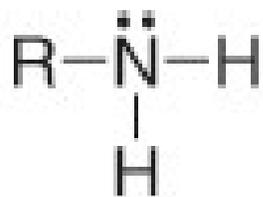
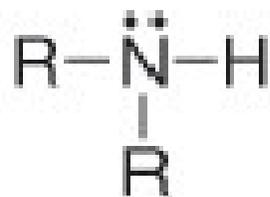


Ammine

# Introduzione



Ammine primarie  
Azoto legato ad un  
solo gruppo  
alchilico



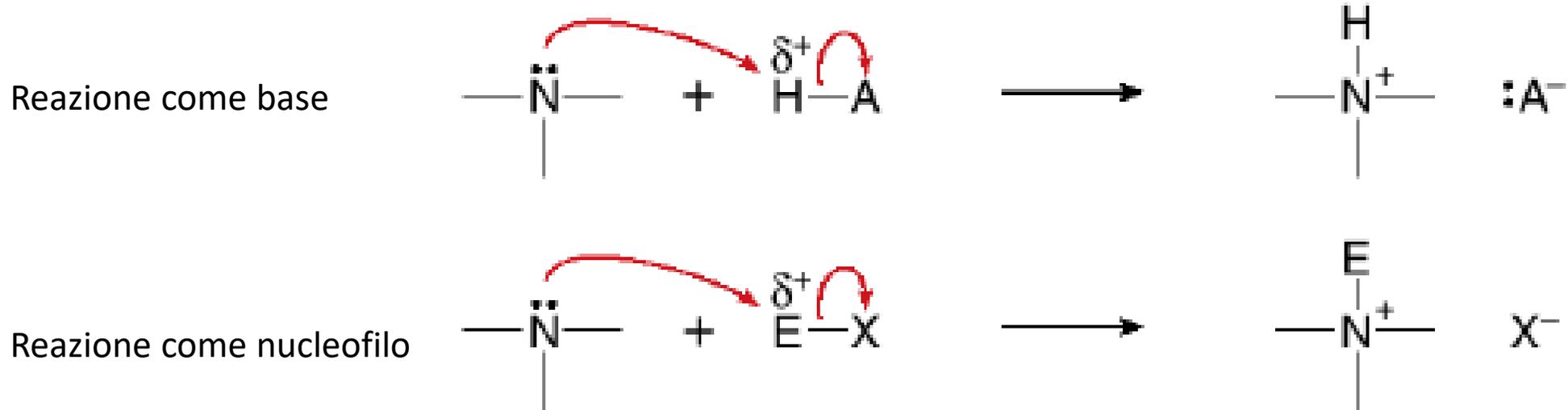
Ammine secondarie  
Azoto legato due gruppi alchilici



Ammine terziarie  
Azoto legato a tre gruppi alchilici

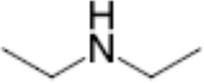
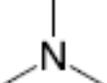
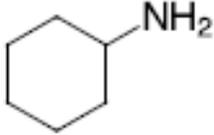
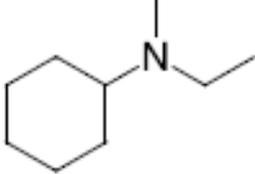
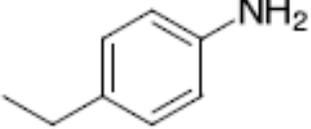
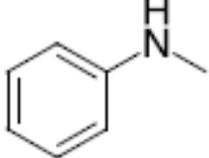
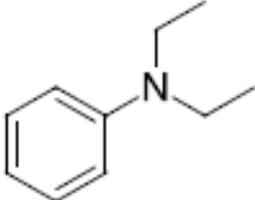
# Introduzione

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

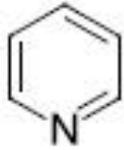


La chimica delle ammine è comandata dalla presenza del doppietto non condiviso sull'azoto

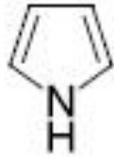
# Nomenclatura

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

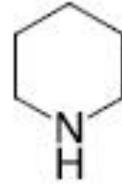
# Ammine eterocicliche



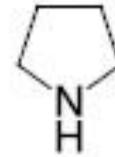
piridina



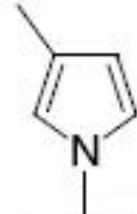
pirrolo



piperidina

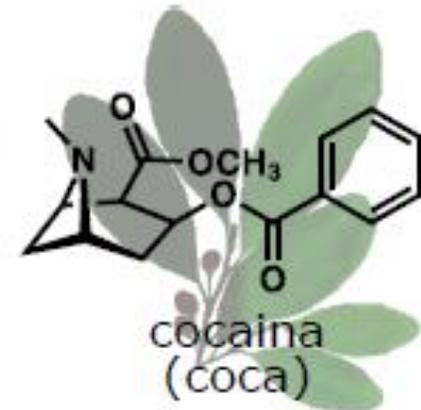
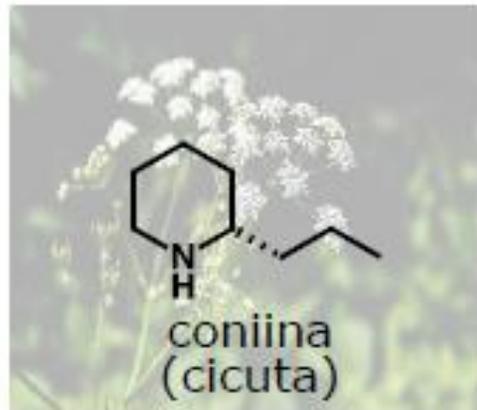
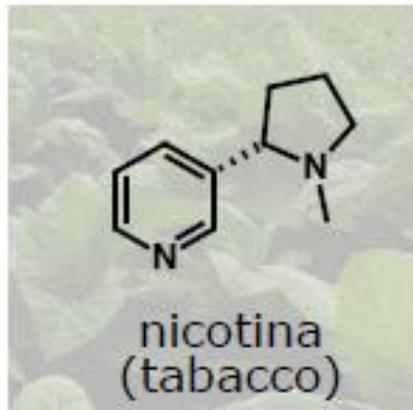


pirrolidina

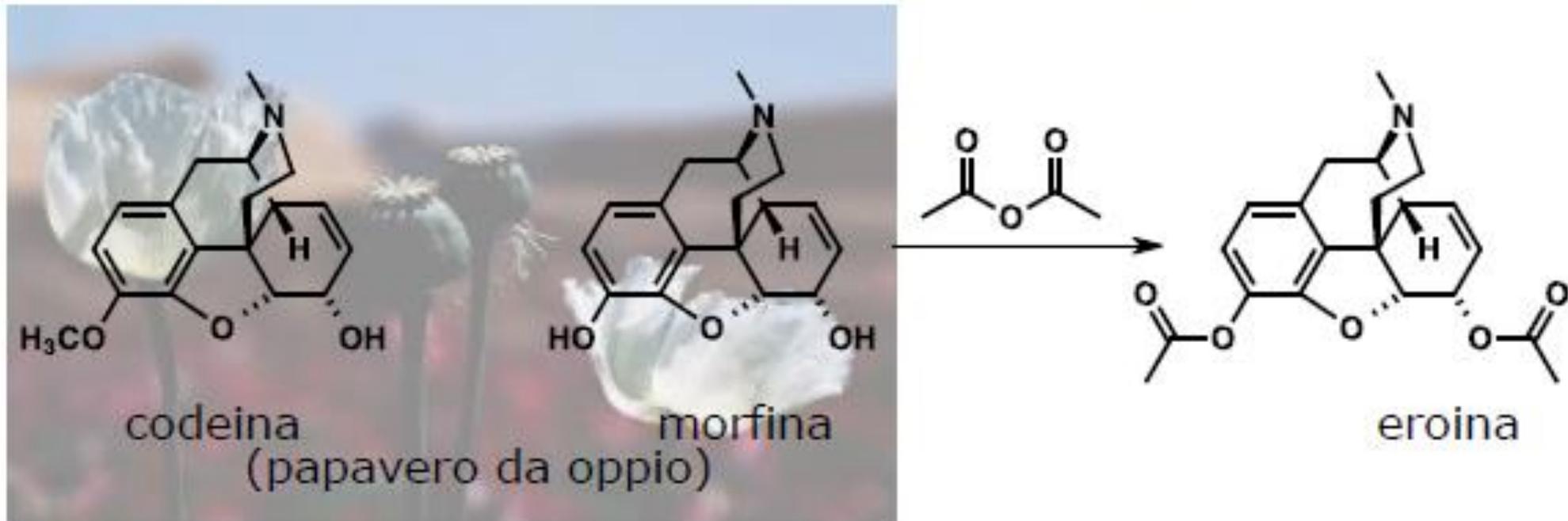


1,3-dimetilpirrolo

## alcaloidi

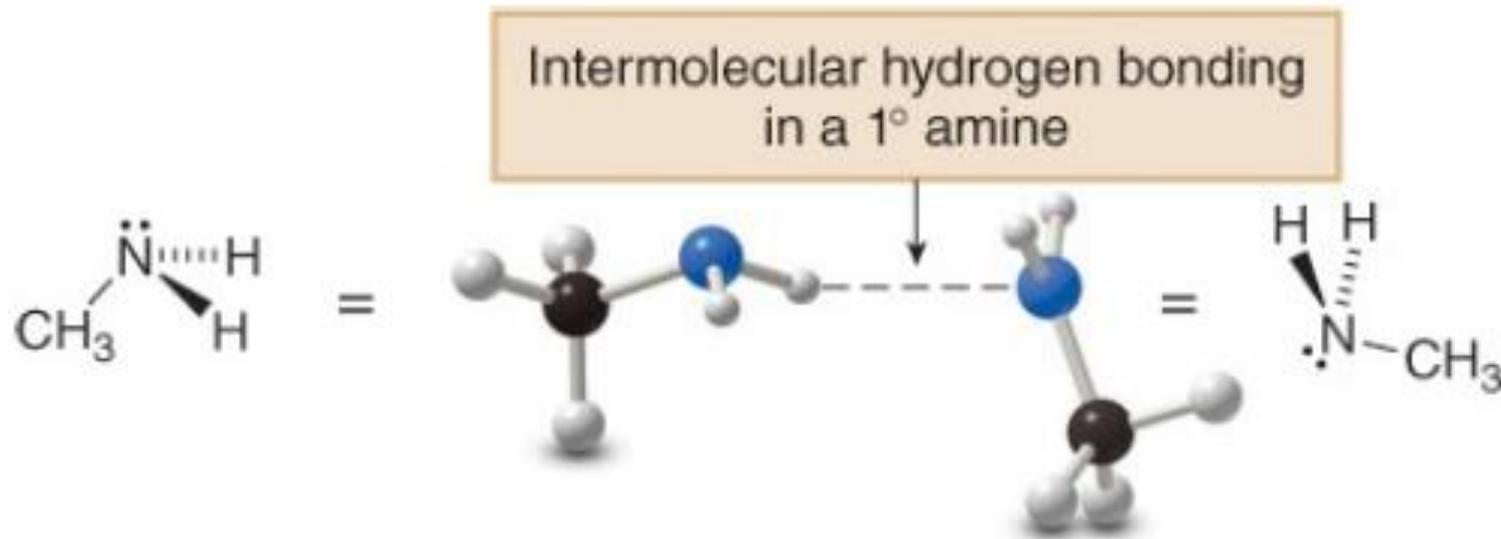


# Ammine eterocicliche



# 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

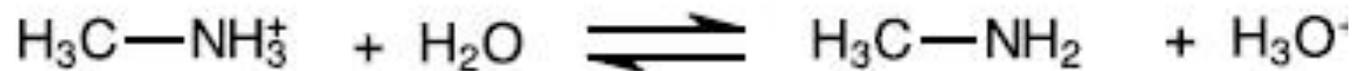


$$K = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2][\text{H}_2\text{O}]}$$



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

# Basicità delle ammine



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



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

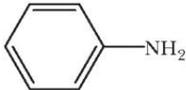
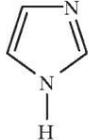
# Basicità delle ammine

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

$$pK_b + pK_a = 14$$

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

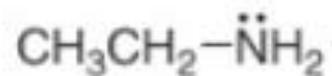
**TABELLA 10.2** Forza basica ( $pK_b$ ) di alcune ammine e forza acida ( $pK_a$ ) dei loro acidi coniugati\*

Ammine	Struttura	$pK_b$	$pK_a$
<b>Ammoniaca</b>	$NH_3$	4.74	9.26
<b>Ammine primarie</b>			
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
<b>Ammine secondarie</b>			
dimetilammina	$(CH_3)_2NH$	3.27	10.73
dietilammina	$(CH_3CH_2)_2NH$	3.02	10.98
<b>Ammine terziarie</b>			
trimetilammina	$(CH_3)_3N$	4.19	9.81
trietilammina	$(CH_3CH_2)_3N$	3.25	10.75
<b>Ammine aromatiche</b>			
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
<b>Ammine aromatiche eterocicliche</b>			
piridina		8.75	5.25
imidazolo		7.05	6.95

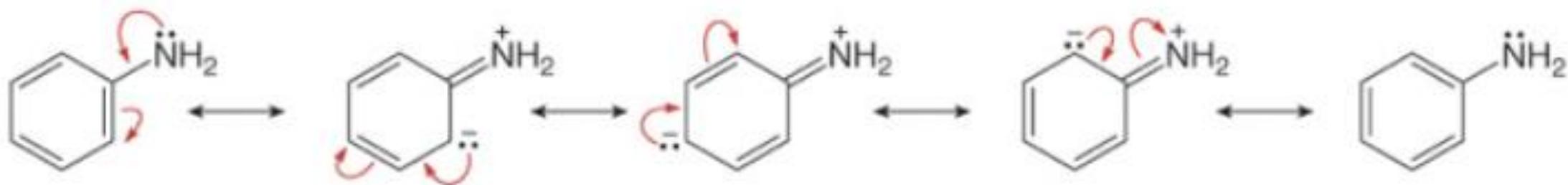
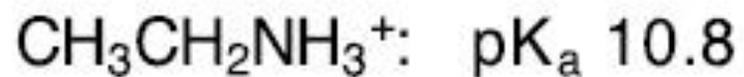
\* Per ciascuna ammina,  $pK_a + pK_b = 14.00$

# Basicità delle ammine

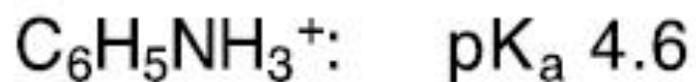
- Le ammine sono leggermente più basiche dell'ammoniaca
- Le ammine aromatiche sono meno basiche delle ammine alifatiche perché il loro doppietto è delocalizzato sull'anello aromatico e quindi meno disponibile per la protonazione



The electron pair is localized on the N atom.



The electron pair is delocalized on the benzene ring.



# Aniline sostituite

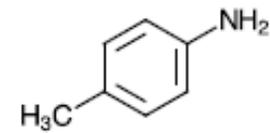
- Sostituenti elettron-donatori (D) aumentano la basicità dell'anilina
- Sostituenti elettron-attrattori (W) diminuiscono la basicità dell'anilina

D
-NH <sub>2</sub>
-OH
-OR
-NHCOR
-R

W	
-X	-CN
-CHO	-SO <sub>3</sub> H
-COR	-NO <sub>2</sub>
-COOR	-NR <sub>3</sub> <sup>+</sup>
-COOH	

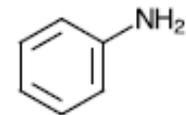
W = electron-withdrawing group

..

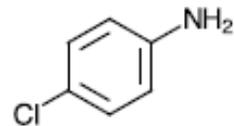


pK<sub>a</sub> (NH<sup>+</sup>)

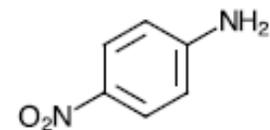
5.1



4.6

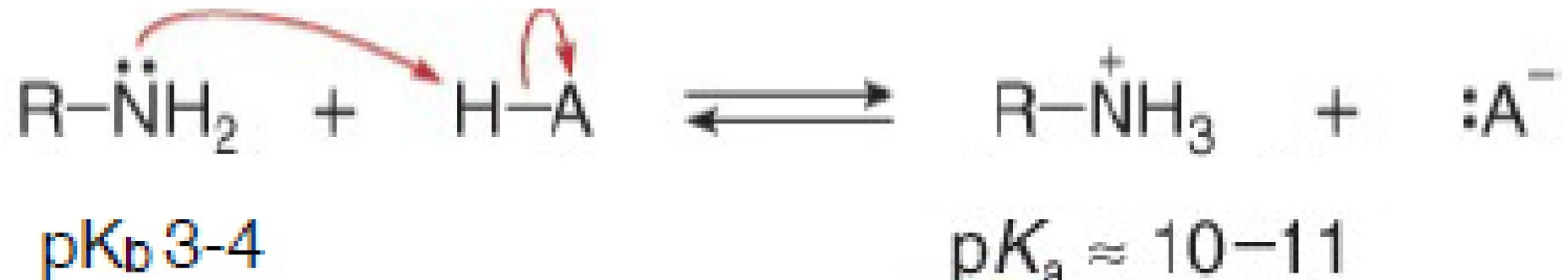


4.2

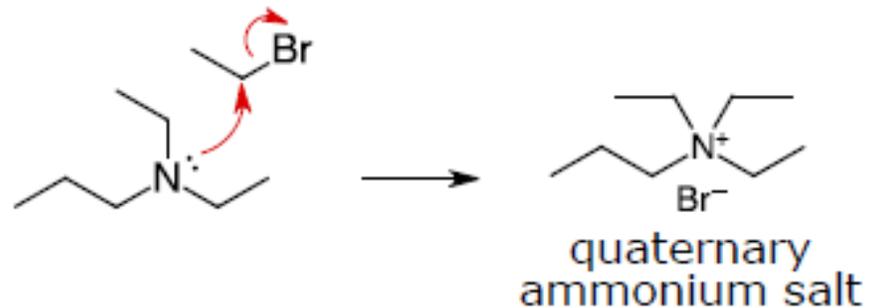
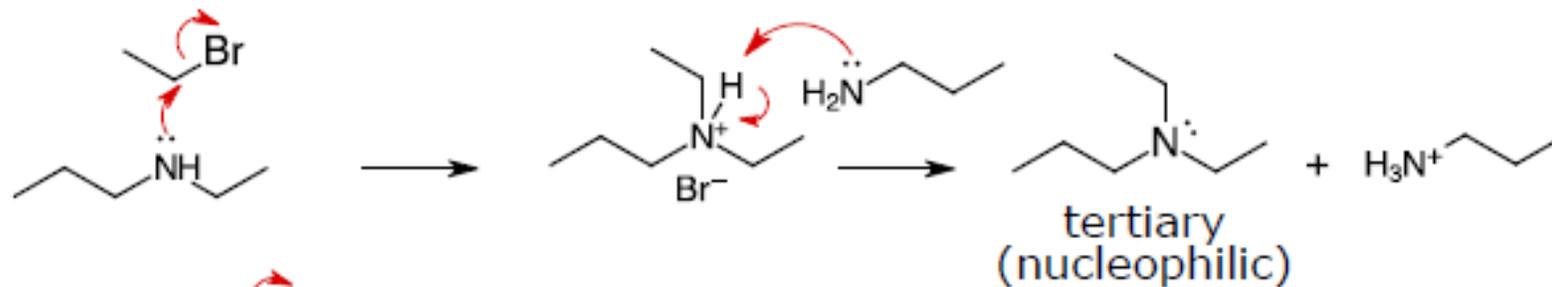
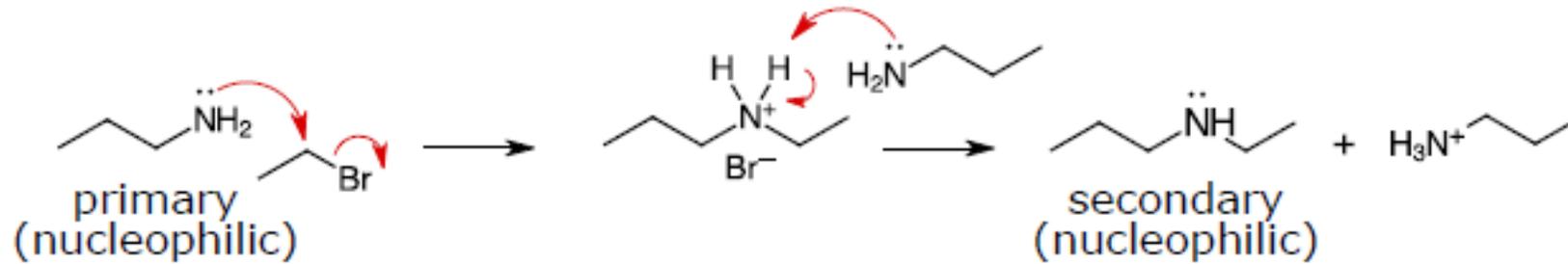


1.0

Le ammine in presenza di un acido si protonano



# Le ammine si comportano da nucleofili



Polialchilazione

si ottiene una miscela di prodotti