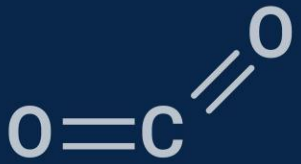
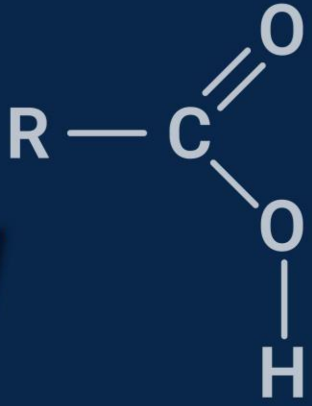
AMINES - L3





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C
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Chemical Properties

- Alkylation
- Acylation
- Carbylamine reaction
- Reaction with nitrous acid
- Reaction with benzene sulphonyl chloride
- Electrophilic substitution reaction

Alkylation

Amines undergo **alkylation** on reaction with **alkyl halides.**

$$CH_3NH_2 + CH_3CH_2Br \longrightarrow CH_3\overset{+}{N}H_2CH_2CH_3 + Br^-$$

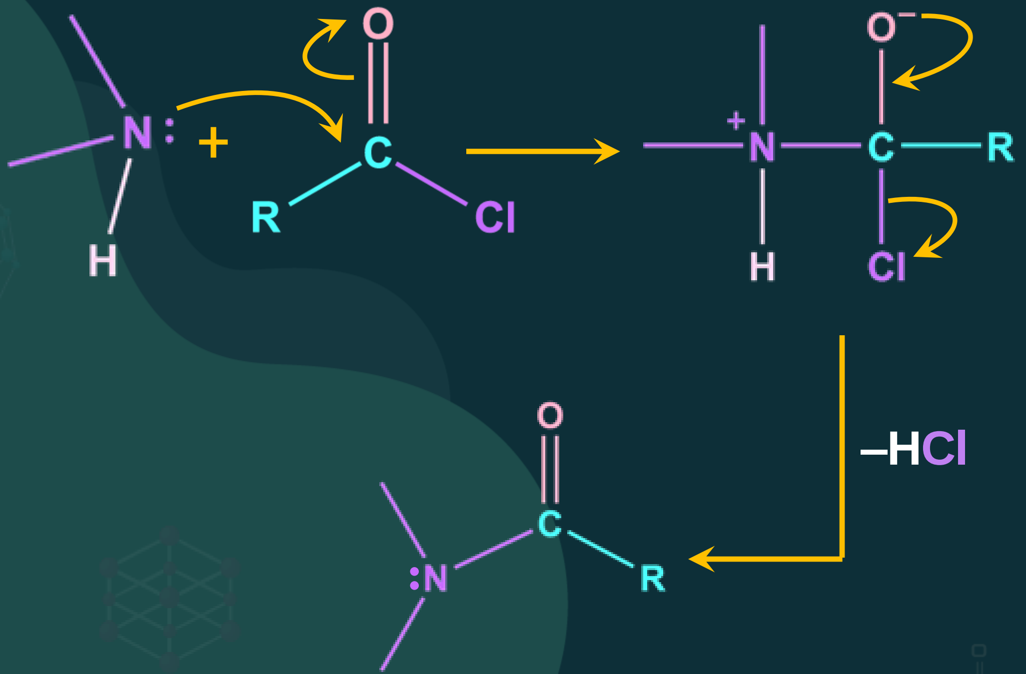
$$\Big\downarrow\ OH^-$$

$$CH_3NHCH_2CH_3$$

The major product in the following reaction is:

Acylation

Aliphatic and aromatic primary and secondary amines react with acyl chlorides, anhydrides, and esters by nucleophilic substitution reaction.

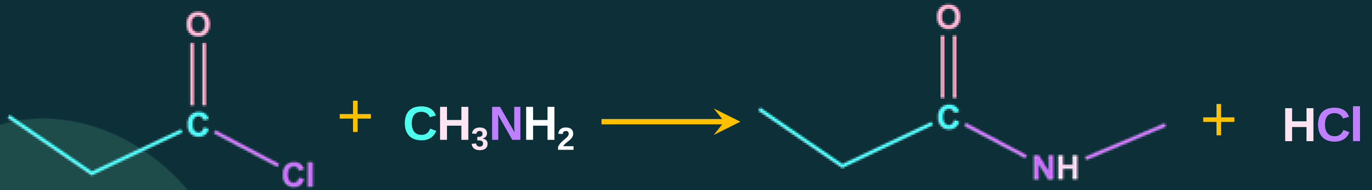


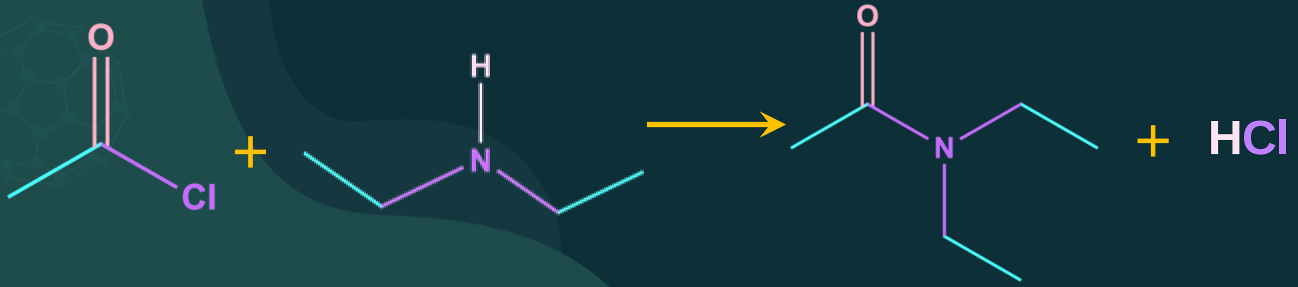
Preparation of Amides

The treatment of **acyl halides with ammonia or amines** is a very general reaction for the preparation of amides.

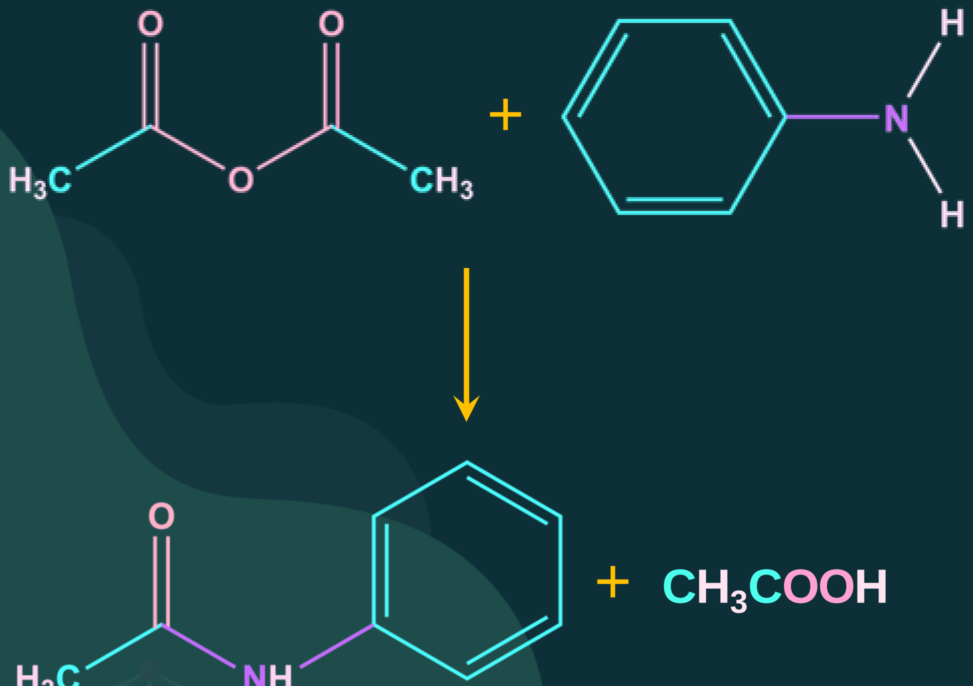
The reaction is **highly exothermic** and must be carefully controlled, usually by cooling or dilution.

Preparation of Amides



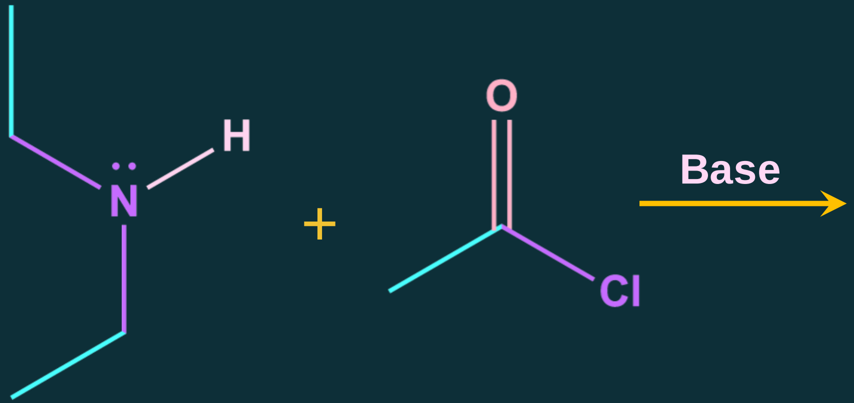


Preparation of Amides



+ CH_3COOH

The major product in the following reaction is:



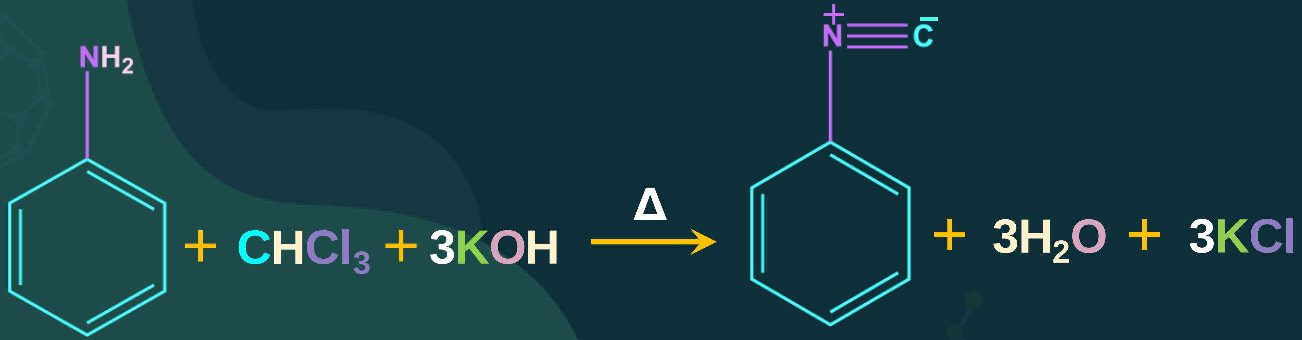
Carbylamine Reaction

Primary amines (aliphatic as well as aromatic) react with chloroform (**$CHCl_3$**) on heating in the presence of ethanolic solution of **KOH** to form **isocyanides** (also known as **carbylamine's**) that are foul smelling substances.

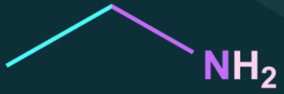
Secondary and tertiary amines **do not** undergo this reaction. It is used as a **test for primary amines** (aliphatic as well as aromatic).

Carbylamine Reaction

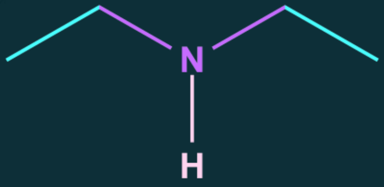
$$RNH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} RNC + 3H_2O + 3KCl$$



Carbylamine Reaction Mechanism



and



can be differentiated by is:

a) Carbylamine reaction

b) Iodoform test

c) Cold $KMnO_4$

d) Br_2 / H_2O

Reaction with Nitrous Acid

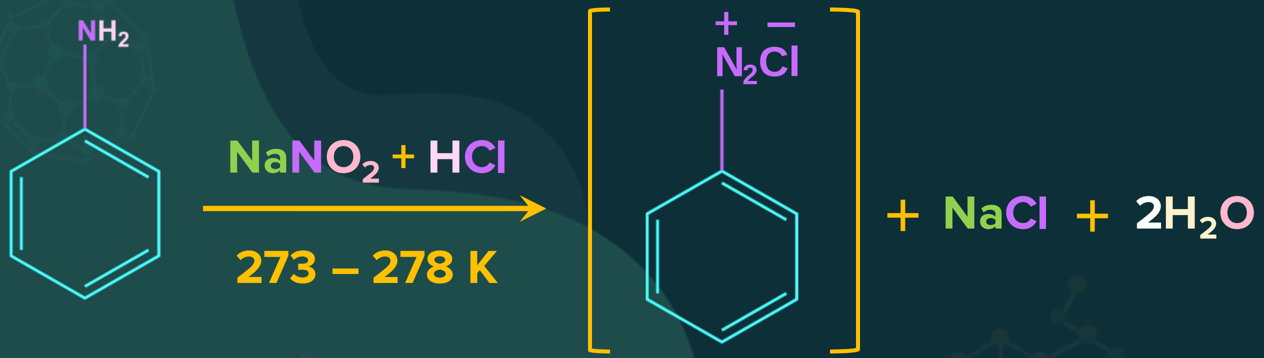
Amines of different classes react with **nitrous acid** (unstable acid).

HNO_2 is prepared in situ by the reaction of sodium nitrite (**$NaNO_2$**) and **dilute HCl**.

Reaction with Nitrous Acid

Primary aromatic amines react with nitrous acid at a low temperature (273-278 K) to give **aromatic diazonium salts**.

This reaction is known as **diazotisation**.



Benzene diazonium chloride

Reaction with Nitrous Acid

Primary aliphatic amines also react with nitrous acid to form diazonium salt.

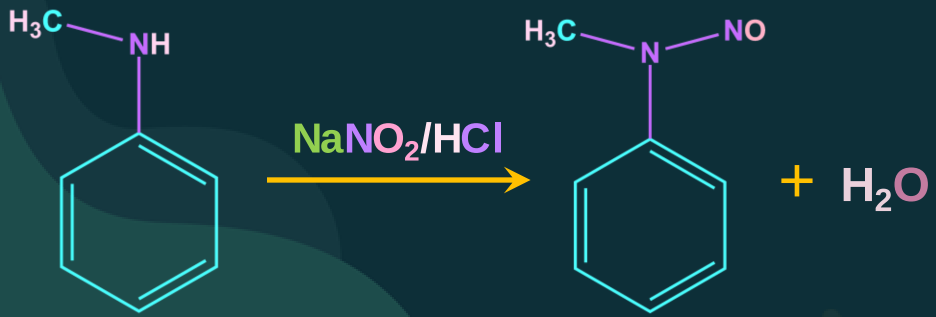
However, the aliphatic diazonium salts being **unstable**, **decompose** to yield mixture of alcohols, nitrogen gas and byproducts.

$$C_2H_5NH_2 \xrightarrow{NaNO_2/HCl} \underset{\text{Unstable}}{[C_2H_5\overset{+}{N_2}\overset{-}{Cl}]} \xrightarrow{H_2O} \underset{\text{(Major)}}{C_2H_5OH} + N_2$$

Reaction with Nitrous Acid

Secondary aliphatic and aromatic amines react with nitrous acid to produce **nitroso-amines.**

Insoluble in aqueous solution and separate out as a **yellow oily layer**.



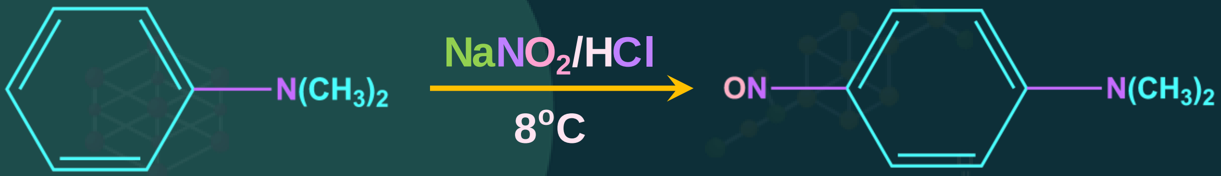
$$(C_2H_5)_2NH + HNO_2 \longrightarrow (C_2H_5)_2NH{-}NO + H_2O$$

Reaction with Nitrous Acid

When a **tertiary aliphatic amine** is mixed with nitrous acid, an **equilibrium** is established among the **tertiary amine, its salt, and an N-nitrosoammonium** compound.

$$2R_3N + HX + NaNO_2 \rightleftharpoons R_3\overset{+}{N}H\overset{-}{X} + R_3\overset{+}{N}{-}N{=}O\overset{-}{X}$$

Tertiary aromatic amines undergo **electrophilic substitution** at the ring.



The compound which gives an oily nitrosamine on reaction with nitrous acid at low temperature, is:

AIIMS 2008

a) CH_3NH_2

b) $(CH_3)_2CHNH_2$

c) $H_3C—NH—CH_3$

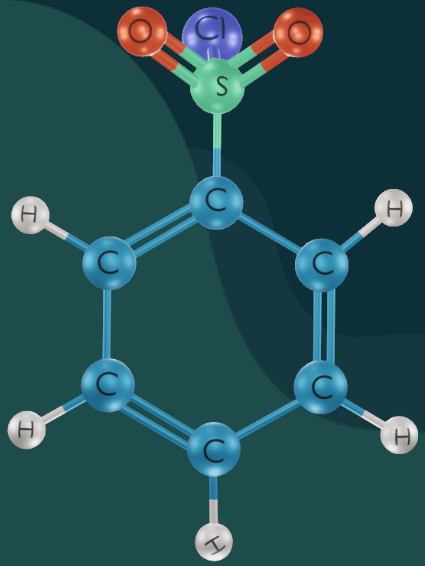
d) $(CH_3)_3N$

Hinsberg Test

Used to **demonstrate** whether an amine is primary, secondary, or tertiary.

Mixture containing a small amount of the amine and **benzenesulphonyl chloride** is shaken with excess **KOH**.

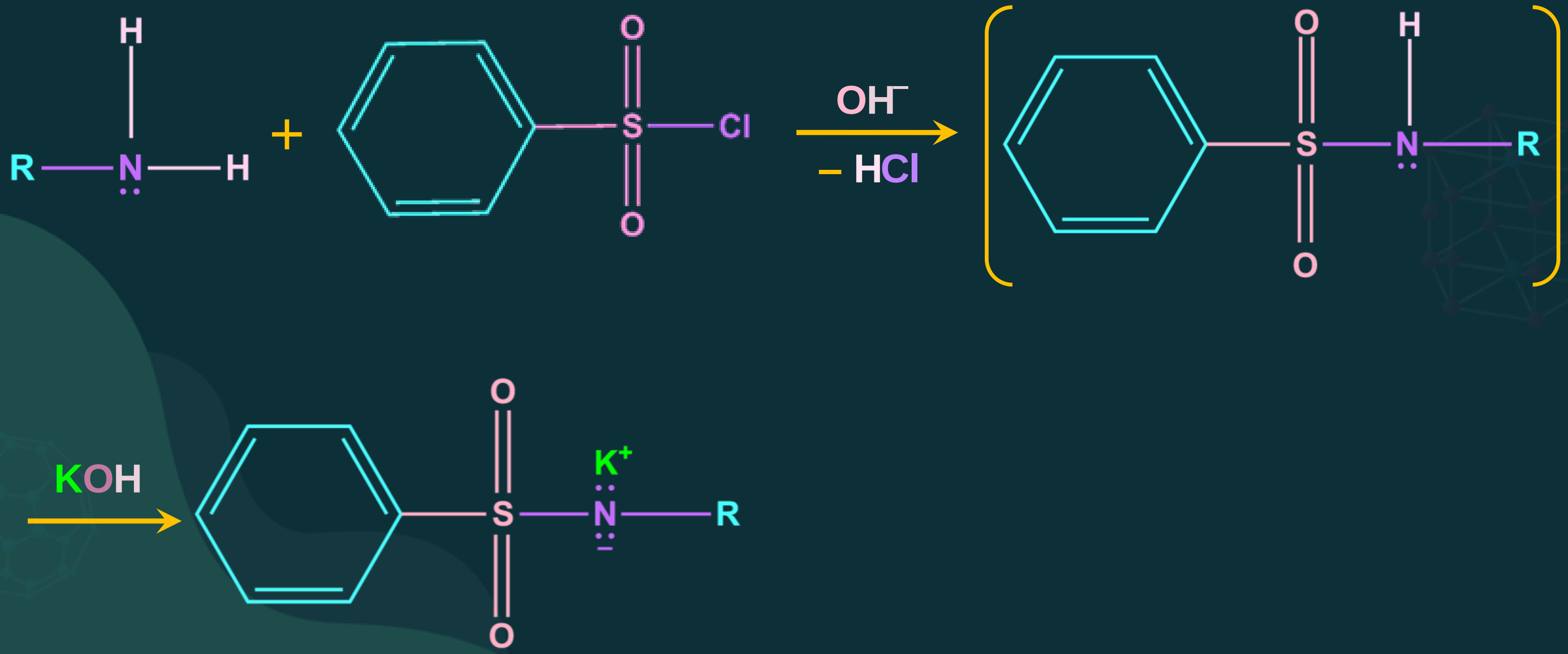
Benzene sulphonyl chloride



Primary Amine

Primary amines react with benzenesulphonyl chloride to form **N-substituted benzenesulphonamides**.

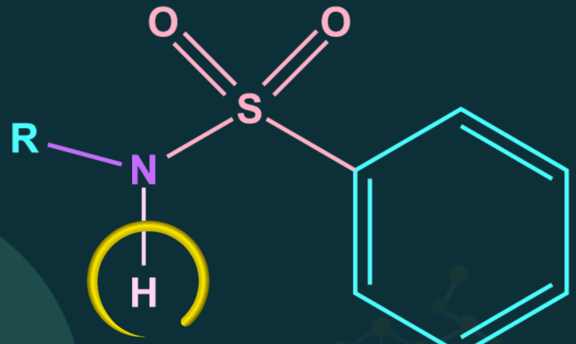
These, in turn, undergo acid-base reactions with the excess potassium hydroxide to form **water-soluble potassium salts.**



Water-soluble
salt (clear solution)

Primary Amine

Acid-base reactions take place because the hydrogen attached to nitrogen is **acidic** due to strongly electron-withdrawing **– SO_2 – group.**)



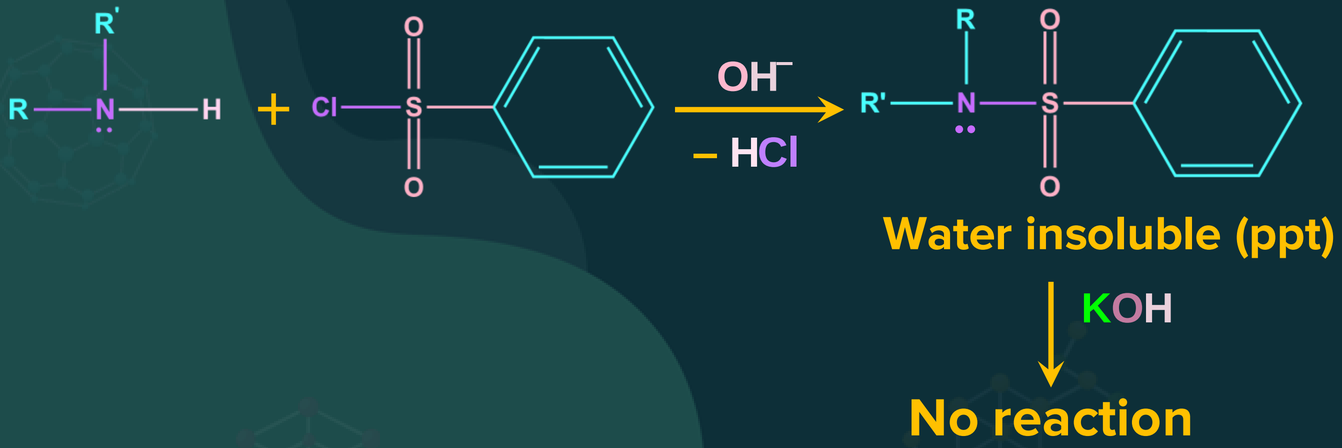
Acidic hydrogen

Secondary Amines

Secondary amines react with benzene sulphonyl chloride in aqueous potassium hydroxide.

→

Insoluble N,N-disubstituted sulphonamides get precipitated.



Water insoluble (ppt)

No reaction

Secondary Amines

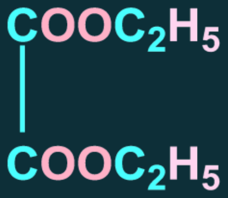
N,N-Disubstituted sulphonamides do not **dissolve** in aqueous potassium hydroxide because they do not have an **acidic hydrogen.**

Tertiary Amine

If the amine is **a tertiary amine** and it is water insoluble, **no apparent change** will take place in the mixture as we shake it with benzene sulphonyl chloride and aqueous KOH.

Heinsberg's reagent is:

AIIMS 2001

a) 

$$\begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array}$$

b) $C_6H_5SO_2Cl$

c) $C_6H_5SO_2NH_2$

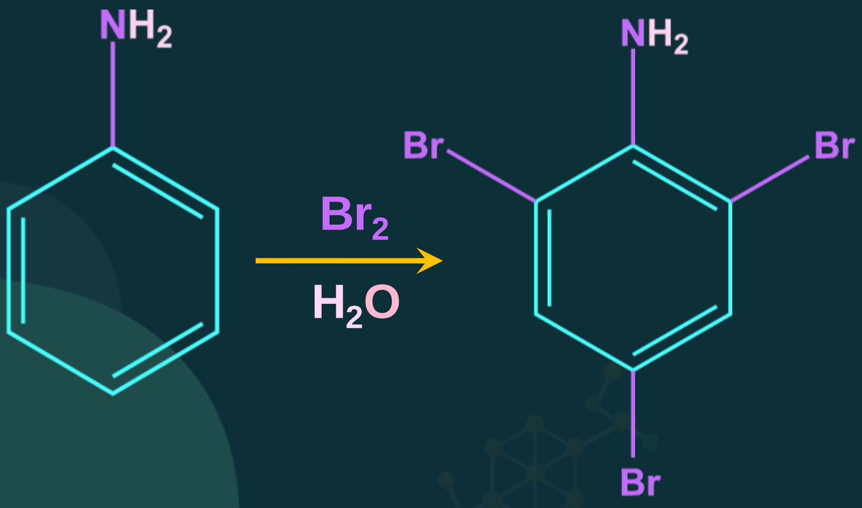
d) $CH_3COCH_2COOC_2H_5$

Electrophilic Substitution in Aniline

-NH_2 group is **ortho-para** directing, and is **activating** groups.

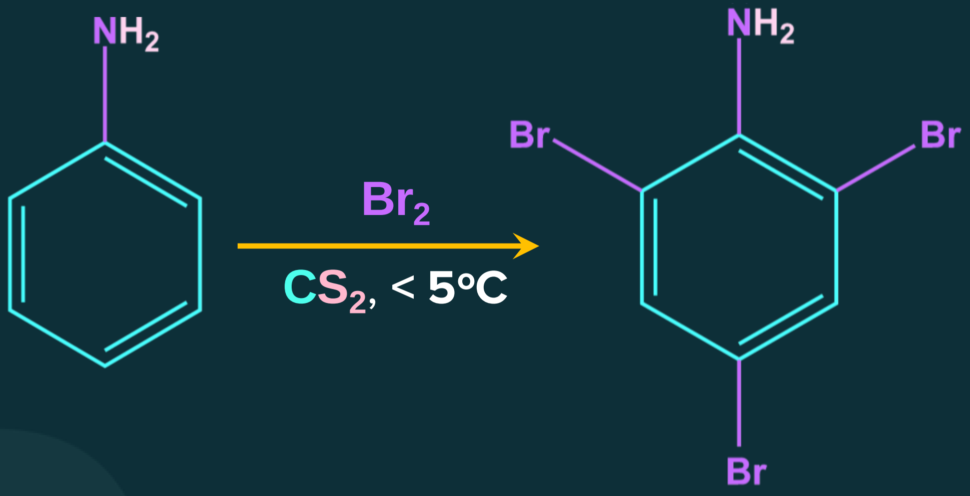
Bromination

Aniline reacts with **bromine in water** (no catalyst is required) at room temperature to produce compounds in which both of the **ortho** positions and the **para** position become **substituted**.



≂ 100%

Bromination



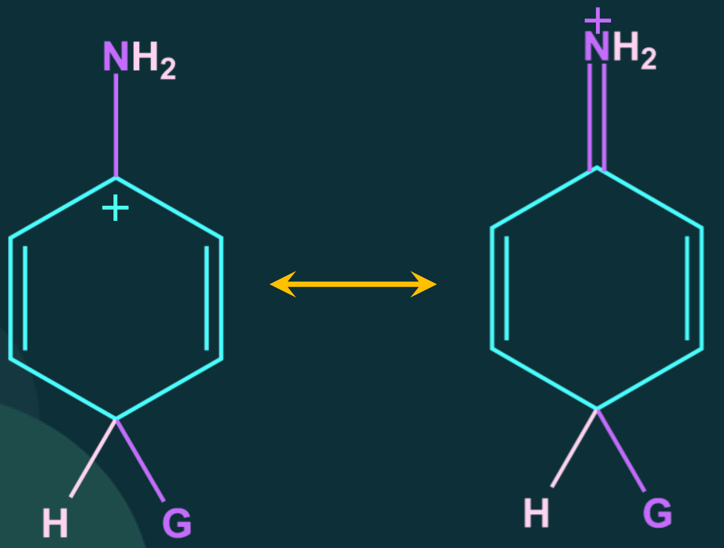
Bromination

In general, substituent groups with **unshared electron pairs** on the atom adjacent to the benzene ring (e.g., **-OH, -NH_2**) are **stronger activating groups** than groups without unshared electron pairs (i.e., alkyl groups).

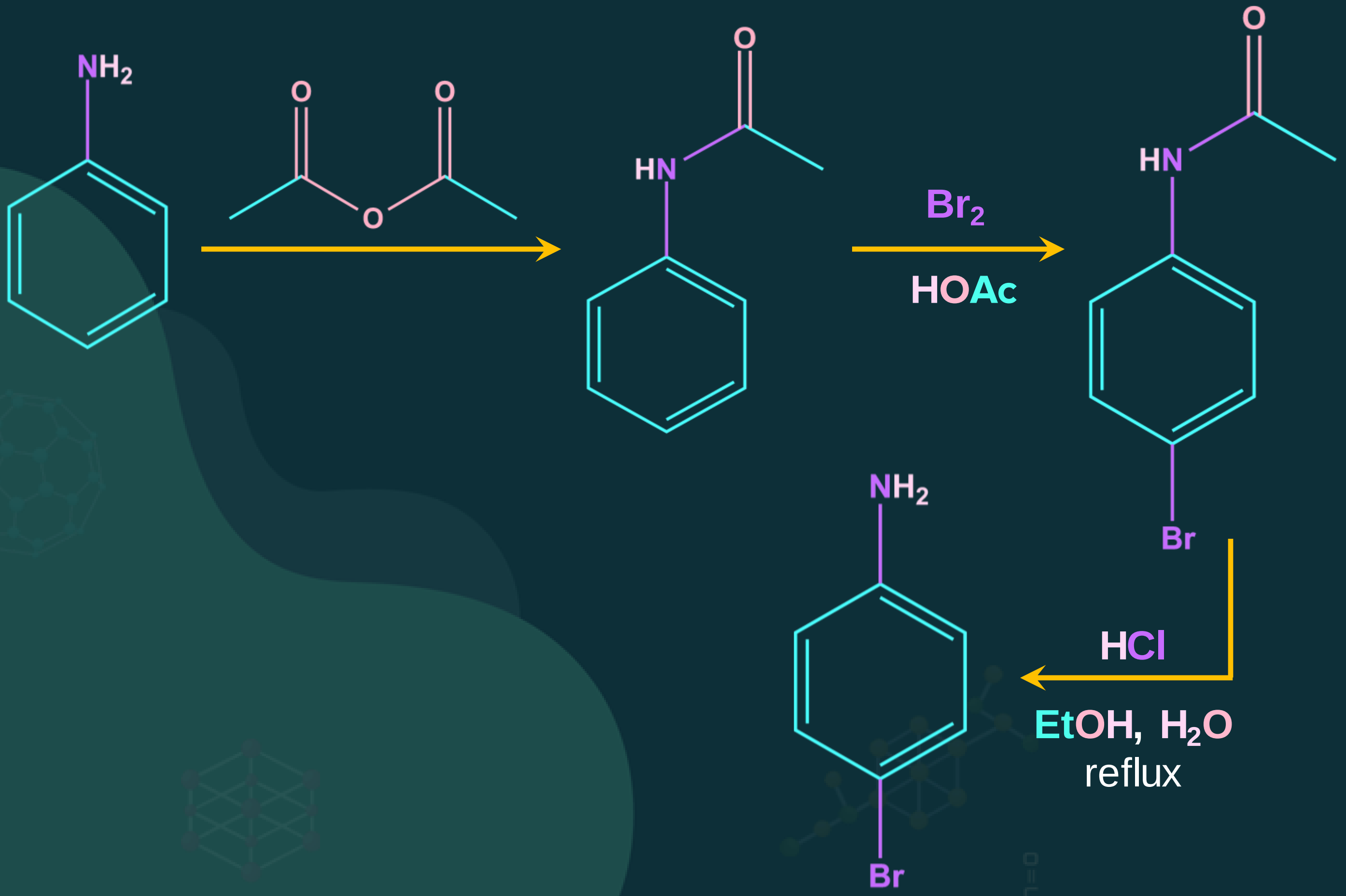
Bromination

Contribution of electron density to the benzene ring through **resonance** is generally **stronger than** through an **inductive** effect.

Arenium ion stabilisation by resonance effect



Bromination

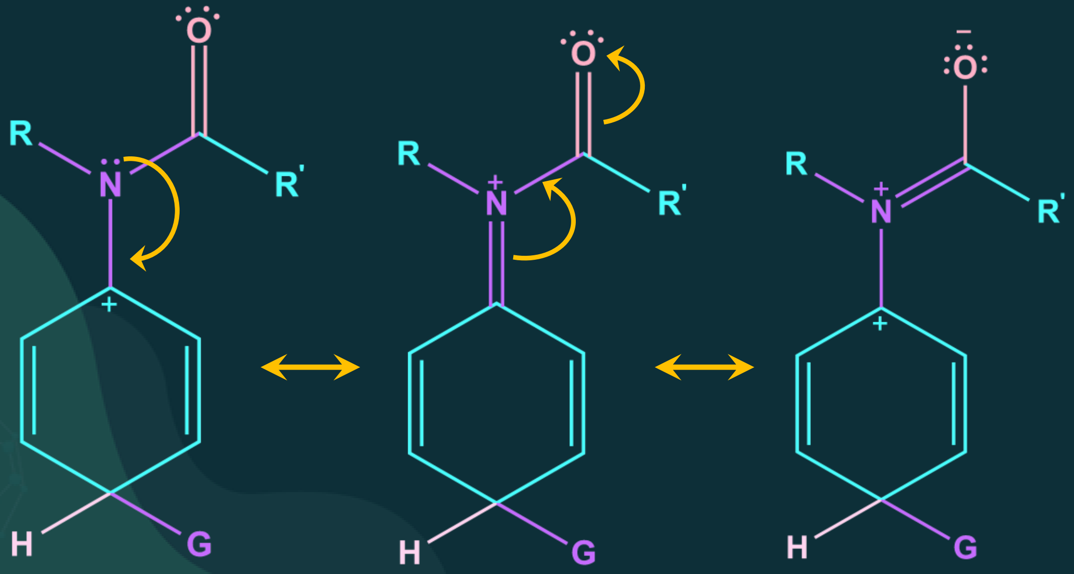


Bromination

Even though amides and esters have an **unshared electron pair** on the atom adjacent to the ring, their **activating effect is diminished**.

Because the carbonyl group provides a resonance effect, where electron density is **directed away** from the benzene ring.

Bromination



Electron donation to the ring by resonance is **reduced** when there is an **alternative resonance pathway** away from the ring.

Bromination

This makes amides and esters **less activating** than groups where the only resonance possibilities involve donation of electron density toward the benzene ring.

Reaction occurs in the **ortho** and **para** positions (mainly para) but it occurs **once only**.

The ortho/para directing group among the following is:

AIIMS 2003

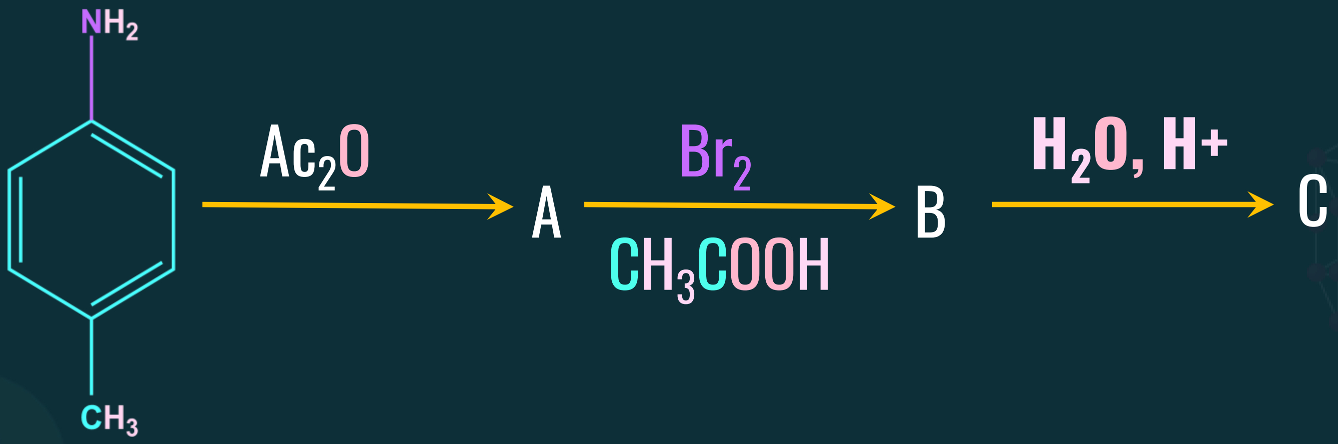
a) $-COOH$

b) $-CN$

c) $-COCH_3$

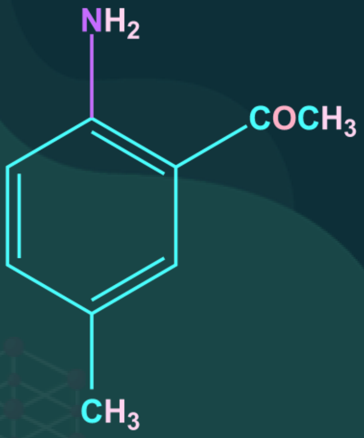
d) $-NHCONH_2$

The final product, obtained in this reaction would be:

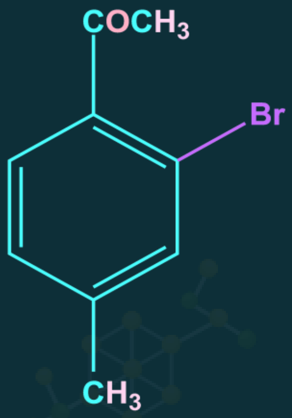


AIPMT 2003

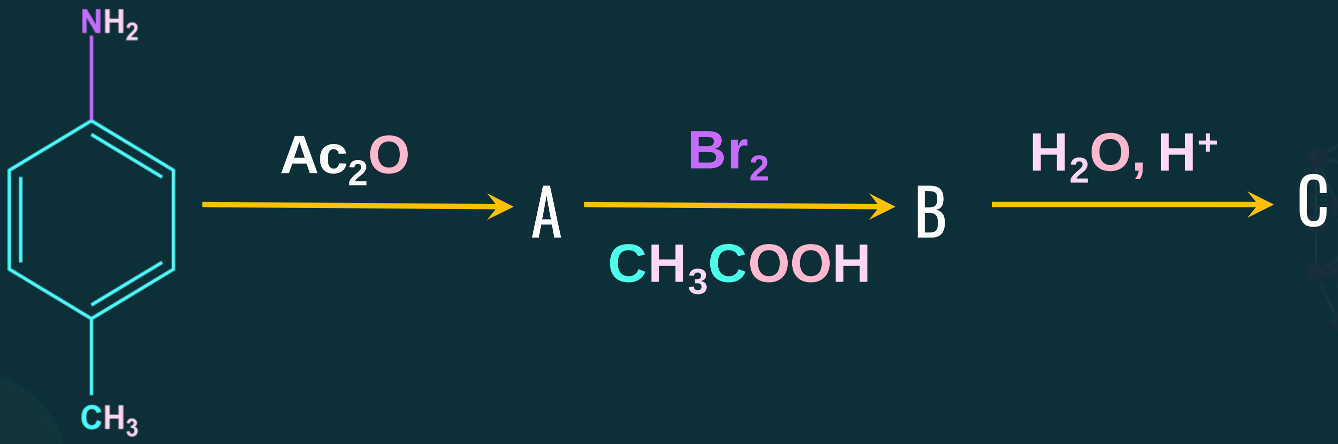
a)



b)

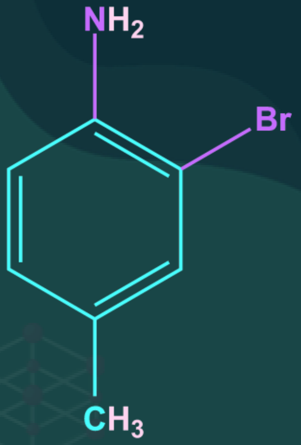


The final product, obtained in this reaction would be:

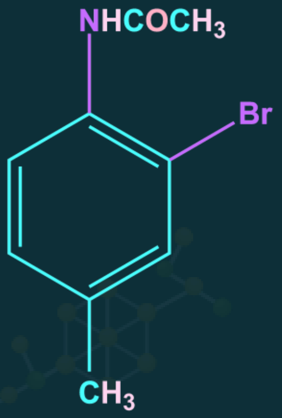


AIPMT 2003

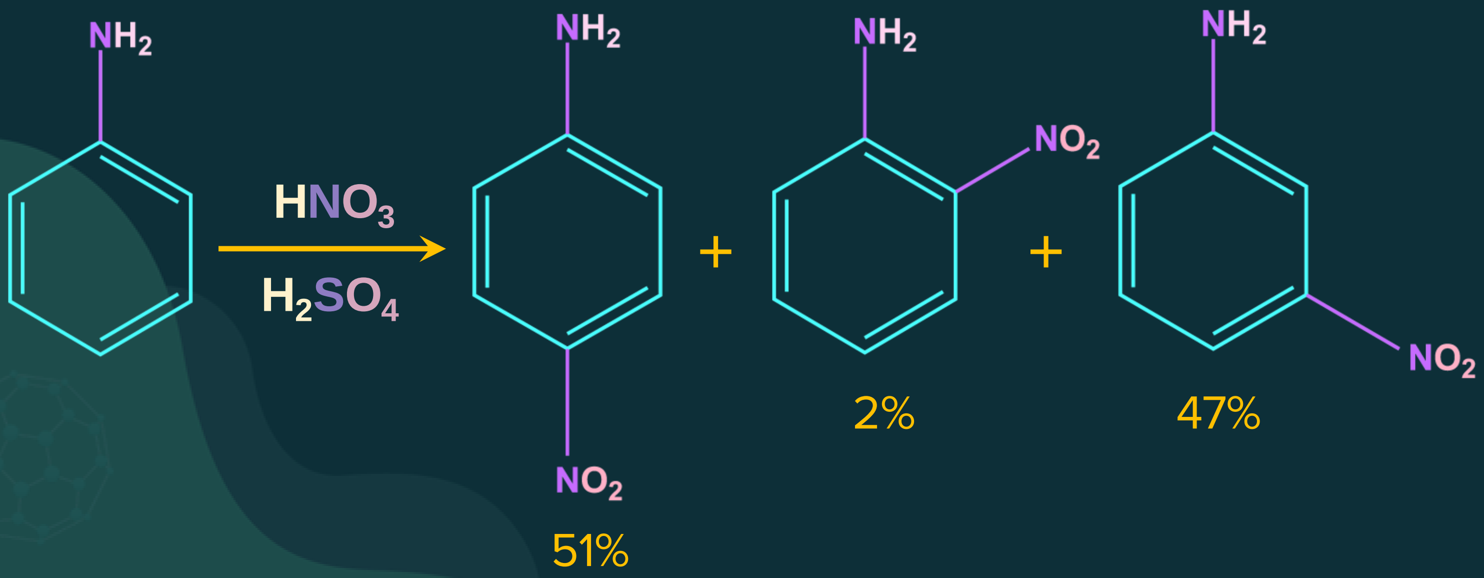
c)



d)



Nitration

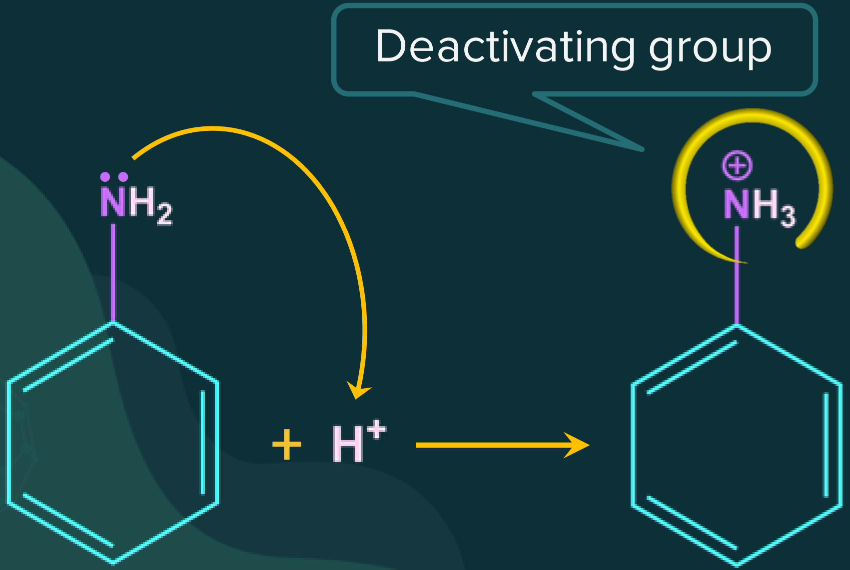


Nitration

When aniline is nitrated under strong acid conditions, **meta orientation** is generally observed.

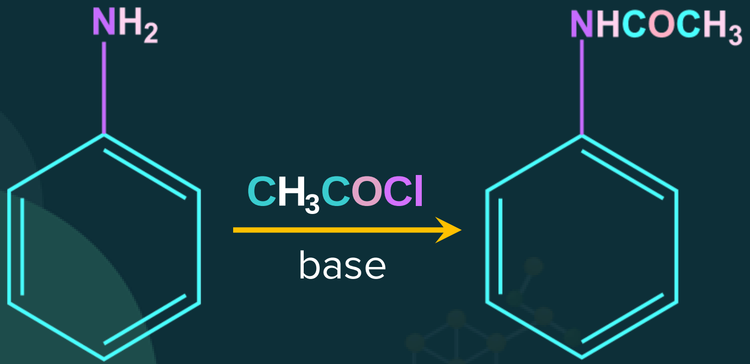
Because the species undergoing nitration is actually the **conjugate acid** of the amine.

Nitration



Nitration

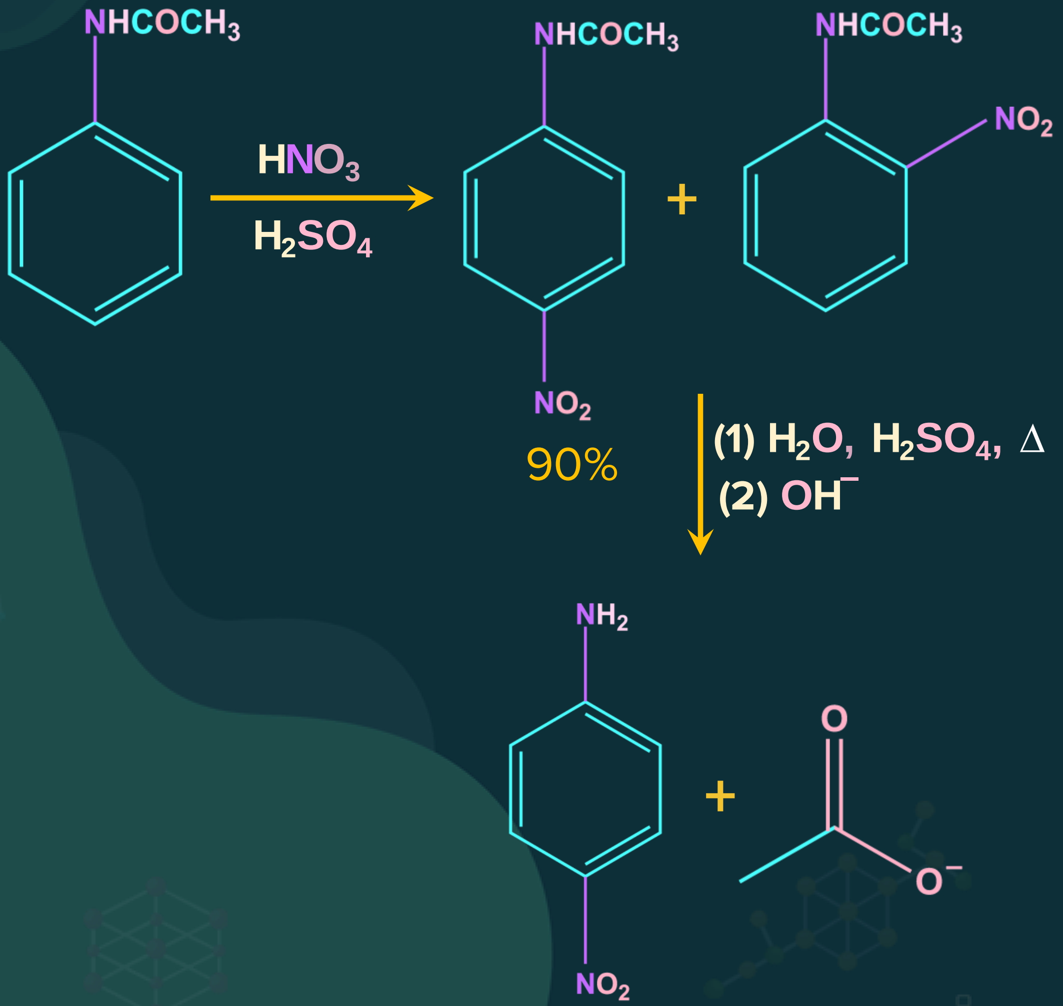
Treating aniline with acetyl chloride, **CH_3COCl**, or acetic anhydride, **$(CH_3CO)_2O$**, converts the **amino group of aniline to an amide**, forming **acetanilide**.



Nitration

An amide group is only **moderately activating**, & it doesn’t make the ring highly susceptible to oxidation during nitration.

If **amino group** of aniline is **blocked** in acetanilide, **direct nitration becomes possible**.

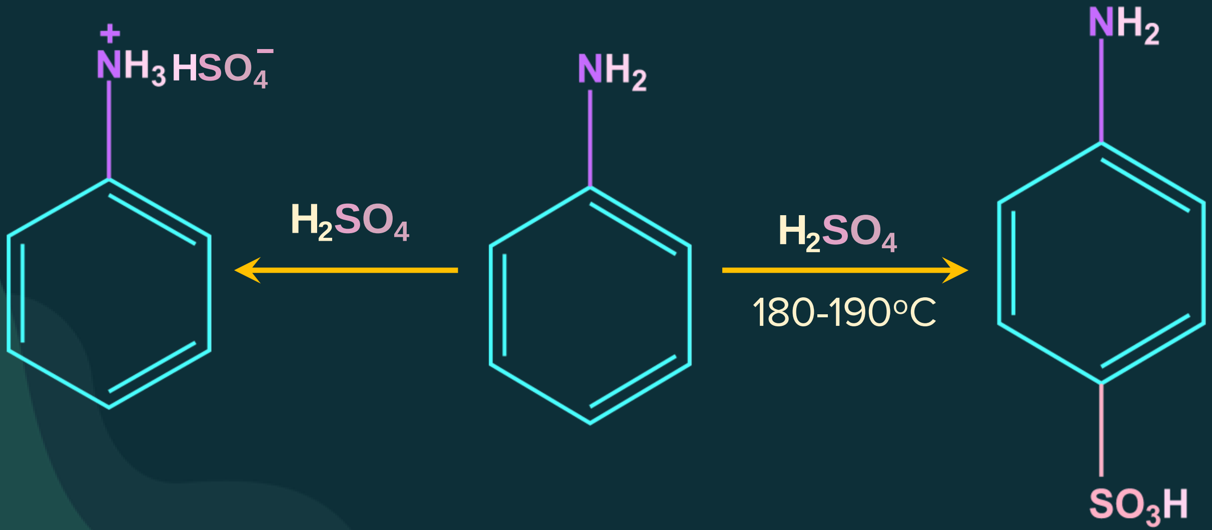

NHCOCH3
HNO3
H2SO4
NHCOCH3
NO2
90%
+
NHCOCH3
NO2
(1) H2O, H2SO4, Δ
(2) OH−
NH2
NO2
+
O
O−

Nitration

Nitration of **acetanilide** gives **p-nitroacetanilide** in excellent yield with only a trace of the ortho isomer.

Acidic hydrolysis of p-nitroacetanilide removes the acetyl group and gives **p-nitroaniline**, also in good yield.

Sulphonation



Sulphonation

In sulphuric acid, all the amines will be **protonated,** so **meta-sulphonic** acid should be formed. But then why **para-sulphonic** acid is forming?

There are two possible explanations for this:

1. Very tiny amount of unprotonated amine **reacts very rapidly** with SO_3 in the para position

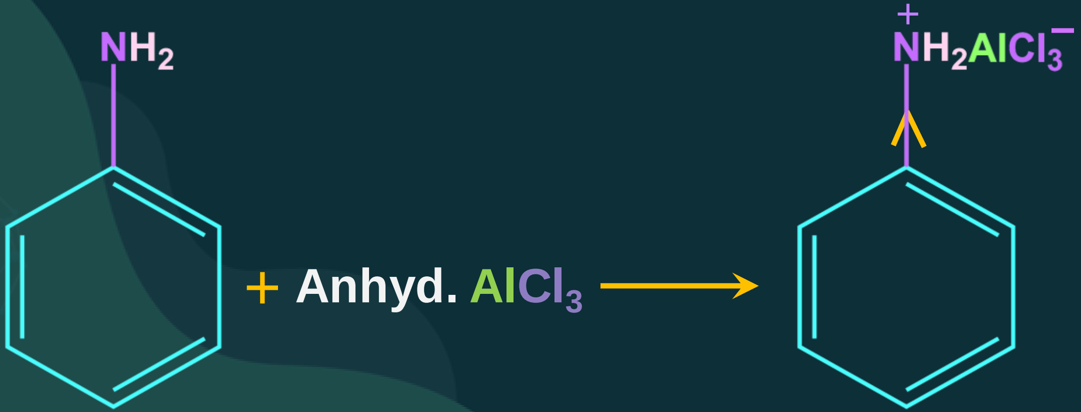
2. The reaction is **reversible** and the para-sulfonic acid is formed because it is **stabilized** by delocalization and is also least hindered.

Friedel Crafts Reaction

Any substituent **more electron withdrawing** (or deactivating) than a halogen, that is, any **meta-directing** group, makes an aromatic ring **too electron deficient** to undergo a Friedel–Crafts reaction.

Friedel Crafts Reaction

The amino groups, -NH_2, -NHR, and -NR_2, are changed into **powerful electron-withdrawing** groups by the Lewis acids used to catalyse Friedel–Crafts reactions.



Does **not** undergo Friedel–Crafts reaction

Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc. H_2SO_4. In the mixture, **nitric acid** acts as a/an:

AIPMT 2009

a) Acid

b) Base

c) Catalyst

d) Reducing agent

Assertion: Nitration of aniline can be conveniently done by protecting the amino group by acetylation.

Reason: Acetylation increases the electron density in the benzene ring.

AIIMS 2010

a) If both assertion and reason are correct and the reason is a correct explanation of the assertion

b) If both assertion and reason are correct but reason is not a correct explanation of the assertion.

Assertion: Nitration of aniline can be conveniently done by protecting the amino group by acetylation.

Reason: Acetylation increases the electron density in the benzene ring.

AIIMS 2010

c) If the assertion is correct but reason is incorrect.

d) If both the assertion and reason are incorrect.

Phenyl isocyanides are prepared by which of the following reaction?

AIPMT 1999

a) Reimer–Tieman reaction

b) Carbylamine reaction

c) Rosenmund's reaction

d) Wurtz reaction

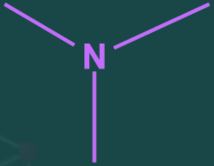
An organic compound (C_3H_9N) (A), when treated with nitrous acid, gave an alcohol and N_2 gas was evolved. (A) on warming with $CHCl_3$ and caustic soda gave (C) which on reduction gave isopropylmethyamine. Predict the structure of (A).

NEET 2012

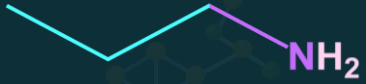
a)

b)

c)



d)

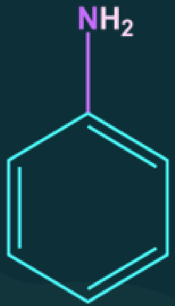


$$A \xrightarrow{\text{reduction}} B \xrightarrow{CHCl_3,\ KOH} C \xrightarrow{\text{reduction}} \text{N-methylaniline}$$

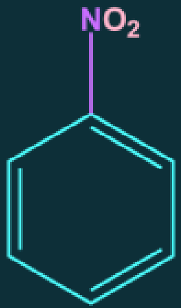
Then A is:

AIPMT 2000

a)



b)



c) CH_3NH_2

d)

Assertion: Acylation of amines gives a monosubstituted product whereas, alkylation of amines gives polysubstituted product.
Reason: Acyl group sterically hinders the approach of further acyl groups.

AIIMS 2016

a) If both assertion and reason are correct and the reason is a correct explanation of assertion.

b) If both assertion and reason are correct, but the reason is not correct explanation of assertion.

Assertion: Acylation of amines gives a monosubstituted product whereas, alkylation of amines gives polysubstituted product.
Reason: Acyl group sterically hinders the approach of further acyl groups.

AIIMS 2016

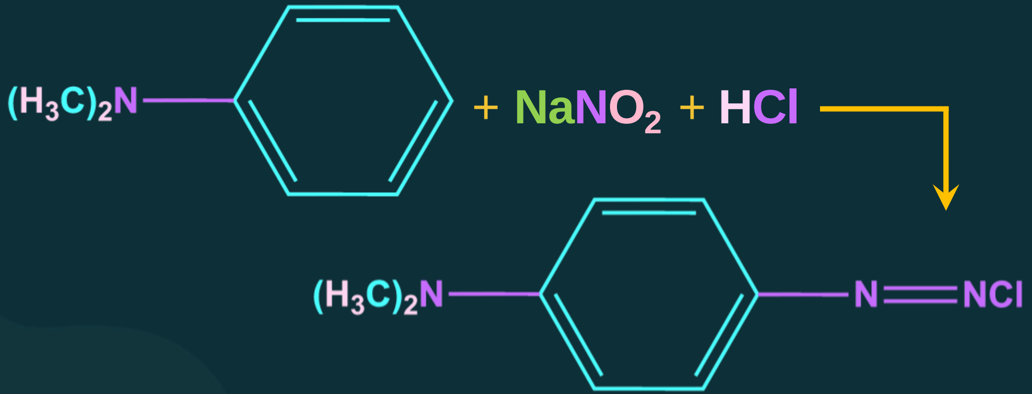
c) If assertion is correct but the reason is incorrect.

d) If both assertion and reason are incorrect.

Some reactions of amines are given. Which one is not correct?

Karnataka NEET 2013

a)



b) $CH_3CH_2NH_2 + HNO_2 \longrightarrow CH_3CH_2OH + N_2$

Some reactions of amines are given. Which one is not correct?

Karnataka NEET 2013

c) $CH_3NH_2 + C_6H_5SO_2Cl \longrightarrow CH_3NHSO_2C_6H_5$

d) $(CH_3)_2NH + NaNO_2 + HCl \longrightarrow (H_3C)_2N{-}N{=}O$

"Stay Positive, Work Hard. Make It Happen!"

THANK YOU