Hydrocarbon

Intro

- Compounds of Carbon & Hydrogen only.
- examples of hydrocarbon in daily life.
  1) LPG → Liquified Petroleum gas
  2) CNG → Compressed Natural gas
  3) LNG → Liquified natural gas (obtained by liquification of natural gas)
  4) Petrol
  5) diesel
  6) kerosene

  } Obtained by fractional distillation of Petroleum.

  7) Coal gas } destructive distillation of Coal.
- Hydrocarbon is also used for manufacture of Polymers
  ex:- polyethene, polypropene, polystyrene

Classification

Hydrocarbon

Saturated
C–C and C–H
Single bond
- → Alkane
  open chain & C–C singlebond
  C_nH_{2n+2}
- → cycloalkane
  Closed chain & C–C Singlebond

Unsaturated
C–C multiplebond
C=C
or
C≡C
or
both
- → alkene
  C–C doublebond
  C_nH_{2n}
- → alkyne
  C–C tripplebond
  C_nH_{2n-2}

Aromatic
Cyclic hydrocarbon containing alternate single and double bond & having $(4n+2)\pi$ electron.

Alkane

- C_nH_{2n+2}
- Paraffin (less reactive)
- CH_4 → first member → methane → Coal mines & marshy places (found in)
- sp^3 hybridization (Tetrahedral) → 109.5°

	C–C	C–H
overlap	$sp^3 - sp^3$	$sp^3 - s$
Bond length	1.54 A°	1.112 A°
Bond energy	80–85 kcal	98.6 kcal

General methods of Preparation

1. From Unsaturated hydrocarbon (Catalytic hydrogenation)
2. — alkyl halide (Wurtz Reaction & Red^n of alkyl halide)
3. — Carboxylic acid → Soda lime decarboxylation
   → Kolbe's electrolysis

} NCERT

(1) Unsatured Hydrocarbon

(2) Zn/CH_3COOH.
(5) Al–Hg couple in C_2H_5OH
(5) Zn–Cu couple in C_2H_5OH

(2) alkyl halide → Reduction by Zn/HCl (1) or $LiAlH_4$ (3) or Red P + HI (4)
→ Wurtz Rxn
→ corey house synthesis
→ Frankland Reaction

(3) Carboxyllic acid → Soda lime decarboxylation
→ kolbe electrolysis
→

(4) Grignard → ROH, HOH, R–NH–H
Reacts with compound having active hydrogen.

→ alkyl halide → higher alkanes.

$$R\text{-}Mg\text{-}X + R'\text{—}X \longrightarrow R\text{–}R' + MgX_2$$

(5) alcohol, aldehyde, Ketone, carboxylic acid, ~~carbox~~ acid derivative $\xrightarrow[150^\circ C]{Red\ P + HI}$ alkane

(6) aldehyde/Ketone → wolf Kishner Reduction
→ Clemmensen Reduction

From unsaturated hydrocarbon

$C=C$ or $C\equiv C$ $\xrightarrow{H_2/Ni, Pd, Pt, Raney\ Ni}$ $C-C$

- $C=C \xrightarrow[200^\circ C]{Ni}$
- $C\equiv C \xrightarrow[300^\circ C]{Ni}$

] Sabatier & Sanderen's rxn

- Raney Ni → Ni/Al + NaOH → Ni → Powder form
- ~~Alkanes~~ Methane are not formed.
- Exothermic rxn (Heat releases i's heat of hydrogenation)
- Syn addition → addition of hydrogen from same side

Ex $H_2C=CH_2 \xrightarrow[200^\circ C]{H_2/Ni} \xrightarrow[room\ temp]{Pt, Pd, Raney\ Ni} CH_3-CH_3$

Ex $CH_3-CH=CH_2 \xrightarrow[200^\circ C]{H_2/Ni} \xrightarrow[room\ temp]{Pt, Pd, Raney\ Ni} CH_3-CH_2-CH_3$

Ex $CH_3-C\equiv C-H \xrightarrow[300^\circ C]{2H_2/Ni} \xrightarrow[room\ temp]{Pt, Pd, Raney\ Ni} CH_3-CH_2-CH_3$

From alkyl halide

Reduction of alkyl halide

① $Zn + HCl$

② $Zn + CH_3COOH$ (metal + acid) $\downarrow H_2$

$$R-X + H_2 \longrightarrow R-H + H-X$$

③ Red P + HI

④ $LiAlH_4$

⑤ Zn–Cu couple in C_2H_5OH

⑥ Al–Hg " " "

Ex

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

$C_2H_5Cl + H_2 \xrightarrow{Zn, H^+} C_2H_6 + HCl$

$CH_3-CH_2-CH_2-Cl + H_2 \xrightarrow[H^+]{Zn} CH_3-CH_2-CH_3 + HCl$

Wurtz Reaction

- 2 mole R–X

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

- Free radical intermediate.
- Higher & Symmetrical alkanes are formed.
  - ↳ double the number of alkyl halide taken.
- When both alkyl halides are different, then 3 alkanes products are formed. So, wurtz is not suitable method for alkanes of odd num of C.

$$C_2H_5I + CH_3I \xrightarrow[\text{dry ether}]{Na} C_2H_5-C_2H_5,\ CH_3-CH_3,\ C_2H_5-CH_3$$

- $2CH_3Br + 2Na \xrightarrow[\text{ether}]{\text{dry}} CH_3-CH_3 + 2NaBr$
- $2C_2H_5Br + 2Na \xrightarrow[\text{ether}]{\text{dry}} C_2H_5-C_2H_5 +$ "

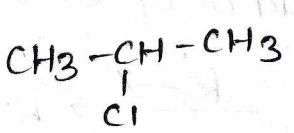
Que 2 moles of isopropyl chloride with 2 mole Na in dry ether gives

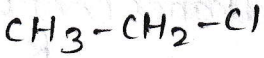
$$2\,CH_3-\underset{Cl}{\underset{|}{CH}}-CH_3 + 2Na \xrightarrow{\text{dry ether}}$$

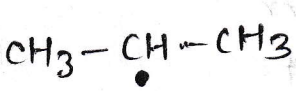
$CH_3-\overset{\bullet}{\underset{|}{CH}}-CH_3$ and $CH_3-\overset{\bullet}{\underset{|}{CH}}-CH_3$

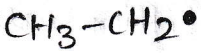
$CH_3-CH(CH_3)-CH_3$ and $CH_3-CH(CH_3)-CH_3$

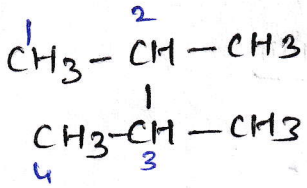
Que of isopropyl chloride & ethylchloride are taken with Na & dryether.





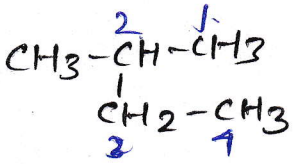






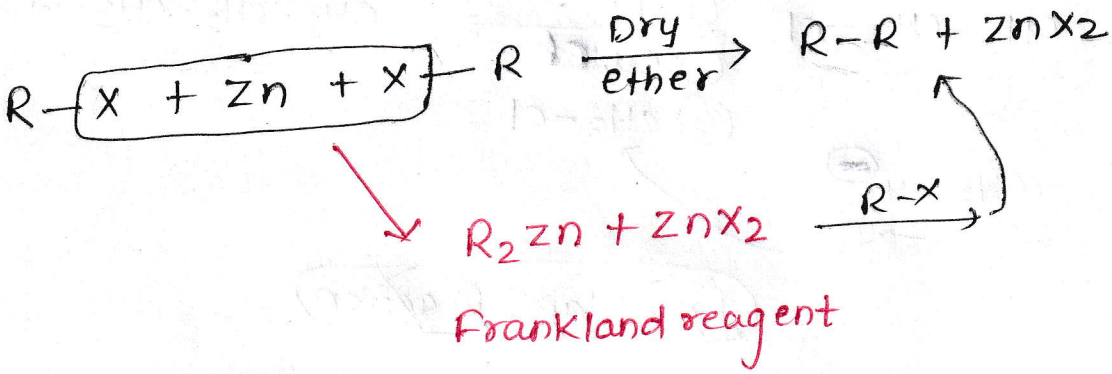
2,3-dimethyl butane

butane



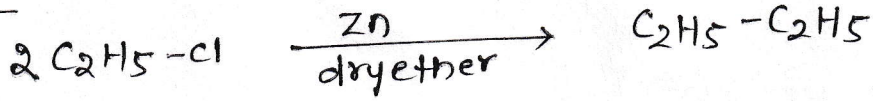
2-methyl butane

Frankland Reaction



Frankland reagent

Que



Corey-house-Synthesis

- Used for preparation of alkanes containing odd no of Carbon.

$$R-X \xrightarrow[CuX]{Li} \underset{\text{Lithiumdialkyl copper}}{\underset{\text{Gilman's reagent}}{R-\overset{R}{\overset{|}{Cu}}-Li}} \xrightarrow{R'-X} R-R' + R-Cu + Li-X$$

⇓ produces $R^{\ominus}$ Carbanion

- Carbanion intermediate
- 1° alkyl halide show have less steric crowding.
- ~~both symmetrical & unsymmetrical alkanes can be formed.~~

Que CH_3-CH_2-Cl

↓

$CH_3-CH_2^{\ominus}$

① Li
② Cu·Et
③ CH_3-Cl

$CH_3-CH_2-CH_3 + Li-Cl$

~~Frankland Reaction~~

Carboxylic Acid

Soda-Lime Decarboxylation

Caustic soda NaOH
Quick lime CaO

- Saturated monocarboxylic acid salt of Na/K.

$$R-\overset{O}{\overset{\|}{C}}-O^{-}\,Na^{+} \xrightarrow[CaO,\,\Delta]{NaOH} R-H + \underset{\downarrow\!\!\downarrow}{CO_2}\uparrow \quad (CO_2 \rightleftharpoons Na_2CO_3)$$

NaOH : CaO ⇒ 3:1

- Process of removal of CO_2 is decarboxylation.
- Remove $-COOH$ group & add H.
- alkane formed is one carbon less than reactant
- step down reaction
- Carbanion intermediate.

Rate of decarboxylation ∝ Stab of carbanion
−M, −I group ↑ decarboxylation

Que

$$H-\overset{O}{\overset{\|}{C}}-O^{-}\,Na^{+} \xrightarrow[\Delta]{NaOH/CaO} H_2 + Na_2CO_3$$

Sodium formate → decarboxylation → Hydrogen gas

Que

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

- methane can be prepared.

- if two COOH groups are present on same carbon atom then decarboxylation occurs simply by heating.

$$CH_2(COOH)_2 \xrightarrow{\Delta} CH_3-COOH + CO_2$$

because

Carbanion $\ominus CH_2-\overset{O}{\overset{\|}{C}}-OH$ → Resonance → Stable

Que Given the reactivity order of following :-

CH_3-CH_2-COOH $\quad$ $CH_2=CH-COOH$ $\quad$ $CH\equiv C-COOH$

$CH_3-CH_2^{\ominus}$ $\quad$ $CH_2=CH^{\ominus}$ $\quad$ $CH\equiv C^{\ominus}$

c > b > a

Kolbe's electrolysis

- electrolysis of saturated monocarboxylic acid salt of Sodium or potassium.

$$2R-\overset{O}{\overset{\|}{C}}-O^{-}Na + 2H_2O \xrightarrow{\text{electrolysis}} \underbrace{R-R + 2CO_2}_{\text{Anode}} + \underbrace{2NaOH + H_2}_{\text{Cathode}}$$

$$2C_2H_5-COONa \xrightarrow{\text{electrolysis}} \underbrace{C_2H_5-C_2H_5 + 2CO_2}_{\text{anode}} + \underbrace{2NaOH + H_2}_{\text{Cathode}}$$

mechanism

$$2C_2H_5COO^{-}Na^{+} \xrightarrow[\text{electrolysis}]{H_2O} 2C_2H_5COO^{-} + 2Na^{+}$$ {break into ions in water}

(ionic compd)

at anode (+)

$2C_2H_5COO^{-}$

↓ 1 e^{-} is taken by anode (2e⁻ loose)

$2C_2H_5COO^{\bullet}$

$$C_2H_5-\overset{O}{\overset{\|}{C}}-O^{\bullet} \rightarrow C_2H_5^{\bullet} + CO_2$$

$$C_2H_5-\underset{O}{\underset{\|}{C}}-O^{\bullet} \rightarrow C_2H_5^{\bullet} + CO_2$$

$$C_2H_5-C_2H_5 + 2CO_2$$

Cathode (−)

$2Na^{+}$ + H_2O (electrolyte)

1 e^{-} of Na will attack on Hydrogen of H_2O and create free radical.

$$Na^{\bullet} + H-OH$$

$$NaOH + H_2$$

$$2Na^{+} + 2e^{-} \rightarrow 2Na$$

$$2Na + H_2O \rightarrow 2NaOH + H_2\uparrow$$

~~mixture of carboxylic acid~~

$$R'COONa + R''COONa \rightarrow R'-R' + R''-R'' + R'-R'' + 2CO_2 + 2NaOH + H_2$$

- Free Radical intermediate
- PH of solution increases. (NaOH formation)
- methane can't be prepared.

Grignard

R^-

(I) It take active hydrogen & forms alkane.

$R-Mg-X + H-O-H \rightarrow R-H + Mg(X)(OH)$

$R-Mg-X + H-O-R \rightarrow R-H + Mg(X)(OR)$

$R-Mg-X + H-NH-R \rightarrow R-H + Mg(X)(NH-R)$

- This method is used to find no of active Hydrogen in compound. (Zerewitinoff's method)

(II) G.R → React → alkyl halide → higher alkane

$RMgX + R'X \rightarrow R-R' + Mg(X)(X)$

$R^{\ominus} \cdots\cdots R'^{\oplus}$

Reduction of alcohol, aldehyde, ketone & Carboxylic acid

$\xrightarrow[150^\circ C]{Red\ P, HI}$

$R-OH \xrightarrow[2HI, 150^\circ C]{Red\ P} R-H + H_2O + I_2$

$R-CHO \xrightarrow[4HI]{''} R-CH_3 + '' + 2''$

$R-\overset{O}{\overset{\|}{C}}-R' \xrightarrow[4HI]{} R-CH_2-R' + '' + 2''$

$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[6HI]{} R-CH_3 + '' + 3''$

$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[6HI]{} R-CH_3$

$R-\overset{O}{\overset{\|}{C}}-OEt \xrightarrow[6HI]{} R-CH_3$

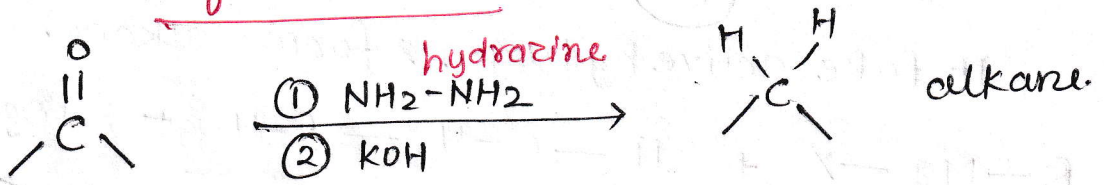
Red P → bcoz alkyl halide will be formed

Red P removes I_2 formed in the rxn.

$2P + 3I_2 \rightarrow 2PI_3$

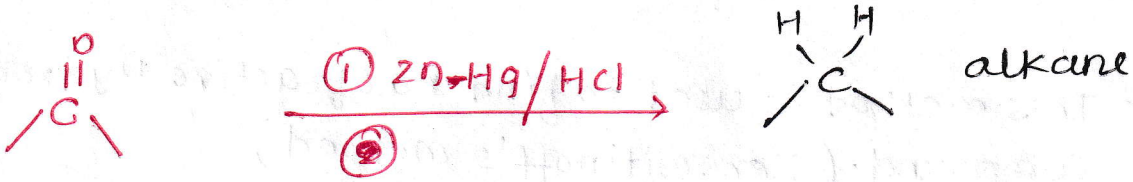
aldehyde, ketone

Wolf Kishner red^n



alkane.

Clemmensen Red^n



alkane

physical property

(i) $C_1 - C_4$ → gas

$C_5 - C_{17}$ – liq

$\geq C_{18}$ – waxy white solid

* neopentane → gas

(ii) B.P. $\propto$ molecular weight

Pentane < hexane < heptane

$$B.P. \propto \frac{1}{\text{no of side chain}}$$

n-pentane > Isopentane > neopentane

(iii) M.P → alkanes having even no of carbon atom has more M.P. than its neighbours.

due to symmetry ↓ Packing efficiency ↑

(iv) alkanes are inert in nature because

① C–C and C–H sigma bonds are strong & hence do not break easily.

② C–C & C–H So, they are non-polar. ↓ vanderwall force

$\Delta En = 0$ $\Delta En \simeq 0$

Chemical property

① Substitution
- → Halogenation
  - Fluorination — exothermic
  - Chlorination — exothermic
  - Bromination — endothermic
  - Iodination — endothermic
- → Nitration
- → Sulphonation
- → Chlorosulphonation (Reed Reaction)

② Combustion
- → ~~Combustion~~
- → ~~Catalytic oxidation~~

③ catalytic oxidation

④ Isomerization

⑤ Aromatization

⑥ pyrolysis

⑦ Reaction with steam.

Halogenation

Hydrogen from alkane is replaced by halogen.

$$R-H + X_2 \xrightarrow{h\nu} R-X + HX$$

Reagent: UV light
$h\nu$
temp (250-400°C)
Peroxide + X_2 (Cl_2, Br_2)

- Reactivity of Hydrogen atom in alkane → $3^\circ H > 2^\circ H > 1^\circ H$
- " " halogen " → $F_2 > Cl_2 > Br_2 > I_2$
  - F_2 ↓ react even in dark
  - Br_2 ↓ required light energy to react
  - I_2 ↓ donot react at room te
    - → very slo
    - → Reversibl
    - → oxidizing a HIO_3 & HN

- Free radical mechanism & involves 3 steps

1) Chain Initiation
2) Chain propagation
3) Chain Termination

~~Chain initiation~~ **Chlorination**

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl \xrightarrow[h\nu]{Cl_2} CH_2Cl_2 \xrightarrow[h\nu]{Cl_2} CHCl_3 \xrightarrow[h\nu]{Cl_2} CCl_4$$

if we want CH_3Cl (major product)

$$\underset{\text{(excess)}}{CH_4} + Cl_2 \longrightarrow CH_3Cl$$

Chain initiation (endothermic)

$$Cl-Cl \xrightarrow[\text{homolysis}]{h\nu} Cl^\bullet + Cl^\bullet$$

Chain propagation

a) $CH_4 + Cl^\bullet \xrightarrow{h\nu} CH_3^\bullet + HCl$

$CH_3^\bullet$ attacks on second molecule of chlorine to form CH_3Cl & $Cl^\bullet$

b) $CH_3^\bullet + Cl-Cl \xrightarrow{h\nu} CH_3Cl + Cl^\bullet$

Step (a) & Step (b) repeats itself and product is formed

many other undesirable products (highly halogenated) are formed

$$CH_3Cl + Cl^\bullet \longrightarrow \dot{C}H_2Cl + HCl$$

$$\dot{C}H_2Cl + Cl-Cl \longrightarrow$$

Chain termination (exothermic)

$$CH_3^\bullet + Cl^\bullet \longrightarrow CH_3-Cl$$

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

$$Cl^\bullet + Cl^\bullet \longrightarrow Cl-Cl$$

Bromination

Chlorination & Bromination are same.

Fluorination

$CH_4 + F_2 \longrightarrow$ Carbon black (highly explosive)

- To obtain product, we used N_2 gas (inert gas)

$$CH_4 + F_2 \xrightarrow{N_2 \text{ gas}} CH_3F + HF$$

Iodination

$$CH_4 + I_2 \rightleftharpoons CH_3I + HI$$
$$HI + HIO_3 \longrightarrow I_2 + H_2O$$

- Reversible
- Carried out in presence of oxidizing agent HIO_3, HNO_3 ------

Que $CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl$
excess

$CH_4 + Cl_2 \xrightarrow{h\nu} CCl_4$
excess

Halogenation of higher alkanes

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

$1^\circ H = 1$
$2^\circ H = 3.8 \sim 4$
$3^\circ H = 4.5 \sim 5$

% = ?? (1° product) | % = ?? (2° product)

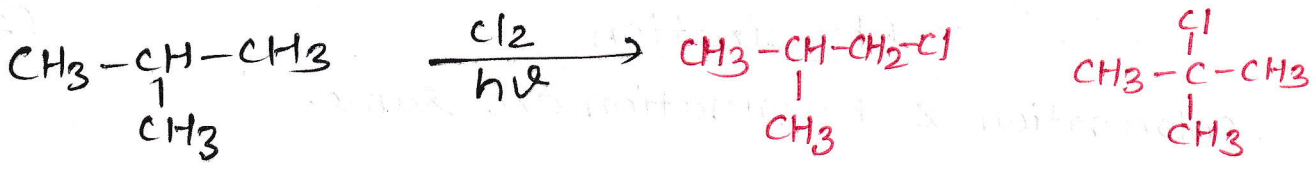
$$\% = \frac{1^\circ H \times 1}{1^\circ H \times 1 + 2^\circ H \times 3.8 + 3^\circ H \times 4.5} \times 100$$

$$= \frac{6 \times 1}{6 \times 1 + 2 \times 3.8 + 0} \times 100$$

$\simeq 45\%$

$\% \frac{2^\circ H \times 3.8}{1^\circ H \times 1 + 2^\circ H \times 3.8}$

$\simeq 55\%$ (major)



1°

$$\% = \frac{1^\circ H \times 1}{1^\circ H \times 1 + 2^\circ H \times 3.8 + 3^\circ H \times 4.5} \times 100$$

$$= \frac{9 \times 1}{9 \times 1 + 0 + 1 \times 4.5} \times 100$$

$$= \frac{9}{13.5} \times 100$$

$\simeq 65\%$

(major)

3°

$$\% = \frac{3^\circ H \times 4.5}{13.5} \times 100$$

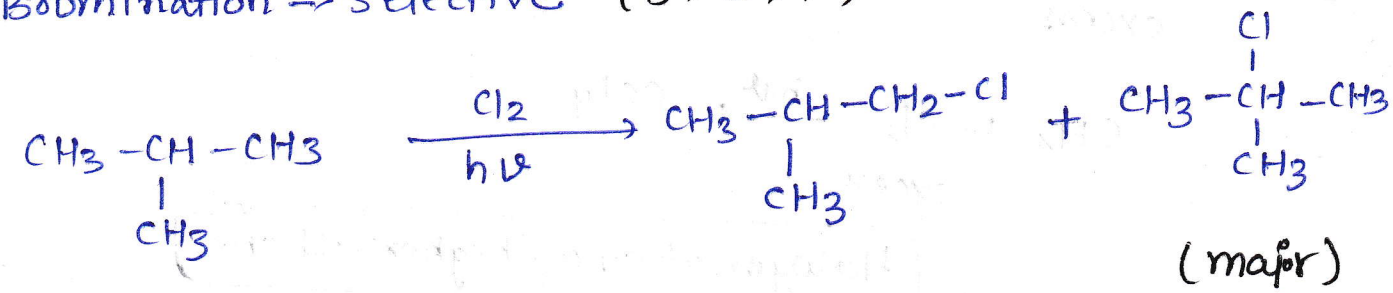
$$= \frac{1 \times 4.5}{13.5} \times 100$$

$$= \frac{4.5}{13.5} \times 100$$

$\simeq 35\%$.

Chlorination → non selective

Bromination → Selective $(3^\circ > 2^\circ > 1^\circ)$



(major)

Nitration

- High temp (400–450°c)
- nitric acid (HNO_3) → Reagent.
- Hydrogen is replaced by NO_2.
- all possible nitroalkanes are formed
  - C–C bond clevage
  - C–H bond clevage.
- free radical substitution.

$$CH_3-CH_3 + HNO_3 \xrightarrow{400-450^\circ c} CH_3-CH_2-NO_2$$

$$CH_3-NO_2$$

$$CH_3-CH_2-CH_3 + HNO_3 \xrightarrow{450^\circ c} CH_3-CH_2-CH_2NO_2$$

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

$$CH_3-CH_2-NO_2$$

$$CH_3NO_2$$

Sulphonation

- High temp (400°c)
- Reagent → Oleum $H_2S_2O_7$ (mixture of SO_3 + conc H_2SO_4)
- Hydrogen is replaced by $-SO_3H$.
- alkane having 6 or more carbon & lower branched alkanes (3°H) gives suphonation.

$$H_3C-C-C-C-C-CH_3 + H_2S_2O_7 \text{ or Fuming } H_2SO_4 \longrightarrow C-C-C-C-C-C-SO_3H$$

$$CH_3-\overset{CH_3}{\overset{|}{\underset{CH}{\underset{|}{C}}}}-H \; + \; \text{"} \longrightarrow CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-SO_3H$$

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lower alkanes, propane, butane, Pentane react with SO_3 in vapour phase to form Sulphonic acid

$$C_3H_8 + SO_3 \longrightarrow C_3H_7SO_3H$$

Chlorosulphonation
(Reed Reaction)

→ Reagent (SO_2 & Cl_2) in presence of $h\nu$

$$C_3H_8 + SO_2 + Cl_2 \xrightarrow{h\nu} C_3H_7SO_2Cl + HCl$$

$$C_3H_7SO_2Cl \xrightarrow{H_2O} C_3H_7SO_3H$$

($C_3H_7SO_3H$ = Sulphonic acid)

Combustion

Combustion

Complete Combustion : $C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O$

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

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

$\Delta H = -ve$ Exothermic

$\Delta H = -ve$ → Heat of Combustion

Incomplete Combustion

$CH_4(g) + O_2(g) \longrightarrow C_{(s)} + 2H_2O(l)$

Carbon black

Heat of Combustion

(1.) Hoc $\propto$ no of Carbon

$C_3H_8 > C_2H_6 > CH_4$

(2) Hoc $\propto \frac{1}{\text{Branching of alkane}}$

$CH_3-CH_2-CH_2-CH_2-CH_3 > CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3 > H_3C-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3$

(3) Hoc $\propto \frac{1}{\text{Size of ring}}$

△ > □ > ⬠ > ⬡

Controlled oxidation

Catalytic oxidation

Alkane $\xrightarrow{\text{oxdn}}$ alcohol

Alkane $\xrightarrow{\text{oxdn}}$ aldehyde

Alkane $\xrightarrow{\text{oxdn}}$ carboxylic acid

$CH_4 + O_2 \xrightarrow[100atm, 523K]{\text{Red hot Cu or Fe tube}} CH_3OH$

alcohol

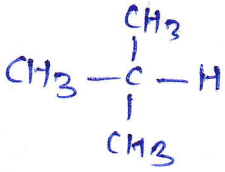
$CH_4 + O_2 \xrightarrow[\Delta]{Mo_2O_3} HCHO$

aldehyde

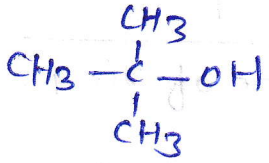
$CH_3-CH_3 + O_2 \xrightarrow[\Delta]{Mn(CH_3COO)_2} CH_3-\overset{O}{\overset{\|}{C}}-OH$

acid

Tertiary alkane $\xrightarrow{KMnO_4}$ alcohol



$\xrightarrow{KMnO_4}$



Isomerization

Straight chain alkane $\xrightarrow[AlCl_3, HCl]{\text{Anhydrous}}$ branched chain isomer.

$$CH_3-CH_2-CH_2-CH_3 \xrightarrow[300^\circ C]{AlCl_3, HCl} CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_3$$

$$CH_3(CH_2)_4CH_3 \xrightarrow{\text{anhy } AlCl_3, HCl} CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_3$$

$$CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3$$

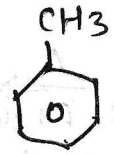
$$CH_3(CH_2)_6CH_3 \xrightarrow{\quad''\quad} CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3$$

iso-Octane

Aromatization

alkane (6 or more Carbon) $\xrightarrow[10-20\ atm]{773K}$ 

Cr_2O_3 or V_2O_5 or Mo_2O_3

$C_7H_{16} \xrightarrow{\quad''\quad}$ 

Toluene

Pyrolysis

- Cracking of hydrocarbon.
- 773K temp → decomposes to lower hydro carbon.
- $CH_4 \xrightarrow{\text{pyrolysis}} C + 2H_2$
- $CH_3-CH_3 \xrightarrow{\quad''\quad} CH_2=CH_2 + H_2$
- $CH_3-CH_2-CH_3 \xrightarrow{\quad''\quad} CH_3-CH=CH_2 + H_2$

  $\xrightarrow{\quad''\quad} CH_4 + CH_2=CH_2$

$C-C-C-C \xrightarrow[773K]{} C=C-C-C + H_2$

$C-C=C-C + H_2$

$C-C\equiv C + CH_4$

$C-C + C=C$

$C-C-C-C-C-C \xrightarrow[773K]{} C-C-C-C=C + H_2$

$C-C-C=C-C + H_2$

$C-C-C-C=C + CH_4 \rightarrow$ minor product

$C-C-C=C + C_2H_6$

$C-C=C + C-C-C$

$C=C + C$

- free radical rxn

Kerosene oil → dodecane

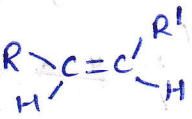
* $C_{12}H_{26} \xrightarrow[Pt,Pd,Ni]{\Delta} C_7H_{16} + C_5H_{10}$ + other product

dodecane — 973K — heptane — pentene.

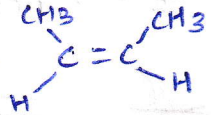
Alkene

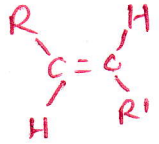
(i) From alkyne { Catalytic hydrogenation with Poision Catalyst }

- Syn Addition of H_2
  - Lindlar's Catalyst: $H_2/Pd\text{-}C$, $CaCO_3$, $Pb(CH_3COO)_2$ & quinoline
  - Rosenumund catalyst: $H_2/Pd\text{-}C$, $BaSO_4$, $Pb(CH_3COO)_2$ & quinoline
  - P_2 Catalyst: Ni_2B (nickel boride)
- Anti addition of H_2 → Na / $liqNH_3$

$R-C\equiv C-R' \xrightarrow[Pd-C]{H_2}$ 

$CH\equiv CH \xrightarrow[CaCO_3]{H_2/Pd} CH_2=CH_2$

$CH_3-C\equiv C-CH_3 \xrightarrow[BaSO_4]{H_2/Pd}$ 

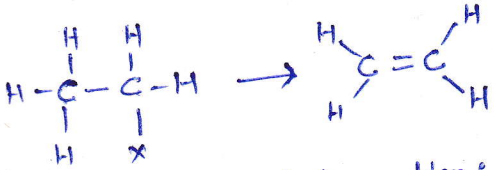
$R-C\equiv C-R' \xrightarrow[Na\ \&\ liqNH_3]{H_2}$ 

- Birch Reduction is not valid in terminal alkynes.

$R-C\equiv CH \xrightarrow[liqNH_3]{Na} R-C\equiv C^{\ominus}Na^{\oplus}$

(ii) From alkyl halide

Monohalide $\xrightarrow[NaNH_2/\Delta]{alc\ KOH\ or}$ (dehydrohalogenation) (β-elimination) (E2-mechanism) (Endothermic)



Rate of dehydrohalogenation: $I > Br > Cl$

3° alkyl $> 2^\circ$ alkyl $> 1^\circ$ alkyl

$CH_3-\underset{X}{CH}-CH_3 \xrightarrow[\Delta]{alc\ KOH}$

$CH_3-CH=CH-CH_3$ $\alpha H=6$ Saytzeff Product (major)

$CH_3-CH_2-CH=CH_2$ $\alpha H=2$ Hoffmann Product

Di-halide

- Geminal
- vicinal → $R-\underset{X}{CH}-\underset{X}{CH_2} \xrightarrow[300^\circ C]{Zn\ dust/\Delta} R-CH=CH_2 + ZnX_2$

$CH_2Br-CH_2Br + Zn \longrightarrow CH_2=CH_2 + ZnBr_2$

$CH_2(-CH_2-CH_2-)\ \xrightarrow[\Delta]{Zn\ dust}$ cycloalkane

1,3-dihalide $\xrightarrow[dust]{Zn}$ cycloalkane

Geminal → $R-CH(X)_2 + 2Zn + (X)_2CH-R \longrightarrow R-CH=CH-R + 2ZnX_2$

$2CH_3-CHCl_2 \xrightarrow{Zn/\Delta} CH_3-CH=CH-CH_3 + 2ZnX_2$

(iii) **From alcohol** : Removal of H_2O : dehydration : β elemination : E1 mechanism : Endothermic

$\xrightarrow[\Delta]{Al_2O_3}$ or $\xrightarrow[\Delta]{\text{mineral acid}}$ H_2SO_4, H_3PO_4

- Carbocation intermediate
- Rate of dehydration : 3° alcohol > 2° alcohol > 1° alcohol

$CH_3-CH_2-OH \xrightarrow[\Delta]{Al_2O_3} CH_2=CH_2$

$CH_3-CH_2-OH \xrightarrow[\Delta]{95\%\ H_2SO_4} CH_2=CH_2$

$CH_3-\underset{OH}{CH}-CH_3 \xrightarrow[\Delta]{60\%\ H_2SO_4} CH_2=CH-CH_3$

$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH \xrightarrow[\Delta]{30\%\ H_2SO_4} CH_3-\overset{CH_3}{C}=CH_2$

mechanism

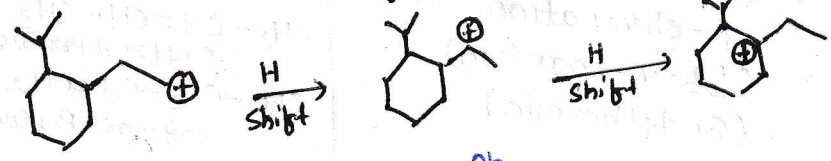
$CH_3-CH_2-\ddot{O}H \xrightarrow{H^+} CH_3-CH_2-\overset{\oplus}{O}H_2 \xrightarrow[RDS]{\text{Slow step}} CH_3-\overset{\oplus}{CH_2} \xrightarrow{HSO_4^-} H_2SO_4 + CH_2=CH_2$

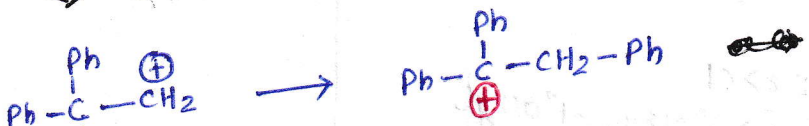
Carbocation intermediate — Catalyst

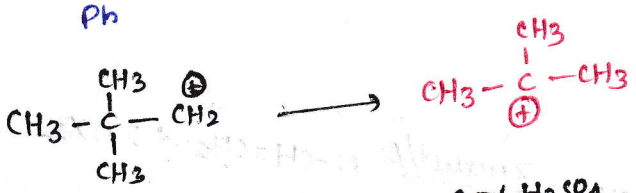
Carbocation Rearrangement

① Hydride shift ② Alkyl shift ③ Phenyl shift

H shift > Phenyl shift > Alkyl shift







$CH_3-CH_2-CH_2-OH \xrightarrow[\Delta]{95\%\ H_2SO_4} CH_3-CH_2-\overset{\oplus}{C}H_2 \longrightarrow CH_3-\overset{\oplus}{C}H-CH_3 \rightarrow CH_2=C-CH_3$

Que $CH_3-CH_2-CH_2-OH \xrightarrow[\Delta]{95\%\ H_2SO_4} CH_3-CH_2-\overset{\oplus}{C}H_2 \longrightarrow CH_3-\overset{\oplus}{C}H-CH_3 \rightarrow CH_2=C-CH_3$

Que $CH_3-\underset{OH}{CH}-\underset{CH_3}{CH}-CH_3 \xrightarrow[\Delta]{60\%\ H_2SO_4} CH_3-\overset{\oplus}{CH}-\underset{CH_3}{CH}-CH_3 \longrightarrow CH_3-CH_2-\underset{CH_3}{\overset{\oplus}{C}}-CH_3$

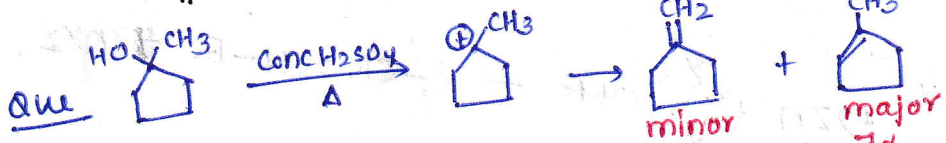
→ $CH_3-CH=C(CH_3)-CH_3$ 92% major — Saytzeff Product

→ $CH_3-CH_2-C(CH_3)=CH_2$ 7% minor — Hoffmann product

Saytzeff/Zaitsev Rule → more Substituted alkene is major product.

Hoffman Rule → less Substituted alkene is minor product. (more αH)

Que



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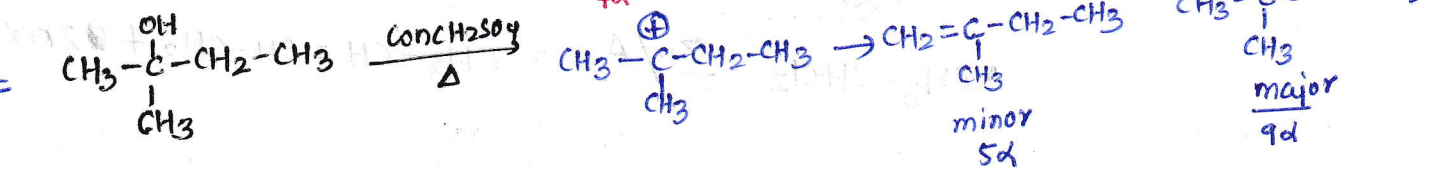
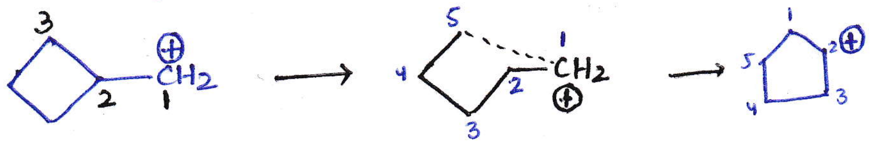


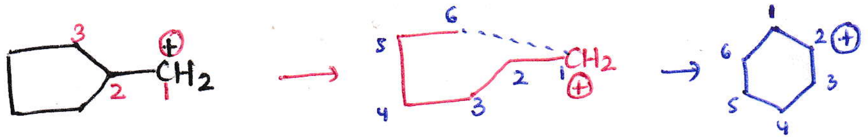
Carbocation – Ring Contraction & Ring Expansion

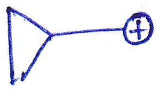
4 member ring → expand → 5 member ring → expand → 6 member ring

7 member ring → contract → 6 member ring

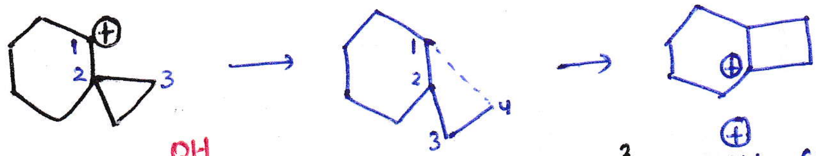


2–3 bond तोड़ो
1–3 bond जोड़ो
1 का charge 2 पर transfer करो





→ X → Stable (dancing Resonance)



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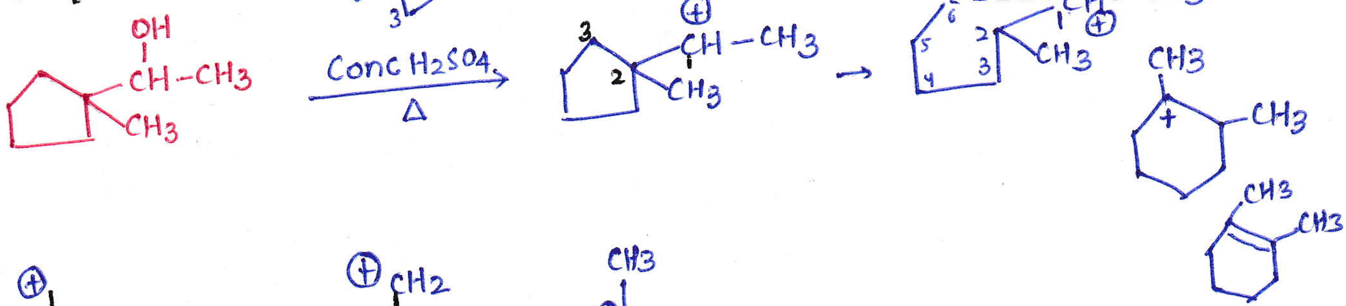
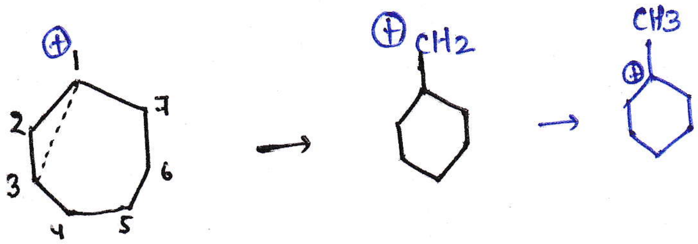




From aldehyde | Ketone

witting Reaction : wittig Reagent → phosphorous ylides $PPh_3=C\begin{smallmatrix}R\\R\end{smallmatrix}$

$R(R)C=O + PPh_3=CR_2 \rightarrow R(R)C=CR_2$

$R(H)C=O + PPh_3=CR_2 \rightarrow R(H)C=CR_2$

From Carboxylic acid | Kolbe's electrolysis $\xrightarrow[\text{electrolysis}]{H_2O}$

$2CH_3-COO^-Na^+ \xrightarrow[\text{electrolysis}]{H_2O} \underbrace{CH_3-CH_3 + 2CO_2}_{\text{Anode}} + \underbrace{2NaOH + H_2}_{\text{Cathode}}$

$CH_3-COO^-Na^+ \,|\, CH_3-COO^-Na^+ \xrightarrow{\;''\;} \underbrace{CH_2=CH_2 + 2CO_2}_{A} + \underbrace{2NaOH + H_2}_{C}$

$CH_2-COO^-Na^+ \,||\, CH_2-COO^-Na^+ \xrightarrow{\;''\;} \underbrace{CH\equiv CH + 2CO_2}_{A} + \underbrace{2NaOH + H_2}_{C}$

From Ester | Pyrolysis of Ester : $\xrightarrow[\text{glass wool}]{\text{Liq } N_2}$

$R-\overset{O}{\overset{||}{C}}-O-R'$

alkanoate → Carboxylic acid ; alkyl part → alkene

$CH_3-\overset{O}{\overset{||}{C}}-O-CH_2-CH_3 \xrightarrow[\text{glass wool}]{\text{Liq } N_2} CH_3COOH + CH_2=CH_2$

Physical properties

- $C_1 - C_3$ → gas
  $C_4 - C_{20}$ → liq
  $> C_{20}$ → Solid
- Colorless & odourless except ethene → faint sweet smell; ↳ colorless
- insoluble in water & Soluble in nonpolar Solvent (Benzene, Petroleum ether)
- B.P → BP ∝ Mwt ; B.P ∝ $\frac{1}{\text{branching}}$
- MP → MP ∝ Mwt ; Trans > cis → more good packing efficiency.

Chemical rxn

- Addition rxn
  - → Addition of H_2 Hydrogen
  - → Addition of X_2 halogen
  - → " " HX halogen acid
  - → " " H_2O water
  - → " " H_2SO_4 sulphuric acid
  - → " " HOX hypohalous acid
  - → Hydroformylation / oxo Rxn
- oxidation
- ozonolysis
- Substitution
- polymerization
- Isomerization

Addition of Hydrogen

$$R-CH=CH-R' \xrightarrow[\text{Ni, Pt, Pd, Raney Ni}]{H_2} R-CH_2-CH_2-R'$$

+ Heat release
⇓
Heat of hydrogenation

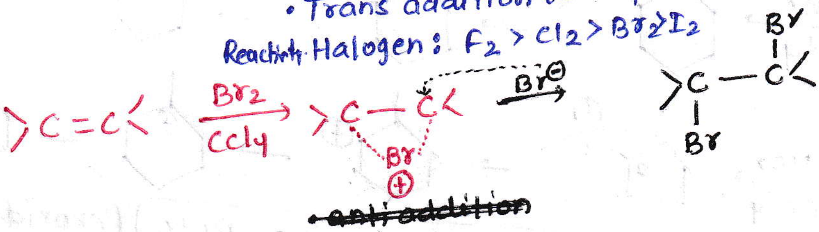
- Syn addition
- CSM → cis + syn → meso
- CAR → cis + anti → Racemic mix, enantiomeric pair
- TAM → Trans + anti → meso
- TSR → Trans + Syn → Racemic mix, enantiomeric pair

Addition of X_2

$$\xrightarrow[CCl_4]{X_2}$$

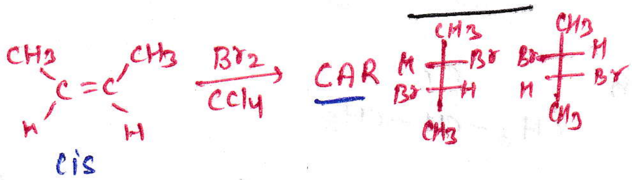
- nonpolar medium
- vicinal dihalide
- Electrophilic addition rxn
- cyclic halonium ion is formed
- Trans addition takes place

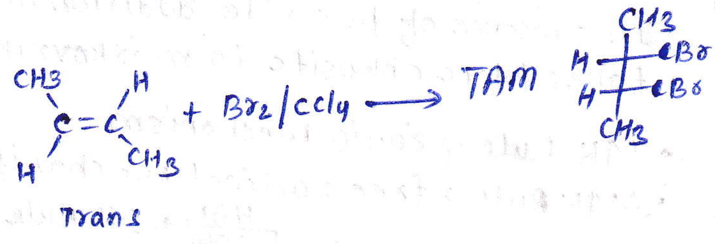
Reactivity Halogen: $F_2 > Cl_2 > Br_2 > I_2$



CAR

TAM





Que $CH_2=CH_2 \xrightarrow[CCl_4]{Br_2} \overset{Br}{CH_2}-\underset{Br}{CH_2}$

Que $CH_2=CH_2 \xrightarrow[aq\ NaCl]{Br_2}$ Polar medium $\rightarrow$ CH_2-CH_2 (bridged Br^{+}) ; $Br^{\ominus}$, $Cl^{\ominus}$, $OH^{\ominus}$

$\overset{Br}{C}-C-Br$; $Br-C-C-Cl$; $Br-C-C-OH$ → **Major**

Test of Unsaturation

$CH_2=CH_2 + Br_2/CCl_4 \longrightarrow \overset{Br}{CH_2}-\underset{Br}{CH_2}$

(Brown color Sol^n) (Brown color disappear)

Addition of HX

- addition of HX on unsymmetrical alkene takes place according to Markovnikov Rule.

~~RCH=CH-R' + HX~~

(H^+X^-) negative part of adding molecule gets attatched to Carbon having less Hydrogen.

mechanism of markovnikov

$CH_3-CH=CH_2 \xrightarrow{H^+}$ ① $CH_3-CH_2-\overset{\oplus}{CH_2}$ → 1° less stable → Minor product

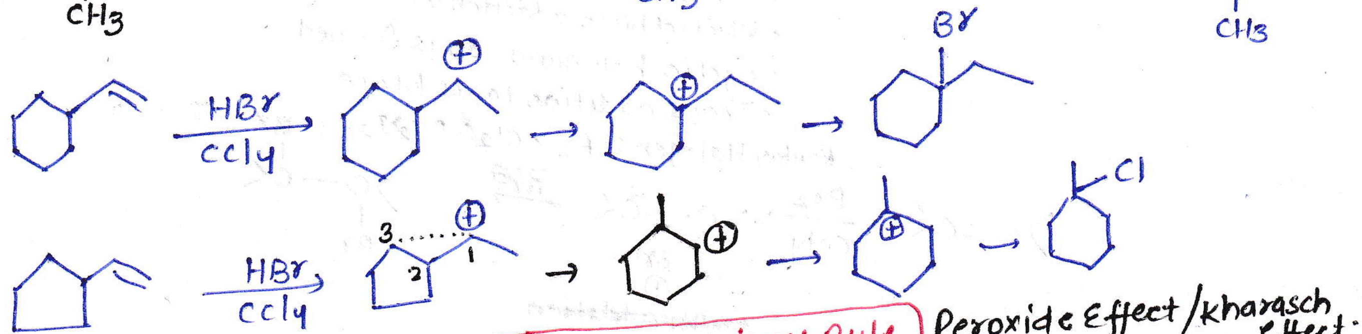
② $CH_3-\overset{\oplus}{CH}-CH_3$ → 2° more stable → major product

- Reactivity order → $HI > HBr > HCl > HF$
- Electrophillic addition
- Carbocation formation (Rarrangement)

Carbocation बनाओ → rearrange कराओ → X^- add कराओ

$CH_3-CH=CH_2 \xrightarrow[CCl_4]{HCl} CH_3-\overset{\oplus}{CH}-CH_3 \rightarrow CH_3-\underset{Cl}{CH}-CH_3$

$CH_3-\underset{CH_3}{CH}-CH=CH_2 \xrightarrow[CCl_4]{HBr} CH_3-\underset{CH_3}{CH}-\overset{\oplus}{CH}-CH_3 \rightarrow CH_3-\underset{CH_3}{\overset{\oplus}{C}}-CH_2-CH_3$; $CH_3-\underset{CH_3}{\overset{Br}{C}}-CH_2-CH_3$



Anti-markovnikov Rule

Peroxide Effect / kharasch effect.

- In presence of peroxide, addition of HBr on unsymmetrical alkene takes place opposite to markovnikov rule.

- MK Rule → ionic mechanism
- AMK Rule → free radical mechanism

$CH_3-CH=CH_2 \xrightarrow[CCl_4]{HBr}$ MK Rule $CH_3-\overset{Br}{CH}-CH_3$

$CH_3-CH=CH_2 \xrightarrow[Peroxide]{HBr}$ AMK Rule $CH_3-CH_2-CH_2Br$

mechanism (i) $R-O-O-R \longrightarrow 2RO^{\cdot}$

(ii) $RO^{\cdot} + H-Br \longrightarrow ROH + Br^{\cdot}$

(iii) $Br^{\cdot} + CH_3-CH=CH_2 \longrightarrow CH_3-CH_2-CH_2Br$ (minor) $+ CH_3-\underset{Br}{CH}-CH_3$ (major)

- HBr only show Peroxide effect
- HCl, HI donot show peroxide effect.

$CH_3-\underset{CH_3}{CH}-CH=CH_2$

- HBr / Peroxide → $CH_3-\underset{CH_3}{CH}-CH_2-CH_2Br$
- HCl / Peroxide → $CH_3-\underset{CH_3}{\overset{Cl}{C}}-CH_2-CH_3$
- HBr / CCl_4 → $CH_3-\underset{CH_3}{\overset{Br}{C}}-CH_2-CH_3$

Addition of water Hydration $H^+ OH^-$

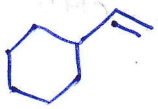
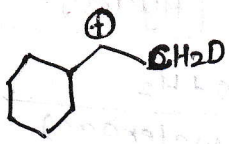
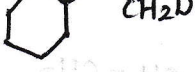
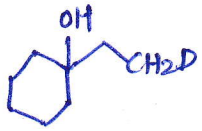
- Carbocation formation → Rearrangement → attack of OH^-

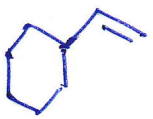
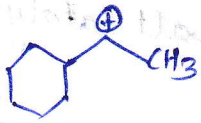
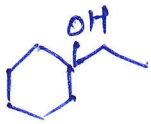
$CH_3-CH=CH_2 + H_2O \xrightarrow{H^+} CH_3-\underset{OH}{CH}-CH_3$

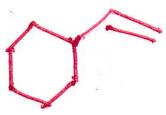
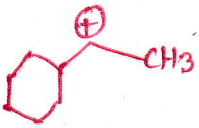
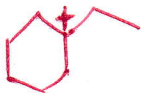
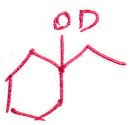
$CH_3-\underset{CH_3}{C}=CH_2 + H_2O \xrightarrow{H^+} CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_3$

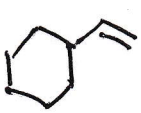
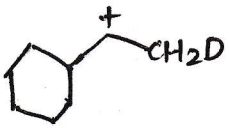
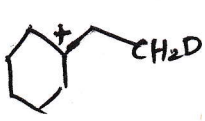
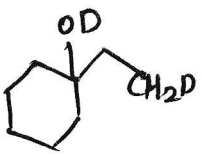
Que $CH_3-\underset{CH_3}{CH}-CH=CH_2$

- H^+/H_2O → $CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_2-CH_3$
- HCl/CCl4 → $CH_3-\underset{CH_3}{\overset{Cl}{C}}-CH_2-CH_3$
- HBr / Peroxide → $CH_3-\underset{CH_3}{CH}-CH_2-CH_2Br$

Que  $\xrightarrow[H_2O]{dil\ D_2SO_4}$  →  → 

Que  $\xrightarrow[H_2O]{dil\ H_2SO_4}$  →  → 

Que  $\xrightarrow[D_2O]{dil\ H_2SO_4}$  →  → 

Que  $\xrightarrow[D_2O]{dil\ D_2SO_4}$  →  → 

Addition of Hypohalous acid HOX

~~$X_2 + H_2O \rightarrow HOX$~~ $\quad HO^{\delta-}-X^{\delta+}$

HOX, HOCl HOBr HOI

~~HOCl~~ $OH^- Cl^+$ $\quad OH^- X^+$ $\quad OH^- Cl^+$ $\quad OH^- Br^+$ $\quad OH^- I^+$

~~HOBr~~ $OH^- Br^+$

~~HOI~~ $OH^- I^+$

- Cyclic halonium ion formation
- anti addition.

~~HOH~~ $HO^{\delta-}-Cl^{\delta+} + R-CH=CH_2 \rightarrow R-CH(Cl)-CH_2^{\oplus} \rightarrow R-CH(OH)-CH_2Cl$

- Reactivity order HOCl > HOBr > HOI

Addition of Sulphuric acid

Conc H_2SO_4

H^+

HSO_4^-

$R-CH=CH_2 + \text{conc } H_2SO_4 \rightarrow$

Carbocation → rearrange → Product

$R-CH^{\oplus}-CH_3 \rightarrow R-CH(OSO_3H)-CH_3$

dil H_2SO_4

H^+

OH^-

$R-CH=CH_2 + \text{dil } H_2SO_4 \rightarrow$

carbocation → rearrange → product

$R-CH^{\oplus}-CH_3 \rightarrow R-CH(OH)-CH_3$

Hydroformylation/oxo reaction

$R-CH=CH_2 \xrightarrow[\text{(watergos)}]{CO+H_2}$

Cobalt Catalyst

$R-CH_2-CH_2-CHO$ (&)

$R-CH(CHO)-CH_3$

Oxidation

→ complete combustion

$$C_nH_{2n} + \frac{3n}{2} O_2 \longrightarrow nCO_2 + nH_2O$$

→ oxidation with acidic $KMnO_4$ (Hot $KMnO_4$)/acidic $K_2Cr_2O_7$ strong oxidizing agent

$R-CH=CH_2 \xrightarrow{\text{acidic } KMnO_4} RCHO + HCHO$

$\hookrightarrow RCOOH + HCOOH - H_2O + CO_2$

$CH_2=CH_2 \xrightarrow{\text{acidic } KMnO_4} 2HCHO \longrightarrow 2HCOOH \longrightarrow 2H_2O + 2CO_2$ ($H_2O + CO_2$)

$CH_3-CH=CH_2 \xrightarrow{\text{acidic } KMnO_4} CH_3CHO + HCHO \longrightarrow CH_3COOH + HCOOH$ ($H_2O + CO_2$)

$CH_3-CH=CH-CH_3 \xrightarrow{"} 2CH_3CHO \longrightarrow 2CH_3COOH$

$CH_3-C(CH_3)=CH_2 \xrightarrow{"} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + HCHO \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + HCOOH$ ($H_2O + CO_2$)

$CH_3-CH(CH_3)-CH=CH_2 \xrightarrow{"} CH_3-CH(CH_3)-CHO + HCHO \longrightarrow CH_3-CH(CH_3)-COOH + H_2O + CO_2$

→ oxidation with alkaline $KMnO_4$/cold $KMnO_4$ {Bayer's Reagent}

$R-CH=CH_2 \xrightarrow{\text{alk } KMnO_4} R-CH(OH)-CH_2(OH)$ (vicinal glycol)

Test of unsaturation.

- Syn addition
- alkaline $KMnO_4$ (Pink Color) → decolorize → Brown ppt (glycol + MnO_2)

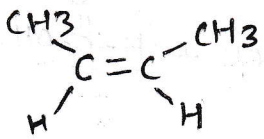
→ oxidation by OsO_4

- syn addition of 2OH group

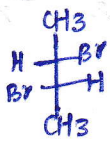
$$R-CH=CH_2 \xrightarrow[H_2O]{OsO_4} R-CH(OH)-CH_2(OH)$$

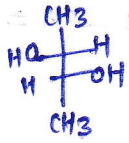
- Syn addition → H_2, Bayer's Reagent, OSO_4/H_2O
- Trans addition → X_2, HOX

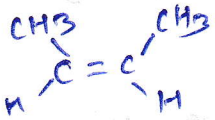
Que



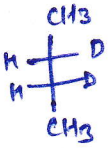
$\xrightarrow[CCl_4]{Br_2}$ CAR

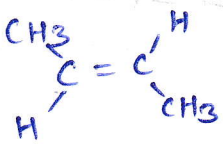




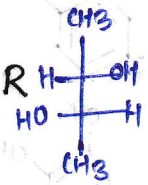


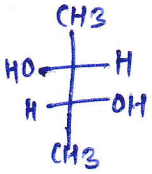
$\xrightarrow[Pt]{D_2}$ CSM

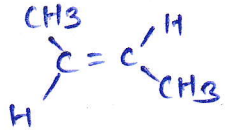




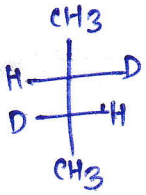
$\xrightarrow[KMnO_4]{\text{cold alkaline}}$ (Bayer's Reagent) TSR

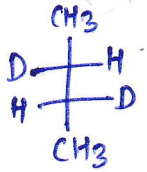






$\xrightarrow[Ni]{D_2}$ TSR



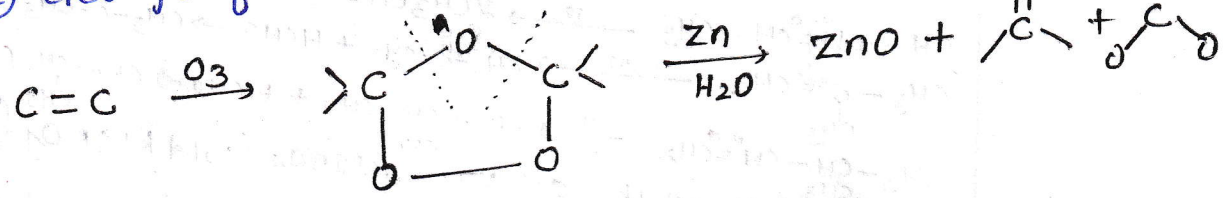


Ozonolysis

Reductive

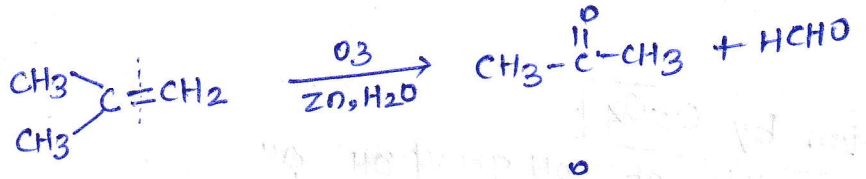
$\xrightarrow[Zn,\ H_2O]{O_3}$

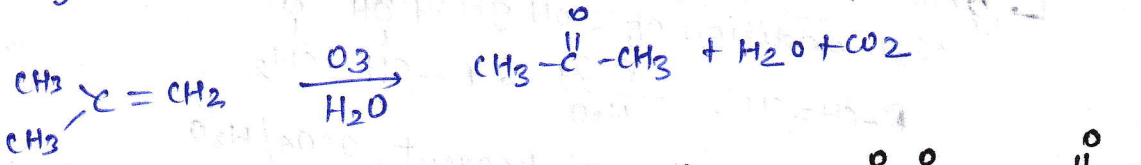
- Two Step reaction :-
  1. ozonide formation
  2. cleavage of ozonide by Zn/H_2O

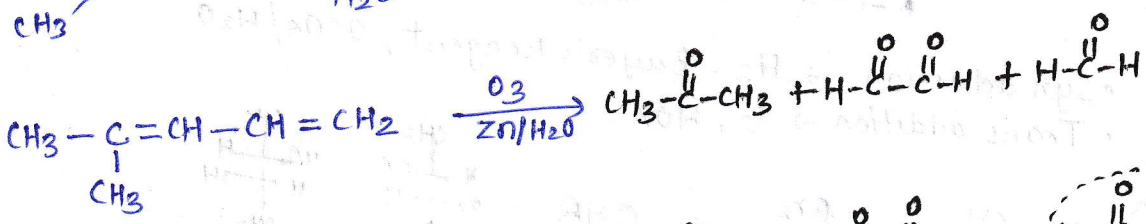


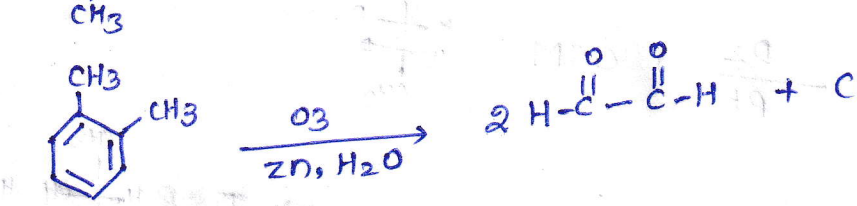
Ex. $CH_3-CH=CH_2 \xrightarrow[Zn,H_2O]{O_3} CH_3CHO + HCHO$

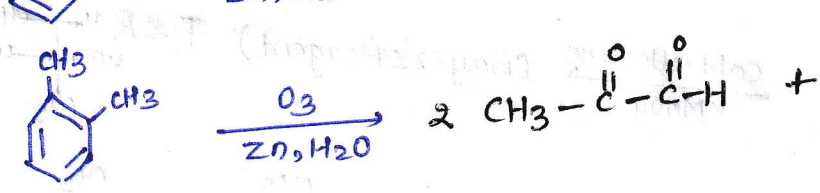
$CH_3-CH=CH_2 \xrightarrow[H_2O]{O_3} \underset{CH_3COOH}{CH_3CHO} + \underset{H_2O+CO_2}{\underset{HCOOH}{HCHO}}$







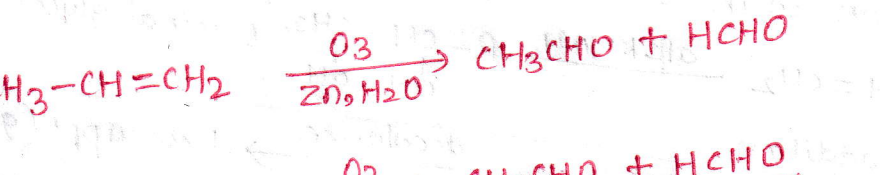


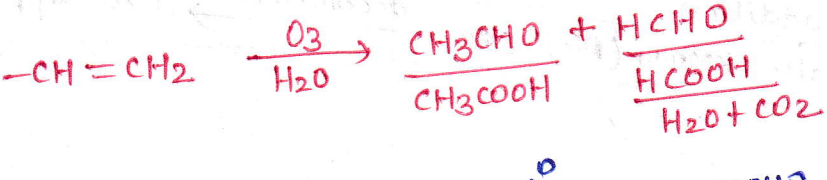


Oxidative

$\xrightarrow[H_2O]{O_3}$

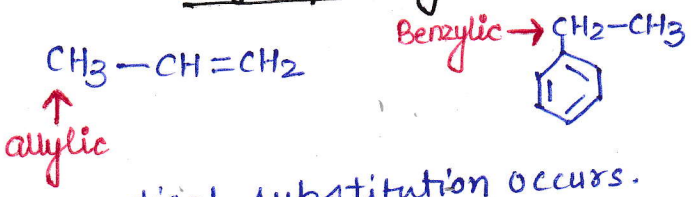
- aldehyde → acid
- $HCHO \rightarrow HCOOH \rightarrow H_2O + CO_2$



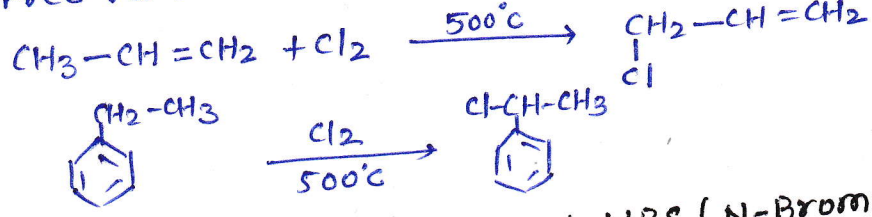


Substitution

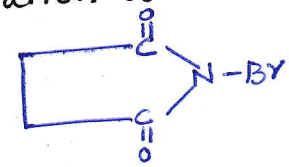
allylic / Benzylic Substitution

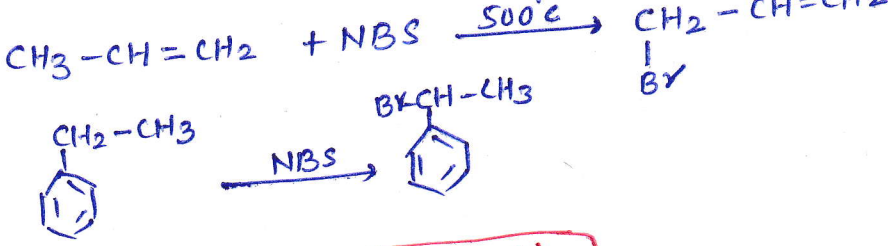


- Free radical substitution occurs.

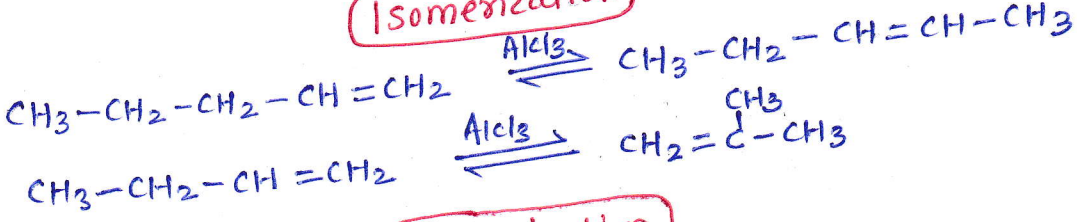


But for Bromination we need NBS (N-Bromosuccinamide)

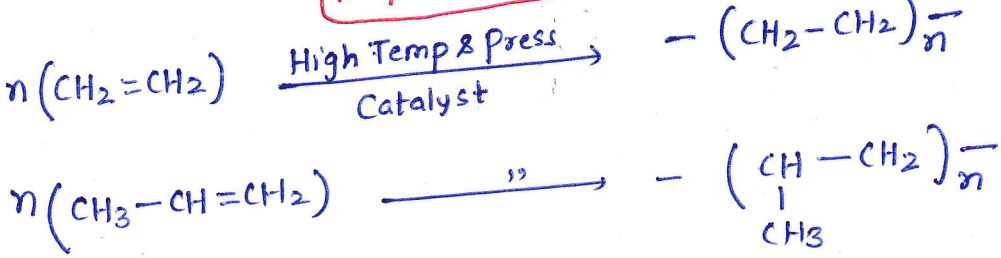




Isomerization



Polymerization



Alkyne

- C_nH_{2n-2}
- $C \equiv C$ bond length 1.20 A°
- bond energy = 192 Kcal/mol
- $C_2H_2 \rightarrow CH \equiv CH \rightarrow$ acetelyene
- welding torch → oxyacetylene fuel.

General methods of Preparation

① From alkyne

(i) with Na/liq NH_3

$$R-C\equiv C-H \xrightarrow[liq\ NH_3]{Na} R-C\equiv C^{\ominus} \xrightarrow{R'-X} R-C\equiv C-R'$$

(ii) with Grignard

$$R-C\equiv C-H + R'MgX \longrightarrow R'-H + R-C\equiv C^{\ominus}MgX \xrightarrow{R-X} R-C\equiv C-R$$

② From alkylhalide

① Gemdihalide $R-\underset{H}{\overset{H}{C}}-\underset{X}{\overset{X}{C}}-R'$ + alc KOH → $R-CH=\underset{X}{C}H$ $\xrightarrow{NaNH_2}$ $R-C\equiv CH$

② vicinal dihalide $R-\underset{X}{CH}-\underset{X}{CH}$ + alc KOH → $R-CH=\underset{X}{C}H$ $\xrightarrow{NaNH_2}$ $R-C\equiv CH$

③ Tetrahaloalkane $R-\underset{X}{\overset{X}{C}}-\underset{X}{\overset{X}{C}}-H$ $\xrightarrow[\Delta]{Zn\ dust}$ $R-\underset{X}{C}=\underset{X}{C}-H$ $\xrightarrow{Zn\ dust}$ $R-C\equiv CH$

③ From Carboxylic acid

$$\begin{matrix} CH-COO^-Na^+ \\ \| \\ CH-COO^-Na^+ \end{matrix} \xrightarrow[\text{electrolysis}]{H_2O} \underset{\text{Anode}}{CH\equiv CH} + 2CO_2 + 2NaOH + \underset{\text{cathode}}{H_2}$$

④ preparation of ethyne/acetylene.

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

→ Pure acetylene iodoform / chloroform + Ag Powder → alkyne

$$CHI_3 + 6Ag + I_3CH \rightarrow CH\equiv CH + 6AgI$$

Physical properties

- $C_2 - C_4$ → gas

  $C_5 - C_{11}$ → liq

  C_{12} → → Solid

- B.P. & MP ∝ Molecular wt ∝ $\frac{1}{\text{branching}}$

Addition of H_2

Chemical Reaction

$R-C\equiv C-R' \xrightarrow[Ni, Pt, Pd, Raney\ Ni]{H_2} R-CH_2-CH_2-R'$

1. addition
2. oxidation
3. substitution
4. cyclic polymerization
5. isomerization.

$R-C\equiv C-R \xrightarrow[CaCO_3, quinoline]{H_2, Pd-C}$ cis-alkene

$R-C\equiv C-R \xrightarrow[BaSO_4]{H_2, Pd-C}$ cis-alkene

$R-C\equiv C-R \xrightarrow[liq\ NH_3]{Na}$ trans-alkene

Addition of X_2

anti addition

M-1 $R-C\equiv C-H \xrightarrow[FeX_3]{X_2} R-C(X)=C(X)-H \xrightarrow{X_2} R-C(X)_2-C(X)_2-H$

M-2 $CH_3-C\equiv CH \xrightarrow[CCl_4]{Br_2} CH_3-C(Br)=C(Br)-H \xrightarrow[CCl_4]{Br_2} CH_3-C(Br)_2-CH(Br)_2$

Br_2/CCl_4 (Reddish orange solution) $\longrightarrow$ decolorized

Addition of HX

MK Rule

$R-C\equiv C-H + H-X \longrightarrow R-C(X)_2-CH_2$

$CH_3-C\equiv CH + HBr \longrightarrow CH_3-C(Br)=CH_2 + HBr \rightarrow [CH_3-C(Br)_2-CH_3]$

Addition of HOX $(OH^- \quad X^+)$

MK Rule

$R-C\equiv CH + HOCl \longrightarrow R-C(OH)(Cl)-CH(OH)(Cl) \rightarrow R-C(=O)-CHCl_2$

Addition of H_2O (Hydration | Kucherov's reaction) → Nucleophilic addition

NAR

$\{1\%\ HgSO_4 + 40\%\ H_2SO_4\}$

$CH\equiv CH + H_2O \xrightarrow[dil\ H_2SO_4]{1\%\ HgSO_4} CH_2=CH-OH \rightleftharpoons CH_3-CHO$ (Aldehyde)

enol

$CH_3-C\equiv CH + H_2O \xrightarrow[dil\ H_2SO_4]{1\%\ HgSO_4} CH_3-C(OH)=CH_2 \rightleftharpoons CH_3-C(=O)-CH_3$ (Ketone)

enol

$CH_3-C\equiv C-CH_3 \xrightarrow[Hg^{+2}]{H^+/H_2O} CH_3-C(OH)(OH)-CH_2-CH_3 \rightarrow CH_3-C(=O)-CH_2-CH_3$

Oxidation Reaction

(a) Combustion $C_nH_{2n-2} + \left(\frac{3n-1}{2}\right) O_2 \rightarrow n\,CO_2 + (n-1)\,H_2O$

(b) oxidation with acidic $KMnO_4$ / $K_2Cr_2O_7$

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

$$H-C\equiv C-H \xrightarrow[H^+/K_2Cr_2O_7]{H^+/KMnO_4} 2HCOOH$$

$$CH_3-C\equiv C-H \xrightarrow{\text{"}} CH_3-\overset{O}{\overset{\|}{C}}-OH + HCOOH$$

(c) oxidation with alkaline $KMnO_4$ (Bayer's reagent)

$$CH\equiv CH \xrightarrow{\text{alk } KMnO_4} HO-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OH$$

oxalic acid

$$CH_3-C\equiv CH \xrightarrow{\text{alk } KMnO_4} CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OH$$

(d) oxidation by Selenium oxide $\{SeO_2\}$ → creates dicarbonyl

$$CH\equiv CH \xrightarrow{SeO_2} CHO-CHO$$

$$H_3C-C\equiv C-CH_3 \xrightarrow{SeO_2} CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$$

(e) ozonolysis → Reductive $\xrightarrow[Zn, H_2O]{O_3}$

oxidative $\xrightarrow[H_2O]{O_3}$

$$CH_3-C\equiv CH \xrightarrow[Zn, H_2O]{O_3} CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H + ZnO$$

$$CH_3-C\equiv CH \xrightarrow[H_2O]{O_3} CH_3-\overset{O}{\overset{\|}{C}}-OH + H-\overset{O}{\overset{\|}{C}}-OH$$

SUBSTITUTION REACTION

(i) Formation of Sodium acetylide

$H-C\equiv C-H \xrightarrow{NaNH_2} H-C\equiv C^{\ominus}Na^{+} \xrightarrow{NaNH_2} Na^{\oplus}\,{}^{\ominus}C\equiv C^{\ominus}\,Na^{\oplus}$

(ii) Formation of Copper & Silver acetylide

$R-C\equiv C-H + Cu_2Cl_2 + NH_4OH \longrightarrow R-C\equiv C\,Cu + NH_4Cl + H_2O$

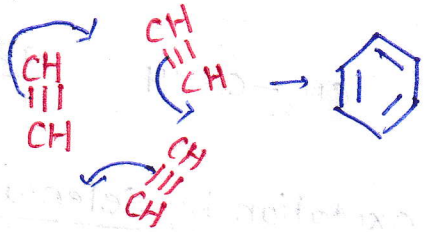
ammonical cuprous chloride — Redppt

$R-C\equiv C-H + AgNO_3 + NH_4OH \longrightarrow R-C\equiv C\,Ag + NH_4NO_3 + H_2O$

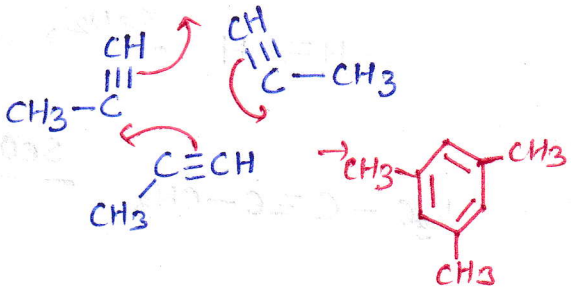
ammonical silver nitrate (Tollen's Reagent) — whiteppt

cyclic polymerization

$3\,CH\equiv CH \xrightarrow{\text{Red hot Fe, Cu, quartz tube}}$



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



Isomerization

1 alkyne

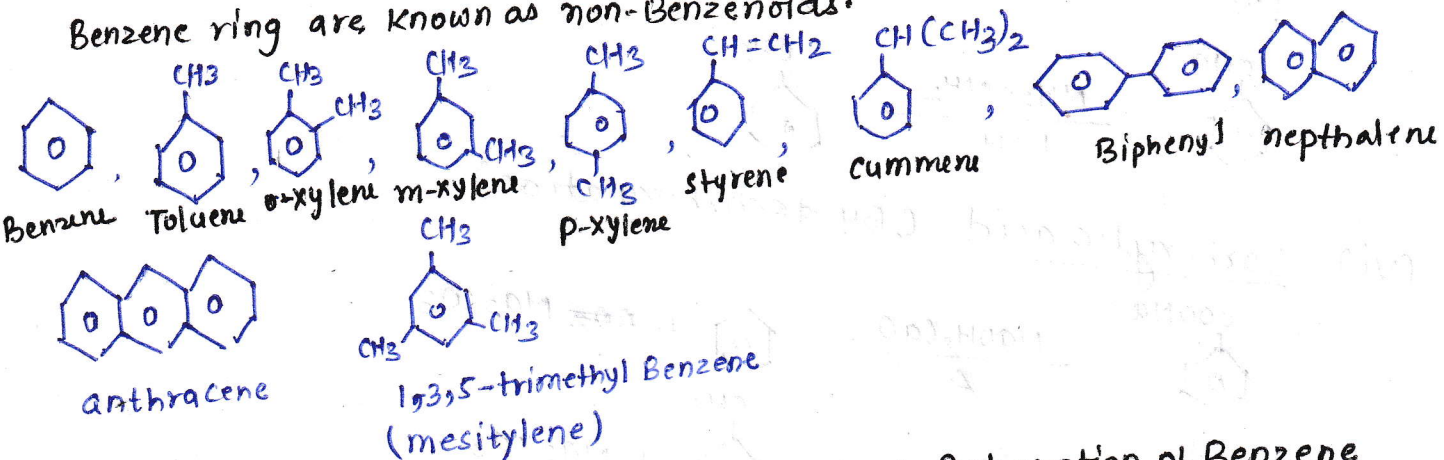
$R-CH_2-C\equiv CH \xrightarrow[\Delta]{\text{alc KOH}} R-C\equiv C-CH_3$

2 alkyne

$CH_3-C\equiv C-CH_3 \xrightarrow{NaNH_2} CH_3-CH_2-C\equiv C\,Na$

Aromatic Hydrocarbon

- also called as arenes.
- cyclic, planar, follow Huckel's rule. $(4n+2)\pi e^-$, $2\pi e^-$, $6\pi e^-$, $10\pi e^-$, $14\pi e^-$ ---
- It shows electrophilic substitution reaction.
- Aromatic comp containing Benzene Ring are K/a Benzenoids. & not containing Benzene ring are known as non-Benzenoids.



General methods of Preparation of Benzene

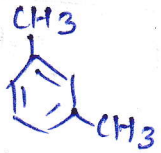
(i) alkane (Aromatization) $\xrightarrow[773K]{Cr_2O_3/Al_2O_3/V_2O_5/MO_2O_3}$

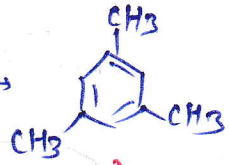
n-Hexane $\xrightarrow[773K]{Cr_2O_3/Al_2O_3}$ 

(ii) alkene (cyclic polymerization) $\xrightarrow{\text{Red hot Fe tube/Cu tube}}$

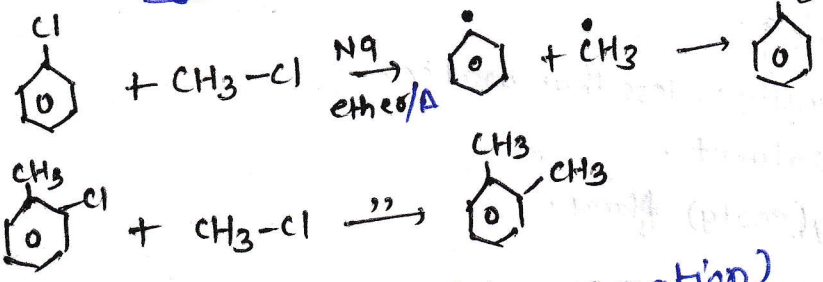
$3CH\equiv CH \xrightarrow[\text{tube}]{\text{Red hot Fe, Cu}}$ 

$2CH\equiv CH + CH_3-C\equiv CH \longrightarrow$ 

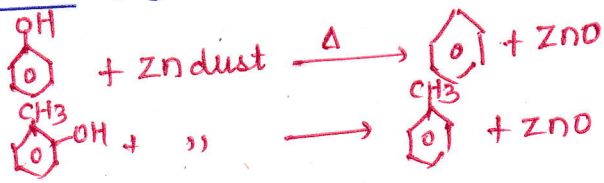
$2CH_3-C\equiv CH + CH\equiv CH \longrightarrow$ 

$3CH_3-C\equiv CH \longrightarrow$ 

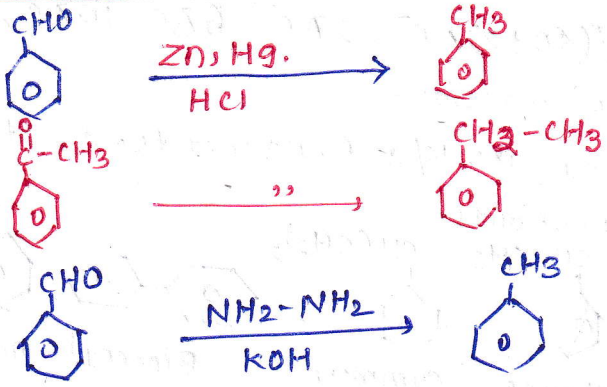
(iii) ~~Haaren~~ Aryl Halide (Wurtz fittig Reaction) $\xrightarrow[\text{dry ether}/\Delta]{Na}$



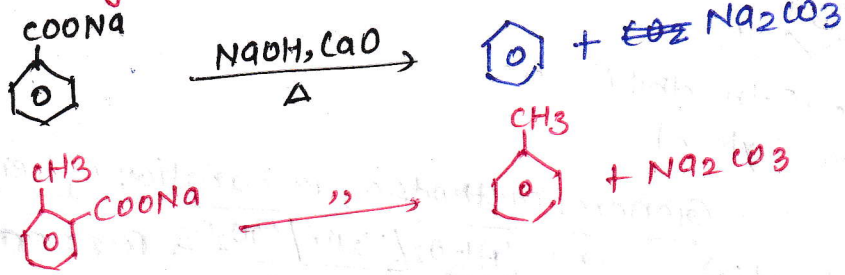
(iv) Phenol (by Reductio) (deoxygenation)



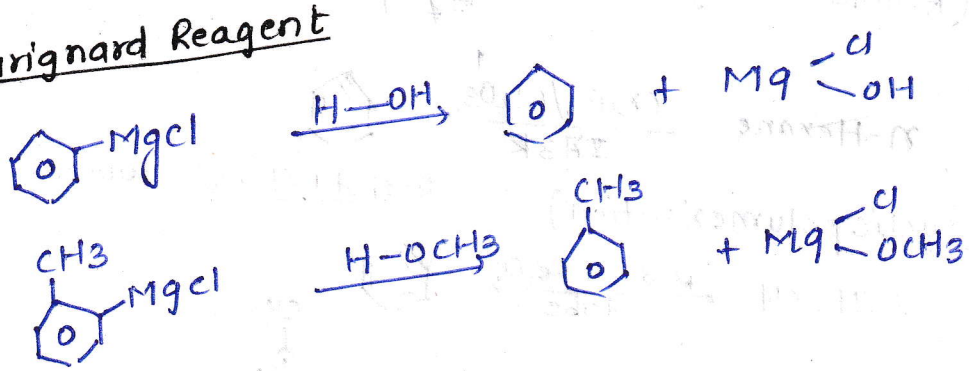
(v) From aldehyde/ketone (By Reduction) → Acidic → clemmensen Rdn
→ Basic → Wolf-kishner Rdn



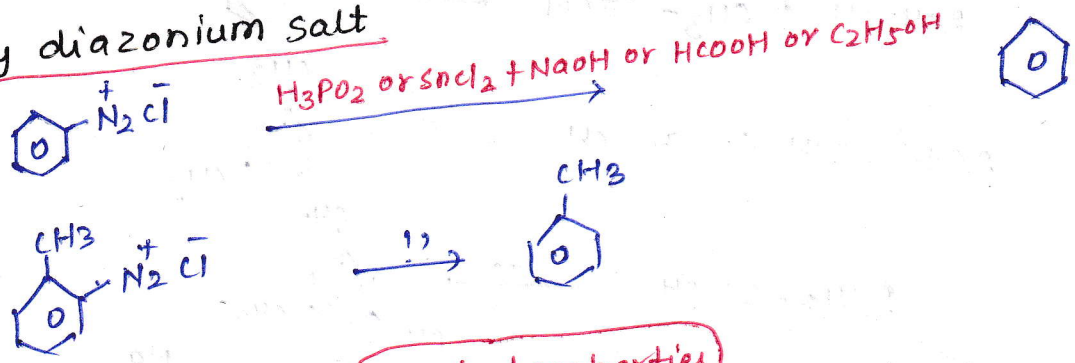
(vi) Carboxylic acid (By decarboxylation)



(vii) Grignard Reagent



(viii) By diazonium salt

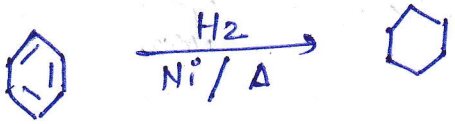


Physical properties

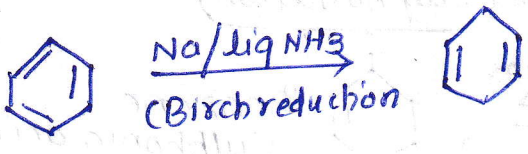
- Benzene → colorless liq.
- Insoluble in H_2O & density is less than water.
- It is used as a solvent.
- Burns with smoky (sooty) flame.

Addition of H_2

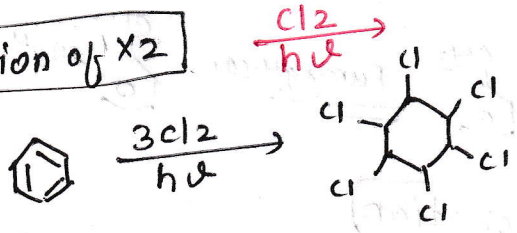
Complete hydrogenation



Partial hydrogenation

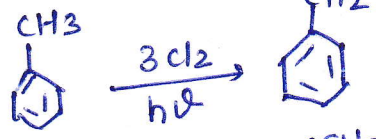


Addition of X_2

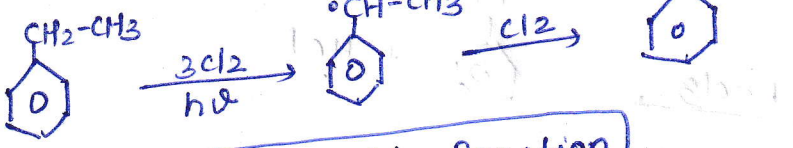


Benzene hexa chloride
BHC
666
Gammaxane
Lindane
- BHC is a powerful insecticide.
- Free radical substitution.

Qul



Qul

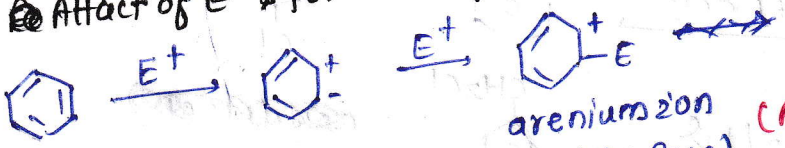


Electrophilic Substitution Reaction

Catalyst → $E^{\oplus} + Nu^{\ominus}$

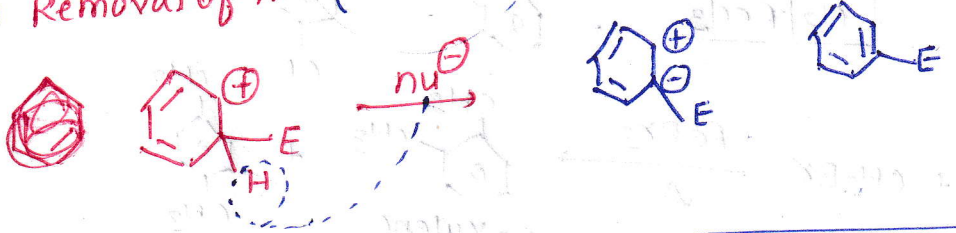
Step 1 Generation of electrophile :- E — Nu

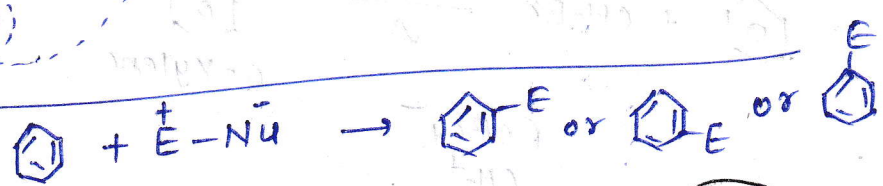
Step 2 Attact of E^+ & formation of carbocation.



arenium ion (Stable by Reso) (Aromaticity is lost)

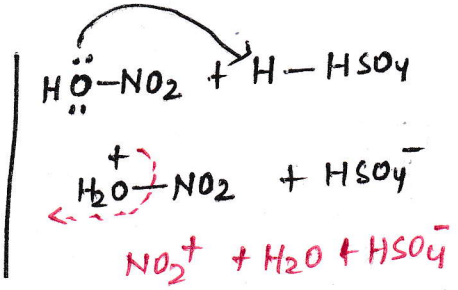
Step 3 Removal of H^+ (To restore aromaticity)

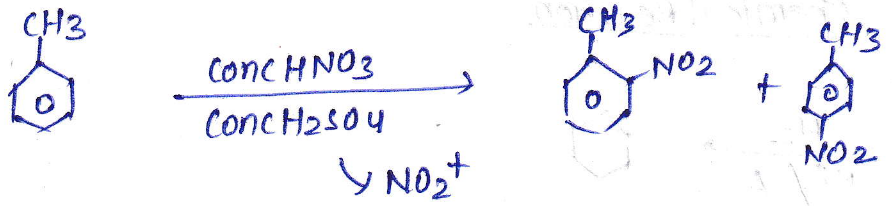


Overall 

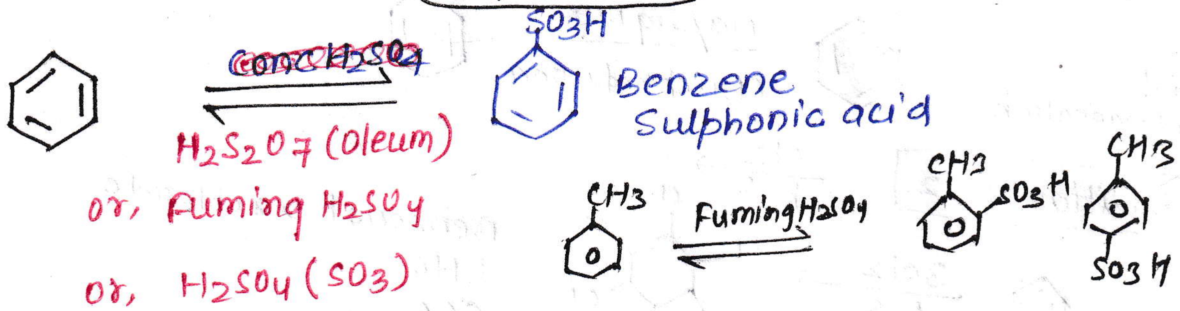
nitration

nitrating mixture → Electrophile → NO_2^+

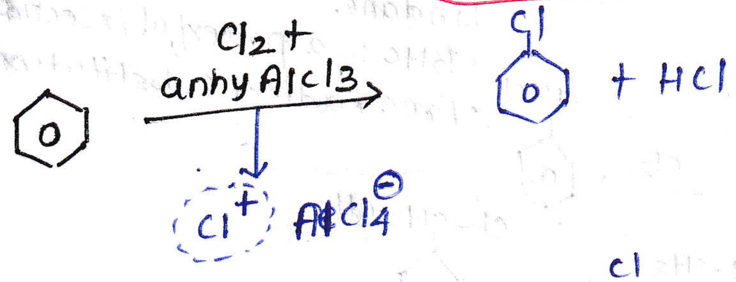


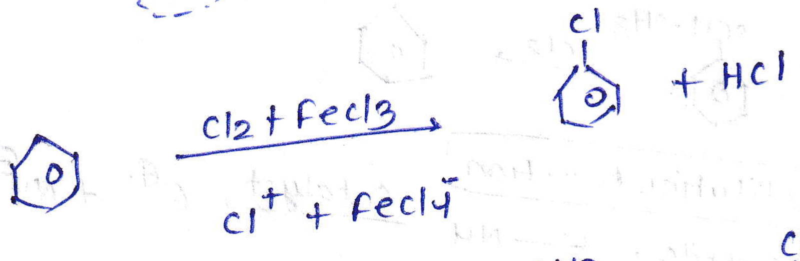


Sulphonation



Halogenation





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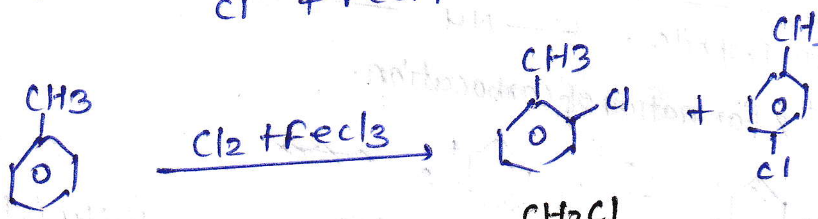
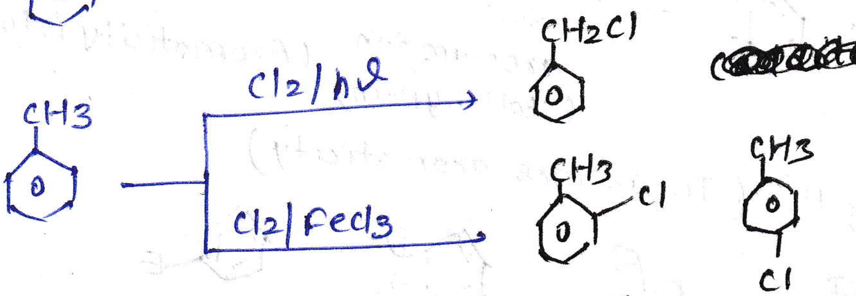
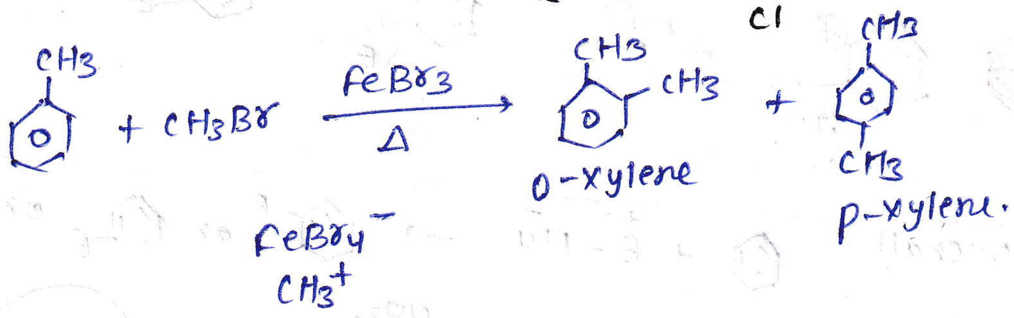


Que

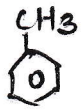


Que

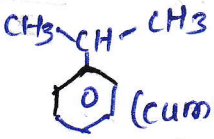


Friedal craft rxn

① Alkylation

①  + CH_3Cl $\xrightarrow{anhy\ AlCl_3}$ 

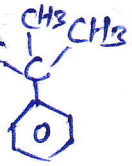
CH_3^+ $AlCl_4^-$

②  + $CH_3-CH_2-CH_2-Cl$ $\xrightarrow{AlCl_3}$  (cummene)

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

↓ Rarrangement

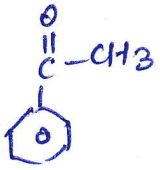
$CH_3-\overset{\oplus}{C}H-CH_3$

③  + $CH_3-\underset{CH_3}{CH}-CH_2-Cl$ $\xrightarrow{AlCl_3}$ 

$H_3C-\overset{\oplus}{C}H-CH_3$ (CH3)

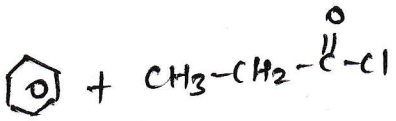
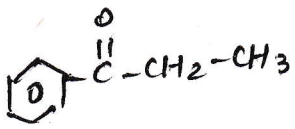
$H_3C-\overset{\oplus}{C}-CH_3$ (CH3)

Acylation

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

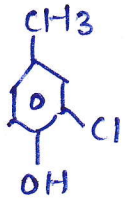
$CH_3-\overset{O}{\overset{\|}{C}}\oplus$

no rerrangement because ⊕ is stable by +M of oxygen.

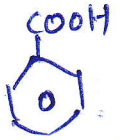
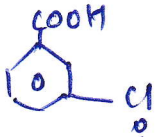
 + $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-Cl$ $\xrightarrow{AlCl_3}$ 

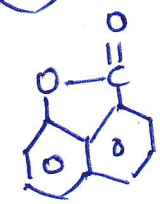
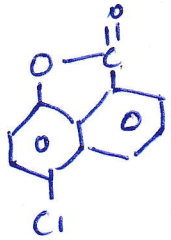
Qu. Find major product

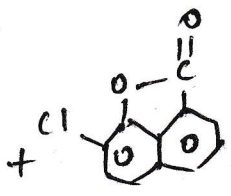
-M group, ortho/para directing

 $\xrightarrow[AlCl_3]{Cl_2}$ 

-M group, meta directing

 $\xrightarrow{''}$ 

 $\xrightarrow[FeCl_3]{Cl_2}$ 

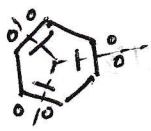
+ 

ESR & +M, +H, -I

Combustion

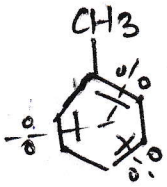
$$C_6H_6 + \frac{15}{2} O_2 \longrightarrow 6CO_2 + 3H_2O$$

Ozonolysis



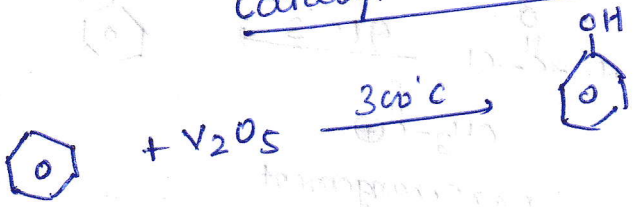
$$\xrightarrow[Zn, H_2O]{O_3} 3\left(H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H\right)$$

$$\xrightarrow[H_2O]{O_3} 3\left(HO-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OH\right)$$



$$\xrightarrow[Zn, H_2O]{O_3} 2\left(H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H\right) + H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$$

Catalytic oxidation



$$+ V_2O_5 \xrightarrow{300^\circ C}$$