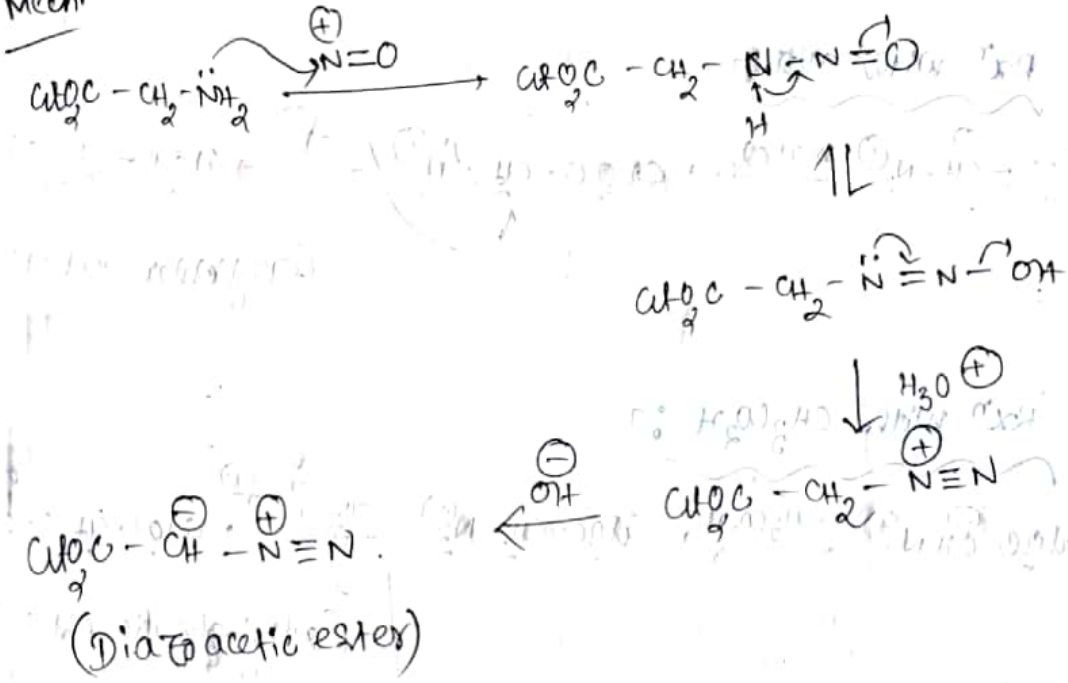
Diazo acetic ester / Ethyl diazo acetate ($CH_3OOCCHN_2$)

Preparation:

Diazoacetic ester can be prepared by treating cold soln of ethyl glycinate in ($HCl + NaNO_2$) soln

$$CH_3OOC-CH_2-NH_2 \xrightarrow[0-5^\circ C]{NaNO_2+HCl} CH_3OOC-CHN_2 + NaCl + H_2O$$

Mech.

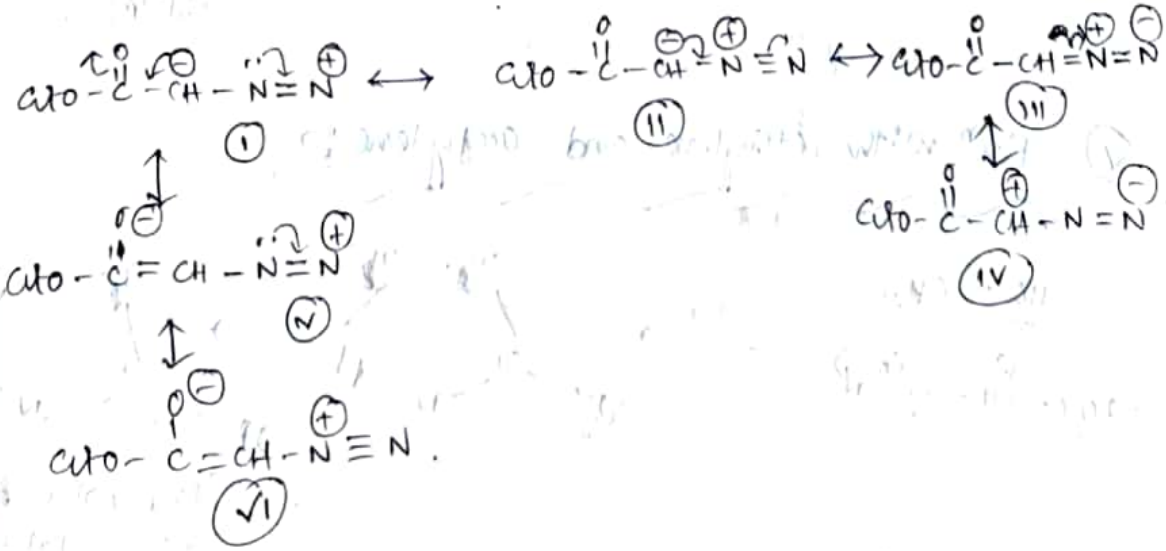


(Diazoacetic ester)

Resonating Structure:

Diazomethane (CH_2N_2) have 4 resonating structure.

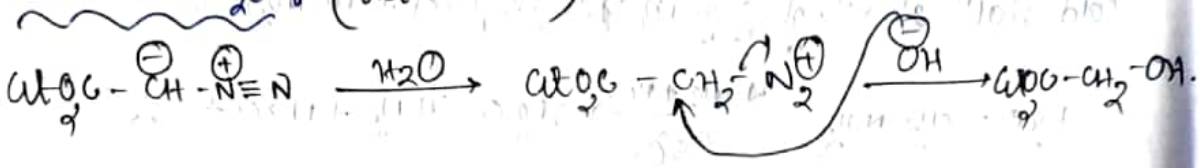
But Diazoacetic ester have 6 resonating structure, i.e it is more stable than diazomethane (CH_2N_2).



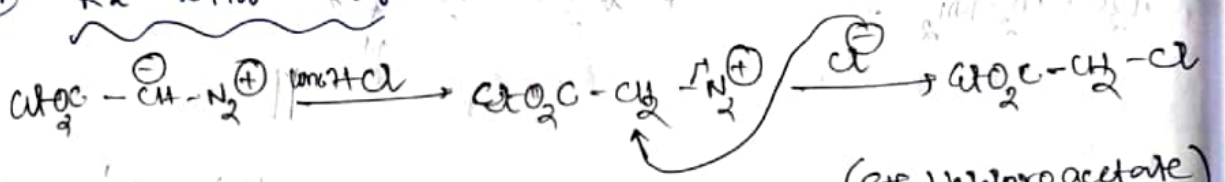
Reaction :-

Diazo acetic ester reacts similar manner like CH_2N_2.

(I) Rxn with H_2O :- (act as base)

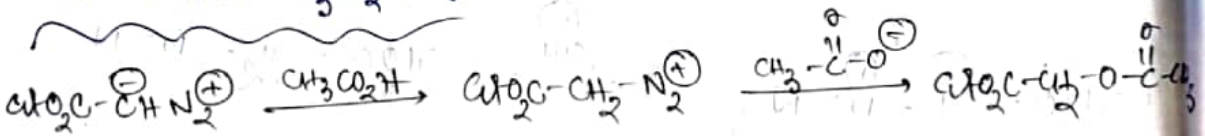


(II) Rxn with HCl :-



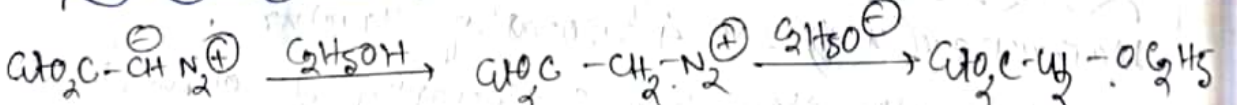
(ethyl chloro acetate)

(III) Rxn with CH_3CO_2H :-



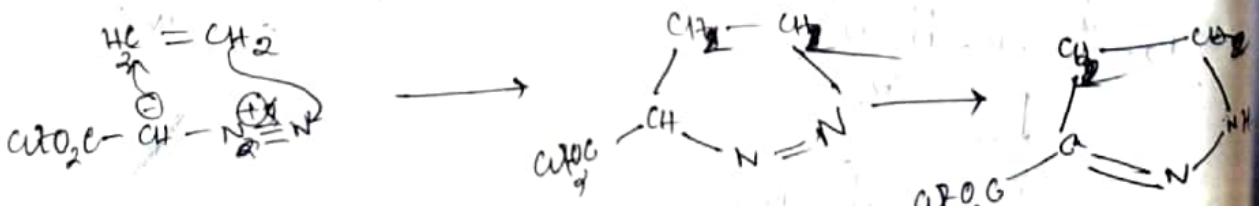
(acetyl glycolic esters)

(IV) Rxn with C_2H_5OH :-

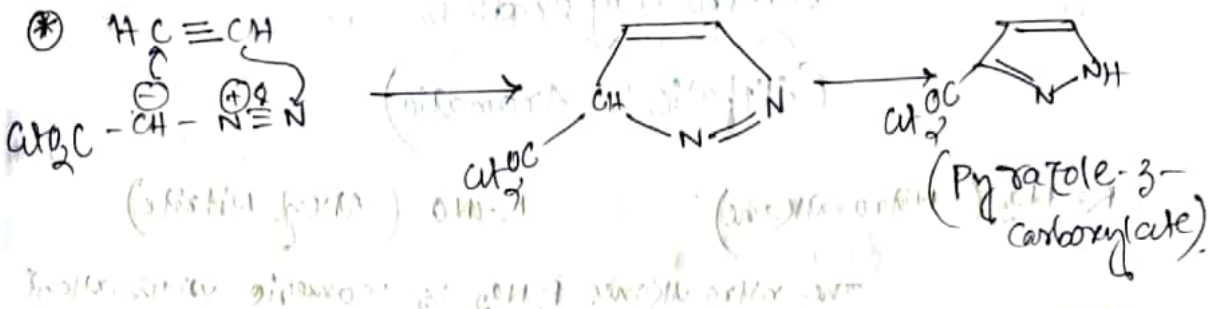


(Ethyl ethers of glycolic esters)

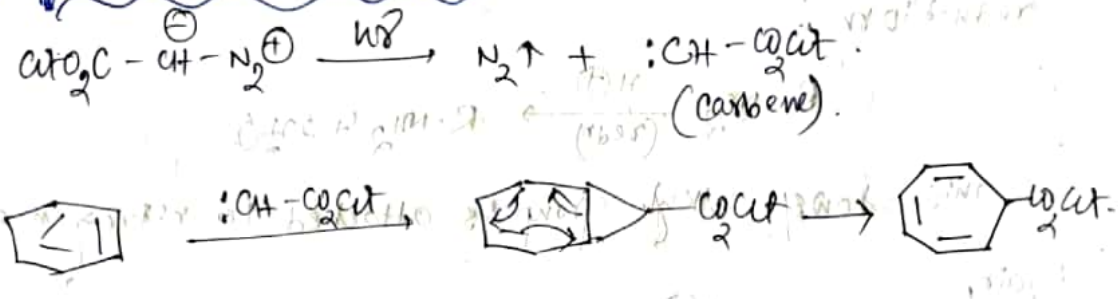
(V) Rxn with ethylene and acetylene :-



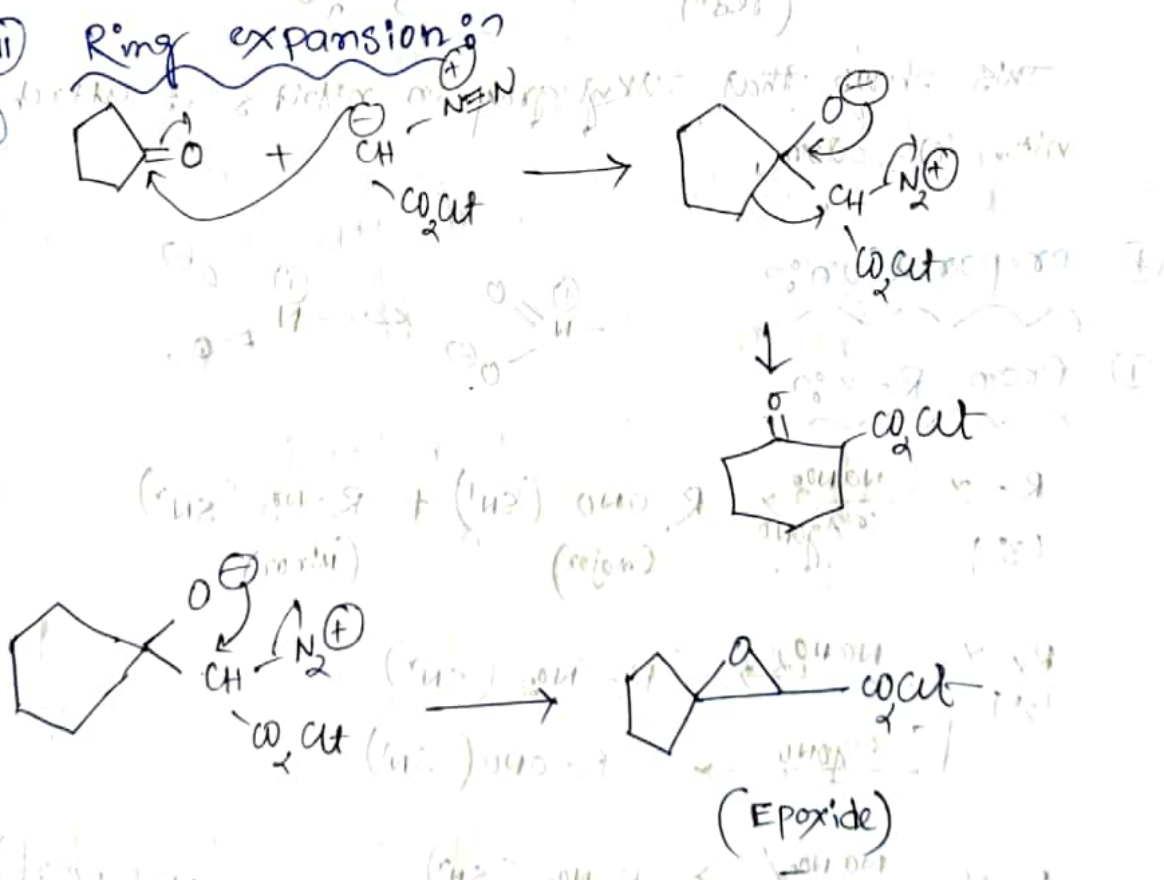
(Pyrazoline-3-carboxylate)



(VI) Carbene formation :-



(VII) Ring expansion :-



Nitro compounds

(Aliphatic & Aromatic)

$R-NO_2$ (Nitro alkane) $R-ONO$ (Alkyl Nitrite).

The nitroalkanes RNO_2 is isomeric with alkyl nitrite RONO. The evidence that may be adduced for these respective formula is to be found in the study of reduction.

$$R-NO_2 \xrightarrow[(red^n)]{H^+} R-NH_2 + 2H_2O$$

This shows alkyl group is attached to nitrogen atom.

Again, $$R-ONO \xrightarrow[(red^n)]{H^+} ROH + NH_3 + H_2O.$$

This shows that alkyl group in nitrites is attached with 'O'- atom.

⊛ preparation:-

$$-\overset{\oplus}{N}(=O)-O^{\ominus} \leftrightarrow -\overset{\oplus}{N}(-O^{\ominus})=O.$$

① From R-X:-

$$R-X \ (3^\circ) \xrightarrow[or\ AgONO]{NaNO_2} \underset{(major)}{R-ONO\ (SN^1)} + \underset{(Minor)}{R-NO_2\ (SN^2)}$$

$$R-X \ (2^\circ) \xrightarrow{NaNO_2} R-NO_2\ (SN^2)$$

$$R-X \ (2^\circ) \xrightarrow{AgONO} R-ONO\ (SN^1)$$

$$R-X \ 1^\circ \xrightarrow[AgONO]{NaNO_2} \underset{(major)}{R-NO_2\ (SN^2)}$$

(HSAB Concept)

- In presence of $NaNO_2$ ⇒ Rxn proceeds through SN^2 & soft end 'N' atom with soft end (base) alkyl gr. (acid) (R^{S-}).
- In presence of AgONO ⇒ Rxn proceeds through SN^1 & Hard end $\overset{\oplus}{R}$ end 'O' atom with hard

(II) From H.V.Z rxn :-

$R-CH_2CO_2H \xrightarrow{red\ P/Br_2} R-\underset{Br}{CH}-CO_2H \xrightarrow[SN^2]{NaNO_2} R-\underset{NO_2}{CH}-C(=O)-OH$

$\downarrow$

$R-CH_2-NO_2 \xleftarrow{H^+} R-\overset{\ominus}{C}H-NO_2 + CO_2$

(stable due to $-NO_2$ gr.)

(III) From R-OH :-

$R-OH \xrightarrow[aq.\ HCl]{NaNO_2} R-O-NO$

$HNO_2 \longrightarrow \overset{+}{N}O$ (Electrophile)

Mech.

$R-\ddot{O}-H \xrightarrow{\overset{+}{N}O} R-\overset{+}{O}(H)-NO \longrightarrow R-O-NO$

(IV) Ritter rxn :-

$Me-\overset{O}{\overset{\|}{C}}-Me \xrightarrow[(ii)\ H_3O^+]{(i)\ MeOH} Me-\underset{Me}{\overset{OH}{C}}-Me \xrightarrow{conc.\ H_2SO_4} Me-\underset{Me}{\overset{+}{C}} \rightleftharpoons \underset{Me}{\overset{Me}{}}C=CH_2$ (elm Pdt)

$\downarrow HCN$

$Me-\underset{Me}{\overset{Me}{C}}-NC \xrightarrow{H_3O^+} Me-\underset{Me}{\overset{Me}{C}}-NH_2 \xleftarrow{KMnO_4} Me_3C-NO_2$

- $Me_3Cl \xrightarrow[Et_2O]{Mg} Me_3CMgBr \xrightarrow{CNCl} Me_3C-CN$

- $Me_3C-Cl \xrightarrow{AgONO} Me_3C-ONO$ (S_N1)

Reaction:-

Reduction under diff. condition:-

- $R-NO_2 \xrightarrow[\text{or } Sn/HCl]{LAH} R-NH_2$.

  $\xrightarrow{Zn/NH_4Cl}$ $R-NHOH$ (N-alkyl hydroxylamine).

- $R-ONO \xrightarrow{Sn/HCl} ROH$.

- $RCH_2NO_2 \xrightarrow[HCl]{SnCl_2} RCH_2NHOH + RCH=NOH$ (oxime)

Tautomerism:-

Primary and secondary nitro compds. i.e. those contain α-hydrogen atoms, exibit tautomerism.

$$R-CH_2-\overset{\oplus}{N}(=O)-O^{\ominus} \rightleftharpoons RCH=\overset{\oplus}{N}(-OH)-O^{\ominus}$$

Psendo-acid form — aci-form.

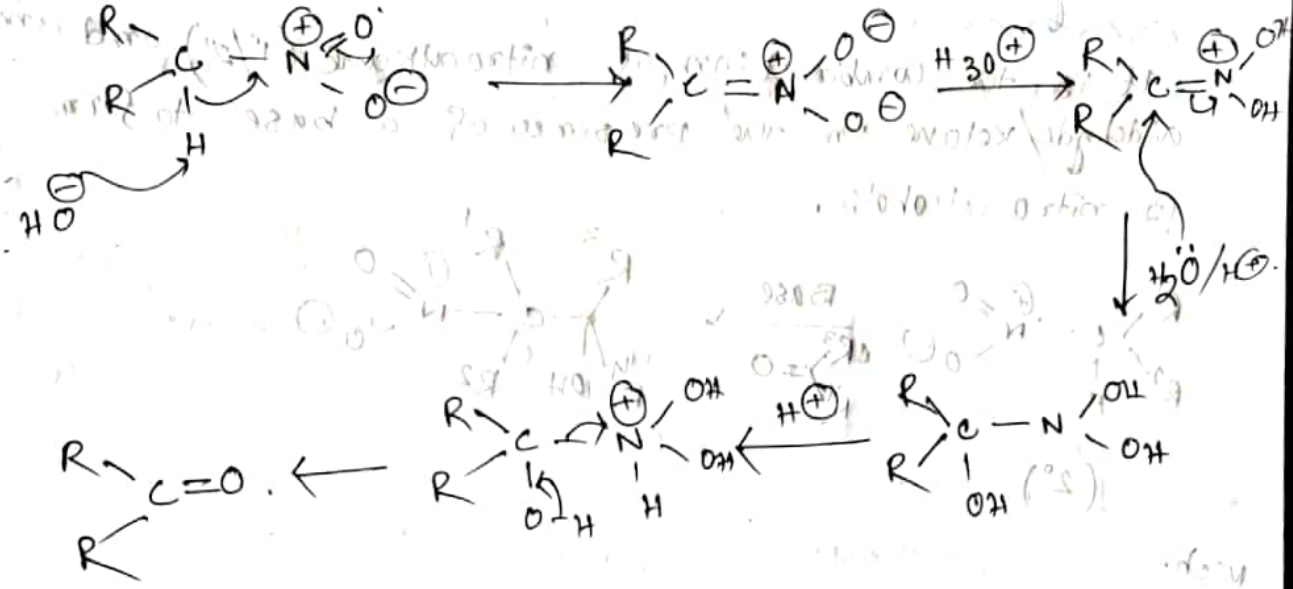
This is the nitro-acinitro system. The equm is almost completely on the left due to the resonance stability of nitro group.

Nef carbonyl synthesis:-

Na/K salt of 1°/2° $R-NO_2$ on treatment with conc H_2SO_4 to give carbonyl compd.

$$\underset{(2^\circ)}{R_2CH-NO_2} \xrightarrow[\text{(ii) } H^{\oplus}/H_2O]{\text{(i) } OH^{\ominus}(NaOH)} \underset{\text{(carbonyl compd.)}}{R_2C=O}$$

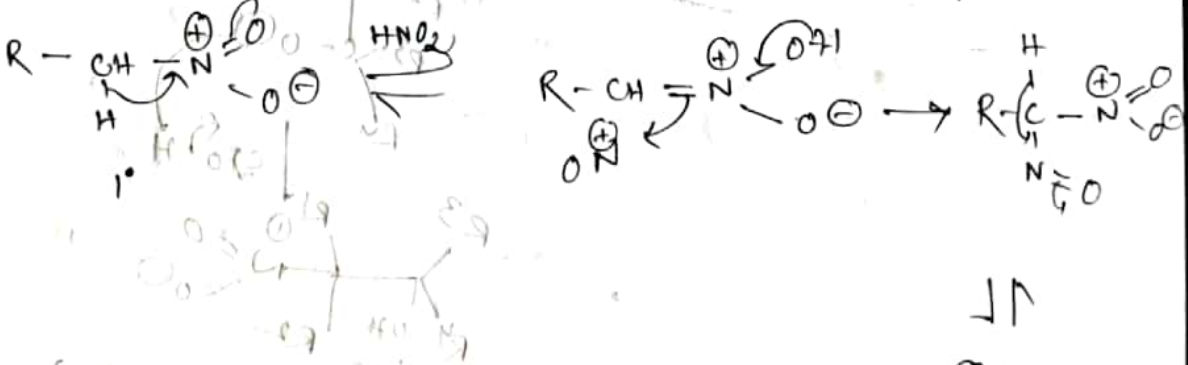
Mech.



- Reaction with HNO_2 :- (Distinguish 1°, 2°, 3° nitroalkane)

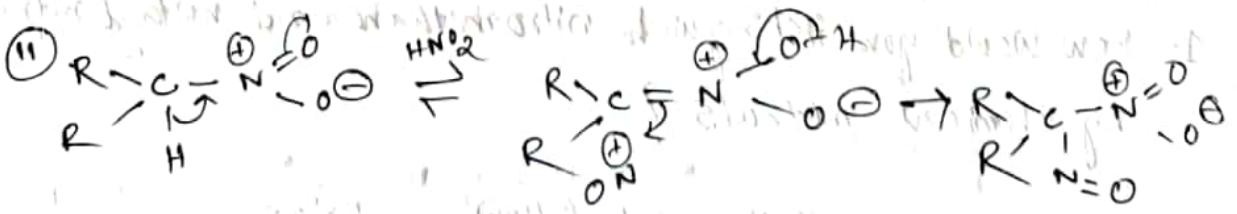
R.B.W Test

All the three nitroalkanes behaves differently with HNO_2.

(I) 

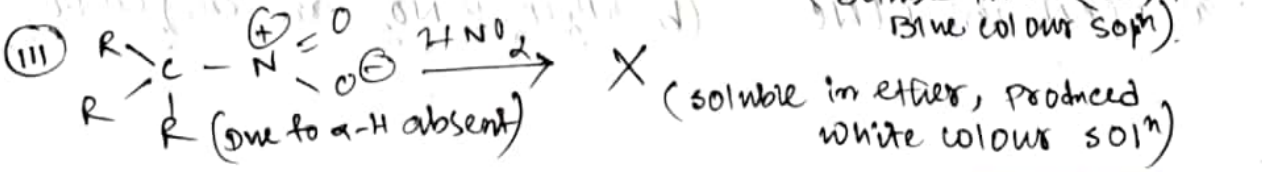
(soluble in alkali, produced red colour soln)

(Nitrolic acid)

(II) 

(Pseudonitrole)

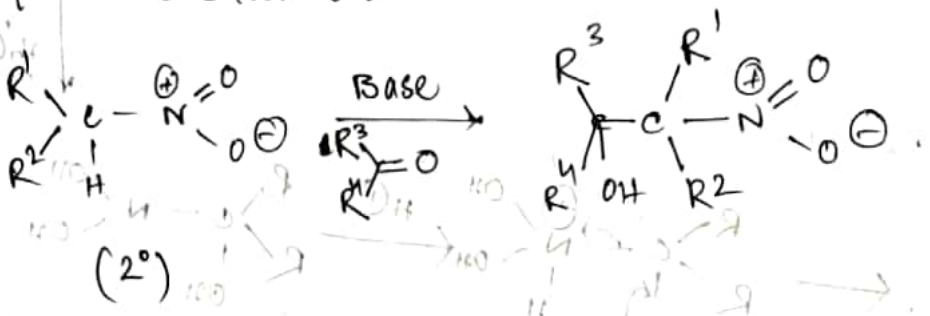
(soluble in alkali, produces blue colour soln)

(III) 

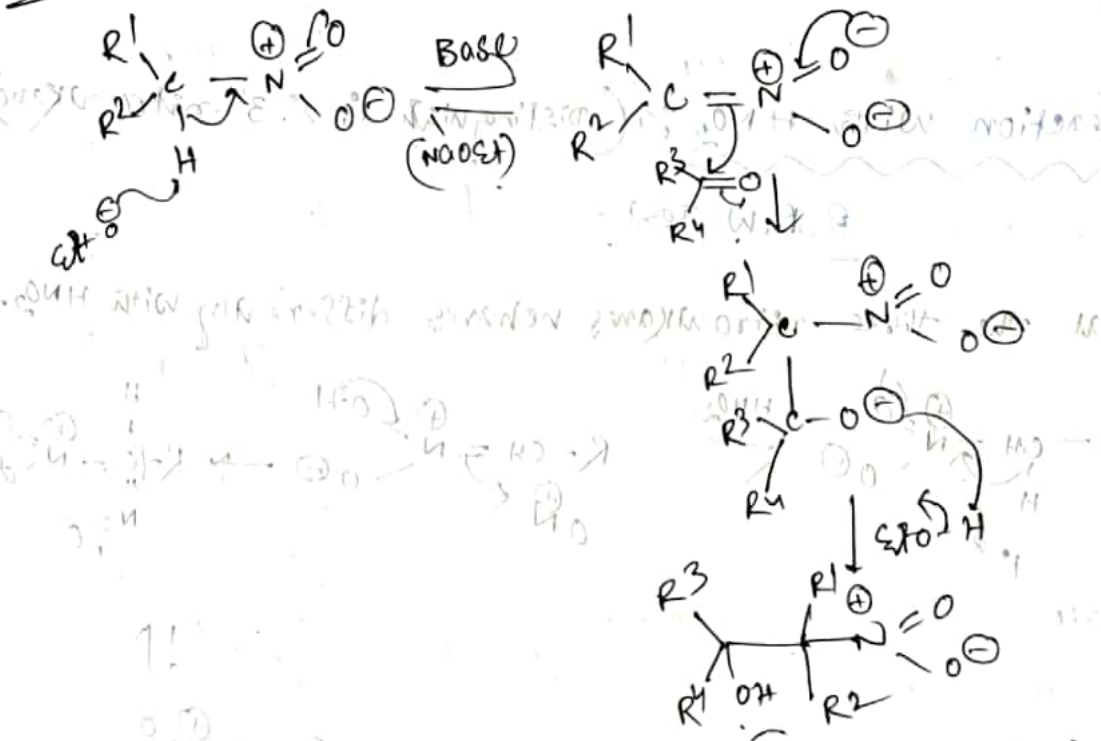
(soluble in ether, produced white colour soln)

Henry reaction :- (Nitro-aldol rxn)

It is the combination of nitroalkane (1°/2°) and an aldehyde/ketone in the presence of a base to form β-nitro alcohols.



Mech.



Questions:

1. How would you distinguish nitromethane and methyl nitrite by chemical methods ?

2. How can you distinguish following pairs -

(a) $EtCN$ and $EtNC$ (b) $CH_3CH_2CH_2NO_2$ and $(CH_3)_2CHNO_2$.

Alkyl nitrile and isonitrile

Alkyl cyanides :- (R-CN)

These are also known as nitriles/carbonitriles.

Preparation :-

(I) From R-X :-

$$R-X + NaCN/KCN \longrightarrow R-CN + NaX/KX.$$

The method is satisfactory only if 1°/2° alkyl groups. If it is 3° very little cyanides is obtained.

(II) From Grignard reagent :-

$$R-X \xrightarrow[Et_2O]{Mg} R-MgX \xrightarrow{ClCN} RCN + MgCl_2$$

- This is the best method of preparing tertiary alkyl cyanides

(III) From Amide :-

$$R-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow[\Delta,\ PCl_5]{Al_2O_3} R-CN + H_2O$$

(IV) From oxime :-

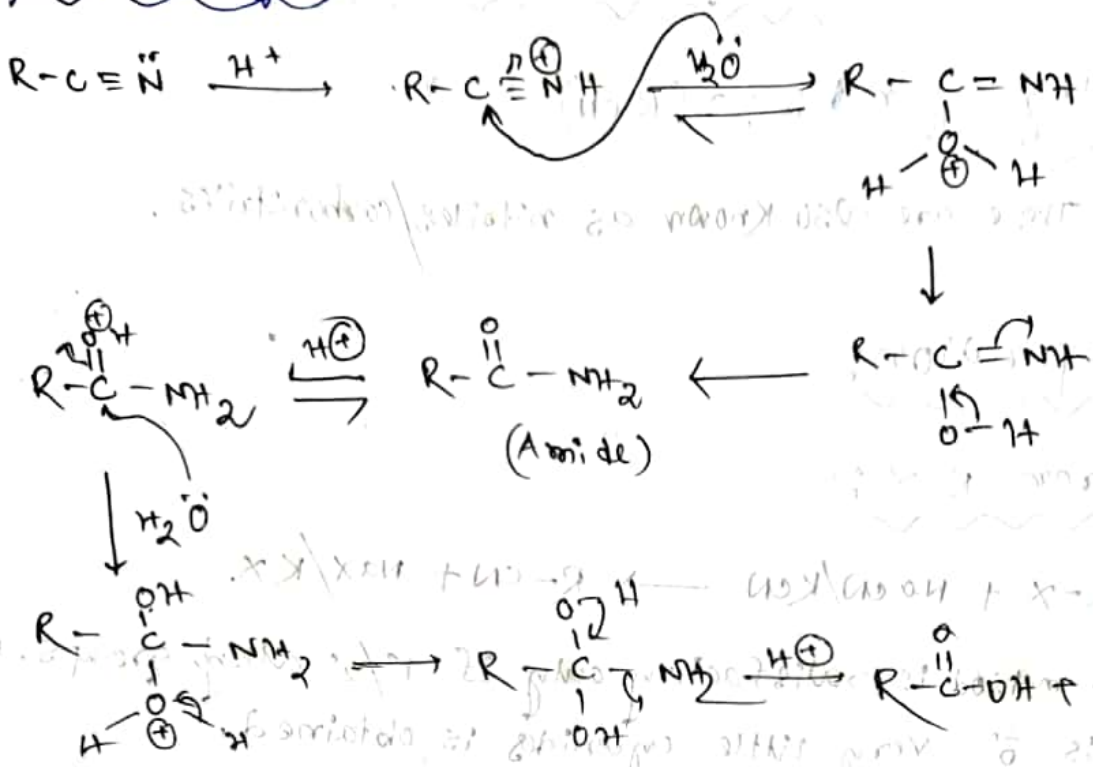
$$R-\underset{H}{C}=N-OH \xrightarrow{P_2O_5} RCN + H_2O.$$

Reactions :-

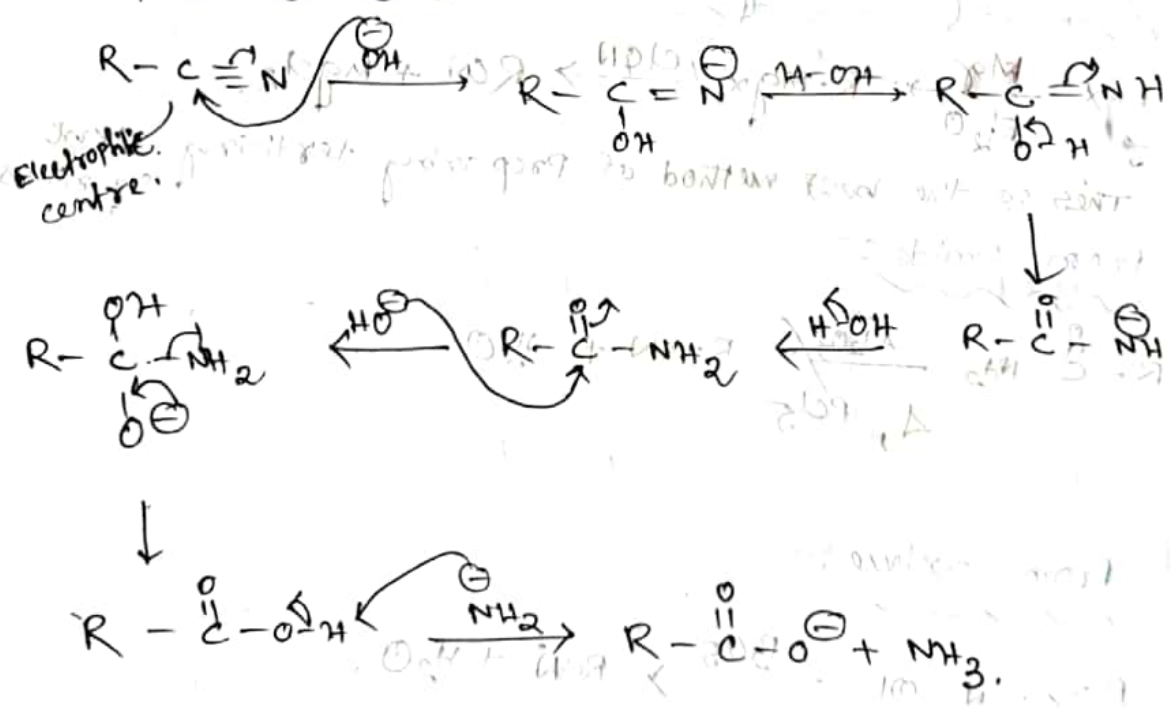
(I) Hydrolysis :-

Alkyl cyanides are hydrolysed by acidic & basic solution as —

(A) Acid catalysed:-



(B) Base catalysed:-

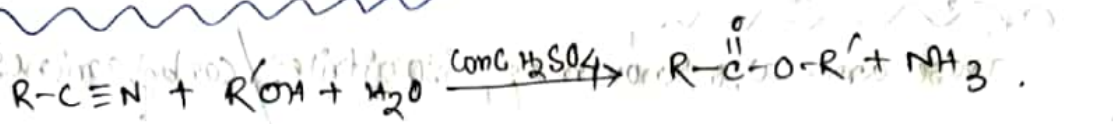


(II) Reduction:-

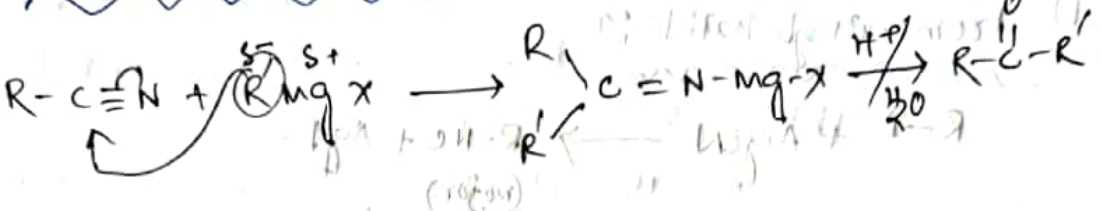
$$R-C\equiv N \xrightarrow[\text{or LAH}]{Na/C_2H_5OH} R CH_2 NH_2 \quad (1^\circ \text{ amine})$$

$$R-C\equiv N \xrightarrow[\text{(II) } H_2O/\Delta]{\text{(I) } SnCl_2/HCl} R-\overset{O}{\overset{\|}{C}}-H \quad (\text{Stephen synthesis}).$$

③ Formation of esters :-

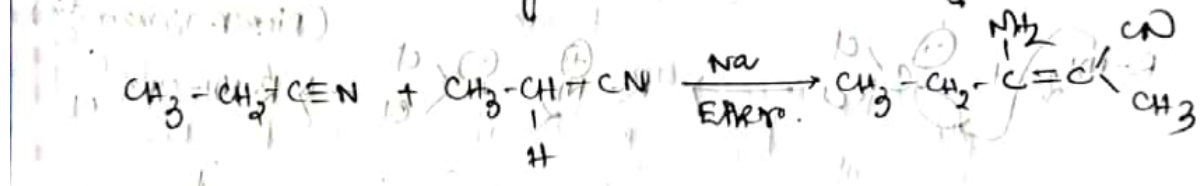


④ Rxn with Grignard reagent :- (Ketone)

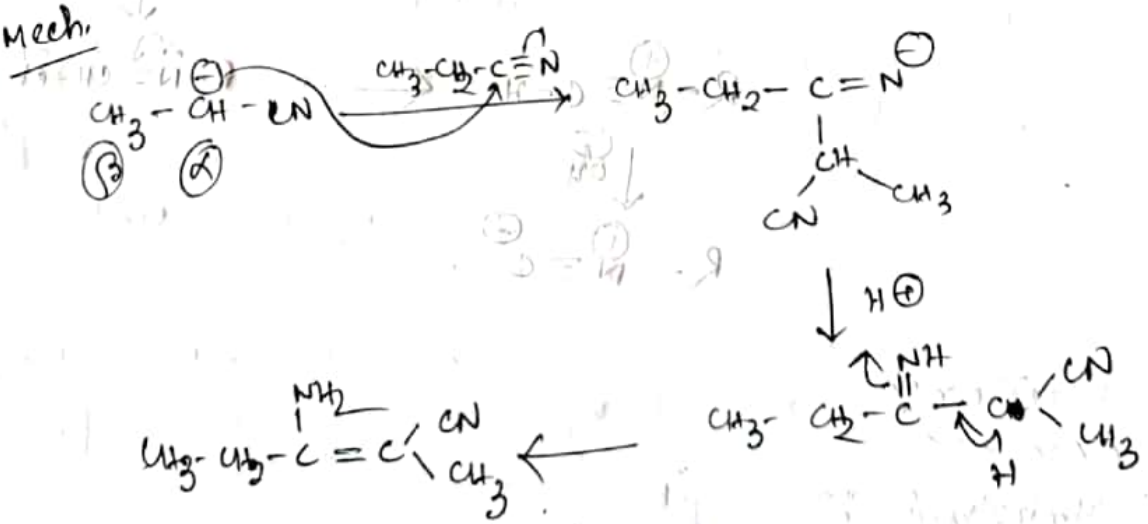


Twrope nitrile condensation :-

Alkyl cyanides undergo condensation rxn in the presence of Na in ethers when two molecules of cyanide condense and only α-H atoms being involved.



Mech.



Alkyl isocyanides :-

These are also known as isonitriles / carbylamines.

Preparation :-

(I) From alkyl halide :-

$$R-I + AgCN \longrightarrow \underset{\text{(major)}}{R-NC} + AgI$$

(II) By carbylamine reaction :-

$$RNH_2 + CHCl_3 + 3KOH \rightarrow RNC + 3KCl + 3H_2O$$

Mech.

$CHCl_3 + KOH \xrightarrow{-H_2O} \overset{\ominus}{C}Cl_3 \xrightarrow{-Cl^{\ominus}} :CCl_2$ (Dichlorocarbene)

(Riemer-Tiemann Rx^n)

$R-\ddot{N}H_2 + :\ddot{C}Cl_2 \longrightarrow R-\overset{\oplus}{N}H_2-\overset{\ominus}{C}Cl_2 \longrightarrow R-NH-CHCl_2$

$\downarrow -HCl$

$R-\ddot{N}=CHCl \longrightarrow R-\overset{\oplus}{N}\equiv C-H$

$\downarrow OH^{\ominus}$

$R-\overset{\oplus}{N}\equiv C^{\ominus}$

Reaction :-

(I) Hydrolysis :-

(Acid catalysed)

$R-\overset{\oplus}{N}\equiv C^{\ominus} \overset{H^+}{\rightleftharpoons} R-\overset{\oplus}{N}\equiv C-H \xrightarrow{H_2O} R-N=C-H$

$R-NH-\overset{\overset{\oplus}{O}H}{\overset{\|}{C}}-H \xleftarrow{H^+} R-NH-\overset{O}{\overset{\|}{C}}-H \longleftarrow R-\overset{\oplus}{N}H=C-H$

$\downarrow H_2O$

$R-NH-\underset{OH}{\overset{OH}{C}}-H \xrightarrow{H^+} RNH_2 + H-\overset{O}{\overset{\|}{C}}-OH$

(*) Isocyanides does not undergo hydrolysis under base catalyst cond^{n} because —

The major resonating str. of isocyanides will be $R-\overset{\oplus}{N}\equiv\overset{\ominus}{C}$. where all the atoms are octet state. The base which is electron dense does not attack $C^{\ominus}$ centre repel each other. $R-\overset{\oplus}{N}\equiv C^{\ominus} \leftrightarrow \overset{\ominus}{OH}$

Repulsion.

Again same base ($\overset{\ominus}{OH}$) can not attack the $\overset{\oplus}{N}$ centre as pentavalent does not exist.

(II) Reduction :-

$$R-\overset{\oplus}{N}\equiv C^{\ominus} \xrightarrow{LAH} R-NHCH_3$$

N-methyl amine (2°).

(III) Isomerisation :-

When alkyl isocyanides are heated for long time, they rearranges to the cyanides.

$$\xrightarrow{heat} R-C\equiv N.$$

(IV)

$$R-\overset{\oplus}{N}\equiv C^{\ominus} \xrightarrow[\Delta]{S} R-N=C=S.$$

Alkyl isothiocyanates.

$$R-\overset{\oplus}{N}\equiv C^{\ominus} \xrightarrow{H_2O} R-NCO.$$

Alkyl isocyanates.

Alkyl halide give mainly cyanides with aq. ethanolic KCN, but with AgCN isocyanides are the main products. — Explain.

→ Alkali cyanides are ionic ($^{\ominus}C\equiv N^{\oplus}$) and so can form a covalent bond either from the carbon or 'N' atom. In cyanide 'C'-atom is soft end & 'N'-atom is hard end of the nucleophile.

~~Ex~~ S_N^2 rxn proceeds in the presence of KCN where soft – soft combination occurs & forms R–CN.

$$N\equiv C^{\ominus} + R{-}X \xrightarrow{S_N^2} \left[N^{\delta-} \cdots C \cdots R \cdots X^{\delta-} \right]^{\neq} \longrightarrow RCN + X^{\ominus}$$

(C: soft, soft; T.S)

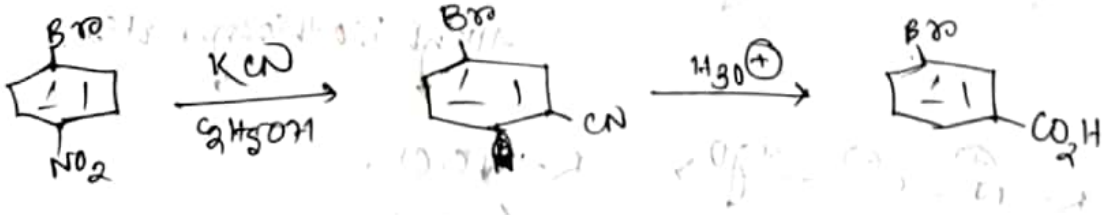
In presence of AgCN, the rxn proceeds through the S_N1 mechanism & to form R-NC by hard – hard combination

$$R{-}X + AgCN \xrightarrow[S_N1]{\text{slow}} AgX + R^{\oplus} + {:}N\equiv C^{\ominus} \longrightarrow R{-}N\equiv C^{\ominus}$$

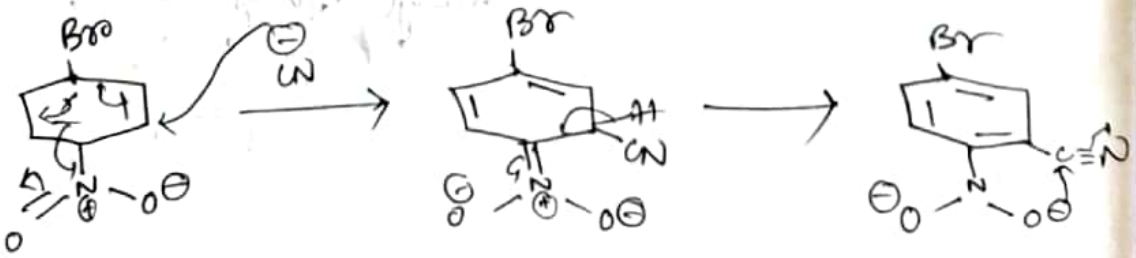
(hard, hard)

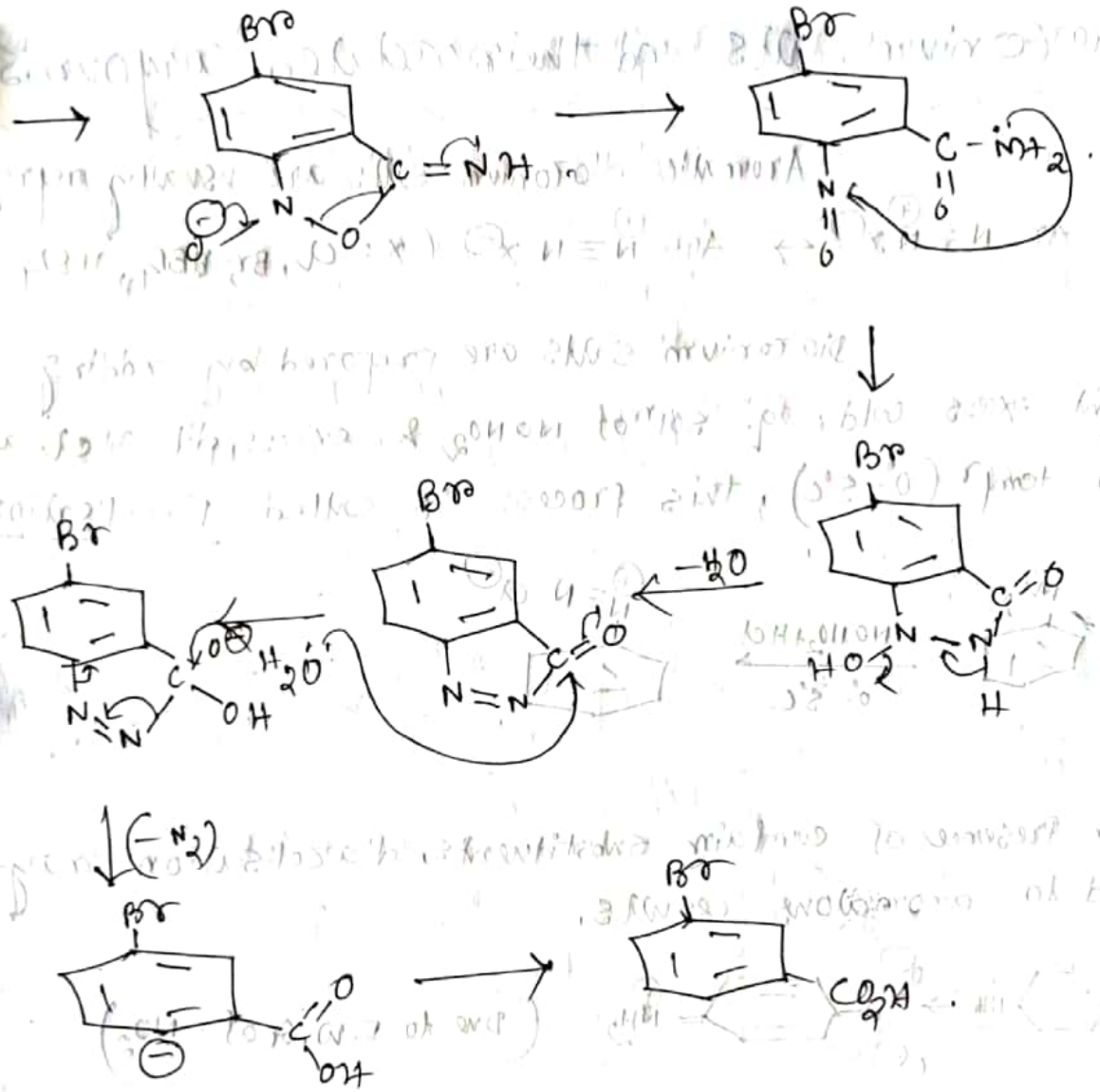
Von Richter Reaction:

This is the example of nucleophilic substitution with rearrangement. It does not occurs by aryne. When halogenated nitrobenzene is heated with KCN, the $-NO_2$ expelled and a $-CN$ gr enter ortho to the $-NO_2$ group.



Mech.

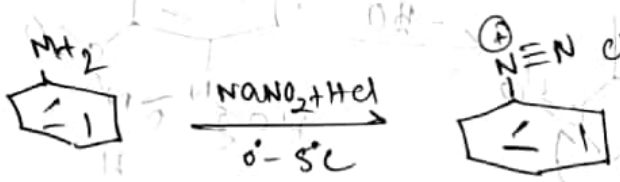




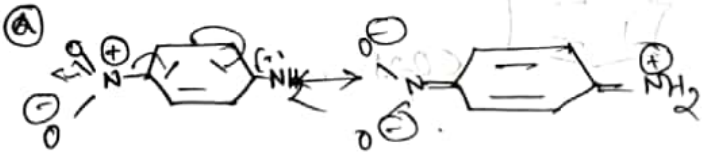
Diazonium salts and their related compounds

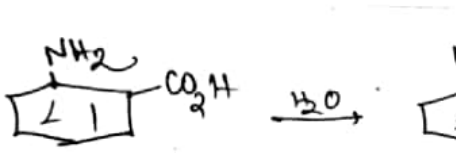
Aromatic diazonium salts are usually represented by $Ar-N=\overset{\oplus}{N}\,X^{\ominus} \leftrightarrow Ar-\overset{\oplus}{N}\equiv N\,X^{\ominus}$ ($X = Cl, Br, BF_4, HSO_4$ etc)

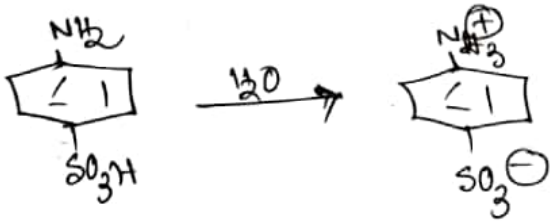
Diazonium salts are prepared by adding slight excess cold aq. soln of $NaNO_2$ & excess dil HCl at low temp^r ($0°-5°C$), this process is called Diazotisation

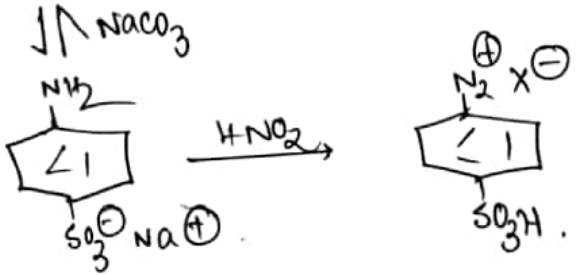


(*) In presence of certain substituents, diazotisation may lead to anomalous results.

(a)  (Due to E.W.G of $-NO_2$)

(b)  (Zwitter ion) $\xrightarrow{HNO_2}$ X

 (Zwitter ion) $\xrightarrow{HNO_2}$ X



Replacement Reaction :-

(I) Replacement by -OH group :- (Hydrolysis)

Diazonium salts are converted into the corresponding Phenol by boiling with H_2O / acidified followed by warming.

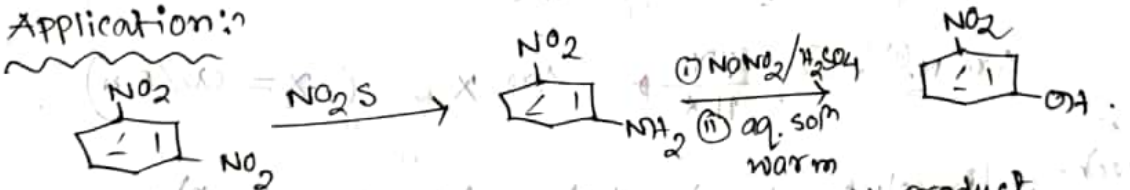
$$Ar\overset{\oplus}{N}\equiv N\ X^{\ominus} \xrightarrow{warm} ArOH + N_2 + HX$$

Mech. (S_N1 pathway).

$$ArN_2^{\oplus}X^{\ominus} \underset{}{\overset{r.d.s}{\rightleftharpoons}} Ar^{\oplus} + N_2 + X^{\ominus}.$$

$$Ar^{\oplus} \xrightarrow[H_2O]{fast} Ar\overset{\oplus}{O}\overset{H}{\underset{H}{}} \longrightarrow ArOH + HX$$

(*) Application :-



(*) If $X = -Cl$ then $Ar-X$ is formed as side product due to Cl is good nucleophile than $HSO_4^{\ominus}$.
But $X = HSO_4^{\ominus}$ then only ArOH is formed.

(II) Replacement by -H :- (Deamination).

A better method is reduction of diazonium salt by H_3PO_2 in presence of $Cu^{\oplus}$ as a catalyst.

$$ArN_2^{\oplus}X^{\ominus} \xrightarrow[Cu^{\oplus}]{H_3PO_2} ArH.$$

* Another Method :-

$$ArN_2^{\oplus}X^{\ominus} \xrightarrow[Boil]{EtOH} ArH + ArOEt.$$

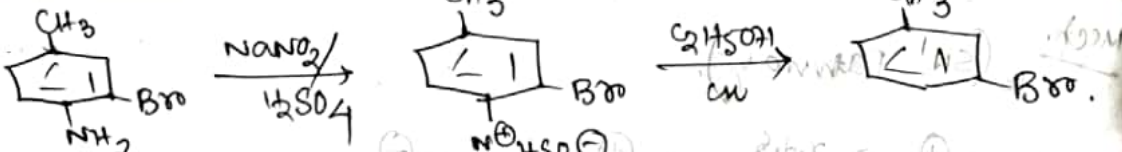
Mech. (Free radical mechanism)

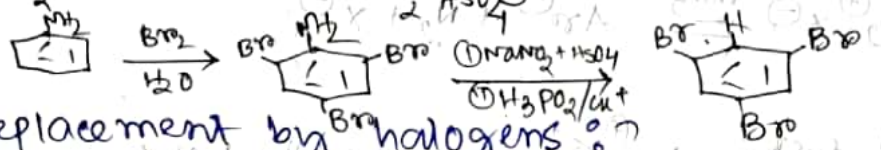
Initiation: $ArN_2^{\oplus} + Cu^{+} \longrightarrow Ar^{\cdot} + N_2 + Cu^{2+}$

propagation: $Ar^{\cdot} + H_3PO_2 \longrightarrow ArH + H_2\dot{P}O_2$

$ArN_2^{\oplus} + H_2\dot{P}O_2 + H_2O \longrightarrow Ar^{\cdot} + N_2 + H_3PO_3 + H^{\oplus}$

- **Application:**

① 

② 

③ Replacement by halogens :-

✱ sandmeyer's reaction :- (replacement by Cl & Br)

$ArN_2^{\oplus}X^{\ominus} \xrightarrow[HX]{CuX} ArX \quad (X = Cl/Br)$

Mech. (involve single electron transfer red^n & then ligand transfer occure.

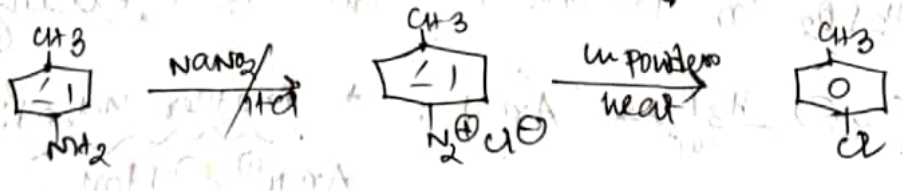
$CuX + X^{\ominus} \longrightarrow CuX_2^{\ominus}$

$ArN_2^{\oplus} + CuX_2^{\ominus} \longrightarrow Ar^{\cdot} + N_2 + CuX_2$ | $Cu(I) \rightarrow Cu(II)$

$Ar^{\cdot} + X\text{-}Cu\text{-}X \longrightarrow Ar\text{-}X + CuX.$ | $Cu(II) \rightarrow Cu(I)$

- Gattermann reaction :- (Modification of sandmeyer's rx^n).

Cu powders is used in place of Cu salts for this type of rx^n (sandmeyer's rx^n).



⊛ Replacement by I :-

$$Ar\overset{\oplus}{N_2}X^{\ominus} \xrightarrow[\text{warmed}]{KI} ArI + N_2 + KX$$

Mech. via single electron transfer (SET).

Initiation: $Ar\overset{\oplus}{N_2} + I^{\ominus} \longrightarrow Ar^{\cdot} + N_2 + I^{\cdot}$

Propagation: $Ar^{\cdot} + I_2 \longrightarrow ArI + I^{\cdot}$

$$I^{\cdot} + I^{\ominus} \longrightarrow I_2^{\cdot-}$$

$$Ar\overset{\oplus}{N_2} + I_2^{\cdot-} \longrightarrow Ar^{\cdot} + N_2 + I_2$$

⊛ Schiemann reaction :- (replacement by -F)

When HBF_4 acid is added to $Ar\overset{\oplus}{N_2}X^{\ominus}$ soln, insoluble fluoroborate is precipitated. It is separated and on heating gives fluorobrene.

$$Ar\overset{\oplus}{N_2}X^{\ominus} \xrightarrow[\Delta]{HBF_4} ArF + N_2 + BF_3$$

Mech. SN^1 pathway.

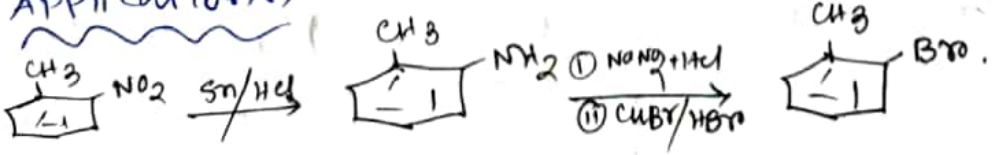
$$Ar\overset{\oplus}{N_2}X^{\ominus} \xrightarrow{HBF_4} Ar\overset{\oplus}{N_2}BF_4^{\ominus} + HX$$

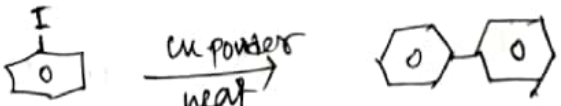
(Insoluble)

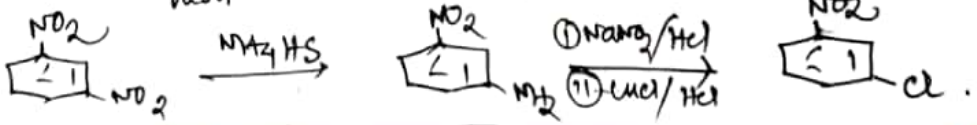
$$Ar\overset{\oplus}{N_2}BF_4^{\ominus} \xrightarrow{\Delta} Ar^{\oplus} + N_2 + BF_4^{\ominus}$$

$$Ar^{\oplus} \leftarrow F\text{-}BF_3^{\ominus} \longrightarrow ArF + BF_3$$

⊛ Application :-

(i) 

(ii) 2 

(iii) 

⊛ Replacement by I :-

$$Ar\overset{\oplus}{N_2}X^{\ominus} \xrightarrow[\text{warmed}]{KI} ArI + N_2 + KX .$$

Mech. via single electron Transfer (SET).

Initiation: $Ar\overset{\oplus}{N_2} + I^{\ominus} \longrightarrow Ar^{\cdot} + N_2 + I^{\cdot}$

Propagation: $Ar^{\cdot} + I_2 \longrightarrow ArI + I^{\cdot}$

$$I^{\cdot} + I^{\ominus} \longrightarrow I_2^{\cdot-}$$

$$Ar\overset{\oplus}{N_2} + I_2^{\cdot-} \rightarrow Ar^{\cdot} + N_2 + I_2 .$$

⊛ Schiemann reaction :- (replacement by -F)

When HBF_4 acid is added to $Ar\overset{\oplus}{N_2}X^{\ominus}$ soln, insoluble fluoroborate is precipitated. It is separated and on heating gives fluorobrene.

$$Ar\overset{\oplus}{N_2}X^{\ominus} \xrightarrow[\Delta]{HBF_4} ArF + N_2 + BF_3$$

Mech. SN^1 pathway.

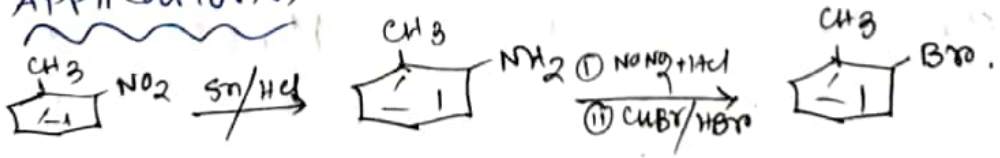
$$Ar\overset{\oplus}{N_2}X^{\ominus} \xrightarrow{HBF_4} Ar\overset{\oplus}{N_2}BF_4^{\ominus} + HX .$$

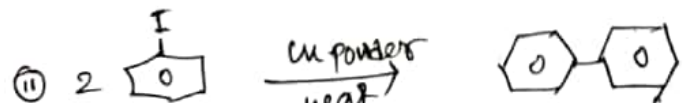
($Ar\overset{\oplus}{N_2}BF_4^{\ominus}$: insoluble)

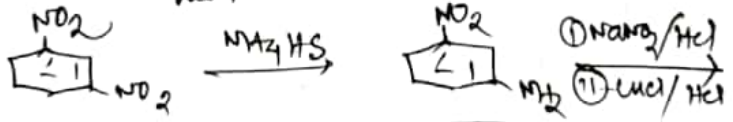
$$Ar\overset{\oplus}{N_2}BF_4^{\ominus} \xrightarrow{\Delta} Ar^{\oplus} + N_2 + BF_4^{\ominus} .$$

$$Ar^{\oplus} \leftarrow F - BF_3^{\ominus} \longrightarrow ArF + BF_3 .$$

⊛ Application :-

(i) 

(ii) 

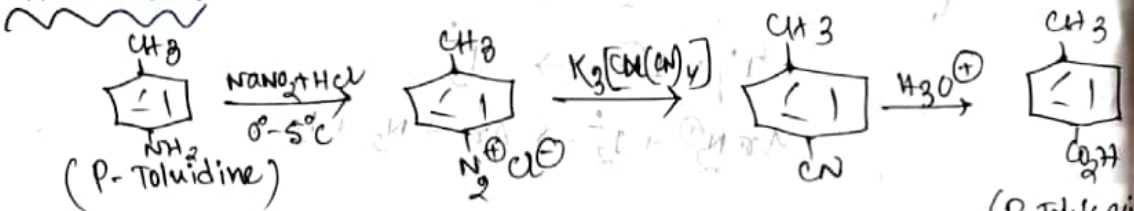
(iii) 

(iv) **Replacement by −CN group in (special case of Sandmeyer rxn).**

When, diazonium salt soln is treated with CuCN in aq. KCN or $K_3[Cu(CN)_4]$, the diazo group is replaced by −CN group and aroyl cyanide is formed.

$$Ar\,N_2^{\oplus}X^{\ominus} \xrightarrow[+\,K_3[Cu(CN)_4]]{CuCN/KCN\ (aq.)} ArCN.$$

- **Application:**



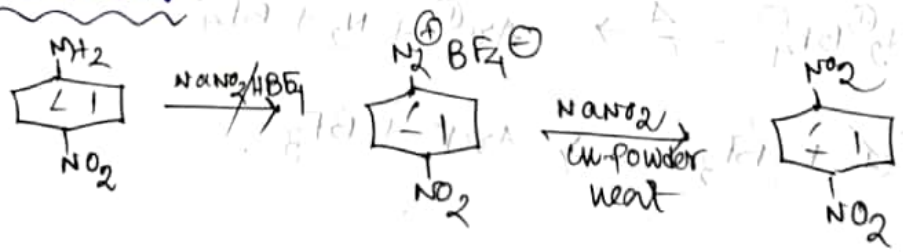
(*) KCN should not be used in large excess otherwise the rxn is retarded due to formation of more stable complex $[Cu^{I}(CN)_4]^{3-}$.

(v) **Replacement by $-NO_2$ group in**

When aromatic diazonium fluoroborate is decomposed with $NaNO_2$ in presence of Cu powder, diazo group is replaced by $-NO_2$ group.

$$Ar\,NH_2 \xrightarrow[NaNO_2,\ 0-5C]{HBF_4} Ar\,N_2^{\oplus}BF_4^{\ominus} \xrightarrow[Cu\text{-}powder,\ heat]{NaNO_2} Ar\,NO_2 + NaBF_4 + N_2$$

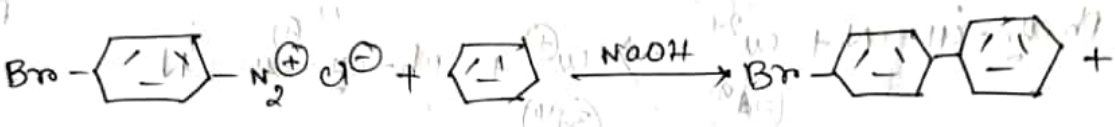
- **Application:**



Gomberg Reaction: (Replacement of aryl group)

Biaryl may be prepared by adding an aromatic compound to an alkaline soln of a diazonium salt. This method of preparation is known as Gomberg reaction.

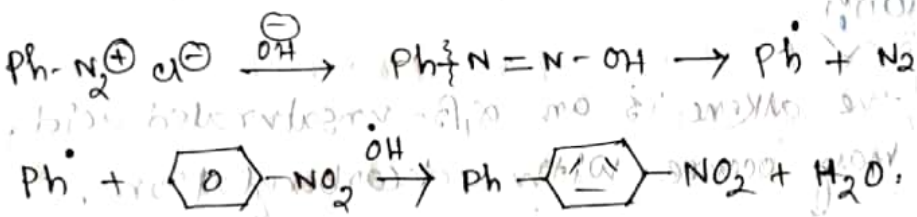
eg:



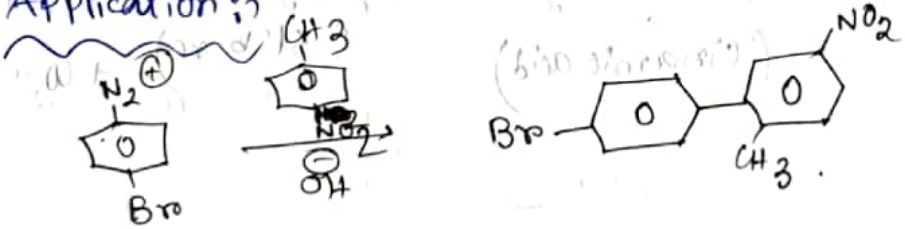
$N_2 + NaCl + H_2O$.

* However improved yield can be obtained in the presence of peroxide.

Mech: The rxn takes place by a free radical mechanism.



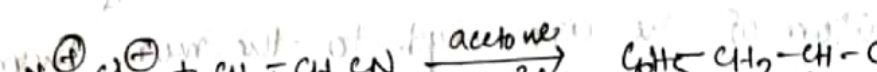
- Application:



Meerwein reaction:

This is the rxn between diazonium salts and compounds containing an activated ethylenic bond to give arylated products. The reaction is carried out in acetone soln in the presence of a cupric salt.

eg:



Mech.

The rxn occure through free radical mechanism.

$$Ph\text{-}N_2^{\oplus}Cl^{\ominus} + Cu^{2+} \longrightarrow Ph^{\cdot} + N_2 + Cu^{2+} + Cl^{\ominus}$$

$$Ph^{\cdot} + CH_2=CH\text{-}CN \longrightarrow Ph\text{-}CH_2\text{-}\dot{C}H\text{-}CN$$ (more stable than $\dot{C}H_2\text{-}CH(Ph)\text{-}CN$)

$$Ph\,CH_2\text{-}\dot{C}H\text{-}CN + Cu^{2+} \longrightarrow Cu^{\oplus} + Ph\text{-}CH_2\text{-}\overset{\oplus}{C}H\text{-}CN$$

(Cu^{2+}: $3d^9$; $Cu^{\oplus}$: $3d^{10}$)

$$\downarrow Cl^{\ominus}$$

$$Ph\text{-}CH_2\text{-}CH(Cl)\text{-}CN$$

⊛ Application:

When the alkene is an α,β-unsaturated acid, then arylation may occure with decarboxylation.

e.g.

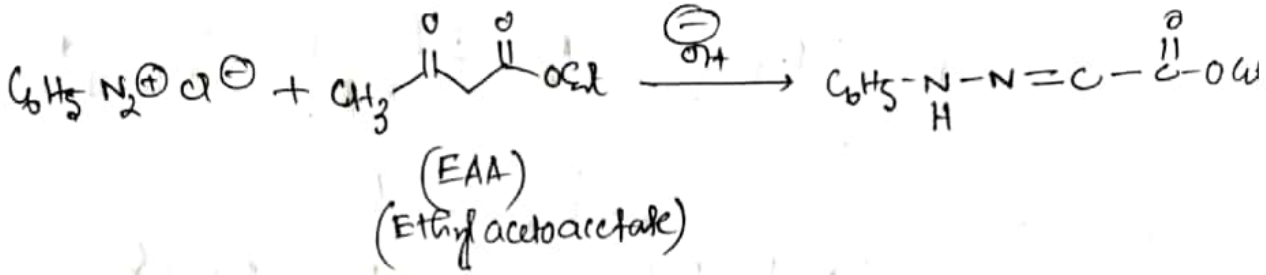
$$PhN_2^{\oplus}Cl^{\ominus} + C_6H_5CH=CHCO_2H \longrightarrow C_6H_5CH=CH\text{-}C_6H_5 + N_2 + CO_2 + HCl$$

(Cinamic acid) (Stibene)

Japp-Klingemann Reaction:

The coupling reaction occures in the presence of sodium acetate with compounds containing an active methylene group e.g. DEM, EAA. The product is usually the phenylhydrazone, formed by the tautomerisation of the azo compd. to the more thermodynamically stable hydrazone.

e.g.



(EAA)
(Ethyl acetoacetate)

Mech.