1am أ.د. محمد مثالي ، محاضرة ، أولى علوم . تكنولوجيا حيوية . ساعات معتمدة .
٢ تربية خاصة / علوم .
٤ تربية أساسي / علوم .

المقرر : أساسيات الكيمياء العضوية . Basic Organic Chemistry .
نقاط مختصرة ومبسطة .

Amines الأمينات

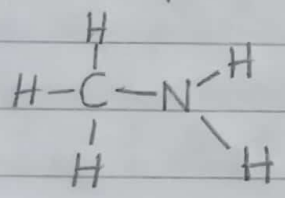
1. Structure :

An amine has the general formula :

RNH_2 , R_2NH or R_3N

R = alkyl or aryl group.

Examples :

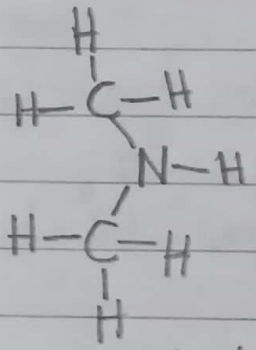


Methylamine
(أمين أحادي)
aliphatic
primary (1°)
amine
أمين أليفاتي
أولي .

CH_3NH_2

1°

أبسط أمين أليفاتي
simplest aliphatic amine

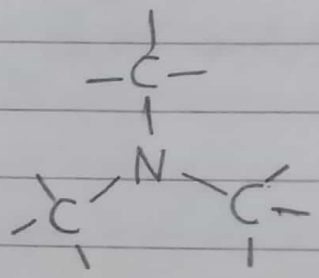


Dimethylamine
(أمين ثنائي)
aliphatic
secondary (2°)
amine
أمين أليفاتي
ثانوي
(وليس ثنائي)

$(CH_3)_2NH$

2°

ثنائي ميثيل أمين



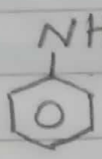
Triethylamine
(أمين ثلاثي)
aliphatic
tertiary (3°)
amine
أمين أليفاتي
ثالثي
(وليس ثلاثي)

$(CH_3)_3N$

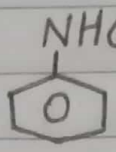
3°

ثلاثي ميثيل أمين

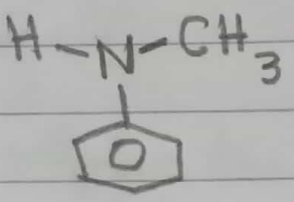
2am



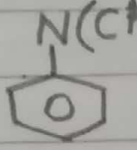
Aniline
1°
أنيلين
Aromatic primary (1°) amine
أمين أروماتي أولي 1°
the simplest aromatic amine
أبسط أمين أروماتي



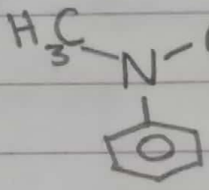
N-Methylaniline
(ثانوي)



Aromatic secondary (2°) amine
أمين أروماتي ثانوي 2°
(وليس ثناءً)



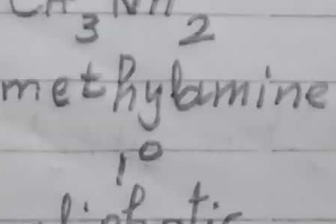
N,N-Dimethyl-aniline
(ثالثي)



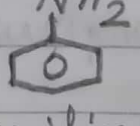
أمين أروماتي ثالثي 3°
(وليس ثلاثي)

2. Classification:

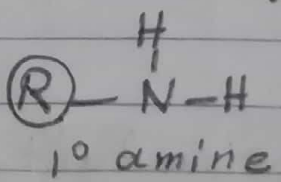
2.1 Primary 1°: one group is attached to nitrogen atom.
(one can also say: two hydrogen atoms are attached to the nitrogen atom).



CH_3NH_2
methylamine
1°
aliphatic



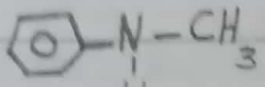
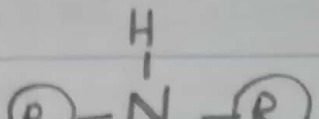
aniline
1°
aromatic



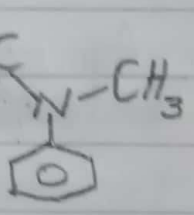
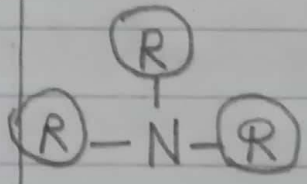
1° amine

3am

2.2 Secondary 2° ; two groups are attached to nitrogen atom.
(one hydrogen atom is attached to the nitrogen atom.).

$(CH_3)NH$ dimethylamine 2° aliphatic	 N-methylaniline 2° mixed (aliphatic-aromatic)	 2° amine

2.3 Tertiary 3° ; three groups are attached to the nitrogen atom.
(no hydrogen atom is attached to the nitrogen atom).

$(CH_3)_3N$ trimethylamine 3° aliphatic	 N, N-dimethyl-aniline (ēp', ādō') 3° mixed (aliphatic-aromatic).	 3° amine

4am

3. Nomenclature :

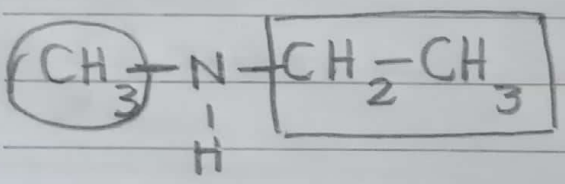
(مع التبسط الحديد)

3.1 Aliphatic amines :

Name the alkyl group(s) attached to nitrogen, and follow this by the word –amine.

CH_3NH_2 $C_2H_5NH_2$ $CH_3CH_2NH_2$

Methylamine Ethylamine

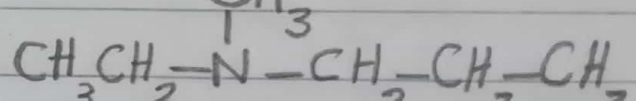


Ethyl methyl amine

أجد يا حرف e يأت قبل حرف m

كلمة واحدة

2° aliphatic amine



Ethylmethylpropyl–amine

كلمة واحدة

3° aliphatic amine

propyl هي أطول سلسلة متصلة بالنيتروجين.

$N(C_2H_5)_3$

Triethylamine

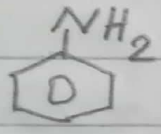
3° aliphatic amine

[ويمكن استخدام تسمية أخرى للأمينات الأكثر تعقيداً في تركيبها].

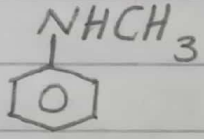
5am

3.2 Aromatic amines :

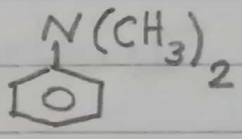
Aromatic amines, where nitrogen is attached directly to an aromatic ring, are generally named as derivatives of aniline.



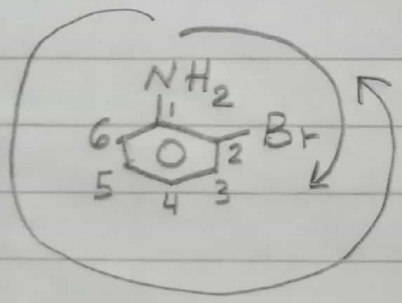
Aniline
the simplest aromatic amine
1°



N-Methylaniline
2°

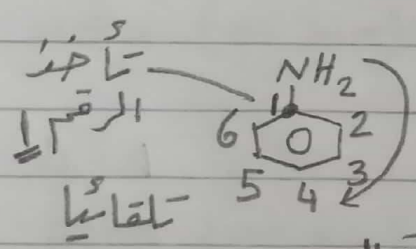


N,N-Dimethyl-aniline
كلمة واحدة
3°

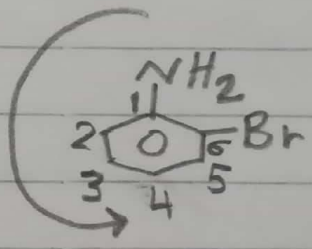


2-Bromoaniline

ذرة الكربون الحاملة للنيتروجين تأخذ الرقم 1. ثم نعد ذرات الكربون في اتجاه عقارب الساعة. فيه 2 ثم في عكس اتجاه عقارب الساعة فيه أطول. ونختار أقل رقم يأخذه البروم.



ذرة البروم في هذا الاتجاه تأخذ الرقم 2



ذرة البروم في هذا الاتجاه تأخذ الرقم 6

إذن ذرة البروم تأخذ الرقم 2 (الأقل)، وهذا (بداهة) يعني أن النيتروجين أخذ الرقم 1

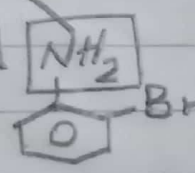
6 am

وحين نعرف من الكيمياء العضوية الأروماتية المبنية على حلقة البنزين أن المجموعة المميزة للمركب تأخذ أقل رقم، أي الرقم ١، ثم بعد ذلك نرقم ذرات الكربون في حلقة البنزين، بحيث تأخذ المجموعة الثانية أقل رقم (بعد الواحد ١).

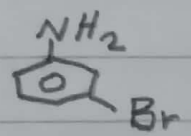
كما نعلم الآن:

رقم المجموعة المميزة	رقم المجموعة الثانية
1	2 ortho (or o-)
1	3 meta (or m-)
1	4 para (or p-)

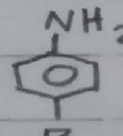
المجموعة المميزة وتأخذ رقم ١ تلقائيًا



2-Bromoaniline
o- "



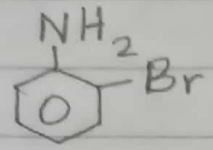
3-Bromoaniline
m- "



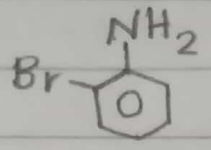
4-Bromoaniline
p- "

7am

لاحظ الآتي:
مجموعة الأمين NH_2 تنشط حلقة البنزين لتستقبل مجموعة ثانية.
ومجموعة الأمين NH_2 توجه المجموعة الثانية إلى المواضعين o- & p-



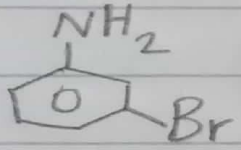
A



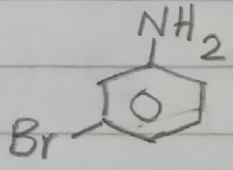
B

A ≡ B 2-Bromoaniline
o-Bromoaniline

هما مركب واحد فقط وليسا مركبين،
ولتتأكد: اكتب اسم كل منهما، ستجده نفس الاسم،
إذاً هما مركب واحد فقط



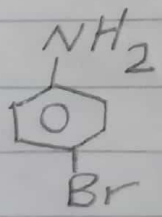
C



D

C ≡ D 3-Bromoaniline
m-Bromoaniline

هما مركب واحد فقط، وليسا مركبين، إذ لهما نفس الاسم،



4-Bromoaniline
p-Bromoaniline

8am

4. Physical properties of amines :

4.1 Form (state) :

4.1.1 Gases :, e.g., the first four amines, e.g.,

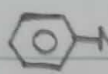
CH_3NH_2 methylamine (1° aliphatic).

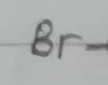
$(CH_3)_2NH$ dimethylamine (2° aliphatic).

$(CH_3)_3N$ trimethylamine (3° aliphatic)

$(C_2H_5)NH_2$ ethylamine (1° aliphatic)

4.1.2 Liquids : e.g., $(C_2H_5)_3N$ triethylamine.

 aniline (1° aromatic)

4.1.3 Solids : e.g.,  4-bromoaniline
p-bromoaniline
(ring-substituted 1° aromatic)

4.2 Polarity :

polar (they are derivatives of ammonia, NH_3  , which is a strong polar compound)

9am

4.3 Odour:

Most of the amines have smell.

Methylamines and ethylamines smell like (ammonia $\ddot{N}H_3$,نشادر).

Higher alkylamines smell like (fish).

4.4 Solubility in highly polar solvents, like water:

$C_1 - C_4$ alkylamines are soluble in water.

As Alkylamines increase in C-number (i.e., the molecular weight) their solubility in water decreases.

Aromatic amines, e.g., aniline  , are insoluble in water.

10am

4.5 Solubility of amines in nonpolar solvents, e.g. benzene (nonpolar): soluble to certain degree (depending on the molecular structure of the amine and solvent).

4.6 Colour: Pure amines (, especially,) in the gas and liquid forms are colourless. In general; impurties, light and air make amines get dark.

5. Biological activity;

Aromatic amines are, generally, very toxic.

11am

6. Salts of amines :

Amines (as derivatives of ammonia $\ddot{N}H_3$) are basic compounds.

Aliphatic amines are, relatively, more basic than aromatic amines.

Aqueous (مائي) mineral acids (inorganic acids, e.g., HCl, H_2SO_4, HNO_3, H_3PO_4) and aqueous carboxylic acids (e.g., CH_3CO_2H) readly convert amines into (amine – acid salts).

Aqueous hydroxides (e.g., $NaOH$, KOH) readly convert the (amine–acid salts) back into the free (original) amines.

انظر المثال التالي :

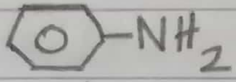
12 am

Amine – acid salt :

Ex. :

$R\ddot{N}H_2$

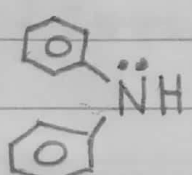
1° amine



aniline

$R_2\ddot{N}H$

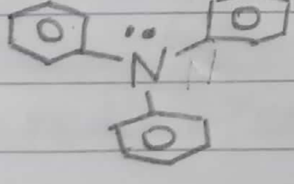
2° amine



diphenylamine

$R_3\ddot{N}$

3° amine



triphenylamine

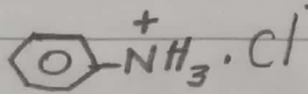
ملح

HCl ⇌ $NaOH$

قلوي

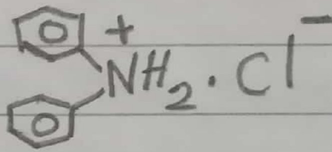
(قاعدة غير قوية)

$R\overset{+}{N}H_3\overset{-}{Cl}$ acid-salt



aniline hyrochloride

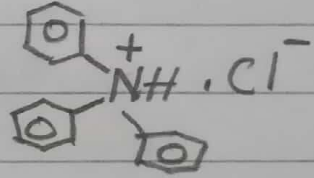
$R_2\overset{+}{N}H_2\overset{-}{Cl}$ acid-salt



diphenylamine hydrochloride

$R_3\overset{+}{N}H, Cl^-$

acid-salt



triphenylamine hydrochloride

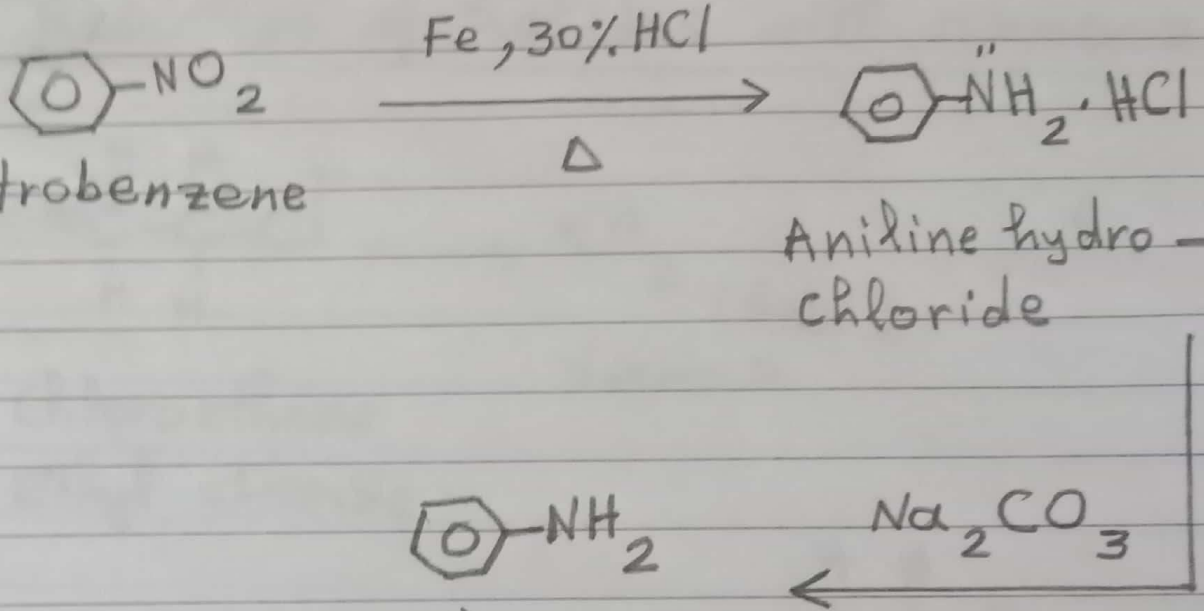
Insoluble in water

Soluble in water

13am

7. Industrial source of amines :

Preparation of aniline by reduction of nitrobenzene (conversion of the nitro group into an amino group) :-



1° aromatic amine

the most important amine

The sodium carbonate, Na_2CO_3, is used - as a base - to neutralize the hydro-chloric acid, HCl, and liberate the free aniline.

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$$

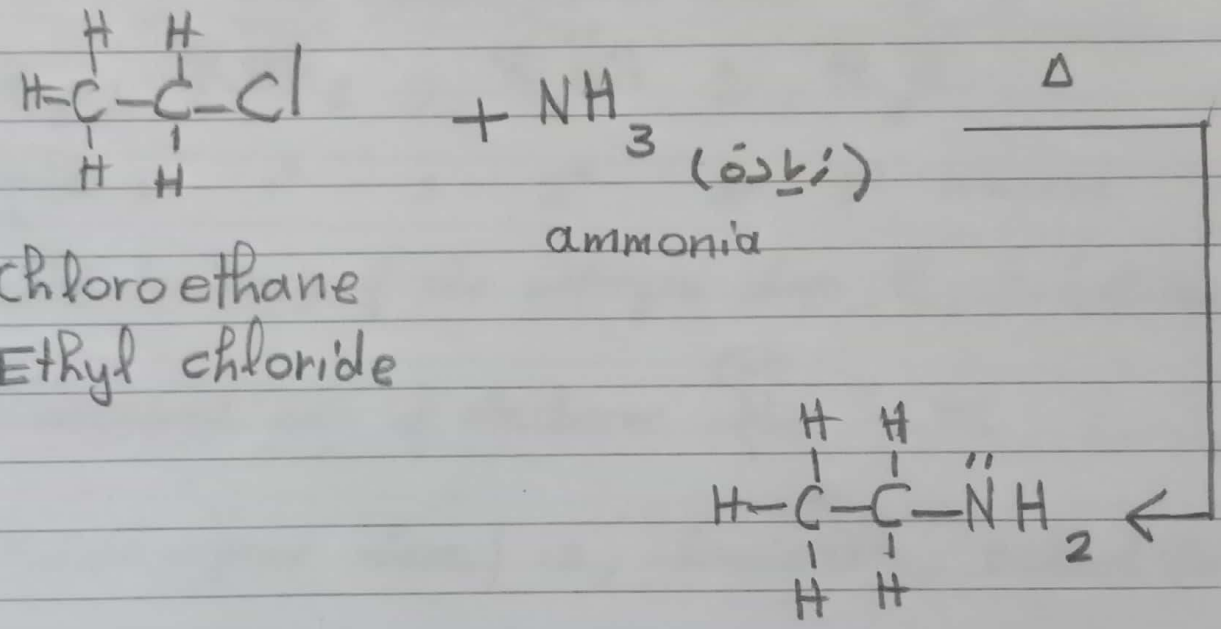
14am

8. Preparation of amines:

8.1 Reduction of nitrocompounds:

انظر تفاعل تحضير الأمينات الأولية ص 13am .

8.2 Reduction of halides with ammonia:



Chloroethane
Ethyl chloride

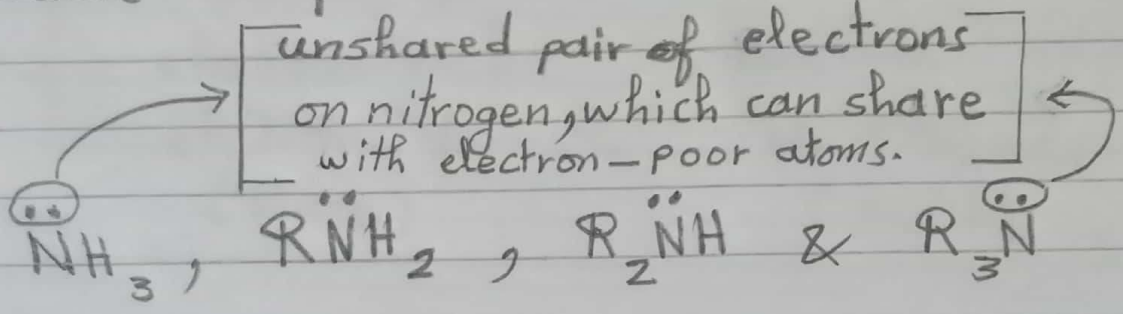
Ethylamine
1° aliphatic amine

16am

15am

9. Reactions of amines:

Ammonia, $\ddot{N}H_3$, and its amine derivatives ($R\ddot{N}H_2$, $R_2\ddot{N}H$ & $R_3\ddot{N}$) are, chemically, basic compounds.



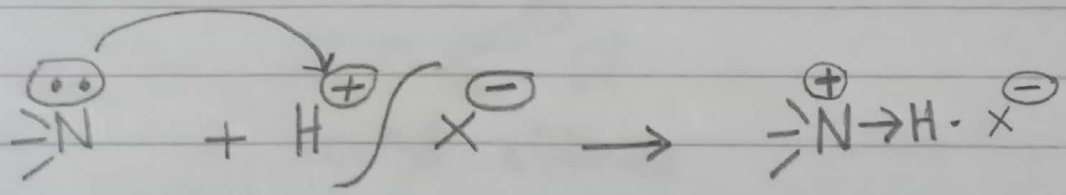
The tendency of the nitrogen atom, $\ddot{N}$, to (share its unshared pair of electrons $-\ddot{N}-$ with electron-poor atoms) is, chemically, called the ("basicity" of amines), i.e. amines are basic organic compounds.

On the other hand, organic and inorganic acids can liberate (hydrogen ions H^+). The hydrogen ion, H^+, has no electrons. The hydrogen ion is, thus, very poor in electrons. Thus, the

hydrogen ion accepts (or receives) the electrons given by nitrogen. The result

N	H
amine-nitrogen	acid-hydrogen ion (proton)
electron-rich	electron-poor
electron-donner (Base)	electron-acceptor (ACid)

is the formation of an (amine-acid salt).



amine	hydrogen ion	amine-acid salt.
(Lewis) (base)	(Lewis) (acid)	(+charge on N).

انظر (ص am12) لأمثلة من هذا النوع.

لويس Lewis هو الباحث الذي صنف الحمض والقاعدة على أساس من «الإلكترونات»: التركيب الإلكتروني للذرة.

electron donner = base; Lewis base.

electron acceptor = acid; Lewis acid.

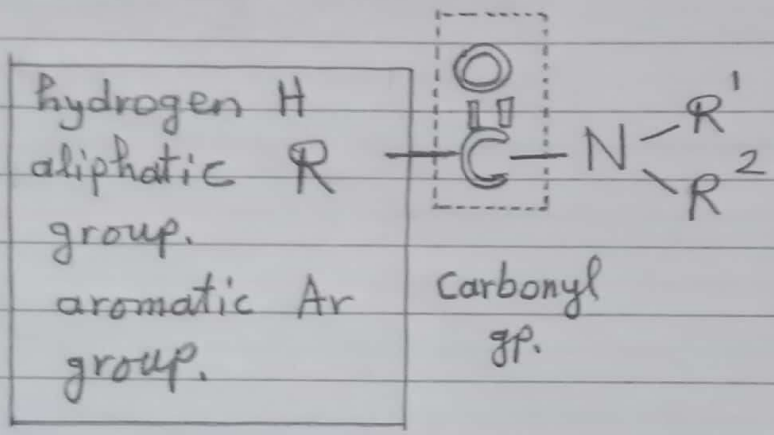
ammonia and its amine derivatives are electron donners, i.e., bases.

the hydrogen ion (proton) is an electron acceptor, i.e., an acid.

17am

9. Conversion into amides;

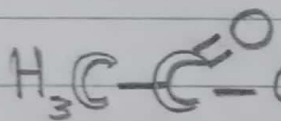
You know that the general structure of the carboxylic acid – amides is;



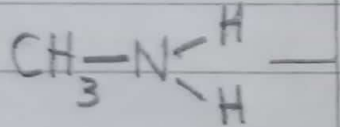
R^1, R^2 may be the same, or different.
R^1; R^2 = H; aliphatic; aromatic gp.s

General representation of the (carboxylic-amide derivative)

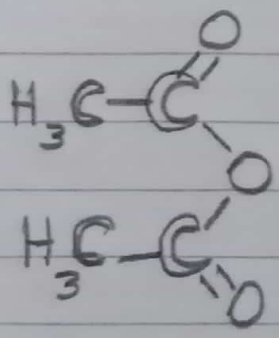
Ex:



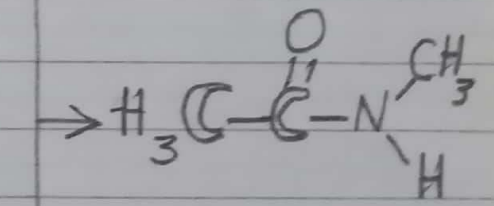
acetyl chloride



Acetamide



acetic anhydride



N-Methylacetamide

18am

10. Uses of amines :

Many amines are used in preparing ;

10.1 Pharmaceutical agents.

10.2 Dyeing materials.