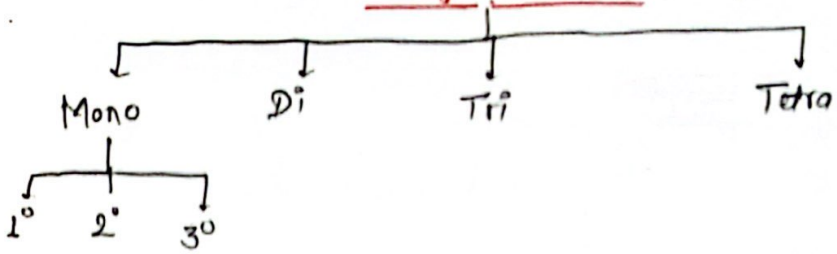
HALO ALKANE (Haloarene)

Alkyl halide

Alkyl Halide (R-X)



CH_3-CH_2-Cl (1°)

$CH_3-CH(Cl)-CH_3$ (2°)

$CH_3-C(CH_3)_2-Cl$ (3°)

Di derivative

* CH_2Cl-CH_2Cl — ethylene (di) chloride (vicinal) (vic)

* CH_3-CHCl_2 — ethylidene (di) chloride, geminal (gem)

Q. Hydrolysis of ethylidiene chloride gives:-

→ $CH_3-CHCl_2 \xrightarrow{aq.KOH} CH_3-CH(OH)_2 \xrightarrow{-H_2O} CH_3-CHO$ acetaldehyde.

Tri derivative

$CHCl_3$ → chloroform

Tetra

CCl_4.

perchloro alkane →

perchloro ethane → $C_2H_6 \rightarrow C_2Cl_6$ (H replaced by X).

Order of reactivity

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

* characteristics rxn → NSR.

* Dipole moment → R-Cl > R-F > R-Br > R-I

but $H-F > H-Cl > H-Br > H-I$

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General Method of Preparation

(1) From Alcohol:

(a) PCl_5

$$R\text{-}\underset{Cl}{O}\text{-}\underset{PCl_3}{H} + PCl_5 \xrightarrow{\Delta} R\text{-}Cl + HCl + POCl_3$$

(b) PCl_3

$$3R\text{-}OH + PCl_3 \longrightarrow 3R\text{-}Cl + H_3PO_3$$

$$3R\text{-}OH + \underset{\text{or. } PI_3}{P + I_2} \longrightarrow 3R\text{-}I + H_3PO_3$$

$$3R\text{-}OH \xrightarrow[\text{or, } PBr_3]{P + Br_2} 3R\text{-}Br + H_3PO_3$$

(c) $SOCl_2$ (Darzen's method)

Thionyl chloride

$$R\text{-}\underset{Cl}{O}\text{-}\underset{SO\,Cl}{H} \xrightarrow{SOCl_2} R\text{-}Cl + SO_2\uparrow + HCl\uparrow$$

→ best method of preparation.

(2) Rxn with HX & alcohol:-

$$R\text{-}OH \xrightarrow{HX} R\text{-}OH_2^{\oplus} \xrightarrow{-H_2O} R^+ \Rightarrow R\text{-}X$$

(X^- attacks R^+)

Reactivity of alc ∝ stability of C^+

→ $R\text{-}OH + H\text{-}X \longrightarrow R\text{-}X + H_2O$

Q. Which alcohol is react fastest with HX.

(a) $CH_3\text{-}CH_2\text{-}\overset{\alpha}{C}H_2\text{-}OH$ — 2 α-H.

(b) $CH_3\text{-}\overset{\alpha}{C}H(CH_3)\text{-}OH$ — 6 α-H.

(c) $CH_3\text{-}\overset{\alpha}{C}(CH_3)_2\text{-}OH$ — 9 α-H.

(1) $CH_3\text{-}CH_2\text{-}\overset{\alpha}{C}H_2\text{-}OH$ — 2 α-H

(2) $CH_3\text{-}\overset{\alpha}{C}H_2\text{-}OH$ — 3 α-H. └ react fastest

$\xrightarrow{HX}$ (2) > (1).

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→ $CH_3-CH_2-CH_2-OH$ & $CH_3-CH_2-CH_2-CH_2-OH$.

ethyl. 2° - H. propyl. 2° - H.

(+I) more ∴ more reactive.

* Groove's method

$$R-OH \xrightarrow[+\ conc.HCl]{anhy.ZnCl_2} R-Cl + H_2O$$

(weak reagent)

(2) By direct halogenation of alkane

$$R-H + Cl_2 \xrightarrow[HRSR]{sunlight} R-Cl + HCl$$

(excess)

e.g. $CH_4 \xrightarrow[Cl_2]{h\nu} CH_3-Cl$.

(excess)

$$CH_3-CH_3 \xrightarrow[Cl_2]{h\nu} CH_3-CH_2-Cl.$$

(excess)

(3) By addition of HX on alkene

$$CH_2=CH_2 \xrightarrow[EAR]{HX} CH_3-CH_2-Cl.$$

$$CH_3-CH=CH_2 \xrightarrow[EAR]{HX} CH_3-\underset{X}{CH}-CH_3 \quad (unsym).$$

$$CH_3-CH=CH-CH_3 \xrightarrow[EAR]{HX} CH_3-CH_2-\underset{X}{CH}-CH_3 \quad (sym).$$

→ Markonikov rxn.

→ $CH_3-CH=CH_2 \xrightarrow[peroxide]{HBr} CH_3-CH_2-CH_2-Br$. → Anti-Markonikov / peroxide effect / Kharash effect.

FAR

only with HBr.

$$CH_3-CH=CH_2 \xrightarrow[peroxide.]{HCl} CH_3-\underset{Cl}{CH}-CH_3$$

(Markonikov rule) (No anti mak) → HCl.

→ $CH_3-\underset{CH_3}{\overset{CH_3}{C}}=CH_2 + \overset{+}{H}\overset{-}{Br} \longrightarrow CH_3-\underset{CH_3}{\overset{Br}{C}}-CH_3$ (Markonikov's rule)

→ $CH_3-CH=CH_2 \xrightarrow[\text{peroxide}]{HCl} CH_3-\underset{Cl}{CH}-CH_3$ (no anti-M)

$\xrightarrow{HCl.} CH_3-\underset{Cl}{CH}-CH_3$

→ $CH_3-CH=CH_2 \xrightarrow[\text{peroxide}]{HBr} CH_3-CH_2-CH_2Br$ (anti).

$\xrightarrow{HBr} CH_3-\underset{Br}{CH}-CH_3$

④ Rxn of ether with HX

→ $R-O-\underset{H}{R} + \underset{\text{excess}}{HX} \longrightarrow R-OH + R-X$

$\downarrow HX$

$R-X.$

$= 2\ R-X.$

⑤ Finkelstein rxn (Halide exchange method).

↳ for prep of iodo alkane.

① $R-Br$
② $R-Cl$ $+ NaI \xrightarrow[\Delta]{\text{Acetone}} R-I$ (iodo) $+$ ① $NaBr$ ② $NaCl$

⑥ Swarts Rxn :- For prep of Floroalkane. (Halide exchange method).

CH_3-CH_2-Cl

- $Hg_2F_2 \longrightarrow CH_3-CH_2-F + Hg_2Cl_2$
- $SbF_3 \longrightarrow CH_3-CH_2-F + SbCl_3$
- $AgF \longrightarrow CH_3-CH_2-F + AgCl$

Properties of Alkyl Halide

① NSR ② Elimination rxn

NSR → typical rxn of Haloalkane

SN¹ ⟷ SN²

$R-\overset{Nu^-}{X} + Nu^- \xrightarrow{NSR} R-Nu + X^-$

① $R-X + KCN \longrightarrow R-CN + KX$

ionic

alkyl cyanide.

$C \equiv N:$

② $R-X + Ag-CN \longrightarrow R-N \equiv C + AgX.$

covalent

alkyl isocyanide

$Ag-C \equiv N:$

adat.

③ Rxn with moist Ag_2O & AgOH.

$R-X + Ag_2O(\text{moist}) \xrightarrow{\Delta} R-OH + AgX.$

AgOH

alc

(but with dry $Ag_2O \rightarrow$ ether)

④ $R-X + NaOR \longrightarrow R-O-R + NaX.$

ether.

⑤ $R-X + NaOH \longrightarrow R-OH + NaX$

alcohol.

⑥ $R-X + NaSH \longrightarrow R-SH + NaX.$

↳ Thioalchol.

* $R-X + KCN \longrightarrow RCN + KX.$

$R-CN$ —

- conc HCl. → partial Hydrolysis or limited supply of H_2O → $R-CONH_2$ (amide)
- dilute HCl. → complete Hydrolysis → $R-COOH$ (C. acid)
- Na/C_2H_5OH → $R-CH_2-NH_2$ [Mandies rxn]
- i) $SnCl_2/HCl$ ② H_3O^+ → $R-CHO$ (aldehyde)
- Sn/HCL → $R-CH_2-NH_2$. (amine)

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• $R-NC \xrightarrow{redn} R-\underset{\underset{H}{|}}{N}-CH_3$ (2° amine)

(7) $R-X + Ag-\underset{\underset{O}{\downarrow}}{N}=O \longrightarrow R-NO_2 + AgX$.
Nitro alkane

(8) $R-X + KNO_2 \longrightarrow R-O-N=O + KX$.
$K^+ \; O-N=O$
Nitrite.

(9) $R-X + \ddot{N}H_3 \longrightarrow R-NH_2 + HX$.
(excess)

$RX + R-NH_2 \longrightarrow R_2NH \xrightarrow{R-X} R_3N \xrightarrow{R-X} R_4N^+X^-$
Quaternary ammonium salt

e.g. $C_2H_5Br + NH_3 \longrightarrow C_2H_5NH_2 + HBr$.
(excess)

$\downarrow$

$(C_2H_5)_2NH \longrightarrow (C_2H_5)_3N$.

$\downarrow$

$\left(C_2H_5-\underset{\underset{C_2H_5}{|}}{\overset{C_2H_5}{N}}-C_2H_5\right)^+ Br^-$

→ $R-X + NH_3 \longrightarrow R-NH_2$.
excess

Elimination Rxn – alkene दिन्ह

$CH_3-CH_2-CH_2-X \longrightarrow CH_3-CH=CH_2$

* $\underset{\beta}{CH_3}-\underset{\alpha}{CH_2}-Cl \xrightarrow{alc.KOH} CH_2=CH_2 + HCl$.
ethene.

* $CH_3-\underset{\beta}{CH_2}-\underset{\alpha}{CH_2}-Cl \xrightarrow{alc.KOH} CH_3-CH=CH_2 + HCl$.

* $\overset{\beta}{CH_3}=\overset{\alpha}{CH}-\overset{\beta}{CH_2}-CH_3 \xrightarrow{alc.KOH} CH_2=CH-CH_2-CH_3$ (Minor) & $CH_3-CH=CH-CH_3$ (Major)
$(2\alpha-H)$ (Hoffman) $(6\alpha-H)$ (Saytzeff).

opposite in case of Fluorine
Hoffman → major

Rxn with metal

① with Na (Wurtz Reaction)

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

$$C_2H_5-\boxed{Br + 2Na + Br}-C_2H_5 \xrightarrow{\text{dry ether}} R-R + 2NaBr$$

② with Zinc (frankland rxn)

$$R-X + Zn + X-R \xrightarrow{\text{dry ether}} R-R + ZnX_2$$

③ with Mg

$$R-X + Mg \xrightarrow{\text{dry ether}} R-MgX.$$

(Grignard reagent).

Reduction

① $R-X + H_2 \xrightarrow[250-300^\circ C]{Ni|pt|pd} R-H + HX.$

② $R-X \xrightarrow[\sim Sn|HCl \;\; \sim Na|C_2H_5OH]{Zn-Cu|C_2H_5OH} R-H + HX.$

2[H]
└ Nascent H हिन्द

③ $R-X \xrightarrow[+HI]{\text{red } P} R-H + HX.$

~~ARYL HALIDE~~

- $CH_3-CH(Cl)-CH_2-CH_3 \xrightarrow[ROH + KOH]{\text{alc. KOH}}$ Hoffman major + Sytzeff minor

└ ROK

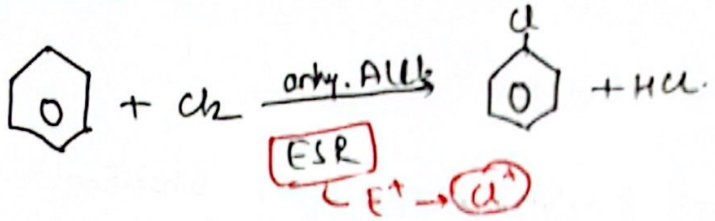
$CH_3-C(CH_3)_2-O^-K^+$

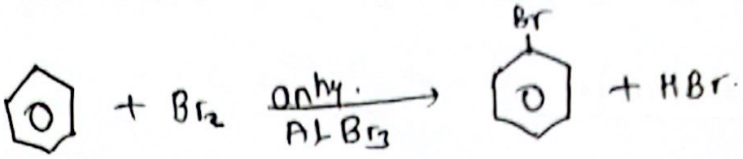
also in R-F

ARYL HALIDE / Haloarene

Preparation

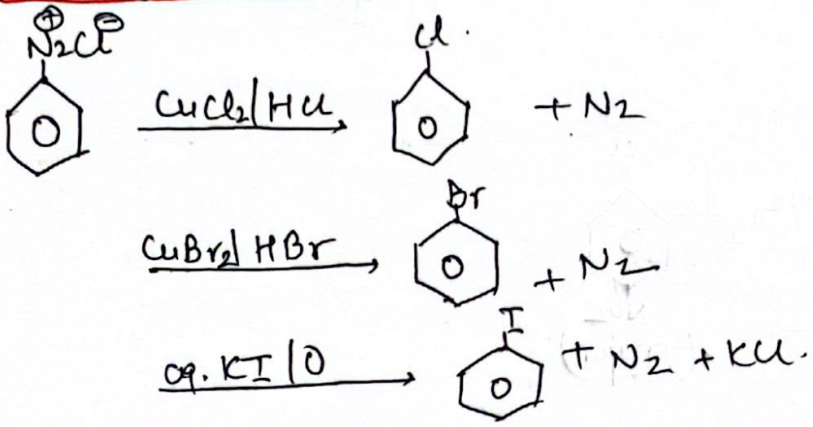
1) By Halogenation



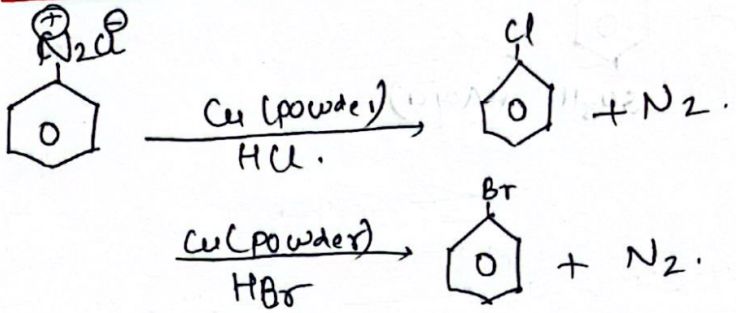


2) From Benzene diazonium salt

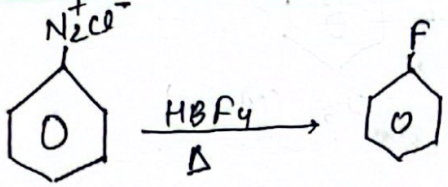
(A) Sandmeyer reaction



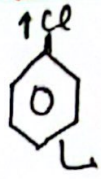
(B) Gattermann reaction



3) Balz-schieman Rxn



+ Relation of Haloarene



→ All O, P director benzene ring activator except halogen.

↳ deactivator.

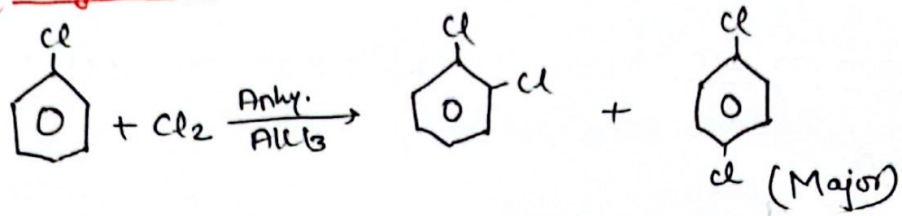
2 types of reaction

① Ring substitution reaction

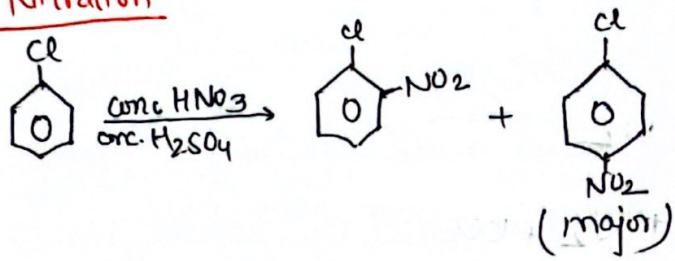
② Reaction involving replacement of halogroup with other substituent.

① Ring electrophilic substitution rxn

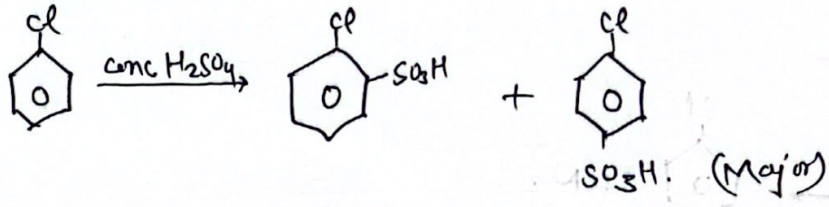
A. Halogenation



B. Nitration

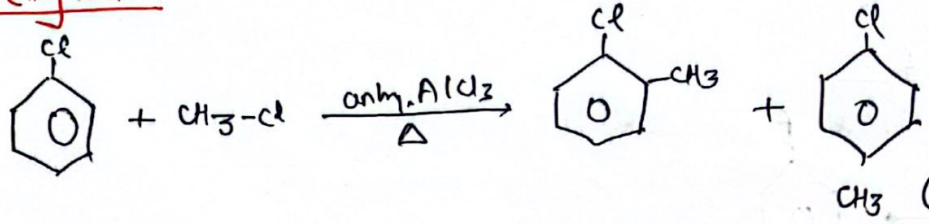


C. Sulphonation

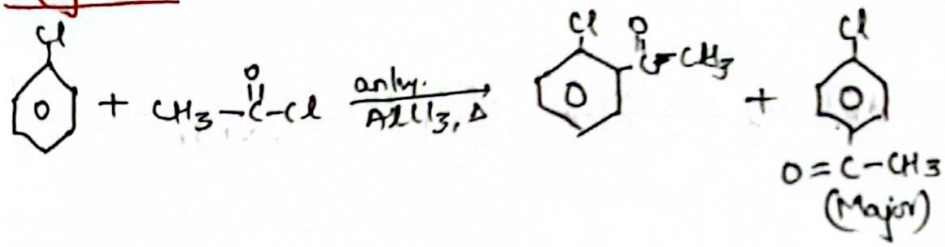


D. Friedel craft rxn

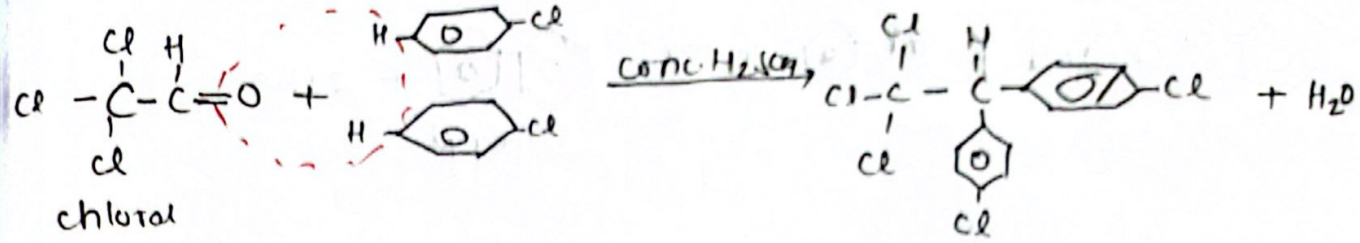
(i) Alkylation



(ii) Acylation



E.→



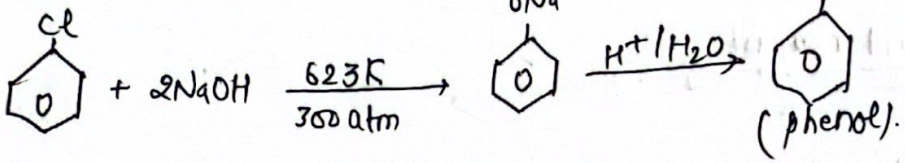
chloral

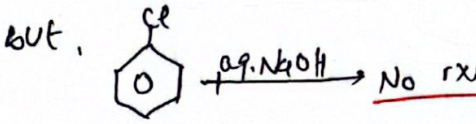
DDT (insecticide)

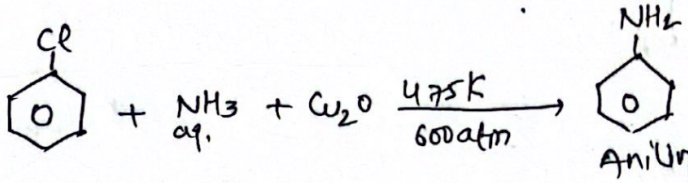
1,1,1-Trichloro-2,2-bis(p-chloro phenyl) ethane.

Bond breaking

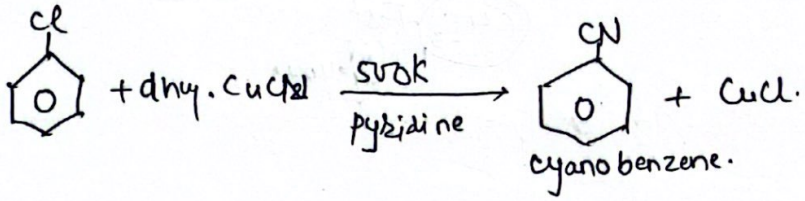
① Dow's process



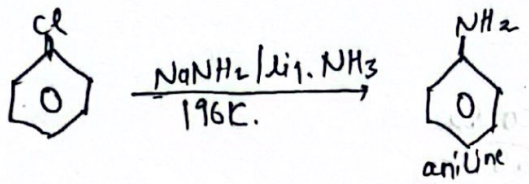


② 

Aniline.

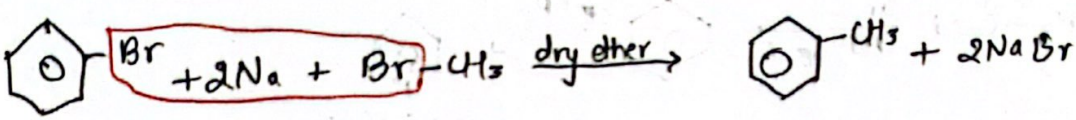
③ 

cyano benzene.

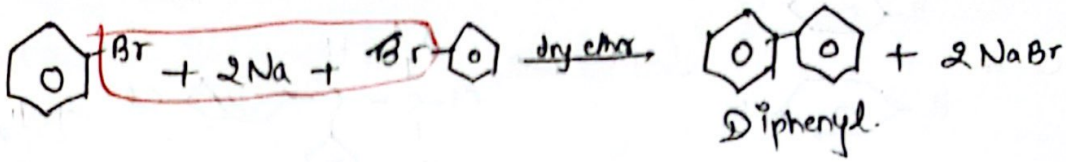
④ 

(intermediate: Benzyne).

* Wurtz fitting Reaction

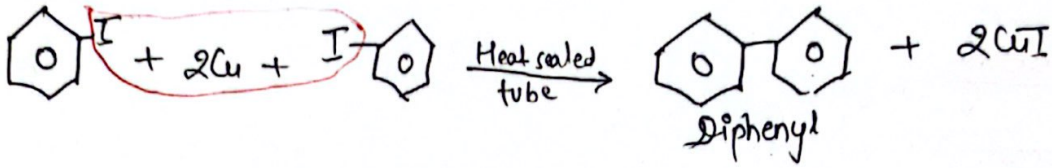


* Fitting Reaction

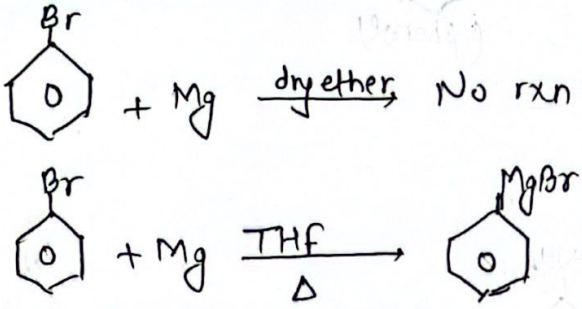


* Ullmann reaction

Given by only iodobenzene.



Formation of Grignard reagent

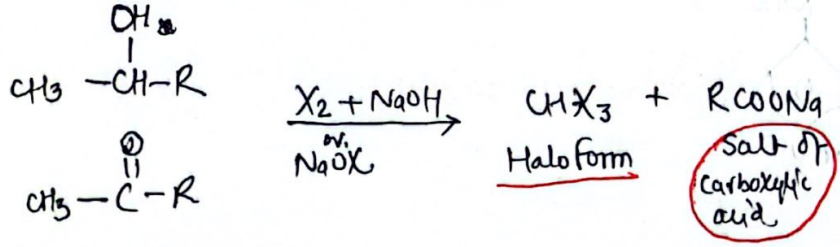


Chloroform

→ Trihalides.
→ Liquid.

CHI_3 – Test – solid yellow

Haloform reaction



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Alcohol

1. Oxidation
2. Halogenation
3. Hydrolysis

Ald / ketone

(i) Halogenation
(ii) Hydrolysis.

* Alcohol

$$CH_3-CH_2-OH \xrightarrow[\text{or } NaOX]{X_2 + NaOH} CH_3-CHO \quad (\text{oxdn})$$

$$CH_3-CHO \xrightarrow{X_2 + NaOH} X-\underset{X}{\overset{X}{C}}-CHO \quad (\text{Halogenation})$$

$$X-\underset{X}{\overset{X}{C}}-\overset{O}{\overset{\|}{C}}-H \xrightarrow{NaOH} CHX_3 + H-\overset{O}{\overset{\|}{C}}-ONa$$

H, ONa

* Iodoform test

$CH_3-\overset{H}{\underset{OH}{C}}-$ & $CH_3-\overset{O}{\overset{\|}{C}}-$ Group हुन पर्‍यो /.
but lone pair हुनु भएन

for iod. test

1. $CH_3-\overset{O}{\overset{\|}{C}}-OH$
2. CH_3-OH. (1 C- no iodoform test)
3. $HCHO$
4. CH_3-CH_2-OH — single 1° alc. which gives iodoform test.
5. $CH_3-CH_2-CH_2-OH$ (1°)
6. $CH_3-CH_2-\underset{OH}{CH}-CH_3$
7. $CH_3-\overset{CH_3}{CH}-OH$
8. $CH_3-\underset{CH_3}{CH}-CH_2-OH$ (1° alc)
9. $CH_3-CH_2-\underset{OH}{CH}-CH_2-CH_3$
10. $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$ (3° alc. never gives iodoform test).
11. $CH_3-\overset{O}{\overset{\|}{C}}-H$ → Acetaldehyde is the single aldehyde that gives iodoform test
12. CH_3-CH_2-CHO
13. $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$
14. $CH_3-\underset{CH_3}{CH}-CHO$
15. $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

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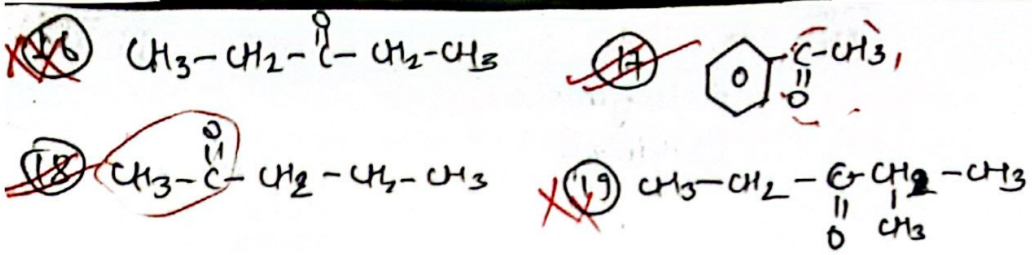
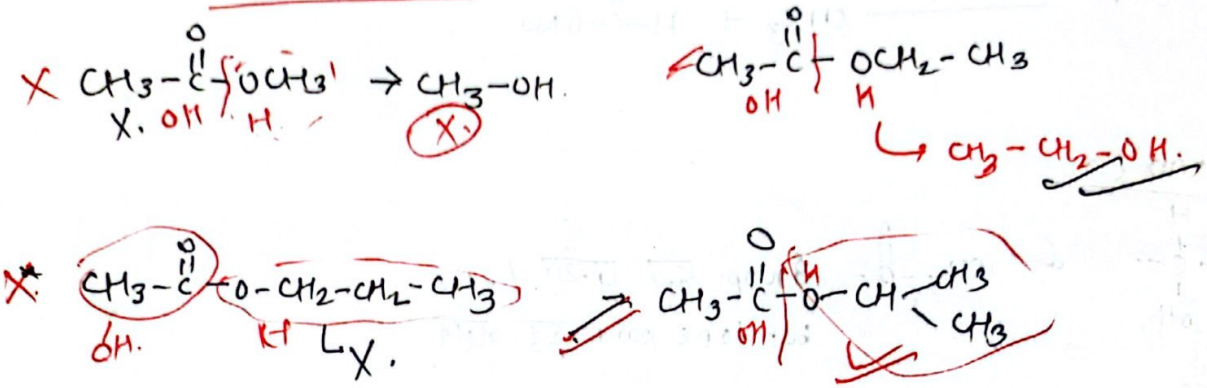


but in ester



2-phenyl ethanol & 2-phenyl ethanol.



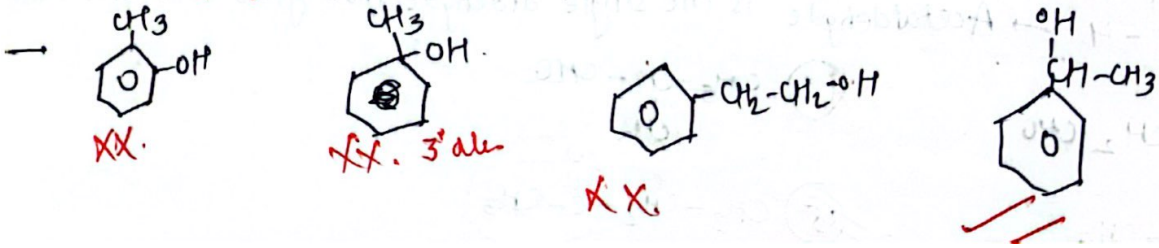
Q. Which compound gives iodoform test?

(a) $CH_3-\overset{O}{\overset{\|}{C}}-H$ (b) $CH_3-\overset{O}{\overset{\|}{C}}-\ddot{O}H$ (c) $CH_3-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2$ (d) All.

Q. Which gives iodoform test?

(a) $CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3$ (b) $CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-CH_3$

(c) $CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3$ (d) $CH_3-\overset{O}{\overset{\|}{C}}-\ddot{O}H$



General Method of preparation of chloroform

Lab Method ✓

alcohol or acetone.

CH_3-CH_2-OH or CH_3COCH_3 $\xrightarrow{\text{Bleaching powder soln}}$ $CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + [Cl]$

$CHCl_3 + (HCOO)_2Ca$ (cal) + $(CH_3COO)_2Ca$ (acet)

Industrial Method

$CH_3-CH(OH)-R$ or $CH_3-C(=O)-CH_3$ $\xrightarrow{\text{aq. NaCl / electrolysis}}$ $NaCl + H_2O \rightarrow [Cl] + NaOH$

CH_3Cl_3 + $HCOONa$ or CH_3COONa.

From chloral hydrate ✓

– pure $CHCl_3$ পাওয়া যায়।

$CCl_3CH(OH)_2 \xrightarrow[\Delta]{NaOH} CHCl_3 + HCOONa + H_2O$

Halogenation of methane

$CH_4 + Cl_2$ (excess) $\xrightarrow{h\nu}$ $CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$

$CHCl_3$ → separate

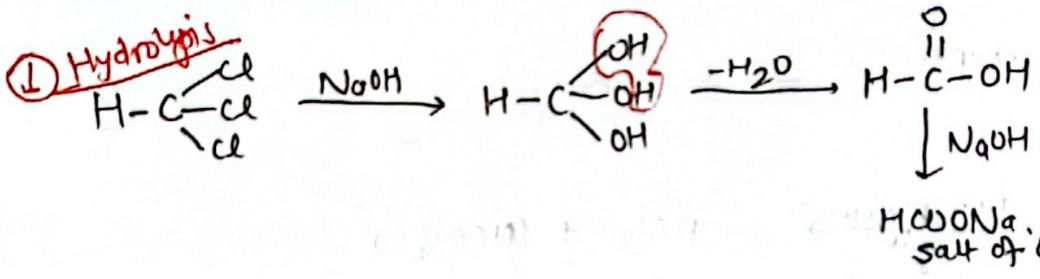
By reduction of CCl_4

– in large scale.

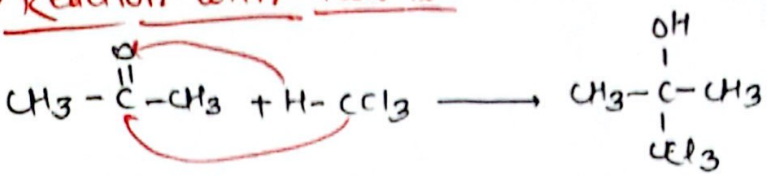
$CCl_4 + 2[H] \xrightarrow[\text{steam}]{Fe/H_2O} CHCl_3 + HCl$.

Chemical properties

① Hydrolysis

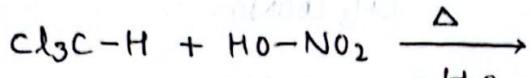


② Reaction with acetone



Chloretone → Hypnotic drug.

③ Reaction with HNO_3 (Nitric acid)



CCl_3-NO_2

Chloropicrin or Nitro-chloroform

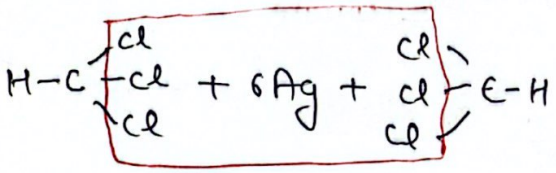
Tear gas

④ Carbylamine rxn / Isocyanide test

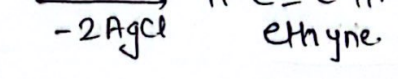
Intermediate :- $:CCl_2$ (6e⁻)

1° amine (aliphatic or aromatic) $\xrightarrow[NaOH]{CHCl_3}$ Isocyanide → offensive smell.

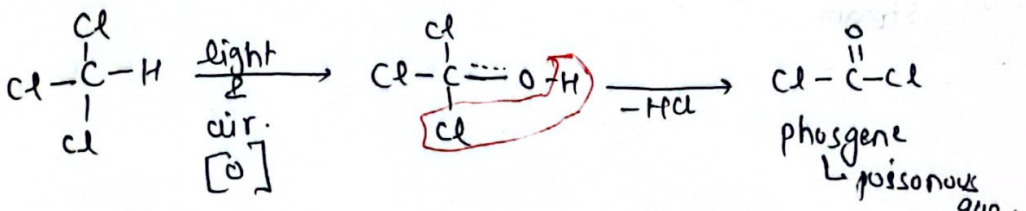
⑤ Reaction with silver



2 moles are used.



⑥ Oxidation



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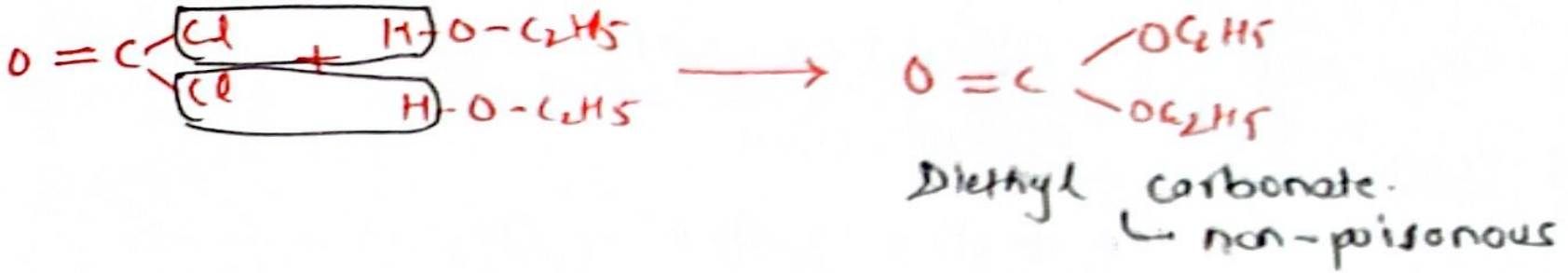
* To prevent from oxidation

→ Kept in dark colored bottles filled upto top to cut of light.

– Small amount of ethyl alc. is mixed with chloroform to neutralize this phosgene.



Diethyl carbonate.
↳ non-poisonous

→ Before using $CHCl_3$ as anesthetics it is tested with $AgNO_3$ soln & KOH.

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