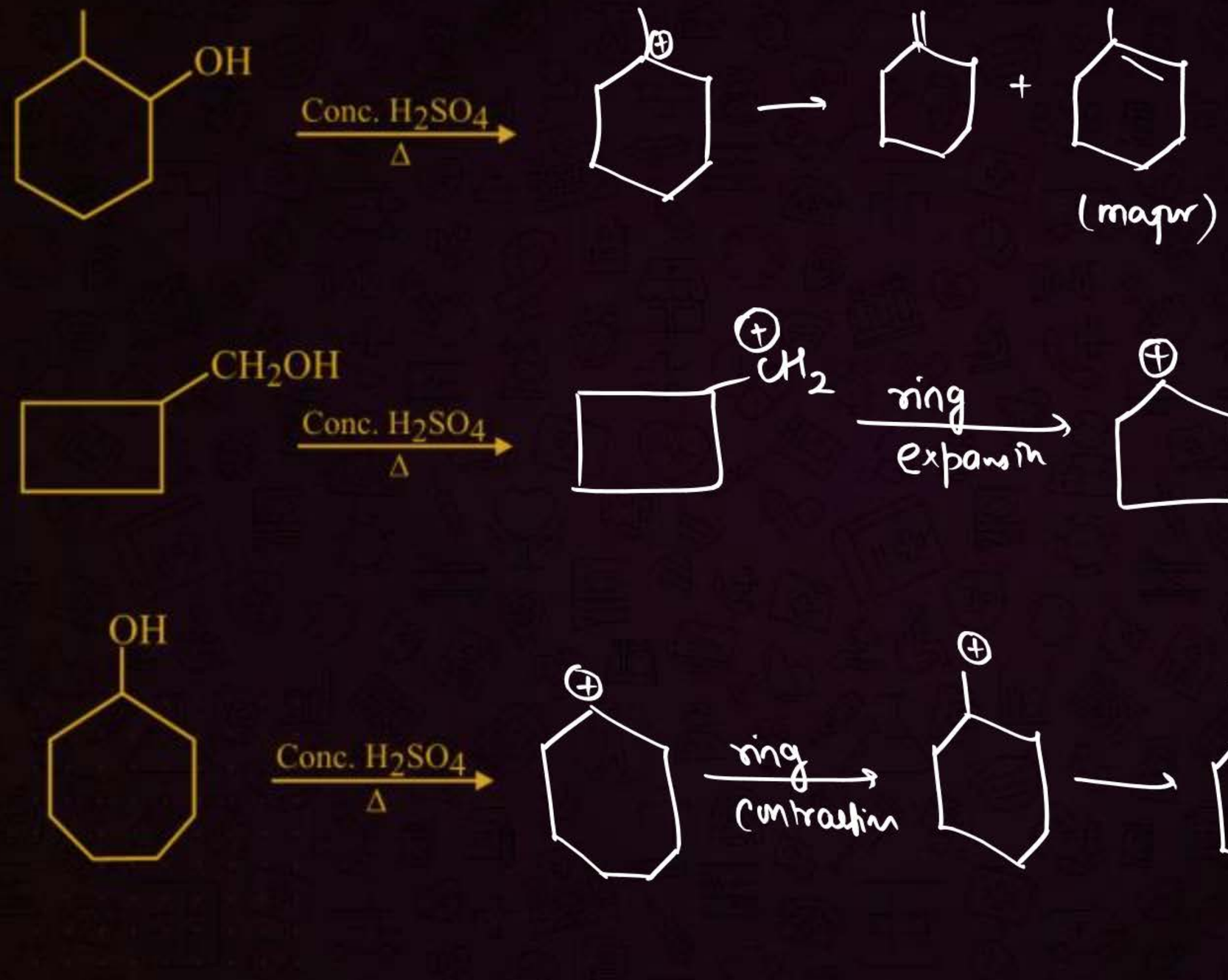
Alkene → less stable alkene — Hoffmann product

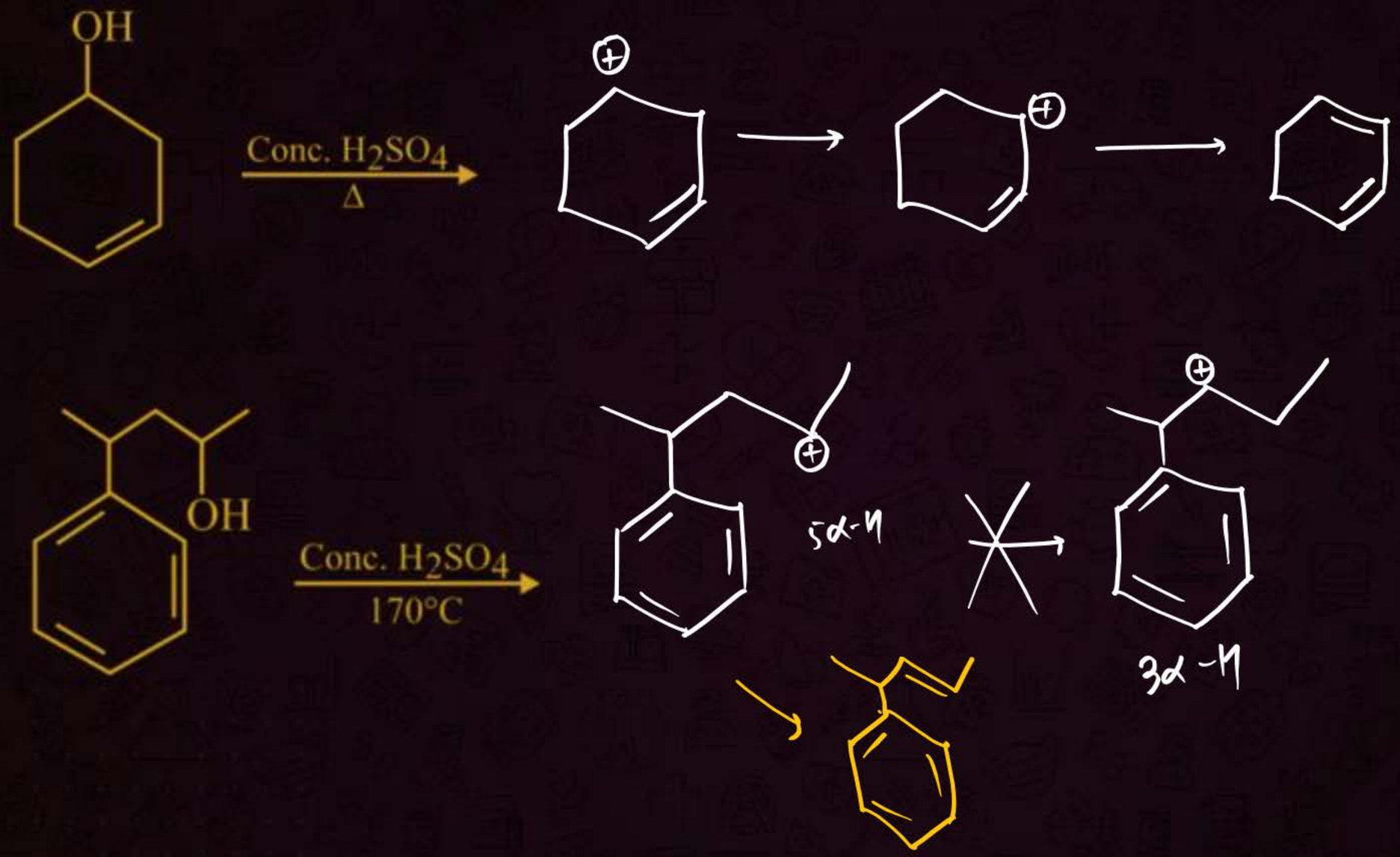
QUESTION

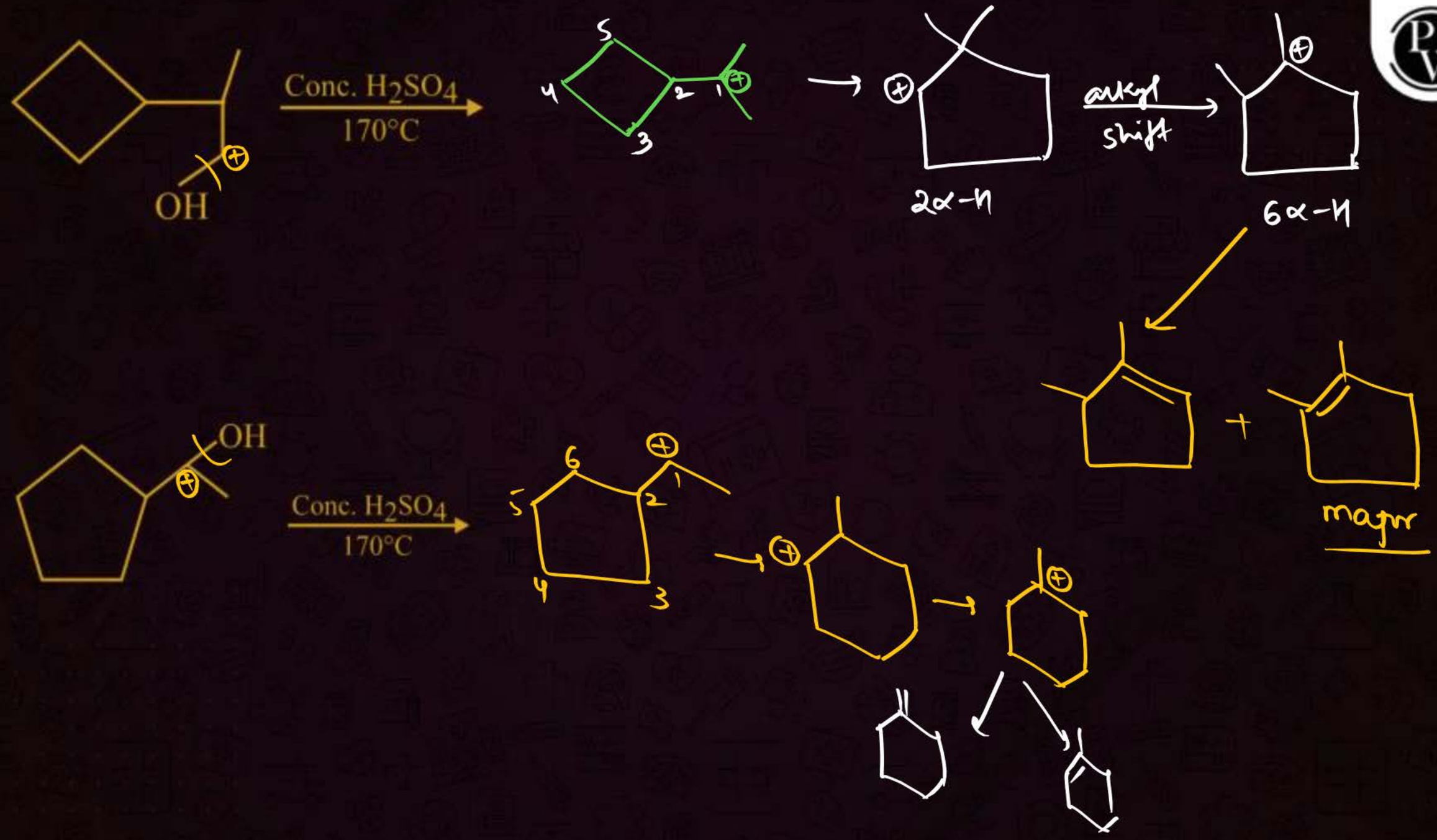






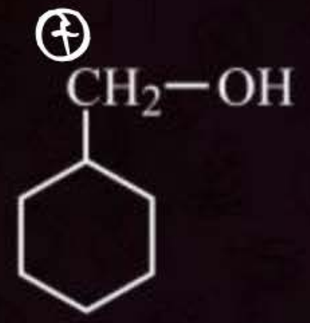

OH
Conc. H_2SO_4
Δ
(major)
CH_2OH
Conc. H_2SO_4
Δ
CH_2
ring expansion
OH
Conc. H_2SO_4
Δ
ring contraction

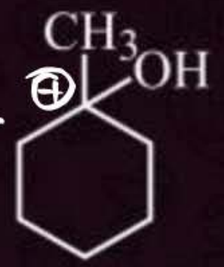

OH
Conc. H_2SO_4
Δ
OH
Conc. H_2SO_4
170°C
5α-H
3α-H

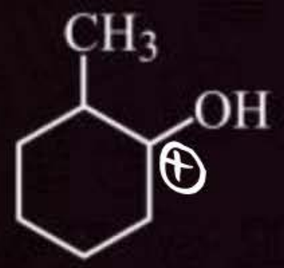

OH
Conc. H_2SO_4
170°C
2α-H
alkyl shift
6α-H
major
OH
Conc. H_2SO_4
170°C

QUESTION

Which will undergoes dehydration fast?

(A) 

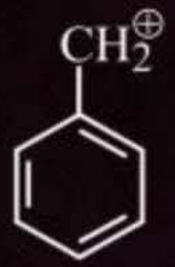
(B) 

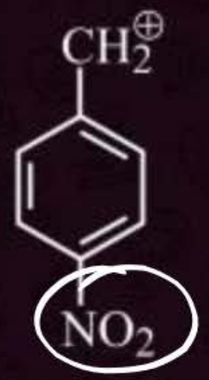
(C) 

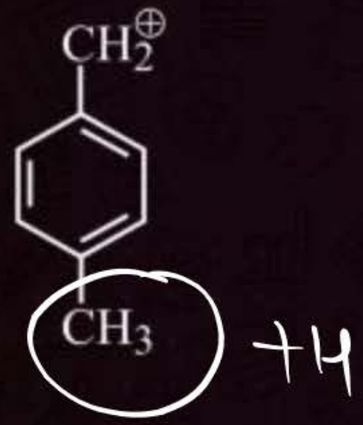
(D) 

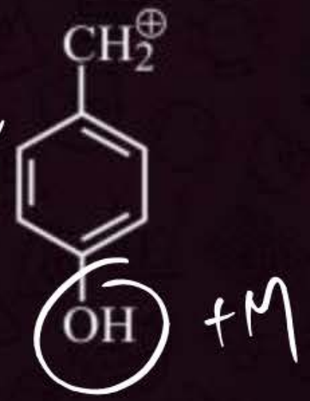
QUESTION

Arrange according to stability of Carbocation?

(A) 

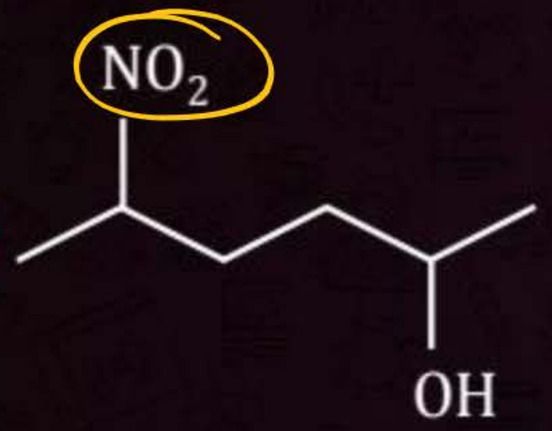
(B) 

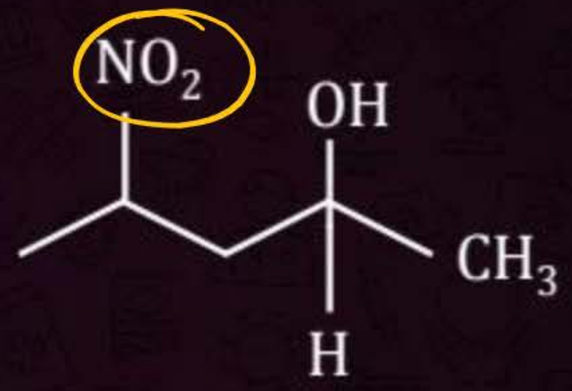
(C) 

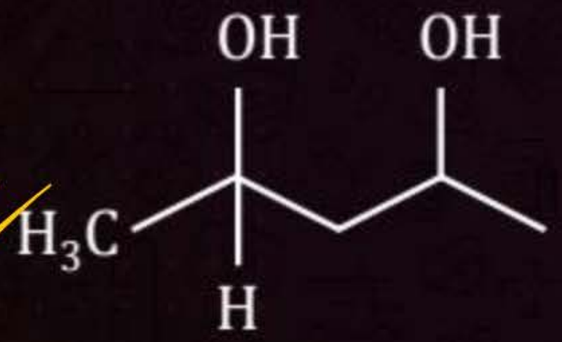
(D) 

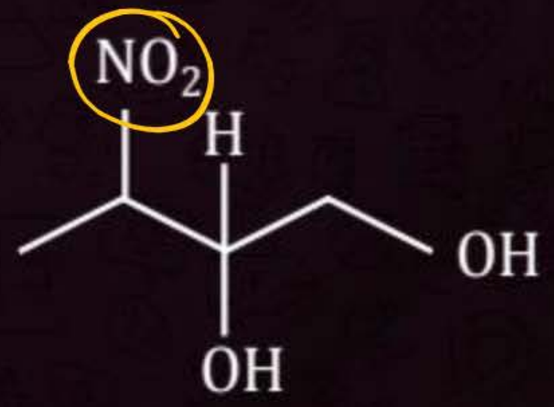
QUESTION

Which amongst the following will be most readily dehydrated under acidic conditions?

A


B


C


D


2. Dehydrohalogenation of Alkyl Halides

Removal of H + X

$$CH_2-CH_2 \xrightarrow[KOH]{\text{alcoholic}} CH_2=CH_2 + HX$$

($RO^{\ominus}$)

→ product ⇒ Saytzeff alkene (in general)

→ But in case of Bulky $t\text{-}O^{\ominus}$ → Hoffmann product

→ anti-elimination

→ 1,2-elimination

→ α,β-elimination

→ E^2 mechanism

→ Rate = K $[CH_3-CH_2-X][RO^{\ominus}]$

→ Order = molecularity = 2

→ Reactivity order ⇒ $I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$

aqueous KOH → Nucleophile $OH^{\ominus}$ → substitution.

alcoholic KOH → $R-O-H + KOH$ → Nucleophile ⇒ $R-O^{\ominus}$ (strong $Nu^{\ominus}$) → elimination

$$CH_3-\underset{\underset{H}{|}}{CH}-\underset{\underset{Br}{|}}{CH_2} \xrightarrow[KOH,\Delta]{alc.} CH_3-CH=CH_2$$

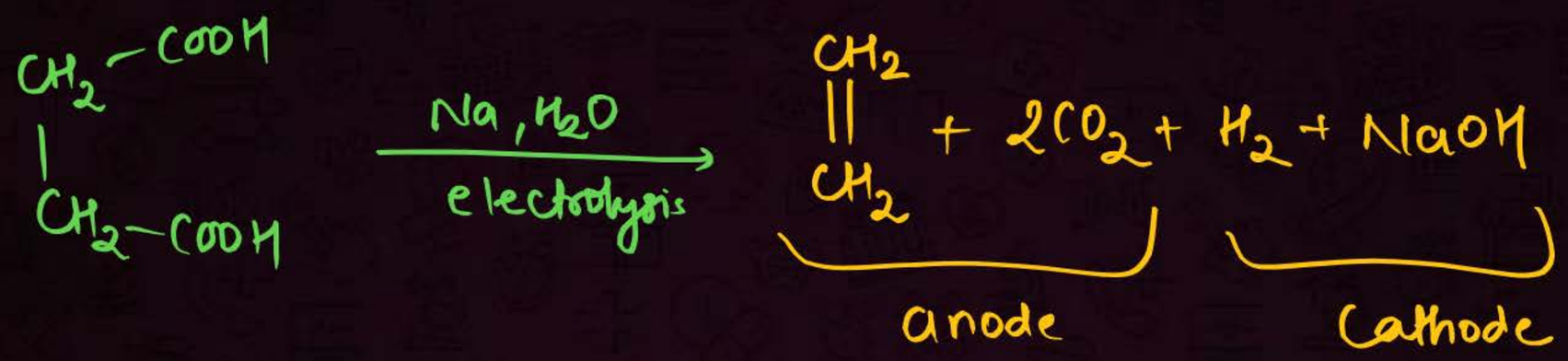
$$\underset{\underset{H}{|}}{CH_2}-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-\underset{\underset{H}{|}}{CH}-CH_3 \xrightarrow[KOH,\Delta]{alc} \underset{(minor)}{CH_2=\overset{\overset{CH_3}{|}}{C}-CH_2-CH_3} + \underset{(major)}{CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH_3}$$

3. Dehalogenation of Vicinal dihalides

$$\underset{\underset{Br}{|}}{CH_2} - \underset{\underset{Br}{|}}{CH_2} \xrightarrow{Zn} CH_2 = CH_2 + ZnBr_2$$

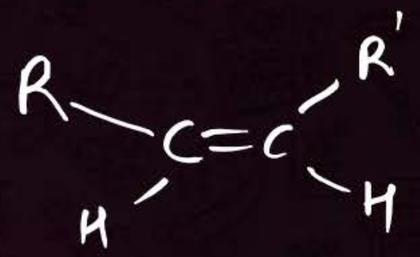
$$CH_3 - CH_2 - \underset{\underset{Br}{|}}{CH} - \underset{\underset{Br}{|}}{CH_2} \xrightarrow{Zn} CH_3 - CH_2 - CH = CH_2$$

4. From Kolbe's Electrolysis



→ Free radical mechanism

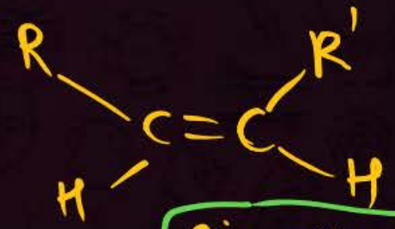
5. Partial Hydrogenation of Alkyne

$R-C\equiv C-R'$ $\xrightarrow{\text{Pd-C or Pd-CaCO}_3 \text{ or Pd-BaSO}_4}$ 

poisoned with 'S', Quinoline

Lindlar's Catalyst

cis-alkene

$R-C\equiv C-R'$ $\xrightarrow[\text{P-2 Catalyst}]{(Ni_2)B \text{ or}}$ 

cis-alkene

$R-C\equiv C-R'$ $\xrightarrow[\text{Birch reduction}]{Na,\ liq.\ NH_3}$ 

trans-alkene

6. Pyrolysis/Cracking of Alkanes → already done

$$C_4H_{10} \xrightarrow[MO_2O_3]{\Delta} C_4H_8 + H_2 \uparrow$$

$$C_6H_{14} \xrightarrow[Cr_2O_3]{\Delta} C_6H_{12} + H_2 \uparrow$$

$$C_6H_{14} \xrightarrow[Al_2O_3]{\Delta} C_3H_8 + C_3H_6$$

Si A Z } (C–C) bond

V M C → (C–H) bond.

1. Dehydration of alcohol → $C^{\oplus}$
2. Dehydrohalogenation of R–X
3. Dehalogenation of R–CH(X)–CH(X)
4. Kolbe's electrolysis
5. Alkynes
6. Pyrolysis

Physical Properties of Alkenes:

1. Heat of Hydrogenation:

always exothermic

$$\Delta H_{hyd} \propto \text{no. of } \pi\text{-bonds}$$
$$\propto \frac{1}{\text{stability}}$$

2. Physical State:

$C_2 - C_4 \rightarrow$ gas
$C_4 - C_{18} \rightarrow$ liquid
$> C_{18} \rightarrow$ solid

$\rightarrow$ all are colorless/odorless except ethene $\rightarrow$ pleasant smell

3. Density:

- always lower than water.
- mass ↑ density ↑
  - density upto 0.8 g/cm³.

4. Melting Point:

- donot follow regular trend
- M.pt ∝ Branching ∝ symmetry
  ∝ stability
  ∝ Packing efficient

M.P order

Trans > Cis

geminal > Trans > Cis → experimental

5. **Boiling Point:**

- follow the regular trend.
- B.pt $\propto$ dipole moment
- In general $\Rightarrow$ cis > trans

6. **Solubility**

- alkenes $\Rightarrow$ non-polar in nature.
- non-polar solvent में Dissolve होगा

Chemical Properties of Alkene:

(1) Electrophilic Addition Reaction:

Addition Rxn

- → Electrophilic addition Rxn (EAR) :- first $E^{\oplus}$ addition, then $Nu^{\ominus}$ is added.
- → Nucleophilic addition rxn (NAR) ⇒ first $Nu^{\ominus}$ addition, then $E^{\oplus}$ is added.

Symmetrical alkene

$$R-CH=CH-R + \overset{\oplus}{H}\overset{\ominus}{Br} \longrightarrow R-\underset{H}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH}}-R$$

Unsymmetrical alkene

$$CH_3-CH=CH_2 + \overset{\oplus}{H}\overset{\ominus}{Br} \longrightarrow CH_3-\underset{Br}{\underset{|}{CH}}-\underset{H}{\underset{|}{CH_2}}$$

Markovnikov's rule (MKR) ⇒ for unsymmetrical alkene,

Negative part of polar reagent attaches to that double bonded 'c' which has less no. of H attached.

$$CH_3-\overset{CH_3}{CH}-CH=CH_2 + HCl \longrightarrow CH_3-\overset{CH_3}{CH}-\underset{Cl}{CH}-\underset{H}{CH_2}$$

$$\longrightarrow CH_3-\overset{CH_3}{\underset{Cl}{C}}-CH_2-CH_3$$

Mechanism of EAR

Rate of EAR $\propto$ stability of $C^{\oplus}$

$$CH_3-CH=CH_2 + HBr \longrightarrow CH_3-\underset{Br}{CH}-\underset{H}{CH_2}$$

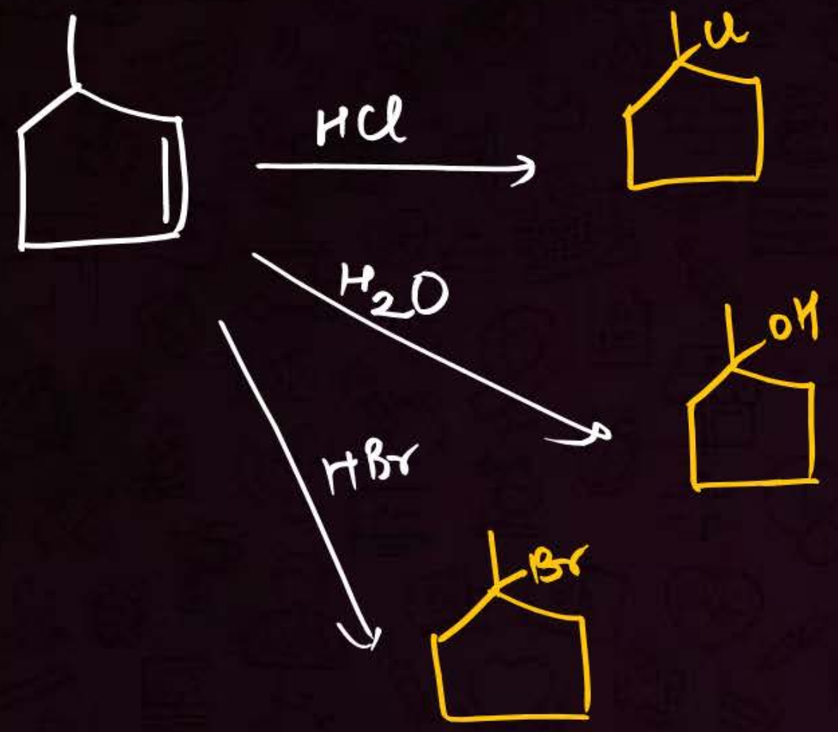
Step-I → attack of $E^{\oplus}$

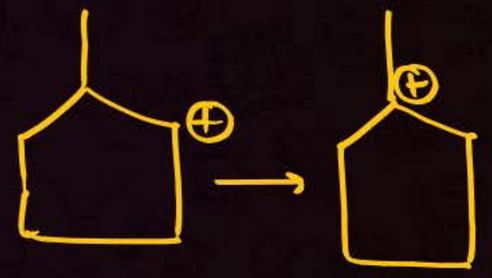
$$CH_3-CH=CH_2 + H^{\oplus} \xrightarrow[\text{rds.}]{\text{slow}} \underbrace{CH_3-\overset{\oplus}{C}H-CH_3}_{\text{Intermediate}}$$

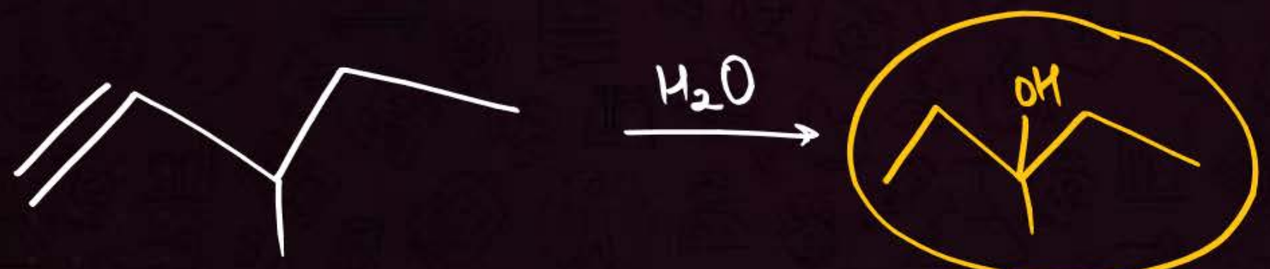
Intermediate → Rearrangement

Step-II → $Nu^{\ominus}$ attack

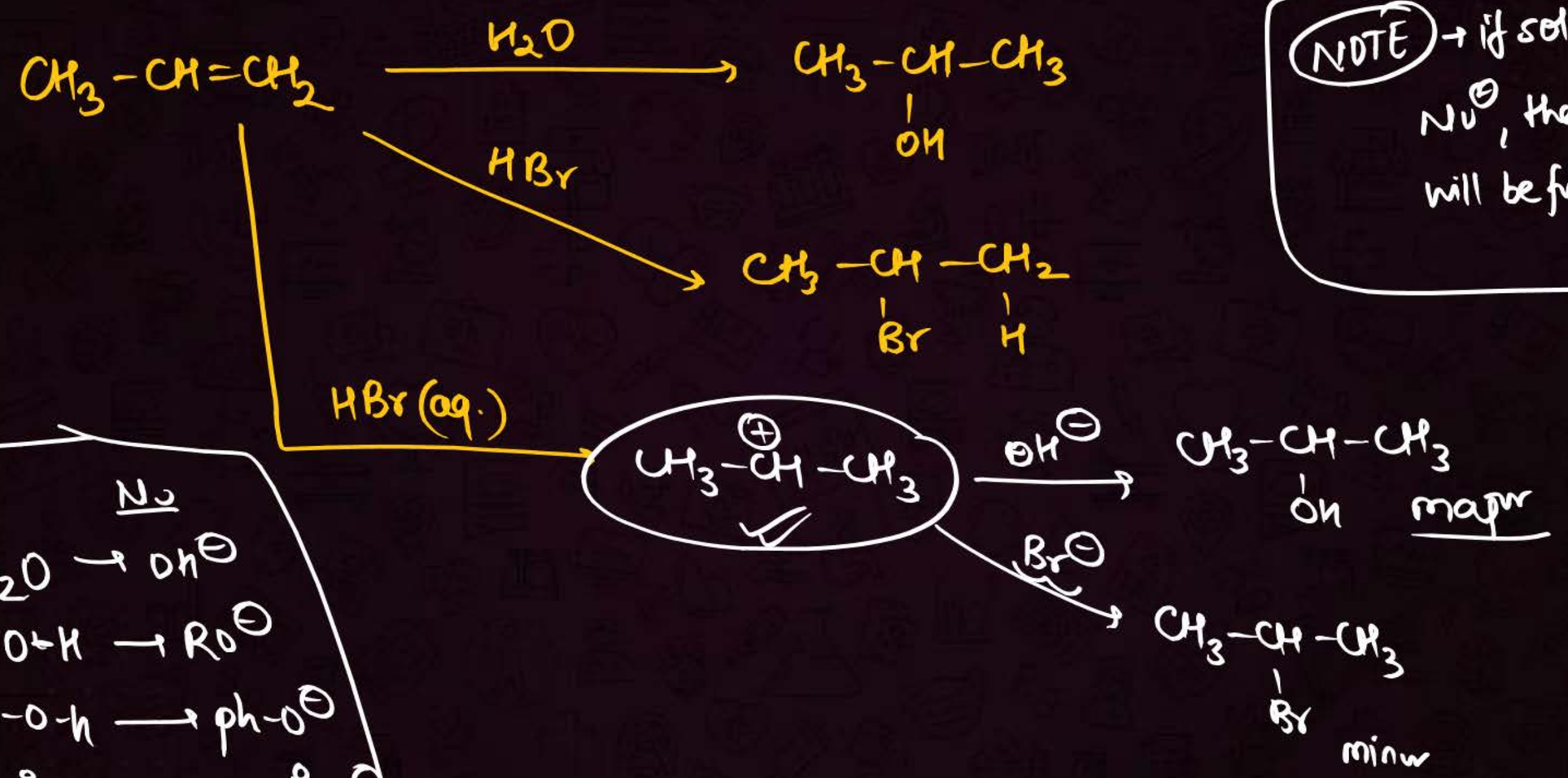
$$CH_3-\overset{\oplus}{C}H-CH_3 + Br^{\ominus} \longrightarrow CH_3-\underset{Br}{CH}-CH_3$$


HCl
Cl
H_2O
OH
HBr
Br




H_2O
OH

Effect of Solvent



NOTE → if solvent can provide $Nu^{\ominus}$, then major product will be formed by solvent $Nu^{\ominus}$

<u>Nu</u>

$H_2O \rightarrow OH^{\ominus}$

$R-O-H \rightarrow RO^{\ominus}$

$Ph-O-H \rightarrow Ph-O^{\ominus}$

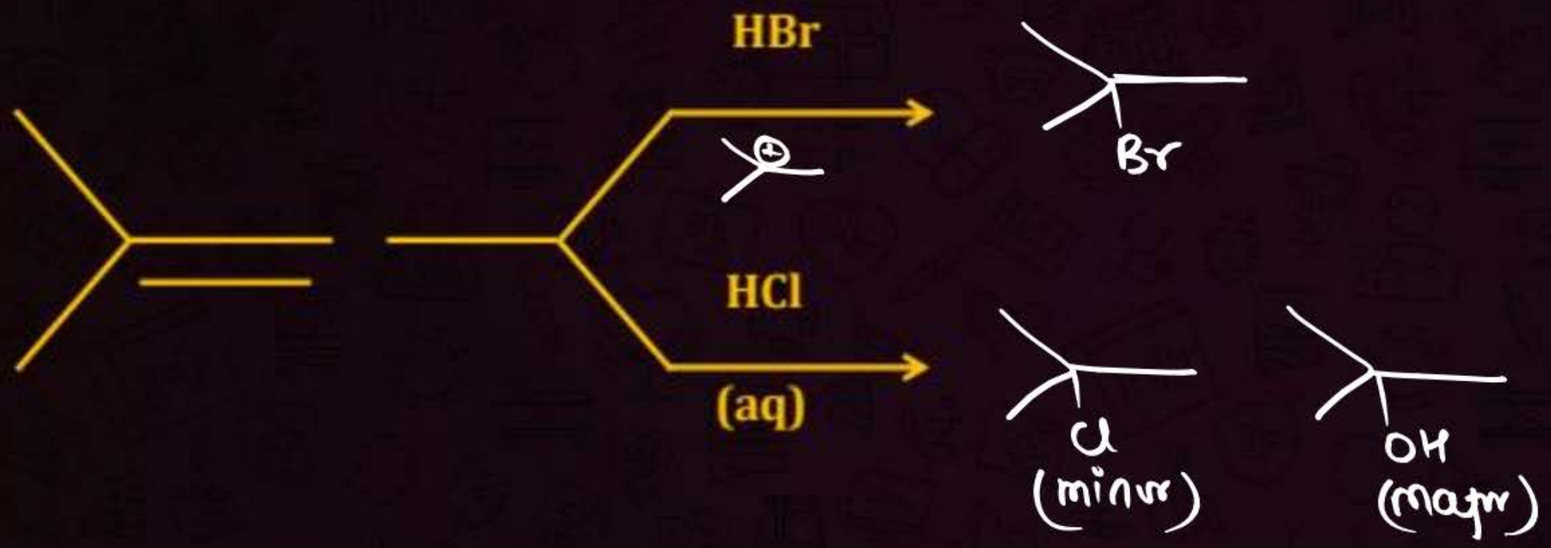
$R-\overset{O}{\overset{\|}{C}}-O-H \rightarrow R-\overset{O}{\overset{\|}{C}}-O^{\ominus}$

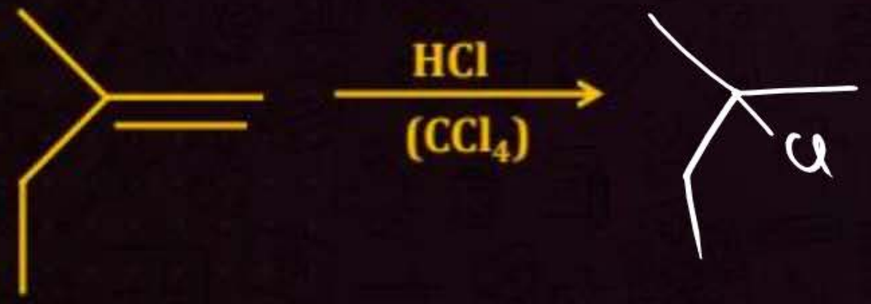
$CH_4 \rightarrow \times$

$$Ph-CH=CH_2 \xrightarrow[(aq)]{HCl} Ph-\overset{\oplus}{C}H-CH_3$$

$Ph-\overset{\oplus}{C}H-CH_3 \rightarrow Ph-\underset{Cl}{CH}-CH_3$ (minor)

$Ph-\overset{\oplus}{C}H-CH_3 \rightarrow Ph-\underset{OH}{CH}-CH_3$ (major)





Effect of Temperature

(a) Kinetically controlled Product (KCP) ⇒ less stable product but most stable intermediate

↳ at low temp.

(b) Thermally controlled Product (TCP) ⇒ more stable product irrespective of stability of intermediate

↳ at high temp.

$$CH_2=CH-CH=CH_2 + HBr \longrightarrow CH_2(H)-CH(Br)-CH=CH_2 + CH_2(H)-CH=CH-CH_2(Br)$$

(1,2-addition) (less stable product) at low temp. (KCP)

(1,4-addition) (stable product) ↳ at high temp. (TCP)

Step-I

$$CH_2=CH-CH=CH_2 + H^{\oplus} \longrightarrow CH_2=CH-\overset{\oplus}{C}H-CH_3 \text{ (more stable)}$$

$$\updownarrow$$

$$\overset{\oplus}{C}H_2-CH=CH-CH_3 \text{ (less stable)}$$

Step-II

$$CH_2=CH-\overset{\oplus}{C}H-CH_3 + Br^{\ominus} \longrightarrow CH_2=CH-CH(Br)-CH_2(H) \text{ (less stable product)}$$

$$\overset{\oplus}{C}H_2-CH=CH-CH_3 + Br^{\ominus} \longrightarrow CH_2(Br)-CH=CH-CH_3 \text{ (more stable)}$$

Comparison of Electrophilic addition in = & –OH:

$$CH_2=CH_2 + H^{\oplus} \longrightarrow \overset{\oplus}{C}H_2-\underset{\underset{H}{|}}{CH_2}$$

$$CH_3-CH_2-\ddot{\underset{..}{O}}-H + H^{\oplus} \longrightarrow CH_3-CH_2-\underset{\underset{H}{|}}{\overset{\oplus}{O}}-H \longrightarrow CH_3-\overset{\oplus}{C}H_2 + H_2O$$

Reactivity order ⇒ $\underbrace{(=)}_{\pi\text{-bond break}} > \underbrace{-OH}_{\sigma\text{-bond break}}$

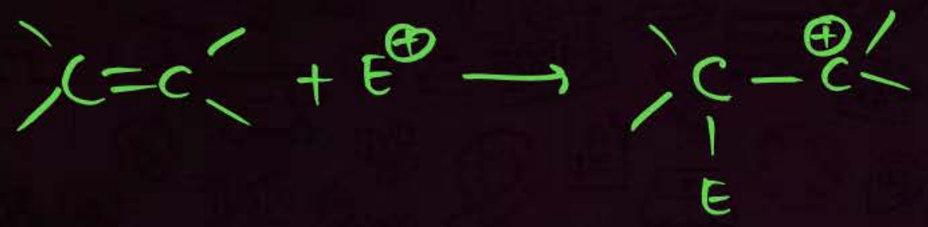
But in case of resonance ⇒ $\underbrace{(=)}_{} < -OH$

QUESTION

$$CH_2 = CH - CH_2 - CH_2 - OH \xrightarrow{HCl} CH_2(H) - CH(Cl) - CH_2 - CH_2 - OH$$

$$CH_2 = CH - \overset{\oplus}{C}H_2 - OH \xrightarrow[ROH]{H^+} CH_2 = CH - CH_2(OR)$$

Comparison of Electrophilic addition in (=) & (≡)

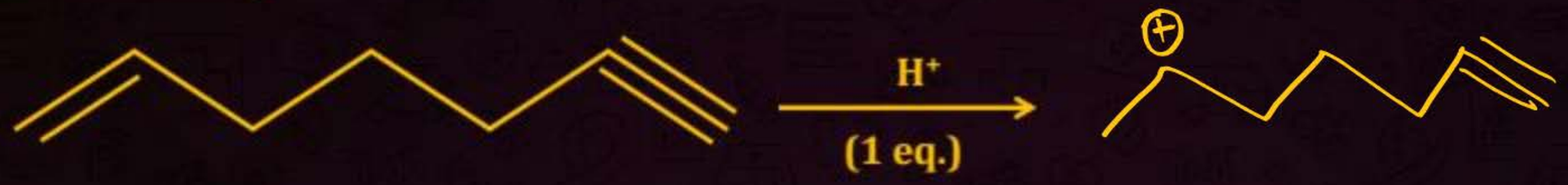


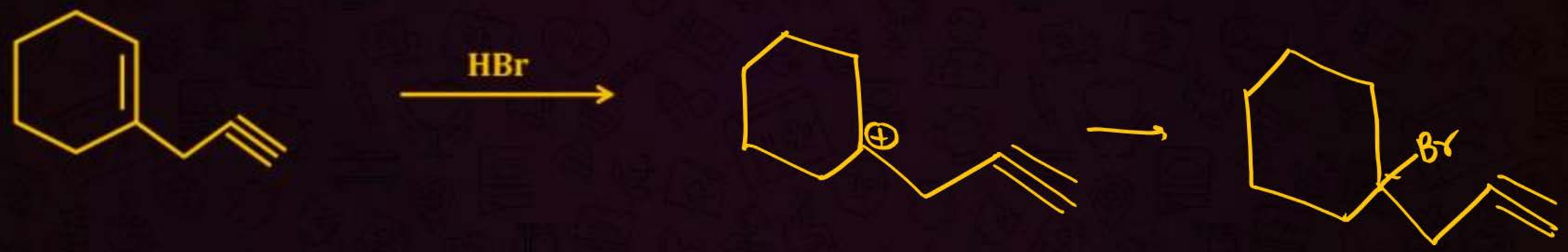
(Vinyl carbocation) → less stable

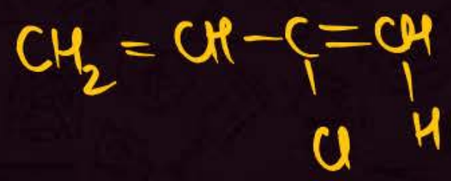
Reactivity for EAR ⇒ (=) > (≡)

except in case of resonance

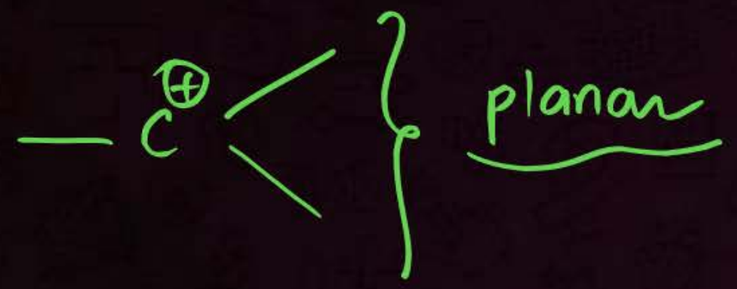
QUESTION



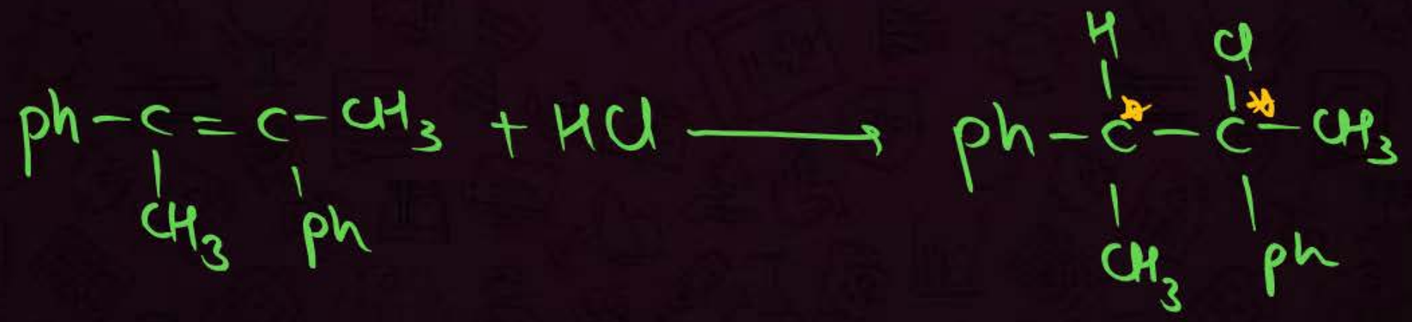


$CH_2 = CH - C \equiv CH \xrightarrow[\text{(1 eq.)}]{HCl}$ 

Stereochemistry of electrophilic addition reaction:



⇒ if chiral centre is present, equal amount of (d) & (l).

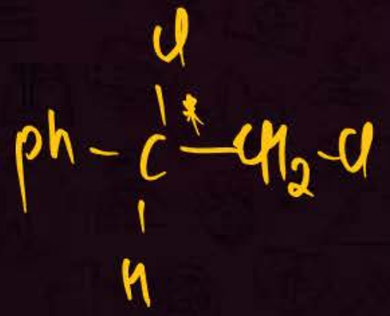


QUESTION

Alkene $\xrightarrow{HCl}$ Enaotiameric pair or Racemic mixture which of the following is possible Alkene?

(A) $CH_3 - CH = CH_2$

(B) $Ph - \underset{\underset{CH_3}{|}}{C} = \underset{\underset{CH_3}{|}}{C} - Ph$

(C) $Ph - CH = CH_2 \xrightarrow{HCl}$ 

(D) $Ph - \underset{\underset{Ph}{|}}{C} = CH_2$

9. Non-Classical Carbocation:

→ No rearrangement

→ partial (+ve) charge on 'c'.

$$CH_2=CH_2 + Br_2 \xrightarrow{CCl_4} CH_2(Br)-CH_2(Br)$$

→ used as test for unsaturation

Br_2/CCl_4 → colored.

When attaches on (=) bond, become colourless.

→ anti-addition

→ stereochemistry

→ In case of unsymmetrical alkene → follow Markovnikov's rule.

CAT / CAR

Cis $\xrightarrow[\text{addition}]{\text{Anti}}$ Racemic mixture | threo.

TAE / TAM

Trans $\xrightarrow[\text{addition}]{\text{anti}}$ Meso | Erythro

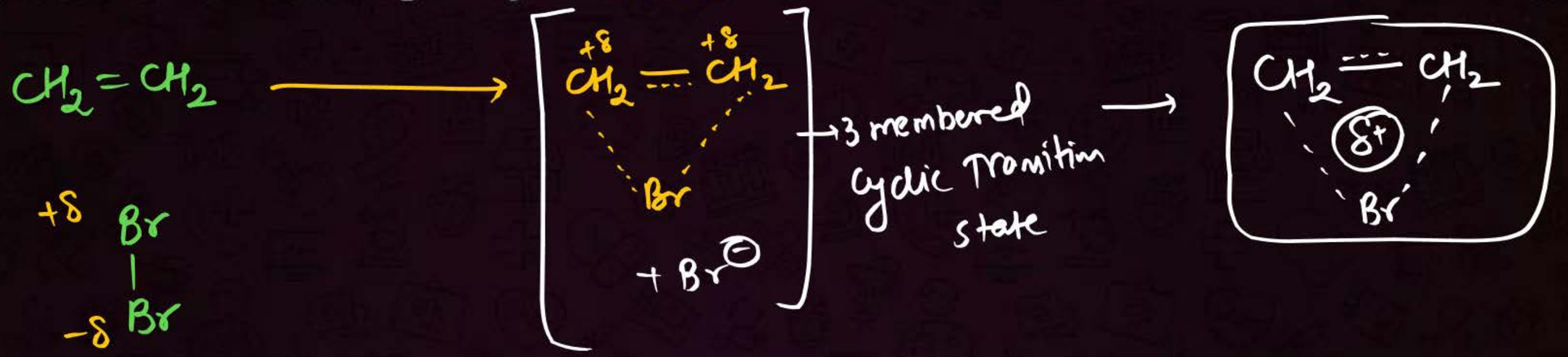
Cis $\xrightarrow[\text{addition}]{\text{syn}}$ Meso | Erythro. (CSM/CSE)

Trans $\xrightarrow[\text{addition}]{\text{syn}}$ Racemic mixture | Threo (TSR/TST)

Mechanism

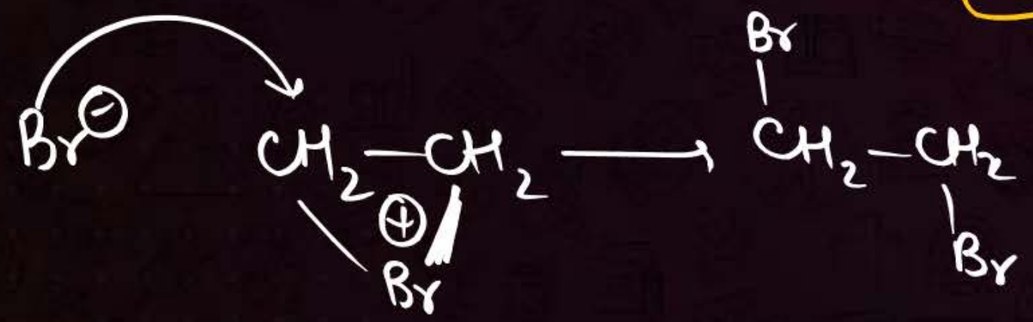
Step-1 (Addition of Electrophile)

$E^{\oplus} = Br_2$

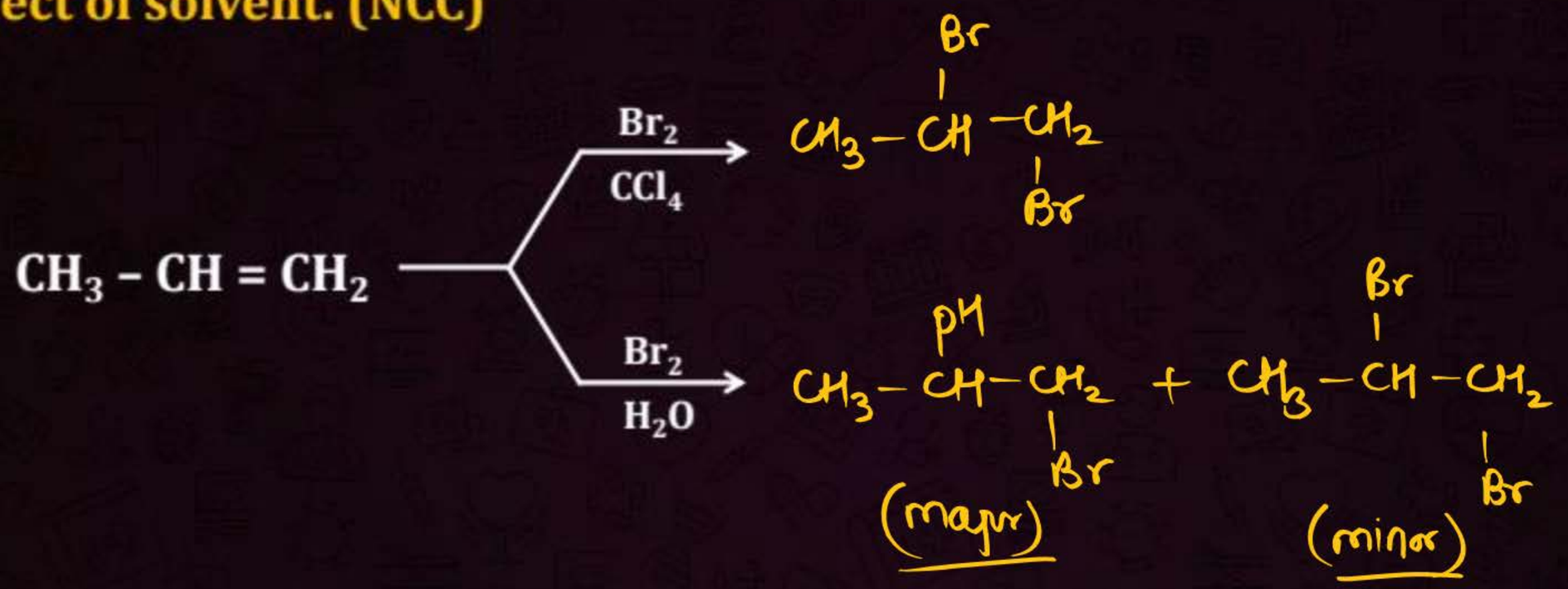


Step-2 (Addition of Nucleophile)

$Nu^{\ominus} = Br^{\ominus}$



Effect of solvent. (NCC)



Reactant	Reagent	E^+	Nu^- (major)	Major Product
$CH_3 - CH = CH_2$	$Br_2/\underline{ROH}$	Br_2	$Br^\ominus / RO^\ominus$	$CH_3-CH(OR)-CH_2Br$
$Ph - CH = CH_2$	$Cl_2/\underline{PhOH}$	Cl_2	$Cl^\ominus / PhO^\ominus$	$CH_3-CH(Ph)-CH_2Cl$
$CH_3 - CH = CH_2$	$Br - Cl$	$Br-Cl$	$Cl^\ominus$	$CH_3-CH(Cl)-CH_2Br$
$Ph - CH = CH_2$	$I - Cl$	ICl	$Cl^\ominus$	$Ph-CH(Cl)-CH_2I$
$CH_3 - CH = CH_2$	$HO - Cl$	$HOCl$	$OH^\ominus$	$CH_3-CH(OH)-CH_2Cl$
$Ph - CH = CH_2$	$HO - I$	HOI	$OH^\ominus$	$Ph-CH(OH)-CH_2I$

QUESTION

What will be the product?

$$\text{Trans-Alkene} \xrightarrow[CCl_4]{Br_2} \text{Product}$$

CAR
TAM

(A) Racemic Mixture

(B) Meso compound

(C) Threo

(D) Both (A) & (C)

(a) Reaction with cold conc. H_2SO_4

$$CH_2=CH_2 + \underbrace{H_2SO_4}_{H^{\oplus} + HSO_4^{\ominus}} \longrightarrow CH_2(H)-CH_2(OSO_3H)$$

$$\boxed{R-O-SO_3H + H_2O \longrightarrow R-OH + H_2SO_4}$$

(b) Reaction with water in presence of acid

$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2+H_2O \xrightarrow{H^+} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

$$CH_3-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH=CH_2+H_2O \xrightarrow{H^+} CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\oplus}{CH}-CH_3 \longrightarrow CH_3-\overset{\oplus}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_3$$

$$\xrightarrow{OH^{\ominus}} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_3$$

(c) Antimarkoni/Peroxide/Kharasch Effect

- Negative part of polar reagent will attach to that double bonded 'C' which has more no. of 'H' attached.
- free radical mechanism.
- No rearrangement
- (HBr in presence of R–O–O–R (Catalyst) Peroxide)

$$CH_3-CH=CH_2 + HBr \longrightarrow CH_3-\underset{Br}{CH}-\underset{H}{CH_2}$$

$$CH_3-CH=CH_2 \xrightarrow[R-O-O-R]{+HBr} CH_3-\underset{H}{CH}-\underset{Br}{CH_2}$$

HF, HCl → all steps are endothermic

H–I → first step exo then endo

all steps are exothermic

Mechanism

initiation

$$R-O-O-R \rightarrow RO^{\bullet} + RO^{\bullet}$$

$$RO^{\bullet} + H-Br \longrightarrow R-O-H + Br^{\bullet}$$

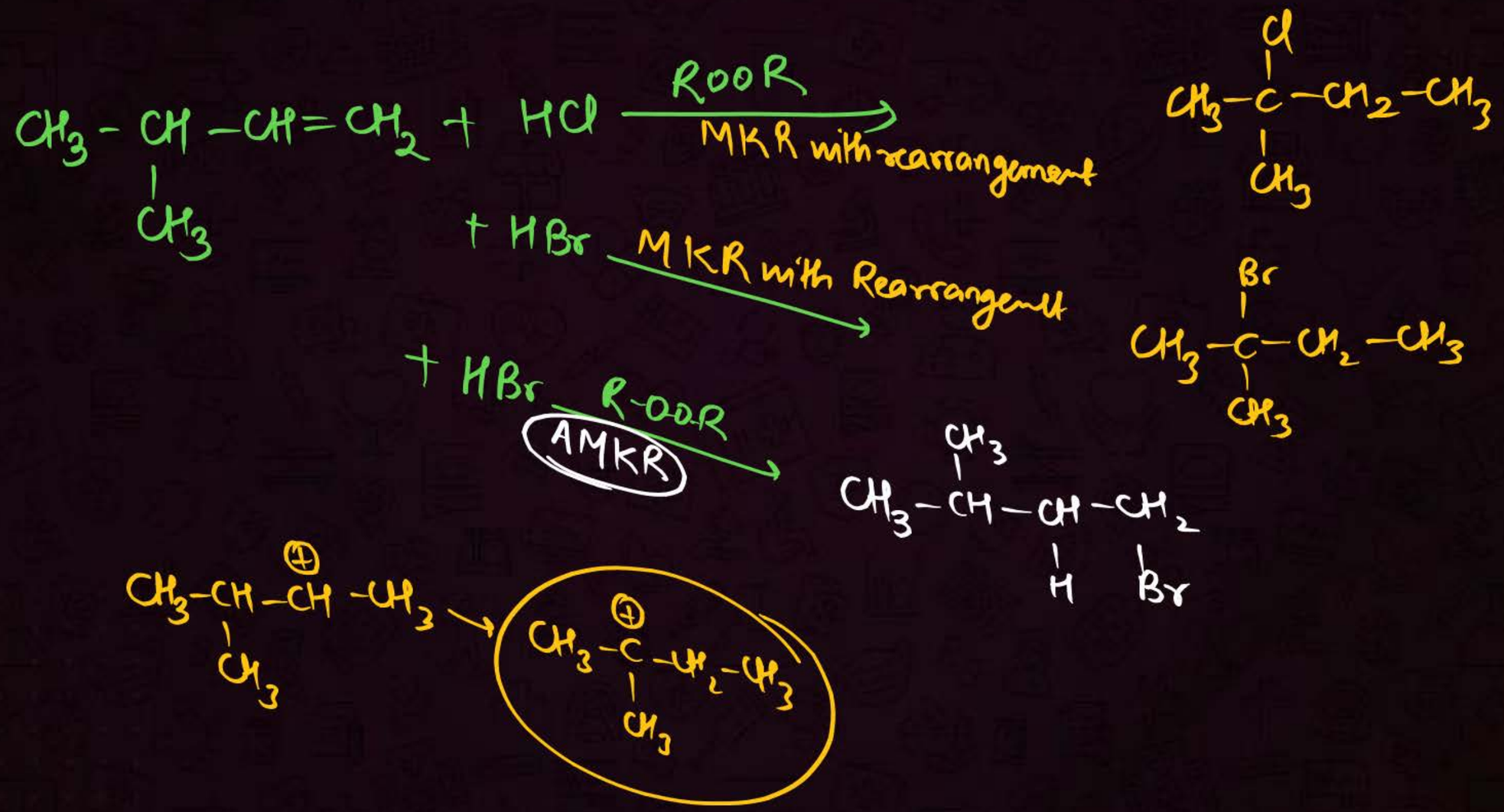
Propagation

$$CH_3-CH=CH_2 \xrightarrow{Br^{\bullet}} CH_3-\overset{\bullet}{C}H-\underset{Br}{CH_2}$$

$$CH_3-\overset{\bullet}{C}H-\underset{Br}{CH_2} + H-Br \longrightarrow CH_3-CH_2-CH_2-Br$$

Termination

$$Br^{\bullet} + Br^{\bullet} \rightarrow Br_2$$


ROOR
MKR with rearrangement
+ HBr
MKR with Rearrangement
+ HBr
R-OOR
AMKR

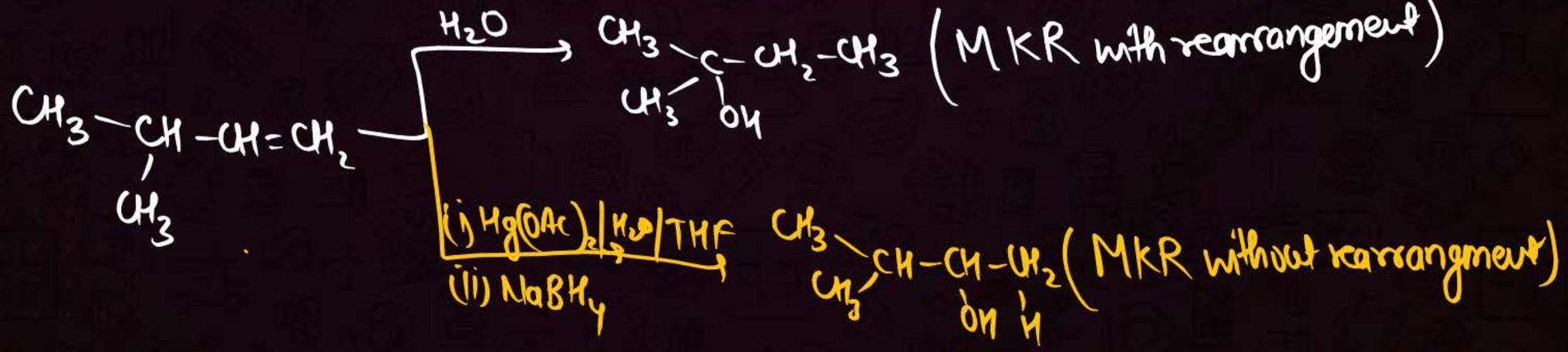
2. Oxymercuration & Demercuration of Alkenes:

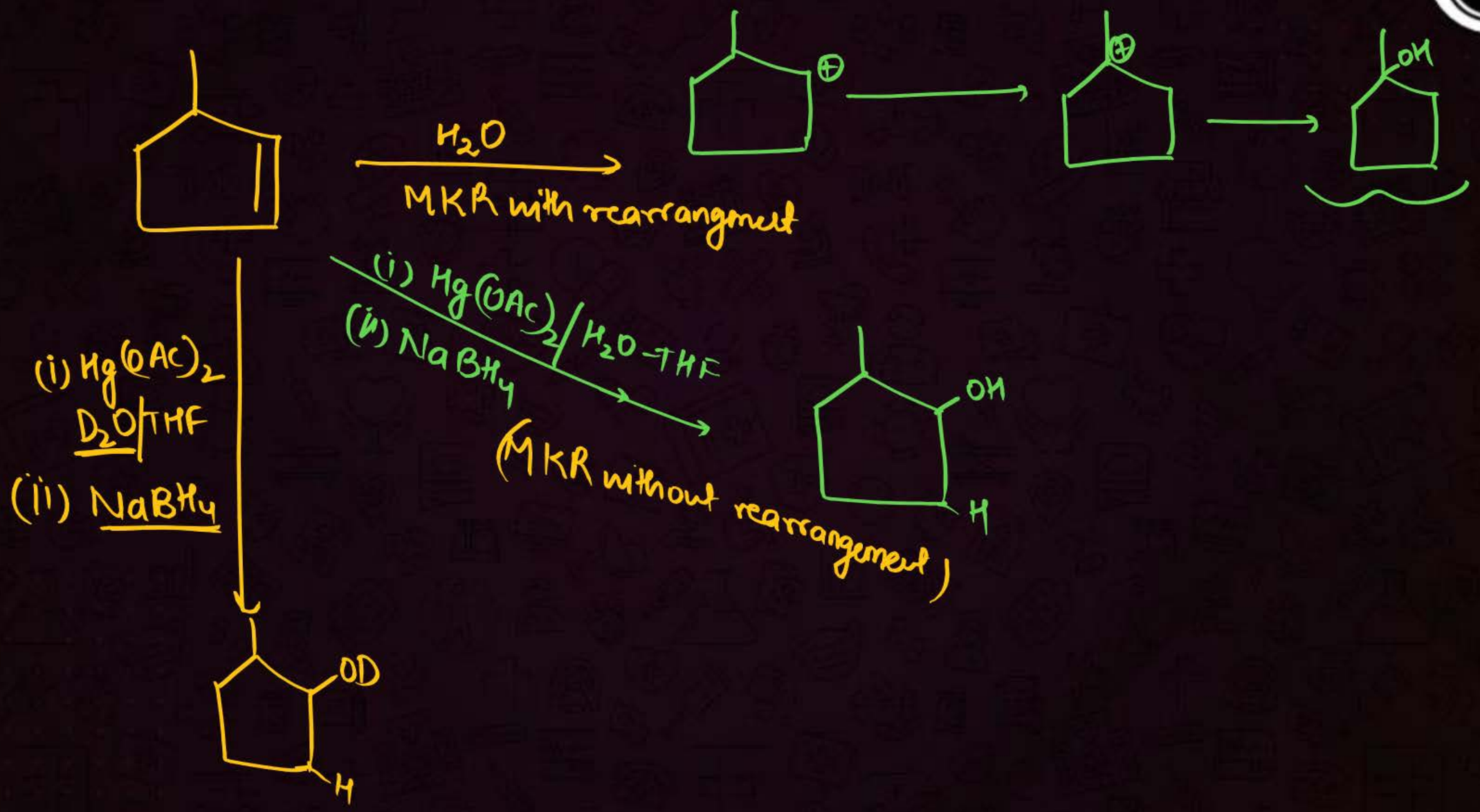
- Reagent ⇒ (i) $Hg(OAc)_2$ / H_2O-THF
  (ii) $NaBH_4$
- anti-addition.
- stereochemistry → CAR/CAT
  TAM/TAE
- product will be formed ⇒ Markovnikov's rule without rearrangement.

Trick

-OH } → from H_2O

-H } → from $NaBH_4$



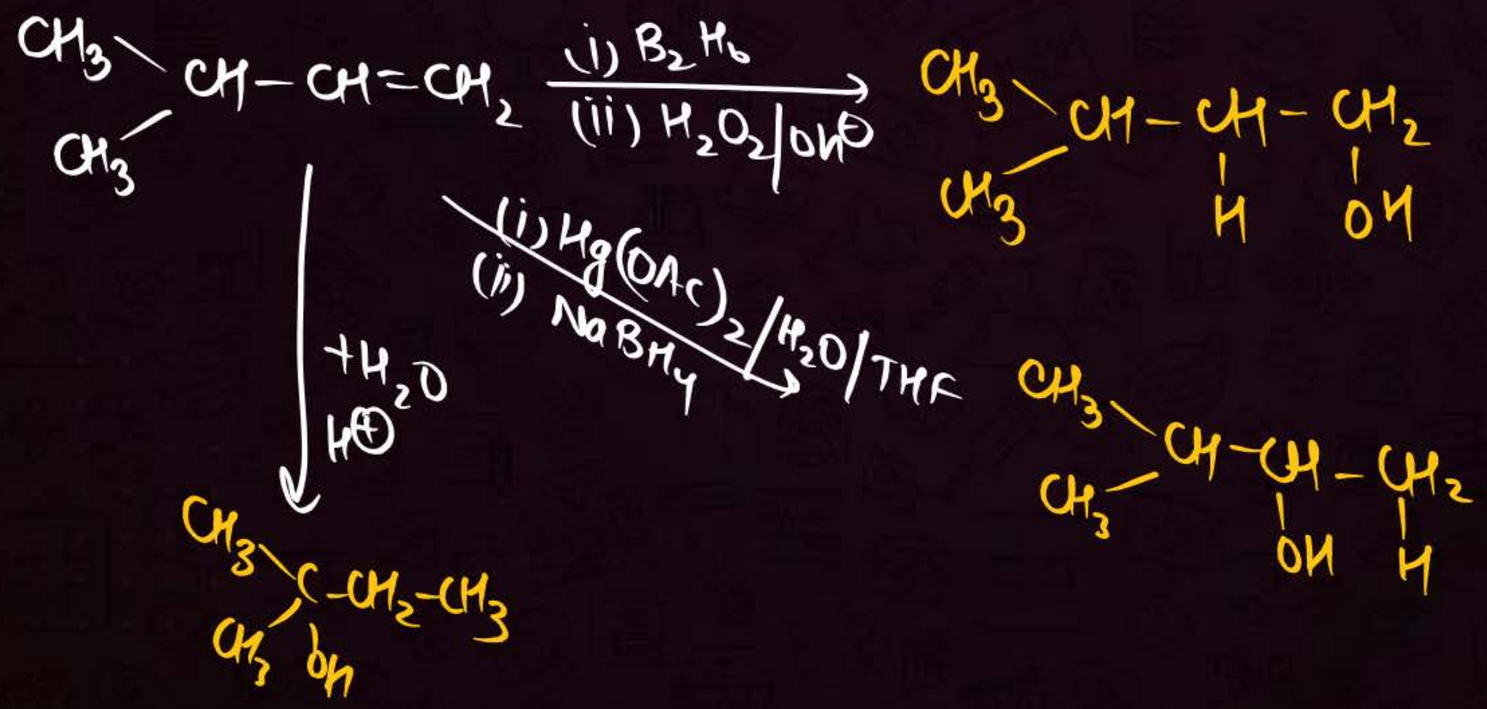

H_2O
MKR with rearrangement
OH
(i) $Hg(OAc)_2$ / H_2O - THF
(ii) $NaBH_4$
(MKR without rearrangement)
OH
H
(i) $Hg(OAc)_2$
D_2O/THF
(ii) $NaBH_4$
OD
H

3. Hydroboration – Oxidation of Alkene:

→ Reagent ⇒ (i) B_2H_6 or $(BH_3)_2$
(ii) $H_2O_2/OH^{\ominus}$

→ water is added by Anti-markonikov's rule

Trick
H ⟶ BH_3/B_2H_6
OH ⟶ H_2O_2



4. Hydroxylation of Alkene:

→ Product → vicinal diol will be formed.

→ Reagent ⇒

(i) cold dilute alkaline $KMnO_4$ (Bayer's reagent) (1%)

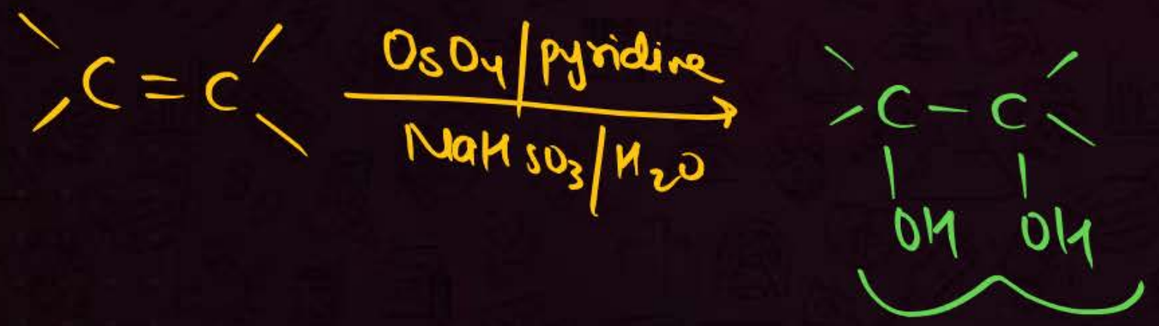
or

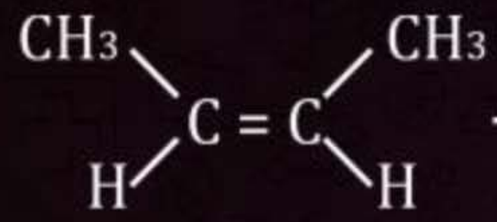
(ii) OsO_4 / pyridine + $NaHSO_3$ / H_2O

syn-addition

CSM / CSE

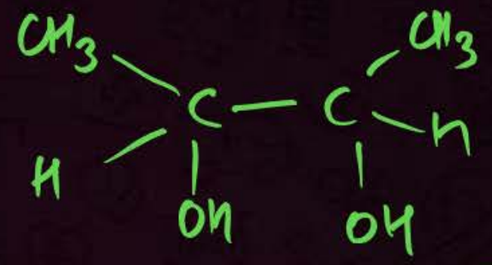
TSR / TST



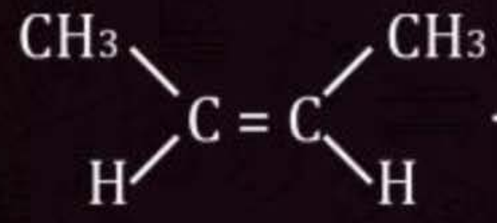
- 

(cis)

$\xrightarrow[\text{NaHSO}_3/\text{H}_2\text{O}]{\text{OSO}_4/\text{Pyridine}}$

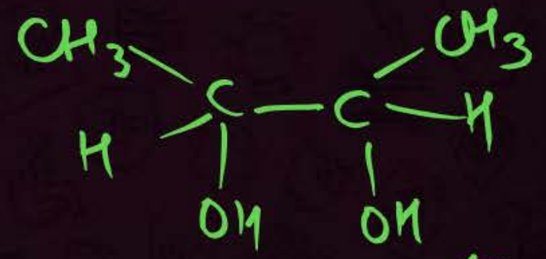


Meso

- 

(Trans)

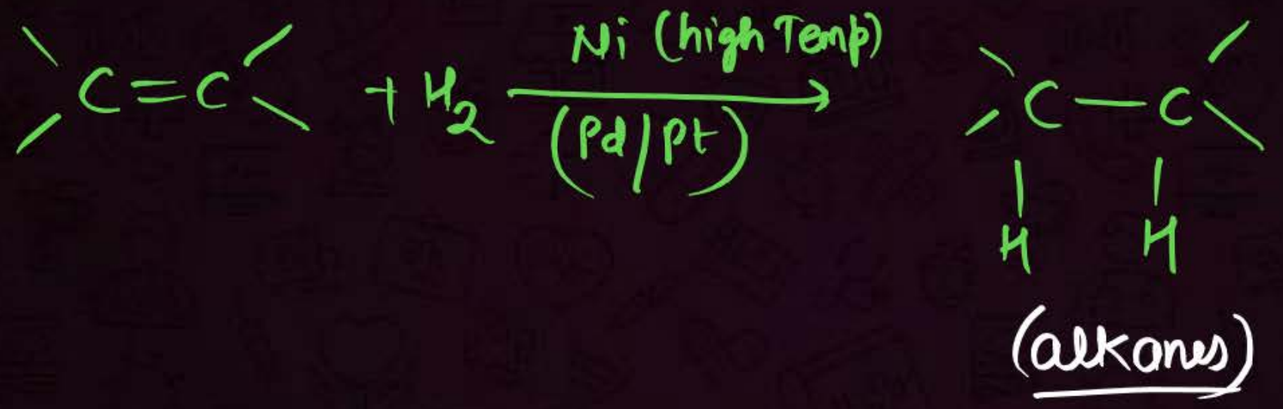
$\xrightarrow[\text{al. KMnO}_4]{\text{Cold dil.}}$



(Racemic mixture)

5. Hydrogenation of Alkenes:

↳ syn-addition

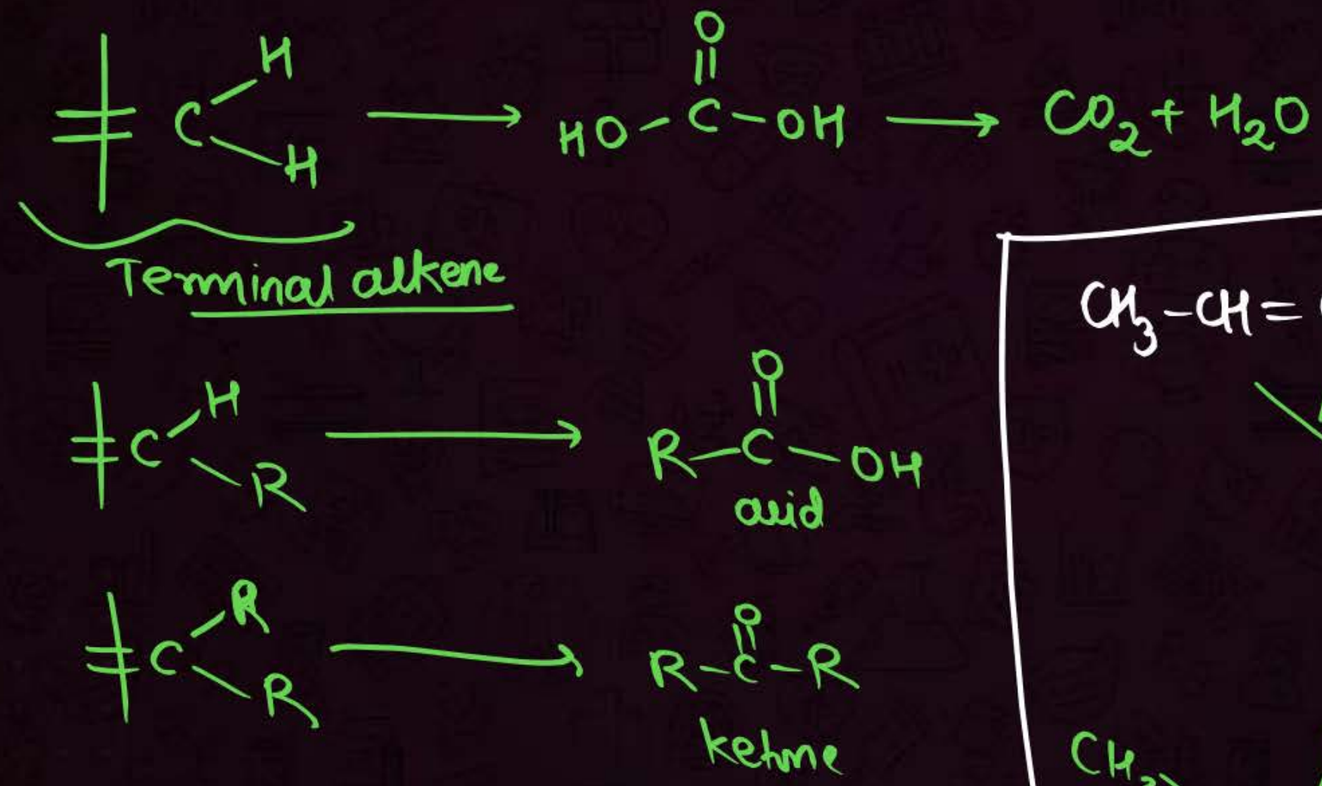


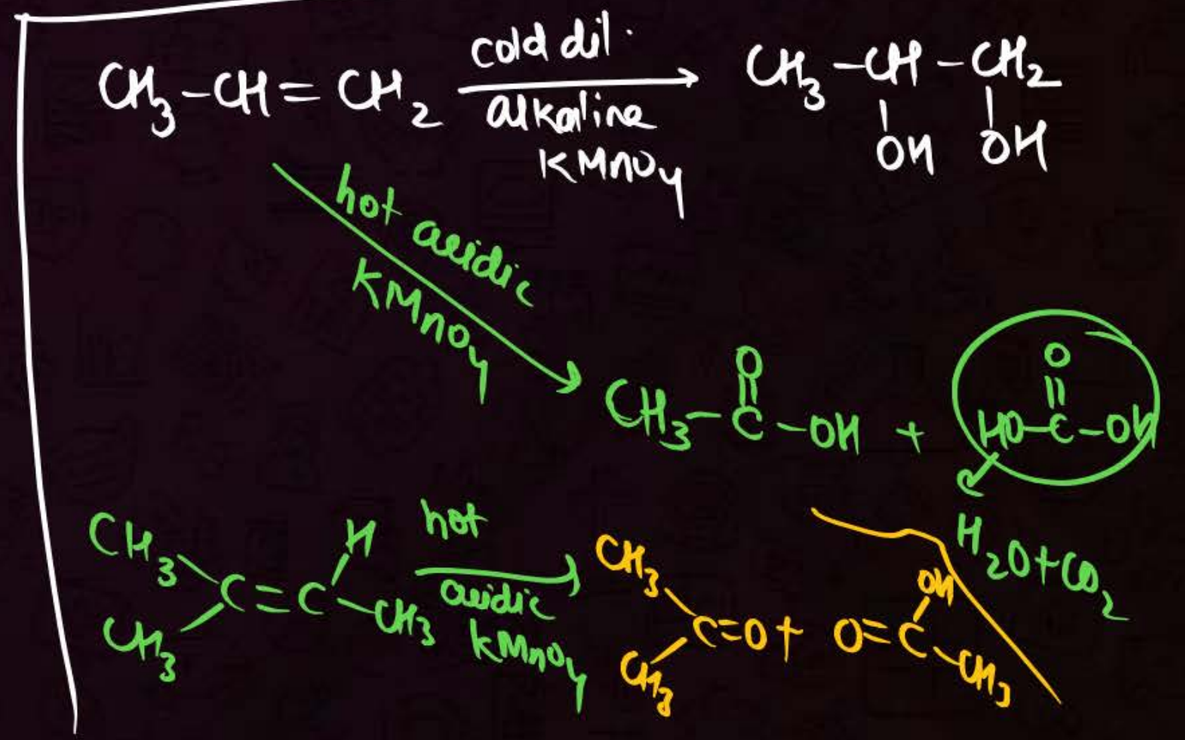
(alkanes)

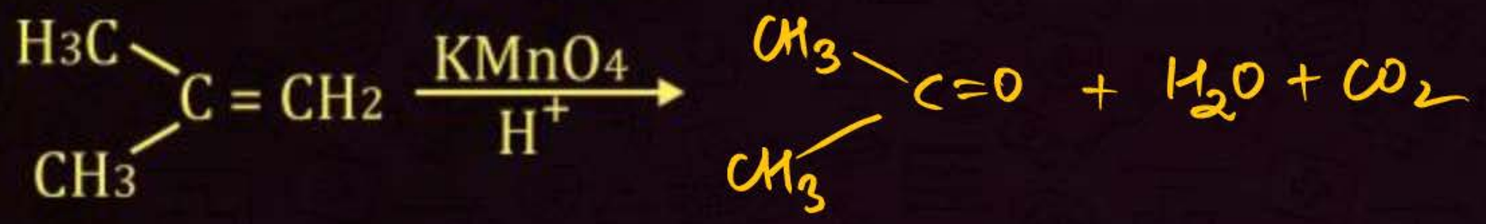
6. Oxidation of alkenes:

a. by Hot Alk. $KMnO_4$ (strong oxidising agent) OR Acidic $KMnO_4$ OR

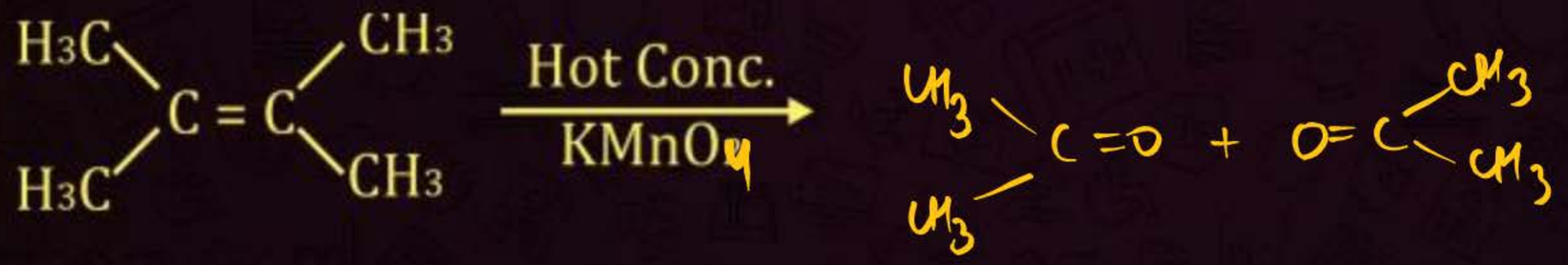
Acidic $K_2Cr_2O_7$

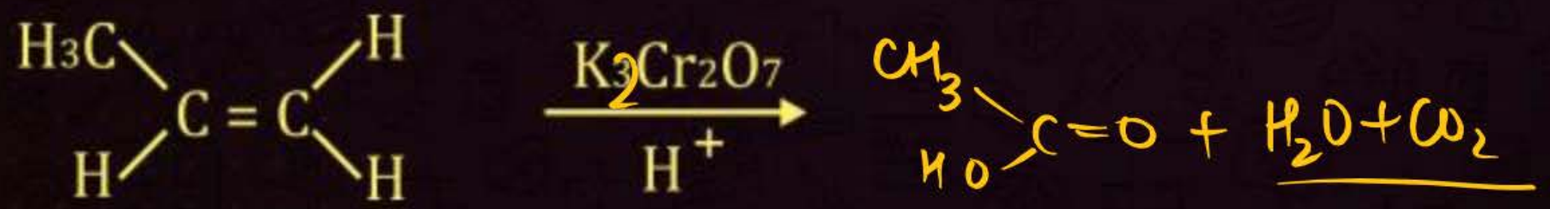





H3C
C = CH2
CH3
KMnO4
H+
CH3
C=O
CH3
+ H2O + CO2


H3C
C = CH2
CH3
Cold
dil. al. KMnO4
CH3
C – CH2
CH3
OH
OH

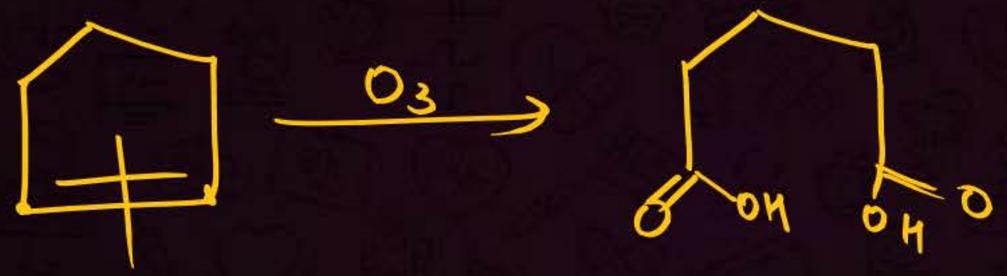

H3C
CH3
C = C
H3C
CH3
Hot Conc.
KMnO4
CH3
C=O
CH3
+ O=C
CH3
CH3


H3C
H
C = C
H
H
K2Cr2O7
H+
CH3
C=O
HO
+ H2O + CO2

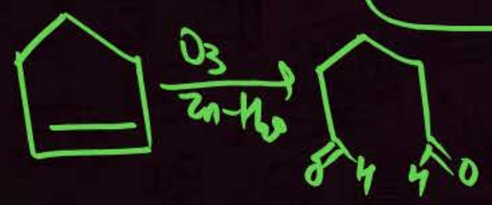
b. By Ozone (Ozonolysis)

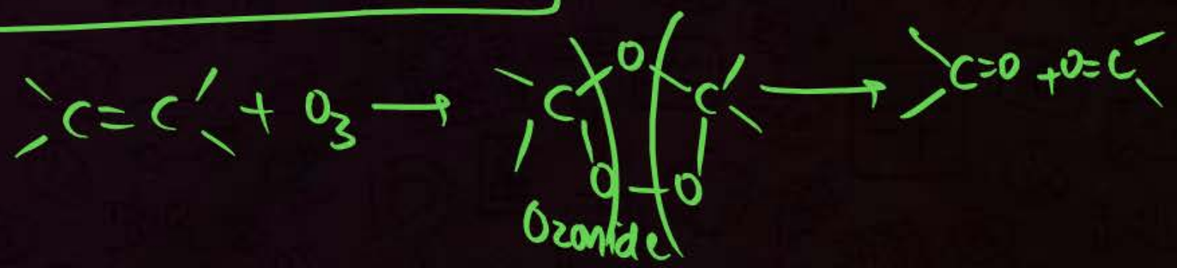
⇒ Oxidative Ozonolysis → Reagent → $\boxed{O_3}$

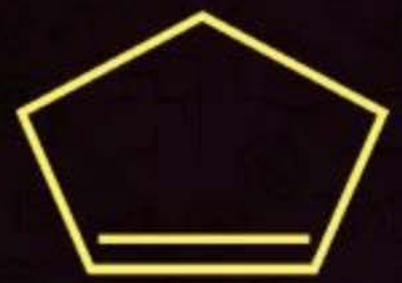
↳ product same as hot $KMnO_4$ / acidic $KMnO_4$ / $K_2Cr_2O_7$.



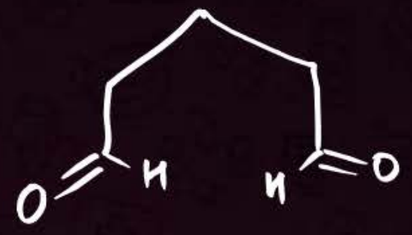
⇒ Reductive Ozonolysis ⇒ Reagent ① O_3
② Zn/H_2O or Pb/H_2O or $(CH_3)_2S$



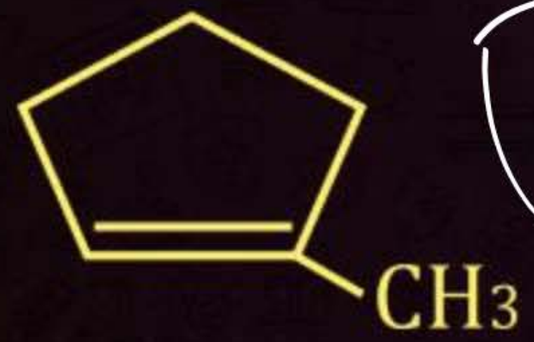




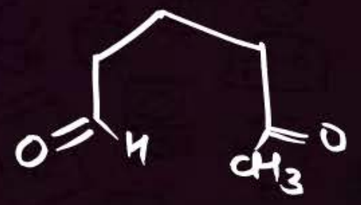
$\xrightarrow[\text{Zn} - H_2O]{O_3}$



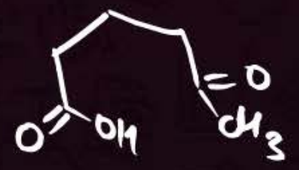
$\xrightarrow{O_3}$

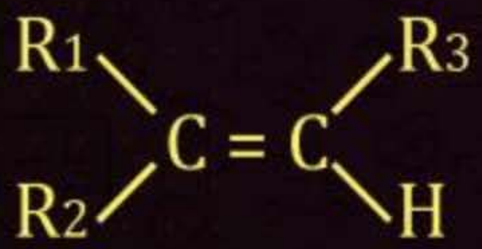


$\xrightarrow[\text{Zn} - H_2O]{O_3}$



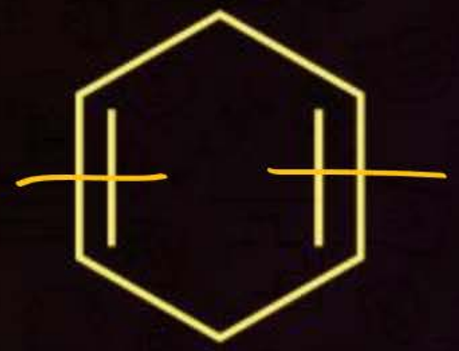
$\xrightarrow{O_3}$



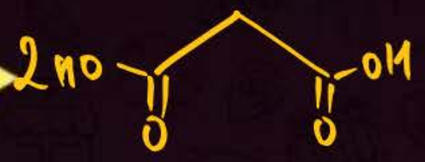


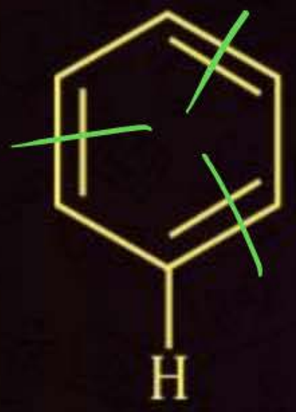
$\xrightarrow[\text{Zn} - H_2O]{O_3}$ $R_1-\overset{O}{\overset{\|}{C}}-R_2 + R_3-\overset{O}{\overset{\|}{C}}-H$

$\xrightarrow{O_3}$ $R_1-\overset{O}{\overset{\|}{C}}-R_2 + R_3-\overset{O}{\overset{\|}{C}}-OH$



$\xrightarrow[\text{Zn} - \text{H}_2\text{O}]{\text{O}_3}$ 2 

$\xrightarrow{\text{O}_3}$ 2 

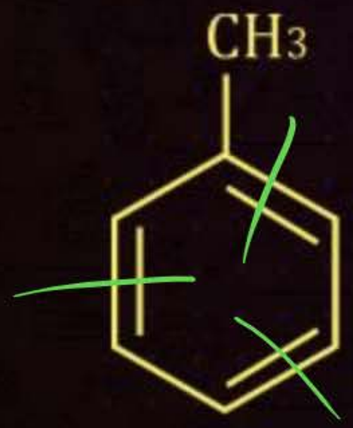


$\xrightarrow[\text{Zn} - \text{H}_2\text{O}]{\text{O}_3}$ 3 H–C(=O)–C(=O)–H

glyoxal

$\xrightarrow{\text{O}_3}$ 3 HO–C(=O)–C(=O)–OH

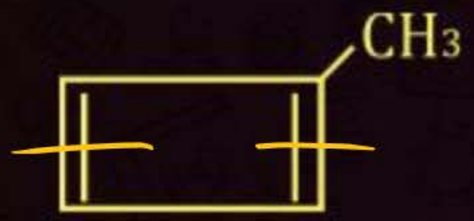
Oxalic acid



$\xrightarrow[\text{Zn} - \text{H}_2\text{O}]{\text{O}_3}$ CH_3–C(=O)–C(=O)–H

2 H–C(=O)–C(=O)–H

$$\xrightarrow[Zn - H_2O]{O_3} 3\,CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H$$

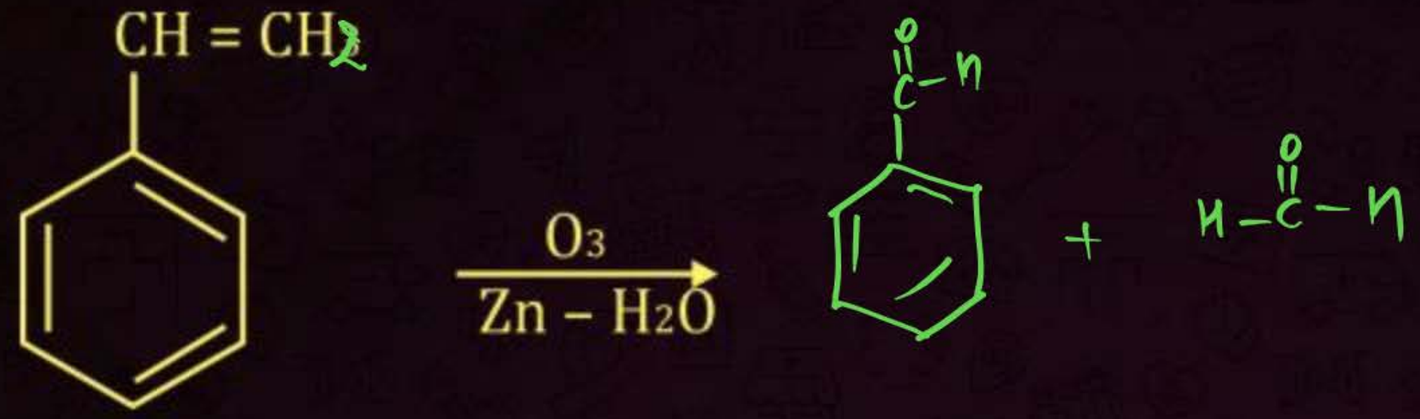


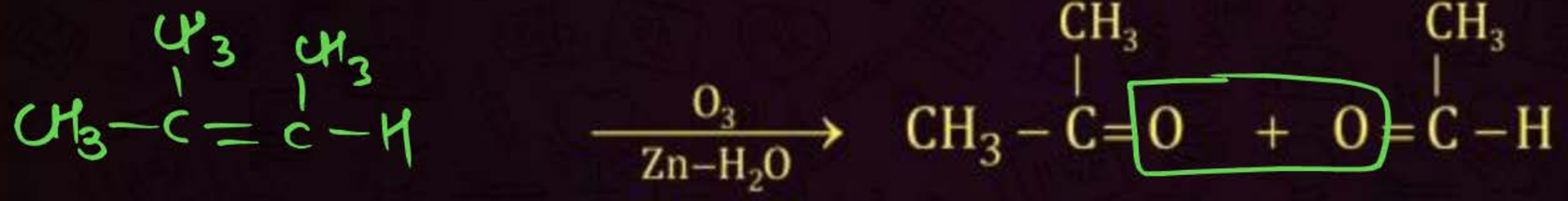
$$\xrightarrow[Zn - H_2O]{O_3}$$

$$+ \quad H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H$$

$$\xrightarrow{O_3} HO-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3 + HO-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OH$$

$$CH_3-CH\equiv C\equiv C\equiv C\begin{matrix}H\\H\end{matrix} \xrightarrow[Zn - H_2O]{O_3} CH_3-\overset{O}{\overset{\|}{C}}-H + \underset{\underset{O}{\|}}{C}=O + O=C=O + H-\overset{O}{\overset{\|}{C}}-H$$

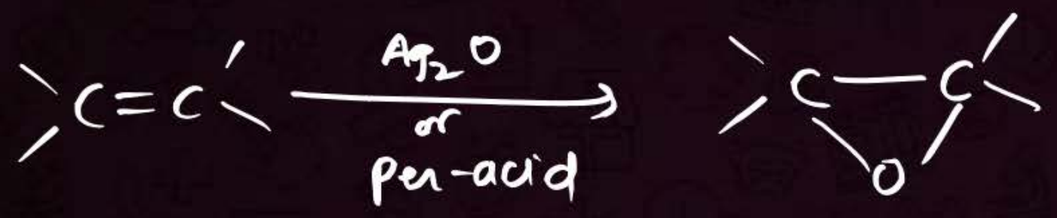




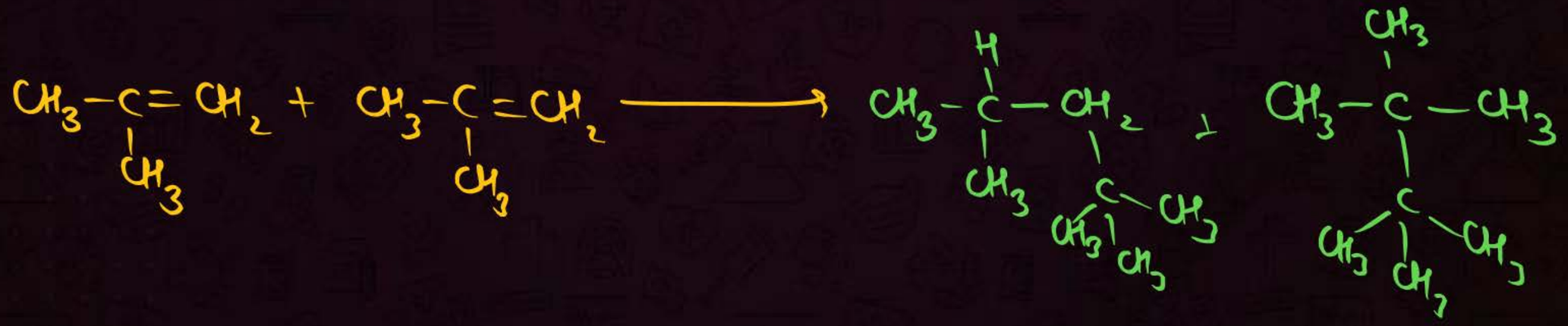
NOTE → ozonolysis is preferred for aliphatic than aromatic

7. Addition of Oxygen:

Reagent: Ag_2O or per-acid ($R-\overset{O}{\overset{\|}{C}}-O-O-H$)



8. Alkylation:



9. Polymerisation:

$$n\,CH_2=CH_2 \xrightarrow{\text{polymerisation}} \left(CH_2-CH_2\right)_n$$

ethene → polyethene

$$n\,CH_3-CH=CH_2 \xrightarrow{''} \left(CH(CH_3)-CH_2\right)_n$$

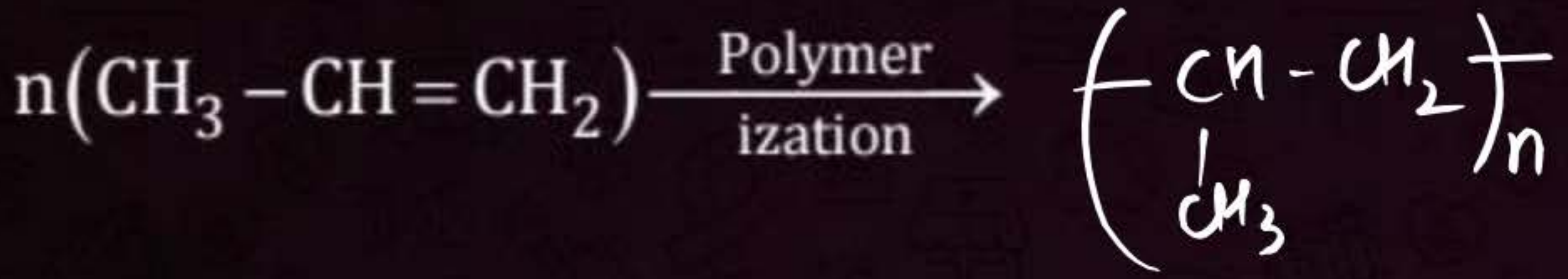
propene → polypropene

$$n\,CH_2=CH-CH=CH_2 \xrightarrow{''} \left(CH_2-CH=CH-CH_2\right)_n$$

$$n\,CH(Cl)=CH_2 \xrightarrow{''} \left(CH(Cl)-CH_2\right)_n$$

vinylchloride → polyvinylchloride (PVC)

QUESTION



$$n(CH_3-CH=CH_2)\xrightarrow[\text{ization}]{\text{Polymer}}\left(\underset{\underset{CH_3}{|}}{CH}-CH_2\right)_n$$

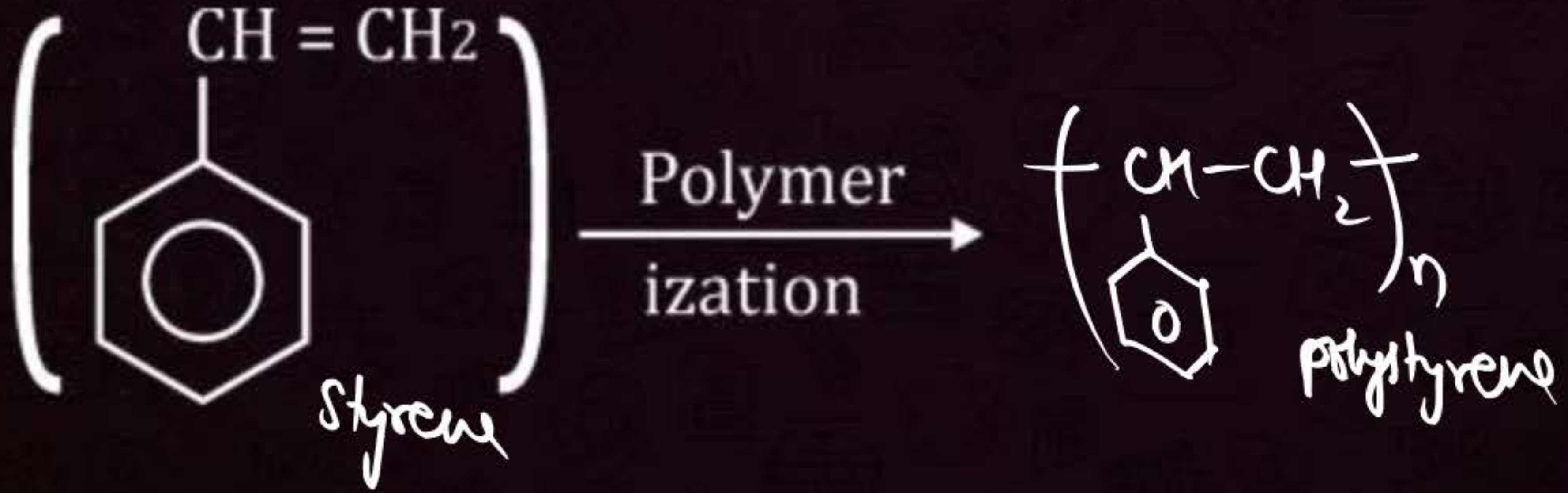
$$n(CN-CH=CH_2)\xrightarrow[\text{ization}]{\text{Polymer}}\left(\underset{\underset{CN}{|}}{CH}-CH_2\right)_n$$

Acrylonitrile

(polyacrylonitrile)

$$n(CF_2=CF_2)\xrightarrow[\text{ization}]{\text{polymer}}\left(CF_2-CF_2\right)$$

Teflon



Styrene

Polystyrene

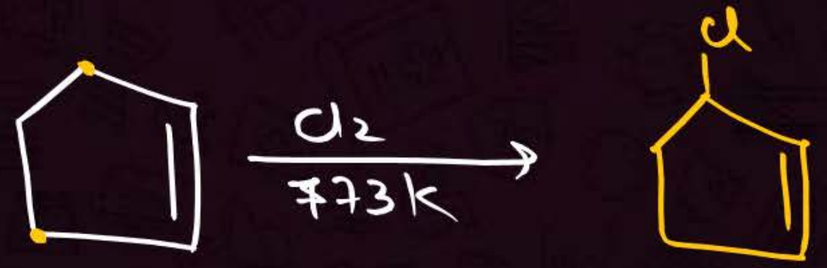
10. Substitution in Alkenes:

↳ allylic substitution → Reagent ⇒ Br_2 / 773K
or
Cl_2 / 773K
or
NBS (N-Bromosuccinamide) 773K
↳ Best for Br°

} free radical mechanism.

$(CH_2 = CH - CH_2)$
allyl group

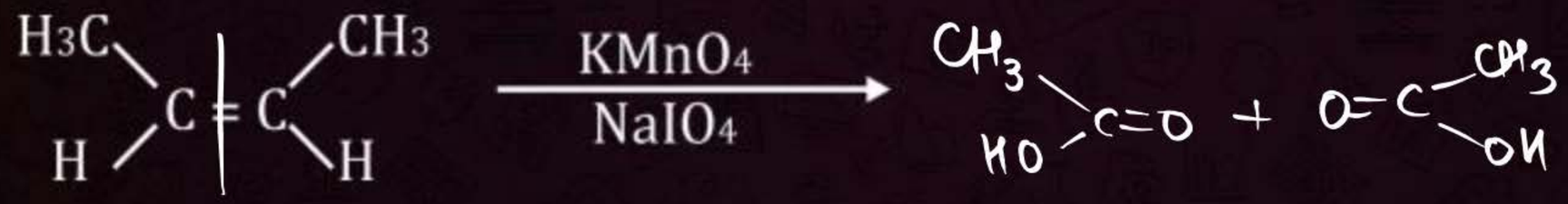
$(CH_2 = CH)$
vinyl group.

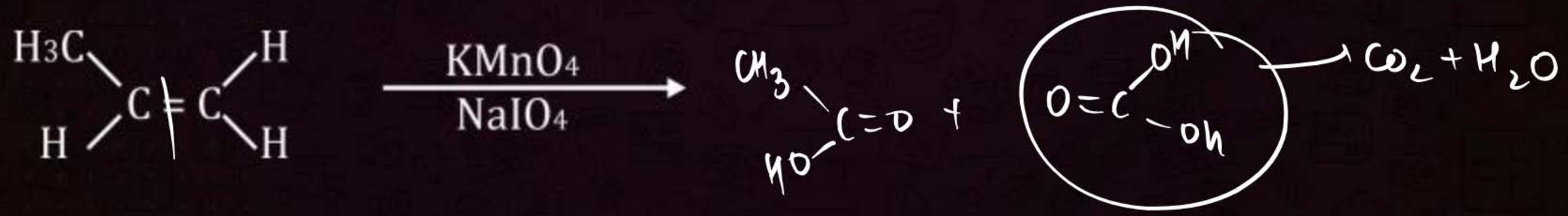


11. Reaction of Alkene with $KMnO_4$ and $NaIO_4$:

Lemux reagent

$KMnO_4/NaIO_4$ → same as oxidative ozonolysis.





QUESTION

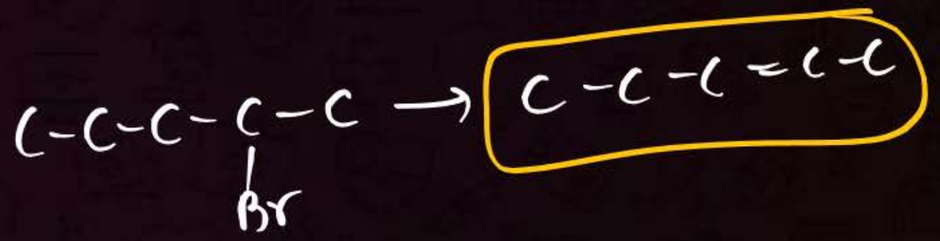
The major product formed in dehydrohalogenation reaction of 2-bromo pentane is pent-2-ene. This product formation is based on **[NEET 2021]**

(A) Saytzeff's rule

(B) Hund's rule

(C) Hoffmann rule

(D) Huckel's rule



QUESTION

2, 3-dimethyl-2-butene can be prepared by heating which of the following compounds with a strong acid: [NEET 2016, P-I]

(A) $(CH_3)_2CH-\underset{\underset{CH_3}{|}}{CH}-CH=CH_3$

(B) $(CH_3)_3C-CH=CH_2$

(C) $(CH_3)_2C=CH-CH_2-CH_2$

(D) $(CH_3)_2CH-CH_2-CH=CH_2$

$$\boxed{C-\underset{\underset{CH_3}{|}}{C}=\underset{\underset{CH_3}{|}}{C}-C}$$

QUESTION

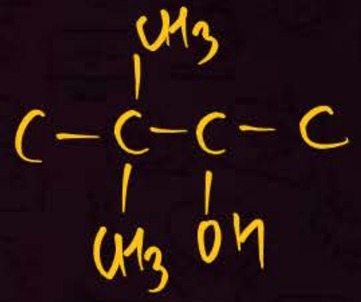
When 3, 3-dimethyl-2-butanol is heated with conc. H_2SO_4, the major product obtained is [CBSE AIPMT 1995]

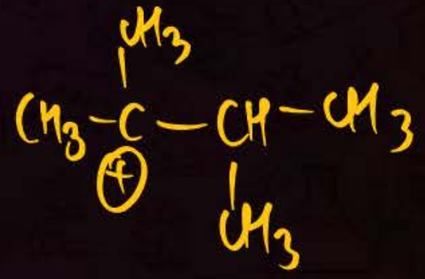
(A) 2, 3-dimethyl-2-butene

(B) 3, 3-dimethyl-2-butene

(C) 2, 3-dimethyl-1-butene

(D) cis and trans-isomers of 2, 3-dimethyl-2-butene





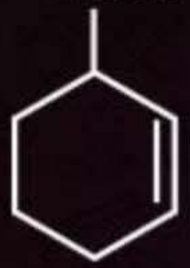
QUESTION

$H-\overset{O}{\overset{\|}{C}}-H$

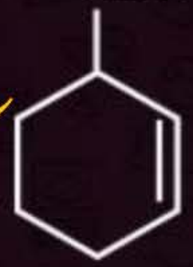
An alkene of ozonolysis gives methanal as one of the product. Its structure is

[NEET Sep.-2020]

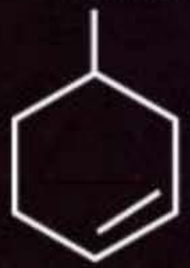
(A) $CH_2 - CH_2 - CH_3$



(B) $CH_2 - CH = CH_2$

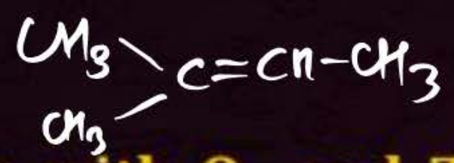


(C) $CH_2\ CH_2\ CH_3$



(D) $CH_2 = CH - CH_3$

QUESTION



An alkene' A' on reaction with O_3 and Zn - H_2O gives propanone and ethanal in equimolar ratio. Addition of HCl to alkene' A'gives' B as the major product. The structure of product' B is [NEET (National) 2019]

(A) $H_3C-CH_2-CH(CH_2Cl)-CH_3$

(B) $H_3C-CH(Cl)-CH(CH_3)-CH_3$

(C) $H_3C-CH_2-C(CH_3)(Cl)-CH_3$

(D) $Cl-CH_2-CH_2-CH(CH_3)-CH_3$

QUESTION

$H_3C-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2 + HBr \rightarrow A$ **A(predominantly) is**

(A) $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH-CH_2Br$

(B) $CH_3-\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2CH_3$

(C) $CH_3-\underset{\underset{Br}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

(D) $CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{Br}{|}}{CH}-CH_3$

QUESTION

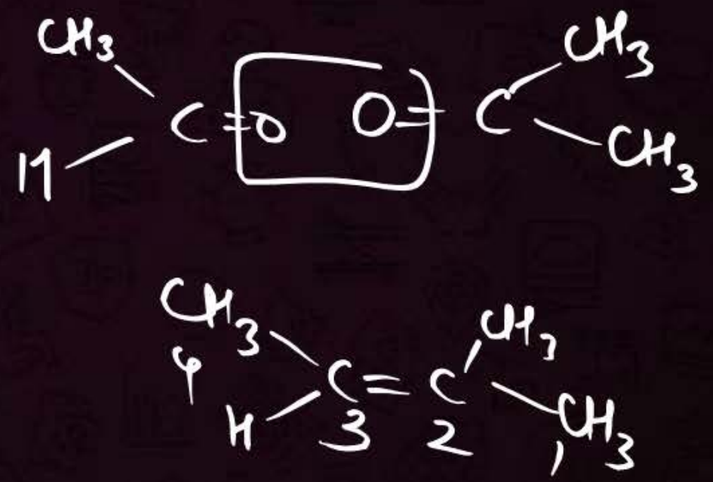
Which of the following compounds with molecular formula, C_5H_{10} yields acetone on ozonolysis? **[CBSE AIPMT 2007]**

(A) 2-methyl-2-butene

(B) 3-methyl-1-butene

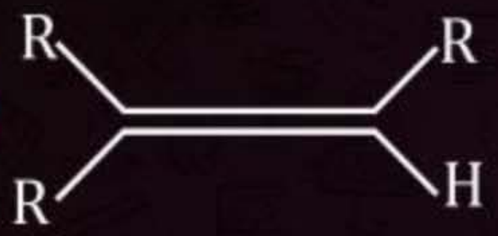
(C) Cyclopentane

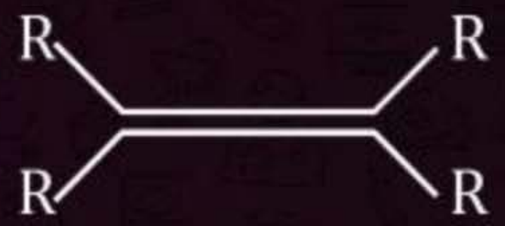
(D) 2-methyl-1-butene

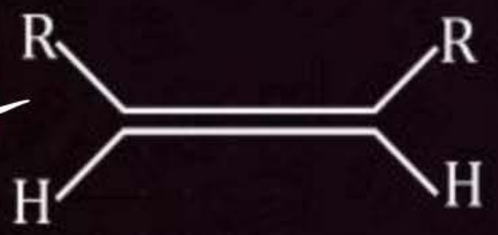


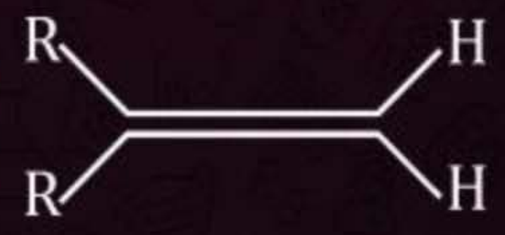
QUESTION

Which one of the following alkenes will react faster with H_2 under catalytic hydrogenation conditions? (R = alky substituent) [CBSE AIPMT-2005]

A


B


C


D


QUESTION

Reaction of HBr with propene in the presence of peroxide gives

[CBSE AIPMT 2004]

(A) iso-propyl bromide

(B) 3-bromo propane

(C) allyl bromide

(D) n-propyl bromide

$$CH_3-CH=CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3-\underset{H}{CH}-\underset{Br}{CH_2}$$

QUESTION

The alkene $R - CH = CH_2$ reacts readily with B_2H_6 and formed the product B which on oxidation with alkaline H_2O_2 produces [CBSE AIPMT 1995]

(A) $R - CH_2 - CHO$

(B) $R - CH_2 - CH_2 - OH$

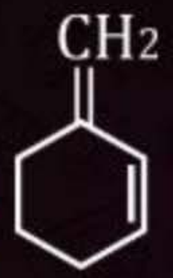
(C) $R - \underset{\underset{CH_3}{|}}{C} = O$

(D) $R - \underset{\underset{OH}{|}}{CH} - \underset{\underset{OH}{|}}{CH_2}$

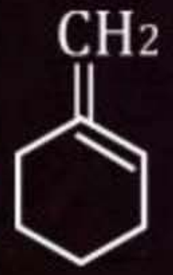
QUESTION

In the reaction with HCl, an alkene reacts in accordance with the Markownikoff's rule, to give a product 1-chloro-1methylcyclohexane. The possible alkane is

[CBSE AIPMT 2015]

(A) 

(B) 

(C) 

(D) (A) and (B)

QUESTION

Among the following alkenes

1-butene	cis-2-butene	trans-2-butene
I	II	III

the decreasing order of stability is [CBSE AIPMT 2000]

(A) II > I > III

(B) III > II > I

$CH_3-CH_2-C=CH_2$

(C) III > I > II

(D) I > II > III

QUESTION

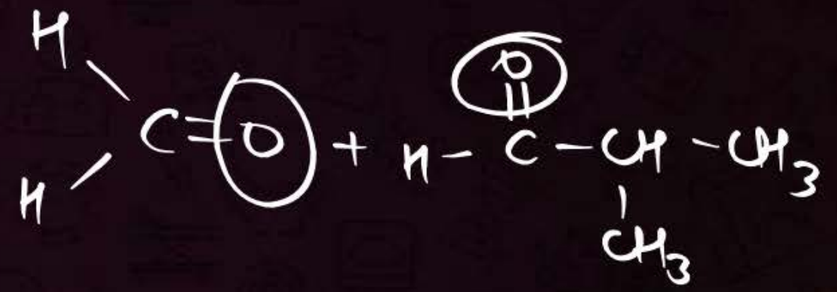
Compound X on reaction with O_3 followed by Zn/H_2O gives formaldehyde and 2-methyl propanal as products. The compound X is: [NEET 2022]

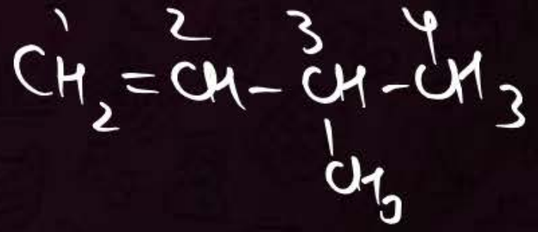
(A) Pent-2-ene

(B) 3-Methylbut-1-ene

(C) 2-Methylbut-1-ene

(D) 2-Methylbut-2-ene





QUESTION

The compound, $CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH_3$ on reaction with $NaOI_4$, in the presence of cold $KMnO_4$ gives [CBSE AIPMT 2003]

(A) $CH_3COCH_3 + CH_3CHO$

(B) $CH_3CHO + CO_2$

(C) CH_3COCH_3

(D) $CH_3COCH_3 + CH_3COOH$

Alkynes

Introduction:

$$\underset{sp}{CH} \equiv \underset{sp}{CH}$$

- S-Character → s-character ↑ acidic nature ↑ Electronegativity ↑

$$CH \equiv CH > CH_2 = CH_2 > CH_3 - CH_3$$

- Type of Alkynes:
  - Terminal alkyne $R-C\equiv \underbrace{CH}_{\text{one acidic H}}$ $\quad \underbrace{CH\equiv CH}_{\text{'2' acidic H}}$
  - non-terminal alkyne $\underbrace{R-C\equiv C-R}_{\text{no acidic H}}$

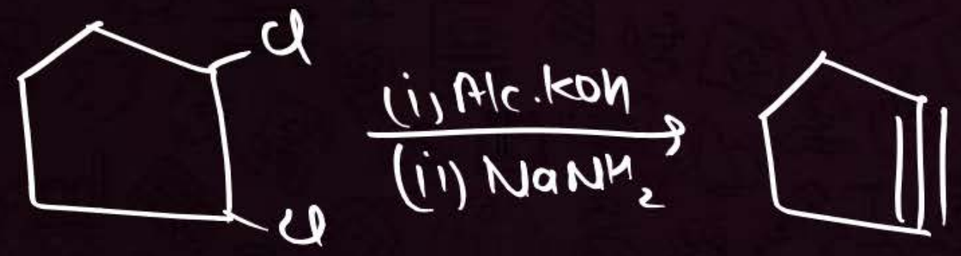
Preparation:

1. Dehydrohalogenation of Vicinal Dihalides

$$CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}} \xrightarrow[\text{KOH}]{\text{alcoholic}} CH_3-CH=\underset{Cl}{\underset{|}{CH}} \xrightarrow[(-HCl)]{NaNH_2} CH_3-C\equiv CH$$

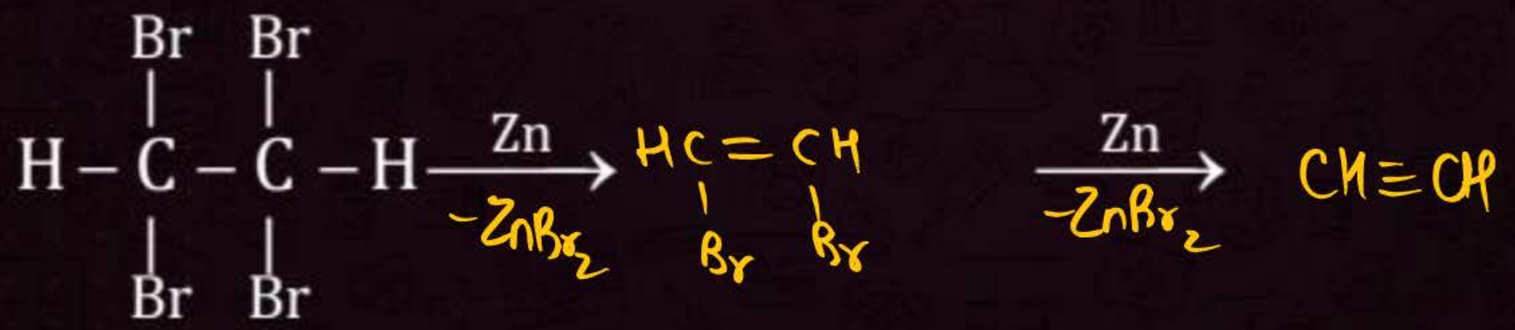
(-HCl) fast

(slow)

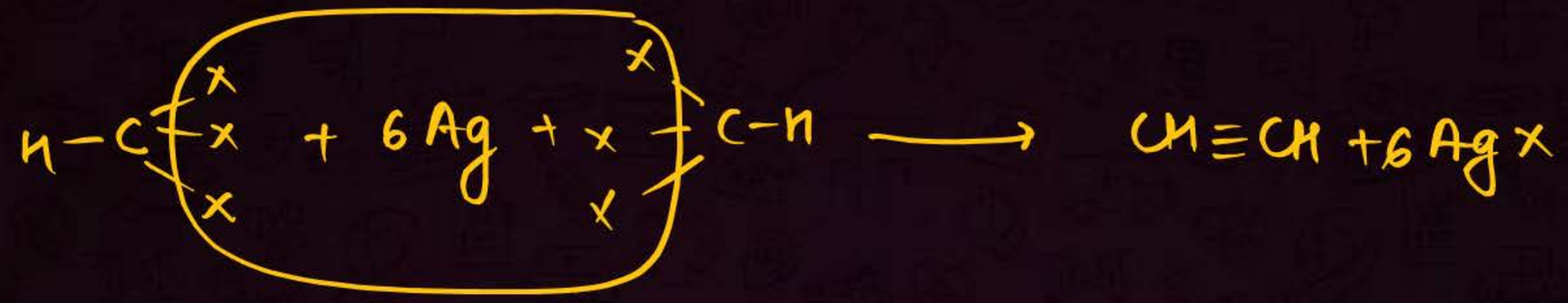


2. Dehydrohalogenation of Geminal Dihalides

3. Dehydrohalogenation of Vicinal Tetrahalides



4. Dehalogenation of Haloform (CHX_3)



→ Symmetrical alkynes will be formed

5. Higher Alkynes from Lower Alkynes

→ having acidic (H)

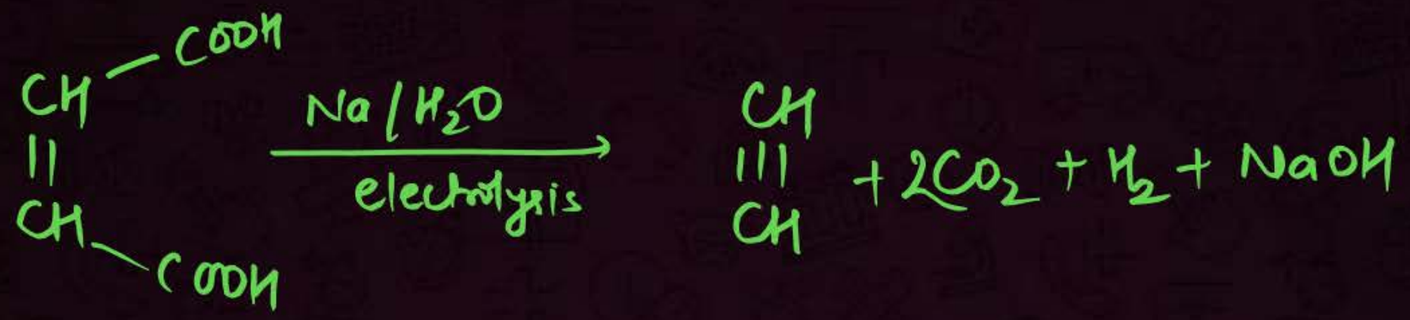
→ Terminal alkyne

$$CH \equiv CH \xrightarrow[(1\ eq.)]{Na} CH \equiv C^{\ominus}\,Na^{\oplus} \xrightarrow{CH_3-CH_2-Cl} CH \equiv C-CH_2-CH_3$$

$$CH \equiv CH \xrightarrow[2(eq.)]{Na} Na^{\oplus}\,C^{\ominus} \equiv C^{\ominus}\,Na^{\oplus} \xrightarrow{2\,CH_3CH_2-Cl} CH_3-CH_2-C \equiv C-CH_2-CH_3$$

6. Preparation of Acetylene only (CH ≡ CH)

(a) From Kolbe's Electrolysis



(b) From Graphite

(c) From Calcium Carbide (Industrial Scale)

$$CaC_2 + H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

$(CH \equiv CH)$

$$Mg_2C_3 + H_2O \longrightarrow Mg(OH)_2 + CH_3-C\equiv CH$$

Al carbide → CH_4
Be carbide → CH_4

Preparation of Calcium Carbide:

$$\left\{\begin{array}{l} CaCO_3 \xrightarrow{\Delta} CaO + CO_2 \\ CaO + C \longrightarrow CaC_2 + CO \end{array}\right\}$$

QUESTION

1. $CH_2 = CH_2 \xrightarrow[CCl_4]{Br_2} CH_2(Br)-CH_2(Br) \xrightarrow[NaNH_2]{Alco.KOH} CH \equiv CH$

2. $CH_4 \xrightarrow{hv/Cl_2} CH_3-Cl \xrightarrow[\text{dry ether}]{Na} CH_3-CH_3 \xrightarrow[uv]{Cl_2} CH_3-CH_2-Cl$

(A) (B) (C)

$CH_3-CH_2-Cl \xrightarrow[KOH, \Delta]{Alc.} CH_2=CH_2 \xrightarrow[CCl_4]{Br_2} CH_2(Br)-CH_2(Br) \xrightarrow[NaNH_2]{Alc\ KOH} CH \equiv CH$

(D) (E) (F)

QUESTION

3. $CH \equiv CH + Na \rightarrow$ $CH \equiv C^{\ominus} Na^{\oplus}$ $\xrightarrow{CH_3CH_2Cl}$ $CH \equiv C - CH_2 - CH_3$

(1eq.)

(A) (B)

4. $CH \equiv CH + \underset{(2eq)}{Na} \rightarrow Na^{\oplus} C^{\ominus} \equiv C^{\ominus} Na^{\oplus}$ $\xrightarrow{2CH_3Cl}$ $CH_3 - C \equiv C - CH_3$

(A) (B)

5. $CH \equiv CH + \underset{(2eq)}{Na} \rightarrow Na^{\oplus} C^{\ominus} \equiv C^{\ominus} Na^{\oplus}$ $\xrightarrow[\& \, CH_3CH_2Cl]{CH_3Cl}$ $CH_3 - C \equiv C - CH_2 - CH_3$

(A) (B)

Physical Properties of Alkynes:

1. Physical state

$C_2 - C_4 \rightarrow$ gas
$C_5 - C_{12} \rightarrow$ liquid
$> C_{12} \rightarrow$ solid

colourless / odourless
except $CH \equiv CH$
→ if pure → pleasant smell
→ if impure → garlic smell.

2. Density → lighter than water.
→ mass ↑ density ↑
→ max upto 0.69 g/cm³

3. Melting Point/Boiling point

- alkyne have higher M.pt/B.pt than alkenes/alkanes
- M.pt $\propto$ symmetry/stability
  B.pt high due to π-bonds

4. Solubility

- non-polar in nature
- soluble in non-polar solvent

Chemical Properties of Alkynes:

- **Electrophilic Addition Reaction**

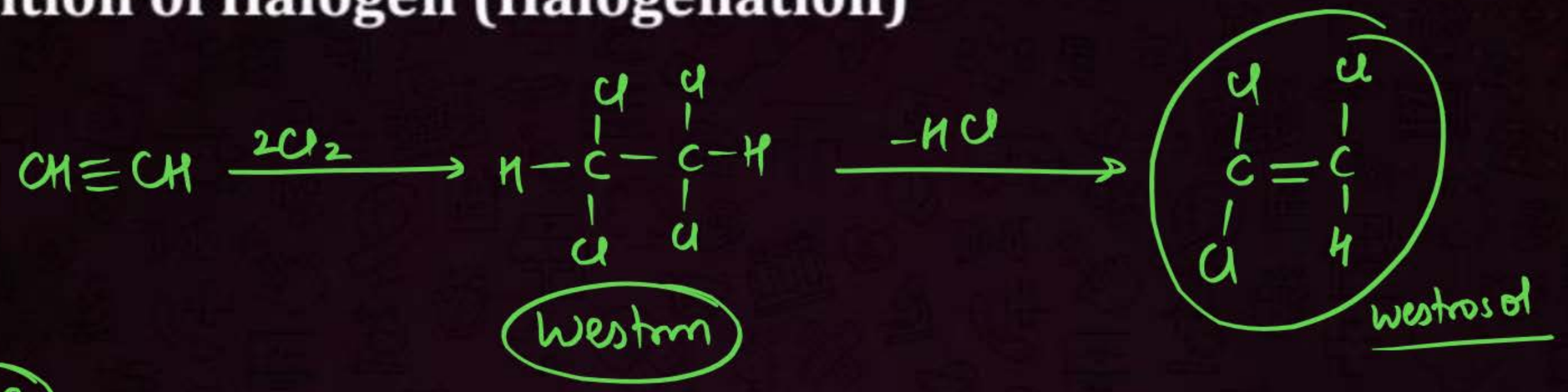
$$-C \equiv C- \xrightarrow{+XY} -\overset{X}{\underset{|}{C}}=\overset{Y}{\underset{|}{C}}- \xrightarrow{+XY} -\overset{X}{\underset{X}{C}}-\overset{Y}{\underset{Y}{C}}-$$

(a) Addition of Hydrogen (Hydrogenation)

$$HC \equiv CH \xrightarrow[\text{Ni/573K}]{+H_2} CH_2 = CH_2 \xrightarrow[\text{Ni/573K}]{+H_2} CH_3 - CH_3$$

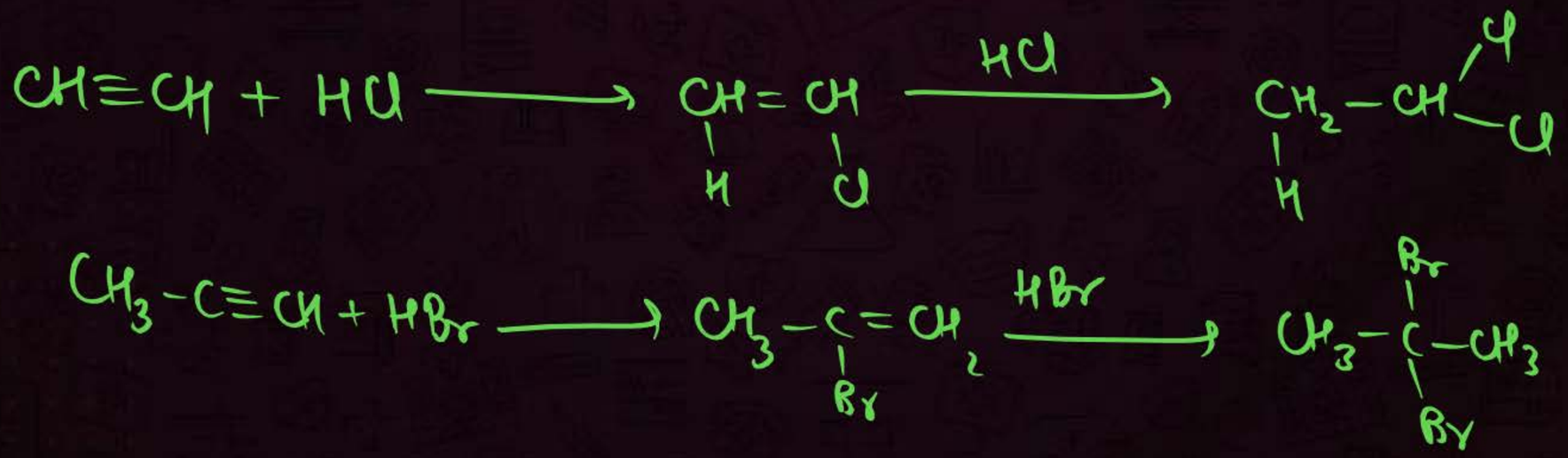
$$HC \equiv CH \xrightarrow[\text{Pd-C or Pd-Baso}_4]{H_2} CH_2 = CH_2$$

(b) Addition of Halogen (Halogenation)



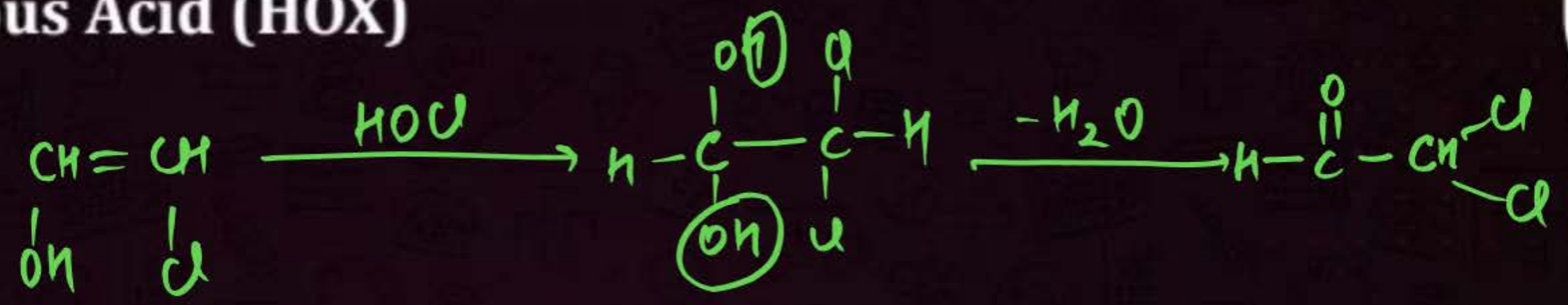
MKR

(c) Addition of Halogen acids (Hydrohalogenation)

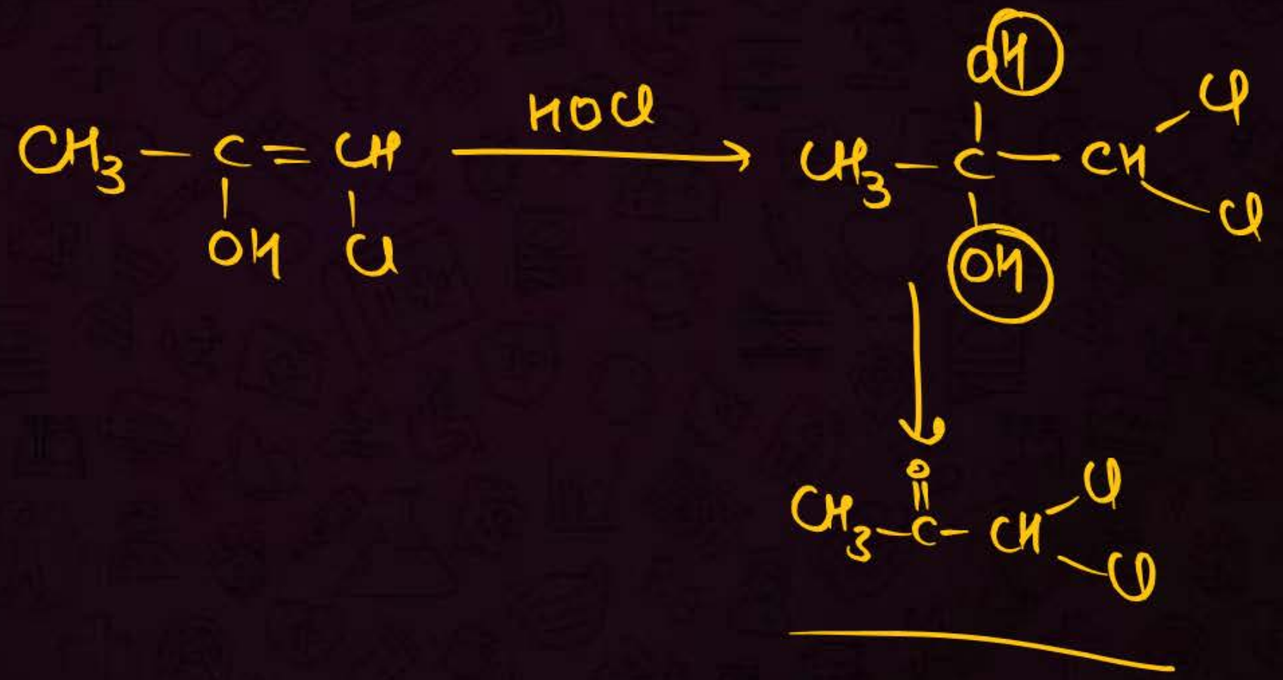


e) Addition of Hypohalous Acid (HOX)

$HC \equiv CH + HOCl \rightarrow$



$CH_3 - C \equiv CH + HOCl \rightarrow$

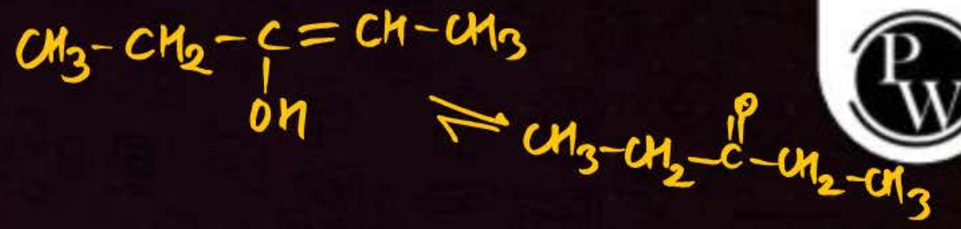


f) Addition of Water in presence of Acid

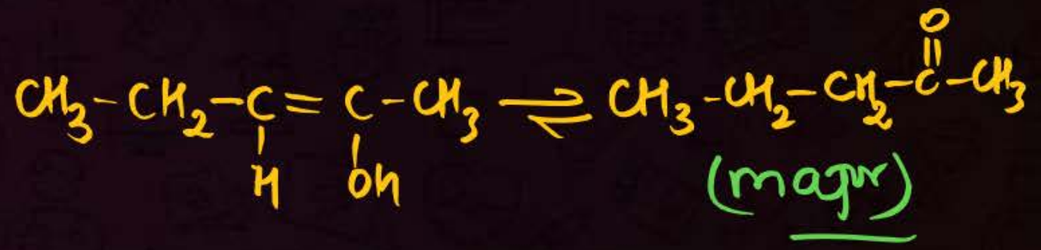
$$CH \equiv CH + H_2O \xrightarrow[HgSO_4,\ H_2SO_4]{H^{\oplus}} \underset{\text{(enol)}}{CH(H)=CH(OH)} \xrightarrow[\text{Tautomerisation}]{} CH_3-\overset{O}{\overset{\|}{C}}-H$$

$$CH_3-C\equiv CH + H_2O \xrightarrow[HgSO_4,\ H_2SO_4]{H^{\oplus}} CH_3-C(OH)=CH(H) \xrightarrow{T} CH_3-\underset{O}{\underset{\|}{C}}-CH_3$$

$$CH_3-CH_2-C\equiv C-CH_3 \xrightarrow[HgSO_4/H_2SO_4,\ \Delta]{+\ H_2O}$$

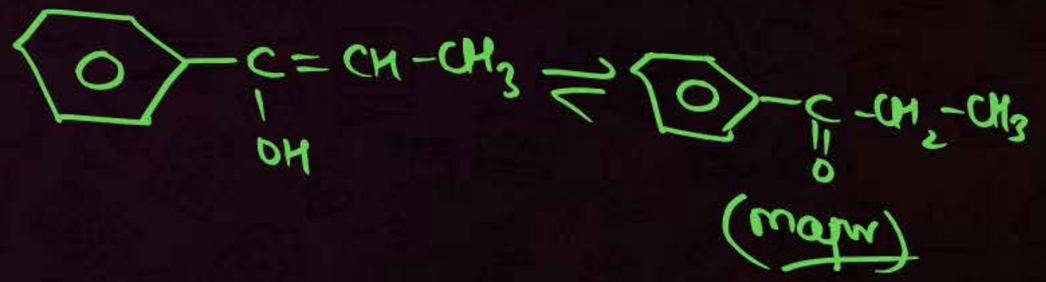


$$CH_3-CH_2-C\equiv C-CH_3 \xrightarrow[HgSO_4/H_2SO_4,\ \Delta]{+\ H_2O}$$

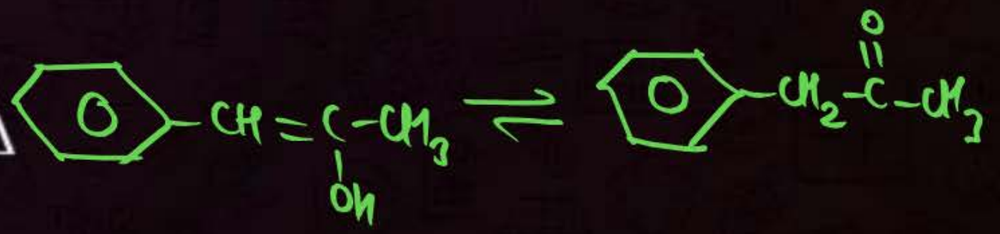


phenyl ketone > methyl ketone > ethyl ketone

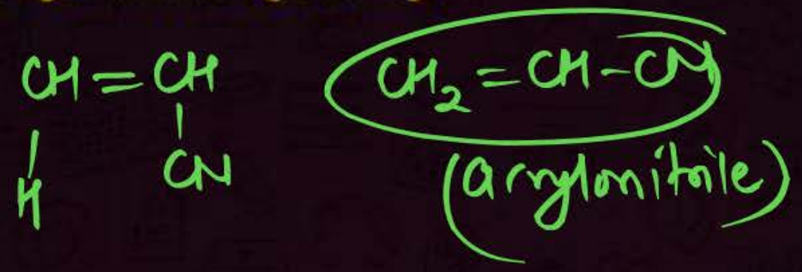
$$C\equiv C-CH_3 \xrightarrow[HgSO_4/H_2SO_4,\ \Delta]{+\ H_2O}$$



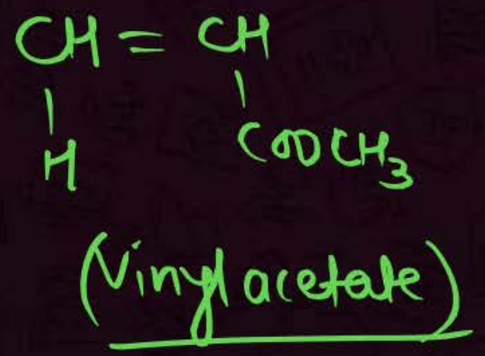
$$C\equiv C-CH_3 \xrightarrow[HgSO_4/H_2SO_4,\ \Delta]{+\ H_2O}$$



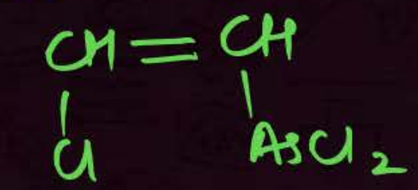
Addition of Hydrogen Cyanide (HCN):

- $CH \equiv CH + HCN \rightarrow$ 

Addition of acetic acid:

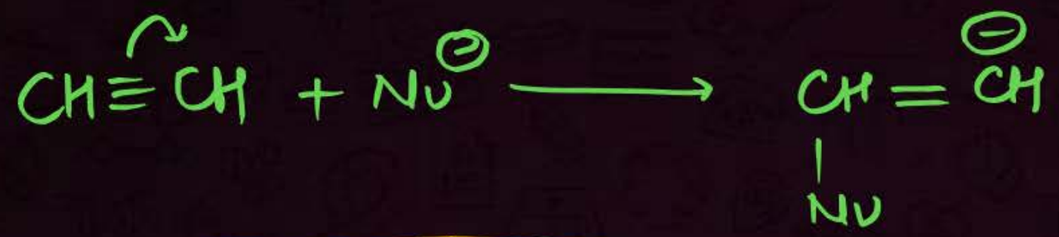
- $CH \equiv CH + CH_3\,COOH \rightarrow$ 

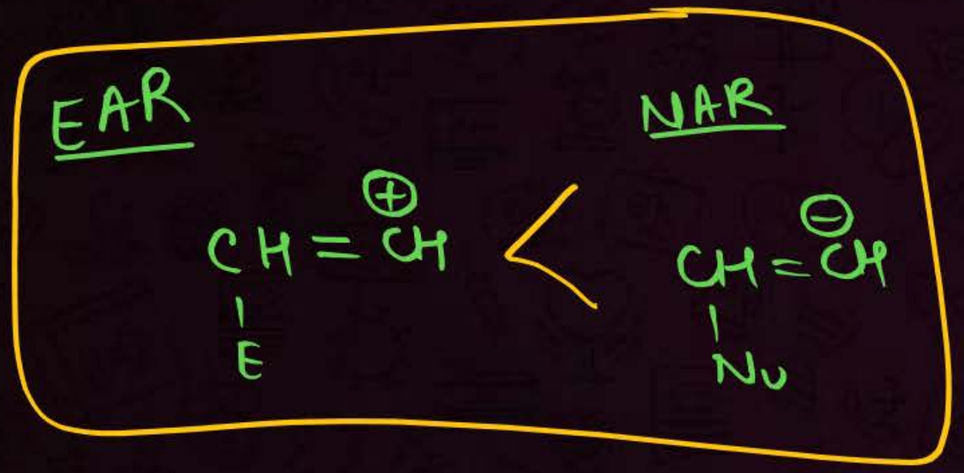
Addition of Arsenic Trichloride:

- $CH \equiv CH + AsCl_3 \longrightarrow$ 

lewisite → poisnous gas

2. Nucleophilic Addition Reaction:





3. Oxidative – Hydroboration (HBO):

→ H_2O ⇒ addition

→ Reagent ⇒ $B_2H_6 / H_2O_2 / OH^{\ominus}$

→ Antimarkonikov's rule

➢ $CH_3 - C \equiv CH$

$$+ H_2O \xrightarrow[H_2O_2,\ OH^{\ominus}]{B_2H_6} CH_3-CH=\underset{\underset{OH}{|}}{CH} \xrightarrow{\oplus} CH_3-CH_2-\overset{\overset{O}{\|}}{C}-H$$

➢ $CH_3 - C \equiv C - CH_3$

$$\xrightarrow[H_2O_2,\ OH^{\ominus}]{B_2H_6} CH_3-\underset{\underset{H}{|}}{C}=\underset{\underset{OH}{|}}{C}-CH_3 \xrightarrow{\oplus} \underline{CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3}$$

4. Acetylide Formation:

(a) Reaction with Ag/Cu:

- $CH \equiv CH + Ag \longrightarrow \overset{\oplus}{Ag}\overset{\ominus}{C} \equiv \overset{\ominus}{C}\overset{\oplus}{Ag}$ (white ppt)
- $CH \equiv CH + Cu \longrightarrow \overset{\oplus}{Cu}\overset{\ominus}{C} \equiv \overset{\ominus}{C}\overset{\oplus}{Cu}$ (Red ppt)

(b) Reaction with Na:

- $RC \equiv CH + Na \longrightarrow R-C \equiv \overset{\ominus}{C}\overset{\oplus}{Na}$
- $CH \equiv CH + Na \longrightarrow \overset{\oplus}{Na}\overset{\ominus}{C} \equiv \overset{\ominus}{C}\overset{\oplus}{Na}$

(c) Reaction with Grignard Reagent:

$$R-C\equiv C-H + R'-MgX \longrightarrow R'-H + Mg(X)-C\equiv C-R$$

(d) Reaction with Tollen's Reagent:

$[Ag(NH_3)_2]OH$

$$R-C\equiv CH + [Ag(NH_3)_2]^{\oplus} \longrightarrow \underbrace{R-C\equiv C^{\ominus}Ag^{\oplus}}_{\text{White ppt}}$$

5. Oxidation of Alkynes:

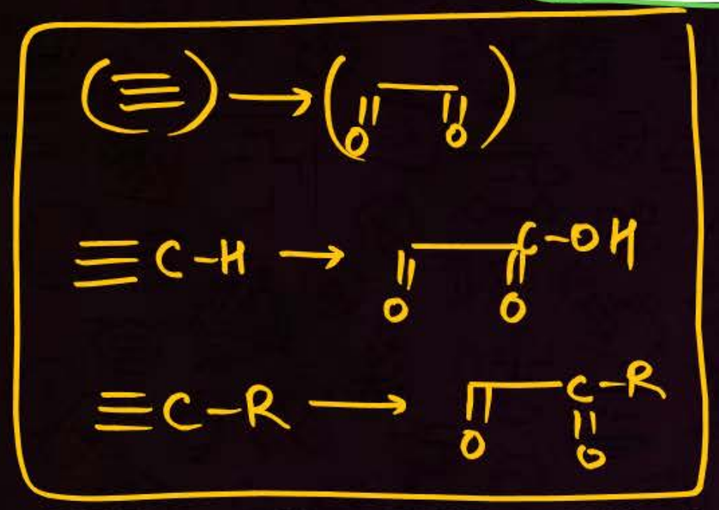
(a) Oxidation in Neutral $KMnO_4$:

↳ Similar to Reductive Ozonolysis.

$$CH \equiv CH \xrightarrow[KMnO_4]{Neutral} H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H$$

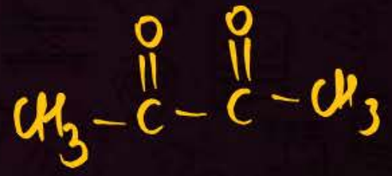
$$CH_3-C \equiv CH \xrightarrow[KMnO_4]{Neutral} CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H$$

(b) Oxidation with cold dil. Alkaline $KMnO_4$ → in case of alkene ⇒ hydroxylation



$$CH_3-C\equiv CH+3(o) \xrightarrow[\text{ii) } H^+]{\text{i) } NaOH,\ KMnO_4,\ \Delta}$$

$$CH_3-C\equiv C-CH_3+(o) \xrightarrow[\text{ii) } H^+]{\text{i) } NaOH,\ KMnO_4,\ \Delta}$$



$$HC\equiv CH+2(o) \xrightarrow[\text{ii) } H^+]{\text{i) } NaOH,\ KMnO_4,\ \Delta}$$

(c) Oxidation By Hot/Acidic $KMnO_4$ → same as Oxidative Ozonolysis.

$$R-C\equiv C-R' \xrightarrow[H^+,\ Heat]{KMnO_4} R-\overset{O}{\overset{\|}{C}}-OH + R'-\overset{O}{\overset{\|}{C}}-OH$$

$$R-C\equiv CH \xrightarrow[\text{"}]{\text{"}} R-\overset{O}{\overset{\|}{C}}-OH + HO-\overset{O}{\overset{\|}{C}}-OH \rightarrow CO_2+H_2O$$

$$HC\equiv CH \xrightarrow[\text{"}]{\text{"}} HO-\overset{O}{\overset{\|}{C}}-OH + OH-\overset{O}{\overset{\|}{C}}-OH$$

$$\downarrow \qquad\qquad \downarrow$$

$$CO_2+H_2O \qquad CO_2+H_2O$$

6. Ozonolysis:

(a) Reductive Ozonolysis (Similar to Neutral $KMnO_4$)

$$CH \equiv CH + O_3 \xrightarrow[-H_2O]{Zn} H-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-H$$

(b) Oxidative Ozonolysis (Similar to Hot/H^+ $KMnO_4$)

$$CH \equiv CH + O_3 \longrightarrow HO-\overset{\overset{O}{\|}}{C}-OH + HO-\overset{\overset{O}{\|}}{C}-OH$$

$$\downarrow \qquad\qquad \downarrow$$

$$CO_2 + H_2O \qquad CO_2 + H_2O$$

- $R-C\equiv C-R' \xrightarrow[\text{ii) } Zn/H_2O \text{ or } Pb/H_2O \text{ or } (CH_3)_2S]{\text{i) } O_3} R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R'$

- $HC\equiv C-H \xrightarrow[Zn/H_2O]{O_3} H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H$

- $R-C\equiv C-H \xrightarrow[Zn/H_2O]{O_3} R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H$

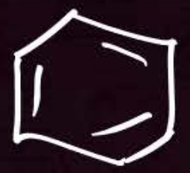
$HC\equiv C-H \xrightarrow{O_3} CO_2 + H_2O$

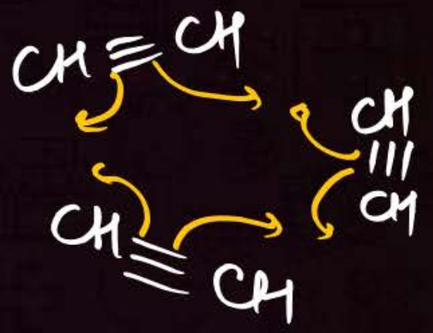
$R-C\equiv C-H \xrightarrow{O_3} R-\overset{O}{\overset{\|}{C}}-OH + HO-\overset{O}{\overset{\|}{C}}-OH$ → CO_2, H_2O

7. Polymerisation Reaction of Alkynes:

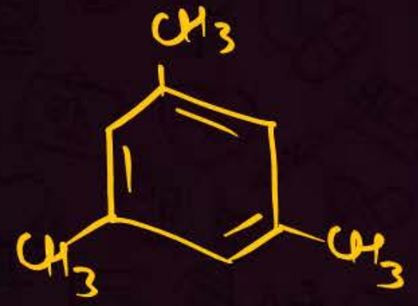
(a) Cyclic Polymerisation

- $3\ HC \equiv CH \xrightarrow[\text{Iron tube}]{\text{Red hot}}$

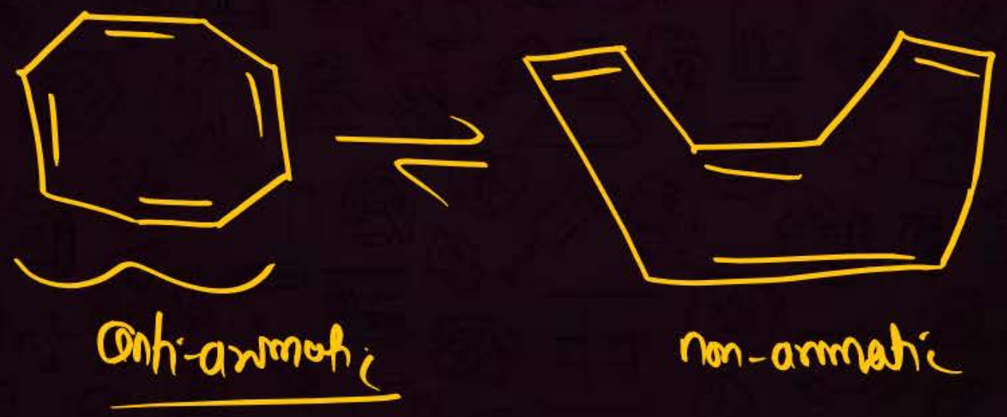




- $3\ CH_3 - C \equiv CH \rightarrow$



- $4\ CH \equiv CH \rightarrow$



(b) Vinylic Polymerisation

- $3\,HC \equiv CH \xrightarrow[CuCl]{NH_4Cl} CH_2=CH-(C\equiv C)-CH=CH_2$

divinylacetylene

c) Linear Polymerisation:

$$\underset{\text{ethyne}}{n\,CH\equiv CH} \xrightarrow{\text{polymerisation}} \underset{\text{Polyethyne}}{-(CH=CH)_n \text{ or } (CH=CH-CH=CH)_n}$$

NCERT

$$CH_3COOH \xrightarrow{NaOH(aq)} \underset{CH_3-\overset{O}{\overset{\|}{C}}-O^{\ominus}Na^{\oplus}}{A} \xrightarrow[\Delta,\ -CO_2]{\text{Soda lime}} \underset{CH_4}{B} \xrightarrow[hv]{Cl_2} \underset{CH_3-Cl}{C} \xrightarrow[\text{Wurtz reaction}]{\text{Na/dry ether}} \underset{CH_3-CH_3}{D}$$

$$\underset{CH_3-CH_3}{\xrightarrow{Cl_2}} \underset{CH_2(Cl)-CH_3}{E} \xrightarrow{\text{alc. KOH,}} \underset{CH_2=CH_2}{F} \xrightarrow{Br_2} \underset{CH_2(Br)-CH_2(Br)}{G} \xrightarrow{\text{alc KOH}} \underset{CH_2=CH(Br)}{H} \xrightarrow{NaNH_2} \underset{CH\equiv CH}{I} \xrightarrow[873\ K]{\text{Red hot iron tube}} J$$

QUESTION

$R-CH_2-CCl_2-R \xrightarrow{\text{Reagent}} R-C\equiv C-R$. The reagent is

(A) Na

(B) HCl in H_2O

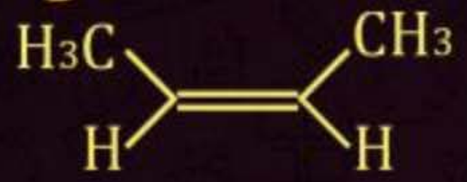
(C) KOH in C_2H_5OH

(D) Zn in alcohol

QUESTION

The most suitable reagent for the following conversion, is:

[NEET (National) 2019]

$H_3C-C\equiv C-CH_3 \rightarrow$ 

cis-2-butene

(A) H_2, Pd/C, quinoline

(B) Zn/HCl

(C) Hg^{2+}/H^+, H_2O

(D) Na/liquid NH_3

QUESTION

Which one is the correct order of acidity? [NEET 2017]

(A) $CH_2 = CH_2 > CH_3 - CH = CH_2 > CH_3 - CH \equiv CH > CH \equiv CH$

(B) $CH \equiv CH > CH_3 - C \equiv CH > CH_2 = CH_2 > CH_3 - CH_3$

(C) $CH \equiv CH > CH_2 = CH_2 > CH_3 - C \equiv CH > CH_3 - CH_3$

(D) $CH_3 - CH_3 > CH_2 = CH_2 > CH_3 - C \equiv CH > CH \equiv CH$

QUESTION

In the reaction, [NEET 2016, P-I]

$CH\equiv C-CH_2-CH_3$

$$H-C\equiv CH \xrightarrow[\text{(ii) } CH_3CH_2Br]{\text{(i) } NaHN_2/\text{liq.}NH_3} X \xrightarrow[\text{(ii) } CH_3CH_2Br]{\text{(i) } NaNH_2/\text{liq. } NH_3} Y$$

$CH_3-CH_2-C\equiv C-CH_2-CH_3$

X and Y are

(A) X = 2-butyne; Y = 3-hexyne

(B) X = 2-butyne; Y = 2-hexyne

(C) X = 1-butyne; Y = 2-hexyne

(D) X = 1-butyne; Y = 3-hexyne

QUESTION

Which of the following reagents will be able to distinguish between 1-butyne and 2-butyne? [CBSE AIPMT 2012]

(A) $NaNH_2$

(B) HCl

(C) O_2

(D) Br_2

$CH_3-C-C\equiv CH$

$CH_3-C\equiv C-CH_3$

QUESTION

When acetylene is passed through dil. H_2SO_4 in presence of $HgSO_4$' the compound formed is [CBSE AIPMT 1999]

(A) ether

(B) ketone

(C) acetic acid

(D) acetaldehyde

$$CH \equiv CH \xrightarrow[H_2SO_4]{HgSO_4} \underset{H}{CH} = \underset{OH}{CH} \overset{T}{\rightleftharpoons} CH_3 - \overset{O}{\overset{\|}{C}} - H$$

QUESTION

The cylindrical shape of an alkyne is due to [CBSE AIPMT 1997]

(A) three sigma C-C bonds

(B) three πC – C bonds

(C) two sigma C – C and one πC – C bonds

(D) one sigma C – C and two πC – C bonds

—C≡C—

QUESTION

A compound is treated with $NaNH_2$ to give sodium salt. Identify the compound.

[CBSE AIPMT 1993]

(A) C_2H_2 $CH \equiv CH$

(B) C_6H_6

(C) C_2H_6

(D) C_2H_4

QUESTION

Reduction of 2-butyne with sodium in liquid ammonia gives predominantly

[CBSE AIPMT 1993]

(A) cis-2-butene

(B) trans-2-butene

(C) no reaction

(D) n-butane

$$CH_3-C\equiv C-CH_3 \xrightarrow{Na/liq.NH_3}$$

QUESTION

Which is the most suitable reagent among the following to distinguish-compound (III) from rest of the compounds? [CBSE AIPMT 1989]

I. $CH_3 - C \equiv C - CH_3$

II. $CH_3 - CH_2 - CH_2 - CH_3$

III. $CH_3 - CH_2 - C \equiv CH$

IV. $CH_3 - CH = CH_2$

(A) Br_2/CCl_4

(B) Br_2/CH_3COOH

(C) Alk. KMO_4

(D) Ammoniacal $AgNO_3$

QUESTION

Acetylenic hydrogens are acidic because **[CBSE AIPMT 1989]**

(A) sigma electron density of C-H bond in acetylene is nearer to carbon which has 50% s-character

(B) acetylene has only one hydrogen on each carbon

(C) acetylene contains least number of hydrogens among the possible hydrocarbons having two carbons

(D) acetylene belong to the class of alkynes with molecular formula C_nH_{2n-2}

Benzene

Benzene

Introduction:

→ D.O.U = 4

→ C_6H_6

C_6H_5 phenyl group.

CH_3 +H

Toluene

OH / NH_2

ortho | para activating for $E^{\oplus}$

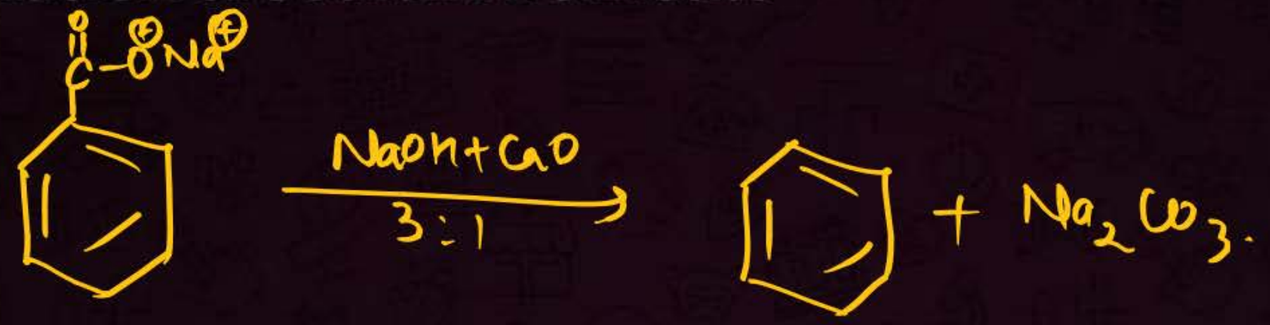
EWG → deactivating group.

Aromatic Compounds → Benzenoid

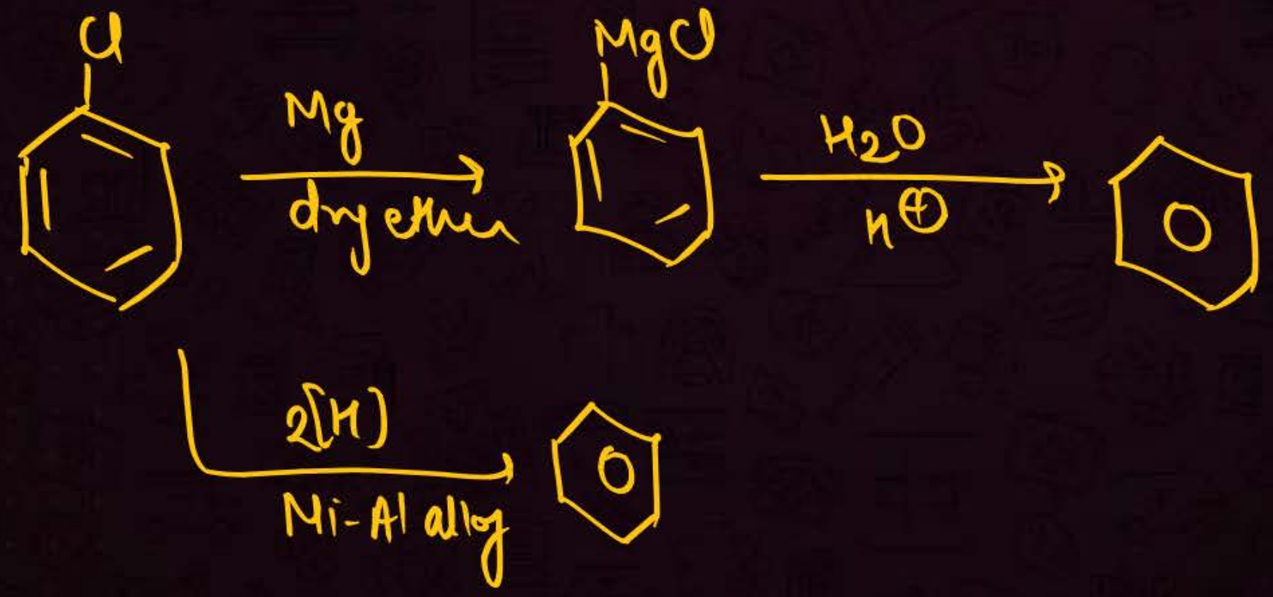
→ non-benzenoid

Preparation:

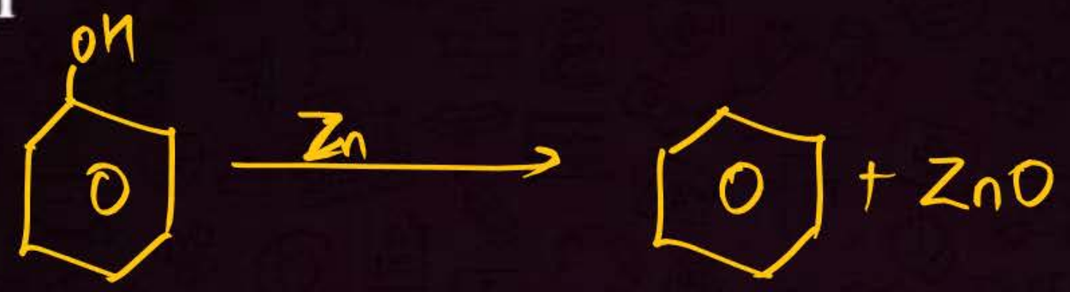
1. Decarboxylation of Sodium Benzoate



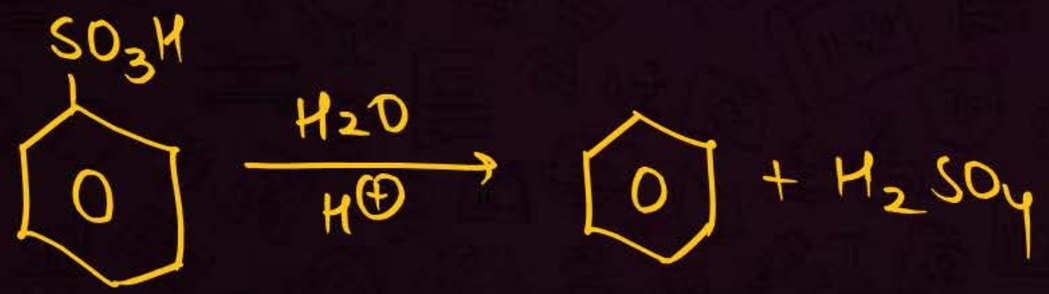
2. From Chlorobenzene



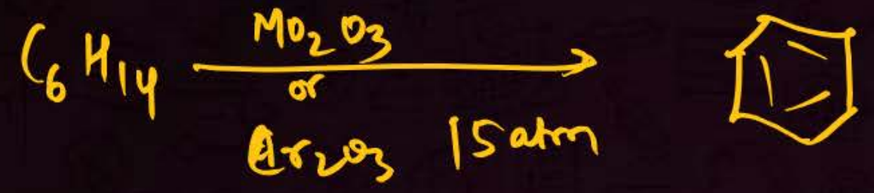
3. From Phenol



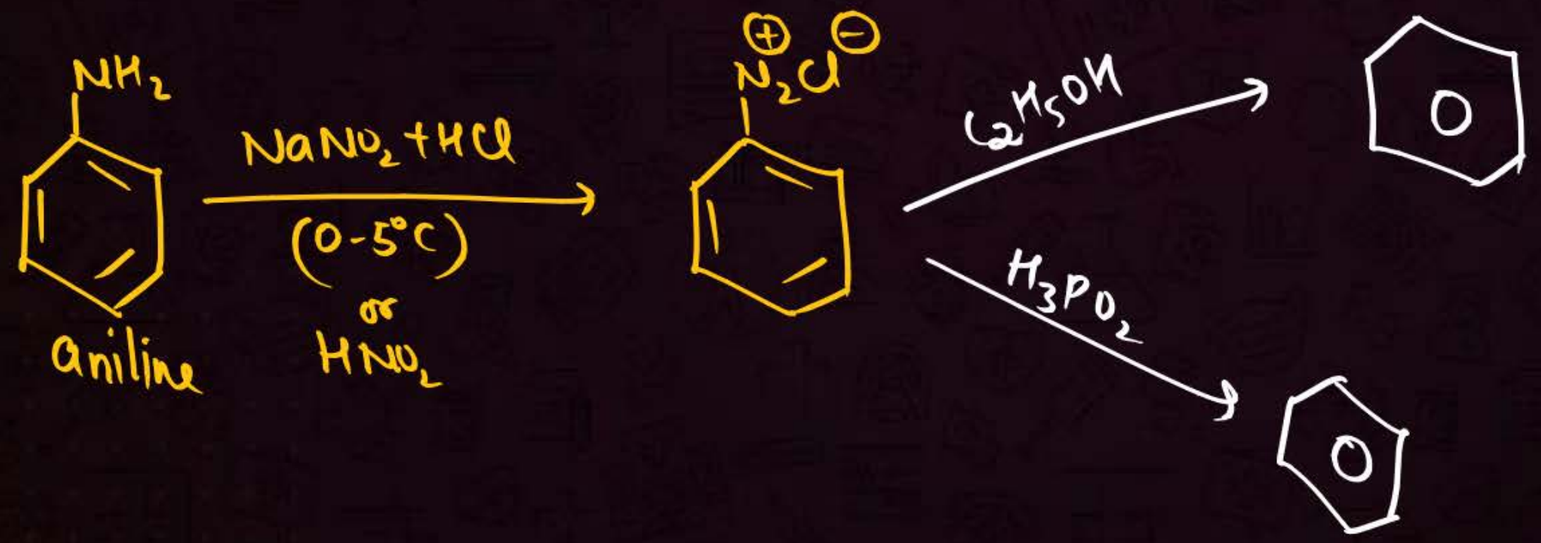
4. From Sulphonic Acid



5. Synthesis/Reforming/Aromatisation



6. From Benzene Diazonium Chloride



7. Manufacture

a. n-Hexane (Reforming/Catalytic Reforming/Aromatisation)

$$C_6H_{14} \xrightarrow[15\ atm]{MoO_3}$$ 

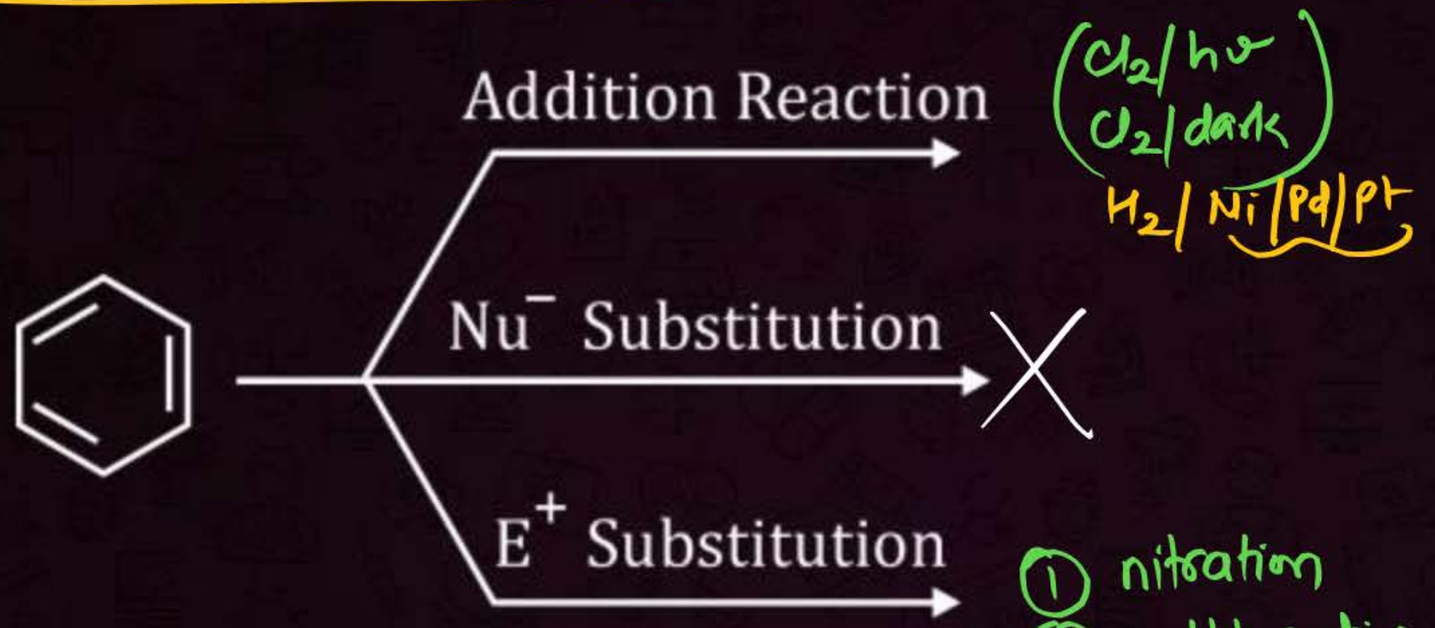
b. Coal Tar

destructive distillation of wood $\longrightarrow$ coal tar $\xrightarrow{\text{fractional}}$ 

Physical Properties of Benzene:

- **Physical State:** liquid
- **M.P./B.P.:** $\propto$ no. of C
- **Nature:** non-polar
- **Solubility:** soluble in non-polar solvent
- **Aromatic Compounds :** producing pleasant smell.
- **On Burning:** Sooty flame
  - ↳ because of high 'C' content

Chemical Properties of Benzene:



($Cl_2/h\nu$, Cl_2/dark)

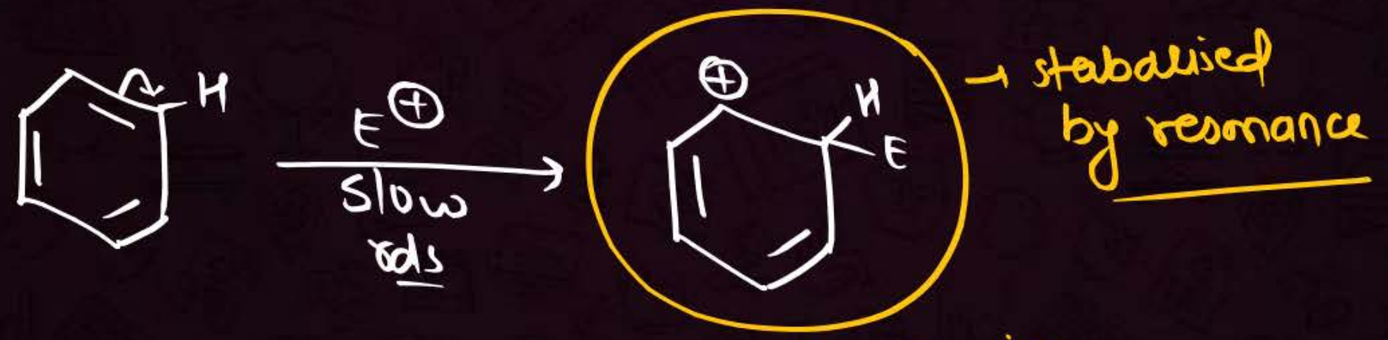
H_2/ Ni/Pd/Pt

1. nitration
2. sulphonation
3. halogenation
4. Friedel-craft alkylation
5. Friedel-craft acylation.

1. Aromatic Electrophilic Substitution Reaction:

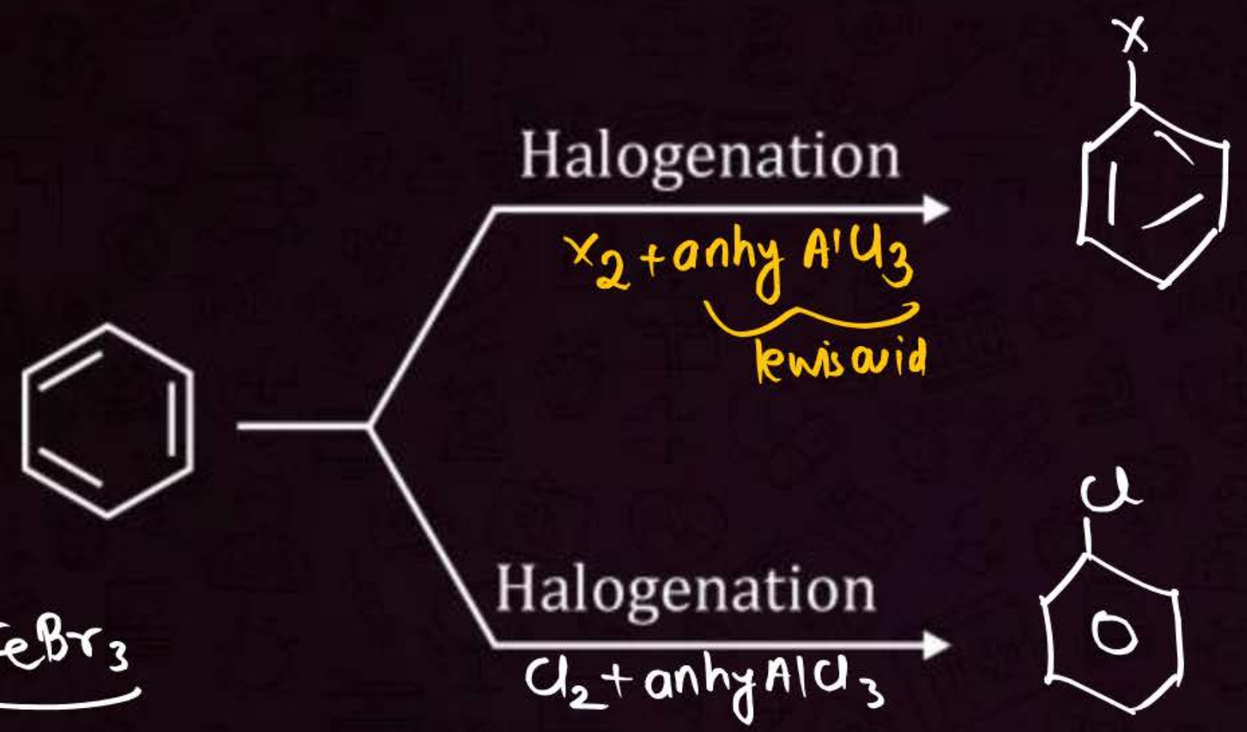
Mechanism

Step-I



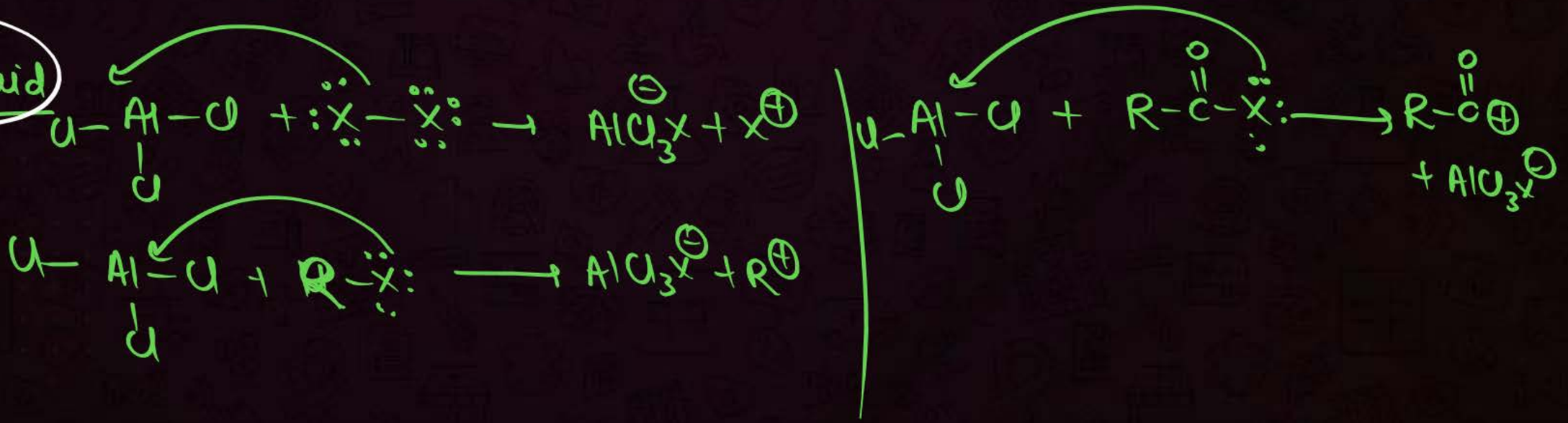
Arenium ion

Step-II

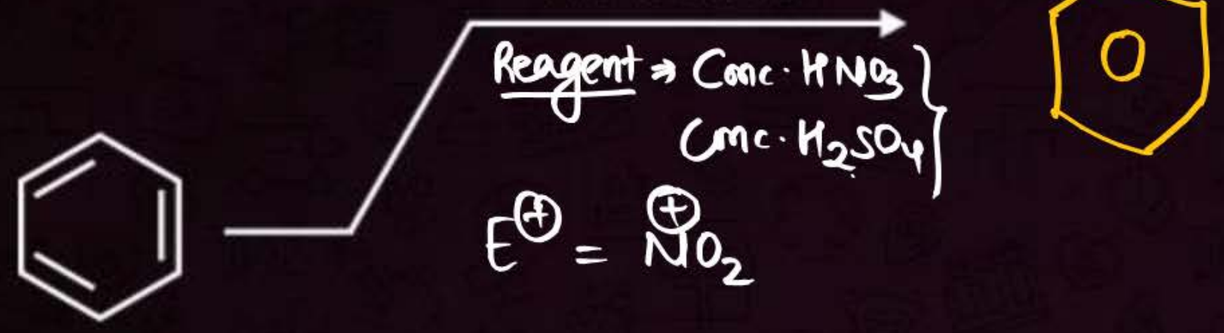


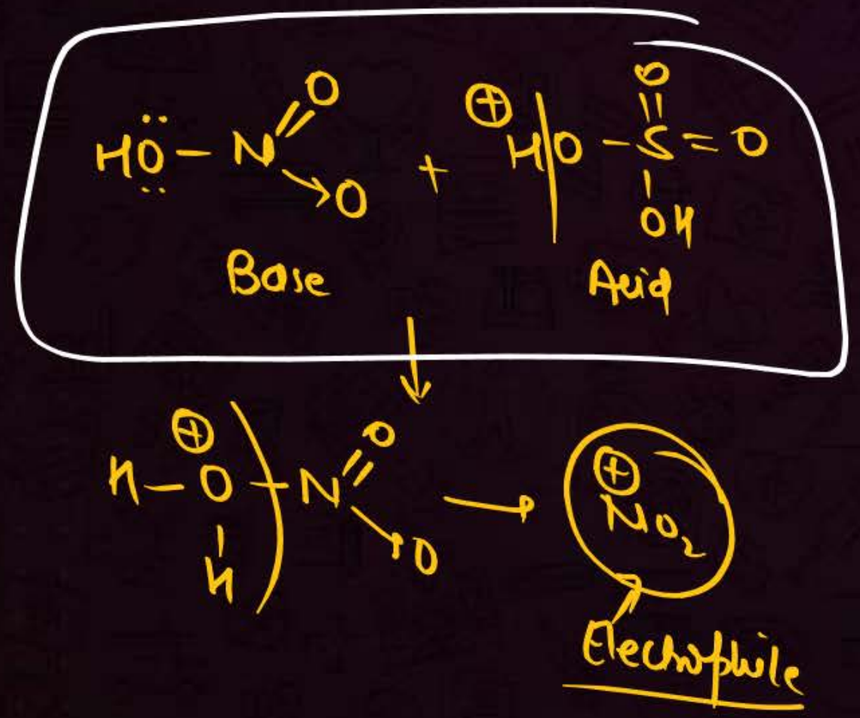
$FeCl_3 | FeBr_3$

lewis acid



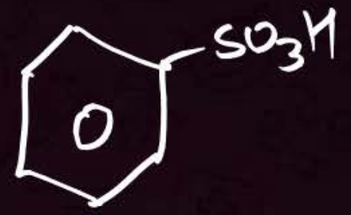
Nitration


Reagent ⇒ Conc. HNO_3
Conc. H_2SO_4
$E^{\oplus} = \overset{\oplus}{N}O_2$
NO_2

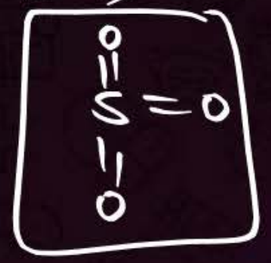

Base
Acid
Electrophile

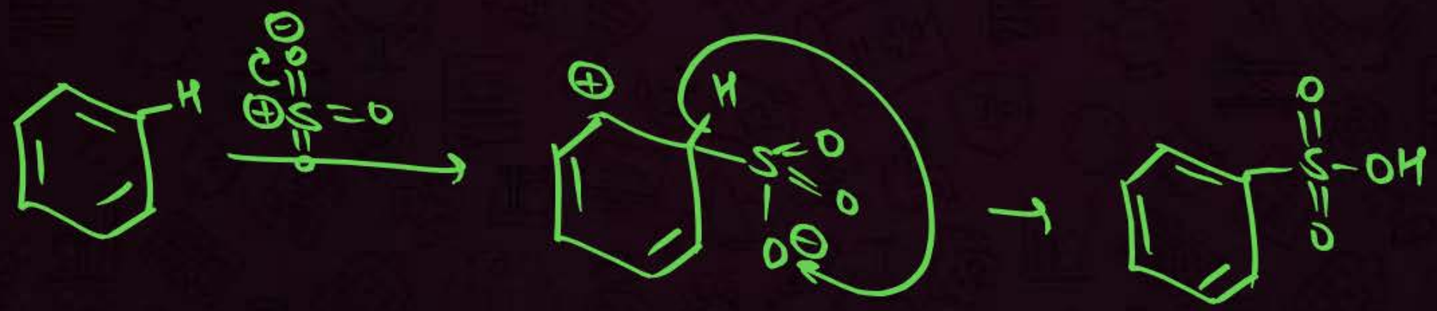
Sulphonation

Reagent ⇒ Conc H_2SO_4
or
Oleum
$H_2SO_4\ (SO_3)$



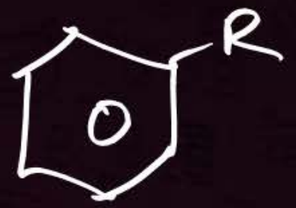
Electrophile ⇒





Friedal Craft Alkylation

$R-X$ + anhy $AlCl_3$



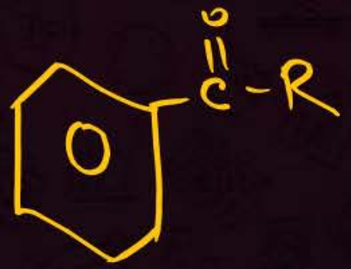
$E^{\oplus} = R^{\oplus}$

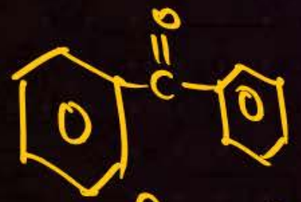
→ Can undergo Rearrangement

$R-\overset{O}{\overset{\|}{C}}-$ acyl group

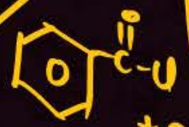
Friedel craft acylation

$R-\overset{O}{\overset{\|}{C}}-Cl$ + anhy $AlCl_3$



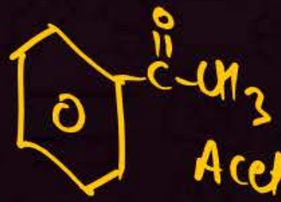


Benzoylation



+ anhy $AlCl_3$

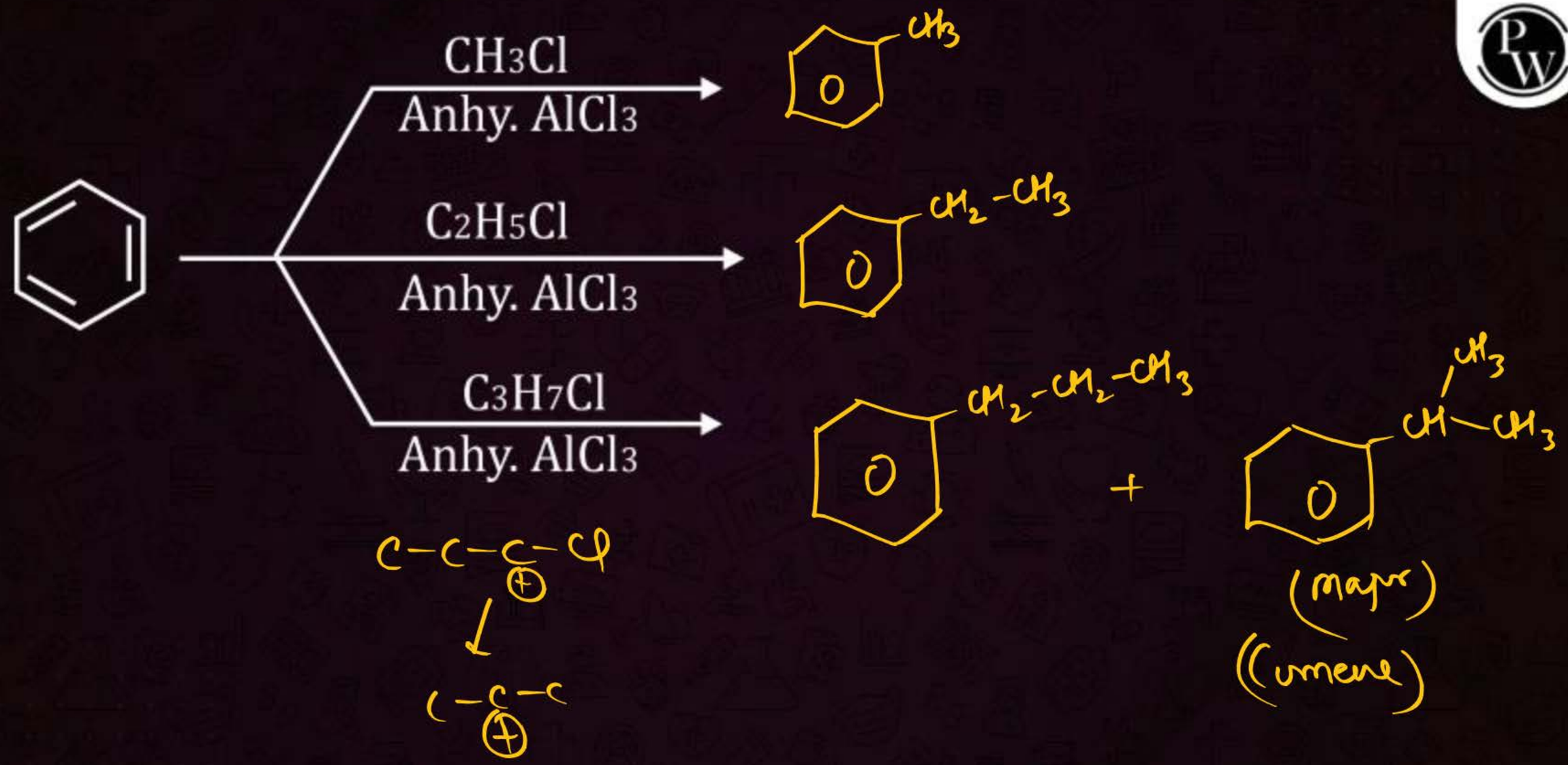
$CH_3-\overset{O}{\overset{\|}{C}}-Cl$ + anhy $AlCl_3$



Acetylation.

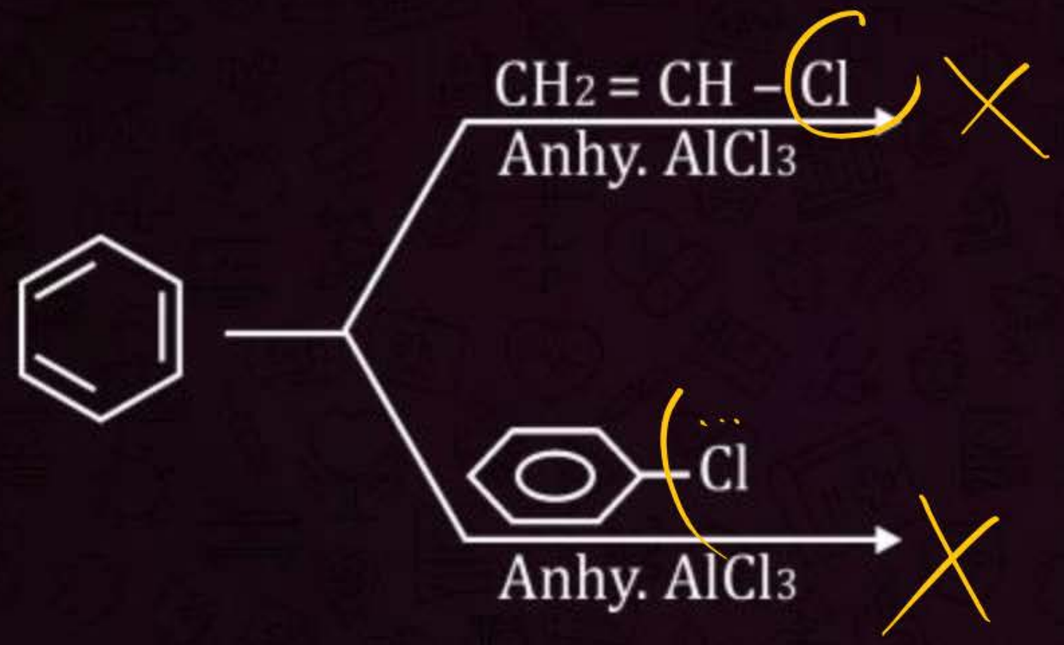
except $R-\overset{O}{\overset{\|}{C}}\oplus$ donot have 3° 'C' in R

if R has 3° C → then that 'C' will be carbocation

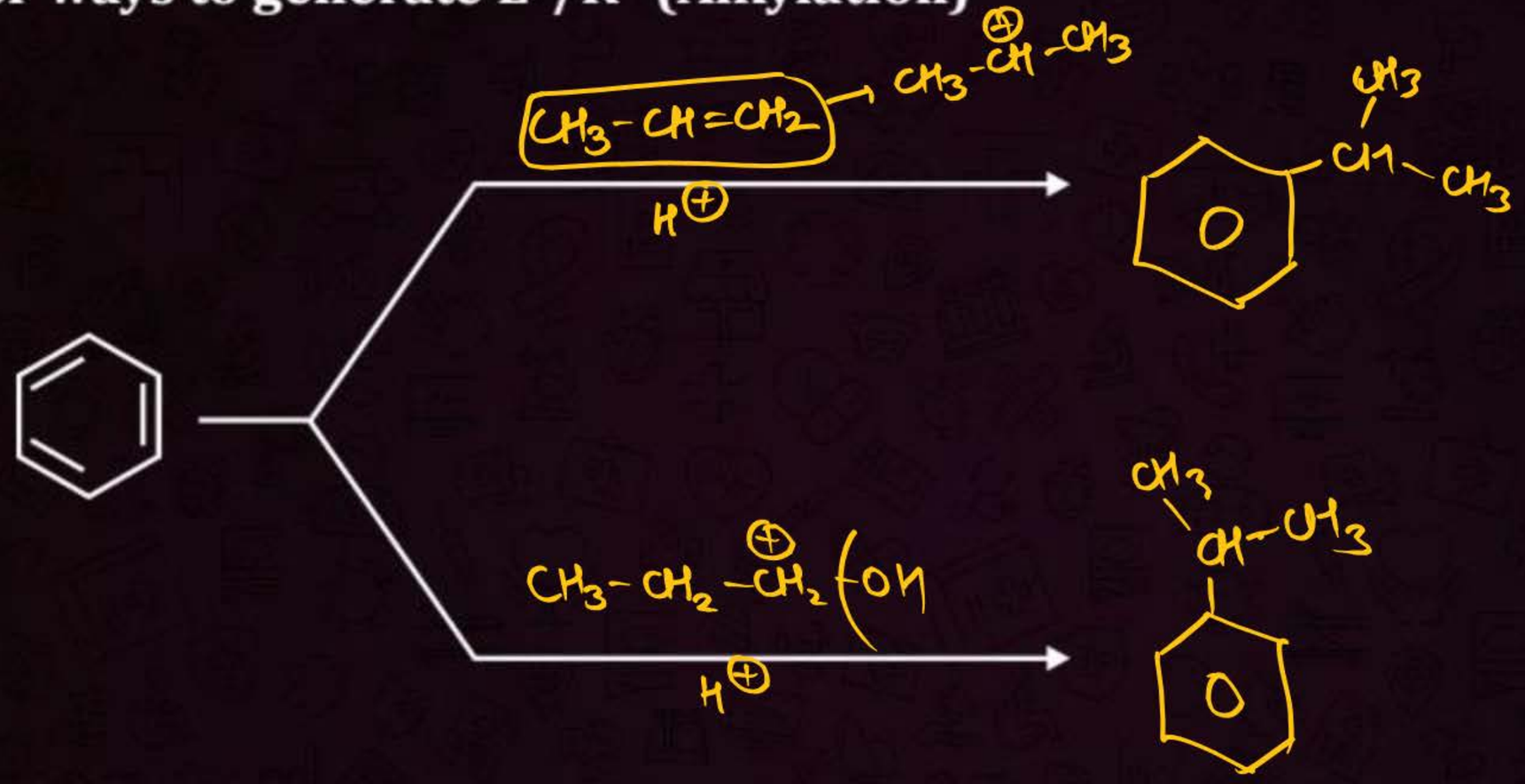

CH3Cl
Anhy. AlCl3
C2H5Cl
Anhy. AlCl3
C3H7Cl
Anhy. AlCl3
(major)
(cumene)

Note:

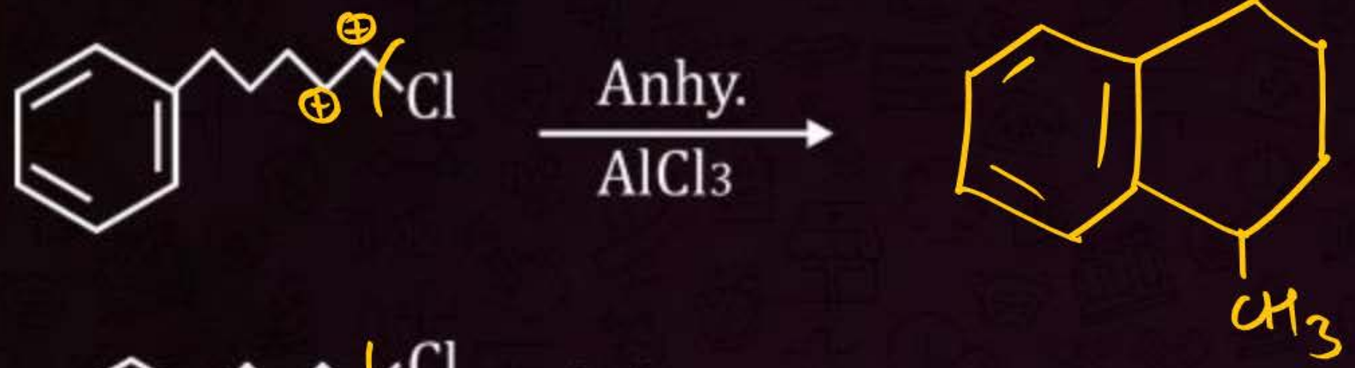
Fridal craft Reaction in Aryl & Vinyl Carbocation.

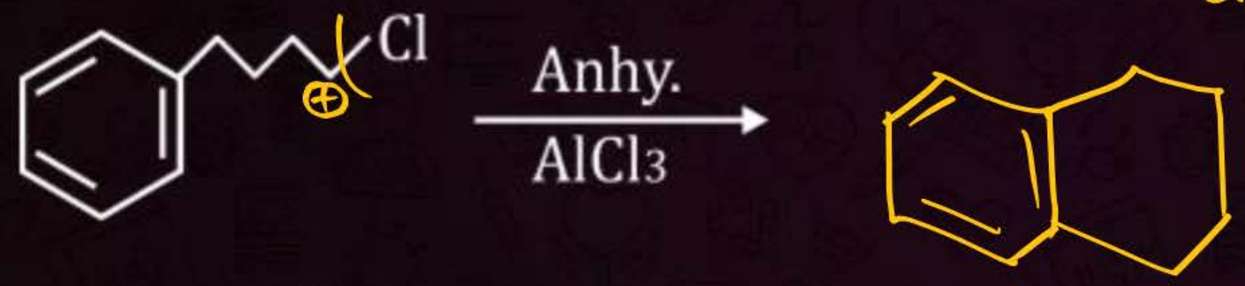


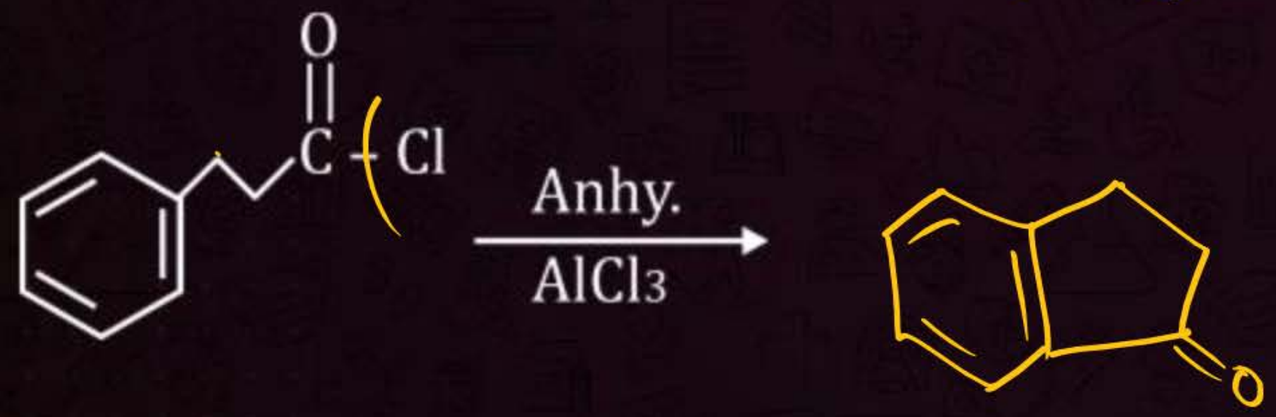
Other ways to generate E^+/R^+ (Alkylation)



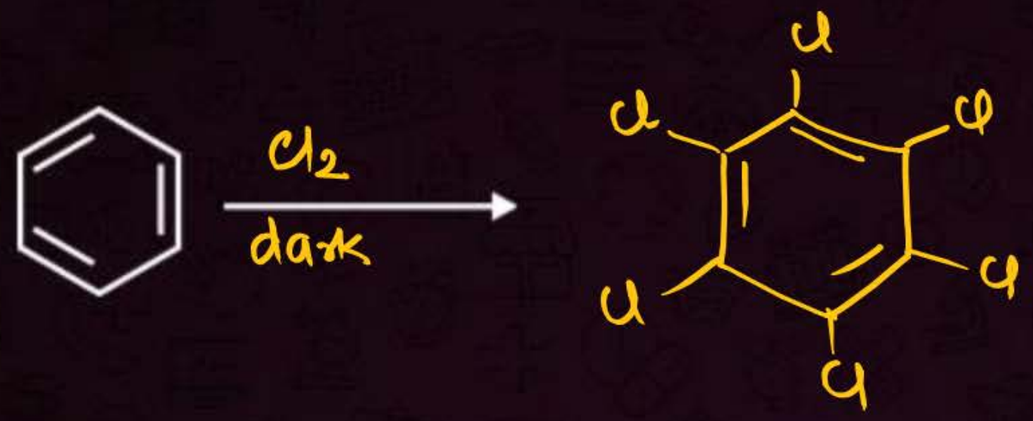
Intramolecular Friedal Craft Reaction: 5/6 membered ring

- 

- 

- 

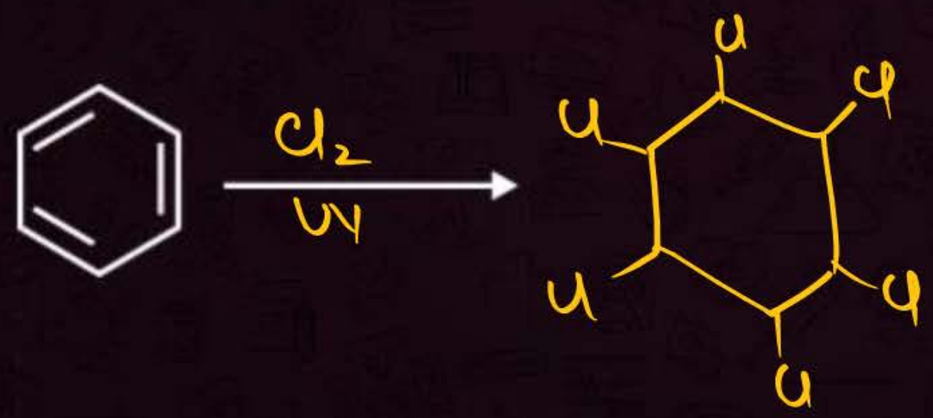
Halogenation in the present of dark:



→ Electrophilic substitution rxn

→ Hexachlorobenzene.

halogenation in the presence of sunlight:



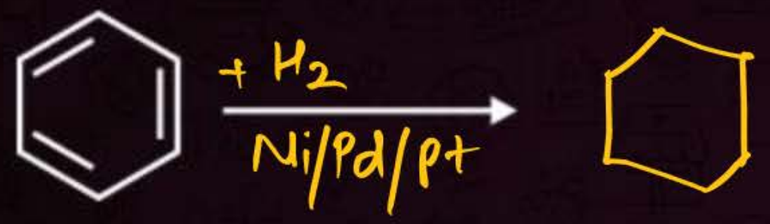
Benzenehexachloride (BHC)

→ Gammoxane

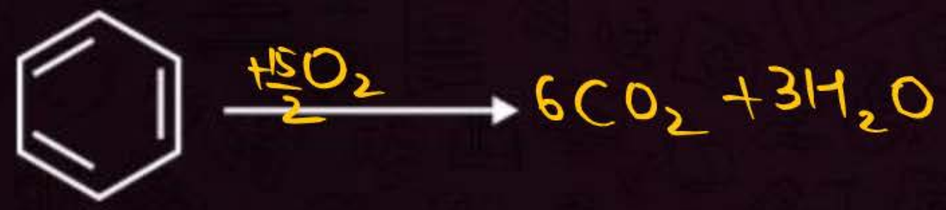
→ insecticide (lindane)

→ C.I = 8

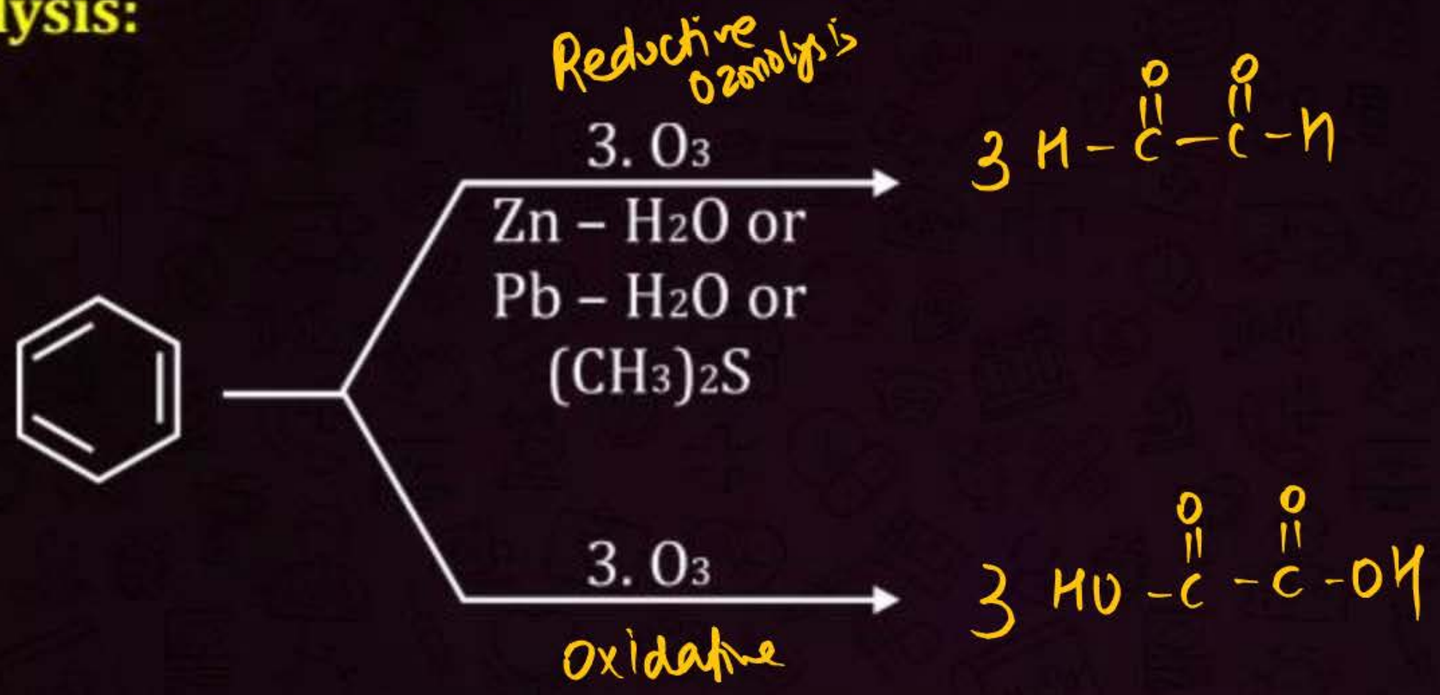
Hydrogenation:



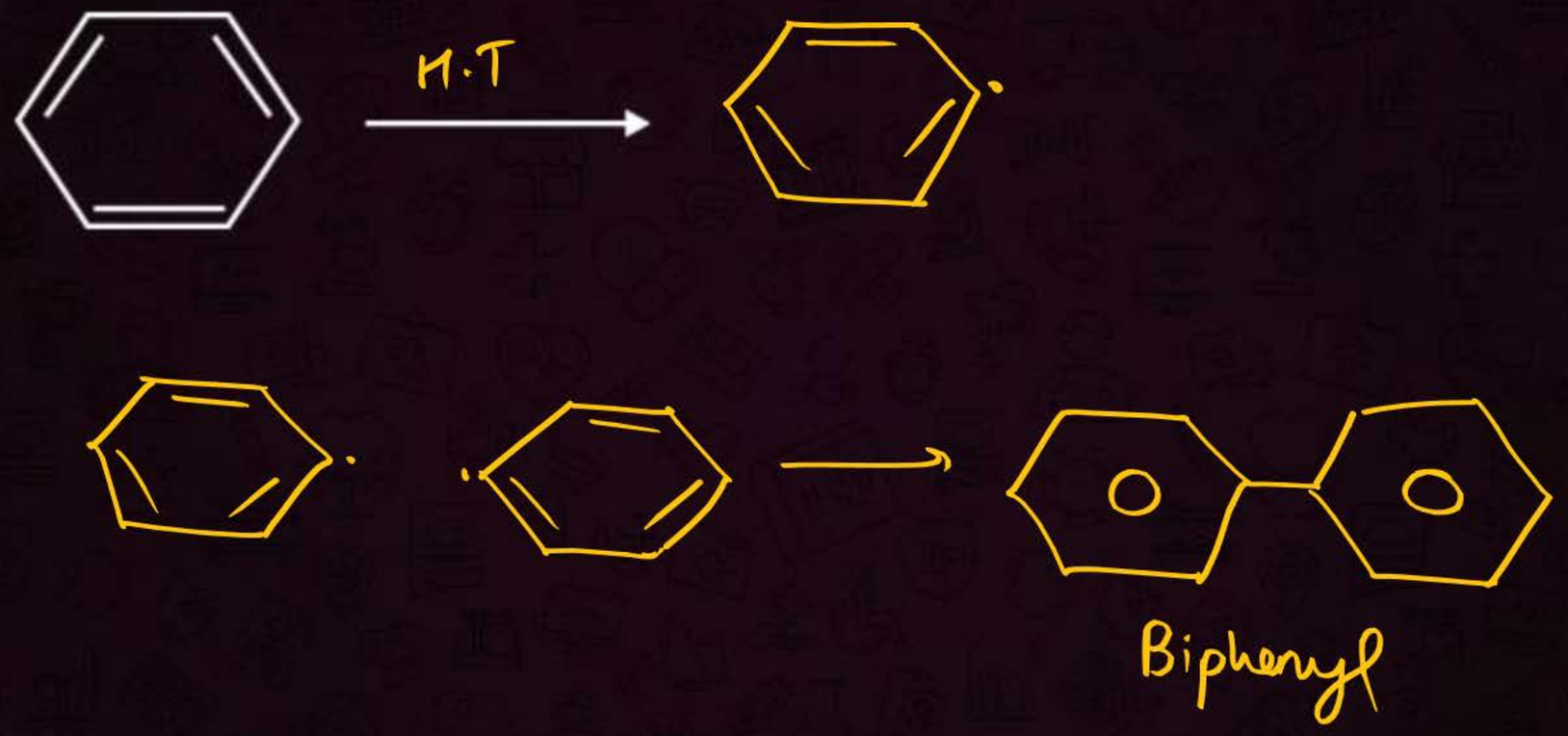
Combustion of Benzene:



Ozonolysis:

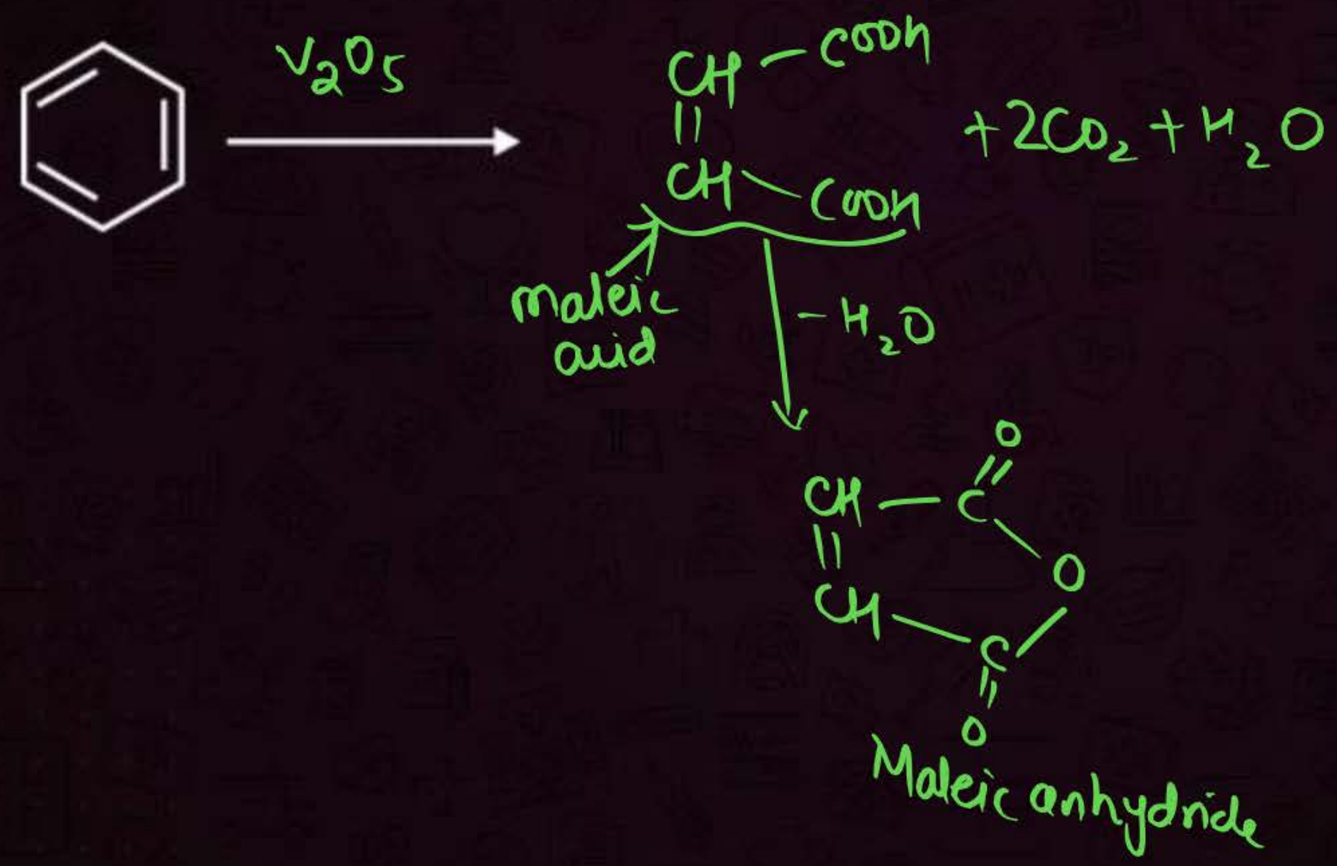

Reductive ozonolysis
3. O3
Zn – H2O or
Pb – H2O or
(CH3)2S
3 H–C(=O)–C(=O)–H
3. O3
oxidative
3 HO–C(=O)–C(=O)–OH

Dehydrogenation:



Oxidation:

(a) Controlled oxidation in Air



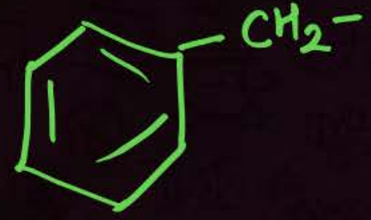
Oxidation of Benzene

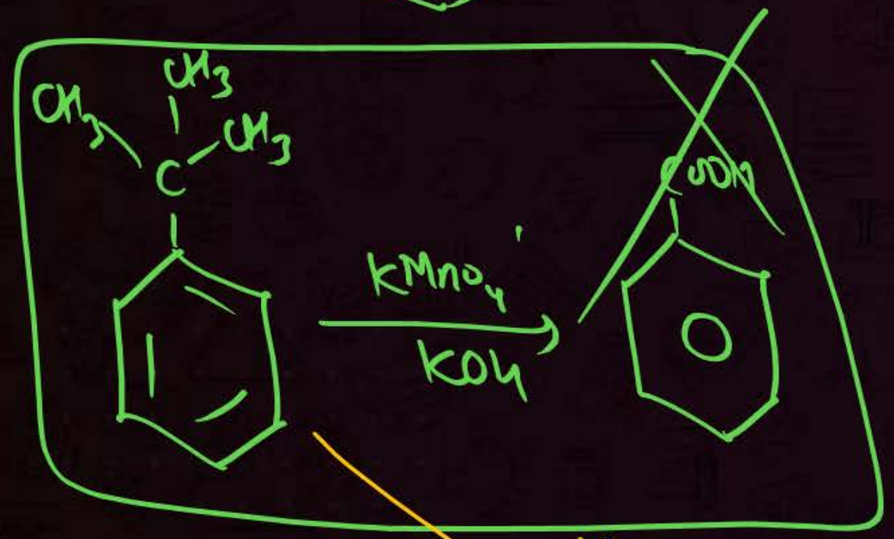
↳ not by oxidising agent

→ under drastic condition.

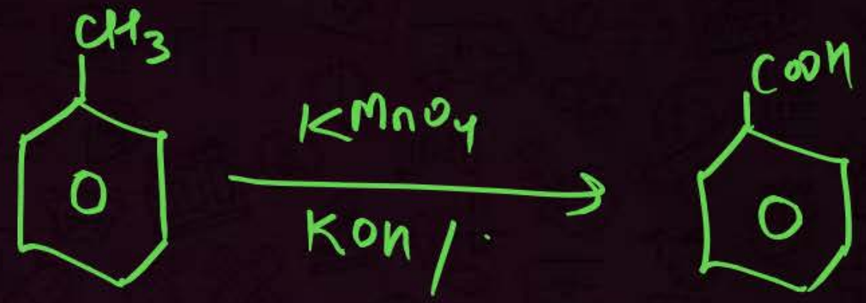
Oxidation of Alkyl Benzene:

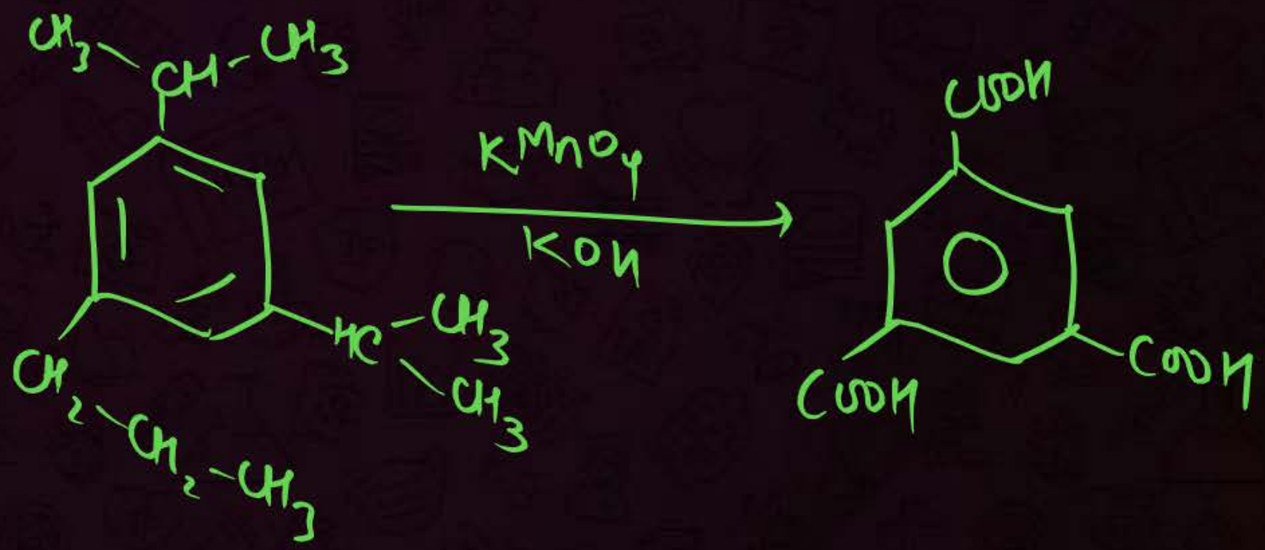
must have one Benzylic (H)





$CH_3-C(CH_3)_2-OH$ + maleic anhydride + CO_2 + H_2O





QUESTION

Some meta-directing substituents in aromatic substitution are given. Which one is most deactivating? [NEET 2013]

(A) $-C = N$

(B) $-SO_3H$

(C) $-COOH$

(D) $-NO_2$

QUESTION

Which of the following compounds will not undergoes Friedel-Craft's reaction easily? [NEET 2013]

(A) Cumene

(B) Xylene

(C) Nitrobenzene

(D) Toluene

QUESTION

Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc. H_2SO_4. In the mixture, nitric acid acts as a/an [CBSE AIPMT 2009]

(A) reducing agent

(B) acid

(C) base

(D) catalysta

QUESTION

Benzene reacts with CH_3Cl in the presence of anhy. $AlCl_3$ to form

[CBSE AIPMT 2009]

(A) toluene

(B) chlorobenzene

(C) benzylchloride

(D) xylene

QUESTION

Which one of these, is not compatible with arenes? [CBSE AIPMT 1998]

(A) Greater stability

(B) Delocalisation of π-electrons

(C) Electrophilic additions

(D) Resonance

QUESTION

Benzene reacts with n-propyl chloride in the presence of anhydrous $AlCl_3$ to give

C-C-C-Cl

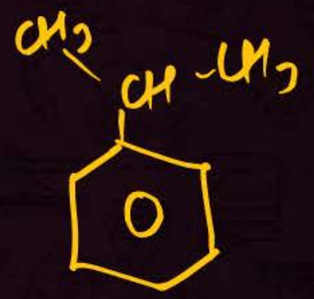
[CBSE AIPMT 1993]

(A) 3-propyl-1-chlorobenzene

(B) n-propyl benzene ✗

(C) no reaction

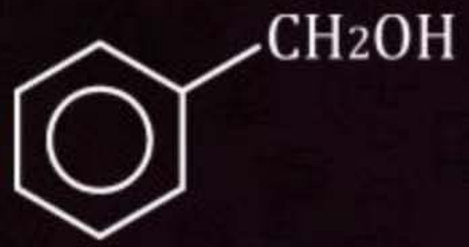
(D) iso-propyl benzene ✓

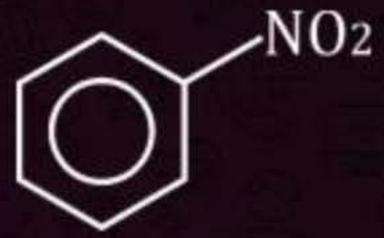


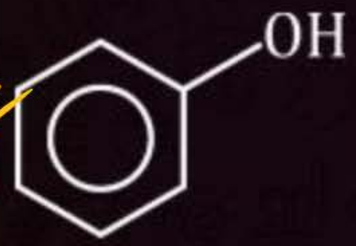
QUESTION

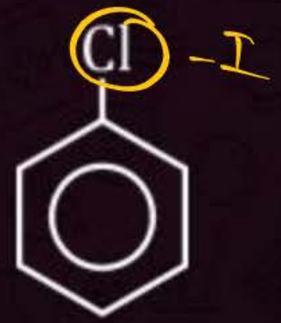
Which one of the following is most reactive towards electrohilie.

[CBSE AIPMT 2008]

(A) 

(B) 

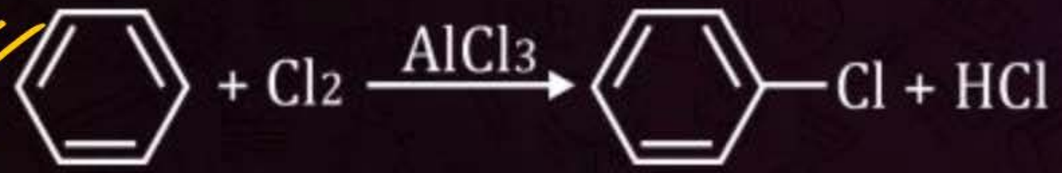
(C) 

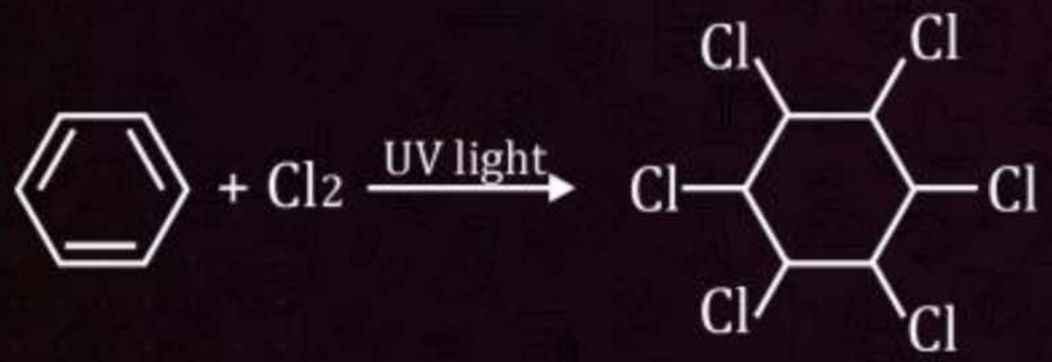
(D) 

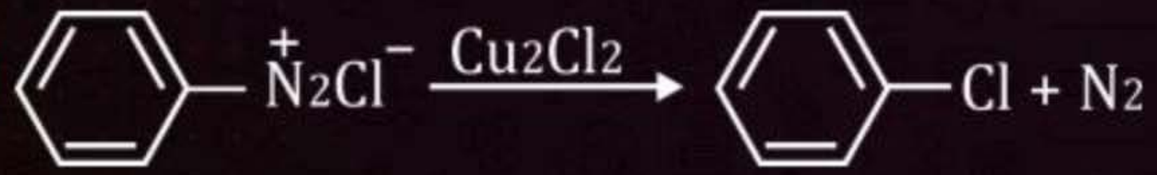
QUESTION

Among the following, the reaction that proceeds through an electrophilic substitution, is [NEET (National) 2019]

(A) 

(B) 

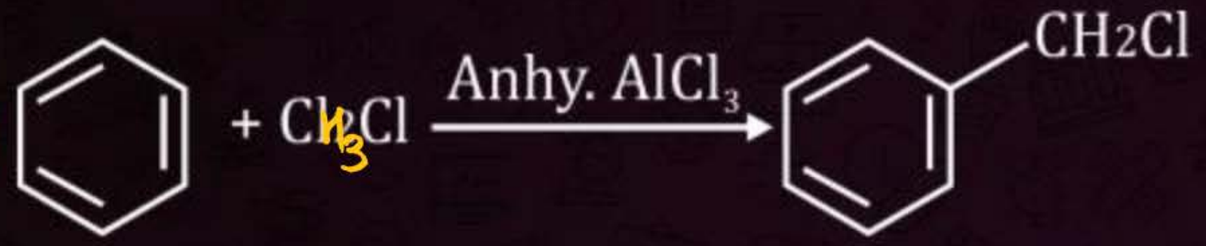
(C) 

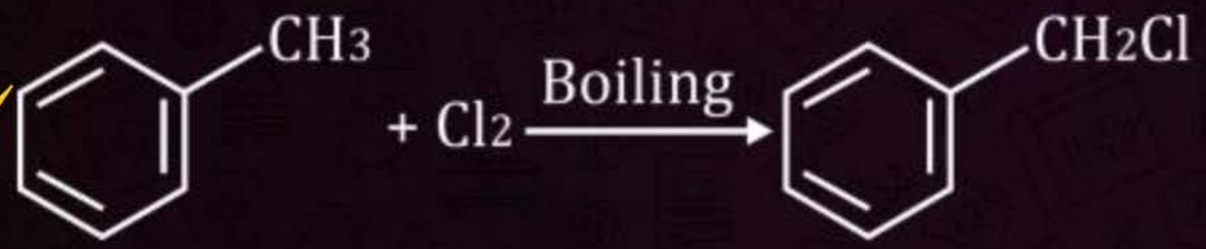
(D) 

QUESTION

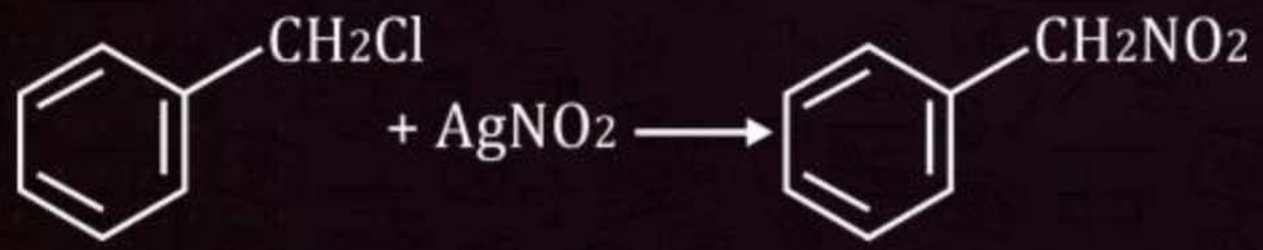
Which one of the following is a free radical substitution reaction?

[CBSE AIPMT 2003]

(A) 

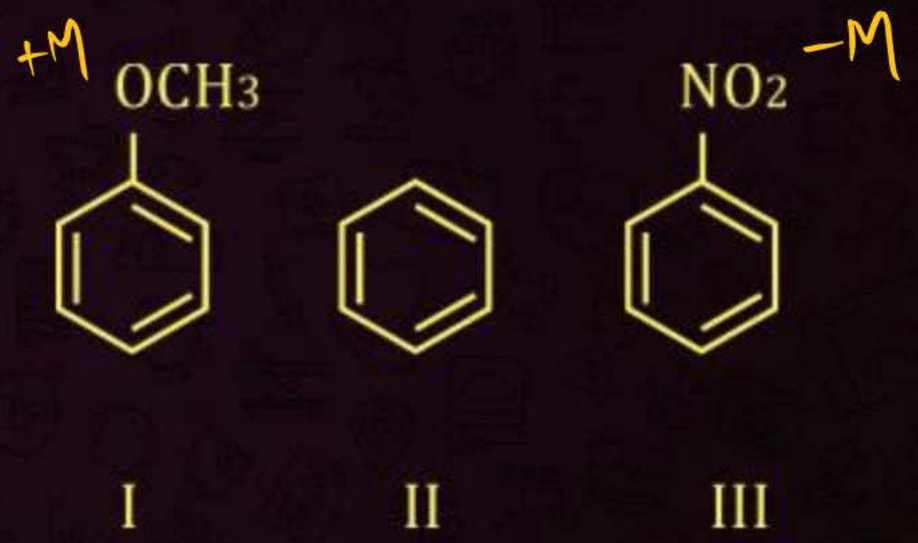
(B) 

(C) $CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$

(D) 

QUESTION

Among the following compounds (I-III), the correct order of reaction with electrophile is [CBSE AIPMT 1997]



(A) II > III > I

(B) III < I < II

(C) I > II > III

(D) I > III > II

Summary

- DPP
- PYQs → NEET
- NCERT

FOR NOTES & DPP CHECK DESCRIPTION

Homework

Selection

FOR NOTES & DPP CHECK DESCRIPTION


THANK YOU