Hydrocarbon

Alkane Alkene Alkyne Benzene

Alkane

→ G.F → C_nH_{2n+2}

R-H | R-R.

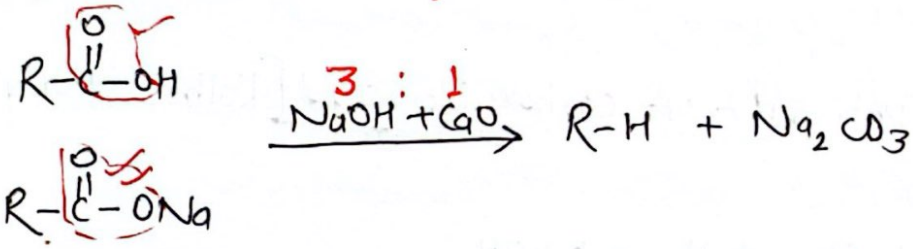
→ C: sp^3

→ BA in alkane : 109°28' (109.5)

→ Tetrahedral

* General Method of preparation

(1) By Sodalime decarboxylation of sod| pot. salt of carboxylic acid (Lab Method)



$R-COONa \xrightarrow{NaOH+CaO} R-H + Na_2CO_3$

eg. $CH_3-COONa \xrightarrow{NaOH+CaO} CH_4 + Na_2CO_3$

→ intermediate → carbanion [C^-]

Rate of decarboxylation ∝ stability of C^-.

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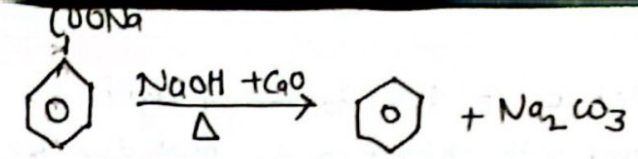


Q. Rate of decarboxylation :-

(a) CH_3-CH_2-COOH (b) $(CH_3)_2CH-COOH$

(c) $(CH_3)_3C-COOH$ (d) CH_3-COOH

order of stability of C^- → $CH_3^- > 1^\circ > 2^\circ > 3^\circ$

↓

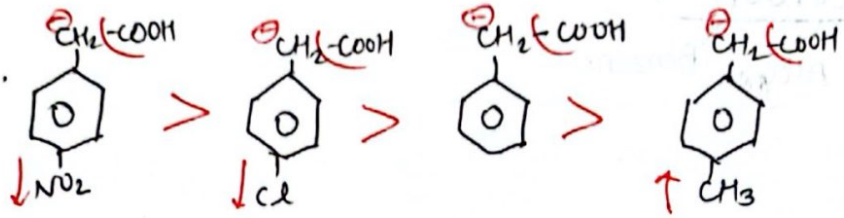
→ d > a > b > c.

$\boxed{C\uparrow \text{ stability } \downarrow \text{es}}$ → in C^-

$\boxed{O^- > N^-}$

Q. $\underset{sp}{CH\equiv\overset{\ominus}{C}-COOH} > \underset{sp^2}{CH_2=\overset{\ominus}{C}H-COOH} > \underset{sp^3}{CH_3-\overset{\ominus}{C}H_2-COOH}$.

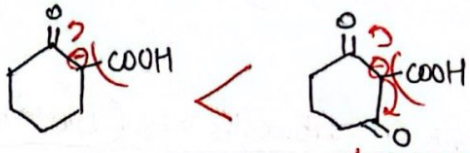
Q.



$\boxed{\text{Carbanion} \propto \frac{EWG}{EDG}}$

- $CH_3-COOH \longrightarrow CH_4$.
- $HCOOH \longrightarrow H_2$

Q.



resonance on both sides.

(2) By electrolysis of sod. or pot. salt of carboxylic acid [Kolbe's electrolysis]

$2RCOONa_{aq.} \xrightarrow{\text{electrolysis}} \underbrace{R-R + CO_2}_{\text{anode}} + \underset{\text{cathode}}{H_2} + \underset{\text{soln.}}{NaOH}$

$RCOONa \rightleftharpoons RCOO^- + Na^+$

$H_2O \rightleftharpoons OH^- + H^+$ (in soln.)

Anode: oxdn

$RCOO^- \longrightarrow RCOO^\cdot + e^-$

$\downarrow$

$R^\cdot + CO_2\uparrow$

$\hookrightarrow R^\cdot + R^\cdot \rightarrow R-R$ (alkane)

Cathode → redn

$H^+ + e^- \longrightarrow \frac{1}{2}H_2$

⇒ $RCOONa$, $RCOONa$ $\longrightarrow R-R$.

→ Methane can't form by this rxn.

$2CH_3COONa \xrightarrow{\text{electrolysis}} CH_3-CH_3$.

- intermediate → free radical.

→ $2CH_3-CH_2-CH_2^\cdot + COONa \xrightarrow{\text{electrolysis}} C-C-C-C-C-C$ Hexane.

→ $CH_3COONa + CH_3CH_2COONa$

$CH_3^\cdot$ — — — $CH_3-CH_2^\cdot$

$C-C$ $C-C-C$ $C-C-C-C$

RCOONa → sod. salt of mono carboxylic acid. (Alkane दि-ह)

→ CH_2-COOH, CH_2-COOH → Succinic acid.

→ $CH_2-COONa$, $CH_2-COONa$ → Sod. succinate or Sod. salt of saturated dicarboxylic acid

$CH_2=CH_2$ (ethene)

Sod. salt of unsatured dicarboxylic acid

$CH-COONa$ ‖ $CH-COONa$

Sod. Maleate → ethene

$CH-COONa$ ‖ CH (COONa)

Sod. Fumarate → ethene.

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- Alkane → sod. salt of Monocarboxylic acid
- Alkene → sod. salt of saturated dicarboxylic acid.
- Alkyne → sod. salt of unsaturated dicarboxylic acid

3) Wurtz rxn

$$R\text{-}X + 2Na + X\text{-}R \xrightarrow{\text{dry ether}} \underset{\text{alkane}}{R\text{-}R} + 2NaX.$$

eg.

$$2CH_3\text{-}CH_2\text{-}Cl \xrightarrow[\text{dry ether}]{2Na} CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 \quad \underset{\text{butane}}{} + 2NaCl.$$

$C^+ \rightarrow 3^\circ > 2^\circ > 1^\circ > CH_3^{\oplus}$

$C^\bullet \rightarrow 3^\circ > 2^\circ > 1^\circ > CH_3^\bullet$

$C^- \rightarrow CH_3^- > 1^\circ > 2^\circ > 3^\circ$

→ $CH_3\text{-}Cl$ $\qquad$ $CH_3\text{-}CH_2\text{-}Cl$.

$CH_3^\bullet$ $\qquad$ $CH_3\text{-}CH_2^\bullet$

C-C $\qquad$ C-C-C $\qquad$ C-C-C-C.

→ $R\text{-}I > R\text{-}Br > R\text{-}Cl > R\text{-}F$

$3^\circ R > 2^\circ R > 1^\circ R.$

elimination.

$$CH_3\text{-}\underset{\substack{\beta \\ CH_3}}{\overset{\substack{CH_3 \\ \alpha}}{C}}\text{-}Cl \xrightarrow[\text{dry ether}]{Na} CH_2=\overset{CH_3}{C}\text{-}CH_3$$

isobutene

elimination.

(No wurtz rxn)
$3^\circ R$.

→ $2CH_3\text{-}\underset{CH_3}{CH}\text{-}Cl \xrightarrow[\text{dry ether}]{Na}$ C-C(C)-C-C =

Q. $C_2H_5\text{-}Cl$ and $CH_3\text{-}CH_2\text{-}CH_2\text{-}Cl$. rxt & which alkane doesn't formed

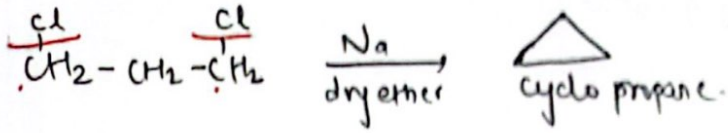
(a) C-C-C-C $\qquad$ (b) C-C-C-C-C $\qquad$ (c) C-C-C-C-C-C

(d) C-C-C

Q. By Wurtz reaction which alkane can be prepared

(a) C_2H_6 (b) C_3H_8 (c) CH_4 (d) C_4H_{10}

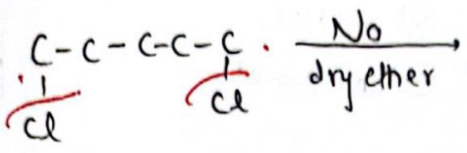
* $CH_2(-Cl)$ / $CH_2(-Cl)$ $\xrightarrow[\text{dry ether}]{Na}$ $CH_2=CH_2$ ethene

* 

cyclo propane

* 

Bicyclic compound

* 

cyclo pentane

* $CH_3-CH(Cl)-CH(Cl)-CH_3$ $\xrightarrow[\text{dry ether}]{Na}$ $CH_3-CH=CH-CH_3$ But-2-ene.

(4) Frankland reaction

$R-X + Zn + R-X \xrightarrow{\text{dry ether}} R-R + ZnX$

(5) From Grignard reagent

(A) $R-MgX$ + active hydrogen containing compound.

HF, H_2O,

$R-MgX + H-OH \longrightarrow R-H + Mg(X)(OH)$.

$R-MgX + H-OR \longrightarrow R-H + Mg(X)(OR)$

(B) Formation of R-R

$R-MgX + R^{\delta+}-X^{\delta-} \longrightarrow R-R + MgX_2$

$CH_3MgBr + C_2H_5Br \longrightarrow CH_3-C_2H_5 + MgBr$

Propane

Hydrolysis of aluminium & Berylium carbide

$$Al_4C_3 + 12H_2O \longrightarrow 3CH_4 + 4Al(OH)_3$$

$$Be_2C + 4H_2O \longrightarrow CH_4 + 2Be(OH)_2$$

but,

$$CaC_2 + 2H_2O \longrightarrow \underset{\text{ethyne}}{C_2H_2} + Ca(OH)_2$$

(F) By reduction of alkyl halide

$$R-X \xrightarrow[\text{agent } 2[H]]{\text{reducing}} R-H + HX$$

(i) Zn + HCl
(ii) Zn-Cu couple + C_2H_5OH
(iii) $LiAlH_4$
(iv) Red P + HI
(v) Sn + HCl
(vi) Zn + NaOH.

$$RI > RBr > RCl > RF$$

(3) By reduction of unsaturated Hydrocarbon or catalytic hydrogenation

$$\underset{\text{alkene}}{>C=C<} + H_2 \xrightarrow{Ni/Pt/Pd} \underset{\substack{H\ \ H \\ \text{syn addition.}}}{>\overset{H}{\underset{|}{C}}-\overset{H}{\underset{|}{C}}<} + \Delta$$

$$\underset{\text{alkyne.}}{-C\equiv C-} + 2H_2 \xrightarrow{Ni/Pt/Pd} -CH_2-CH_2- + \Delta$$

→ In presence of Pt or Pd, hydrogenation takes place at room temp^r.
→ In presence of Ni, hydrogenation takes place at higher temp^r (200–300°C).
  └ Sabatier & Senderen's reaction

* Raney Ni → Rxn occurs at room temp^r.
  └ Nickel in powder form.

– Exothermic [heat of hydrogenation].

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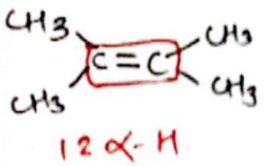
Heat of hydrogenation $\propto \frac{1}{\text{Stability}}$

Stability of alkene $\propto$ no. of α-H.

- $CH_3-CH=CH_2$ (3 α-H) $<$ $CH_3-CH=CH-CH_3$ (6 α-H) (stability)

-  (12 α-H)

- $CH_3-C\equiv CH$ (3 α-H) $>$ $CH\equiv C-CH_2-CH_3$ (2 α-H)

(9) Red P + HI

↳ All functional group into alkane.

$R-CH_2OH \xrightarrow{\text{Red P + HI}} R-CH_3 + I_2 + H_2O$

$R-CHO \xrightarrow{\text{Red P + HI}} R-CH_3$

$R-\overset{O}{\overset{\|}{C}}-R \xrightarrow{\text{"}\ \text{"}} R-CH_2-R$

$R-COOH \longrightarrow R-CH_3$

$R-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow R-CH_3$

$R-Br \longrightarrow R-H.$

(10) Clemmenson reduction

$HIR-\overset{O}{\overset{\|}{C}}-HIR \xrightarrow[\text{conc. HCl}]{Zn-Hg} R/H-CH_2-HIR$

(11) Wolf-Kishner redn

$HIR-\overset{O}{\overset{\|}{C}}-HIR \xrightarrow[KOH]{NH_2-NH_2} HIR-CH_2-HIR$

(12) Corey House synthesis

→ Both symmetrical as well as unsymmetrical alkane.

$R-X \xrightarrow[\text{(ii) CuI}]{\text{(i) Li}} R-R'$

(11) $R'-X$

$R-X \xrightarrow{Li} RLi$

$RLi \xrightarrow{CuI} R_2CuLi$ (Gilliman's reagent)

$R_2CuLi \xrightarrow{R'-X} R-R'.$

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9. $CH_3-Cl \xrightarrow{Li} CH_3Li$

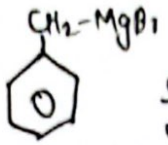
$CH_3Li \xrightarrow{CuI} (CH_3)_2CuLi \xrightarrow{C_2H_5-Br} CH_3-C_2H_5$ propane

CH_3^-

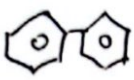
Q. $CH_3-CH_2-CH_3$ not formed by:-

(a) wurtz rxn (Hardly form) (b) corey House synthesis

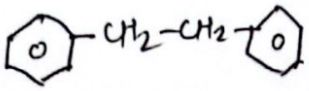
(c) Decarboxylation of acid salt

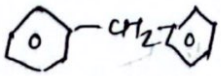
Q. 

$\xrightarrow[\text{(ii) } Cl_2/h\nu \text{ (iii) Na/ether dry}]{\text{(i) } H_2O}$?

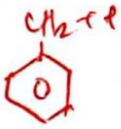
(a) 

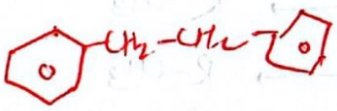
(b) 

(c) 

(d) 

(i) 

(ii) 

(iii) 

Q. $CH_3-CH(CH_3)-MgBr + CH_3-C(CH_3)_2-OH \longrightarrow$

(a) $CH_3-CH_2-CH_3$

(b) $CH_3-CH(CH_3)-CH_3$

(c) $CH_3-C(CH_3)_2-CH_3$

(d) $CH_3-CH(CH_3)-C(CH_3)_2-CH_3$

Chemical properties of Alkane

(i) F.S.R (ii) other rxn.

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① Free Radical substitution rxn

A. Halogenation

$$R-H + X_2 \xrightarrow[\Delta]{h\nu} R-X + HX.$$

Mechanism : 3 step.

① Chain initiation

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

② Propagation

$$R-H + X^{\cdot} \longrightarrow R^{\cdot} + HX$$

Rate determining step or slowest step

$$R^{\cdot} + X-X \longrightarrow R-X + X^{\cdot}$$

③ Termination

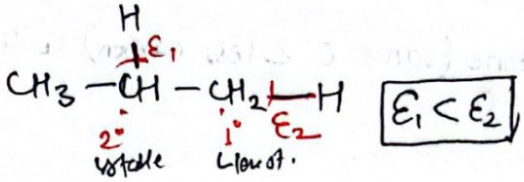
$$R^{\cdot} + X^{\cdot} \longrightarrow R-X \qquad X^{\cdot} + X^{\cdot} \longrightarrow X_2$$

$$R^{\cdot} + R^{\cdot} \longrightarrow R-R.$$

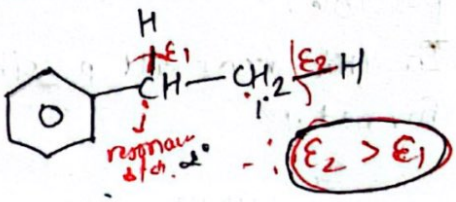
- **Bond dissociation energy (BDE)**

B.D.E of C-H bond $\propto \frac{1}{\text{reactivity of C-H}} \propto \frac{1}{\text{stability of } \geq C^{\cdot}}$

e.g. $CH_2=CH-\overset{2^{\circ}}{CH}(H)-\overset{1^{\circ}}{CH_2}-H$ (ε_1, ε_2) → B.D.E more $\varepsilon_1 > \varepsilon_2$



$\varepsilon_1 < \varepsilon_2$



$\varepsilon_2 > \varepsilon_1$

- **Reactivity of Halogen**

$$F_2 > Cl_2 > Br_2 > I_2$$

- **Fluorination :-** Rxn is controlled by some inibitors (N_2 or inert gas).
  → No need of sunlight / Rxn is possible in dark.

$$CH_4 + F_2 \xrightarrow[\text{inert gas}]{\text{dark}} CH_3F + HF.$$

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but

$CH_4 + 2F_2 \xrightarrow{\text{sunlight}} C + 4HF$

- **Iodination**

$CH_4 + I_2 \underset{\text{Red. agent}}{\overset{h\nu}{\rightleftharpoons}} CH_3-I + HI$

but,

$CH_4 + I_2 \xrightarrow[\text{O. agent}]{h\nu,\ HIO_4,\ HNO_3} CH_3-I + HI$ → (no reversible)

Q. $CH_3-\overset{\overset{CH_3}{|}}{\underset{3^\circ}{CH}}-CH_3 \xrightarrow{Cl_2/h\nu} CH_3-\overset{\overset{CH_3}{|}}{\underset{Cl}{C}}-CH_3$ more stable

B. Nitration

$R-H + HO-NO_2 \xrightarrow{400^\circ C} R-NO_2 + H_2O$

(alkane; conc. HNO_3)

spcl. point

- In this reaction, reactant react in vapour phase due to very high Temp. It is called vapour phase nitration.
- → Reactivity of alkane ∝ stability of $R^\bullet$.
  i.e. $3^\circ > 2^\circ > 1^\circ > CH_3^\bullet$
- In this rxn, tempr is too high. so, C-C bond cleavage is also possible.
- In this rxn, all possible nitroalkane (same C & less carbon) will be formed.

Q. $CH_4 \xrightarrow[400^\circ C]{\text{conc } HNO_3} CH_3-NO_2$

→ $CH_3-CH_3 \xrightarrow[400^\circ C]{\text{conc } HNO_3} \underset{\text{Major}}{C-C-NO_2} + \underset{\text{Minor}}{CH_3-NO_2}$

→ $CH_3-CH_2-CH_3 \xrightarrow[400^\circ C]{\text{conc } HNO_3} \underset{1^\circ}{C-C-\overset{\overset{NO_2}{|}}{C}} + \underset{\text{Major}}{C-\overset{\overset{NO_2}{|}}{\underset{2^\circ}{C}}-C} + C-C-NO_2 + C-N$ (Mi...)

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Q. Sulphonation

$R-H + HO-SO_3H \xrightarrow{\Delta} R-SO_3H$

$HO-SO_3H$ → fuming H_2SO_4 → $H_2SO_4 + SO_3$ → $H_2S_2O_7$ → deum.

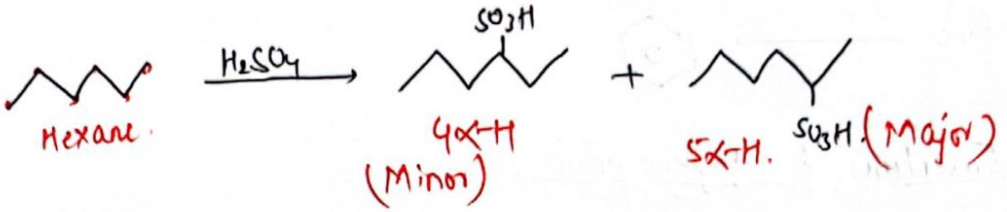
$R-SO_3H$ → Sulphonic acid.

→ This rxn is only possible over if min C ≥ 6. in unbranched alkane
↳ Hexane ~~are~~ start.

in branched alkane → 3° CH bond must be present

e.g. $CH_3-C(CH_3)_2-CH_3 \xrightarrow{H_2SO_4}$ No rxn.
↳ No 3°

→ $CH_3-CH(CH_3)-CH_3 \xrightarrow{H_2SO_4} C-C(SO_3H)(C)-C$ (3°)

→ 

→  $\xrightarrow{H_2SO_4}$ No rxn.

Q. Which is most reactive towards Halogenation | Nitration | Sulphonation | F.R.S.R?

(a) $CH_3-C(CH_3)_2-C(CH_3)_2-CH_3$

(b) $CH_3-CH(CH_3)-C(CH_3)_2-CH_3$ (3°) Stable F.R

(c) $CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

(d) CH_3-CH_3

Other reactions

A. Isomerisation of alkane

→ It is rearrangement reaction.

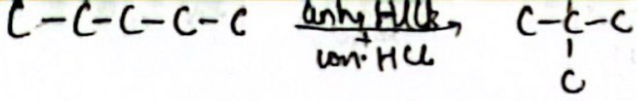
→ In this reaction, unbranched alkane is converted into branched alkane and branched alkane is converted into more branched alkane.

→ This rxn is used to ↑ octane no. of hydrocarbon. by which quality of fuel is improved.

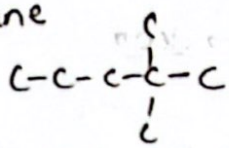
e.

$C-C-C-C \xrightarrow[\text{conc. HCl}]{\text{anhy. } AlCl_3} C-C(C)-C$

iso-butane



n-octane $\xrightarrow[\text{conc. HCl}]{\text{anhy. AlCl}_3}$ iso-octane



2, 2, 4 - Trimethyl pentane

octane no. $\Rightarrow$ 100

② Aromatisation / cyclisation

→ $C \geq 6$

$CH_3-(CH_2)_4-CH_3 \xrightarrow[500°C-600°C,\ 15\ atm]{Cr_2O_3/Al_2O_3}$ 

n-heptane $\xrightarrow{\Delta}$ 

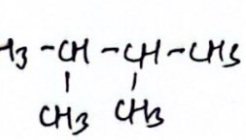
③ ~~Toluene~~ Insertion of methylene group

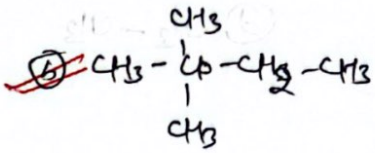
$R-H \xrightarrow[-N_2]{CH_2N_2/\Delta} R-CH_3$

↳ Next homologue.

$R-R \xrightarrow{CH_2N_2/\Delta} R-CH_2-R$.

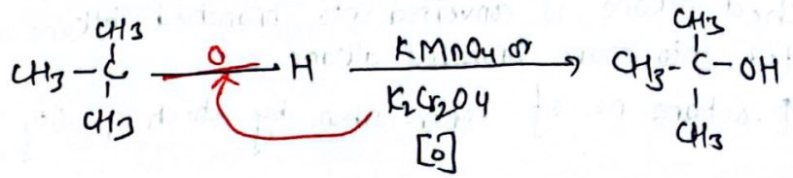
Q. $CH_3-\overset{3^\circ}{CH}(CH_3)-CH_2-CH_3 \xrightarrow{CH_2N_2/\Delta}$

(a) 

~~(b)~~ 

④ Oxidation by strong oxidising agent

→ This rxn is possible only when $3^\circ C-H$ is present.



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Q. Which doesnot oxidise by $KMnO_4$? — no 3°CH

(a) $CH_3-CH_2-CH_3$ (b) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$ (c) $CH_3-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$ (d) All

Q. $CH_3-\overset{\overset{CH_3}{|}}{\underset{3°}{CH}}-CH_2-CH_3 \xrightarrow{KMnO_4}$?

(a) $CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-CH_3$ (b) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-CH_3$

Q. Which does not show isomerisation.

(a) CH_3-CH_3 (b) $CH_3-CH_2-CH_3$ (c) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$ (d) All

(5) Combustion

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right) O_2 \longrightarrow nCO_2 + (n+1)H_2 + \Delta H_{eat}.$$

→ exothermic.

$$C_5H_{22} + 8O_2 \longrightarrow 5CO_2 + 6H_2O$$

$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$$

Q. Soda lime is specific reagent for:-

(a) Dehalogenation (b) Decarboxylation
(c) Dehydration (d) Dehydrogenation

Q. The compound X produces methane when treated with water. The compound X is

(a) Calcium carbonate (b) Beryllium carbide
(c) Calcium phosphide (d) Aluminium nitride

Q. Which of Following can't be prepared by Kolbes electrolysis process?

(a) C_2H_2 (b) C_2H_6 (c) CH_4 (d) C_2H_4

Q. Indicate the result when ethyl magnesium bromide is reacted with heavy water (D_2O)?

(a) $C_2H_5-C_2H_5$ (b) C_2H_5OD (c) Sodium benzoate (d) C_2H_5D

$$C_2H_5MgBr + D_2O \longrightarrow C_2H_5-D$$

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Q. Which of the following on treatment with Zn/Cu couple produce propane?

(a) Propanal (b) Isopropyl bromine (c) Isopropyl amine (d) Isopropyl alc

$R-X \xrightarrow{Zn/Cu} CH_3-\underset{Pr.}{CH}-CH_3$

Q. Which of the following alkane contains 1°, 2° & 3° as well as quaternary carbon?

(a) $(CH_3)_3CH$ (b) $(C_2H_5)_3CH$ (c) $(CH_3)_3CCH_2CH(CH_3)_2$ (d) $(CH_3)_4C$

Q. Electrolytic decarboxylation of sodium propionate produces?

(a) propane (b) ethane (c) Methane (d) butane

$CH_3CH_2COONa \longrightarrow CH_3-CH_2-CH_2-CH_3$

Q. The compound which produces propane on heating with HI in presence of phosphorus is:-

(a) $CH_3CH_2CH_2I$ (b) CH_3CH_2CHO (c) $CH_3CH_2CH_2OH$ (d) All of these

Red P + HI → alkane

Q. Which of the following will not produce ethane?

(a) reduction of CH_3COOH with HI/P_4

(b) Reduction of CH_3COOCH_3 with HI/P_4. → propane

(c) Sodalime decarboxylation of sodium propionate

(d) Hydrogenation of ethene in the presence of Ni.

Q. What is X in the rxn?

$X \xrightarrow[-\frac{1}{2}H_2]{Na} Z \xrightarrow{NaOH/CaO} CH_4\uparrow$

X: Carboxylic acid. Z: Sod. salt of carboxylic acid.

(a) Methane (b) ethanoic acid (c) propane (d) None.

Q. Which reaction not yield alkane?

(a) Rxn of acetone with Mg/H_2O

(b) Hydrogenation of alkene

(c) Treatment of ethanol with methyl magnesium bromide.

(d) Sodalime decarboxylation of sodium propionate

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Q. The reagent used to convert a carboxyl group (-COOH) into $-CH_3$ group is:-

(a) $LiAlH_4$ (Late.) (b) Na & alcohol (Late.) (c) Red P + HI (d) Zn + HCl

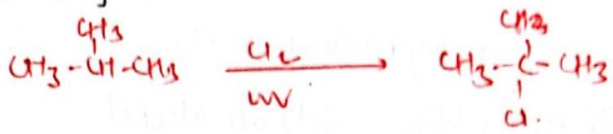
Q. Reaction of alkanes with halogen is explosive in case of :—

(a) F_2 (b) Cl_2 (c) Br_2 (d) I_2

Q. The major product obtained when isobutane is treated with chlorine in presence of diffused sunlight is:-

(a) isobutyl chloride (b) n-butyl chloride (c) tert-Butylchloride

(d) sec-butyl chloride

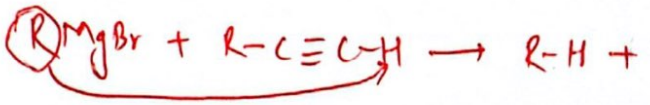


Q. Which of the following alkanes can be easily sulphonated?

(a) n-butane (b) Isobutane (c) n-pentane (d) n-heptane

Q. The treatment of $RMgBr$ with $R'C \equiv CH$ produces:-

(a) RH (b) R'H (c) R-R (d) R-R'



Q. During the chlorination of methyl chloride the propagation step is represented by:-

(a) $Cl-Cl \xrightarrow{h\nu} Cl^{\cdot} + Cl^{\cdot}$ - initiation

(b) $CH_3^{\cdot} + Cl^{\cdot} \longrightarrow CH_3Cl$ - Termination

(c) $CH_4 + Cl^{\cdot} \longrightarrow \dot{C}H_3 + HCl$

(d) $Cl^{\cdot} + Cl^{\cdot} \longrightarrow Cl_2$ - Termination

Q. Which of the following is not an oxidation product of alkane?

(a) Alcohol (b) Aldehyde (c) C acid (d) ether

Q. Iodination of alkane is carried out in the presence of :-

(a) Alcohol (b) HNO_3 or HIO_3 (S.O.A) (c) any reducing agent (d) Benzene

Q. Domestic cooking gas consists of mostly:-

(a) Methane & ethane (b) Liquified butane & isobutane

(c) ethylene & CO (d) Acetylene & hydrogen

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Q. The rxn:- $CH_3-CH_2-CH_2-CH_3 \xrightarrow[\text{conc HCl}]{\text{anhy. } AlCl_3} CH_3-CH(CH_3)-CH_3$ is an eg of:-

(a) ~~Fuse~~ Isomerisation (b) Polymerisation (c) Cracking
(d) Dehydrogenation

Q. Which alkane (Mol. mass 72) would yield three different monochl. derivative?

(a) n-pentane (b) Isopentane (c) n-Hexane (d) Isohexane

Q. The final product of oxidation of a hydrocarbon is:

(a) acid (b) alldehyde (c) $H_2O + CO_2$ (d) an alcohol

Alkene

→ C_nH_{2n}

→ $>C=C<$

→ bond angle 120°. (sp^2)

II General Method of preparation

(1) Dehalogenation of vicinal or geminal dihalides

$R-\overset{X}{CH}-\overset{X}{CH_2} + Zn\,(dust) \longrightarrow R-CH=CH_2 + ZnX_2$.
vicinal.

$CH_2(Cl)-CH_2(Cl) + Zn\,(dust) \longrightarrow CH_2=CH_2 + ZnCl_2$.

→ $CH_3-CH(Cl)-CH(Cl)-CH_3 \xrightarrow{Zn} CH_3-CH=CH-CH_3 + ZnCl_2$.

→ $CH_3-CH\left\langle\begin{matrix}Cl\\Cl\end{matrix}\right. + 2Zn + \left.\begin{matrix}Cl\\Cl\end{matrix}\right\rangle CH-CH_3 \longrightarrow CH_3-CH=CH-CH_3 + ZnCl_2$
geminal.

→ but $CH_2-CH_2-CH_2 \xrightarrow{Zn} \triangle$

$CH_2-CH_2-CH_2-CH_2-CH_2$ (Cl, Cl) $\xrightarrow[\text{dist.}]{Zn}$ 

cyclo pentane

② By dehydrohalogenation of alkyl halide | β-elimination

Reagent → alc. KOH (ROH + KOH)
↳ ROK or RONa.

→ $NaNH_2$ (sodamine)
→ E^2 mechanism.
- no C^+ formation.
- Transition state.

- In this rxn, if 2 or more alkene is formed then major product is given by saytzeff & Hoffmann.

$CH_3-\overset{\beta}{CH_2}-\overset{\alpha}{CH_2}$ (Cl) $\xrightarrow[\text{or ROK}]{\text{alc. KOH}}$ $CH_3-CH=CH_2$

$R = CH_3, -C_2H_5, -C_3H_7$ → Saytzeff product

$R = -C(CH_3)_3$ (tert butyl) → Hoffmann

- X = Cl, Br, I
- no bulky group at β-C.

- X = F.
- If Bulky group at β-C.

e.g. $CH_3-CH_2-\overset{Cl/Br}{CH}-CH_3$ (β', α, β) $\xrightarrow[\text{or ROK}]{\text{alc. KOH/}\Delta}$ $CH_3-CH_2-CH=CH$ + $CH_3-CH=CH-CH_3$

Hoffman (Minor). Saytzeff (Major).

Q. $CH_3-CH_2-CH_2-CH_3$ (F) $\xrightarrow{\text{alc. KOH/}\Delta}$? major

Hoffman major.

(a) 2-butene ~~(b)~~ 1-butene

Q. $CH_3-CH_2-CH(Cl)-CH_3$

- $\xrightarrow{C_2H_5ONa}$ $CH_3-CH=CH-CH_3$ Saytzeff
- $\xrightarrow{CH_2-C(CH_3)_2-ONa}$ $CH_3-CH_2-CH=CH_2$ Hofman

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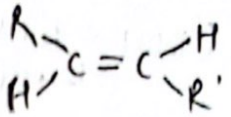
Q. $CH_3-CH_2-CH_2-CH_2-Cl \xrightarrow[\Delta]{C_2H_5ONa}$ 1-butene.

(3) Partial hydrogenation of alkyne

Case (1) Birch Redn

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

(trans alkene)

Note: This rxn is not applicable for terminal alkyne because they're acidic H.

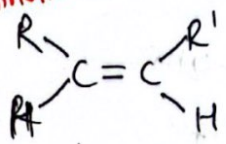
$R-C\equiv C-H \xrightarrow{Na} R-C\equiv C^{\ominus}\,Na^{\oplus} + \frac{1}{2}H_2\uparrow$

(H is acidic)

Case (2) Synthesis of cis-alkene.

$R-C\equiv C-R' + H_2 \xrightarrow{Pd-BaSO_4}$ (Rosenmund catalyst.)

$\xrightarrow{Pd-CaCO_3}$ (Lindlar catalyst.)

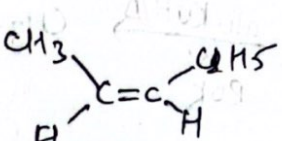


cis-alkene

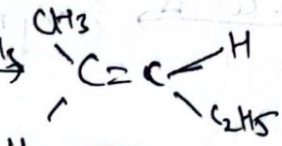
but

$R-C\equiv C-R + H_2 \xrightarrow{Pd} R-CH_2-CH_2-R'$

$CH_3-C\equiv C-C_2H_5$

$\xrightarrow{H_2/Pd/BaSO_4}$ 

(cis)

$\xrightarrow{Na/liq\,NH_3}$ 

(trans)

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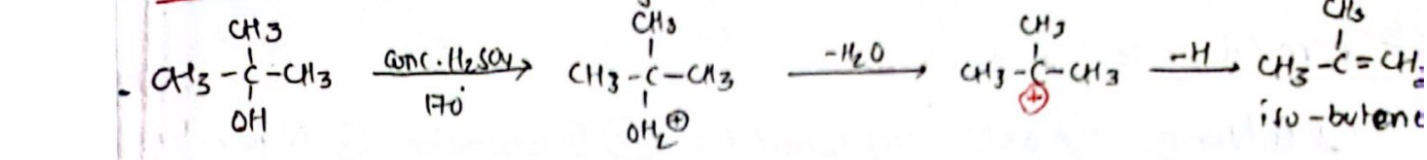
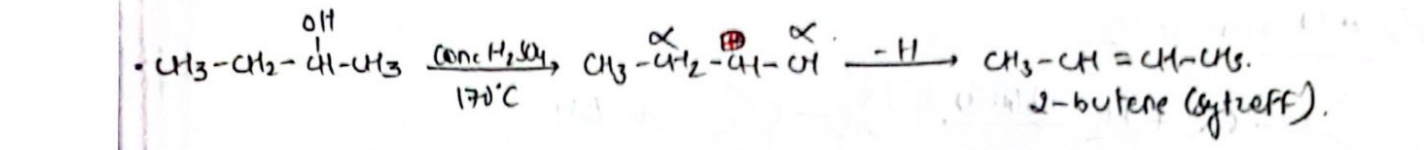
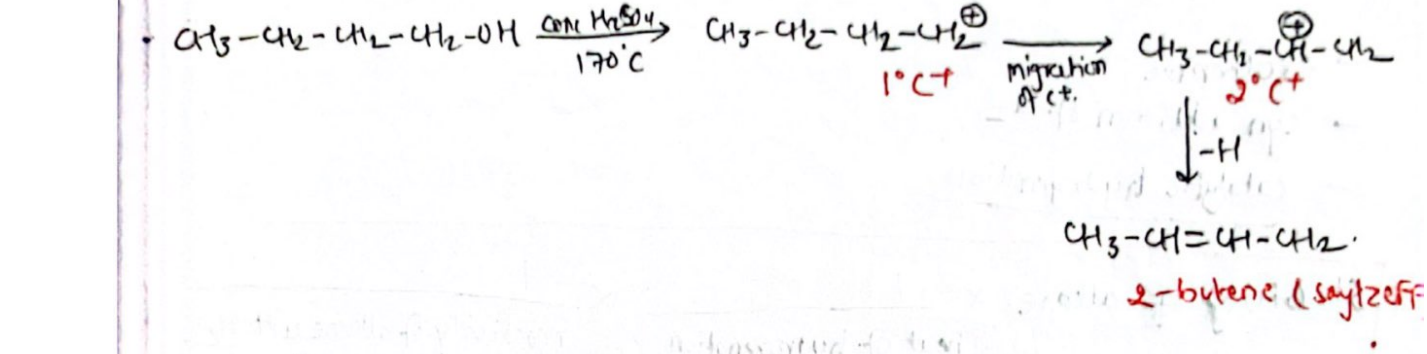
4) By acid catalysed dehydration of alcohol

- → E1 mechanism.
- In this rxn, C^+ is formed.
- → Reactivity of R-OH ∝ stability of R^+.
- In this rxn, if 2 or more alkene is then major product is given by saytzeff rule → more stable alkene is major.

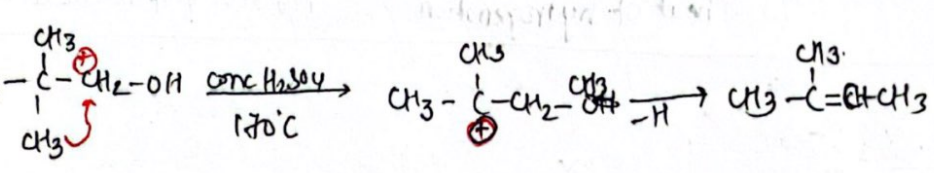






- $CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3 \xrightarrow[170^\circ]{conc.\ H_2SO_4} CH_3-\underset{OH_2^{\oplus}}{\overset{CH_3}{C}}-CH_3 \xrightarrow{-H_2O} CH_3-\underset{\oplus}{\overset{CH_3}{C}}-CH_3 \xrightarrow{-H} CH_3-\overset{CH_3}{C}=CH_2$ iso-butene

- $CH_3-CH_2-\overset{OH}{CH}-CH_3 \xrightarrow[170^\circ C]{conc\ H_2SO_4} CH_3-\overset{\alpha}{CH_2}-\overset{\oplus}{CH}-\overset{\alpha}{CH} \xrightarrow{-H} CH_3-CH=CH-CH_3$ 2-butene (Saytzeff).



- $CH_3-CH_2-CH_2-CH_2-OH \xrightarrow[170^\circ C]{conc\ H_2SO_4} CH_3-CH_2-CH_2-CH_2^{\oplus} \xrightarrow[\text{migration of } C^+]{} CH_3-CH_2-\overset{\oplus}{CH}-CH_2$ ($1^\circ C^+$ → $2^\circ C^+$)

$\downarrow -H$

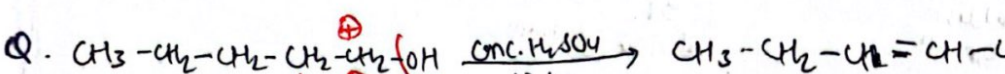
$CH_3-CH=CH-CH_2$ 2-butene (saytzeff)

Q. $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{\oplus}{C}H_2-OH \xrightarrow[170^\circ C]{conc\ H_2SO_4} CH_3-\underset{\oplus}{\overset{CH_3}{C}}-CH_2-CH_3 \xrightarrow{-H} CH_3-\overset{CH_3}{C}=CH-CH_3$

Note:- If Al_2O_3 is given then high temp^r will be required and it will follow E^2 mechanism. So, one step elimination in which no C^+ & no rearrangement.

Q. $CH_3-CH_2-CH_2-CH_2-CH_2-OH \xrightarrow[350^\circ C]{Al_2O_3} CH_3-CH_2-CH_2-CH=CH_2$ (β, α) 1-pentene.

Q. $CH_3-CH_2-CH_2-CH_2-\overset{\oplus}{C}H_2-OH \xrightarrow[170^\circ C]{conc.\ H_2SO_4} CH_3-CH_2-CH=CH-CH_2$ 2-pentene



Q. Which is most reactive towards H_2SO_4?

(a) CH_3-CH_2-OH (b) $CH_3-\underset{CH_3}{\overset{C_2H_5}{C}}-OH$ (8α-H) (c) $CH_3-\overset{CH_3}{CH}-OH$ (6α-H) (d) $CH_3-CH_2-CH_2-OH$ (2α-H)

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Kolbe's electrolysis

$CH_2-COONa$
$CH_2-COONa$
sod. succinate

$\xrightarrow{\text{electrolysis}}$ $CH_2=CH_2 + CO_2 + H_2 + NaOH$

$CH_2=CH_2$: anode; H_2 : cathode; $NaOH$: soln.

Chemical properties of alkene

(I) Addition (II) oxdn (III) substitution (IV) Isomerization (V) Polymeri.

(1) Addition of H_2 :-

$$>C=C< + H_2 \xrightarrow{Ni/Pt/Pd} >\underset{H}{C}-\underset{H}{C}< + \Delta H$$

- exothermic
- syn addition of H_2
- catalytic hydrogenation

Stability of alkene $\propto \frac{1}{\text{heat of hydrogenation}} \propto \frac{1}{\text{reactivity of alkene with } H_2}$

(2) Addition of X_2 :-

$$>C=C< + X_2 \xrightarrow{CCl_4} >\underset{X}{C}-\underset{X}{C}<$$

(anti addition)

$$>C=C< + Br_2 \xrightarrow{CCl_4} >\underset{Br}{C}-\underset{Br}{C}<$$

Br_2: reddish brown; product: colorless solution.

→ This is used for detecting the presence of $C=C$ / $C\equiv C$.

$F_2 > Cl_2 > Br_2 > I_2$

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⑤ Reaction with HX [Markonikov's] — EAR

$CH_3-CH=CH_2 \xrightarrow{H^{\oplus}X^{\ominus}} CH_3-\underset{X}{CH}-CH_3$

↳ $CH_3-\overset{\ominus}{C}H=CH_2 \xrightarrow{HX} CH_3-\overset{\oplus}{C}H-CH_3 \xrightarrow{X^-} CH_3-\underset{X}{CH}-CH_3$

(H^+/X^-)

④ Antimarkonikovs :- FAR

$CH_3-CH=CH_2 \xrightarrow[\text{peroxide}]{HBr} CH_3-CH_2-\underset{Br}{CH_2}$

⑤ Addition of hypohalous acid (HOX)

↳ $X_2 + H_2O$

$H\overset{\ominus}{O}\overset{\oplus}{X}$

$CH_3-CH=CH_2 \xrightarrow{H\overset{\ominus}{O}\overset{\oplus}{Cl}} CH_3-\underset{OH}{CH}-CH_2-Cl$

↳ anti-addition

↳ Halohydrin.

~~ethy~~ ethylene chlorohydrine.

⑥ Addition of water / Hydration of alkene

$CH_3-CH=CH_2 \xrightarrow[\text{or } dil.H_2SO_4]{H^+/H_2O} CH_3-\underset{OH}{CH}-CH_3$

(H^+ OH^-)

$CH_3-\underset{CH_3}{\overset{|}{C}}=CH_2 \xrightarrow{dil.H_2SO_4} CH_3-\underset{OH}{\overset{CH_3}{\overset{|}{C}}}-CH_3$

(H^+/OH^-)

⑦ Addition of NOCl (Nitrosyl chloride) ↳ Tilden's reaction

$\overset{\oplus}{N}O\overset{\ominus}{Cl}$

$CH_3-CH=CH_2 \xrightarrow{\overset{\oplus}{N}O\overset{\ominus}{Cl}} CH_3-\underset{Cl}{CH}-\underset{NO}{CH_2}$ (anti-addition)

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8) Addition of oxygen

$$R\text{-}CH{=}CH_2 + \tfrac{1}{2}O_2 \xrightarrow[\Delta]{Ag} R\text{-}CH\text{-}CH_2 \quad (O)$$

epoxy compound

$$CH_2{=}CH_2 + \tfrac{1}{2}O_2 \xrightarrow[0]{Ag} CH_2\text{-}CH_2 \quad (O)$$

epoxy ethane (oxirane)

$$CH_2\text{-}CH_2 \;(O) \xrightarrow{H_2O} CH_2(OH)\text{-}CH_2(OH)$$

glycol.

Q. $CH_2{=}CH_2 + \tfrac{1}{2}O_2 \xrightarrow[\Delta]{Ag} A \xrightarrow{H_2O} B$

A: $CH_2\text{-}CH_2$ (O)

B: $CH_2(OH)\text{-}CH_2(OH)$

9) Addition of sulphur monochloride

$$CH_2{=}CH_2 + S_2Cl_2 \longrightarrow CH_2Cl\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2Cl + S$$

Mustard gas

10) Oxidation rxn

I) Complete oxidation

$- CO_2 + H_2O$

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$$

$$C_nH_{2n} + \tfrac{3}{2}nO_2 \longrightarrow nCO_2 + nH_2O$$

$$C_4H_8 + 6O_2 \longrightarrow 4CO_2 + 4H_2O$$

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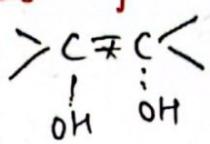
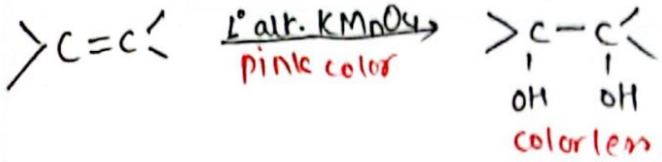
Hydroxylation:



① Hydroxylation by Bayers reagent

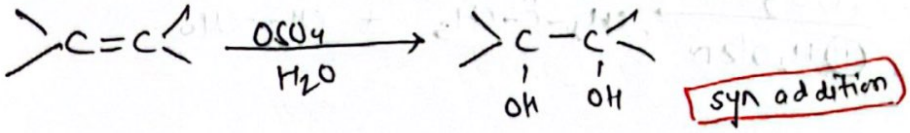
- cold and dil. alkaline $KMnO_4$.
- 1° alkaline $KMnO_4$. → pink color.

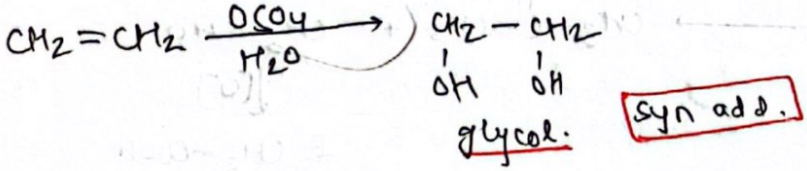


→ Decolorization of Bayeric reagent is test of unsaturation.

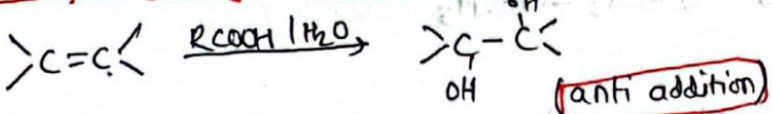
→ Benzene doesnot give test of unsaturation.

② Hydroxylation by OSO_4 (osmium tetraoxide)

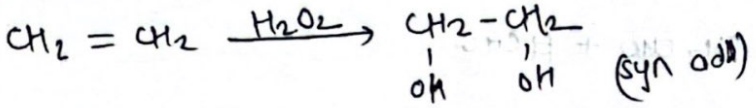




③ Hydroxylation by RCOOH / H_2O :-



④ Hydroxylation by H_2O_2 :-



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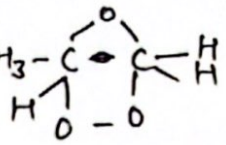
(11) Ozonolysis

$CH_3-CH=CH_2 \xrightarrow{O_3}$  $\xrightarrow{H_2O/Zn} CH_3-\overset{O}{\overset{\|}{C}}-H + CH_2(-\overset{O}{\overset{\|}{C}}-H) + H_2O_2$

ozonide.

$H_2O_2 + ald \rightarrow R-COOH$.

$H_2O_2 + ket \rightarrow X$.

$Zn + H_2O_2 \rightarrow ZnO + H_2O$.

→ $CH_3-CH(=O)-CH(=O)-CH_3 \xrightarrow[(ii)\ H_2O/Zn]{(i)\ O_3} 2\ CH_3-CHO$

$\xrightarrow[(ii)\ H_2O]{(i)\ O_3} 2CH_3-CHO \xrightarrow{[O]} 2CH_3-COOH$.

→ $CH_3-C(CH_3)(=O)-CH(=O)-CH_3 \xrightarrow[(ii)\ H_2O/Zn]{(i)\ O_3} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3-CHO$.

$\xrightarrow[(ii)\ H_2O]{(i)\ O_3} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3-CHO$

$\xrightarrow{[O]}$ $2\ CH_3-COOH$

→ $CH_3-C(CH_3)=C(CH_3)-CH_3 \xrightarrow[(ii)\ H_2O/Zn]{(i)\ O_3\ [R:O]} 2\ CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

$\xrightarrow[(ii)\ H_2O]{(i)\ O_3\ [R:O]} 2CH_3-\overset{O}{\overset{\|}{C}}-CH_3$.

→ $CH_3-CH=CH_2 \xrightarrow[(ii)\ H_2O/Zn]{(i)\ O_3} CH_3CHO + HCHO$

$\xrightarrow[(ii)\ H_2O]{(i)\ O_3} CH_3COOH + HCOOH$

$\xrightarrow{[O]}$

$CO_2 + H_2O$.

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iv) SeO_2

$CH_2=CH-CH_3 \xrightarrow{SeO_2} CH_2=CH-\overset{OH}{CH_2}$

$CH_2=CH-CH_2-CH_3 \xrightarrow{SeO_2} CH_2=CH-\overset{OH}{CH}-CH_3$

allylic C.

i) oxidation by strong oxidizing agent

- Hot alk. $KMnO_4$
- acidic $K_2Cr_2O_7$
- acidic $KMnO_4$.
  - product - oxidative ozonolysis [O.O]

$CH_3-CH=CH-CH_3 \xrightarrow[KMnO_4]{\text{hot alk.}} 2CH_3COOH$

$CH_3-\overset{CH_3}{C}=CH-CH_3 \xrightarrow[\text{acidic } KMnO_4]{\text{hot alk. } KMnO_4} CH_3-\overset{O}{C}-CH_3 + CH_3-COOH$

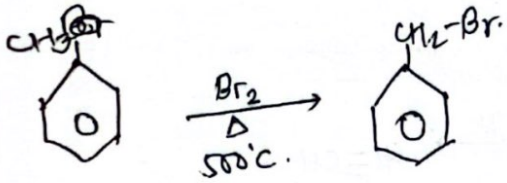
c) Allylic substitution

- It is free radical substitution.
- When alkene is treated with Cl_2 / Br_2 at high temp one of the allylic hydrogen is replaced by halogen atom.

$CH_2-CH=CH_2 + Br_2 \xrightarrow{500^\circ C} CH_2(Br)-CH=CH_2$

H allylic H.

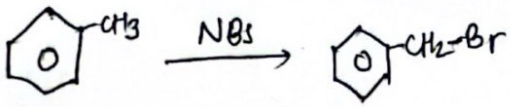
Allylic bromination



NBS → N-bromo succinamide

$CH_2=CH-CH_3 \xrightarrow{NBS} CH_2=CH-CH_2-Br$

allylic



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$$CH_2=CH-CH_2-CH_3 \xrightarrow[\text{or } Br_2 | 500^\circ C]{NBS} CH_2=CH-\underset{\underset{Br}{|}}{CH}-CH_3$$

→ ethene ले yo rxn दिन्न।

D) Isomerization

$$CH_3-CH_2-CH=CH_2 \xrightarrow[H_2SO_4]{AlCl_3} C-C=C-CH_3 + C=\underset{\underset{CH_3}{|}}{C}-CH_3$$

E) Polymerization

$$nCH_2=CH_2 \xrightarrow[1500\,atm]{200^\circ C} \text{Polyethene}$$

Alkyne

- C_nH_{2n-2}
- bond angle → 180°, (sp).
- shape → linear.

$C=C$ → olefinic bond.
$C\equiv C$ → Acetylenic bond

- $CH_2=CH-\overset{\overset{O}{\|}}{C}-C\equiv C-CH_2-CH_2-C\equiv N$.
  - Double bond → 2
  - Olefinic bond → 1.
  - Triple bond → 2.
  - Acetylenic bond → 1.

General Method of preparation

① From dihalides (By dehydrohalogenation)

$$H-\underset{\underset{Br}{\alpha|\beta}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{\alpha|\beta}}{\overset{\overset{Br}{|}}{C}}-H \xrightarrow{\text{alc. KOH}} H-\underset{\underset{Br}{|}}{C}=\underset{\underset{Br}{|}}{C}-H \xrightarrow[\text{or } NaNH_2]{\text{alc. KOH}} CH\equiv CH$$

ethyne

$$CH_3-\overset{\overset{Br}{|}}{CH}-\overset{\overset{Br}{|}}{CH_2} \xrightarrow[\text{or } NaNH_2]{\text{alc. KOH}} CH_3-C\equiv CH$$

propyne.

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$CH_3-CH(Cl)_2 \xrightarrow{alc.KOH} CH_2=CH-Cl \xrightarrow{NaNH_2} CH\equiv CH.$

$CH_3-CH_2-CH(Cl)_2 \xrightarrow{alc.KOH} CH_3-CH_2=CH-Cl \xrightarrow{NaNH_2} CH_3-C\equiv CH.$

$CH_2=CH_2$ (ethene) $\downarrow Br_2/CCl_4$

$CH_2(Br)-CH_2(Br) \xrightarrow[\Delta]{al.KOH} CH\equiv CH$ (ethyne)

② Hydrolysis of calcium carbide

$CaC_2 + H_2O \longrightarrow CH\equiv CH + Ca(OH)_2$ (ethyne)

→ Wohler reaction → lab method.

CaC_2 ↓ Ca^{++} C^- ||| C^- $\pi \rightarrow 1+1 = 2$, $\sigma = 1$.

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

③ From Trihalides (chloroform & iodoform)

$H-C(Cl)_3 + 6Ag + (Cl)_3C-H \xrightarrow{\Delta} H-C\equiv C-H + 6AgCl.$

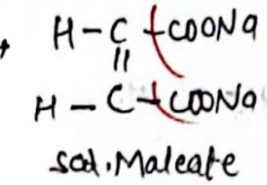
$H-C(I)_3 + 6Ag + (I)_3C-H \xrightarrow{\Delta} H-C\equiv C-H + 6AgI$

④ From tetrahalides (By dehalogenation)

$H-C(X)_2-C(X)_2-H \xrightarrow[\Delta]{Zn} H-C\equiv C-H.$ (ethyne.)

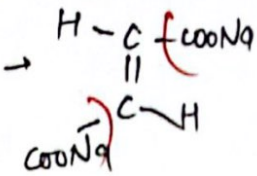
$CH_3-C(Cl)_2-C(Cl)_2-CH_3 \xrightarrow[\Delta]{Zn} CH_3-C\equiv C-CH_3$ (but-2-yne.)

⑤ By electrolysis of sod. salt of unsaturated dicarboxylic acid

→ 

sod. Maleate

electrolysis → H – C ≡ C – H.
ethyne.

→ 

Sod. Fumrate

electrolysis → H – C ≡ C – H

⑥ Formation of higher alkyne

R – C ≡ C – H $\xrightarrow{Na}$ R – C ≡ C$^{\ominus}$ Na$^{\oplus}$ + ½ H$_2$

R – C ≡ C$^{\ominus}$ Na$^{\oplus}$ $\xrightarrow[\text{NSR}]{R-X}$ R – C ≡ C – R
Alkyne

e.g. H – C ≡ C – H $\xrightarrow{Na}$ H – C ≡ C$^{\ominus}$ – Na$^{\oplus}$

H – C ≡ C$^{\ominus}$ – Na$^{\oplus}$ $\xrightarrow[\text{NSR}]{CH_3-Cl}$ H – C ≡ C – CH$_3$

Chemical properties

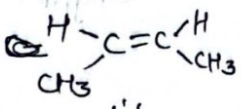
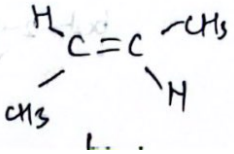
Acidic → Alkyne > Alkene > Alkane.

EAR → Reactivity: Alkene > Alkyne.

(A) Addition rxn

(1) Addition of H$_2$ (Hydrogenation)

CH$_3$ – C ≡ C – CH$_3$ + 2H$_2$ $\xrightarrow{Pd/Pt/Ni}$ CH$_3$ – CH$_2$ – CH$_2$ – CH$_3$
butane

CH$_3$ – C ≡ C – CH$_3$ →
- Lindlar's catalyst: H$_2$ + Pd/CaCO$_3$ →  (cis)
- Birch Redn: Na/Li's, NH$_3$ → 

partial hydrogenation.

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1) Addition of Halogen

$$H-C\equiv C-H \xrightarrow{Cl_2/CCl_4} H-\underset{Cl}{\overset{Cl}{C}}-\underset{Cl}{\overset{Cl}{C}}-H \xrightarrow{Ca(OH)_2} CCl_2=CHCl$$

westron

Westrosol

$$CH_3-C\equiv C-H \xrightarrow{Br_2/CCl_4} CH_3-\underset{Br}{\overset{Br}{C}}-\underset{Br}{\overset{Br}{C}}-H$$

reddish brown

colorless

(Test of unsaturation)

3) Addition of H-X

$$CH_3-C\equiv C-H \xrightarrow{2\overset{\oplus}{H}-\overset{\ominus}{X}} CH_3-\underset{X}{\overset{X}{C}}-CH_3$$

$$H-C\equiv C-H \xrightarrow{2\overset{\oplus}{H}-\overset{\ominus}{X}} H-\underset{X}{\overset{X}{C}}-CH_3$$

4) Addition of HOCl [$Cl_2 + H_2O$]

$$CH_3-C\equiv C-H \xrightarrow{\overset{\ominus}{H}O\overset{\oplus}{Cl}} CH_3-\underset{OH}{\overset{OH}{C}}-CHCl_2 \xrightarrow{-H_2O} CH_3-\overset{O}{\overset{\|}{C}}-CHCl_2$$

$$H-C\equiv C-H \xrightarrow{\overset{\ominus}{H}O\overset{\oplus}{Cl}} H-\underset{Cl}{\overset{Cl}{C}}-\overset{OH}{CH}-OH \xrightarrow{-H_2O} CHCl_2-\overset{O}{\overset{\|}{C}}-H$$

5) Hydration of Alkyne / Kucherox reaction

$$H-C\equiv C-H \xrightarrow[dil.\ H_2SO_4]{HgSO_4} H-\underset{H}{C}=\overset{OH}{C}-H \xrightarrow{Tautomerisation} CH_3-\overset{O}{\overset{\|}{C}}-H$$

ethyne. enol form acetaldehyde.

[ethyne मात्रै acetaldehyde दिन्छ अरु सबै ketone दिन्छन]

$$CH_3-C\equiv C-H \xrightarrow[dil.\ H_2SO_4]{HgSO_4} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

propyne. acetone

$$CH_3\equiv C-CH_2-CH_3 \xrightarrow{\text{"}} C-\overset{O}{\overset{\|}{C}}-C-C$$

$$C-C\equiv C-C \xrightarrow{\text{"}} C-\overset{O}{\overset{\|}{C}}-C-C$$

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Oxidation by Baeyer's reagent

$$R-C\equiv C-R \xrightarrow[KMnO_4]{(\%\ alk.)} R-\overset{OH}{\underset{OH}{C}}-\overset{OH}{\underset{OH}{C}}-R \xrightarrow{-H_2O} R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R$$

pink color. ↳ Hydroxylation

colorless.

[Test of unsaturation].

Oxidation by SeO_2

$$R-C\equiv C-R \xrightarrow{SeO_2} R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R$$

Dicarbonyl compound.

Oxidation by strong oxidizing agent

$$R-C\equiv C-R \xrightarrow[\text{or } K_2Cr_2O_7/H^+]{OH^-/KMnO_4} R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R \longrightarrow 2R-\overset{O}{\overset{\|}{C}}-OH$$

OH, OH.

$$CH_3-C\equiv C-CH_3 \xrightarrow{H^+/K_2Cr_2O_7} 2\,CH_3-\overset{O}{\overset{\|}{C}}-OH$$

acetic acid.

Ozonolysis

$$R-C\equiv C-R \xrightarrow[(ii)\ H_2O/Zn]{(i)\ O_3} R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R \quad \text{(Reductive)}$$

$$\xrightarrow[(ii)\ H_2O]{(i)\ O_3} R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R \longrightarrow 2R-\overset{O}{\overset{\|}{C}}-OH \quad \text{(oxidative)}$$

OH OH

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

$$\xrightarrow[(ii)\ H_2O/Zn]{(i)\ O_3} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$$

$$\xrightarrow[(ii)\ H_2O]{(i)\ O_3} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH + CH_3-\overset{O}{\overset{\|}{C}}-OH$$

$$\xrightarrow{K_2Cr_2O_7/H^+} \text{"} \quad + \quad \text{"}$$

Same

Rxn with Tollen's reagent

→ only terminal alkyne react due to the presence of acidic -H.

$$R-C\equiv C-H \xrightarrow[\text{or } NH_4OH + AgNO_3]{\text{ammonical } AgNO_3 \text{ soln}} R-C\equiv C^{\ominus}-Ag^{\oplus}$$

white ppt

Rxn with ammonical Cu_2Cl_2 soln

↳ $NH_4OH + Cu_2Cl_2$.

(Terminal alkyne).

$$R-C\equiv C-H \xrightarrow{NH_4OH + Cu_2Cl_2} R-C\equiv C^{\ominus}-Cu^{\oplus}$$

Red ppt

$$R-C\equiv C-H \xrightarrow{Na} R-C\equiv C^{\ominus}-Na^{\oplus} + \tfrac{1}{2}H_2\uparrow$$

$$R-C\equiv C-H \xrightarrow{NaNH_2} R-C\equiv C^{\ominus}-Na^{\oplus} + NH_3\uparrow$$

$$R-C\equiv C-H \xrightarrow{NaH} R-C\equiv C^{\ominus}-Na^{\oplus} + H_2\uparrow$$

$$R-C\equiv C-H \xrightarrow{CH_3MgBr} CH_4 + R-C\equiv C^{\ominus}Mg^{\oplus}Br$$

acidic nature of alkyne

Q. Propene and propyne can be distinguished by:—

(a) Br_2/CCl_4 (b) Alkaline $KMnO_4$ (c) $AgNO_3$ in NH_4OH (d) None.

Q. 1-butyne & 2-butyne can be distinguished by:-

(a) ammonical Cu_2Cl_2 (b) $(Ag(NH_3)_2^{+})OH^-$ (c) Br_2/CCl_4 (d) both a & b.

Polymerization

$$3\,H-C\equiv C-H \xrightarrow[\text{Fe tube}]{\text{red hot}} \text{(benzene)}$$

$$3\,CH_3-C\equiv C-H \longrightarrow$$

1,3,5-Trimethyl benzene (Mesitylene)

$$3CH-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[H_2SO_4]{\text{conc}}$$

Mesitylene