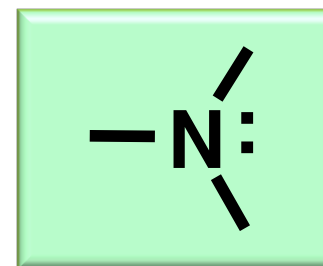


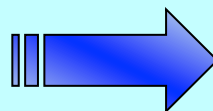
# AMMINE

Caratteristica strutturale delle ammine

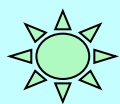


## Caratteristiche Spettrali

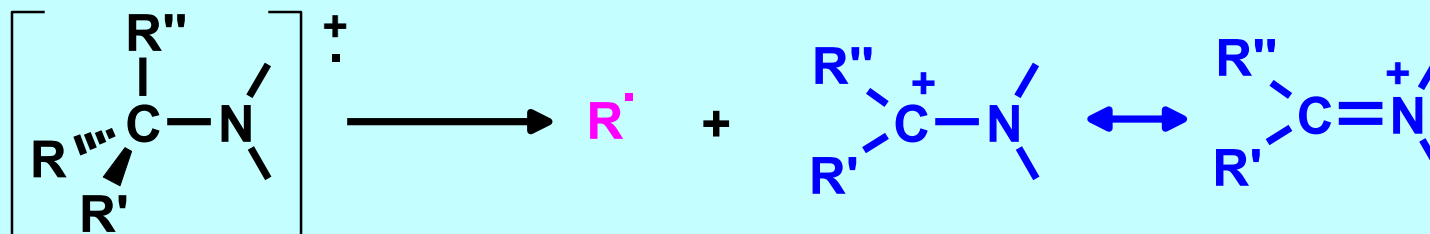
Spettrometria di massa



Lo ione molecolare è quasi sempre presente



La frammentazione più importante avviene tra il C  $\alpha$  all' N ed il C  $\beta$  (carbocatione stabile)



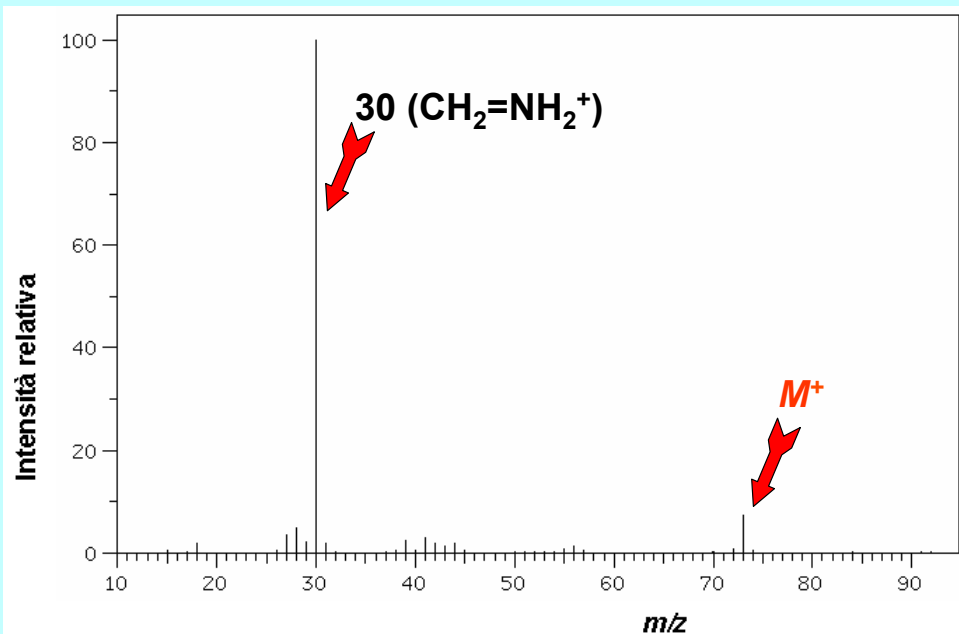
Per le ammine vale la “regola dell’ azoto”

# La regola dell'azoto

E' una regola universale che riguarda sia gli ioni molecolari che i frammenti con una singola carica.

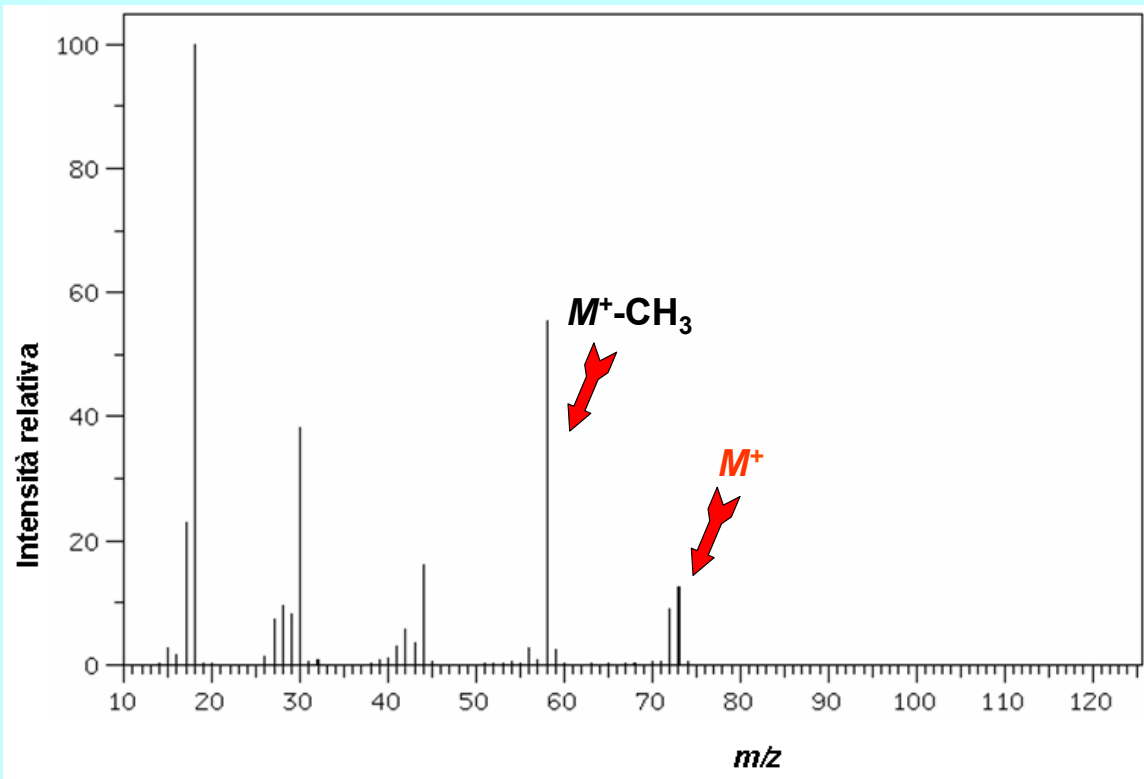
***“tutti gli ioni con numero dispari di elettroni hanno valori  $m/z$  pari, tranne quando contengono un numero dispari di atomi di azoto”***

Questa regola viene dal fatto che l'azoto ha massa atomica pari e valenza dispari.

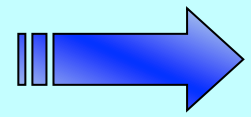


1-butanamina, P.M. 73

# dietilammina, P.M. 73

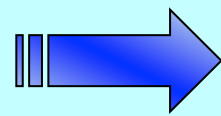


**UV-visibile**



Solo legami  $\sigma$ : le transizioni  $n \rightarrow \sigma^*$  richiedono  $\lambda = 185-195$  nm (lontano UV): fuori dal comune intervallo

**IR**



**stretching N-H** 3500-3300  $cm^{-1}$

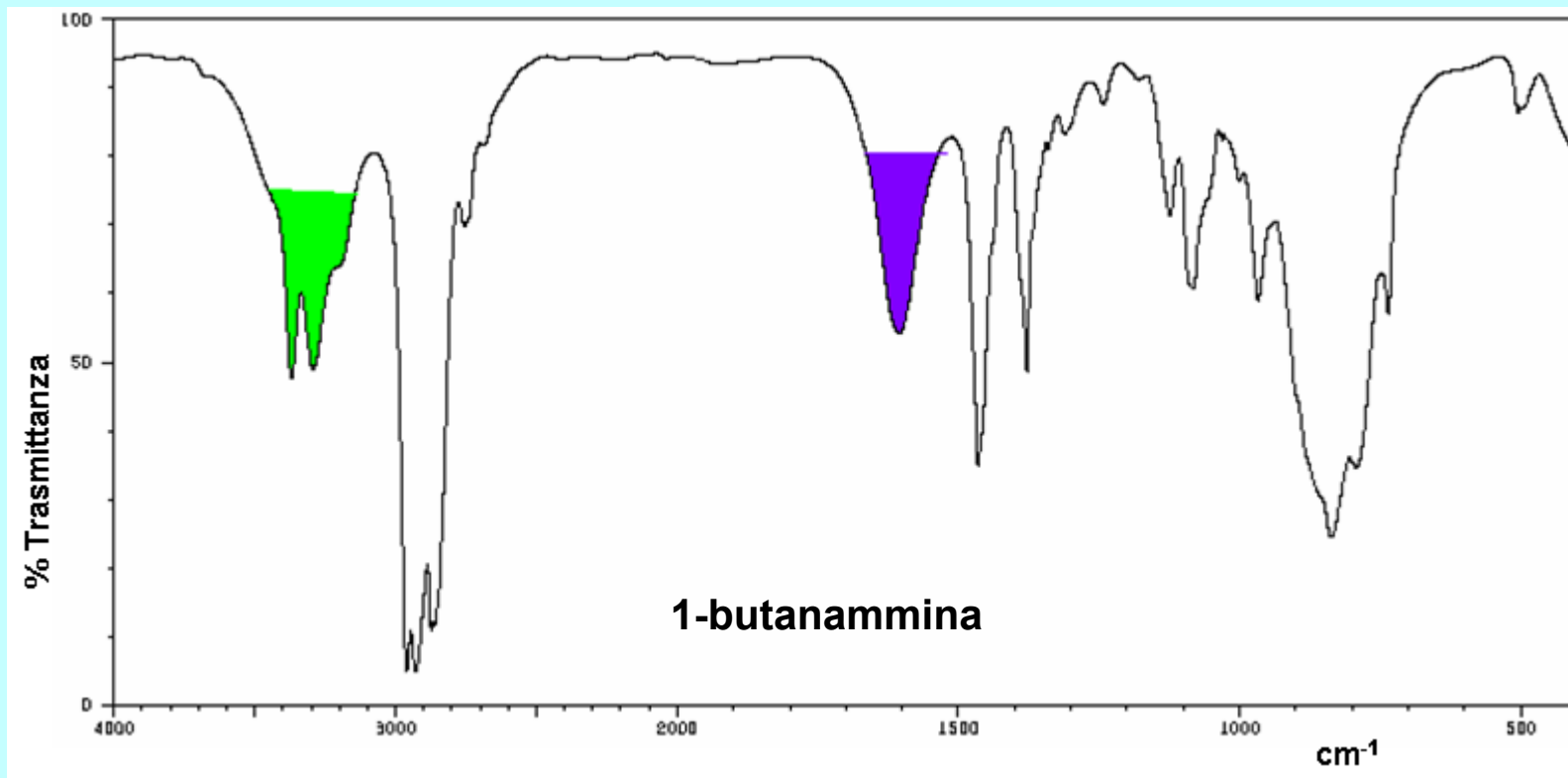
**DUE bande per le ammine primarie; una banda per le ammine secondarie (debole se alifatiche, forte se aromatiche). Le amine terziarie non hanno assorbimento**

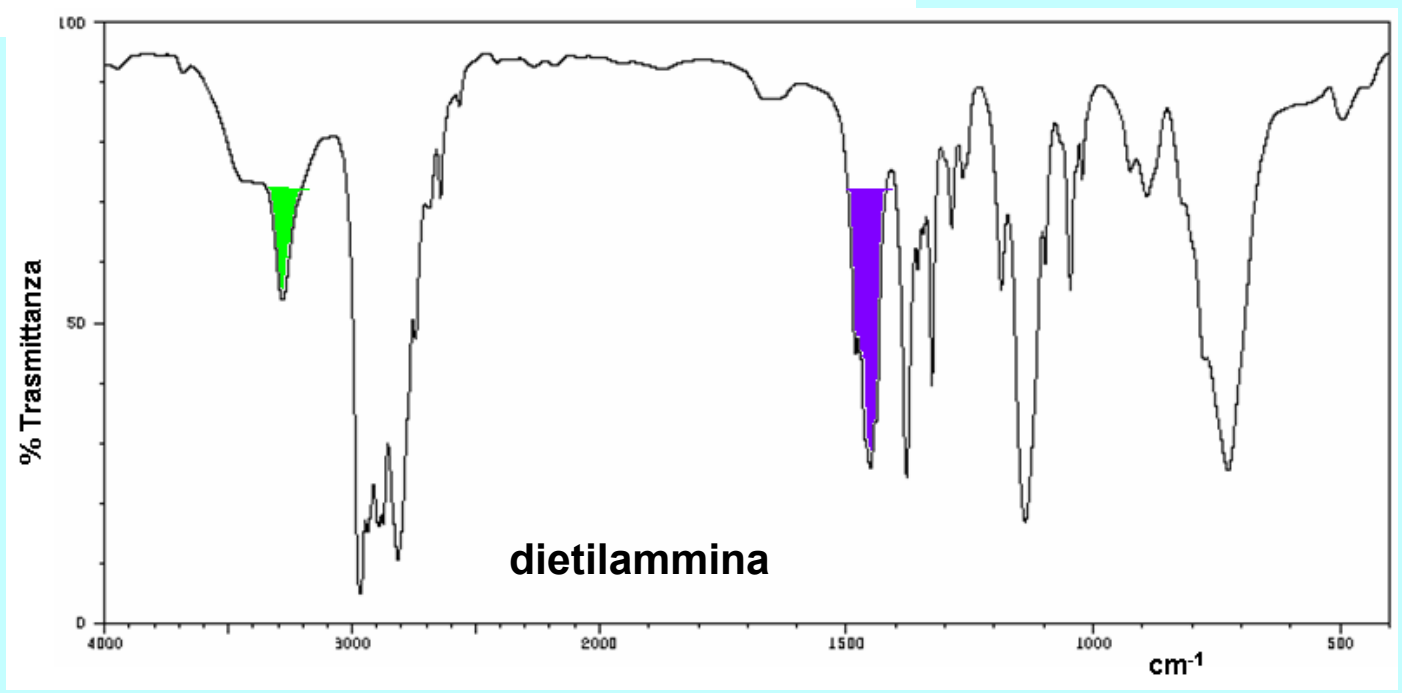
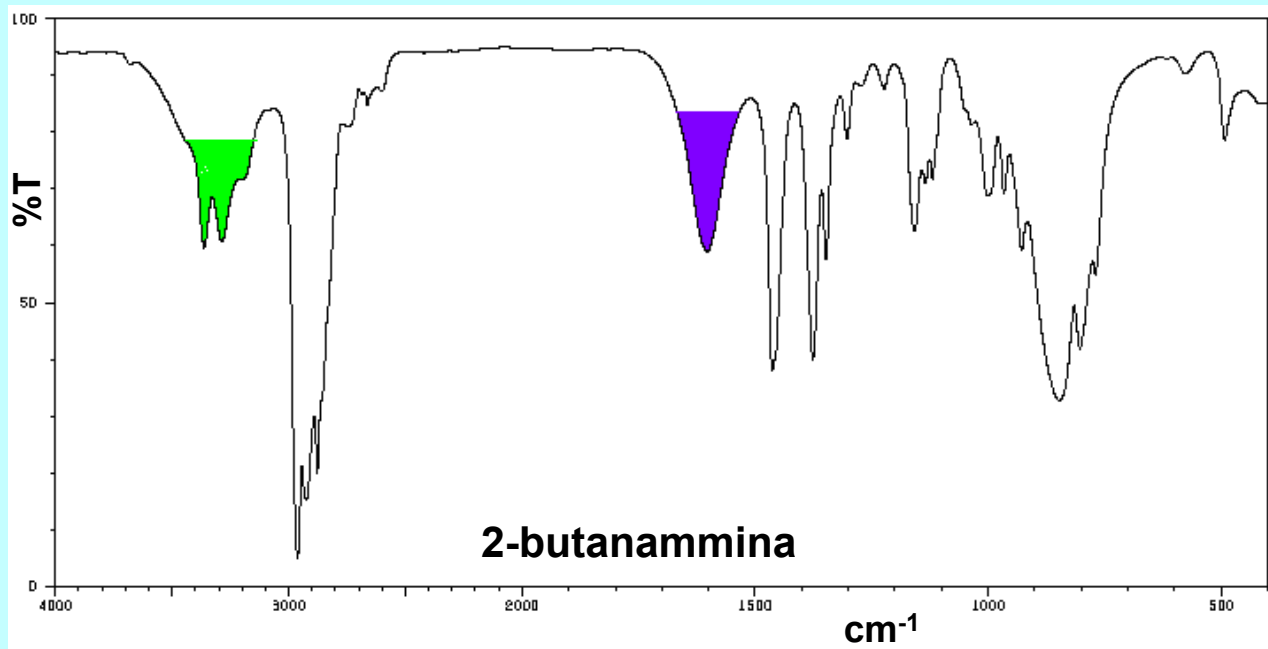
**bending N-H**

nelle ammine primarie, banda larga 1640-1560  $\text{cm}^{-1}$   
nelle ammine secondarie verso 1500  $\text{cm}^{-1}$

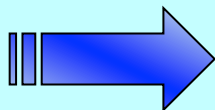
**stretching C-N**

1350-1000  $\text{cm}^{-1}$

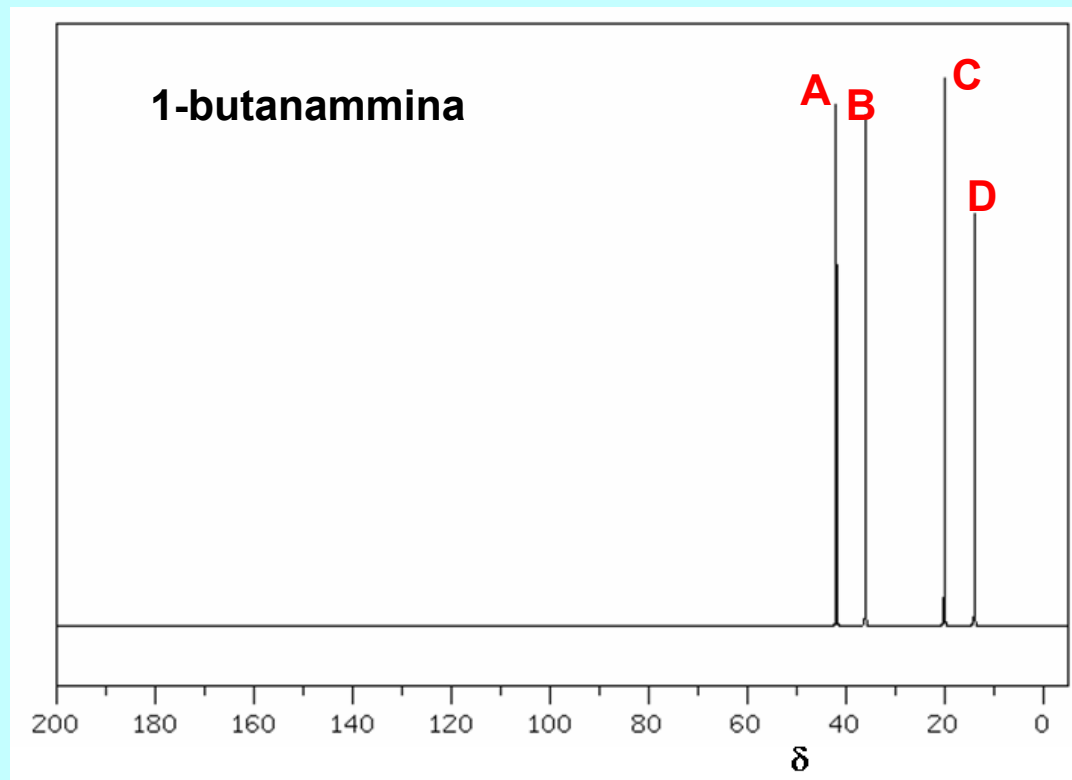
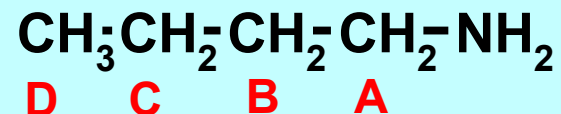




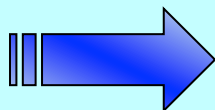
# $^{13}\text{C}$ NMR



L'effetto -I dell' N diminuisce la densità elettronica attorno al nucleo del  $^{13}\text{C}$ : deschermato

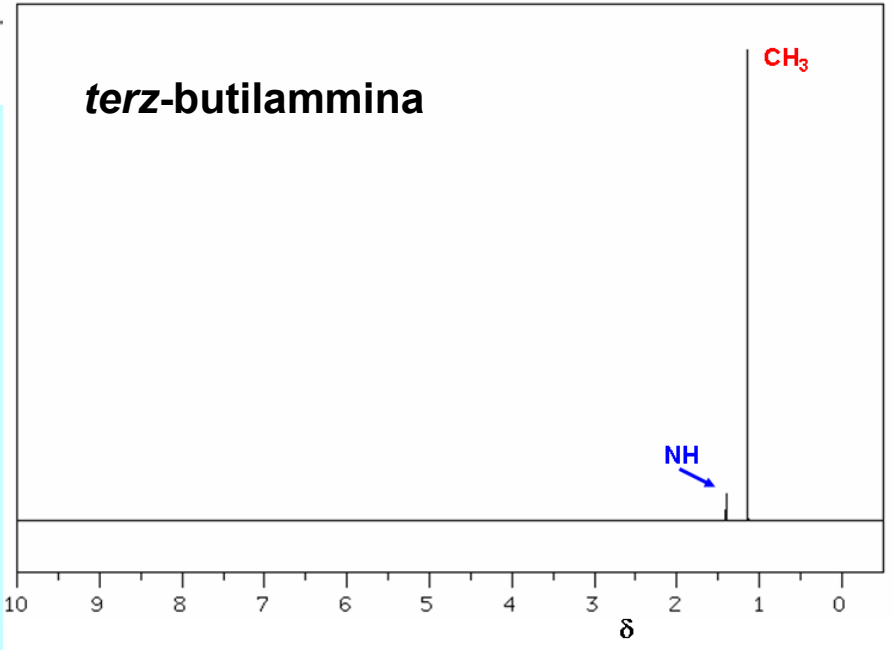
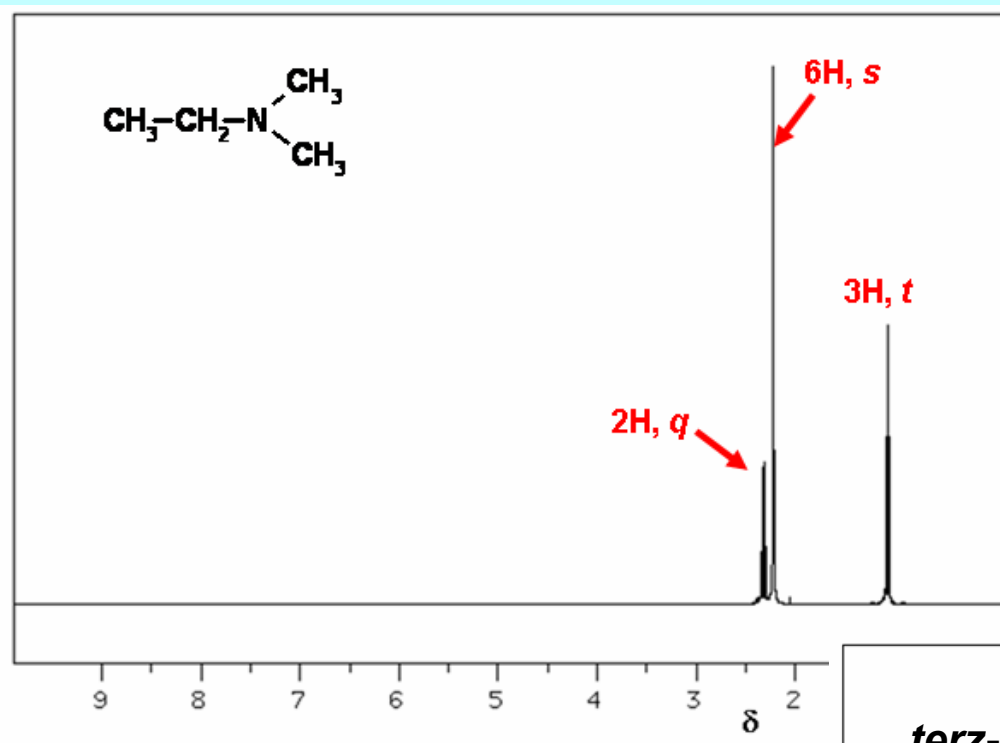


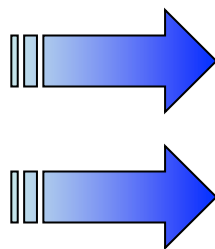
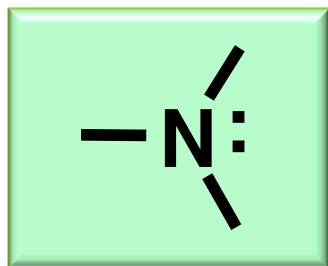
# $^1\text{H}$ NMR



L'effetto -I dell' N diminuisce la densità elettronica attorno al nucleo del  $^1\text{H}$ : deschermato a 2.5-3  $\delta$

Anche l' H sull' N è mobile: scambia abbastanza rapidamente da non dare accoppiamento con nuclei adiacenti





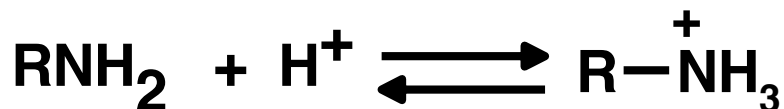
atomo basico, atomo nucleofilo

cattivo gruppo uscente, *anche in seguito a protonazione*



### 1. N come atomo basico o nucleofilo

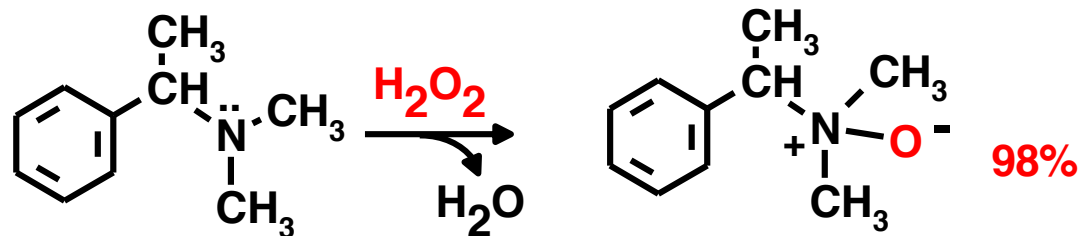
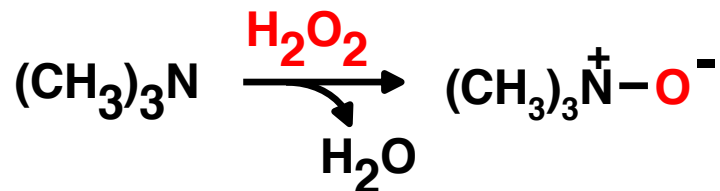
con acidi



con O come elettrofilo

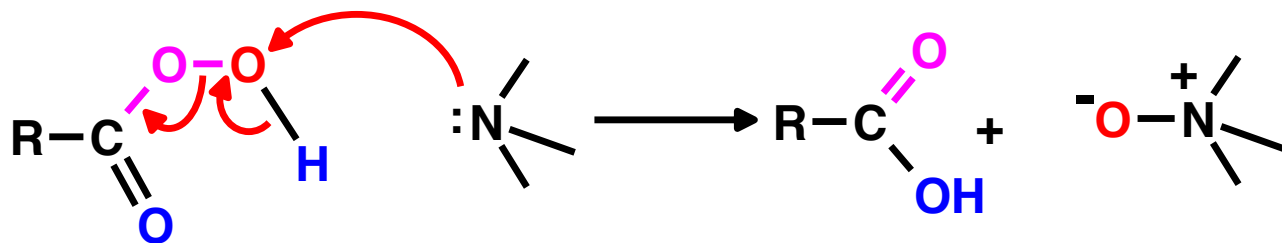


SOLO con ammine terziarie



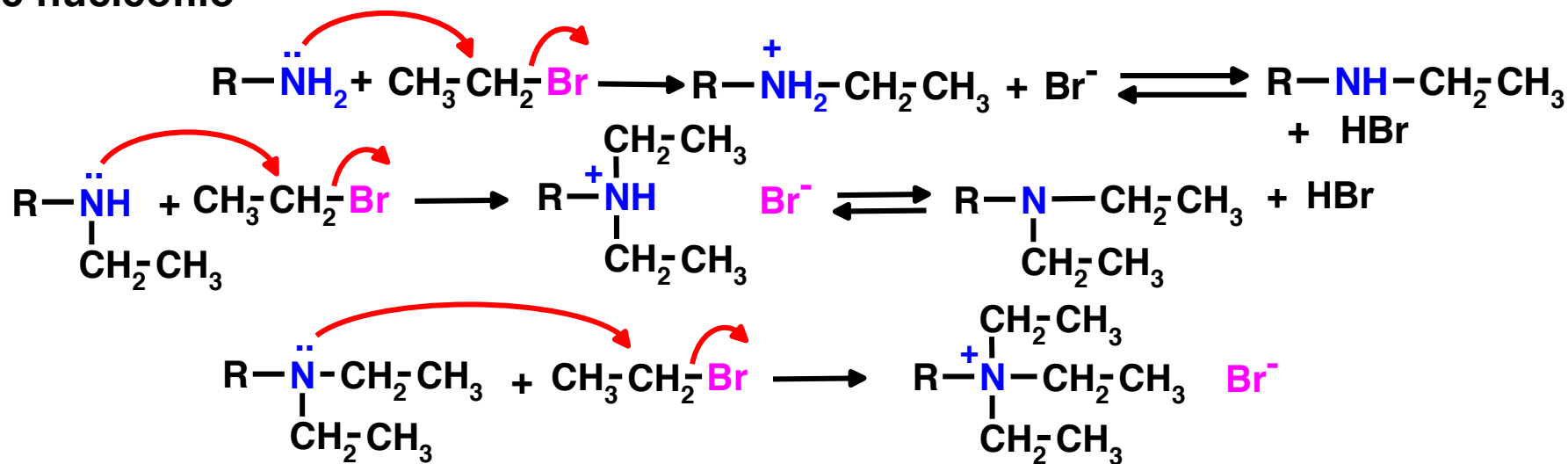


invece di  $\text{H}_2\text{O}_2$  si possono usare peracidi  $\rightarrow \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{OH}$



**con alogenuri alchilici**

La reazione dà miscele di prodotti, perché anche il prodotto della sostituzione è nucleofilo

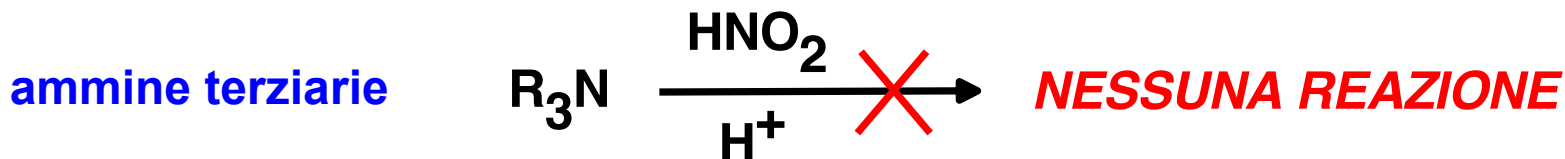


Quando l'alchilazione dell'ammina si esegue fino al sale di ammonio si parla di **METILAZIONE ESAURIENTE**

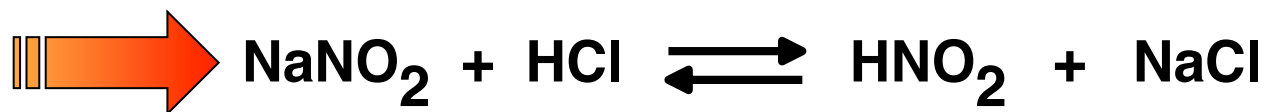


La reazione con HNO<sub>2</sub> è la reazione più caratteristica delle ammine, che permette di distinguere tra ammine primarie, secondarie e terziarie.

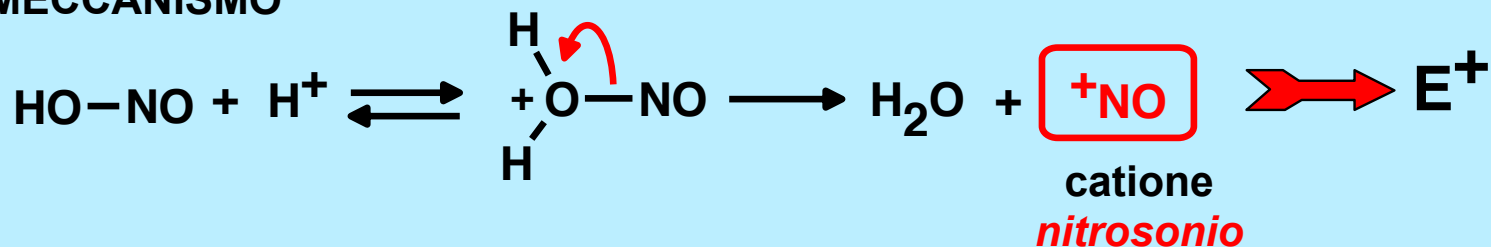
**Fatti sperimentali:**



L'acido nitroso si genera *in situ*

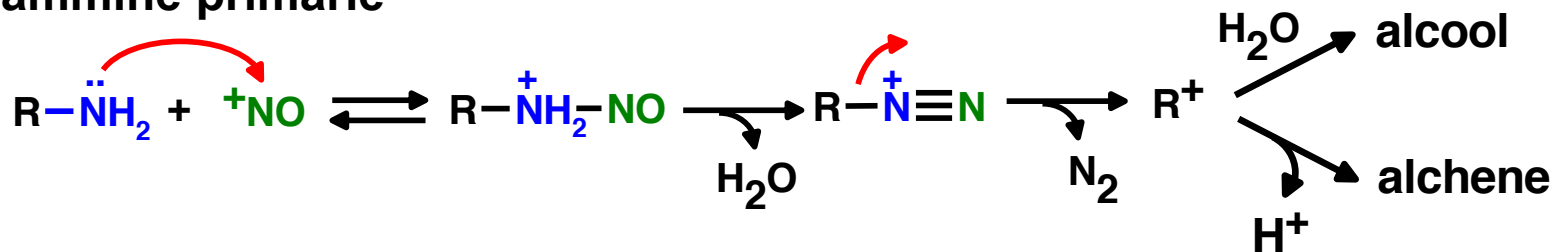


## MECCANISMO

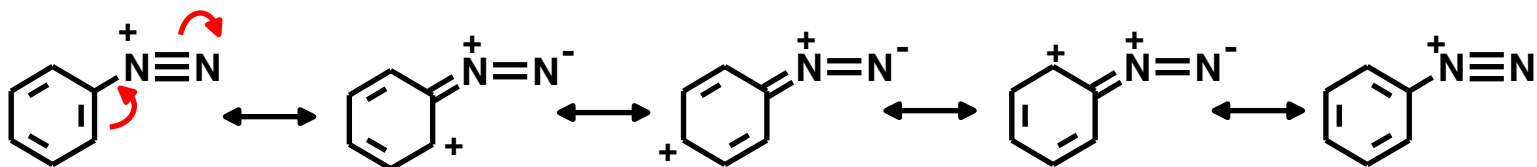
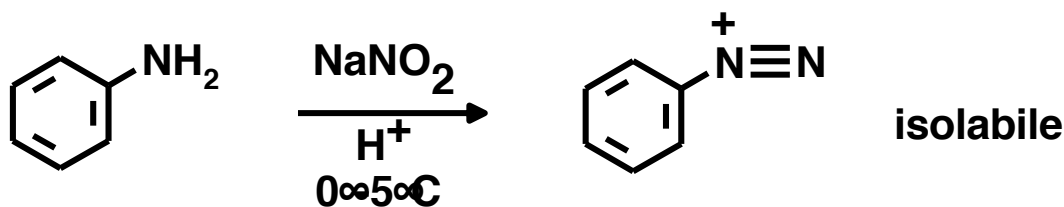


in comune ai diversi  
tipi di ammina

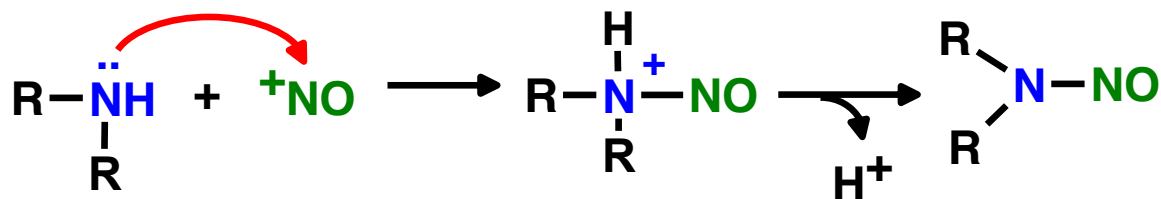
## ammine primarie



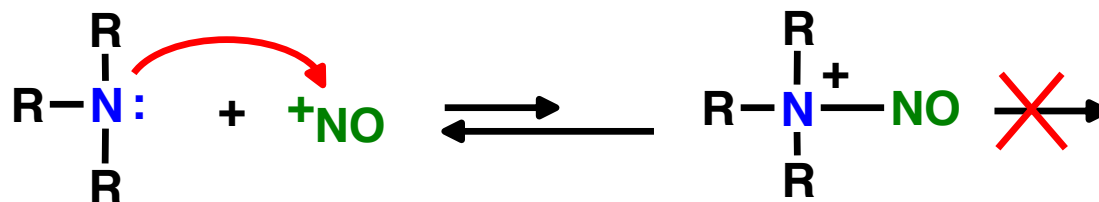
i sali di diazonio si possono isolare solo con le ammine aromatiche



## ammine secondarie

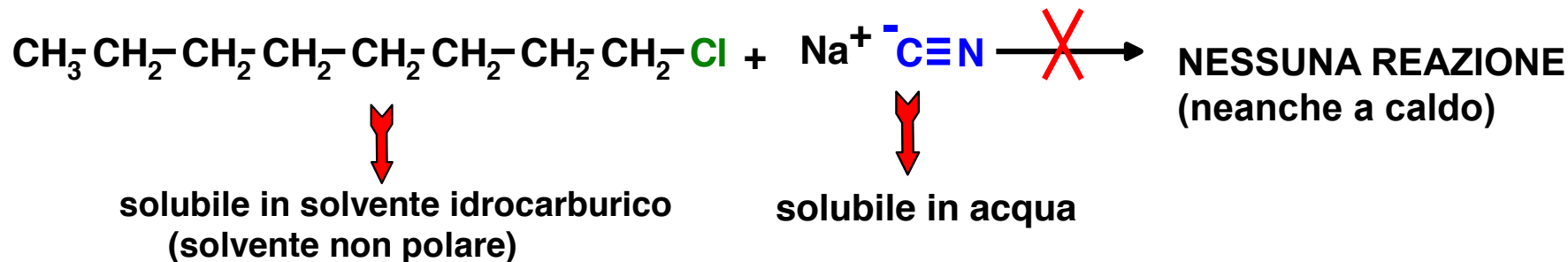


## ammine terziarie

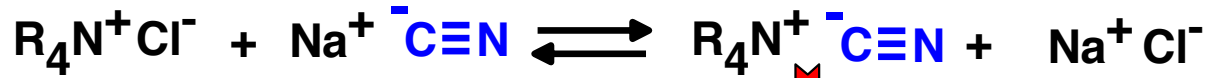


i sali di ammonio quaternari possono essere usati come

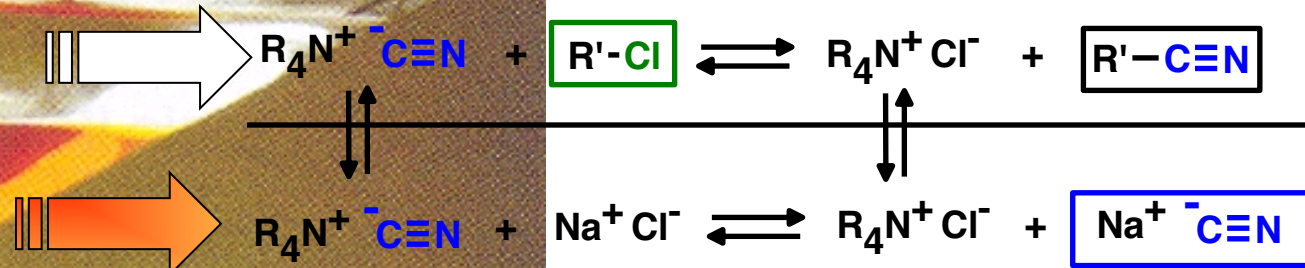
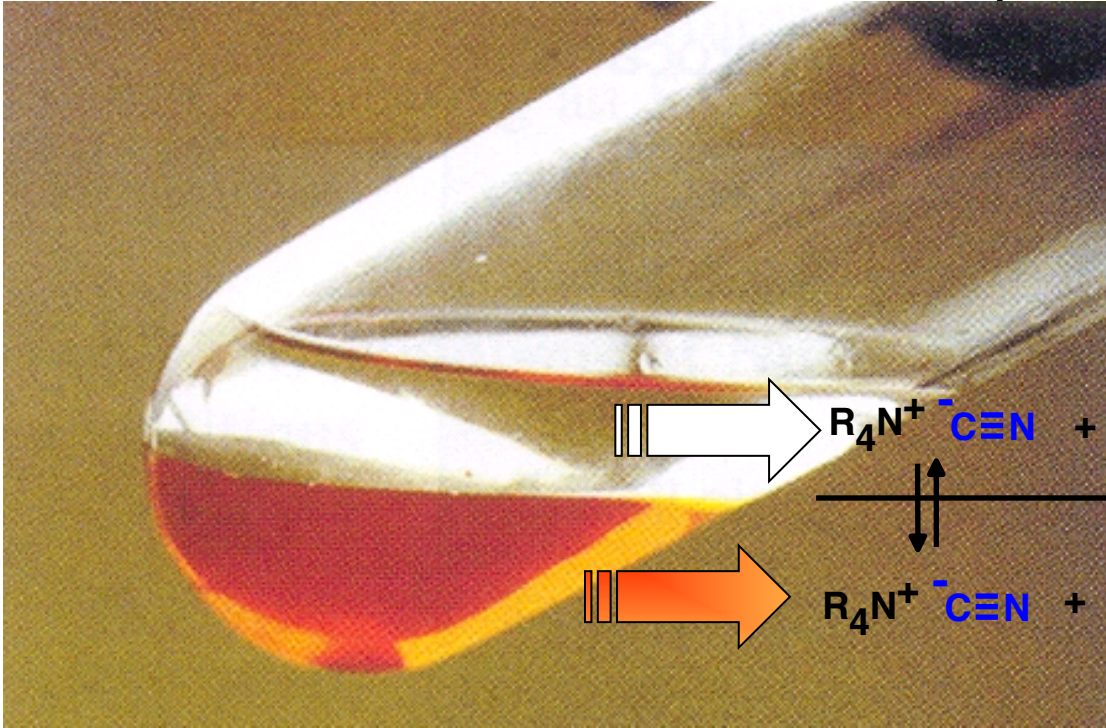
***catalizzatori di trasferimento di fase***



$R_4N^+$   $\rightarrow$  se R contiene almeno 4 atomi di C, è solubile sia in acqua (per l'N positivo) che in solventi non polari (per R)



$\downarrow$   
porta in fase organica il reagente nucleofilo



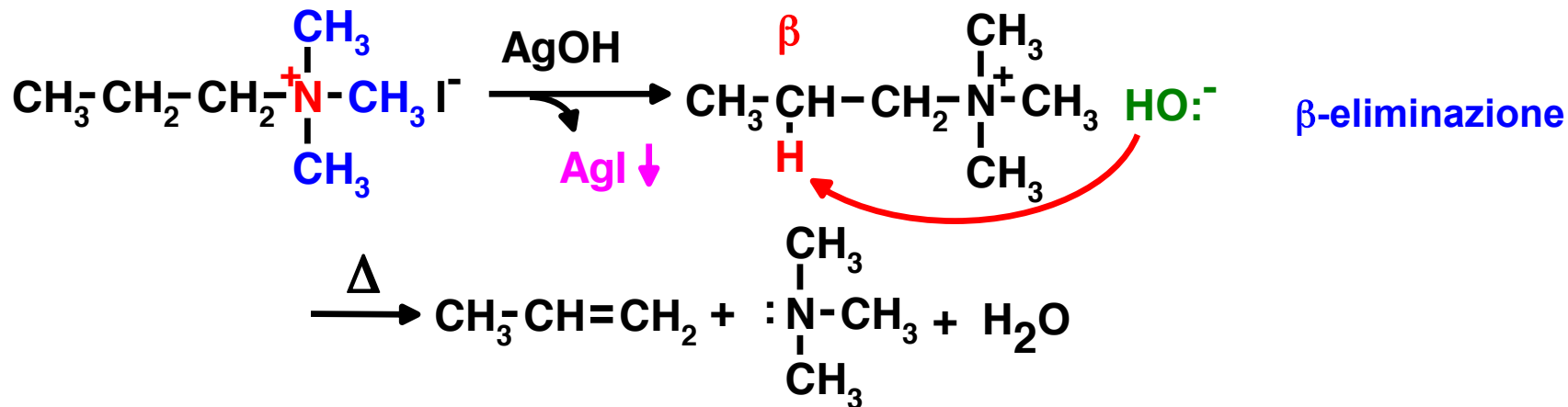
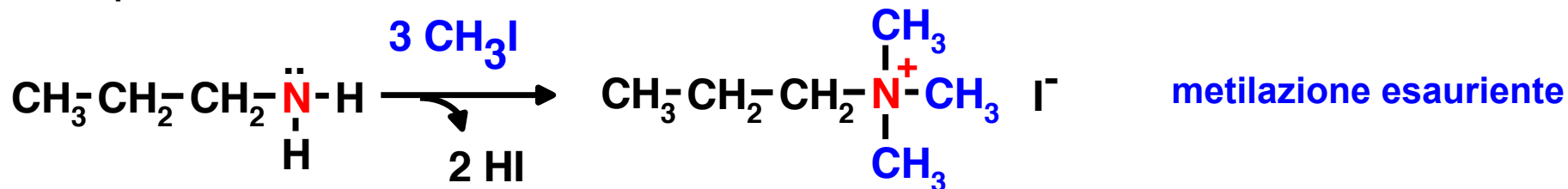
$\rightarrow R_3N^+$   $\rightarrow$  pessimo gruppo uscente

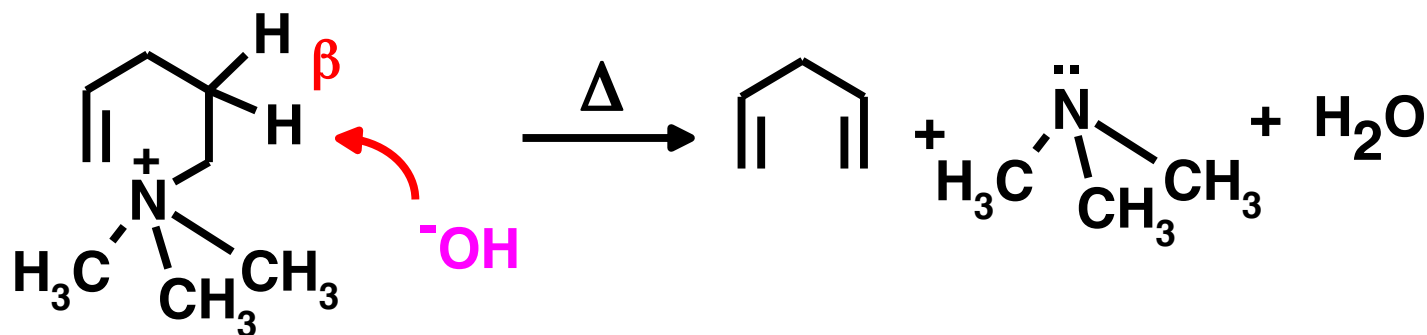
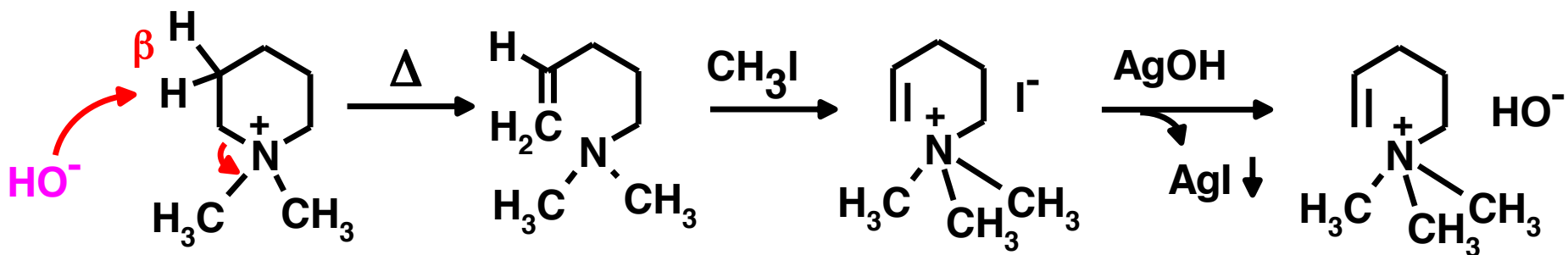
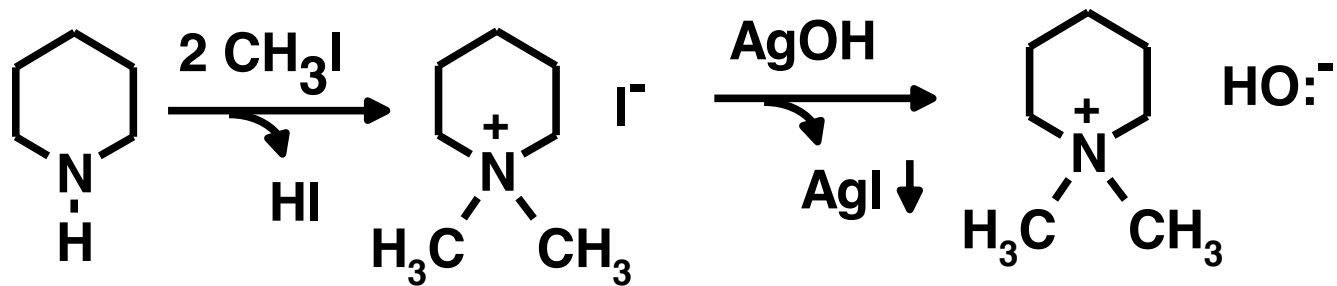
# Metilazione esauriente - Degradazione di Hofmann

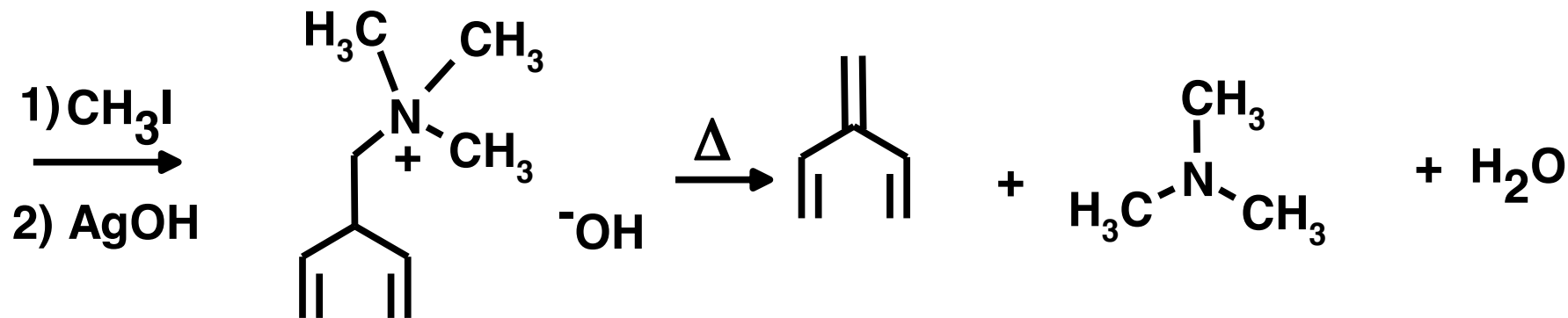
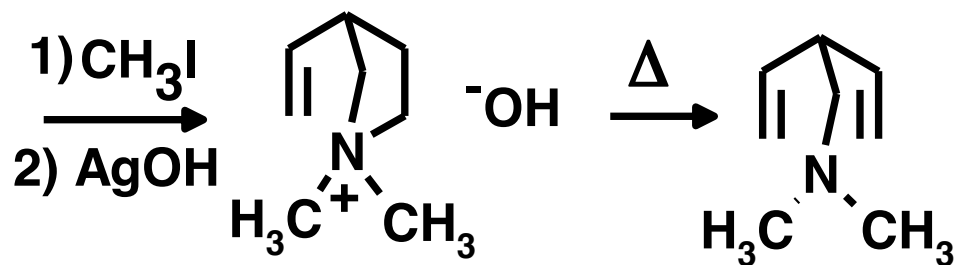
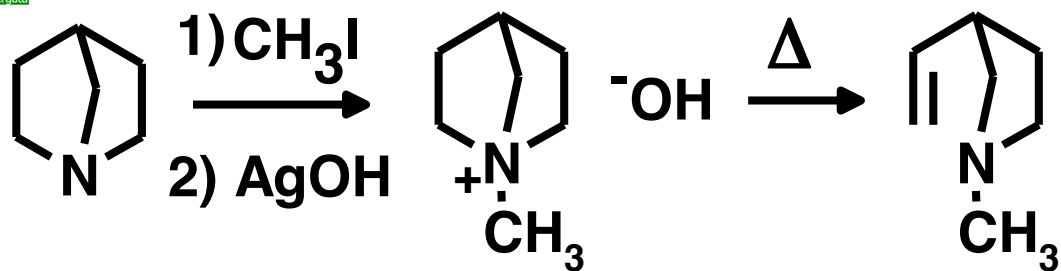


Reazione utilizzata per la determinazione della struttura di ammine

Esempi:

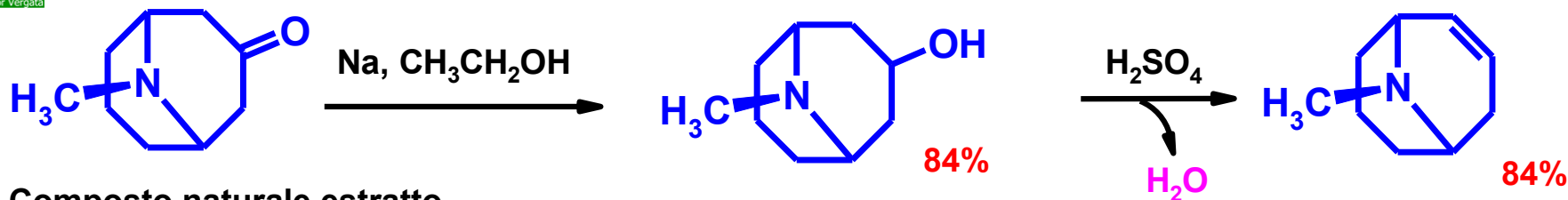




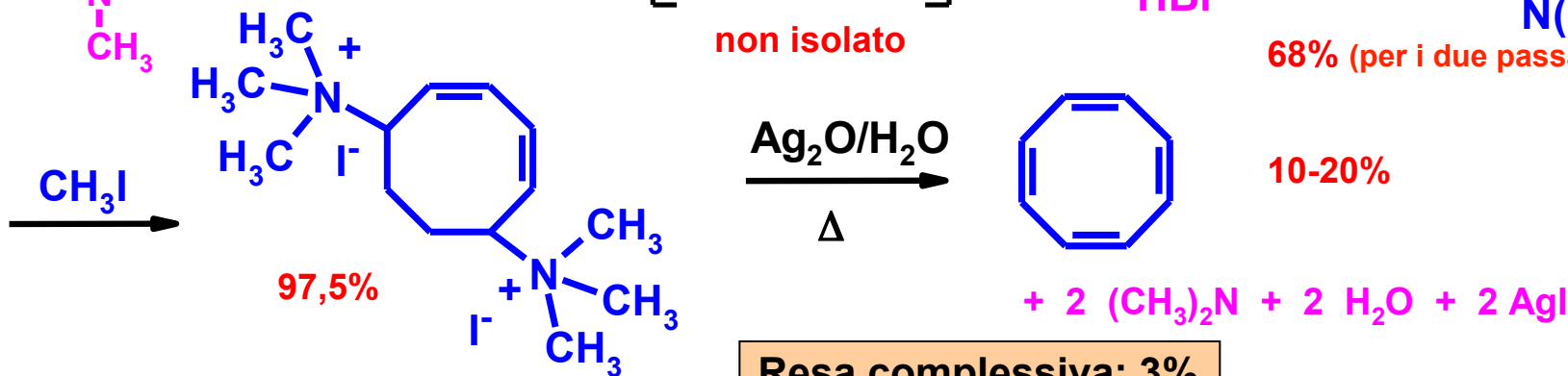
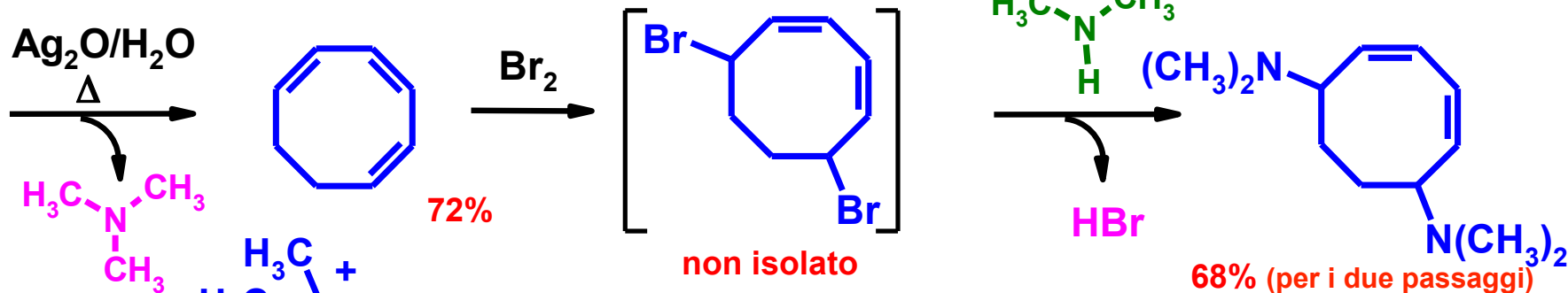
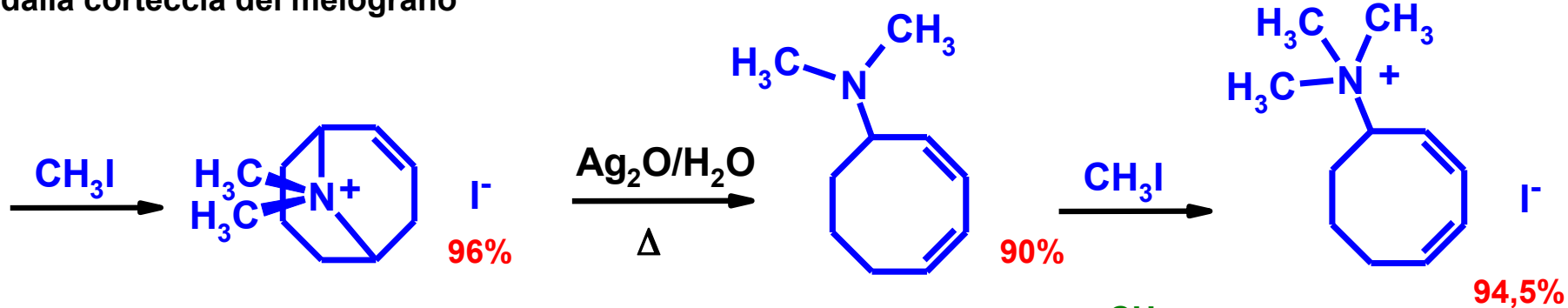




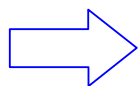
# Applicazione: sintesi del cicloottatetraene (Wilstätter)



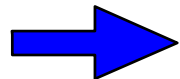
Composto naturale estratto dalla corteccia del melograno



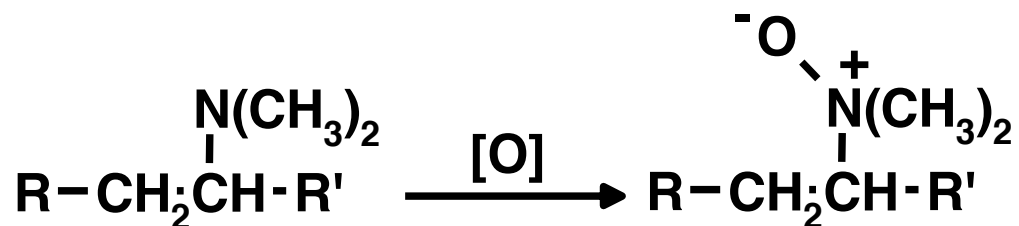
Resa complessiva: 3%



Gli N-ossidi delle ammine terziarie danno  $\beta$ -eliminazione

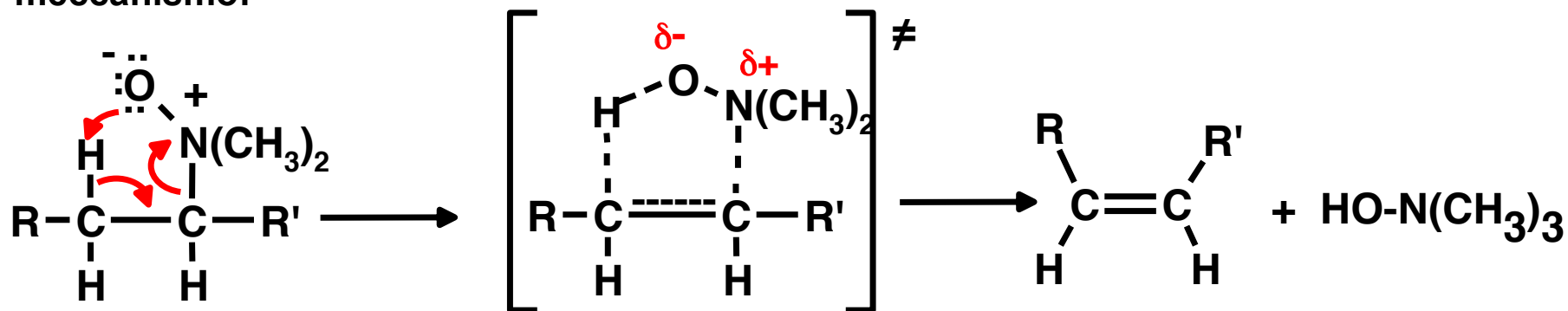


## Eliminazione di Cope

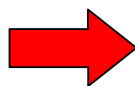


([O] = reagente ossidante, per esempio  $\text{H}_2\text{O}_2$ )

meccanismo:



reazione stereospecifica



eliminazione *sin*