Halogen Derivative :-

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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. Hunsdicker Reac^n :-

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

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

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

Mech :

$$R-\underset{\underset{O}{\|}}{C}-O-Ag \xrightarrow{X_2/CCl_4} R\overset{\cdot}{-}\underset{\underset{O}{\|}}{\overset{\cdot}{C}}-O\cdot + X\cdot + AgX$$

$X\cdot$: $Br\cdot$ $Cl\cdot$ $I\cdot$ → I_2

$R\cdot + CO_2$ ← Br_2 → $R-Br$

$R\cdot + CO_2$ ← Cl_2 → $R-Cl$

$R\cdot + CO_2$ ← I_2 → $R-\underset{\underset{O}{\|}}{C}-O-R$

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

From Tildane :-

$$R-\underset{1^\circ}{\overset{N}{\overset{N}{(}}}\overset{H_2}{\overset{O}{)}}Cl \xrightarrow{NOCl} R-Cl + N_2 + H_2O$$

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

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 $R-I > R-Br > R-Cl > R-F$
$> H_2O >$

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

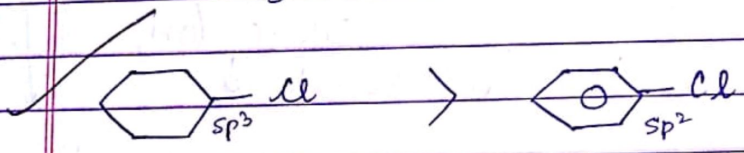
$R-I > R-Br > R-Cl > R-F$

B.P. $R-OH > R^{\delta+}-X^{\delta-} > R-H$
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



ΔEN ↑ ΔEN ↓

Test for Halides :

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

Chemical Reac^n

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

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Dihalide :-

General Method of Preparation :-

1. From alkane FR^1SR
2. From alkene EAR X_2/CCl_4
3. From Alkyne $\frac{EAR}{FRAR}$
4. from carbonyl sub. $>C=O + Cl-P(Cl)(Cl)Cl \rightarrow >C(Cl)Cl$

Chemical Properties :-

(1) Reaⁿ with aq KOH SN^2

(2) Reaⁿ with alc. KOH → Elimination

(3) with Zn/Δ → α elimination

Reaⁿ with KCN

$CH_3-CH(Cl)-Cl$ (geminal) $\xrightarrow[SN^2]{KCN} CH_3-CH(CN)-CN \xrightarrow{H_2O/H^\oplus} CH_3-CH(C(=O)-OH)-C(=O)-OH \xrightarrow[-CO_2]{\Delta} CH_3-CH_2-COOH$

OC or IC

$CH_2(Cl)-CH_2-Cl$ (vicinal) $\xrightarrow[SN^2]{KCN} CH_2(CN)-CH_2-CN \xrightarrow{H_2O/H^\oplus} CH_2(C(=O)-OH)-CH_2-C(=O)-OH \xrightarrow[-H_2O]{\Delta}$ Succinic anhydride

Succinic acid — 2C or 3C

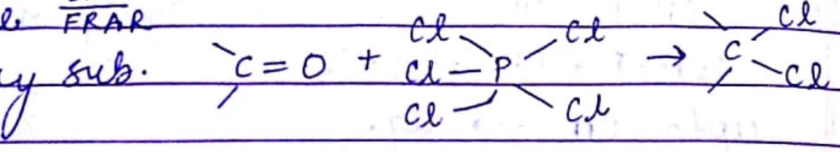
$CH_2(Cl)-CH_2-Cl$ $\xrightarrow[SN^2]{KCN} CH_2(CN)-CH_2-CN \xrightarrow{H_2O/H^\oplus} CH_2(C(=O)-OH)-CH_2-C(=O)-OH$

4C or 5C — adipic acid

Dihalide :-

General Method of Preparation :-

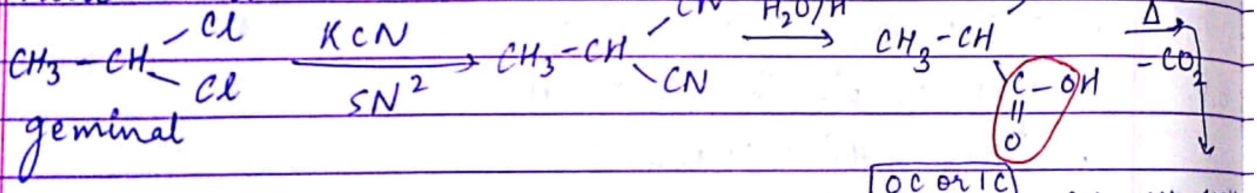
1. From alkane FR SR
2. From alkene EAR X_2/CCl_4
3. From Alkyne $\frac{EAR}{FRAR}$
4. from carboxy sub.



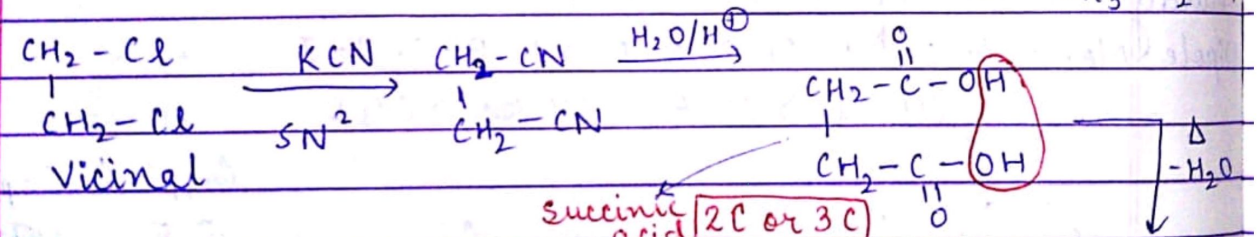
Chemical Properties :-

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

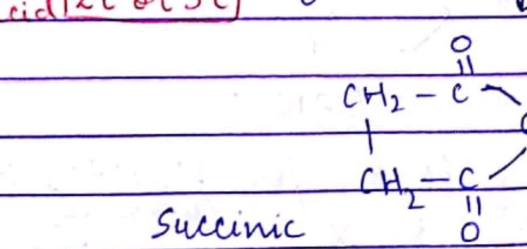
Reaⁿ with KCN



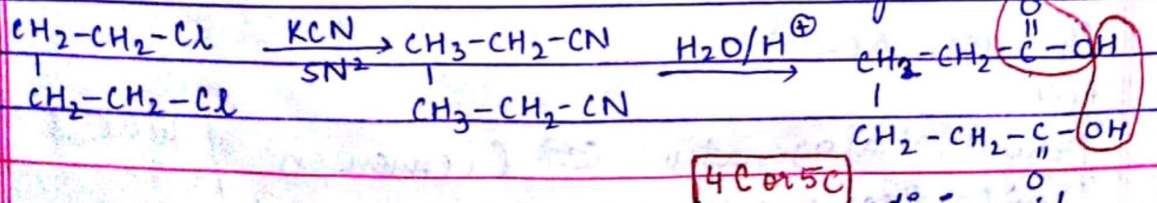
geminal



Vicinal



Succinic anhydride



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$\xrightarrow{\Delta}$ $-CO_2$ $-H_2O$ CH_2-CH_2, CH_2-CH_2, $C=O$ cyclo Pentanone

Note: ① When OC or IC 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 $R-\underset{\underset{OH}{|}}{CH}-CH_3$ $\xrightarrow[\text{eg } I_2/NaOH,\ Cl_2/KOH,\ I_2/KOH,\ I_2/Na_2CO_3,\ I_2/Ca(OH)_2]{X_2/\text{alkali}}$ $CHX_3 + R-\underset{\underset{O}{\|}}{C}-O^{\ominus}Na^{\oplus} + NaX + H_2O$

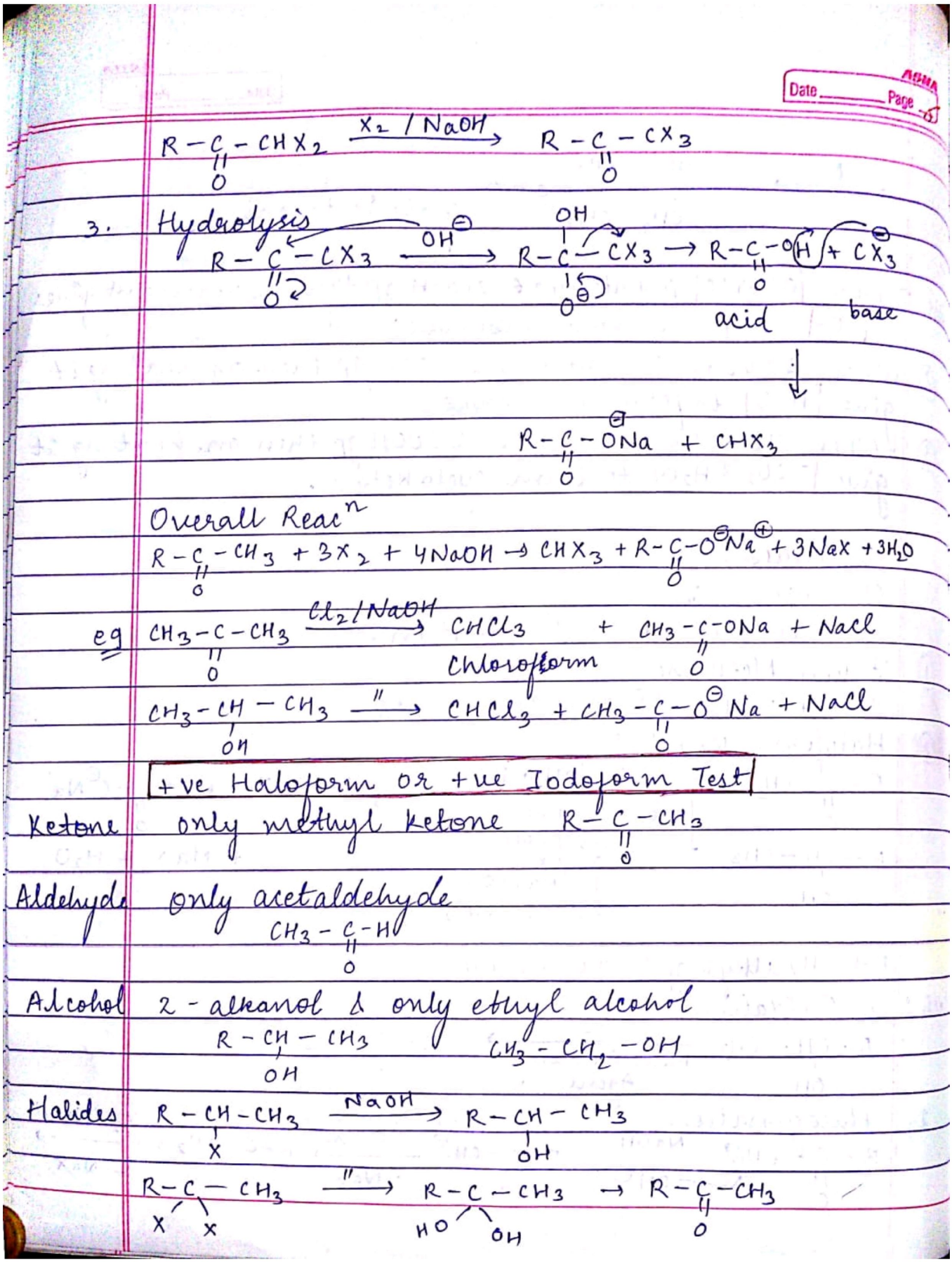
$R \rightarrow -H$ / alkyl gp / $-CHO$ / $-COOH$

Meth: 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

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



$X_2 \rightarrow OBr^{\ominus}$

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-Ve Haloform or -ve Iodoform Test :-

$CH_3-\overset{\overset{O}{\|}}{C}-\ddot{Z}$ ↔ (Reso) ; acidic H(↓) ; only lp conj.

$\ddot{Z} \rightarrow \ddot{N}H_2, -\ddot{N}H-\overset{\overset{O}{\|}}{C}-R, -\ddot{O}R, -\ddot{O}H, -\ddot{X}:$

Idoform test :-

$R-\overset{\overset{O}{\|}}{C}-CH_3$ or $R-\underset{OH}{\underset{|}{CH}}-CH_3$ $\xrightarrow[\text{or}]{I_2/\text{alkali}}$ $CHI_3 + R-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{O}Na +$

$I_2/NaOH$, I_2/KOH, I_2/Na_2CO_3, $I_2/Ba(OH)_2$

Idoform ; Yellow ; V.D. = 197 ; $NaI + H_2O$

R = -H / alkyl gp / -CHO / -COOH

Which of the following will give +ve Idoform Test?

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

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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

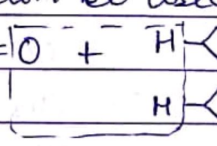
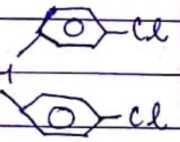
$CH_3-CHO + Cl_2 \xrightarrow{Ca(OH)_2} CCl_3-CHO + CaCl_2$ (Halogenation)

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

(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

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

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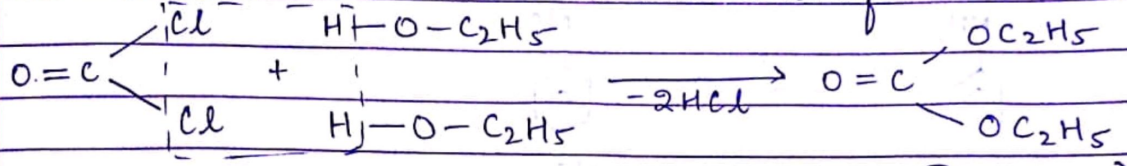
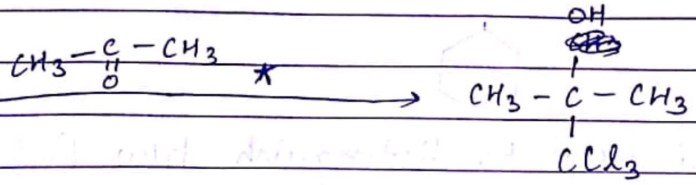
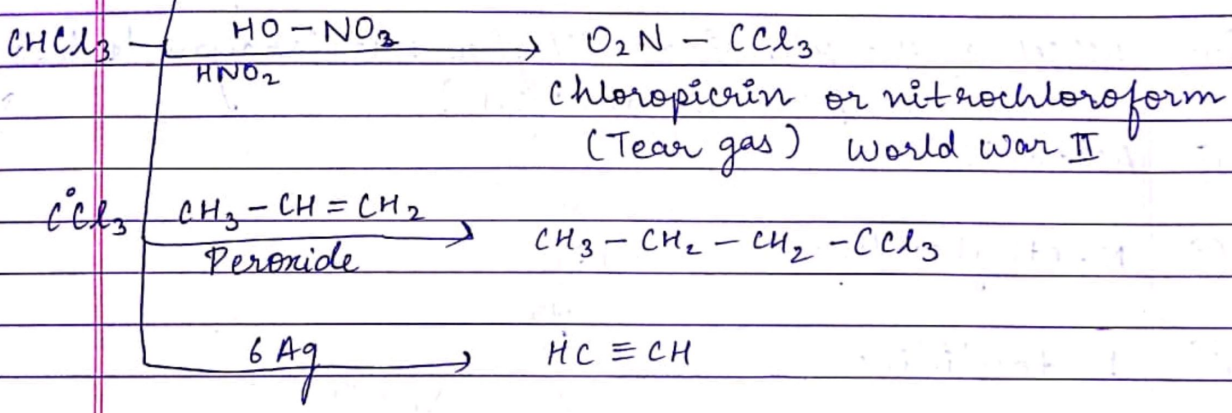
$CHCl_3$ is stored in dark coloured bottles which are filled upto brim to prevent oxidation of $CHCl_3$ into $COCl_2$ & 1% ethanol is also added to chloroform.



(non Poisonous)



Chloritone (Hyptonic)



Chloropicrin or nitrochloroform (Tear gas) World War II

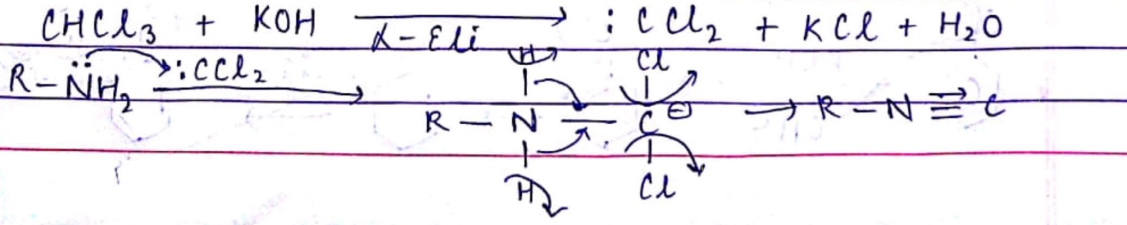
Hoffmann Carbelamide test

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

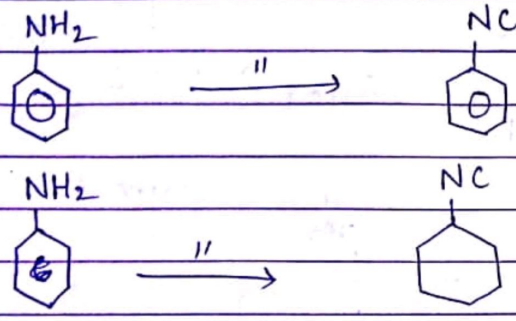
Mech:



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

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

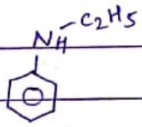
$CH_3-CH_2-NC \xrightarrow{H_2O/H^+} CH_3-CH_2-NH_2 + H-\underset{\underset{O}{\|}}{C}-OH$

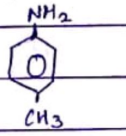


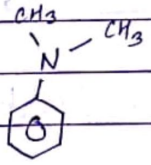
This test is used to distinguish b/w 1° & 2°/3° amines

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

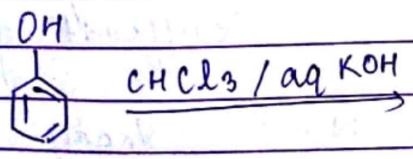
① Acetanilide 

② N-ethylaniline 

③ P-toulidine 

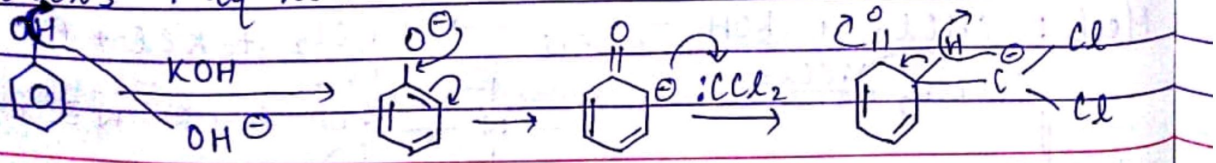
④ N,N-dimethyl aniline 

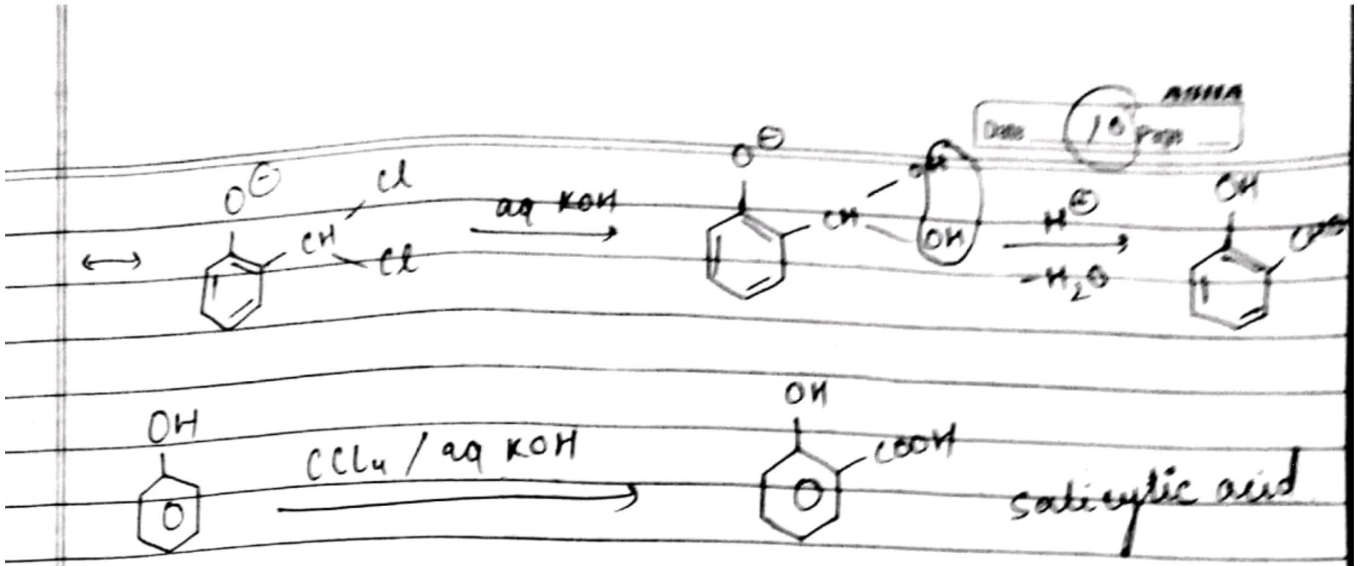
~~Ric~~ Reimer Tiemann Reac^n :-



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 to ozone layer.

Haloarenes :-