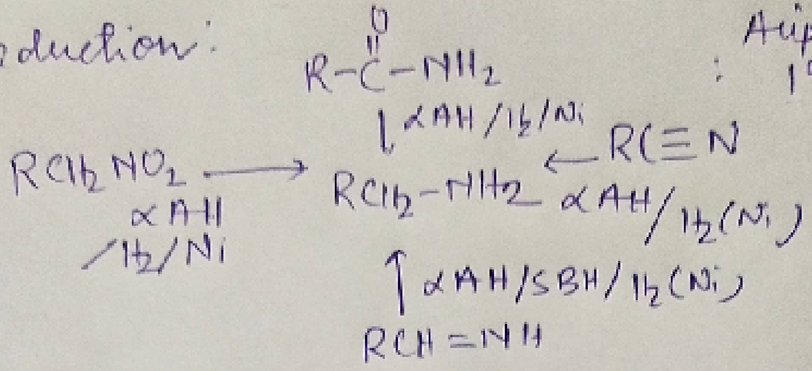
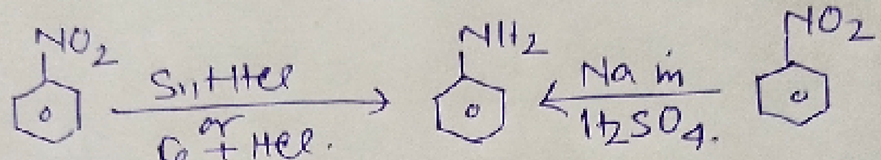
Amine (Aliphatic / Aromatic):

i) : Reduction:

Aliphatic : 1° Amine



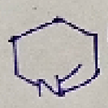
ii)



Aromatic 1° amine.

iii) $R-\underset{\underset{O}{\|}}{C}-NHR$ (N alkyl substituted amide)

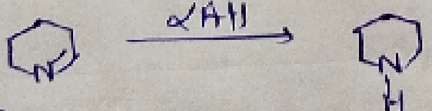
$R-\overset{+}{N}\equiv\overset{-}{C}:$ (Alkyl isocyanide)


(Cyclic 3° amine system)

all when undergo reaction with LiAlH4 they will give 2° amine.

a) $R-\underset{\underset{O}{\|}}{C}-NHR \xrightarrow{LiAlH_4} RCH_2-NHR$

b) $R-\overset{+}{N}\equiv\overset{-}{C}: \xrightarrow{LiAlH_4} RNH-CH_3$

c) 

iv) $R-\underset{\underset{O}{\|}}{C}-N\begin{matrix}R\\-R\end{matrix}$ (N,N dialkyl substituted amide)

when undergoes reaction with LiAlH4, it gives 3° amine $R-\underset{\underset{O}{\|}}{C}-N\begin{matrix}R\\-R\end{matrix} \xrightarrow{LiAlH_4} RCH_2-N\begin{matrix}R\\-R\end{matrix}$.

v) Reductive amine of carbonyl compound can give 1°/2°/3° amine.

a) $>C=O + NH_3 \longrightarrow >C=NH \xrightarrow{\text{reduction}} >CH-NH_2$ (2)
aminahi

b) $>C=O + RNH_2 \longrightarrow >C=NR \xrightarrow{\text{reduction}} >CH-NHR$.

vi) Ammonolysis of alkyl halide can give 1°/2°/3° amine using NH_3/RNH_2/R_2NH excess.

$RCH_2X \xrightarrow[(XS)]{+NH_3} RCH_2NH_2$.

$RCH_2X \xrightarrow[(XS)]{RNH_2} RCH_2NHR$

$RCH_2X \xrightarrow[(XS)]{R_2NH} RCH_2NR_2$

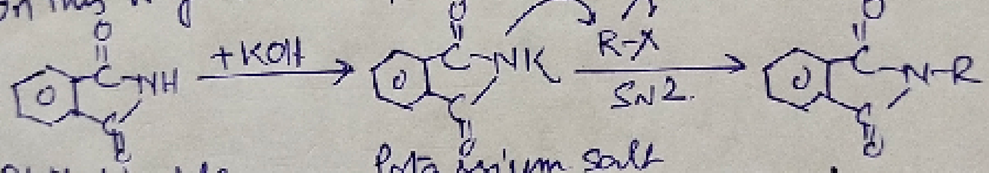
All are example of S_N2 reaction.

So alkyl halide used should not be 3° R-X, In this case elimination reaction takes place.

$PhNH_2$ & $CH_2=CH-NH_2$ can not be prepared because  & $CH_2=CH-X$ is unreactive towards S_N2 reaction.

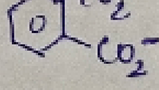
vii) Gabriel Phthalimide Synthesis

In this way we can prepare 1° amine



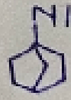
Phthalimide

Potassium salt of Phthalimide

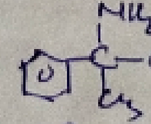
$\xrightarrow[\Delta]{OH/H_2O}$  $+ RNH_2$

Limitation:

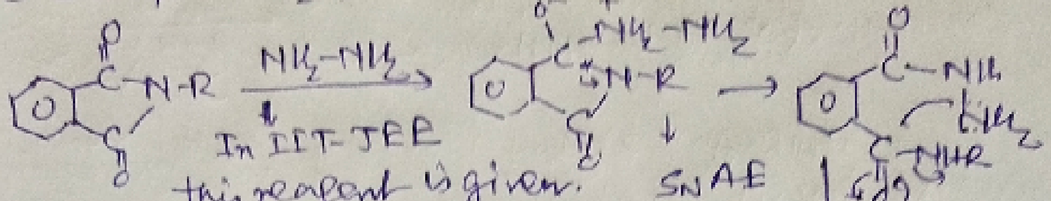
i) The following 1° amine can't be prepared by this way

a)  (b) $CH_2=CH-NH_2$ (c) 

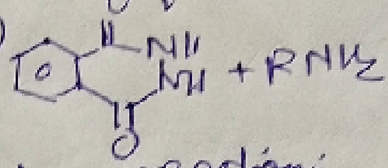
Because corresponding halide is unreactive towards S_N2 reaction.

(d) Me_3C-NH_2, (e) Et_3C-NH_2 (f)  can not be prepared because corresponding 3° R-X very unreactive towards S_N2 mechanism.

In Gabriel Phthalimide synthesis in last step ③ instead of OH/H_2O, we can also use NH_2-NH_2.



We can not prepare R-C(=O)-NH2 (Amide) R_2NH, R_3N by this reaction



Amine Preparation (1° RNH_2) by stepdown reaction:

	Name of reaction	Starting cpd. / Reagent.	R.I.P / Intermediate
i)	Hoffman Bromamide Reaction (degradation)	$R-C(=O)-NH_2 + KOBr$	$RNH_2 / R-N=C=O$
ii)	Curtius reaction	$RCOCl + NaN_3/\Delta$	$RNH_2 / R-N=C=O$
iii)	Schmidt Reaction.	$R-C(=O)-OH / HN_3 + H_2SO_4$.	$RNH_2 / R-N=C=O$
iv)	Lossen Rearrangement.	$R-C(=O)-NHOH / H^+$	$RNH_2 / R-N=C=O$

Hoffman Bromamide reaction:

i) The reagent used $KOH + Br_2$ / KOBr.
organic substrate used is $R-C(=O)-NH_2$

$$R-C(=O)-NH_2 \xrightarrow{KOH} R-C(=O)-NHK \xrightarrow{Br-Br} R-C(=O)-NHBr$$

$$R-C(=O)-NHBr \xrightarrow{KOH} R-C(=O)-\overset{\ominus}{N}-Br \xrightarrow{r.d.s} R-N=C=O.$$

$$R-N=C=O + \overset{\cdot\cdot}{\bar{O}}H/H_2O \rightarrow R-\overset{\ominus}{N}=C(-O^-)-OH_2^+$$

$$R-NH-C(=O)-O-H \rightarrow R-NH_2 + CO_2$$

$CO_2 + KOH \rightarrow K_2CO_3$.

4eq KOH/NaOH is consumed up.

$$RCONH_2 + Br_2 + 4NaOH \rightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

featureg this reaction

⇒ 1st step acid base reaction.

⇒ $R-\underset{\underset{O}{\|}}{C}-NHBr$; $R-\underset{\underset{O}{\|}}{C}-\overset{\ominus}{N}-Br$; $R-N=C=O$ are formed as intermediate in this reaction

⇒ r.d.s involves loss of leaving group & shift of alkyl group. So more migrating tendency of alkyl group, faster will be reaction.

⇒ Alkyl isocyanate is formed as intermediate.

⇒ Here nitrene is formed as intermediate which can not be isolated. (electron defficient N : one valency :NH is called nitrene)

⇒ $R-\underset{\underset{O}{\|}}{\overset{14}{C}}-NH_2 \xrightarrow{KOH} K_2\overset{14}{C}O_3$ Carbonate ion is formed as products which has ^{14}C.

⇒ It's example of step down reaction where carbon no is reduced by 1 unit.

⇒ It is example of intramolecular rearrangement.

$$R-\underset{\underset{O}{\|}}{C}-NH_2 + R-\underset{\underset{O}{\|}}{C}-\overset{15}{N}D_2 \longrightarrow R-NH_2 + R\overset{15}{N}H D_2$$

Curtius reaction: (Mechanism).

$$R-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow[SNAE]{NaN_3} \underset{\text{Acid azide}}{R-\underset{\underset{O}{\|}}{C}-\overset{+}{N}=\overset{+}{N}=\overset{-}{N}} \xrightarrow[\Delta]{r.d.s} R-N=C=O \xrightarrow{H_2O} R-NH_2 + CO_2$$

Acid chloride

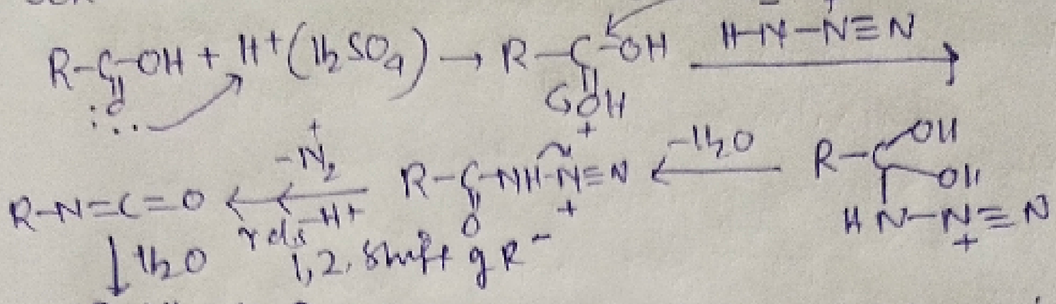
⇒ r.d.s involves loss of leaving group R migration of alkyl group. Nitrene formed as intermediate can not be isolated

Lossen Rearrangement (Mechanism)

$$R-\underset{\underset{O}{\|}}{C}-NHOH \xrightarrow[-H_2O]{H^+} R-\underset{\underset{O}{\|}}{C}-NH-\overset{+}{O}H_2 \xrightarrow{r.d.s} R-N=C=O + H_2O \xrightarrow{} R\overset{\downarrow}{N}H_2 + CO_2.$$

⇒ r.d.s involves loss of H & R migrate of alkyl group.

Schmidt Reaction (Mechanism)



=) r.d.s involves loss of $-N_2$ & shift of R^-. Nitrene is formed as intermediate which can not be isolated.

Questions:

i) $ROH \xrightarrow{PBr_3} X_1 \xrightarrow{NH_3} X_2$ $X_1 \Rightarrow R-Br$; $X_2 \Rightarrow RNH_2$.

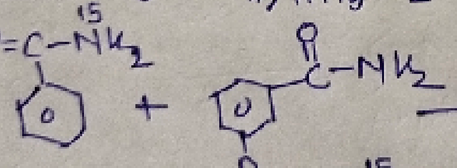
ii) $RCO_2H \xrightarrow{LAH} X_1 \xrightarrow{SOCl_2} X_2 \xrightarrow{NH_3} X_3$

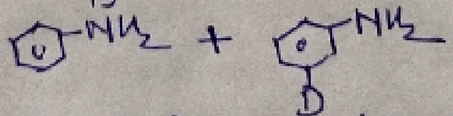
$X_1 \Rightarrow RCH_2OH$; $X_2 \Rightarrow RCH_2Cl$; $X_3 \Rightarrow RCH_2NH_2$

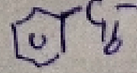
iii) Which of the following reaction gives $Et-NH_2$ as major final product.

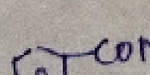
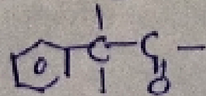
a) $EtCN \xrightarrow[ii)\ NH_3\ iii)\ NaOBr]{i)\ H_3O^+}$ b) $Et-\underset{O}{\overset{}{C}}-Cl \xrightarrow[+H_2O]{NaN_3}$

c) $EtMgBr \xrightarrow[ii)\ HN_3+K_2SO_4]{i)\ Cu_2I_2/H^+}$ d) $EtMgBr \xrightarrow{NH_2-Cl}$

iv)  $\xrightarrow[+Br]{KOH}$ Whatare the products?

Products are 

v) Which can't give Hoffmann bromamide reaction a) $CH_3-\underset{O}{\overset{}{C}}-NH-CH_3$ b) 

c)  d)  .

vi) conversion

$n C_{15}H_{31}CO_2H \longrightarrow n C_{15}H_{31}NH_2$ —(1)

$\longrightarrow n C_{16}H_{33}NH_2$ —(2)

$\longrightarrow n C_{17}H_{35}NH_2$ —(3)

$\longrightarrow n C_{16}H_{33}-\underset{\underset{NH_2}{|}}{CH}-n C_{15}H_{31}$.

Reagent used for (i) $NH_3 + KOBr$.

Reagent used for (ii) LAH; PBr_3; NH_3 (XS).

Reagent used for (iii) LAH, PBr_3, KCN; LAH.

$n C_{15}H_{31}CO_2H \xrightarrow{SOCl_2} n C_{15}H_{31}COCl \xrightarrow[(R)_2Cd \text{ or } (R)_2CuLi]{} n C_{15}H_{31}CO-n C_{16}H_{33}$.

[R =) $n C_{16}H_{33}$]

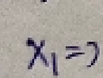
$\downarrow NH_3$.

$n C_{15}H_{31}\underset{\underset{NH_2}{|}}{CH}-n C_{16}H_{33} \xleftarrow{H_2/Ni} n C_{15}H_{31}\underset{\underset{NH}{||}}{C}-n C_{16}H_{33}$

vii) $HC\equiv CH \xrightarrow[(Lindlar)]{H_2} X_1 \xrightarrow{M.C.P.B.A} X_2 \xrightarrow{NH_3} X_3$

$X_2 \xrightarrow{NMe_3} X_4$.

$X_1 =) CH_2=CH_2$. $X_3 =) \underset{OH}{CH_2}-\underset{NH_2}{CH_2}$.

$X_2 =)$  $X_4 =) \underset{OH}{CH_2}-\underset{\overset{(+)}{N}Me_3}{CH_2}$

viii) $HO-CH_2-(CH_2)_8-CH_2OH \xrightarrow{PBr_3} X_1$

$X_1 =) Br-CH_2-(CH_2)_8-CH_2Br$

$\downarrow NH_3$

$X_2 \xrightarrow[(XS)]{MeBr} X_3$

$X_2 =) H_2N-CH_2-(CH_2)_8-CH_2-NH_2$

$X_3 =) Br^- \overset{+}{N}Me_3-(CH_2)_{10}-\overset{+}{N}Me_3\,Br^-$

ix) $CH_2=CH-CH=CH_2 \xrightarrow[+H_2O_2]{HBr\ (XS)} X_1 \xrightarrow[(XS)]{KCN} X_2 \xrightarrow{LAH\ (XS)} X_3$

Ans: $X_1 =) Br-(CH_2)_4-Br$ $X_3 =) H_2N-(CH_2)_6-NH_2$

$X_2 =) NC-(CH_2)_4-CN$

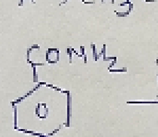
Q.1. Urea $\xrightarrow[Br_2]{KOH} X \xrightarrow{\text{Acetone}} Y$.

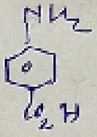
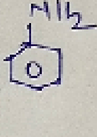
X ⇒ NH_2-NH_2 Y ⇒ $>C=N-NH_2$

Q2. $CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[2.\ H^+]{1.\ KOH + Br_2} X$ + yellow ppt.

$X \xrightarrow{SOCl_2} Y \xrightarrow{NH_3} Z_1 \xrightarrow[+Br_2]{KOH} Z_2$

X ⇒ CH_3CO_2H Y ⇒ $CH_3-\underset{\underset{O}{\|}}{C}-Cl$ Z_1 ⇒ $CH_3-\underset{\underset{O}{\|}}{C}-NH_2$ Z_2 ⇒ CH_3-NH_2

Q3.  $\xrightarrow[ii)\ H^+]{i)\ KOH + Br_2\ (X)} X_1 \xrightarrow[+CaO/\Delta]{NaOH} Y$

X_1 ⇒  Y ⇒ 

Q4. $CH_3-\underset{\underset{OH}{|}}{CH}-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow[+Br_2]{KOH} X \xrightarrow[+I_2]{NaOH} Y$.

Ist reaction is called Hoffman bromamide reaction

$CH_3-CH(OH)-\overset{\oplus}{N}H_2 \rightarrow CH_3CH=O\ (X) + NH_3$.

2nd reaction is called Iodoform reaction

$CH_3CH=O \xrightarrow[+I_2]{NaOH} HCO_2^-Na^+ + CHI_3$.

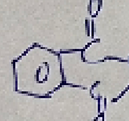
Q5 $CH_2(\underset{\underset{O}{\|}}{C}-N-Br)_2 \xrightarrow[+Br_2]{+KOH} CH_2(NH_2)_2$ Pdt ??

(NBS)

It also participates in Hoffman bromamide reaction

Pdt: $CH_2(CO_2H)_2$

$CH_2(NH_2)_2$

Q6.  (Phthalimide) $\xrightarrow[+Br_2]{KOH}$ Pdt ??

Ans:  (Anthranilic acid)

Q7 $CH_3-\underset{\underset{(R)}{|}}{\overset{Et}{CH}}-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow{KOH + Br_2} CH_3-\underset{\underset{Et}{|}}{\overset{(R)}{CH}}-NH_2$

In Hoffman bromamide reaction retention of configuration take place.

Q. Example of step down reaction.

a) Haloform reaction. c) Arndt Eistert Synthesis

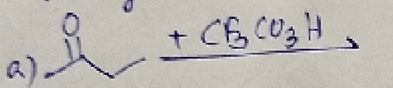
b) Hoffman bromamide reaction d) Hunsdiecker reaction

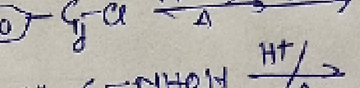
Q. Example of step up reaction

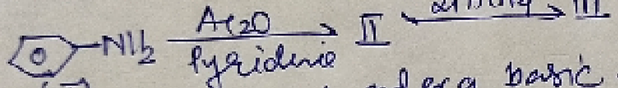
a) Oakwood reaction. c) Reaction of $H_2C{=}O$ with RMgX/H^+

b) Curtius reaction d) Schmidt reaction.

Q. In which of the following reaction electron deficient nitrogen is found as linker mediate.

a)  b) $CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[CH_2N_2]{SOCl_2}$

c)  d) $CH_3-\overset{O}{\overset{\|}{C}}-NHOH \xrightarrow[\Delta]{H^+}$

Q. 

(I) The correct order of basic strength.

a) III > I > II b) I > II > III c) III > II > I d) II > I > III.

Q. $R-\overset{O}{\overset{\|}{C}}-NH-O-\overset{O}{\overset{\|}{C}}-R' \xrightarrow{\Delta}$ Pdt.

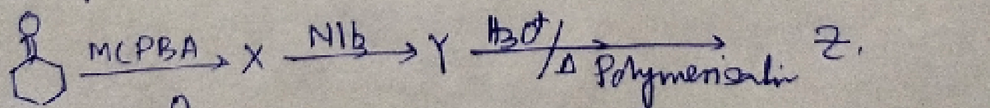
reaction rate is highest if

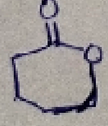
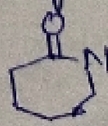
a) R, R' both are example of electron donating group.

b) R, R' both are example of electron withdrawing group

c) If R is electron donating & R' is elec. withdrawing.

d) If R is electron withdrawing & R' is electron donating.

Q. 

X =>  (7 membered cyclic ester) Y =>  (7 membered cyclic amide)

Z => Nylon-6. Caprolactum.

Detection of amine:

Carbylamine Test: This is the test of 1° amine only. Aliphatic & Aromatic 1° amine when reacts with $CHCl_3$ & alcoholic KOH, it gives foul smell product. 2° & 3° amine can not give +ve test. So this reaction is used to distinguish 1° amine & 2° amine or 1° amine & 3° amine.

$RNH_2 + CHCl_3 + KOH \longrightarrow R-\overset{+}{N}\equiv\overset{-}{C}:$

foul smell / obnoxious smell of organic

Also applicable for $PhNH_2$.

mechanism:

$CHCl_3 + KOH \longrightarrow \overset{\ominus}{C}Cl_3 + H_2O$ (Carbanion & carbene are generated as intermediate.)

$\downarrow$

$:CCl_2 + Cl^-$

(singlet carbene / electrophile)

$RNH_2 + :CCl_2 \longrightarrow RN\overset{+}{H}_2 - \overset{-}{C}Cl_2$

$\downarrow -HCl.$

$RNH-CCl \longleftrightarrow R\overset{+}{N}H=\overset{-}{C}-Cl$

$\downarrow +HCl$

$R-\overset{+}{N}\equiv\overset{-}{C}:$

2° amine R_2NH & 3° amine R_3N give −ve test.

To distinguish all types of amine, Hinsberg reagent is used up. $PhSO_2Cl$ is used in basic medium for this purpose.

Hinsberg Test: $RNH_2 + PhSO_2Cl \longrightarrow RNH-\overset{O}{\overset{\|}{S}}(=O)-Ph + HCl$

Benzene sulfonyl chloride

[water insoluble product]

It becomes water soluble on addition of KOH.

$RNH-\overset{O}{\overset{\|}{S}}(=O)-Ph + NaOH/KOH \longrightarrow R\overset{\ominus}{N}-\overset{O}{\overset{\|}{S}}(=O)-Ph\ Na^+/K^+$

water soluble.

$R_2NH + Ph-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-Cl \longrightarrow R_2N-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-Ph$

2° amine — water insoluble product remains water insoluble in basic medium because KOH/NaOH can not abstract acidic H.

$R_3N + PhSO_2Cl \longrightarrow$ No observation / no reaction because 3° amine does not have acidic H.

By this way we can distinguish all types of amine.

To distinguish aliphatic 1° amine & aromatic 1° amine we can use $NaNO_2 + HCl$ followed by PhOH/β-naphthol in basic medium.

Reaction of RNH_2 (Aliphatic 1° amine) with $NaNO_2 + HCl$ is called diazotisation.

$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$

$HNO_2 + HCl \longrightarrow H_2\overset{+}{N}O_2 + Cl^-$

(Bad) Acid

$H_2O + NO^+$

$R\ddot{N}H_2 + \overset{+}{N}O \longrightarrow R\overset{+}{N}H_2-N=O \xrightarrow{-H^+} R-NH-N=O$

$R-\overset{+}{N}_2 \leftarrow R-N=N-\overset{+}{O}H_2 \xleftarrow{H^+} RN=N-OH$

alkyl diazonium ion (very unstable / can not be found as pure)

$\downarrow -N_2$

$R^+ \xrightarrow{H_2O} R-\overset{+}{O}H_2 \xrightarrow{-H^+} R-OH$ (Colorless liquid which gives red colour with CAN solution).

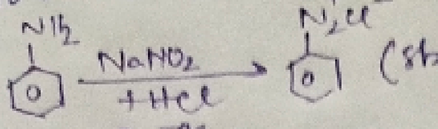
$R_2NH \xrightarrow[+HCl]{+NaNO_2} R_2N-N=O$ (yellow colour oily layer formed.)

2°/secondary amine — N-nitroso dialkyl amine.

$R_3N \xrightarrow[+HCl]{NaNO_2}$ equilibrium mixture of $R_3\overset{+}{N}HCl^-$ + $R_3\overset{+}{N}-N=O\,X^-$

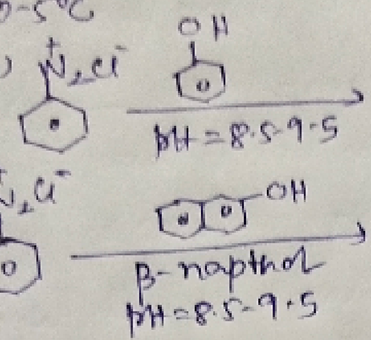
3°/Tertiary amine — N-nitroso ammonium compound

Aromatic amine: (Reaction with $NaNO_2 + HCl$)



(stable; resonance, can be isolated at 0-5°C).

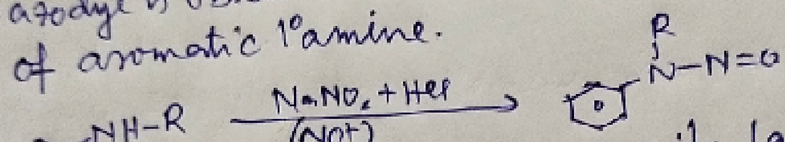
(1° amine)



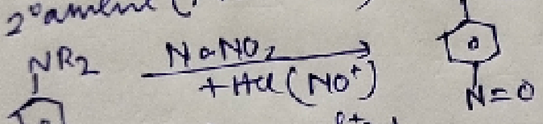
(Red colour azodye)

(Red/orange colour azodye)

If azodye is observed then it indicates the presence of aromatic 1° amine.



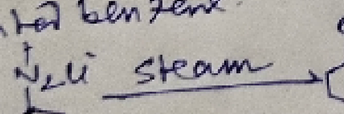
2° amine (Aromatic) — yellow oily layer.

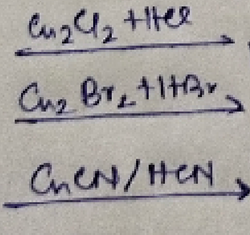


(green colour solution)

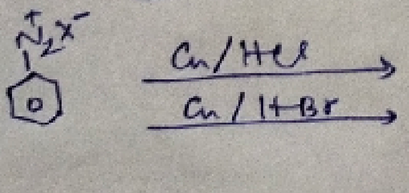
3° amine (Aromatic)

is called benzene diazonium chloride which can be used to prepare benzene / monosubstituted benzene.

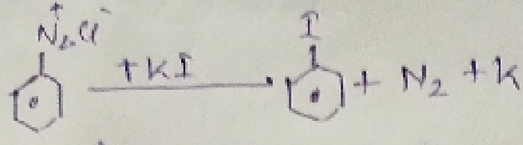


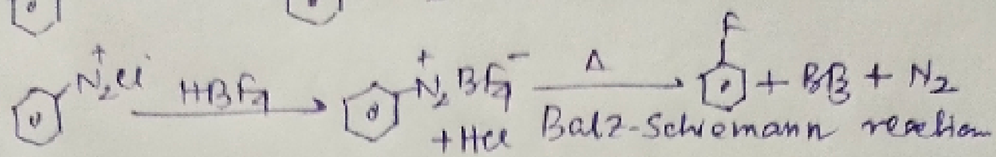


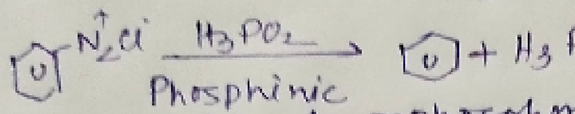
Example of Sandmayer reaction



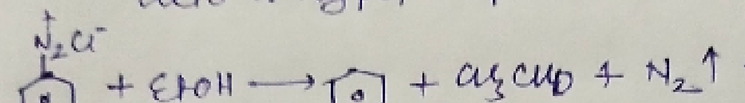
Gattermann reaction

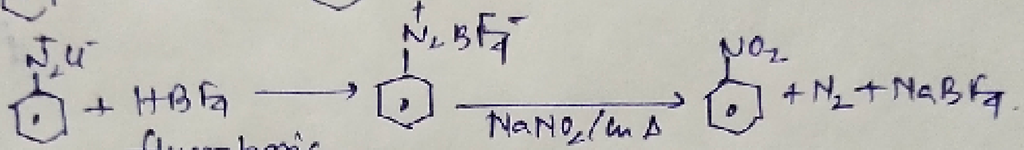




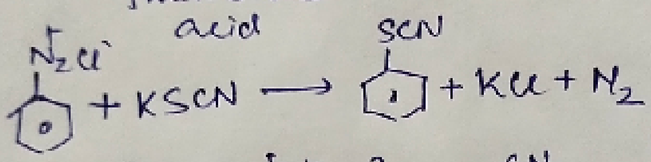


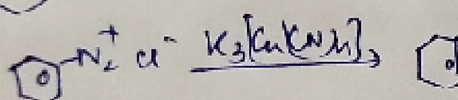
Phosphinic acid or hypophosphorous acid.



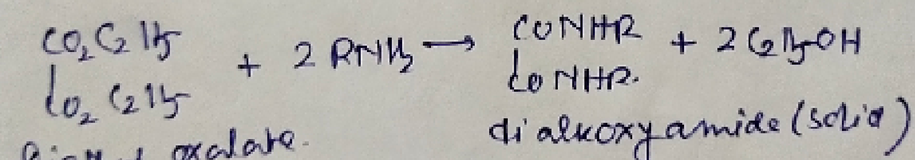


fluoroboric acid

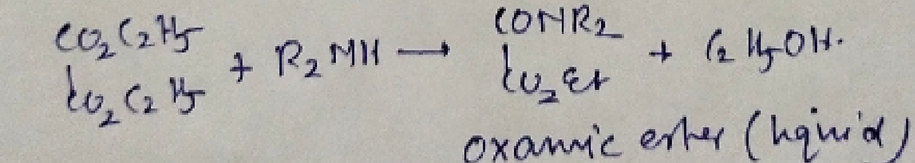




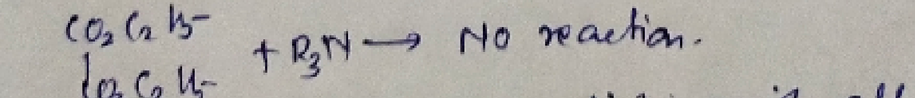
: Reaction with Diethyl oxalate:



Diethyl oxalate. dialkoxyamide (solid)



oxamic ester (liquid)



By this way also we can distinguish all types of amine.

Hoffmann Mustard oil reaction.

Primary amine when warmed with alcoholic CS_2 followed by heating with excess of mercuric chloride ($HgCl_2$) forms isothiocyanates having pungent smell similar to mustard oil.

$Et/RNH_2 + S=C=S \longrightarrow S=C(-NHEt/R)-SH$.

$S=C(-NHEt)-SH + HgCl_2 \longrightarrow Et/R-N=C=S. + H_2S\downarrow + HCl$

alkyl isothiocyanate

Mustard oil smell

Et_2N By this way we can identify 1° amine.

Oxidation of different types of amine using different oxidising reagents.

$R_3C-NH_2 \xrightarrow{KMnO_4} R_3C-NO_2$

1° amine (attached with 3° carbon)

$R_3C-NH_2 \xrightarrow{H_2SO_5} R_3C-NO$

1° amine (attached with 3° carbon)

$RCH_2-NH_2 \xrightarrow{KMnO_4} RCH=NH \xrightarrow[H_3O^+]{} RCH=O + \overset{+}{N}H_4$

(1° amine (attached with 1° carbon)

$R_2CH-NH_2 \xrightarrow{KMnO_4} R_2C=NH \xrightarrow[H_3O^+]{} R_2C=O + \overset{+}{N}H_4$

1° amine (attached with 2° carbon).

$R_3N \xrightarrow{H_2SO_5/H_2O_2} R_3\overset{+}{N}-O^-$

(3° amine) (Tertiary amine oxide)

$R_2NH \xrightarrow{KMnO_4} R_2N-NR_2$

(2° amine)

$R_2NH \xrightarrow{H_2SO_5} R_2N-OH$

(2° amine)

: Preparation of amide:

When aliphatic/aromatic 1°amine reacts with carboxylic acid/acid derivative then amide is formed as product.

$RNH_2 + CH_3CO_2H \rightarrow RNH-\overset{O}{\overset{\|}{C}}-CH_3$.

$RNH_2 + AcCl/CH_3-\overset{O}{\overset{\|}{C}}-Cl \rightarrow RNH-\overset{O}{\overset{\|}{C}}-CH_3$.

} Amide

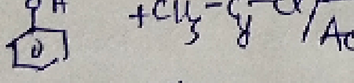
$RNH_2 + Ac_2O + (CH_3CO)_2O \xrightarrow[N/R_3N]{} RNH-\overset{O}{\overset{\|}{C}}-CH_3$

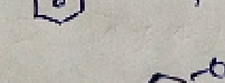
The above process is called acylation of amine where molecular weight is increased by 42 unit. If the same reaction is carried out in presence of $PhCOCl + RNH_2$, then it is called Benzoylation molecular weight is increased by 104 unit.

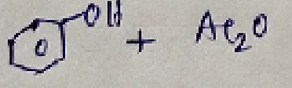
$RNH_2 + PhCOCl \rightarrow RNH-\overset{O}{\overset{\|}{C}}-Ph + HCl$.

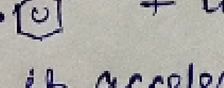
Acylation is applicable not for 1°amine but also alcoholic OH / phenolic OH / 2° amine. But it is not applicable for 3°amine / amide group.

$ROH + CH_3-\overset{O}{\overset{\|}{C}}-OH \longrightarrow RO-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O$.



$+ CH_3-\overset{O}{\overset{\|}{C}}-Cl/AcCl \longrightarrow$  $+ HCl$.



$+ Ac_2O \xrightarrow[\text{or } R_3N]{}$  $+ CH_3CO_2H$

$/R_3N$, being stronger base it accelerates acylation process by removing H from $-NH_2/-OH$ group & increase nucleophilicity.

$Ph-\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}-Cl + RNH_2/R_2NH \rightarrow Ph-\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}-NHR/NR_2$

(sulphonamide)

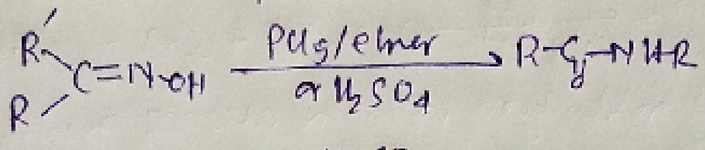
: Beckman Rearrangement:

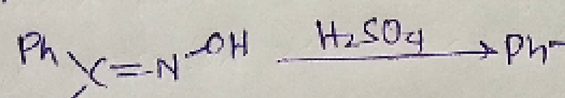
The acid Catalysed conversion of ketoximes to N-substituted amide is called Beckmann rearrangement.

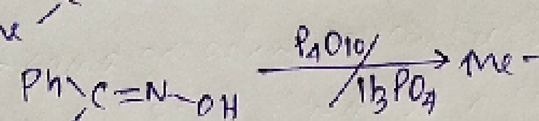
Acid used can be Bronsted/Lewis acid

H_2SO_4 / H_3PO_4 (Bronsted) ; PCl_5 / P_4O_{10}

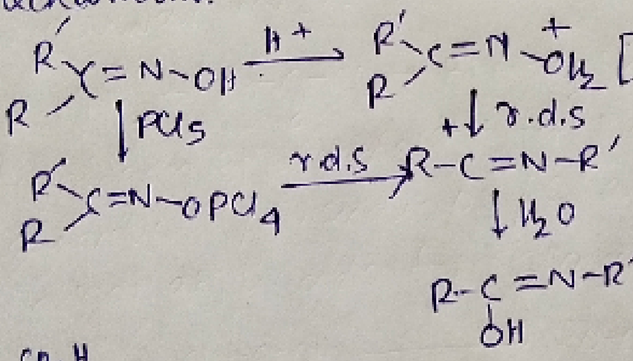
In this rearrangement which is anti position w.r.t L.G in the oxime is shifted & attached with N of amide.



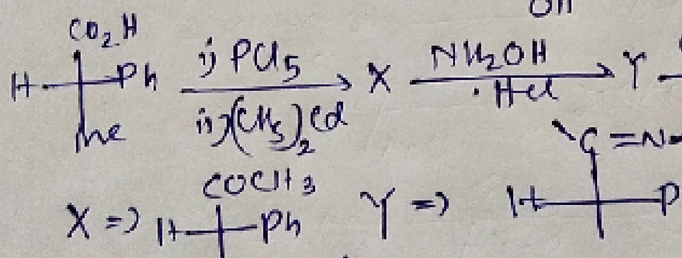


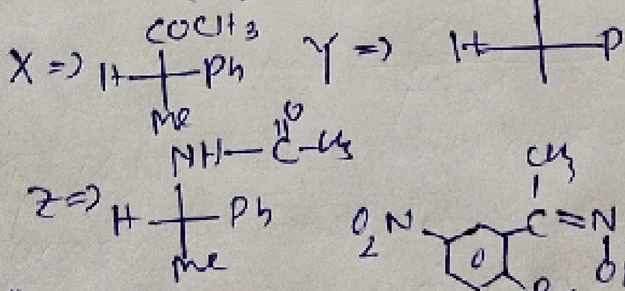


Mechanism: [Here migration takes place to $\bar{e}$ deficient N].

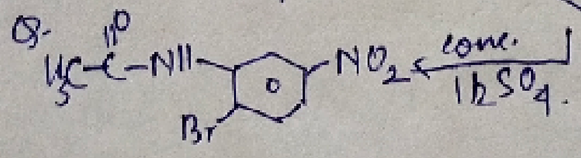


Q.





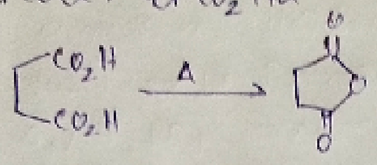
Q.



Qustions based on acid & amine.

Q. $EtCOCl + EtCO_2Na \longrightarrow Et-C(=O)-O-C(=O)-Et$ (Preparation of linear anhydride)

(1)

(2)  (Preparation of cyclic anhydride)

(3) $Me-C(=O)-O-C(=O)-Me$

(4) $Me-C(=O)-OMe + EtO^- \longrightarrow Me-C(=O)-OEt + MeO^-$ (Trans esterification)

(5) $Ph-C(=O)-NH_2 + Me_2NH \longrightarrow Ph-C(=O)-NMe_2 + NH_3$

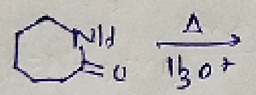
(6) $Me-C(=O)-OH + ROH \xrightarrow{Py} Me-C(=O)-OR$ [Acylation]

(7) $Me-C(=O)-Cl + NH_3 \longrightarrow Me-C(=O)-NH_2 + HCl$.

(8) $PhNH_2 + PhC(=O)-Cl \longrightarrow PhNH-C(=O)-Ph + HCl$ [Benzoylation].

(9) $RNH_2 + PhSO_2Cl \longrightarrow RNH-SO_2Ph$ [water insoluble pdt].

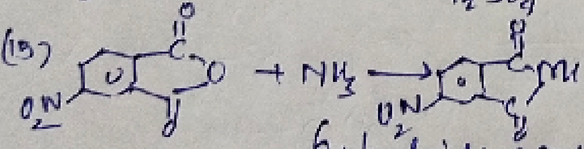
(10) $ROH + KCN \longrightarrow$ no reaction.

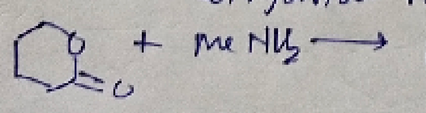
(11) 

(12) $Me-C(=O)-NH_2 \xrightarrow[\Delta]{NaOH/Br_2} MeCO_2H + NH_3$.

(13) $Me-C(=O)-NH_2 \xrightarrow[\Delta]{PCl_5} MeC\equiv N$ [PCl_5 here acts as oxidising agent

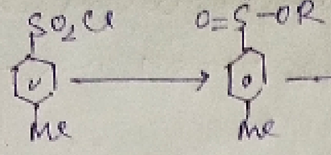
(14) $EtCO_2H + EtCO_2H \xrightarrow[H_2SO_4]{conc.} Et-C(=O)-O-C(=O)-Et$ [conc. H_2SO_4 acts as dehydrating agent

(15)  (Anhydride reacts with NH_3 to give amide)

(16)  (Ester reacts with amine to give amide)

(17) $Me-C(=O)-Cl + EtOK \longrightarrow Me-C(=O)-OEt$.

(18) $PhNH_2 + MeCOCl \longrightarrow PhNH-C(=O)-Me$

(18) ROH +  → RCN.

(19) $R_2NH + PhSO_2Cl \longrightarrow R_2NSO_2Ph$ (Hinsberg's reagent)

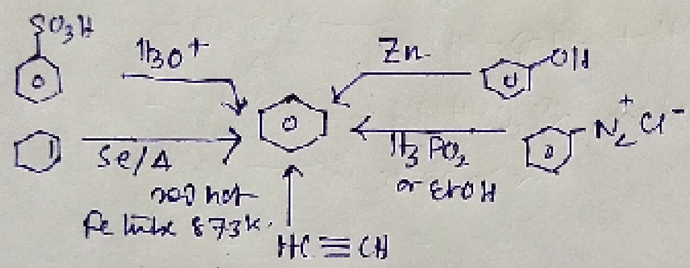
(20) $EtCONH_2 + P_4O_{10} \longrightarrow EtC\equiv N$

(21) $EtN\overset{\oplus}{=}\overset{\ominus}{C}: + H_2O/H^+ \longrightarrow EtNH_2 + HCO_2H$

(22) $EtCN + H_3O^+ \longrightarrow EtCO_2H + NH_4$

(23) $CH_3CO_2Na + Ac_2O +$  →

(24)

(25) 

(26) $PhCH=O \xrightarrow[+ NR_3 / \text{Pyridine}]{CH_2(CO_2Et)_2} X_1 \xrightarrow[\Delta]{H_3O^+} X_2$

$X_1 \Rightarrow PhCH=C(CO_2Et)_2$ $\quad X_2 \Rightarrow PhCH=CHCO_2H$

Reaction is called Knoevenagel Reaction

(27) $PhCH=O \xrightarrow[CH_2(CN)_2]{CN} X_1 \xrightarrow[\Delta]{H_3O^+} X_2$

NR_3 + Pyrrolidine

$X_1 \Rightarrow PhCH=C(CN)_2$ $\quad X_2 \Rightarrow PhCH=CHCO_2H$

(28) $PhCH=O \xrightarrow[\text{ii) } H^+]{\text{i) } CH_2(CO_2Et)_2,\ Br,\ Zn} X_1 \xrightarrow[H_3O^+]{\Delta} X_2 \xrightarrow{\Delta} X_3$

$X_1 \Rightarrow PhCH(OH)-CH_2-CO_2Et$ $\quad X_2 \Rightarrow PhCH(OH)-CH_2CO_2H$

$X_3 \Rightarrow PhCH=CHCO_2H$

The reaction is called Reformatsky reaction.