Handwritten Notes

On

Halogen Derivative

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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. 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 :

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

$X^{\cdot}$: $Br^{\cdot}$ $Cl^{\cdot}$ $I^{\cdot} \rightarrow I_2$

$R\cdot$ + $\underset{\underset{O}{\|}}{C}-O^{\cdot}$ → $R' + CO_2$

$R' \xleftarrow{Br_2} R-Br$

$R' \xleftarrow{Cl_2} R-Cl$

$R' \xleftarrow{I_2} R-\underset{\underset{O}{\|}}{C}-O-R$

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

From Tildane :-

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

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1st $CH_3-CH_2-NH_2 \xrightarrow{NOCl} CH_3-CH_2-Cl + N_2 + H_2O$

Physical Property :-

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

Density $R-I > R-Br > R-Cl > R-F$
($> H_2O >$)

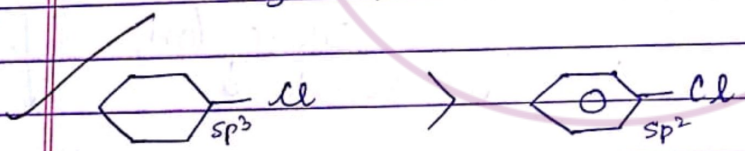
B.P. B.P. $\propto$ Mw. $\propto \frac{1}{\text{Branching}}$

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

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



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

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

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

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

1C or 1C

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

Succinic acid 2C or 3C

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

4C or 5C adipic acid

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Dihalide :-

General Method of Preparation :-

1. From alkane FR SR
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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 ~~Re~~ Reaⁿ with alc. KOH → Elimination

③ with Zn / Δ → α elimination

Reaⁿ with KCN

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

OC or TC

$CH_2(Cl)-CH_2(Cl)$ (Vicinal) $\xrightarrow[SN^2]{KCN} CH_2(CN)-CH_2(CN) \xrightarrow{H_2O/H^\oplus} CH_2(C(=O)-OH)-CH_2(C(=O)-OH)$ (Succinic acid) 2C or 3C $\xrightarrow{\Delta} -H_2O$ Succinic anhydride

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

4C or 5C

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$\xrightarrow[-CO_2 \\ -H_2O]{\Delta}$ CH_2-CH_2 (C=O) CH_2-CH_2 — Cyclo Pentanone

Note: ① When OCOR/C 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

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

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$R-\underset{\underset{O}{\|}}{C}-CHX_2 \xrightarrow{X_2 / NaOH} R-\underset{\underset{O}{\|}}{C}-CX_3$

3. Hydrolysis

$R-\underset{\underset{O}{\|}}{C}-CX_3 \xrightarrow{OH^{\ominus}} R-\underset{\underset{O^{\ominus}}{|}}{\overset{\overset{OH}{|}}{C}}-CX_3 \rightarrow R-\underset{\underset{O}{\|}}{C}-OH + CX_3^{\ominus}$

acid base

$\downarrow$

$R-\underset{\underset{O}{\|}}{C}-O^{\ominus}Na + CHX_3$

Overall Reac^{n}

$R-\underset{\underset{O}{\|}}{C}-CH_3 + 3X_2 + 4NaOH \rightarrow CHX_3 + R-\underset{\underset{O}{\|}}{C}-O^{\ominus}Na^{\oplus} + 3NaX + 3H_2O$

eg $CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{Cl_2/NaOH} CHCl_3$ (Chloroform) $+ CH_3-\underset{\underset{O}{\|}}{C}-ONa + NaCl$

$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{''} CHCl_3 + CH_3-\underset{\underset{O}{\|}}{C}-O^{\ominus}Na + NaCl$

+ve Haloform or +ve Iodoform Test

Ketone — only methyl ketone $R-\underset{\underset{O}{\|}}{C}-CH_3$

Aldehyde — only acetaldehyde $CH_3-\underset{\underset{O}{\|}}{C}-H$

Alcohol — 2-alkanol & only ethyl alcohol $R-\underset{\underset{OH}{|}}{CH}-CH_3$ $\quad CH_3-CH_2-OH$

Halides $R-\underset{\underset{X}{|}}{CH}-CH_3 \xrightarrow{NaOH} R-\underset{\underset{OH}{|}}{CH}-CH_3$

$R-\underset{\underset{X}{|}}{\overset{\overset{X}{|}}{C}}-CH_3 \xrightarrow{''} R-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3 \rightarrow R-\underset{\underset{O}{\|}}{C}-CH_3$

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$X_2 \rightarrow OBr^{\ominus}$

ASHA
Date _____ Page ___

-ve Haloform or -ve Iodoform Test :-

$CH_3-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{C}}-\ddot{Z}$ ← $\ddot{Z} \rightarrow \ddot{N}H_2, -\ddot{N}H-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{C}}-R, -\ddot{O}R, -\ddot{O}H, -\ddot{X}:$

acidic H(↓) only lp conj.

Idoform test :-

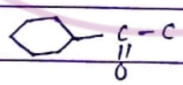
$R-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{C}}-CH_3$ or $R-\underset{\underset{OH}{\downarrow}}{CH}-CH_3$

$\xrightarrow[\text{or } I_2/KOH,\ I_2/Na_2CO_3,\ I_2/Ba(OH)_2]{I_2/\text{alkali}, \text{ or } I_2/NaOH}$ ~~CHI~~ $CHI_3 + R-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{C}}-\ddot{O}^{\ominus}Na^{\oplus} + NaI + H_2O$

Idoform Yellow, V.D. = 197

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

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By Haloform Reac^n [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

$Cl_3C-CH=O + H-C_6H_4-Cl \xrightarrow[-H_2O]{\text{conc. } H_2SO_4} Cl_3C-CH(C_6H_4-Cl)_2$

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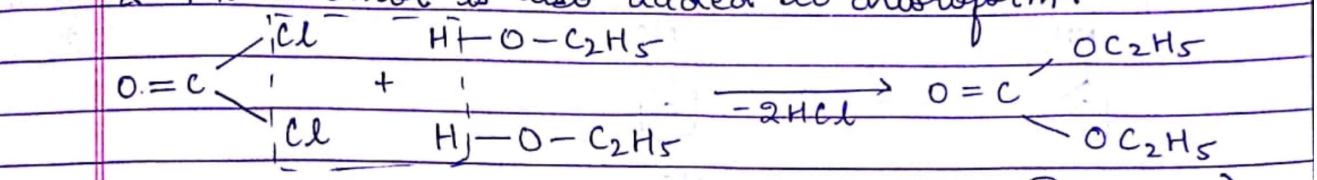
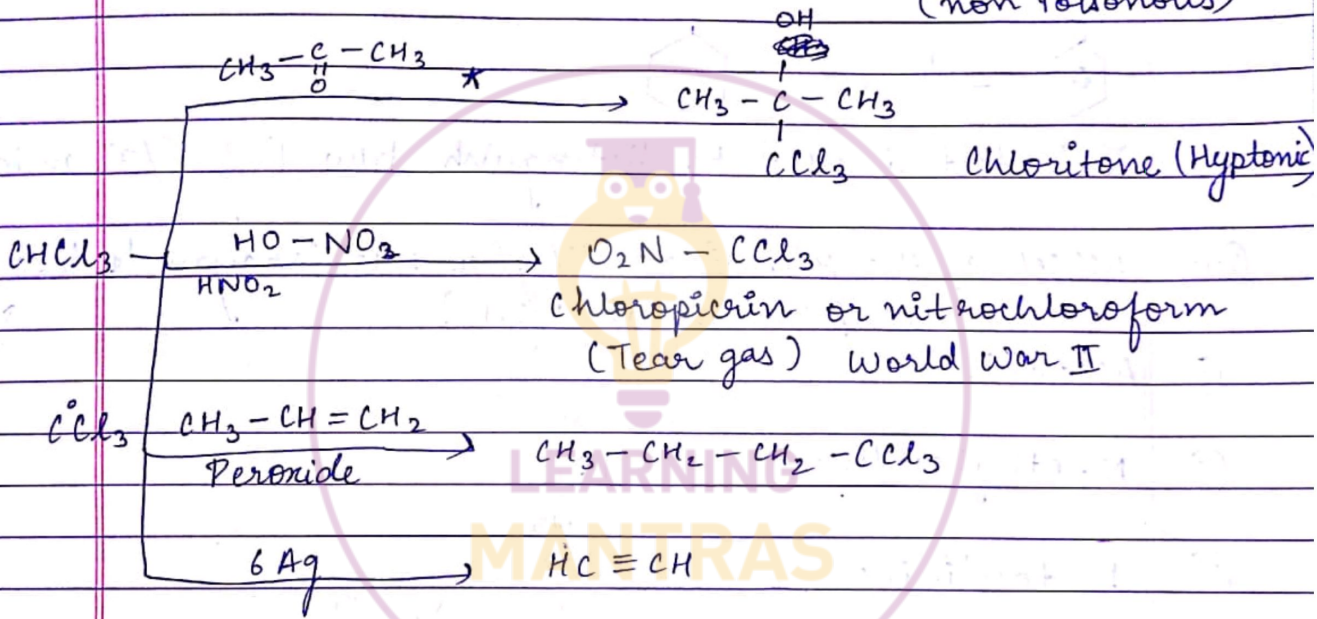
$CHCl_3$ is stored in dark coloured bottles which are filled upto brim to prevent oxidation of $CHCl_3$ into $COCl_2$ & 1% ethanol is also added to chloroform.



(non Poisonous)



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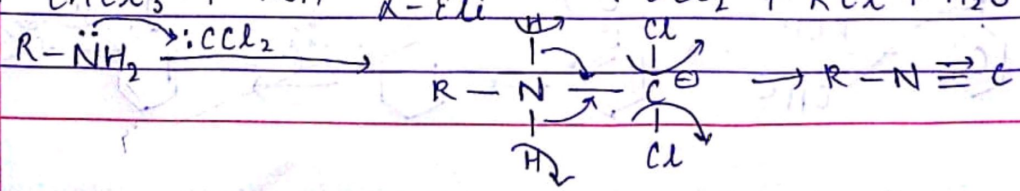
Hoffmann Carbelamide test

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

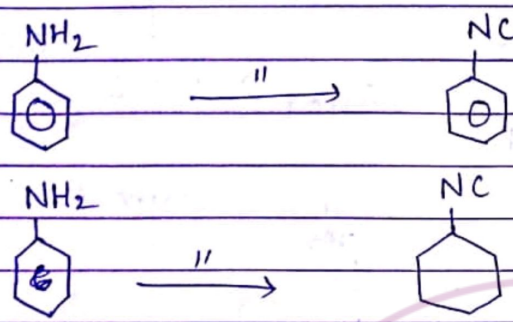
Mech: $CHCl_3 + KOH \xrightarrow{\alpha\text{-}Eli} :CCl_2 + KCl + H_2O$



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

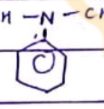
$CH_3-CH_2-NC \xrightarrow{LiAlH_4/H^+} CH_3-CH_2-NH-CH_3$

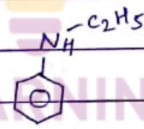
$CH_3-CH_2-NC \xrightarrow{H_2O/H^+} CH_3-CH_2-NH_2 + H-C(=O)-OH$

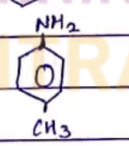


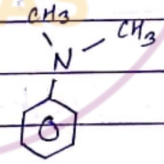
This test is used to distinguish b/w 1° & 2°/3° amines

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

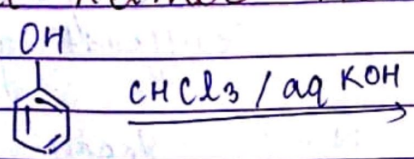
① Acetanilide 

② N-ethylaniline 

③ P-toulidine 

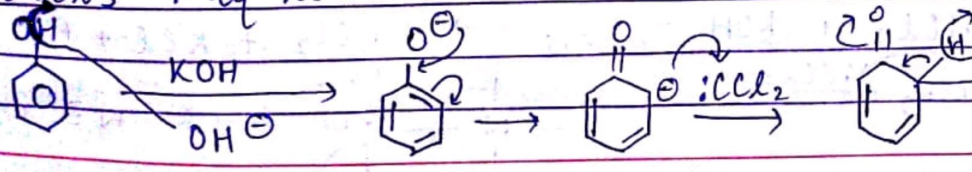
④ N,N-dimethyl aniline 

Rie Reimer Tiemann Reac^n :-



Salialdehyde

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



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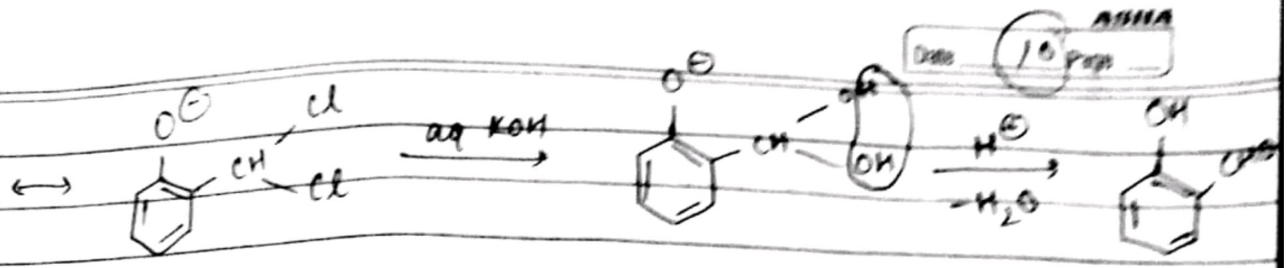

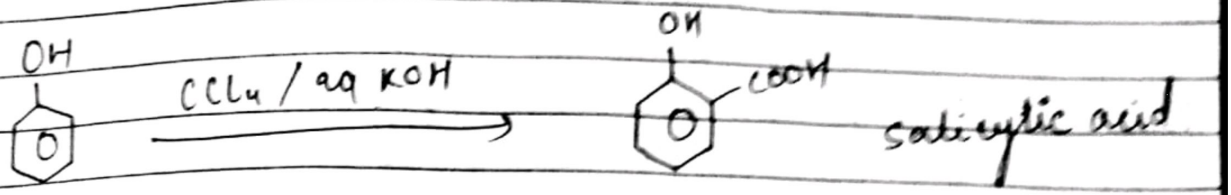

salicylic acid

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 :-

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

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.

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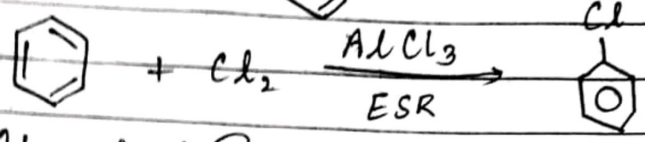
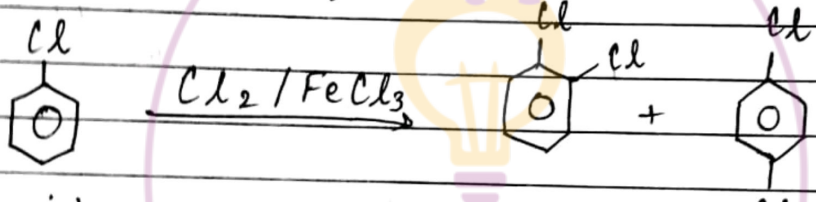
Haloarenes :-

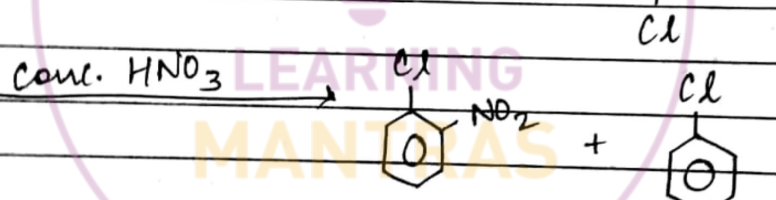
Prep :

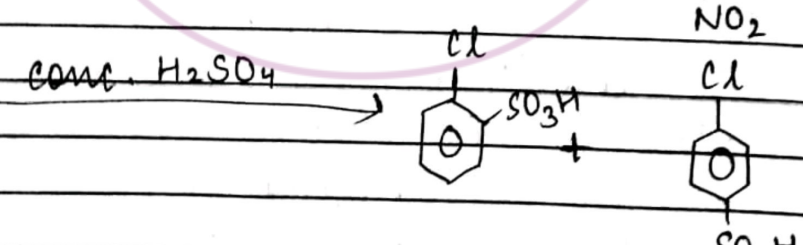


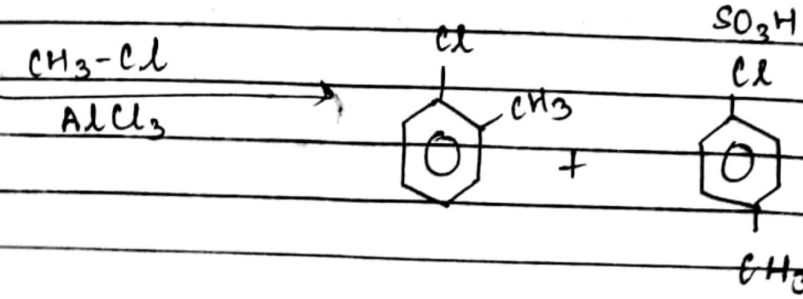
Chemical Properties :-

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









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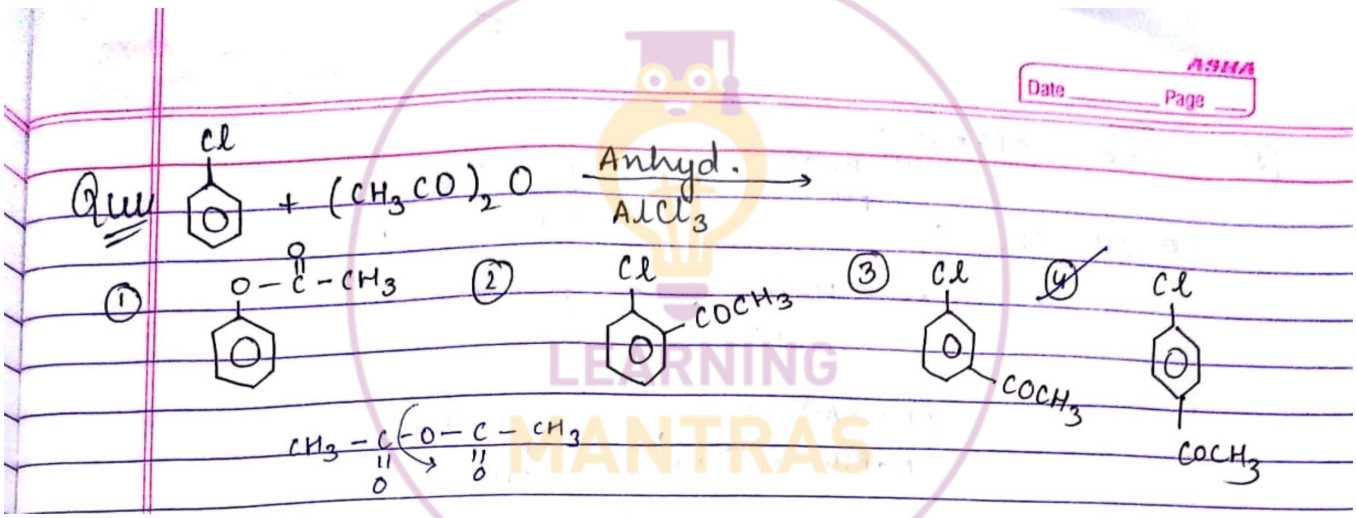

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