Halogen Derivative :-

Mono Chloro Derivative :-

1. By halogenation of alkane (FRSR)
2. " " " alkene — EAR → MK; FRAR → AMK
3. " Halogen exchange Method — Swartz's Reac^n SN^2; Finkelstein Reac^n SN^2
4. From Alcohol
   - → with HX / Δ
   - → with PCl_5
   - → with $SOCl_2$ Darzen's Reac^n
5. From ether
6. Huns Dicker Reac^n :-

$$R-\underset{\underset{O}{\parallel}}{C}-O-Ag \xrightarrow{Br_2 / CCl_4} R-Br + CO_2 + AgBr$$

$$R-\underset{\underset{O}{\parallel}}{C}-O-Ag \xrightarrow{Cl_2 / CCl_4} R-Cl + CO_2 + AgCl$$

$$R-\underset{\underset{O}{\parallel}}{C}-O-Ag \xrightarrow{I_2 / CCl_4} R-\underset{\underset{O}{\parallel}}{C}-O-R + AgI$$

Mech : $R-\underset{\underset{O}{\parallel}}{C}-O-Ag \xrightarrow{X_2 / CCl_4} R-\underset{\underset{O}{\parallel}}{C}-O^{\bullet} + X^{\bullet} + AgX$ ($Br^{\bullet}$, $Cl^{\bullet}$, $I^{\bullet}$ ⇌ I_2)

$$\downarrow$$

$$R^{\bullet} + CO_2$$

$R^{\bullet} \xrightarrow{Br_2} R-Br$

$R^{\bullet} \xrightarrow{Cl_2} R-Cl$

$\xrightarrow{I_2} R-\underset{\underset{O}{\parallel}}{C}-O-R$

$$CH_3-CH_2-COOH \xrightarrow[T.R.]{NH_4OH + AgNO_3} CH_3-CH_2-\underset{\underset{O}{\parallel}}{C}-O.Ag \xrightarrow{Br_2/CCl_4} CH_3-CH_2-Br$$

From Tildane :-

$$\underset{1^{\circ}}{R}-NH_2 \xrightarrow{NOCl} R-Cl + N_2 + H_2O$$

(N N, H_2 O Cl circled)

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III) $CH_3-CH_2-NH_2 \xrightarrow{NOCl} CH_3-CH_2-Cl + N_2 + H_2O$

Physical Property :-

State : CH_3F, CH_3-Cl, CH_3-Br] Gas
C_2H_5F, C_2H_5-Cl
upto C11 → liq.
higher → solid

Density $R-I > R-Br > \underbrace{R-Cl > R-F}_{> H_2O >}$

B.P. B.P. $\propto$ Mw. $\propto \frac{1}{\text{Branching}}$

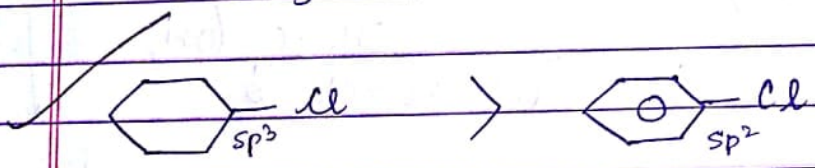
$R-I > R-Br > R-Cl > R-F$

B.P. $R-OH > \overset{\delta+}{R}-\overset{\delta-}{X} > R-H$
H-bonding ↓ due to Polar bond

Polarity $RF > RCl > R-Br > R-I$

Dipole Moment : $R-Cl > R-F > R-Br > R-I$
$CH_3Cl > CH_3F > CH_3Br > CH_3I$

$C_{sp^3} < C_{sp^2}$ EN
2.5 2.75



$\Delta EN \uparrow$ $\Delta EN \downarrow$

Test for Halides :

$R-X \xrightarrow[\text{Beilstein Test}]{\text{Cu-wire}}$ green Flame

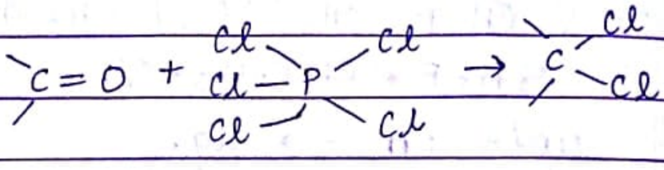
Chemical Reac^n

① NSR
② Dehydrohalogenation Clemenson] GOC II
③ Wurtz Reac → alkanes

Dihalide :-

General Method of Preparation :-

1. From alkane FR SR
2. From alkene EAR X_2/CCl_4
3. From Alkyne $\frac{EAR}{FRAR}$
4. from carbony sub.



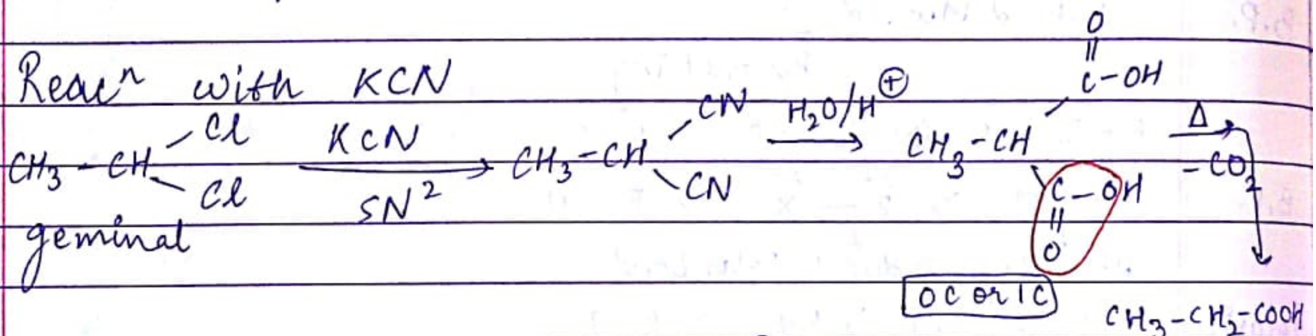
Chemical Properties :-

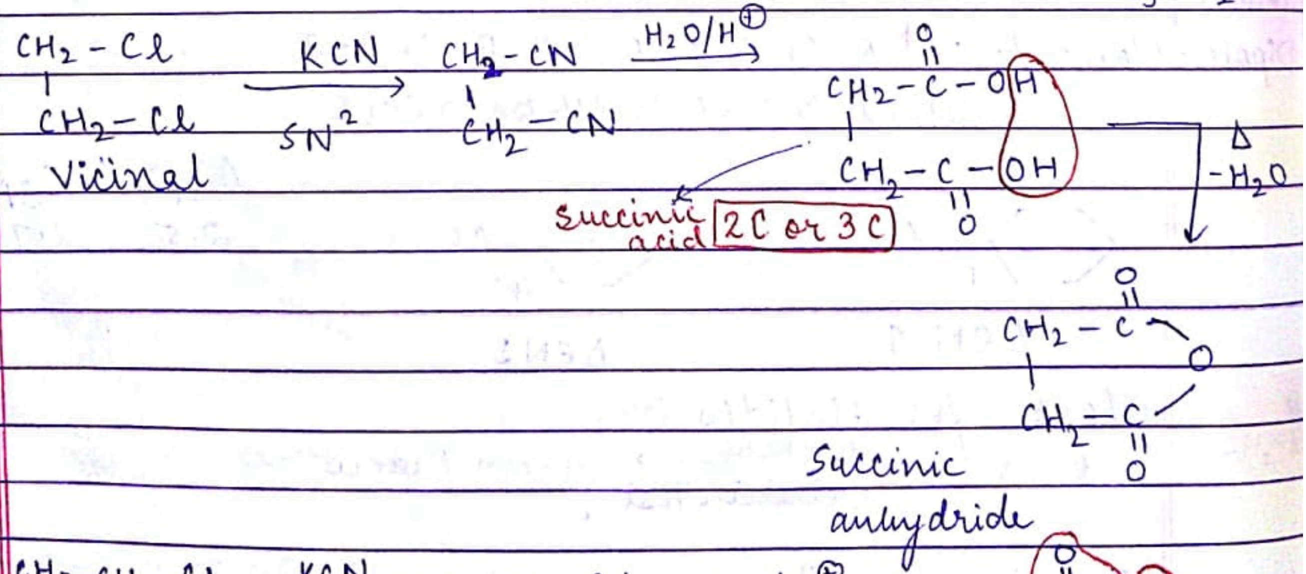
① Reacⁿ with aq KOH SN^2

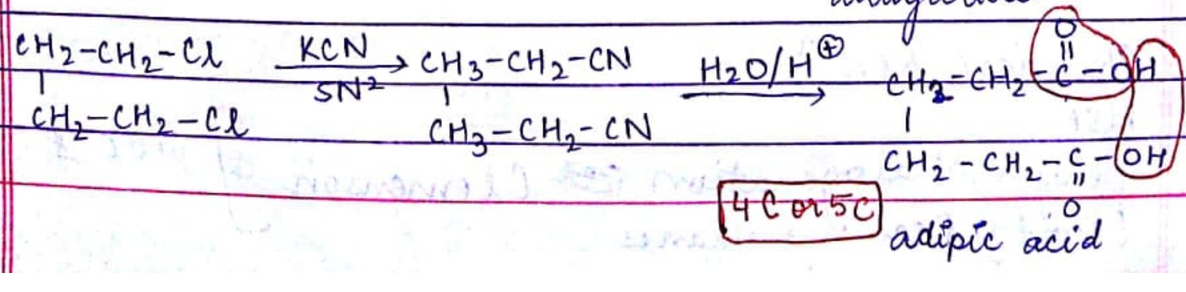
② Reacⁿ with alc. KOH → Elimination

③ with Zn/Δ → α elimination

Reacⁿ with KCN







Dihalide :-

General Method of Preparation :-

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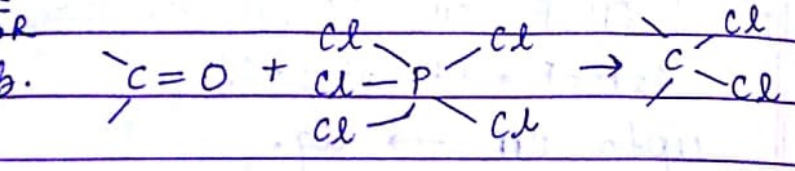
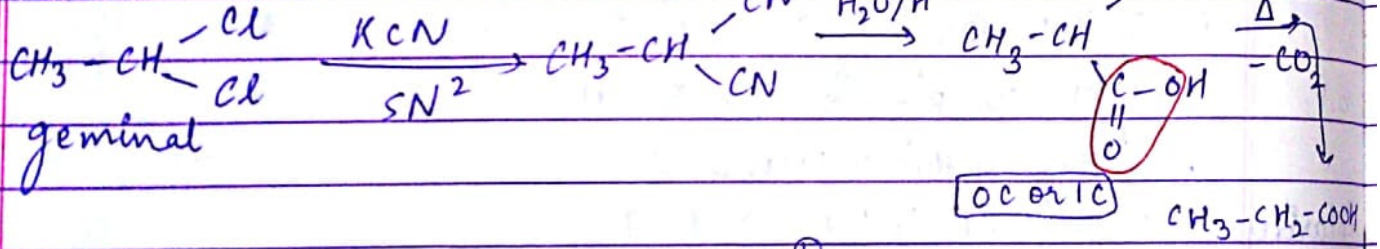
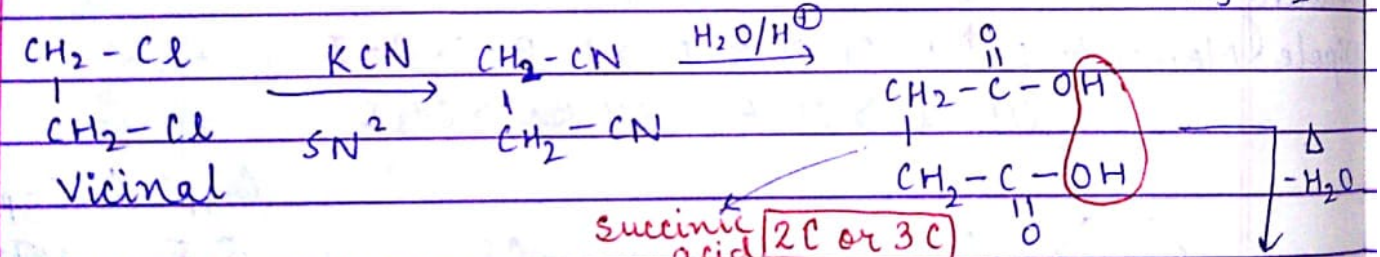
4. from carbonyl sub. 

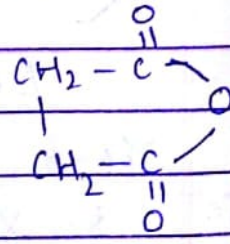
Chemical Properties :-

(1) Reac^n with aq KOH SN^2
(2) Reac^n with alc. KOH → Elimination
(3) with Zn/Δ → α elimination

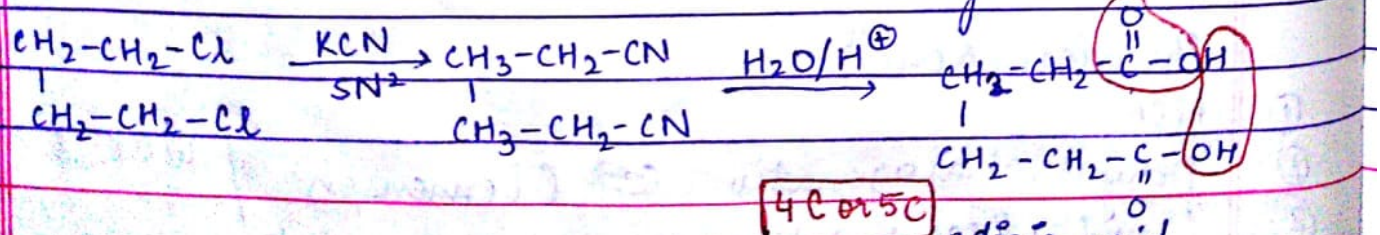
Reac^n with KCN







Succinic anhydride



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$\xrightarrow{\Delta}$ ($-CO_2$, $-H_2O$) CH_2-CH_2 with $C=O$ bridging CH_2-CH_2 — cyclo Pentanone

Note: ① When OCOrIC is +nt b/w 2 COOH gp then on heating it gives CO_2 to form mono carboxylic acid

② When 2C or 3C is +nt b/w 2 COOH gp then on heating it give H_2O to form. anhydride

③ When 4C or 5C is +nt b/w 2 COOH gp then on heating it give $-CO_2$ & H_2O to form cyclo ketone.

Trihalides :-

Chloroform :-

General Method of Preparation :-

① From Methane

$$CH_4 + 3Cl_2 \xrightarrow{h\nu} CHCl_3 + 3HCl$$

② Haloform Reac^n :-

$R-\underset{\underset{O}{\|}}{C}-CH_3$ or $R-\underset{\underset{OH}{|}}{CH}-CH_3$ $\xrightarrow[\text{eg } I_2/NaOH,\ Cl_2/KOH,\ I_2/KOH,\ I_2/Na_2CO_3,\ I_2/Ca(OH)_2]{X_2/\text{alkali}}$ $CHX_3 + R-\underset{\underset{O}{\|}}{C}-O^{\ominus}Na^{\oplus} + NaX + H_2O$

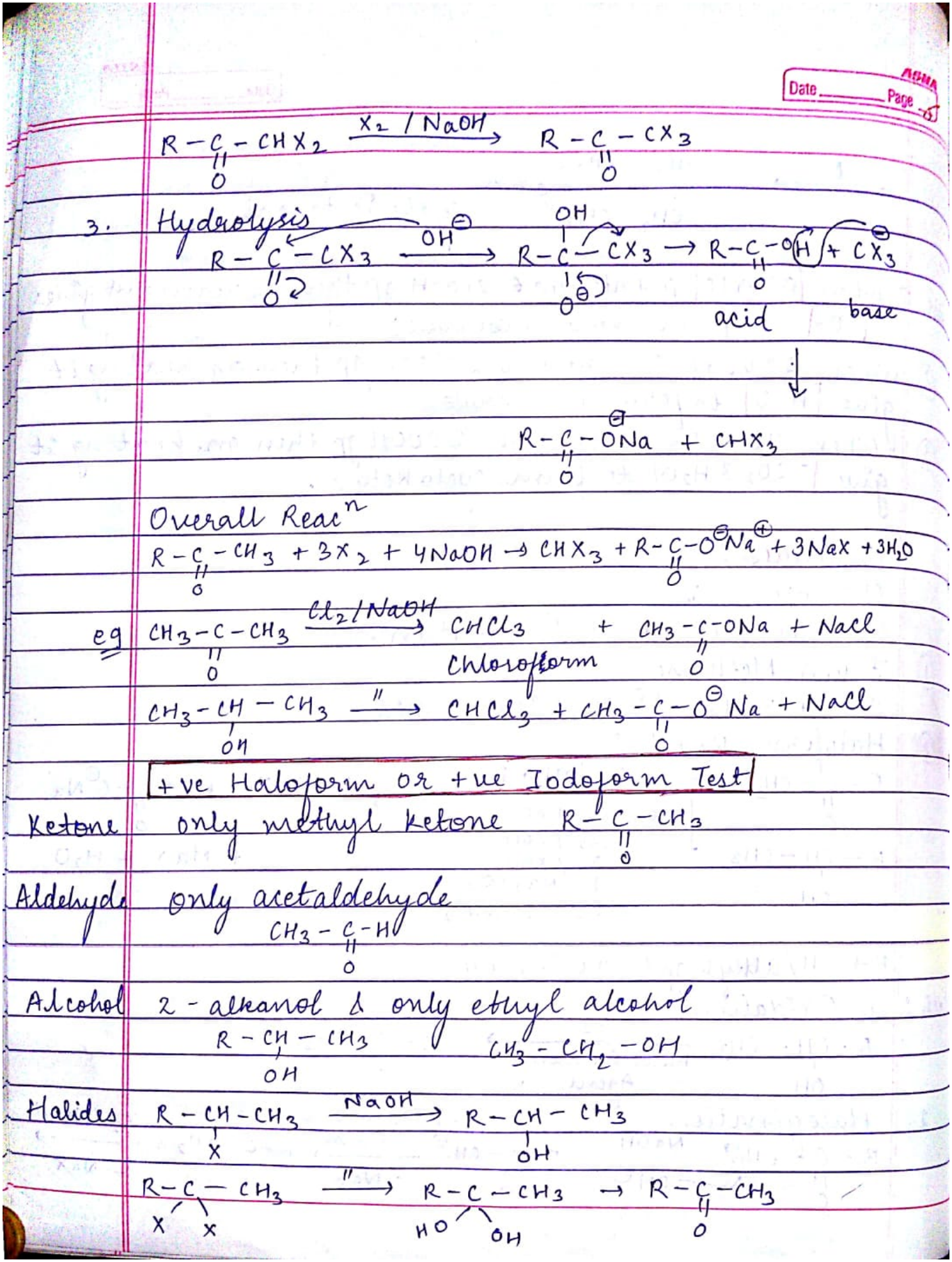
R → -H / alkyl gp / -CHO / -COOH

Mech: 1. Oxidation

$R-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow[\text{Mild Oxidising Agent}]{X_2} R-\underset{\underset{O}{\|}}{C}-CH_3$

2. Halogenation

$R-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{NaOH} R-\underset{\underset{O}{\|}}{C}-CH_2^{\ominus}$ ($OH^{\ominus}$) $\xrightarrow[-NaX]{X-X} R-\underset{\underset{O}{\|}}{C}-CH_2X \xrightarrow[-NaX]{X_2/NaOH}$



$X_2 \rightarrow OBr^{\ominus}$

−ve Haloform or −ve Iodoform Test :-

$CH_3 - \overset{O}{\overset{||}{C}} - \ddot{Z}$ (Reso) — $\ddot{Z} \rightarrow \ddot{N}H_2, -\ddot{N}H-\overset{O}{\overset{||}{C}}-R, -\ddot{O}R, -\ddot{O}H, -\ddot{X}:$

acidic H(↓) only lp conj.

Idoform test :-

$R-\overset{O}{\overset{||}{C}}-CH_3$ or $R-\underset{OH}{\underset{|}{CH}}-CH_3$ $\xrightarrow[\text{or } I_2/NaOH,\ I_2/KOH,\ I_2/Na_2CO_3,\ I_2/Ba(OH)_2]{I_2/\text{alkali}}$ $CHI_3 + R-\overset{O}{\overset{||}{C}}-O^{\ominus}Na + NaI + H_2O$

Idoform Yellow V.D. = 197

R = −H / alkylgp / −CHO / −COOH

which of the following will give +ve Idoform Test?

1. CH_3-CHO ✓
2. Propanal ×
3. Formaldehyde HCHO ×
4. acetone $CH_3-\overset{O}{\overset{||}{C}}-CH_3$ ✓
5. 3-Pentanone ×
6. benzaldehyde ×
7. acetophenone $C_6H_5-\overset{O}{\overset{||}{C}}-C$
8. 2-butanol ✓
9. Benzoic acid ×
10. acetic acid CH_3-COOH −ve
11. acetamide
12. $CH_3-\overset{O}{\overset{||}{C}}-CH_2-CH_3$ ✓
13. $CH_3-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-CH_3$ ×
14. $CH_3-C(Cl)(Cl)-CH_3$ ✓
15. CH_3-CH_2-OH ✓
16. $CH_3-CH_2-CH_2-OH$ ×
17. CH_3-CH_2-Cl ✓
18. $CH_3-\overset{O}{\overset{||}{C}}-\ddot{O}-C_2H_5$ ×
19. $CH_3-\overset{O}{\overset{||}{C}}-CH_2-\overset{O}{\overset{||}{C}}-\ddot{O}-C_2H_5$ (Most acidic H at CH_2) ×
20. $CH_3-\overset{O}{\overset{||}{C}}-CHO$ ✓
21. $CH_3-\overset{O}{\overset{||}{C}}-COOH$ ✓
22. CH_2I-CHO ✓

By Haloform Reacⁿ [By lab. Method] :-

CH_3-CH_2-OH or $CH_3-\underset{\underset{O}{\|}}{C}-CH_3$ $\xrightarrow[CaOCl_2 \; H_2O/\Delta]{\text{Bleaching Powder}}$ $CHCl_3 +$ $(HCOO)_2Ca$ or $(CH_3COO)_2Ca$

Mech: $CaOCl_2 + H_2O \longrightarrow Cl_2 + Ca(OH)_2$

$CH_3-CH_2-OH + Cl_2 \longrightarrow CH_3-CHO$ Oxidation

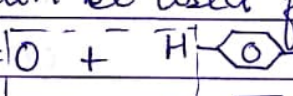
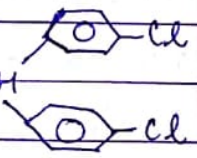
$CH_3-CHO + Cl_2 \xrightarrow{Ca(OH)_2} CCl_3-CHO + CaCl_2$ (Halogenation)

$Cl_3C-CHO \xrightarrow{Ca(OH)_2} CHCl_3 + (HCOO)_2Ca$ Hyrolysis

(3) Prep. of Pure chloroform from Chloral hydrate

$CCl_3-CHO \cdot 2H_2O \xrightarrow[\Delta]{NaOH} CHCl_3 + HCOONa + H_2O$

Chloral can be used for prep. of DDT

$Cl_3C-CH=O$ +  $\xrightarrow[-H_2O]{conc.\,H_2SO_4}$ 

Dichloro Diphenyl Trichloro ethane (DDT)

Physical Properties :-

1. $CHCl_3$ is colourless & sweet smelling liquid.
2. B.P. → 61°C
3. Insoluble in water but soluble in non-polar solvents
4. $CHCl_3$ has higher density than water
5. used as anaesthetic.

Chemical Properties :-

1. Oxidation : $CHCl_3 + [O] \xrightarrow{light} COCl_2 + HCl$

Phosgene gas or Carbonyl chloride (Poisonous gas)

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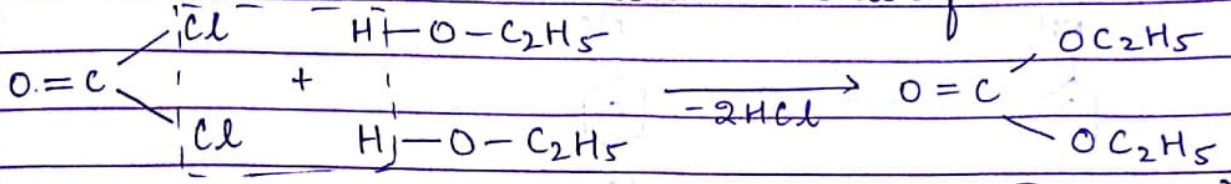
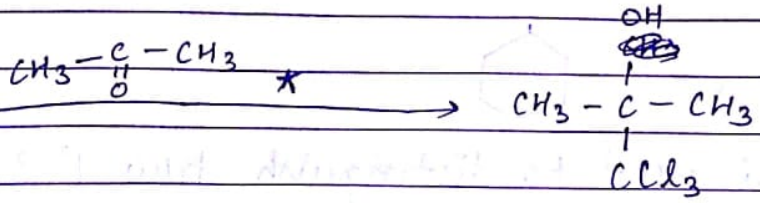
$CHCl_3$ is stored in dark coloured bottles which are filled upto brim to prevent oxidation of $CHCl_3$ into $COCl_2$ & 1% ethanol is also added to chloroform.



(non Poisonous)



Chloritone (Hyptonic)

$CHCl_3 \xrightarrow[HNO_2]{HO-NO_2} O_2N-CCl_3$

Chloropicrin or nitrochloroform (Tear gas) World war II

$\dot{C}Cl_3 \xrightarrow[\text{Peroxide}]{CH_3-CH=CH_2} CH_3-CH_2-CH_2-CCl_3$

$\xrightarrow{6Ag} HC \equiv CH$

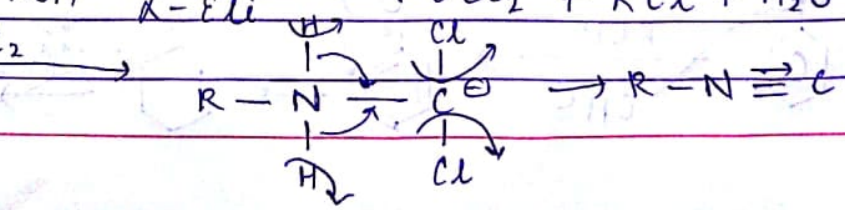
Hoffmann Carbelamide test

Only Primary amine $\xrightarrow{CHCl_3/aq\ KOH}$ Isocyanide (suffocating odour)

iso cyanide Test.

$R-\underset{1^\circ}{NH_2} \xrightarrow{CHCl_3/aq\ KOH} R-N\equiv C$ Isocyanide

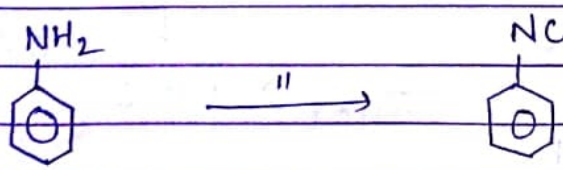
Mech: $CHCl_3 + KOH \xrightarrow{\alpha\text{-Eli}} :CCl_2 + KCl + H_2O$

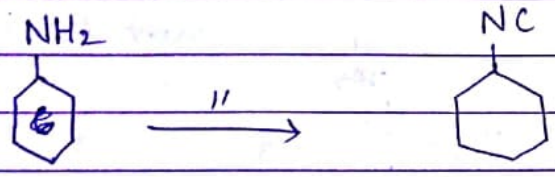


$CH_3-CH_2-NH_2 \xrightarrow{CHCl_3 / aq.\ KOH} CH_3-CH_2-NC$

$CH_3-CH_2-NC \xrightarrow{LiAlH_4/H^+} CH_3-CH_2-NH-CH_3$

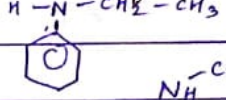
$CH_3-CH_2-NC \xrightarrow{H_2O/H^+} CH_3-CH_2-NH_2 + H-\underset{\underset{O}{\|}}{C}-OH$

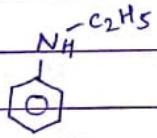


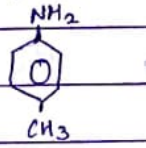


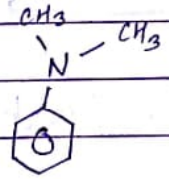
This test is used to distinguish b/w 1° & 2°/3° amines

Ques = Which of the following will give +ve isocyanide test with chloroform in aq. KOH ?

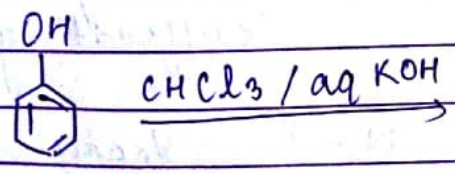
① Acetanilide 

② N-ethylaniline 

③ P-toulidine 

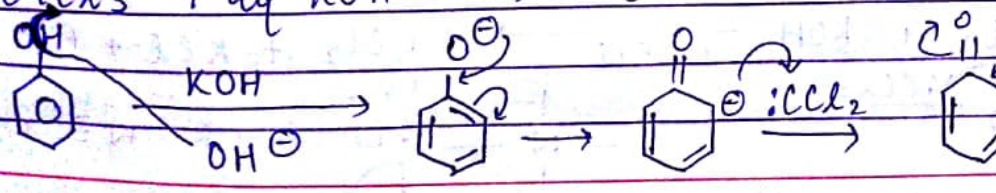
④ N,N-dimethyl aniline 

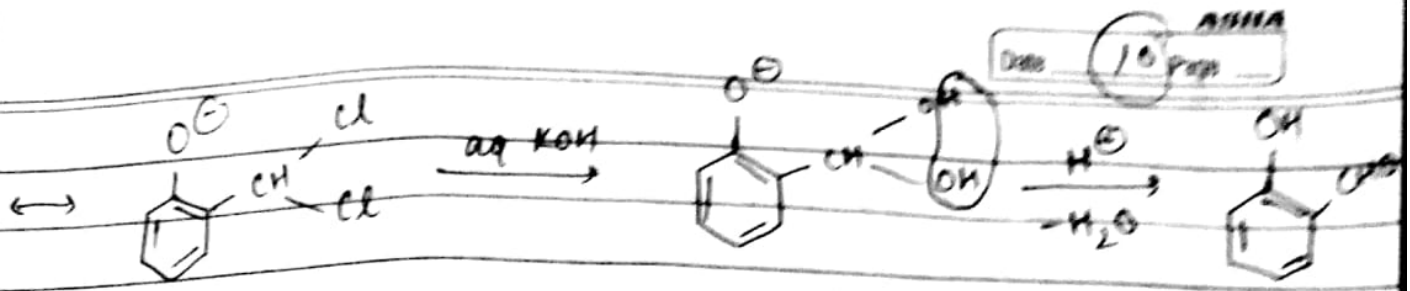
Rie Reimer Tiemann Reac^n :-

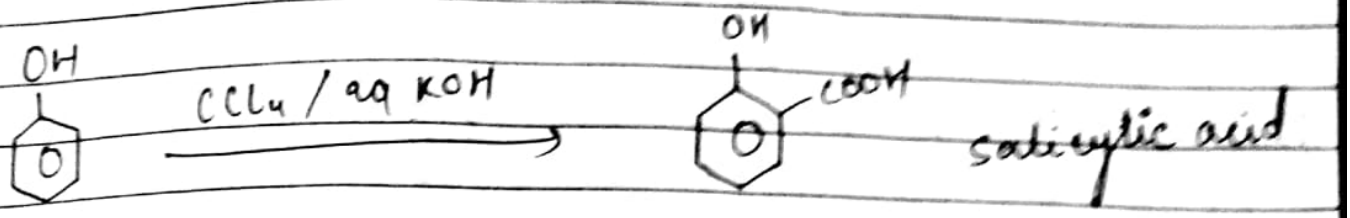


Salialdehyde

Mech $CHCl_3 + aq\ KOH \longrightarrow :CCl_2$







salicylic acid

Test of $CHCl_3$

Reagent	Pure $CHCl_3$	Impure $CHCl_3$ ($COCl_2 + HCl$)
Blue litmus	X	turns into red
*$AgNO_3$	X	white ppt of AgCl
conc H_2SO_4	X	Yellow soln

Tetrahalo Derivative :-

$CH_4 \xrightarrow[\text{excess}]{Cl_2 / hv} CCl_4 + HCl$

Freons : CF_2Cl_2 dichloro difluoro methane

Freon (0, 1, 2)

$C_aH_bF_cCl \rightarrow$ Freon $(a-1, b+1, c)$

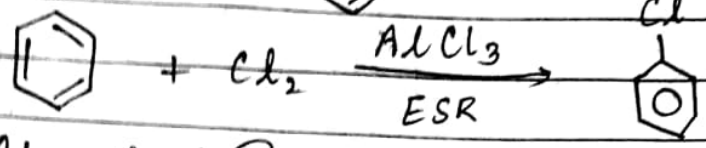
$C_2F_2Cl_4$ Freon (1, 1, 2)

Freon (1, 1, 3) $C_2F_3Cl_3$

Freons are used in refrigerants.

Freons are harmful on ozone layer.

Haloarenes :-

Prep : 

Chemical Properties :-

1. NSR → Revise from GIOC - II
2. Wurtz Fittig → Revise from GIOC - II
3. ESR :  → +M o/p director