By Mohammad Alkhawaldeh

Morphin 💊🩺

Chapter-8: Amines

+ MCQ

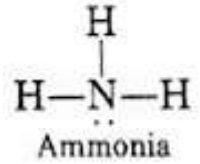
Structure and Classification of Amines

NH_3

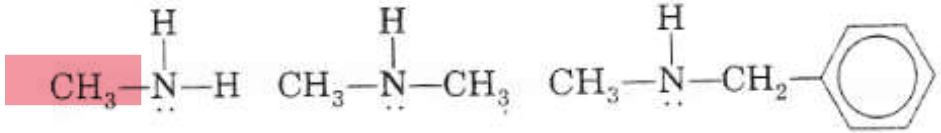
- Amines are compounds that derived from ammonia by replacement of one, two, or three hydrogens by alkyl or aryl groups.

Amines هي مركبات طالعة من ammonia (NH_3)
و شلنا منه hydrogen حطينا مكانه الكيل أو اريل

alkyl = aliphatic
aryl = aromatic

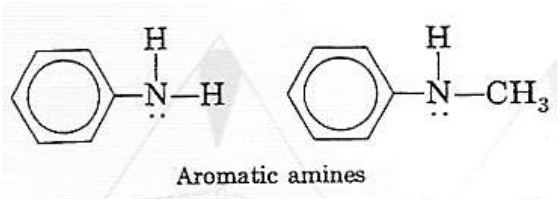

Ammonia

- Aliphatic amines contain *only alkyl* groups bonded directly to the nitrogen atom.


Aliphatic amines

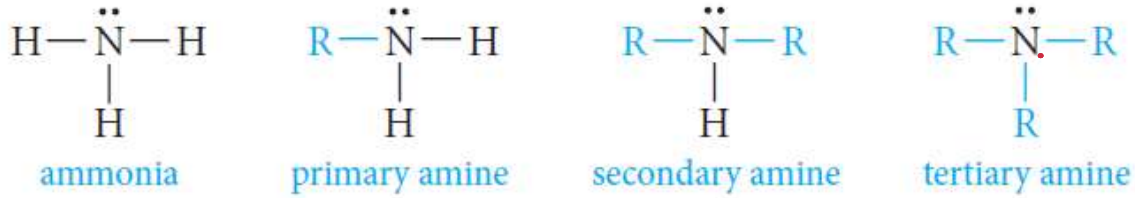
(حلقة بنزين)

- Aromatic amines are those in which one or more aryl groups are bonded directly to nitrogen.


Aromatic amines

Classification and Structure of Amines

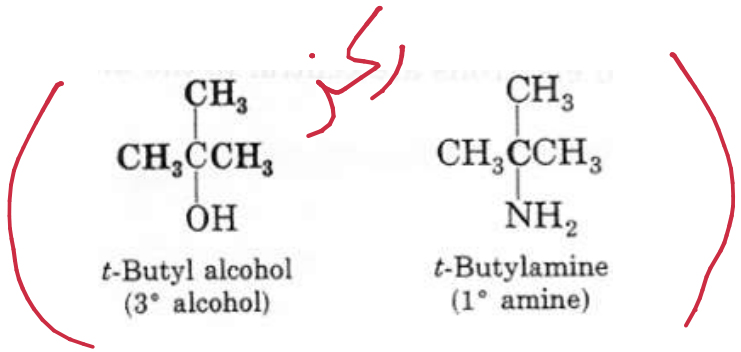
- The relation between **ammonia and amines** is illustrated by the following structures:



- **Amines** are classified as **primary**, **secondary**, or **tertiary**, *depending on whether one, two, or three organic groups are attached to the nitrogen*.

- **NOTE:**

Primary amine (1° amine)
مرتبط بـ كربون واحد N
الصيغة: $R-NH_2$



Secondary amine (2° amine)
مرتبط بـ كربونين N
الصيغة: R_2-NH

Tertiary amine (3° amine)
مرتبط بـ 3 كربونات N
الصيغة: R_3-N

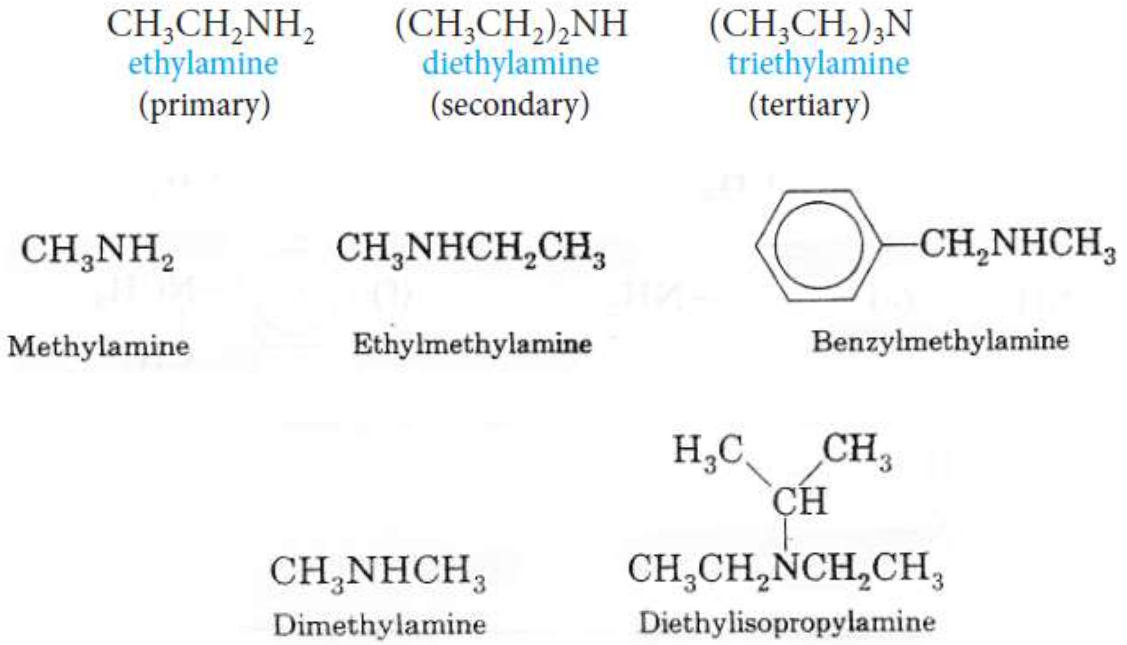
- ***t*-butyl alcohol** is a **tertiary alcohol** (because three carbons are attached to the carbinol carbon).
- ***t*-butyl amine** is a **primary amine** (because only one carbon is attached directly to the nitrogen atom).

التصنيف دايمًا حسب عدد الكربونات المرتبطة مباشرة بالـ nitrogen مش حسب شكل المركب.

Nomenclature of Amines

Common Names

- **Amines** are named by specifying the alkyl groups attached to the nitrogen and adding the suffix –*amine* (*Alkylamine*).amine وبنضيف كلمة alkyl groups بنسمي الأمين حسب أسماء

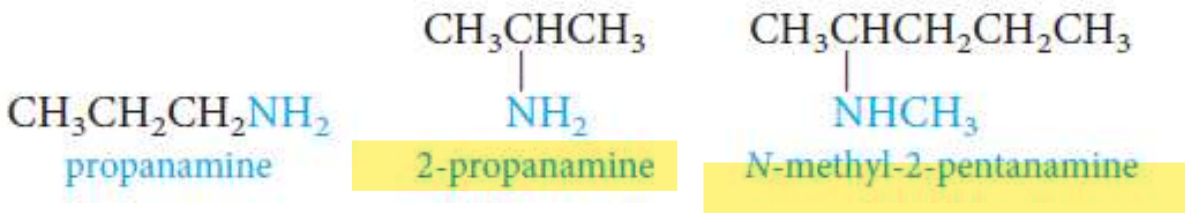


Nomenclature of Amines

IUPAC System

بنعتبر الأمين مشتق من alkane وبنضيف amine

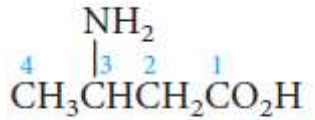
- Amines can be named as **alkanamines**.



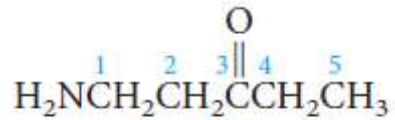
Nomenclature of Amines

IUPAC System

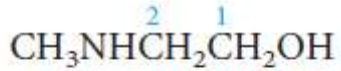
- When **other functional groups** are present, the amino group, **-NH_2, is named as a substituent.**



3-aminobutanoic acid



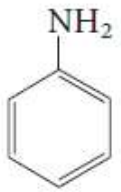
1-amino-3-pentanone



2-methylaminoethanol

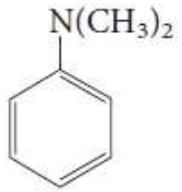
إذا في functional أهم: group
مجموعة NH_2 بتتحول لـ substituent
اسمها: amino–

- **Aromatic amines** are named as derivatives of aniline.
- In the IUPAC system, aniline is called benzenamine.

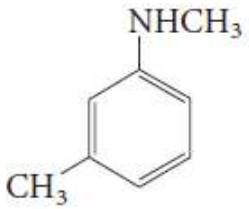


aniline
(benzenamine)

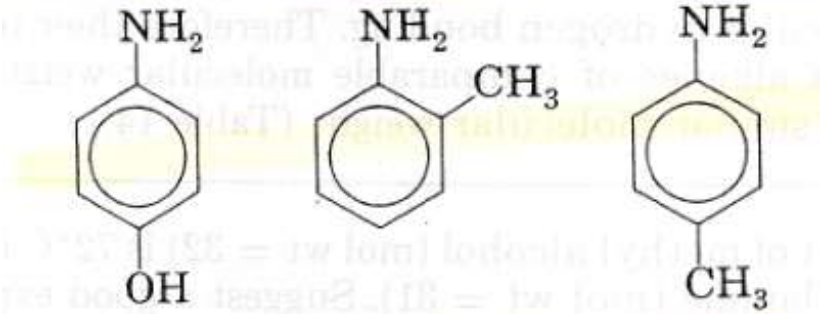
p-bromoaniline
(4-bromobenzenamine)



N,*N*-dimethylaniline
(*N*,*N*-dimethylbenzenamine)



m-methyl-*N*-methylaniline, or
N-methyl-*m*-toluidine
(*N*-methyl-3-methylbenzenamine)



p-Hydroxyaniline
(*p*-Aminophenol)

o-Toluidine

p-Toluidine

Physical Properties of Amines

Boiling Point

أمينات فيها 3 carbons أو أكثر → liquids

- **Methylamine and ethylamine are gases,** but primary amines with three or more carbons are liquids.
- **Primary amines** boil well above alkanes with comparable molecular weights, but below comparable alcohols. درجة الغليان فعليا أعلى من alkanes أقل من alcohols

Intermolecular N-H· · ·N hydrogen bonds are important and raise the boiling points of primary and secondary amines but are not as strong as the O-H· · ·O bonds of alcohols. The reason for this is that nitrogen is not as electronegative as oxygen.

alkane	CH_3CH_3 (30) bp −88.6°C	$CH_3CH_2CH_3$ (44) bp −42.1°C
amine	CH_3NH_2 (31) bp −6.3°C	$CH_3CH_2NH_2$ (45) bp +16.6°C
alcohol	CH_3OH (32) bp +65.0°C	CH_3CH_2OH (46) bp +78.5°C

الأمينات تعمل Hydrogen bonding بس أضعف من الكحول ، لأن Nitrogen أقل electronegativity من Oxygen

Physical Properties of Amines

Boiling Point

ما فيها N–H ف بالتالي ما بتعمل hydrogen bonding مع بعض

- **Tertiary amines** are also polar compounds, but because hydrogen is not bonded to nitrogen, these amines are incapable of intermolecular hydrogen bonding.

درجة غليان أقل من primary & secondary لكن أعلى من alkanes

Their boiling points are Lower than primary and secondary amines of identical molecular weights and Higher than those of alkanes of similar molecular weight.

Solubility in Water

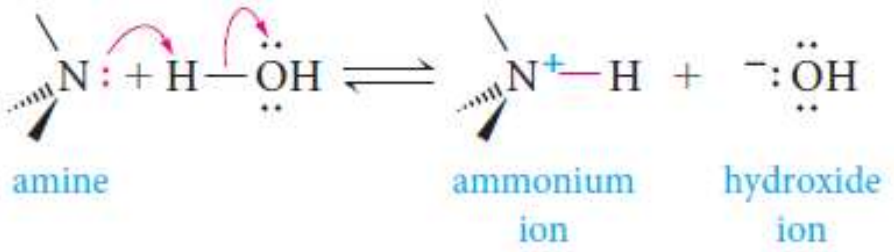
- **All three classes of amines** can form hydrogen bonds with the -OH group of water (that is, O-H· · ·N). كل الأمينات بتعمل H–bond مع الماء
- **Primary and secondary amines** can also form hydrogen bonds with the oxygen atom in water: N-H· · ·O.
- **Amines** with up to six carbons show appreciable solubility in water.

الامينات حتى ⇒ 6 carbons amines → soluble in water

The Basicity of Amines

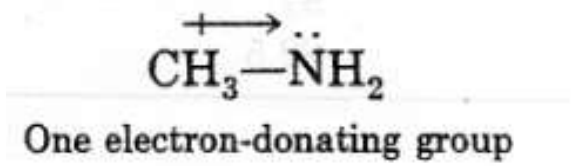
ليش الامينات Basic
لأن عندها Lone pair electrons على Nitrogen

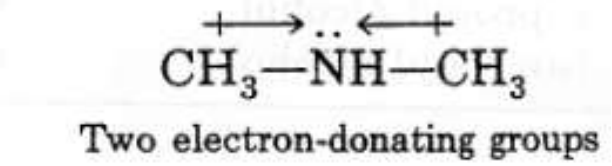
- The **unshared pair of electrons** on the nitrogen atom dominates the chemistry of amines.
- Because of this electron pair, **amines are both basic and nucleophilic.**
- Aqueous solutions of amines are basic because of the following equilibrium:



- Electron-donating groups increase the basicity of amines.
- Electron-withdrawing groups decrease their basicity.

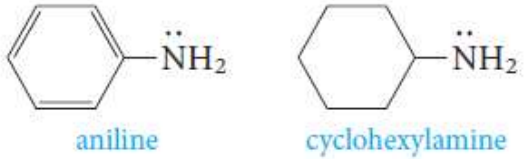
(I+)->⬆️ basicity
(I-)->⬇️ basicity
عكس الحموض الي أخذنا بالشابتر السابق ✔️



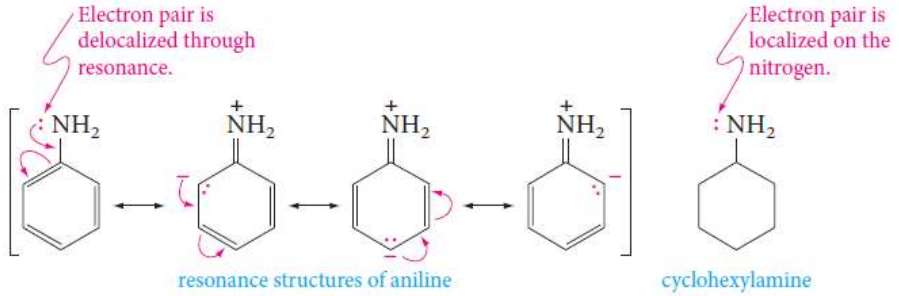


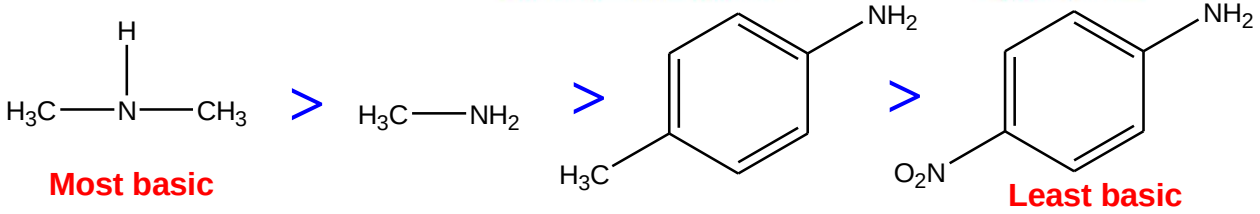
The Basicity of Amines

- **Aromatic amines are much weaker than aliphatic amines or ammonia.**
  - **Example:** aniline is less basic than cyclohexylamine.



The reason is the resonance delocalization of the unshared electron pair that is possible in aniline, but not in cyclohexylamine:





ليش طيب ؟

لأن lone pair في aniline داخل في resonance، فهو مش متاح يستقبل proton

Preparation of Amines

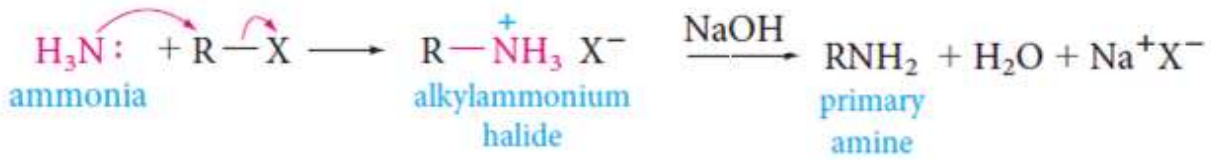
تحضير الامينز بطرق سهلة و مجربة و مواد موجودة بكل بيت

1) Alkylation of Ammonia

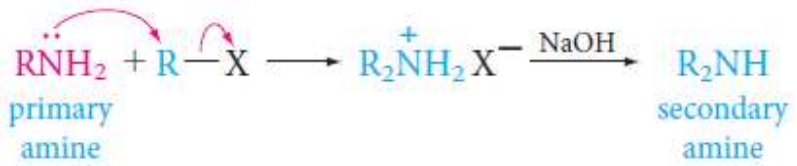
Nucleophilic Substitution نوع التفاعل

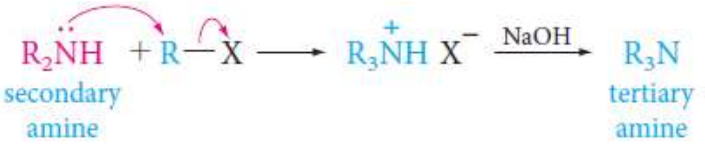
- **Ammonia** reacts with alkyl halides to give amines via a two-step process.

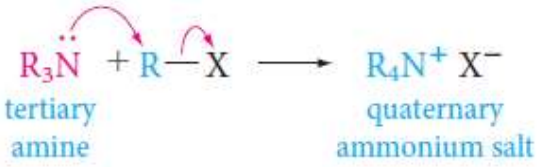
  ***The first step** is a nucleophilic substitution reaction. **The free amine** can then be obtained from its salt by treatment with a strong base*



- **Primary, secondary, and tertiary amines** can be similarly alkylated.







NH_3 تهاجم alkyl halide
amine salt يتكون
strong base نضيف
free amine نحصل على

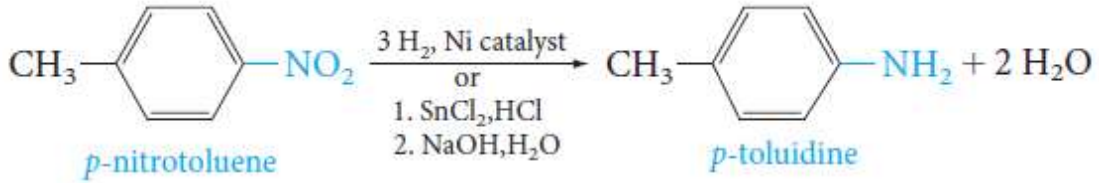
لأن الأمين اللي طلع ممكن يرجع يتفاعل مرة ثانية وثالثة

2) Reduction of Nitro Groups

إذا عندك Nitro compound ($-NO_2$)
وبتعمله reduction
بتحوله لـ Amine ($-NH_2$) ←

- The best route to **aromatic primary amines** is by reduction of the corresponding nitro compounds.

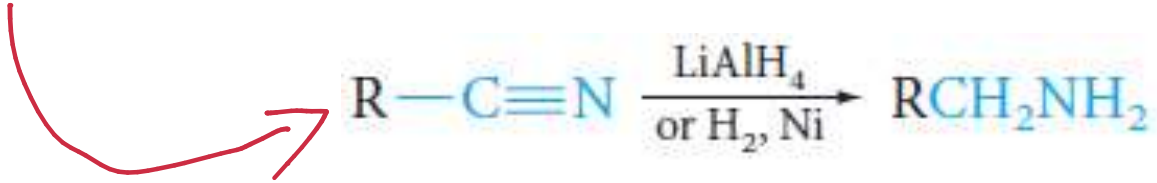
The nitro group is easily reduced, either catalytically with hydrogen or by chemical reducing agents.



3) Reduction of Nitriles

❗ يعطوا Primary amines فقط

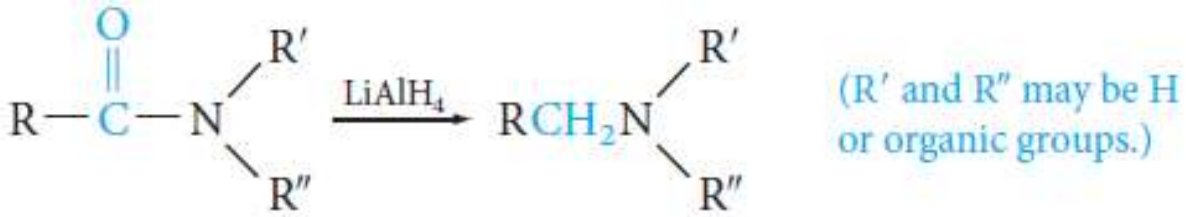
- Reduction of nitriles (cyanides) gives primary amines.



بتفاعلين الاختزال كان
العامل المختزل هو
$LiAlH_4$
او كما يسميه البعض ليلى

4) Reduction of Amides

- Amides can be reduced to amines with lithium aluminum hydride.

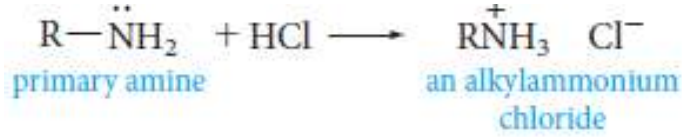


(R′ and R″ may be H or organic groups.)

Reactions of Amines

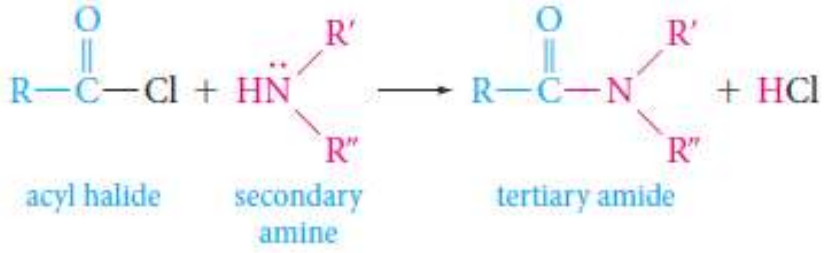
1) Reactions with Acids: Salt Formation

Amines react with strong acids to form alkylammonium salts.



2) Acylation of Amines: Amides Formation

Primary and secondary amines react with acyl halides to form amides.



Primary amine ($R-NH_2$) + Aldehyde or Ketone
acidic buffer بوجود
Imine بعطيني

3) Imines Formation

Primary amines, R-NH_2 or ArNH_2, undergo nucleophilic addition with aldehydes or ketones in an acidic buffer to give substituted imines.

Preparation of Amines🤯
Alkylation of ammonia → mixture of amines
Nitro reduction → أفضل طريقة للأمينات العطرية
Nitrile reduction → primary amine
Amide + $LiAlH_4$ → amine

Reactions of Amines 🤯
Acid → ammonium salt
Acyl halide → amide (1° & 2° only)
Aldehyde/Ketone → imine (1° only)

Advanced MCQ Exam – Amines

Choose the correct answer for each question.

1. Why are aromatic amines less basic than aliphatic amines?
A. Larger molecular size
B. Inductive effect only
C. Absence of lone pair
D. Resonance delocalization of lone pair

2. Which amine has the lowest boiling point?
A. Propylamine
B. Trimethylamine
C. Ethylamine
D. Diethylamine

3. Alkylation of ammonia produces a mixture of amines because:
A. Alkyl halides are unstable
B. Ammonia is weakly basic
C. Formed amines are more nucleophilic
D. Reaction is reversible

4. Best reagent to reduce amides into amines:
A. $NaBH_4$
B. H_2/Pd
C. Zn/HCl
D. $LiAlH_4$

5. Most basic amine:
A. Aniline
B. p-Nitroaniline
C. Ammonia
D. Cyclohexylamine

6. Tertiary amines cannot form intermolecular hydrogen bonding because:
A. They are nonpolar
B. Nitrogen is less electronegative
C. They lack N–H bonds
D. They are bulky

7. Reduction of nitriles yields:
A. Secondary amines
B. Primary amines
C. Amides
D. Imines

8. Reaction of amines with HCl results in:
A. Imine
B. Amide
C. Alkyl halide
D. Ammonium salt

9. Which amine is most soluble in water?
A. Octylamine
B. Hexylamine

C. Aniline
D. Methylamine

10. Which functional group is best converted to amine by reduction?
A. Ester
B. Nitro
C. Ether
D. Alkene

11. IUPAC name of aniline:
A. Phenylamine
B. Aminobenzene
C. Benzenamine
D. Benzylamine

12. Which amine forms imines with aldehydes?
A. Secondary
B. Tertiary
C. Primary
D. Aromatic only

13. Which decreases amine basicity most?
A. Alkyl substitution
B. Resonance
C. Hydrogen bonding
D. Steric hindrance

14. Hydrogen bonding in primary amines occurs via:
A. N–H···N
B. C–H···N
C. O–H···N
D. N···N

15. Reduction of nitrobenzene gives:
A. Cyclohexylamine
B. Benzylamine
C. Aniline
D. Phenol

16. Acyl halides react with which amines?
A. Primary only
B. Secondary only
C. Primary and secondary
D. Tertiary

17. Lone pair on nitrogen makes amines:
A. Electrophilic
B. Neutral
C. Acidic
D. Basic

18. $LiAlH_4$ acts as reducing agent because:
A. Lithium is reactive
B. Aluminum is electronegative
C. It donates hydride ions
D. It releases hydrogen gas

19. Which amine has boiling point between alkane and alcohol?
A. Alkanes
B. Primary amines
C. Alcohols
D. Aromatic hydrocarbons

20. Product of primary amine + ketone (acidic medium):
A. Enamine
B. Amide
C. Salt
D. Imine

Answer Key

1. D
2. B
3. C
4. D
5. D
6. C
7. B
8. D
9. D
10. B
11. C
12. C
13. B
14. A
15. C
16. C
17. D
18. C
19. B
20. D