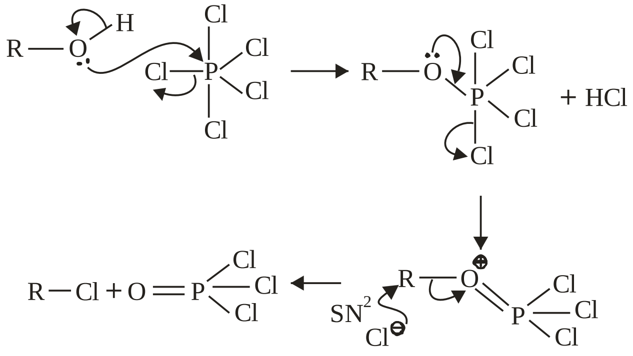
Glimpse of Alkyl Halide

General Preparation:

1. $R - H \xrightarrow[UV]{X_2} R{-}X$
2. $R - OH + PCl_5 \longrightarrow R\text{-}Cl + POCl_3$



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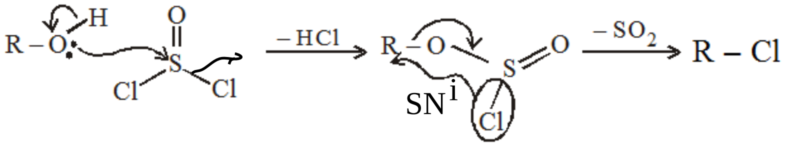
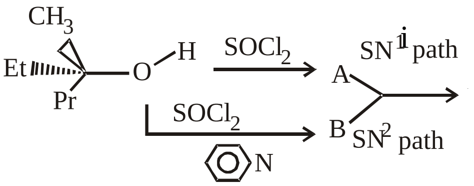
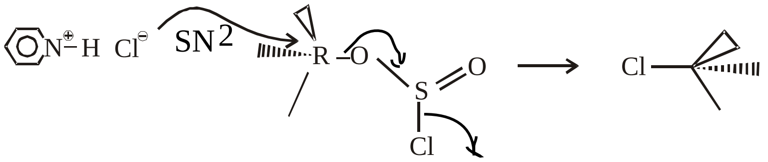


- Between $SOCl_2$ and PCl_5, $SOCl_2$ is preferred. Because, SO_2 is released from product side, so the equillibrium point is shifted to the right-hand direction. That is yield increases.



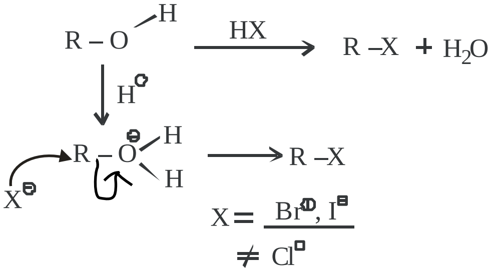
- In presence of pyridine, pyridinium chloride ($NH^+\ Cl^-$) is synthesized. This free $Cl^{(-)}$ attacks the chiral centre through SN^2 manner. Thus inversion takes place



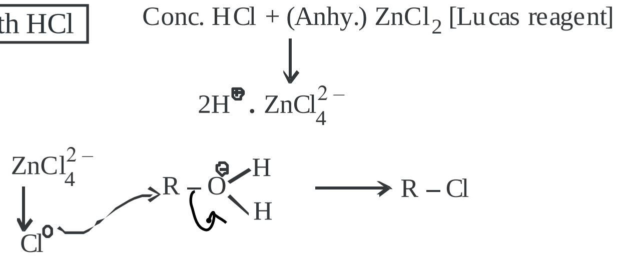
- In place of $SOCl_2$ if $COCl_2$ (phosgene) is used same R-Cl and CO_2 are released through SNi process.
- It is found that using polar solvent, rate of SN^i increases.

  R-O-SO-Cl practically exists as $R^+.{}^-O$-SO-Cl intimate ion pair which is favoured in polar medium. Thus rate of SN^i increases.

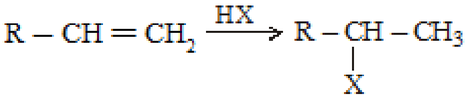
4.



To make with HCl



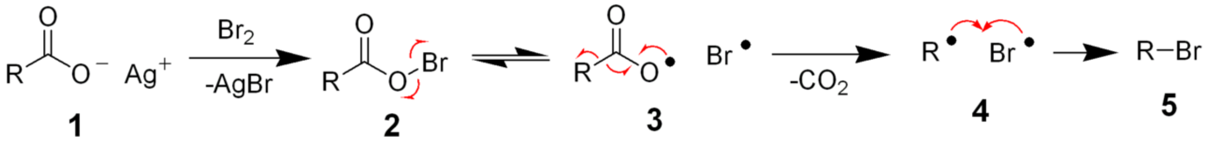
Anhydrous $ZnCl_2$ enhances the ionic character of HCl by forming $2H^{\oplus}.ZnCl_4^{2-}$ complex. Thus protonation of alcoholic oxygen is favoured and water elimination takes place.

5. 

$$R-CH=CH_2 \xrightarrow{HX} R-\underset{\displaystyle X}{\underset{|}{CH}}-CH_3$$ [M-Rule is obeyed]

$R-CH=CH_2 + HBr\ (R_2O_2) \rightarrow R-CH_2-CH_2-Br$ [anti M-rule]

6. **Hunsdiecker reaction:**



7. **Halide Exchange Reaction:**

Finkelstein reaction:

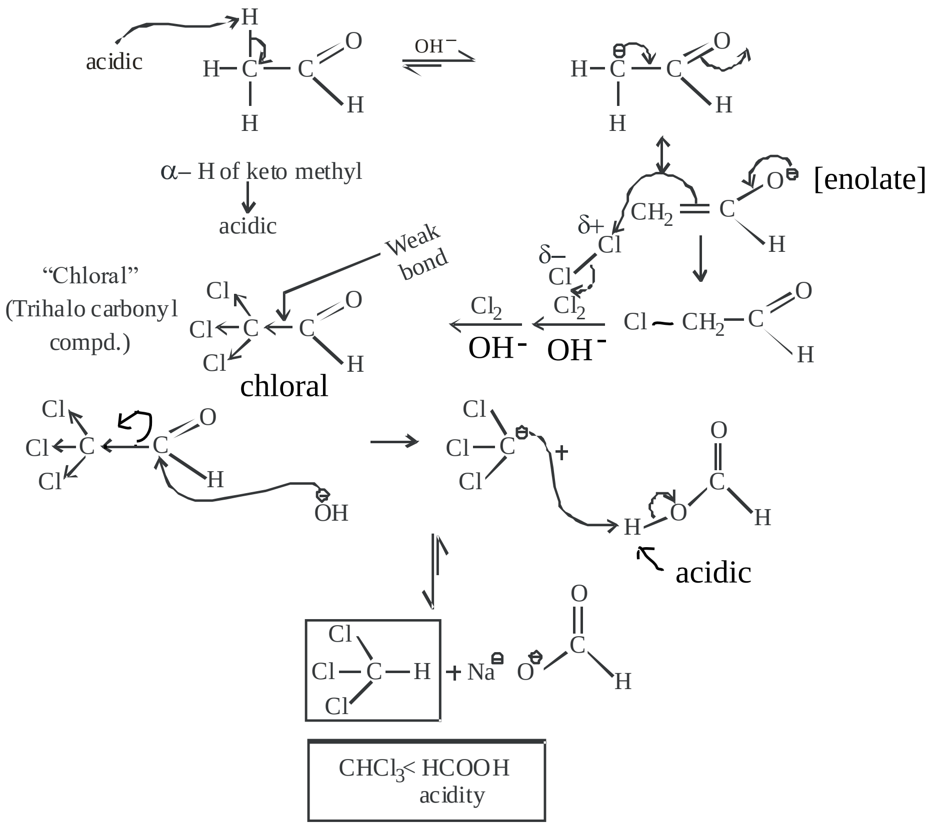
R-X + NaI in Acetone → R-I + NaX↓ [X = Cl, Br]

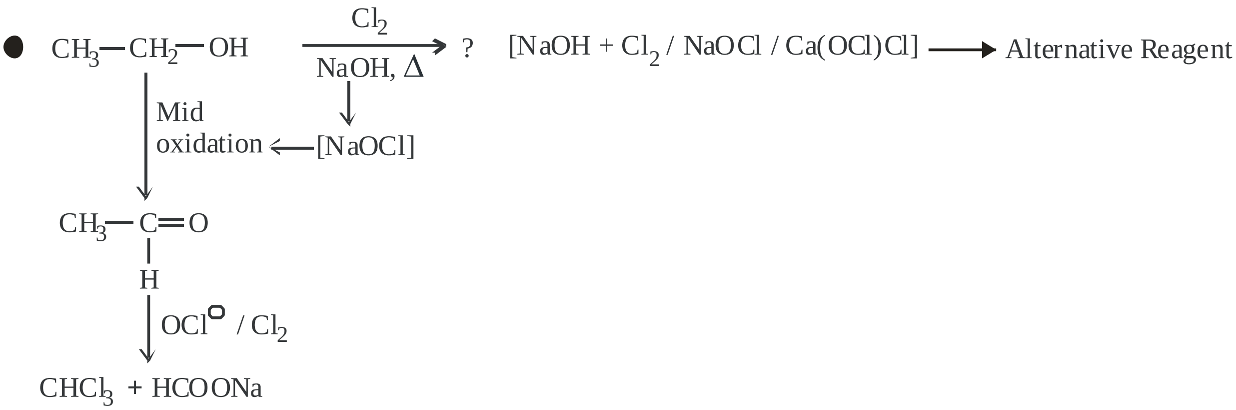
In dry acetone medium NaX (X = Cl, Br) so formed are precipitated which facilitates the forward reaction according to Le- Chatelier's Principle.

Swarts reaction:

$R-Br + AgF\ (SbF_3, CoF_2) \rightarrow R-F + AgBr\downarrow$

Haloform Reaction:

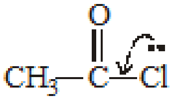


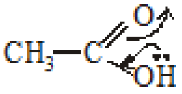


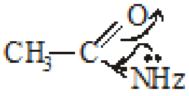
Criteria of a compound to exhibit haloform reaction:

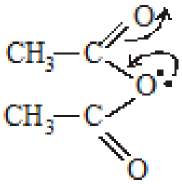
(i) The compound must have keto-methyl group directly or indirectly (i.e. generated by oxidation)
(ii) The methyl protons of ketomethyl group should be sufficiently acidic, so that trihalo-derivative is synthesized as an intermediate

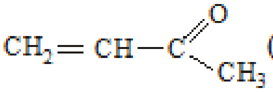
Which of the following molecules give (+) ve haloform test?

(i) 

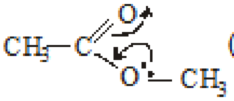
(ii) 

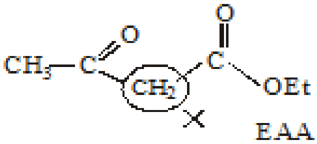
(iii) 

(iv) 

(v) 

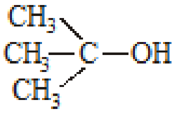
MVK
methyl Vineyl Ketone

(vi) 

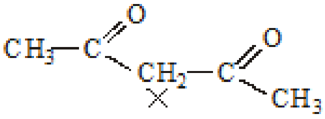
(vii) 

EAA

(viii) CH_3-OH

(ix) 

(x) $CH_3-CH_2-CH_2-OH$

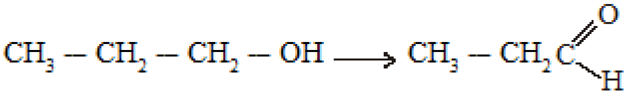
(xi) 

acetyl acetone (acac)

- From (i) to (iv) & (vi) there are cross-resonances which lowers the acid strength of methyl protons of CH_3-CO group. That's why they can't give haloform reaction.

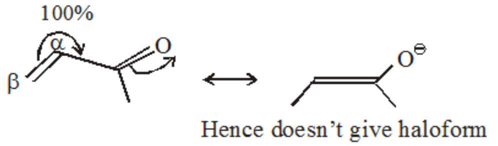
- (vii) & (xi) → acidity of $\boxed{>CH_2}$ -Hydrogen i.e methylene protons is greater than methyl hydrogen. So Cl substitution occurs there.

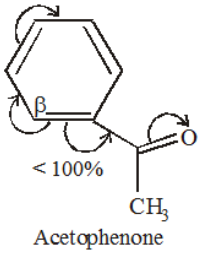
- (viii) , (ix) & (x) → can't produce CH_3-CO group after oxidation.



$CH_3-CH_2-CH_2-OH \longrightarrow CH_3-CH_2CHO$

- (v)





Gives haloform

In acetophenone α–β double bond is involved in resonance within the ring as well as with the external keto group. So chance of resonance with external keto is < 100%. Thus acidity of – CH_3 proton is not reduced significantly which favours haloform reaction.

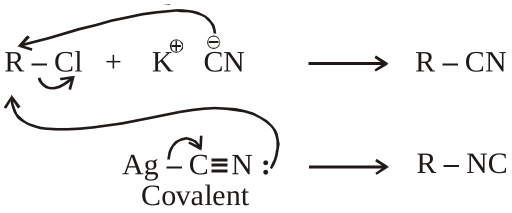
- Et-OH & CH_3-CO-CH_3 How will you distinguish, by haloform reaction?

CH_3 -CH_2 -OH gives iodoform reaction through oxidation. If we use I_2 and weak alkali, like NH_4OH as there is no dismutation / disproportionation reaction, i.e hypoiodide (NH_4OI) is not synthesized, so keto methyl intermediate formation does not happen. Thus iodoform is not synthesized.
But in acetone, as there is ketomethyl group directly, I_2 and NH_4OH can generate iodoform where NH_4OH is acting as proton abstractor. So normal iodoform reaction takes place from acetone.

PROPERTIES:

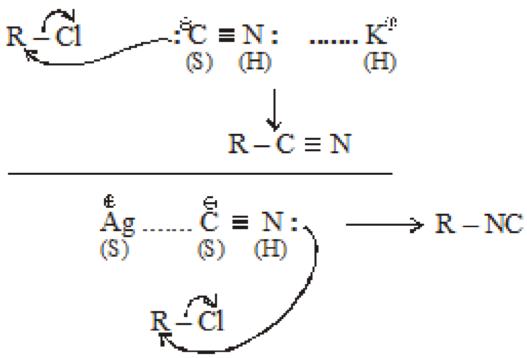
1. ● **R-Cl + KCN→ ? & R-Cl + AgCN→?**

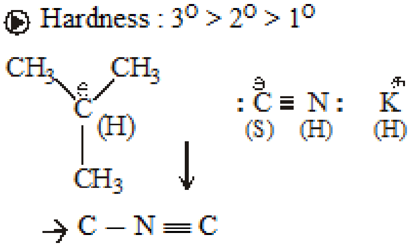
I. KCN being ionic, free CN^- ion having (-) ve charge on carbon can attack the alkyl group producing R-CN as major product. But AgCN being covalent cyanide, it's nitrogen lone pair is free to attack resulting alkyl isocyanide as major product.



II.

SHAB mode





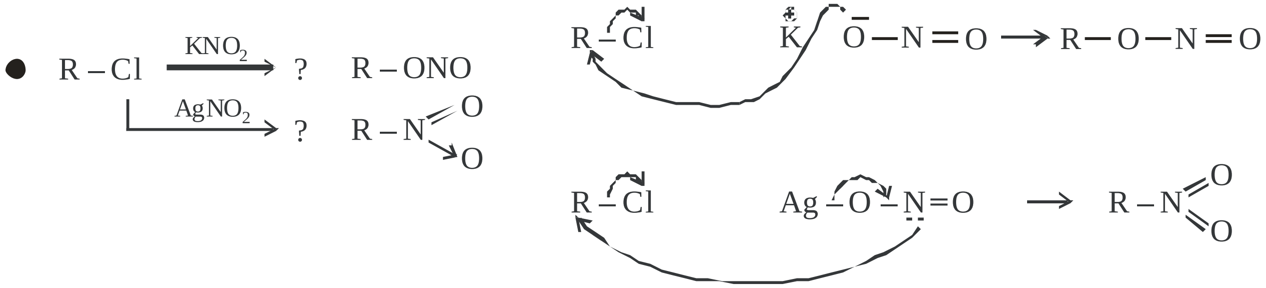
Carbon is relatively softer than nitrogen so K^+ being relatively hard cation, it prefers N-end of CN^- i.e C-end is free to react. Ag^+ being softer it prefers C-end of CN^- i.e N-end is free to attack.

III.

R-Cl + Ag-CN → AgCl (ppt) + R^+ (even 1^o) Due to precipitation of AgCl, R-Cl is ionized so it follows SN^1 path. Now free R^+ cation being hard ion, N-hard- end of CN^- prefers to bind with R^+ resulting R-NC as major product.

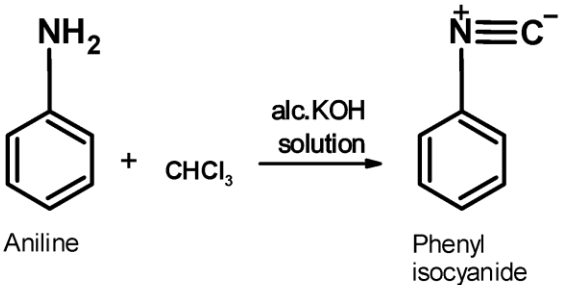
R-Cl + KCN → As KCl is not precipitated R^+ is not generated at all i.e relatively softer C-end of CN^- attacks softer $^{\delta+}$R of R-Cl in SN^2 manner affording R-CN as major product.

2.

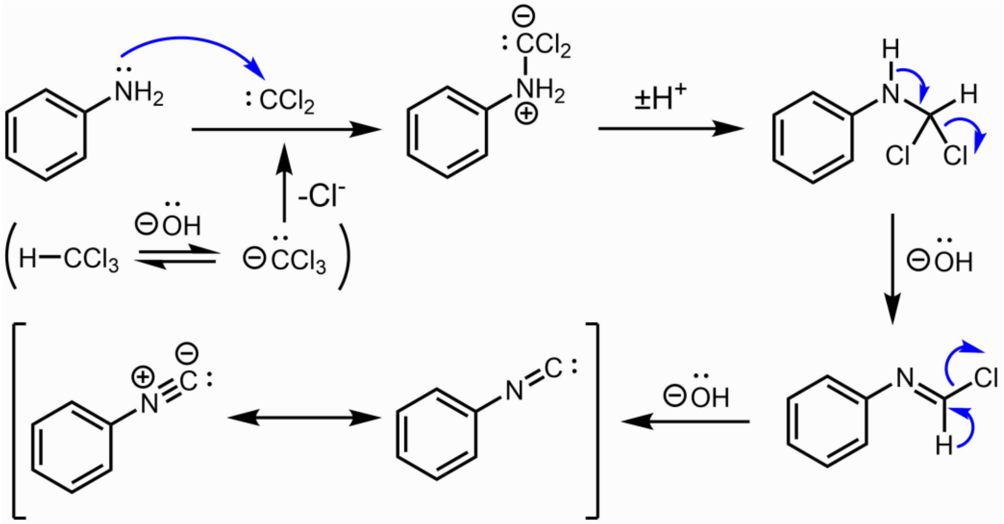


For NO_2 system, SHAB method cannot be applied because in presence of two hard centres (O) hardening of N takes place (symbiosis). So covalent and ionic pathway is the correct pathway to explain the observation.

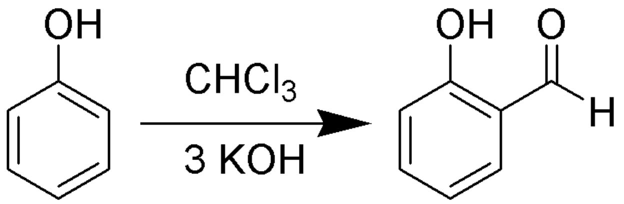
3. • Carbylamine Reaction:



Mechanism:

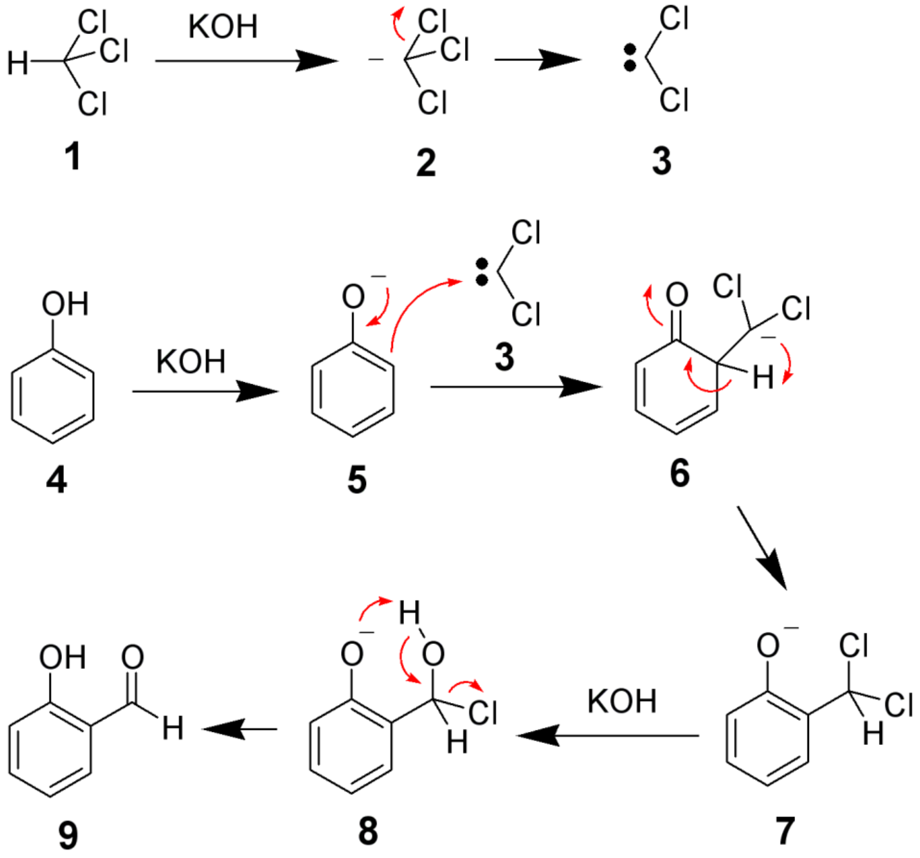


4. • Reimer-Tiemann Reaction:



Salicyladehyde

Mechanism:



5. • Oxidation of CHCl3:

$$CHCl_3 + O_2 \xrightarrow{\text{light}} \underset{\textbf{Phosgene}}{COCl_2} + 2\,HCl$$

$$COCl_2 + 2C_2H_5OH \longrightarrow \underset{\textbf{Ethyl carbonate}}{CO(OC_2H_5)_2} + 2HCl$$

Chloroform when exposed to sunlight, it slowly decomposes to phosgene ($COCl_2$) which is extremely poisonous gas. To use chloroform as an anaesthetic agent, it is necessary to prevent the above reaction.

The following two precautions are taken when chloroform is stored:

a) It is stored in a dark brown or blue coloured bottle so that light can not pass through it.
b) 1% ethyl alcohol is added. This retards the oxidation of chloroform and converts the phosgene so formed into harmless diethyl carbonate.

6. • Reduction of $CHCl_3$:

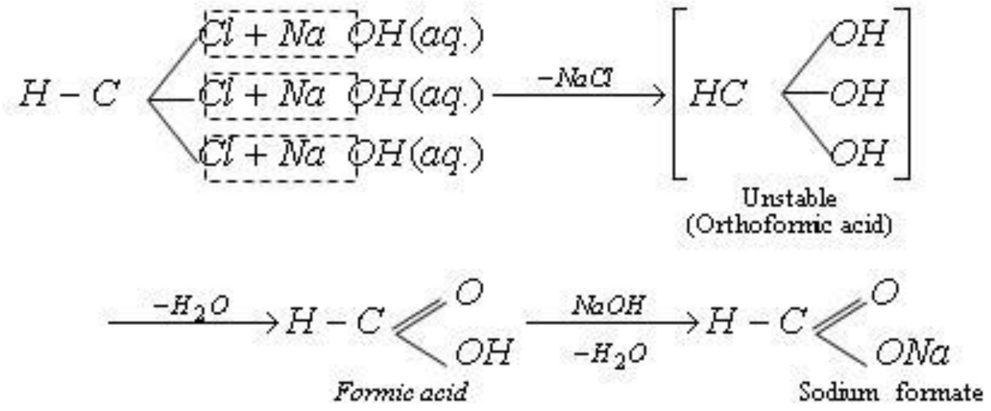
$$CHCl_3 + 2[H] \xrightarrow{Zn/HCl} CH_2Cl_2 + HCl$$

(methylene chloride)
(dichloromethane)

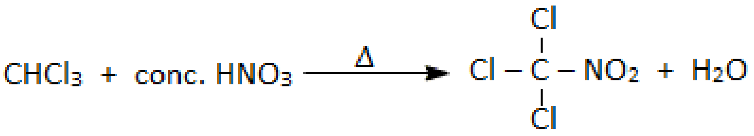
$$CHCl_3 + 6[H] \xrightarrow{Zn/H_2O} CH_4 + 3HCl$$

(methane)

7. • Hydrolysis of $CHCl_3$:



8. • Nitration of $CHCl_3$:

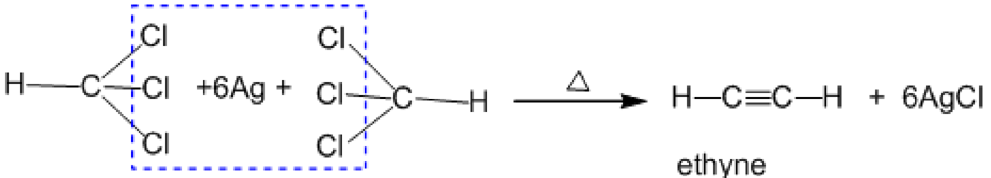


$$CHCl_3 + \text{conc. } HNO_3 \xrightarrow{\Delta} CCl_3NO_2 + H_2O$$

(chloropicrin)
trichloro(nitro)methane

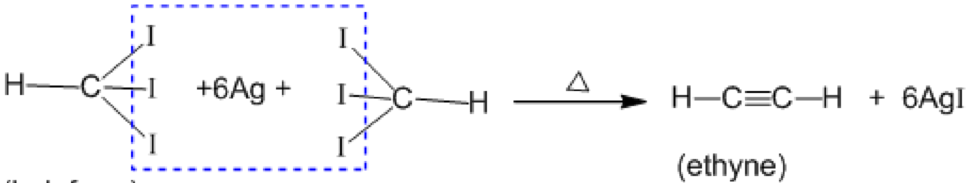
Chloropicrin or nitro chloroform is a poisonous liquid and used as an **insecticide** as well as **tear gas**.

9. • $CHCl_3$ heated with Ag powder:



(trichloromethane)
(chloroform)

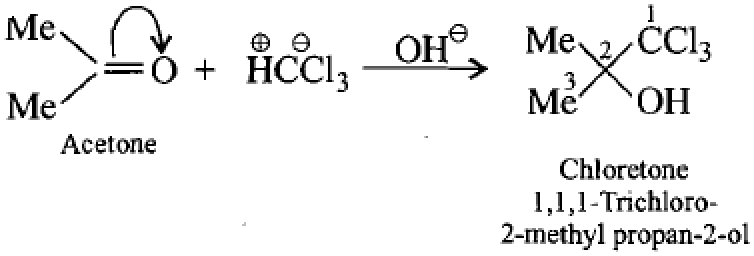
ethyne
(acetylene)



(iodoform)

(ethyne)

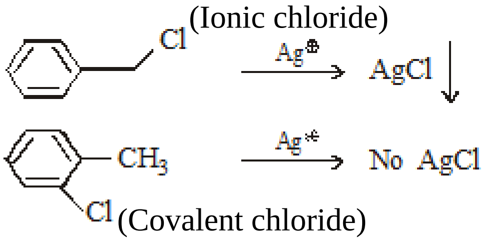
10. ● Condensation with Acetone:



Chloretone is used as **hypnotic** drug i.e sleep producing drug.

Related Questions:

1. ●



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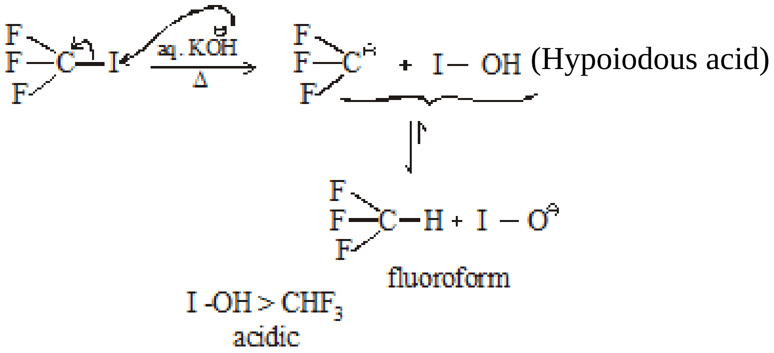

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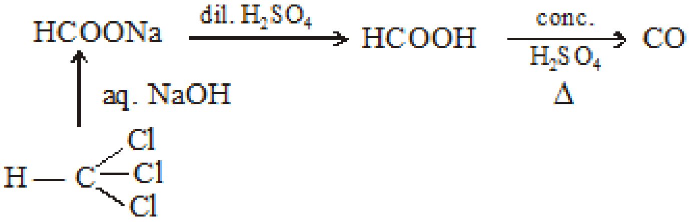

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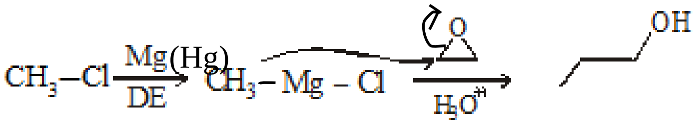

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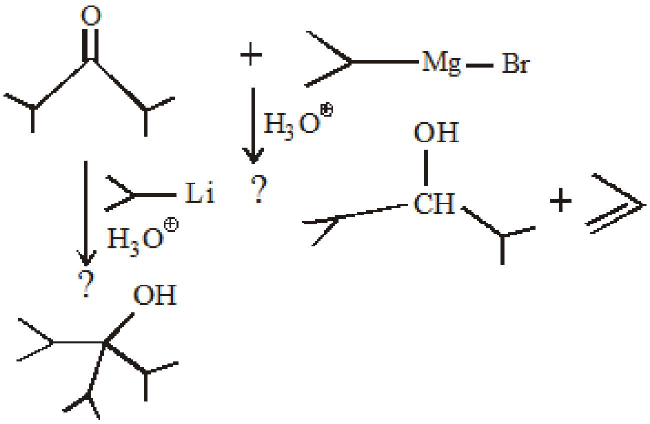

Li$^{\oplus}$ being alkali metal ion, it can’t form six-membered complex like Transition State. Whereas Mg^{++} being alkaline earth metal, its complexing ability is greater than Li. So unusual reducing behaviour of sterically hindered Grignard reagent is not observed by Li-analogue.