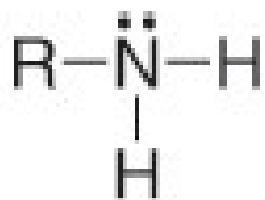
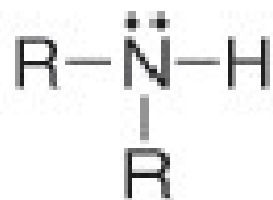


Ammine

Introduzione



Ammine primarie
Azoto legato ad un
solo gruppo
alchilico



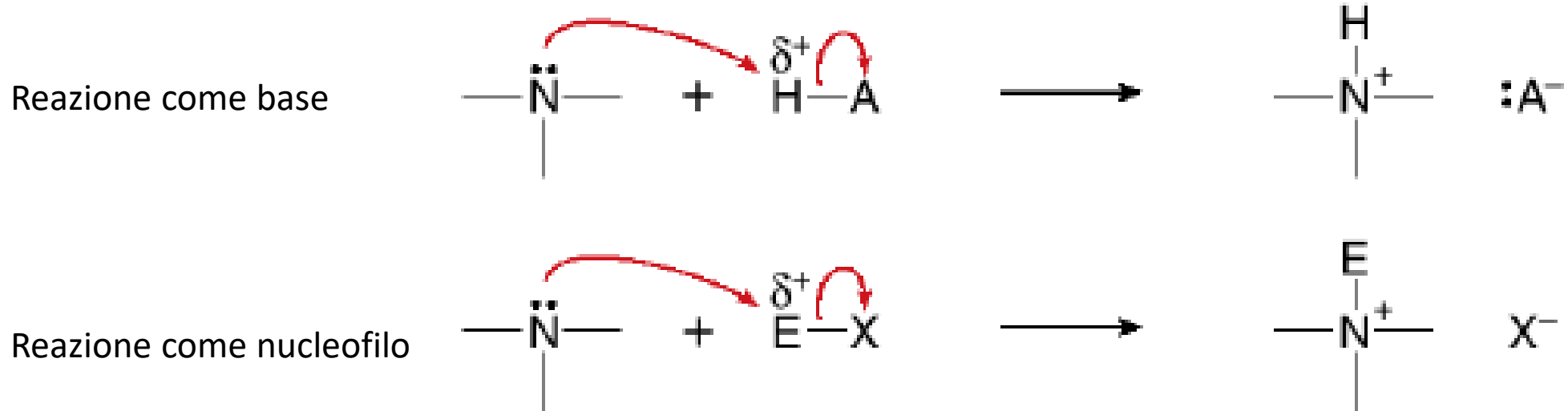
Ammine secondarie
Azoto legato due gruppi alchilici



Ammine terziarie
Azoto legato a tre gruppi alchilici


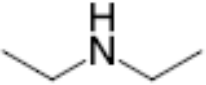
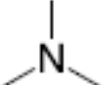
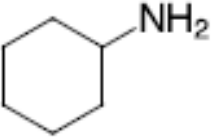
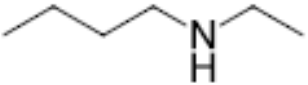
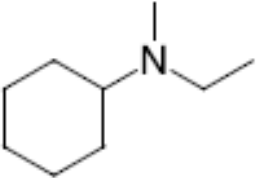
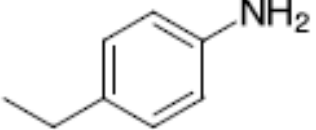
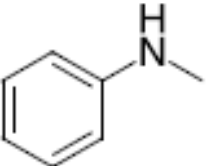
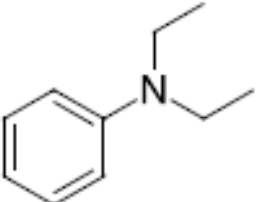
Introduzione

- Le ammine sono le basi organiche più forti
- Le ammine sono i più forti nucleofili organici neutri

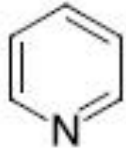


La chimica delle ammine è comandata dalla presenza del doppietto non condiviso sull'azoto

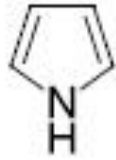
Nomenclatura

| | primarie | secondarie | terziarie |
|------------|---|--|---|
| alifatiche |  butanammina (butil ammina) |  dietilammina |  trimetilammina |
| aromatiche |  cicloesanammina (cicloesil ammina) |  N-etilbutanammina |  N-etil-N-metil- cicloesanammina |
| |  |  |  |

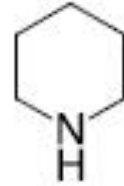
Ammine eterocicliche



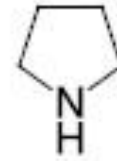
piridina



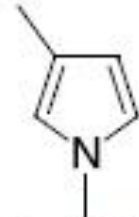
pirrolo



piperidina

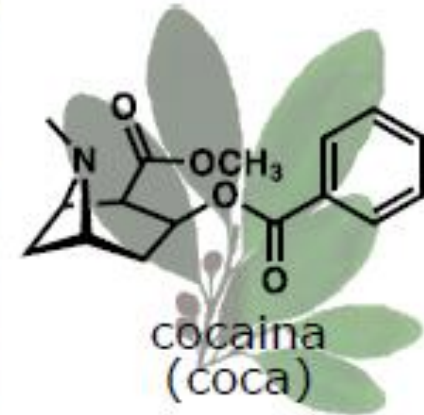
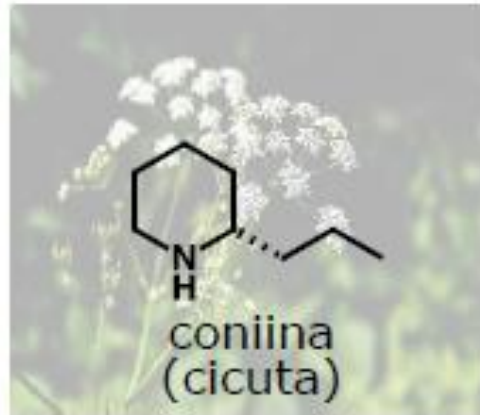
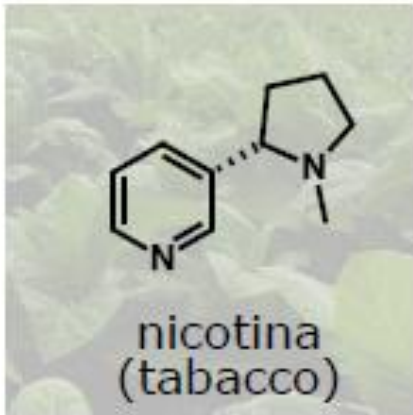


pirrolidina

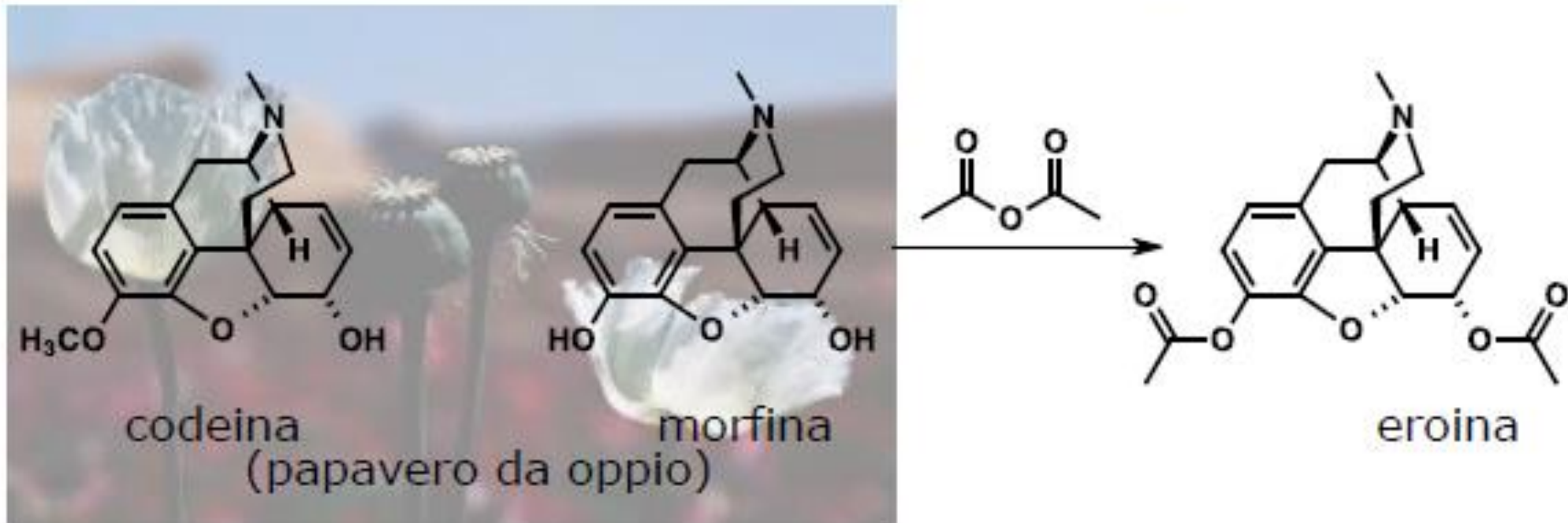


1,3-dimetilpirrolo

alcaloidi

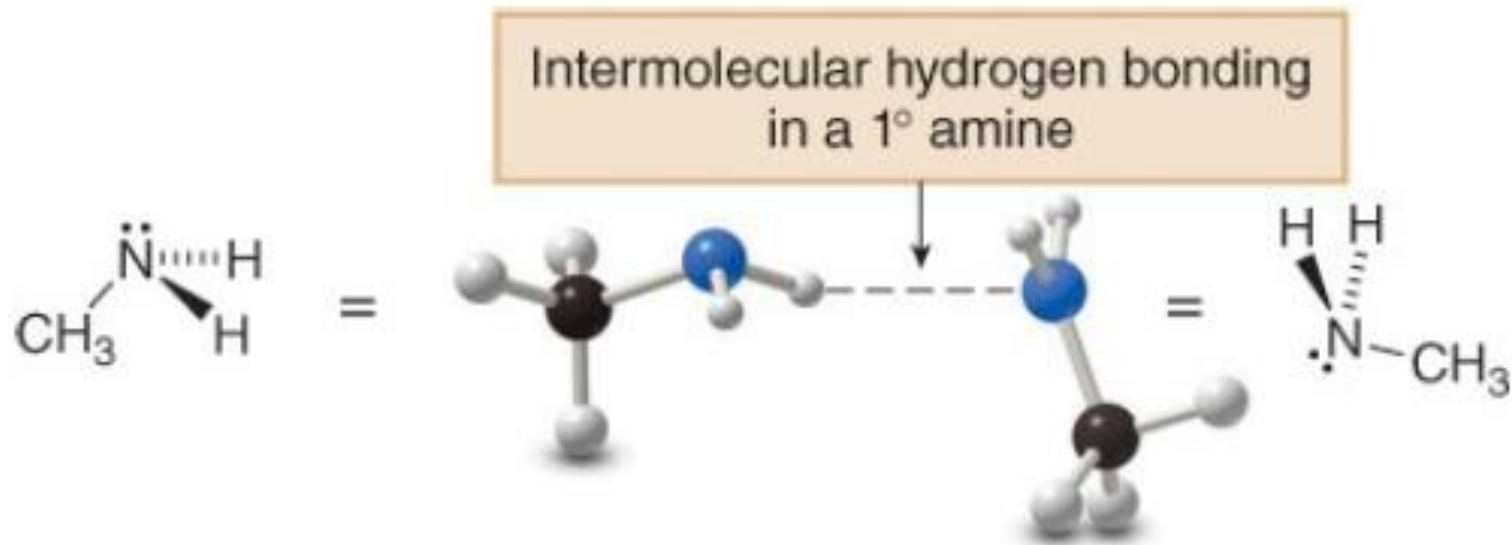


Ammine eterocicliche



Proprietà fisiche

- Le ammine mostrano interazioni dipolo-dipolo tra molecole per la presenza dei legami polari C-N e N-H
- Le ammine primarie e secondarie sono in grado di formare legami idrogeno tra loro perché contengono legami N-H



Proprietà fisiche



MW = 74

bp 38 °C



MW = 73

bp 78 °C



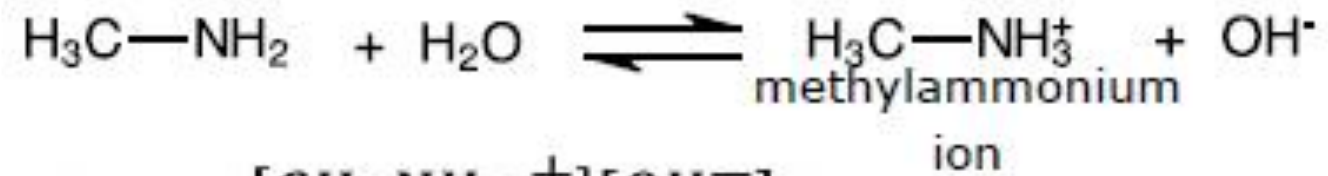
MW = 74

bp 118 °C



Aumentando le forze intermolecolari, aumenta il punto di ebollizione

Basicità delle ammine

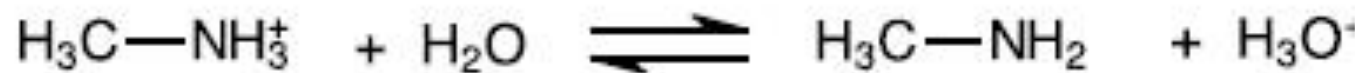


$$K = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2][\text{H}_2\text{O}]}$$



$$K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]}$$

Basicità delle ammine



$$K = \frac{[\text{CH}_3\text{NH}_2][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{NH}_3^+][\text{H}_2\text{O}]}$$



$$K_a = \frac{[\text{CH}_3\text{NH}_2][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{NH}_3^+]}$$

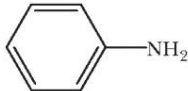



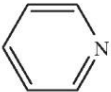
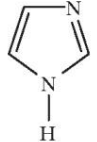
Basicità delle ammine

$$K_b \times K_a = [\text{OH}^-][\text{H}_3\text{O}^+] = 10^{-14}$$

$$pK_b + pK_a = 14$$

| amine | K_b | pK_b | pK_a (NH ⁺) |
|--|-------------------------|--------|---------------------------|
| NH ₃ , RNH ₂ , R ₂ NH, R ₃ N | $10^{-3} \div 10^{-5}$ | 3 ÷ 5 | 9 ÷ 11 |
| NH ₃ | | 4.7 | 9.3 |
| CH ₃ NH ₂ | | 3.4 | 10.6 |
| (CH ₃) ₂ NH | | 3.3 | 10.7 |
| (CH ₃) ₃ N | | 4.2 | 9.8 |
| ArNH ₂ , ArNHR, ArNR ₂ | $10^{-8} \div 10^{-10}$ | 8 ÷ 10 | 4 ÷ 6 |
| PhNH ₂ | | 9.4 | 4.6 |

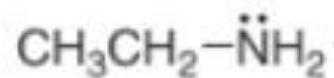
TABELLA 10.2 Forza basica (pK_b) di alcune ammine e forza acida (pK_a) dei loro acidi coniugati*

| Ammine | Struttura | pK_b | pK_a |
|--|---|--------|--------|
| Ammoniaca | NH_3 | 4.74 | 9.26 |
| Ammine primarie | | | |
| metilammina | CH_3NH_2 | 3.36 | 10.64 |
| etilammina | $CH_3CH_2NH_2$ | 3.19 | 10.81 |
| cicloesilammina | $C_6H_{11}NH_2$ | 3.34 | 10.66 |
| Ammine secondarie | | | |
| dimetilammina | $(CH_3)_2NH$ | 3.27 | 10.73 |
| dietilammina | $(CH_3CH_2)_2NH$ | 3.02 | 10.98 |
| Ammine terziarie | | | |
| trimetilammina | $(CH_3)_3N$ | 4.19 | 9.81 |
| triethylammina | $(CH_3CH_2)_3N$ | 3.25 | 10.75 |
| Ammine aromatiche | | | |
| anilina |  | 9.37 | 4.63 |
| 4-metilammina (<i>p</i> -toluidina) |  | 8.92 | 5.08 |
| 4-cloroanilina |  | 9.85 | 4.15 |
| 4-nitroanilina |  | 13.0 | 1.0 |
| Ammine aromatiche eterocicliche | | | |
| piridina |  | 8.75 | 5.25 |
| imidazolo |  | 7.05 | 6.95 |

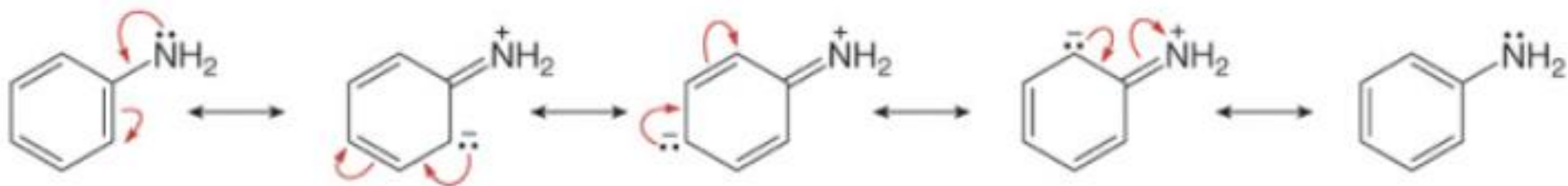
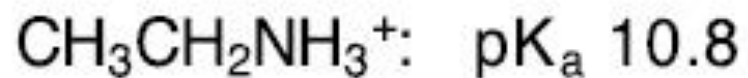
* Per ciascuna ammina, $pK_a + pK_b = 14.00$

Basicità delle ammine

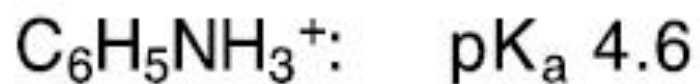
- Le ammine sono leggermente più basiche dell'ammoniaca
- Le ammine aromatiche sono meno basiche delle ammine alifatiche perché il loro doppietto è delocalizzato sull'anello aromatico e quindi meno disponibile per la protonazione



The electron pair is localized on the N atom.



The electron pair is delocalized on the benzene ring.



Aniline sostituite

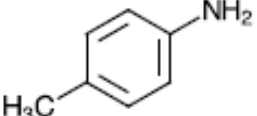
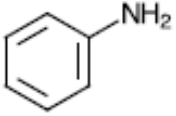
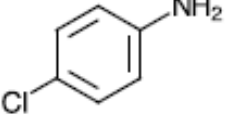
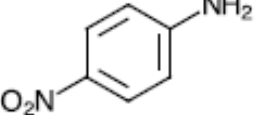
- Sostituenti elettron-donatori (D) aumentano la basicità dell'anilina
- Sostituenti elettron-attrattori (W) diminuiscono la basicità dell'anilina

| D |
|------------------|
| -NH ₂ |
| -OH |
| -OR |
| -NHCOR |
| -R |

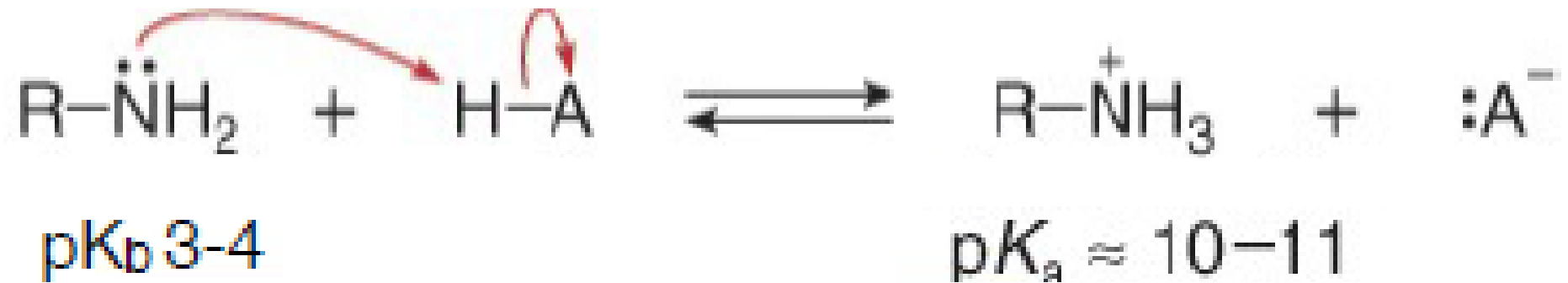
| W | |
|-------|-------------------------------|
| -X | -CN |
| -CHO | -SO ₃ H |
| -COR | -NO ₂ |
| -COOR | -NR ₃ ⁺ |
| -COOH | |

W = electron-withdrawing group

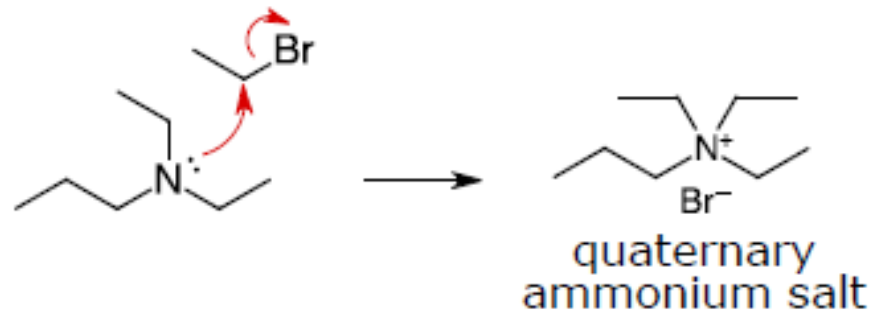
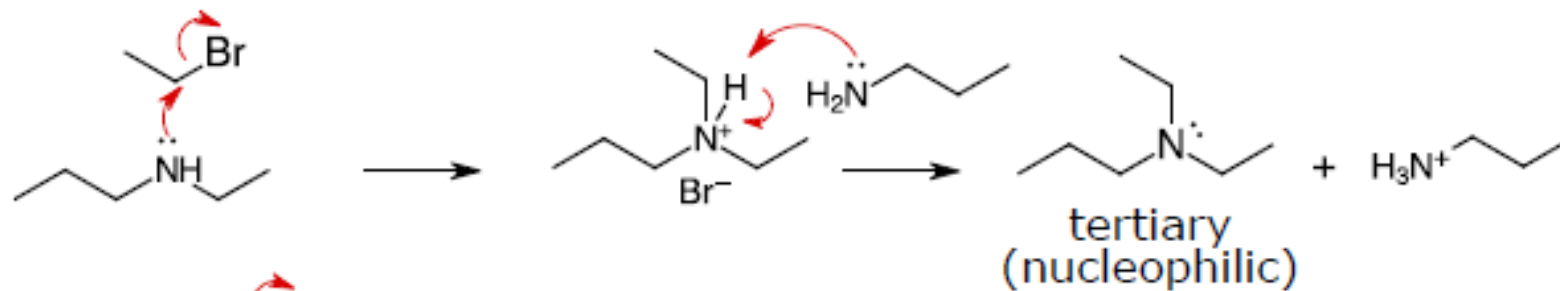
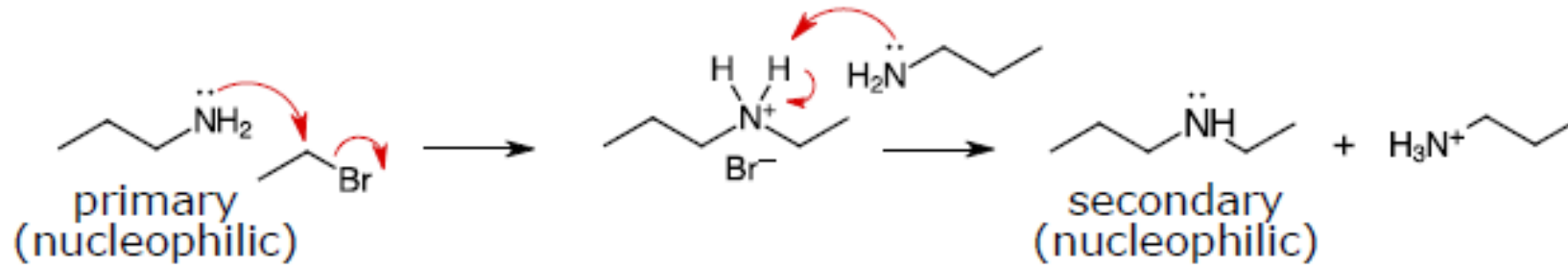
..

| | pK _a (NH ⁺) |
|---|------------------------------------|
|  | 5.1 |
|  | 4.6 |
|  | 4.2 |
|  | 1.0 |

Le ammine in presenza di un acido si protonano



Le ammine si comportano da nucleofili



Polialchilazione

si ottiene una miscela di prodotti