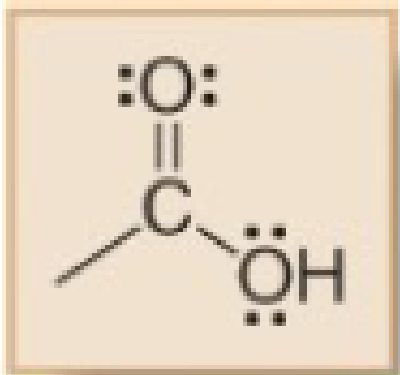
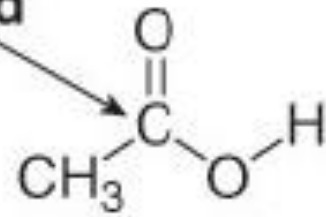


# Acidi Carbossilici e Derivati

# Gruppo carbossilico

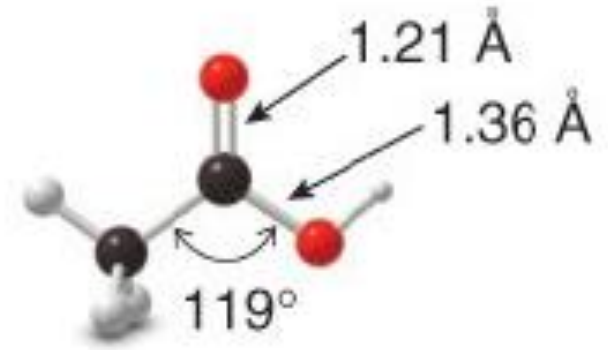


$sp^2$  hybridized



acetic acid

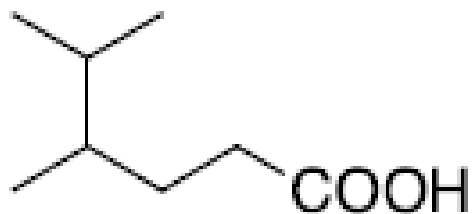
=



**TABELLA 14.1 Alcuni acidi carbossilici alifatici e i loro nomi comuni**

Struttura	Nome IUPAC	Nome comune	Derivazione
HCOOH	acido metanoico	acido formico	Latino: <i>formica</i> , formica
CH <sub>3</sub> COOH	acido etanoico	acido acetico	Latino: <i>acetum</i> , aceto
CH <sub>3</sub> CH <sub>2</sub> COOH	acido propanoico	acido propionico	Greco: <i>propion</i> , primo grasso
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COOH	acido butanoico	acido butirrico	Latino: <i>butyrum</i> , burro
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COOH	acido pentanoico	acido valerianico	Latino: <i>valere</i> , esser forte
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> COOH	acido esanoico	acido caproico	Latino: <i>caper</i> , capra
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> COOH	acido ottanoico	acido caprilico	Latino: <i>caper</i> , capra
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOH	acido decanoico	acido caprico	Latino: <i>caper</i> , capra
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> COOH	acido dodecanoico	acido laurico	Latino: <i>laurus</i> , lauro
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>12</sub> COOH	acido tetradecanoico	acido miristico	Greco: <i>myristikos</i> , fragrante
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOH	acido esadecanoico	acido palmitico	Latino: <i>palma</i> , albero di palma
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> COOH	acido ottadecanoico	acido stearico	Greco: <i>stear</i> , grasso solido
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>18</sub> COOH	acido eicosanoico	acido arachidico	Greco: <i>arachis</i> , arachide

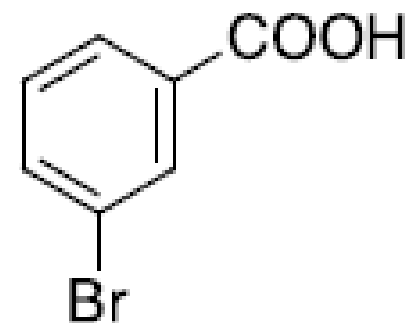
# Nomenclatura degli acidi carbossilici



Acido 4,5-dimetilesanoico

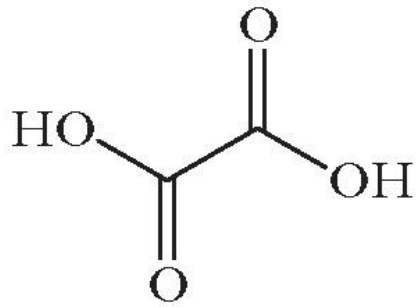


Acido 3-pentenoico

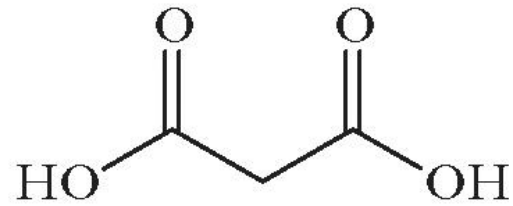


Acido 3-bromobenzoico

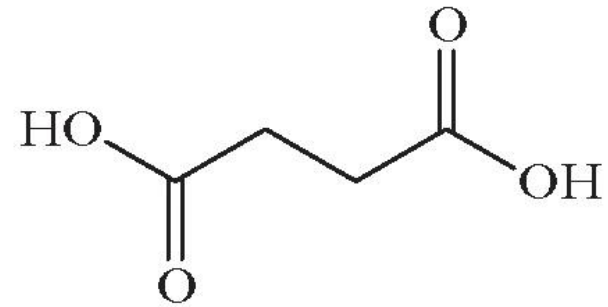
# Acidi dicarbossilici



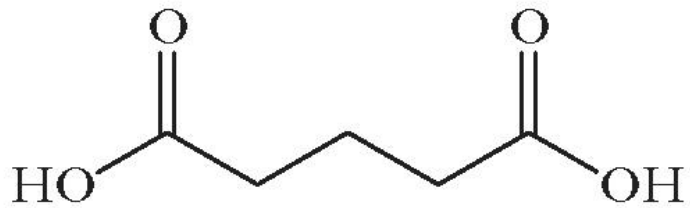
Acido etandioico  
(acido ossalico)



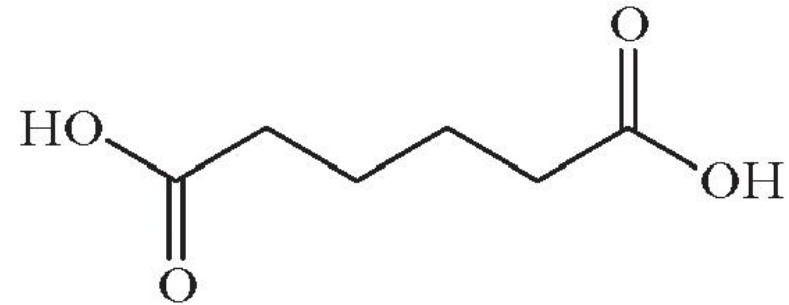
Acido propandioico  
(acido malonico)



Acido butandioico  
(acido succinico)



Acido pentandioico  
(acido glutarico)



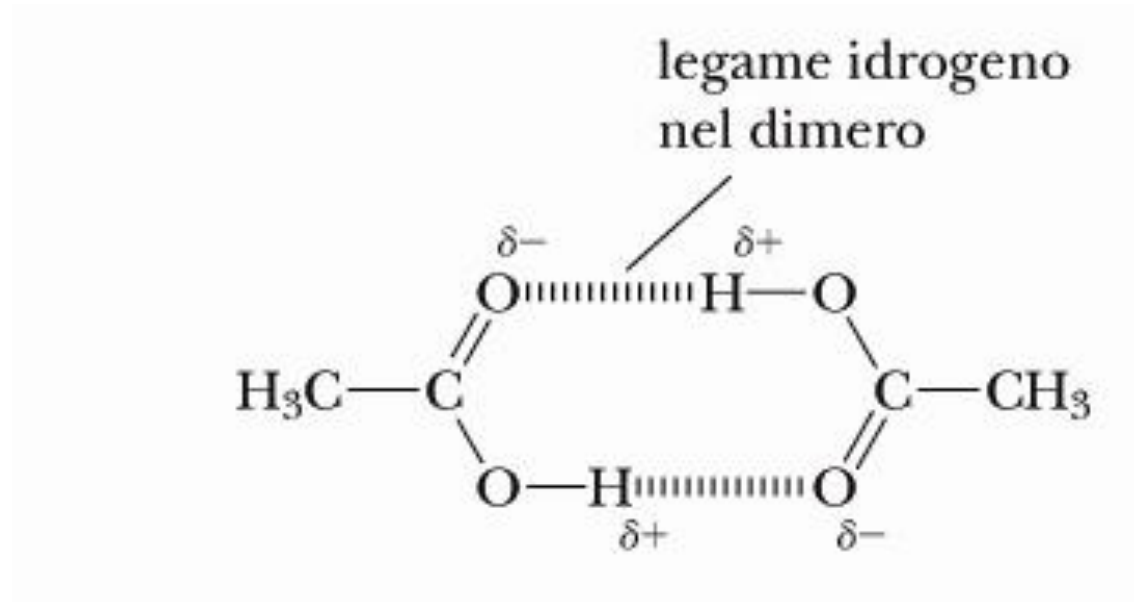
Acido esandioico  
(acido adipico)

# Proprietà fisiche degli acidi carbossilici

**TABELLA 14.2** Punti di ebollizione e solubilità in acqua di alcuni acidi carbossilici, alcoli e aldeidi di peso molecolare paragonabile

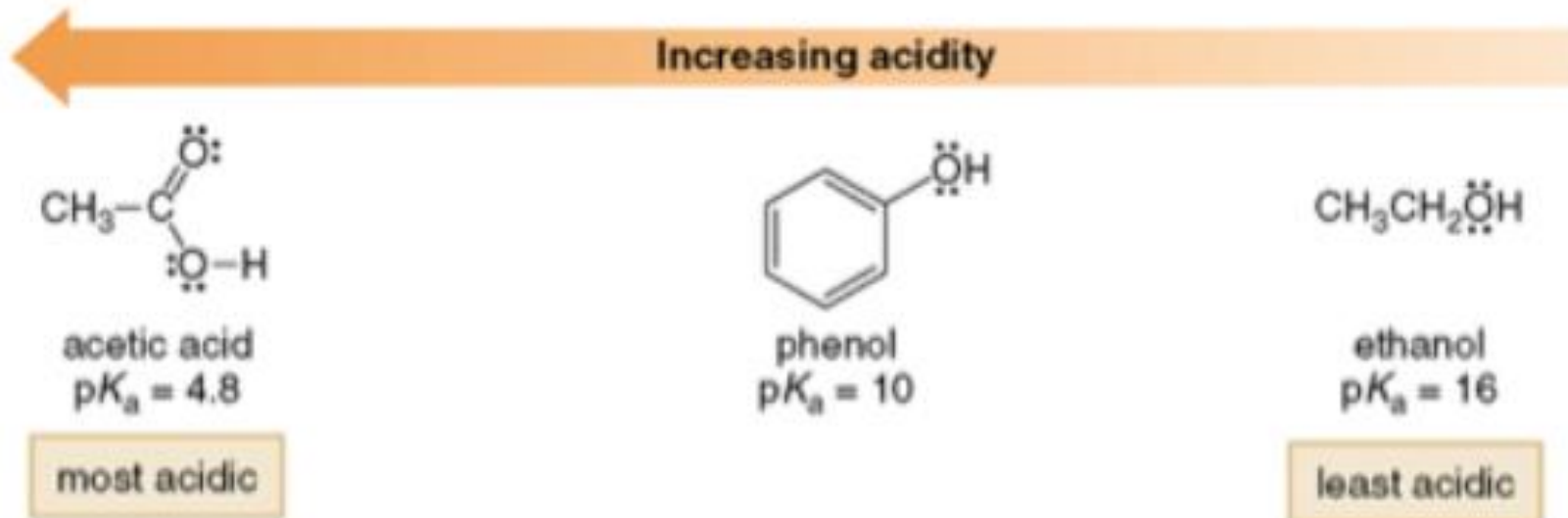
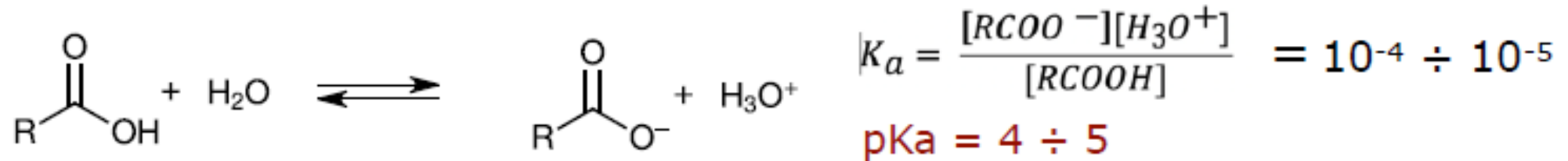
Struttura	Nome	Peso molecolare	Punto di ebollizione(°C)	Solubilità (g/100 mL H <sub>2</sub> O)
CH <sub>3</sub> COOH	acido acetico	60.5	118	infinita
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	1-propanolo	60.1	97	infinita
CH <sub>3</sub> CH <sub>2</sub> CHO	propanale	58.1	48	16
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COOH	acido butanoico	88.1	163	infinita
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub> OH	1-pentanololo	88.1	137	2.3
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CHO	pentanale	86.1	103	bassa
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> COOH	acido esanoico	116.2	205	1.0
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH <sub>2</sub> OH	1-eptanololo	116.2	176	0.2
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CHO	eptanale	114.1	153	0.1

# Proprietà fisiche



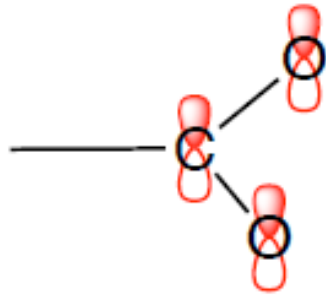
Gli acidi carbossilici si associano in dimeri tramite legami idrogeno intermolecolari

# Acidità degli acidi carbossilici

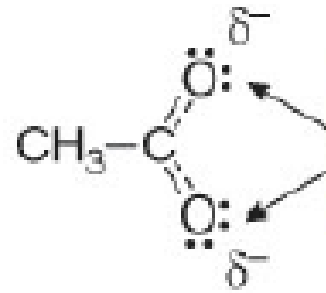
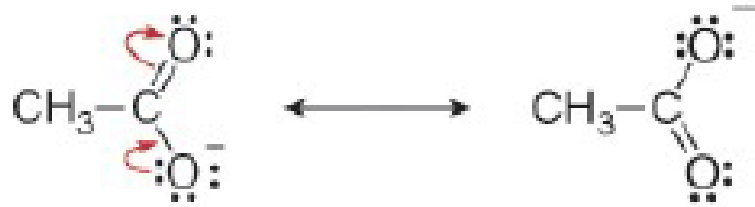




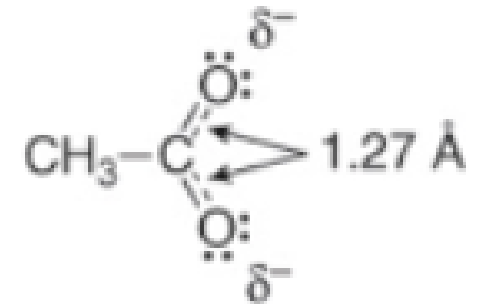
# Struttura dell'anione carbossilato



4 elettroni  $\pi$  delocalizzati in 3 orbitali 2p

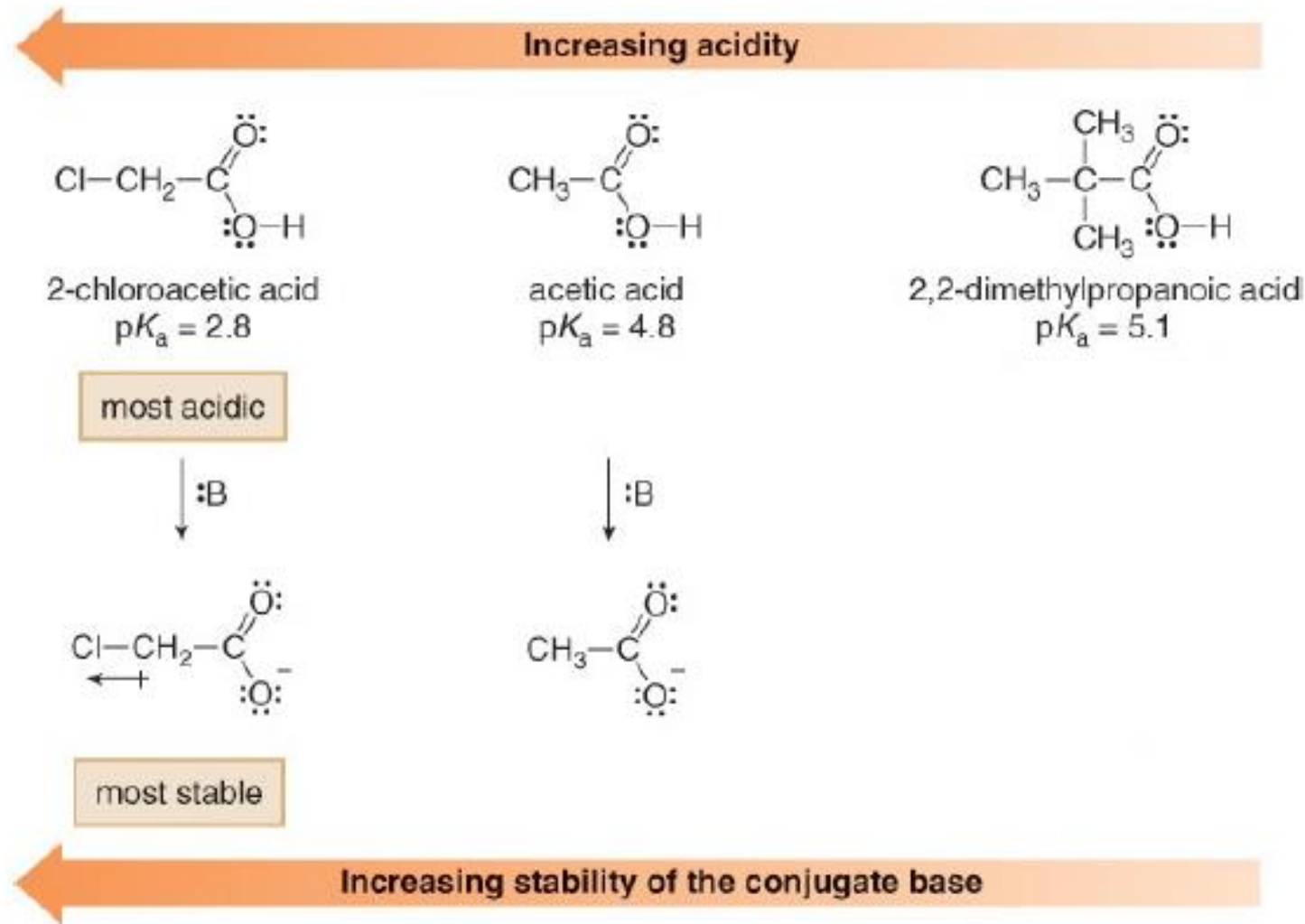


La carica negativa è delocalizzata sui due ossigeni



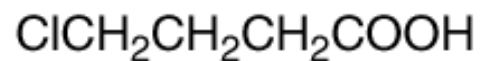
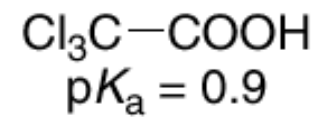
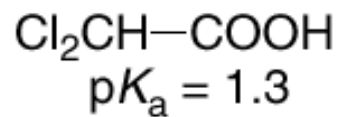
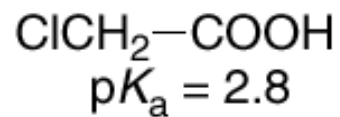
Ibrido di risonanza

# Acidi carbossilici sostituiti

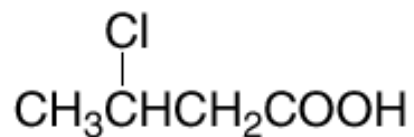


Atomi elettronegativi stabilizzano l'anione carbossilato e di conseguenza l'acidità dell'acido aumenta

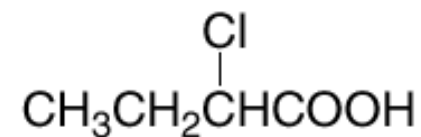
# Acidi carbossilici sostituiti



4-chlorobutanoic acid  
 $pK_a = 4.5$

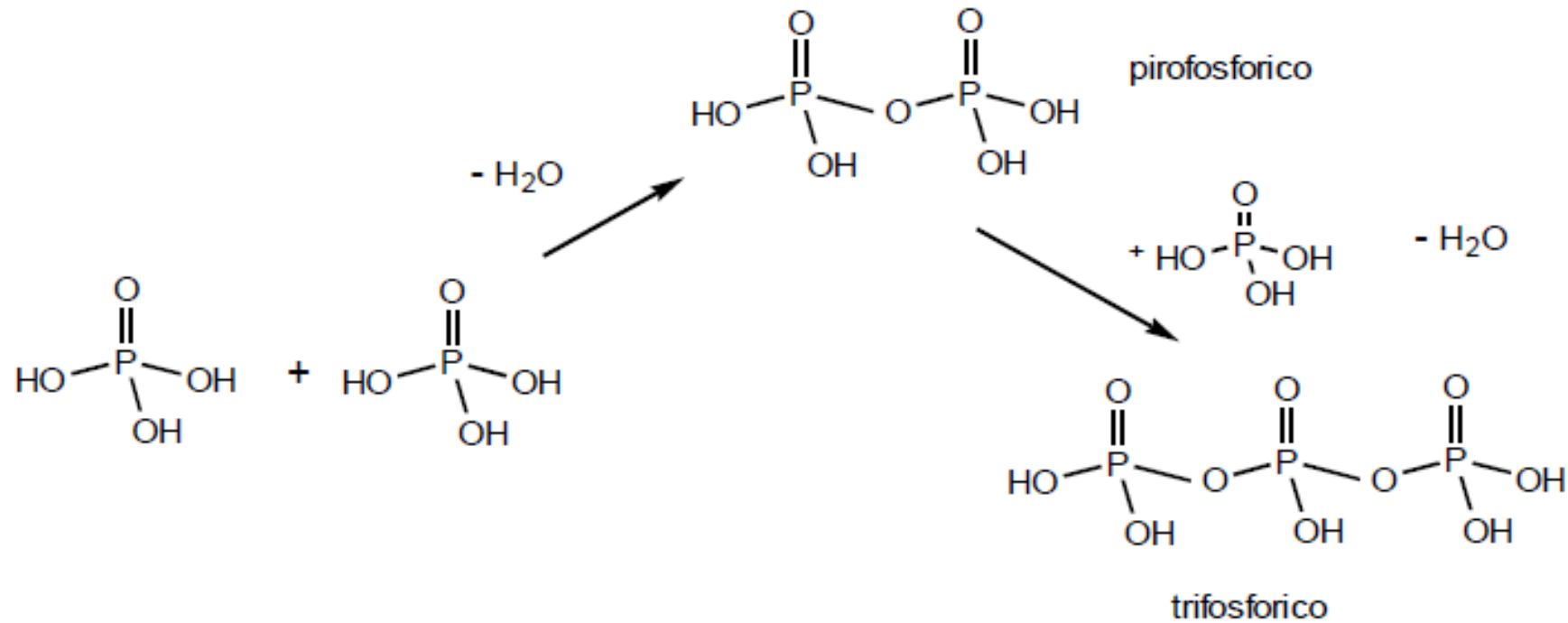


3-chlorobutanoic acid  
 $pK_a = 4.1$



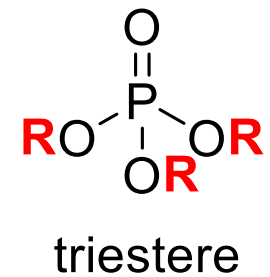
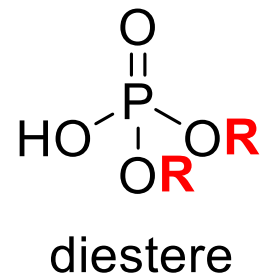
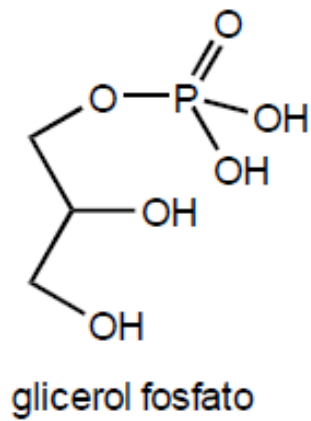
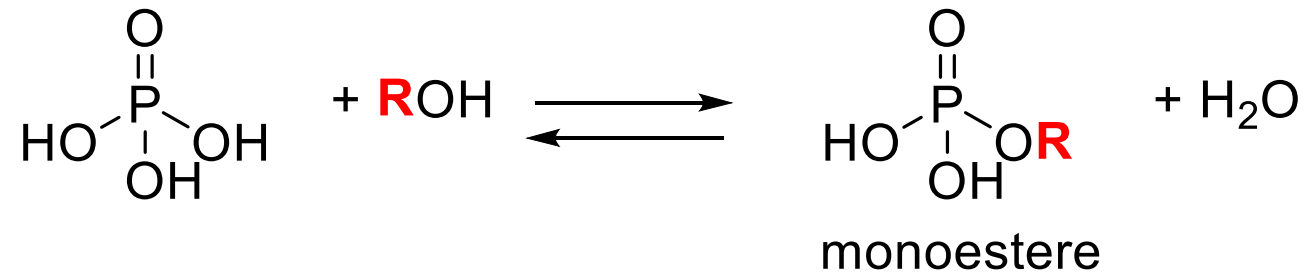
2-chlorobutanoic acid  
 $pK_a = 2.9$

# Esteri e anidridi dell'acido fosforico $\text{H}_3\text{PO}_4$



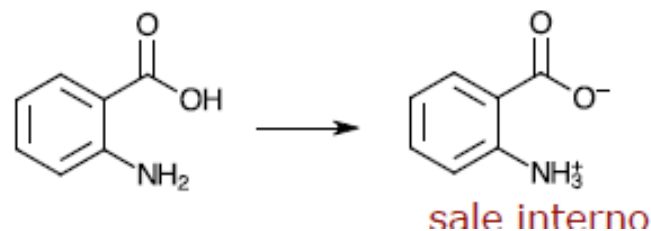
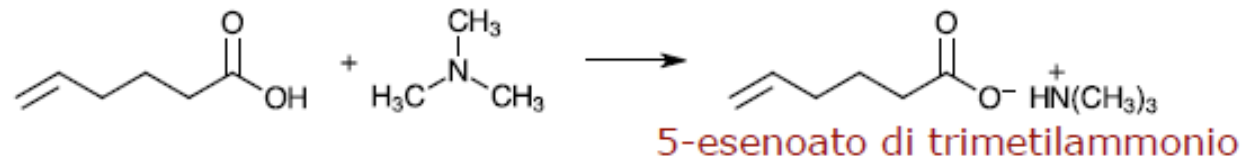
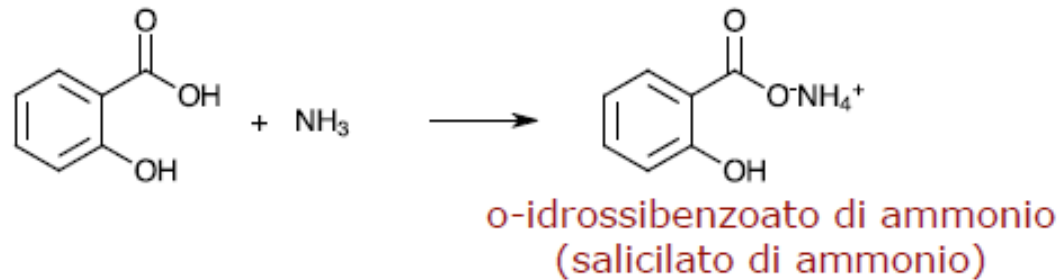
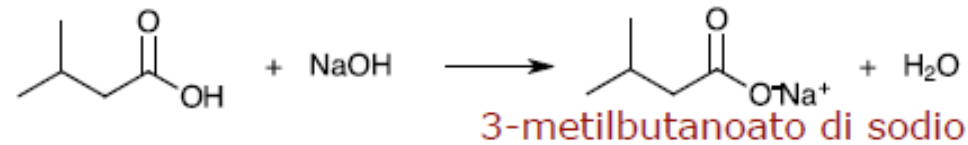
*Le due anidridi che si ottengono sono estremamente importanti in biochimica, infatti sono capaci di **trasferire energia** essendo il legame **P -O -P** un legame definito ad "**alta energia**".*

# Esteri e anidridi dell'acido fosforico

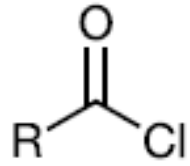


# REAZIONI CON BASI

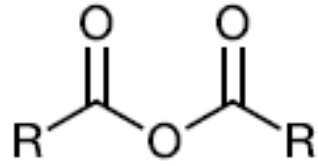
- Gli acidi carbossilici reagiscono irreversibilmente con le basi per dare i corrispondenti sali



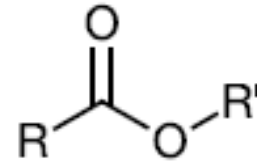
# DERIVATI DEGLI ACIDI CARBOSSILICI



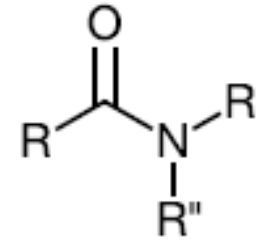
cloruri acilici



anidridi



esteri

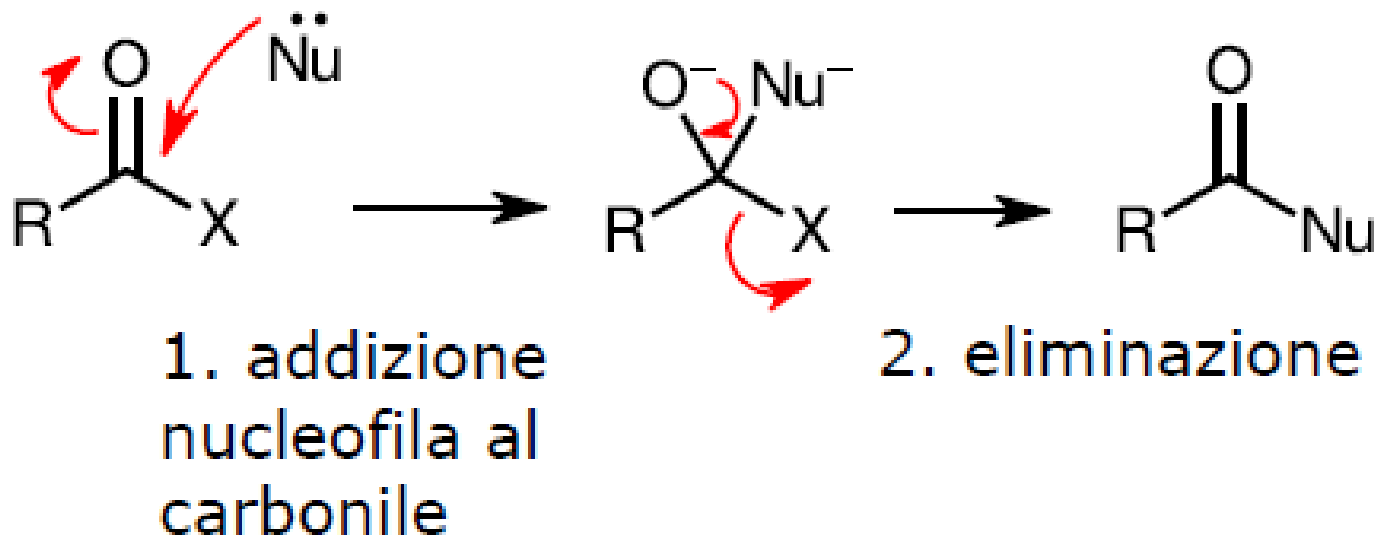


ammidi

comuni reagenti  
non presenti in  
natura

importanti in  
natura

# REAZIONI DI ACIDI CARBOSSILICI E DERIVATI: SOSTITUZIONE NUCLEOFILA ACILICA



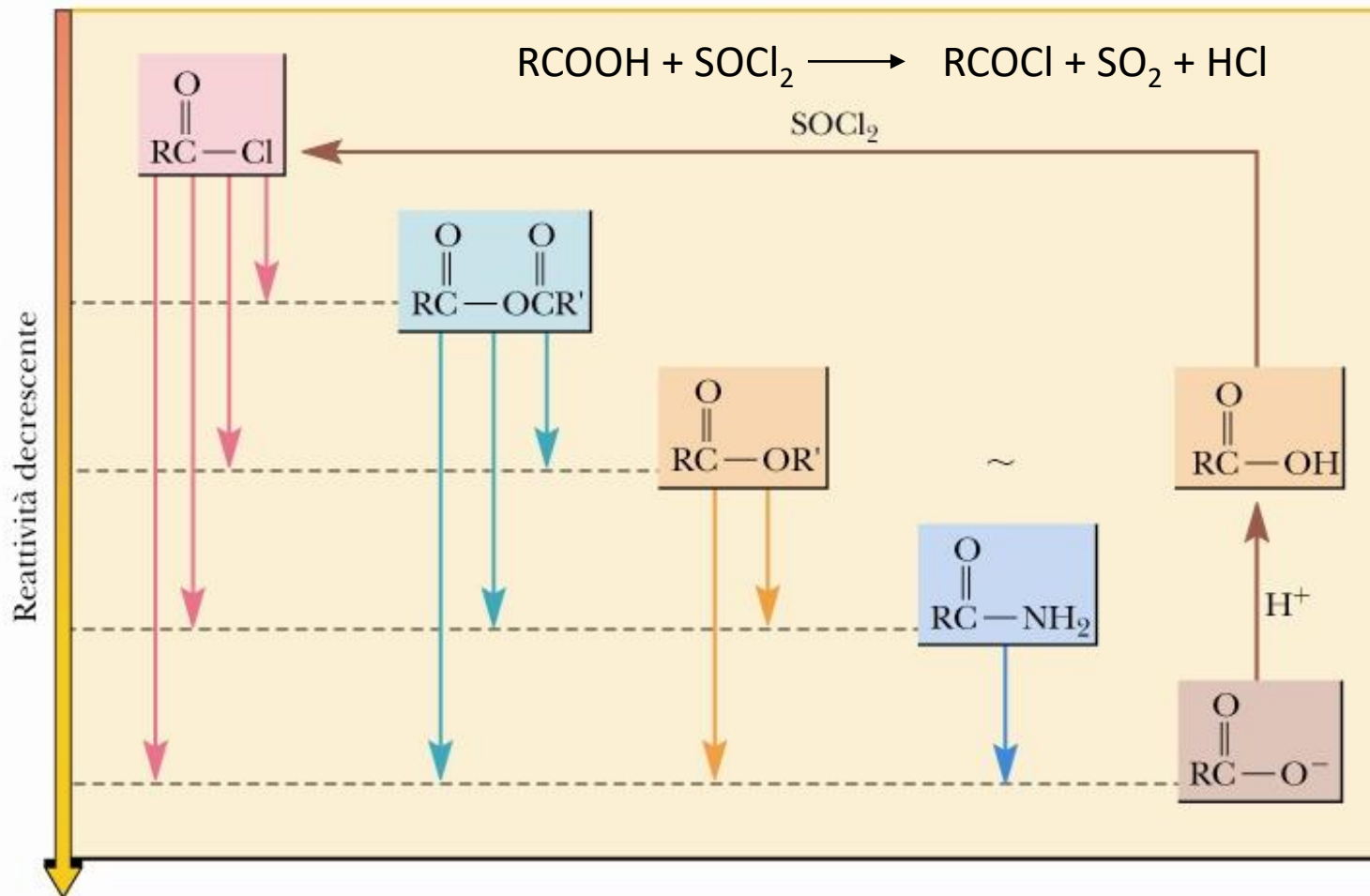
X = Cl, OCOR, OR', NHR'



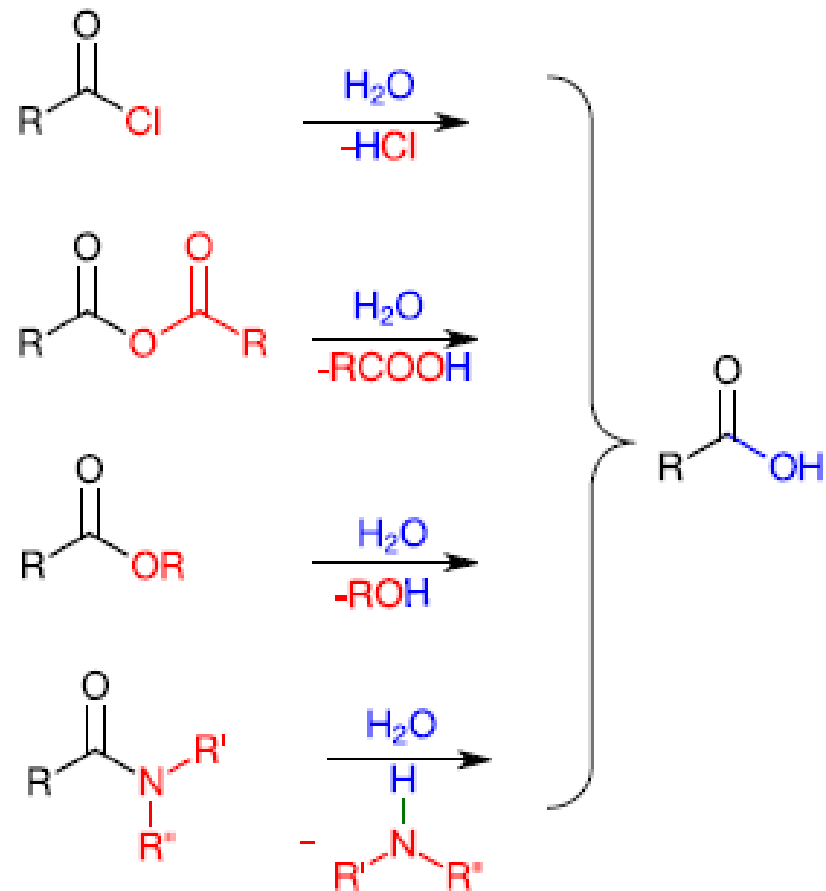
Con quale nucleofilo converto il cloruro acilico in anidride? In estere? In ammido ? In acido?  
 Con quale nucleofilo converto l'anidride in estere? In ammido ? In acido?  
 Con quale nucleofilo converto l'estere in ammido ? In acido?  
 Con quale nucleofilo converto l'ammido in acido?

**Figura 15.1**

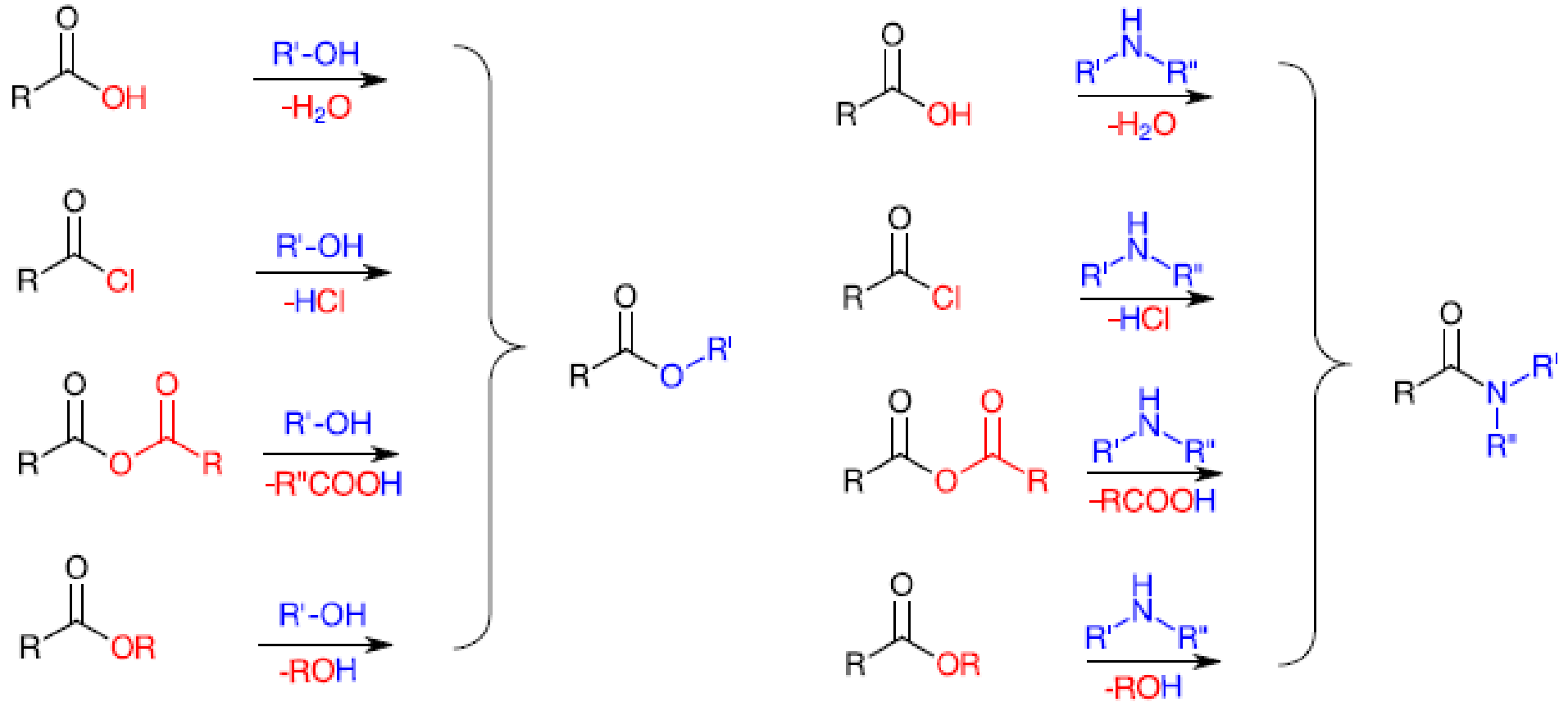
Reattività relative dei derivati degli acidi carbossilici verso la sostituzione nucleofila acilica. Un derivato più reattivo può essere convertito in uno meno reattivo per trattamento con un appropriato reagente. Il trattamento di un acido carbossilico con il cloruro di tionile lo converte nel più reattivo cloruro acilico. Gli acidi carbossilici sono reattivi circa quanto gli esteri in condizioni acide, ma vengono trasformati nei non reattivi anioni carbossilato in ambiente basico.



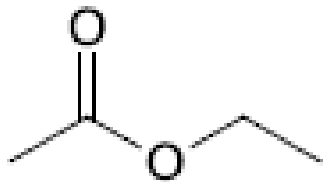
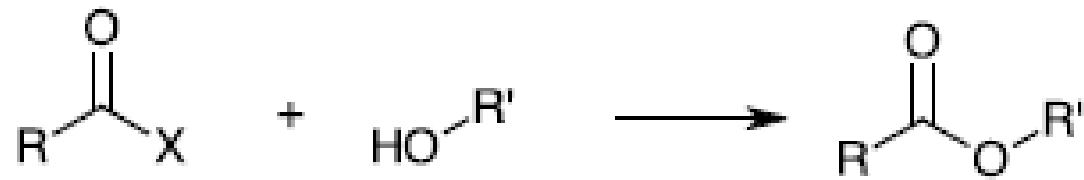
# REAZIONI DI ACIDI CARBOSSILICI E DERIVATI: IDROLISI



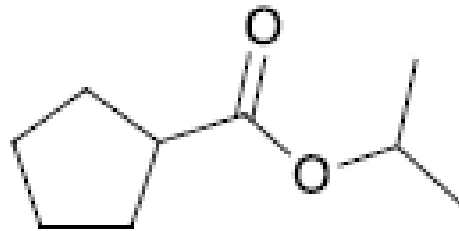
# SINTESI DI ESTERI E AMMIDI



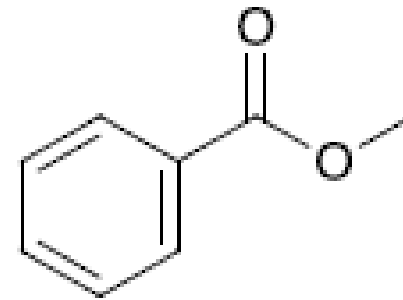
# Nomenclatura degli esteri



Etil acetato



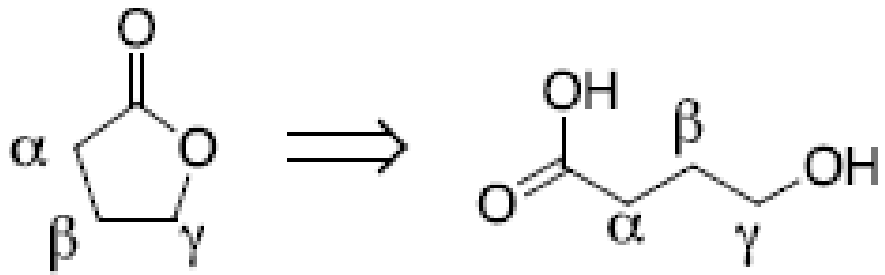
Isopropil ciclopentancarbossilato



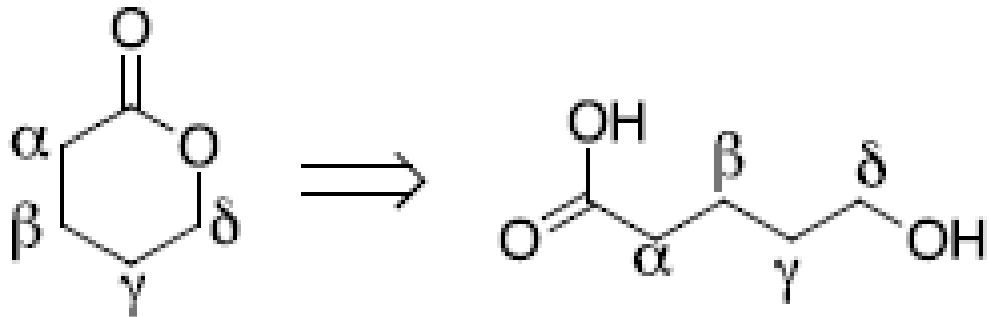
Metil benzoato

# Lattoni

I lattoni sono esteri ciclici



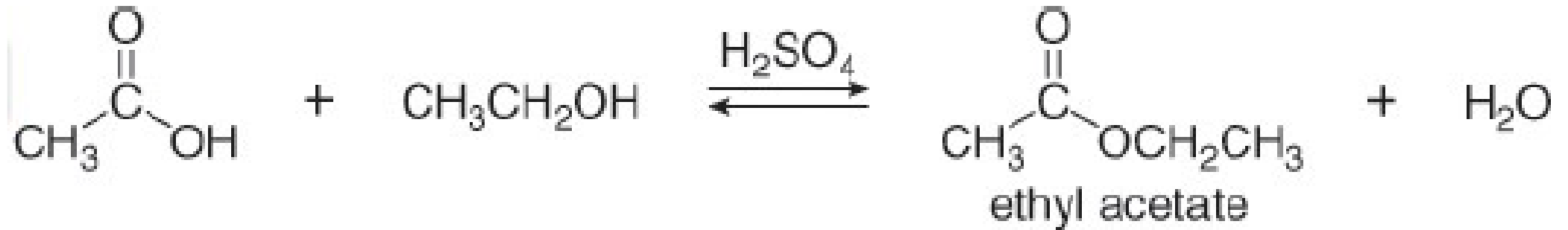
$\gamma$ -lattoni



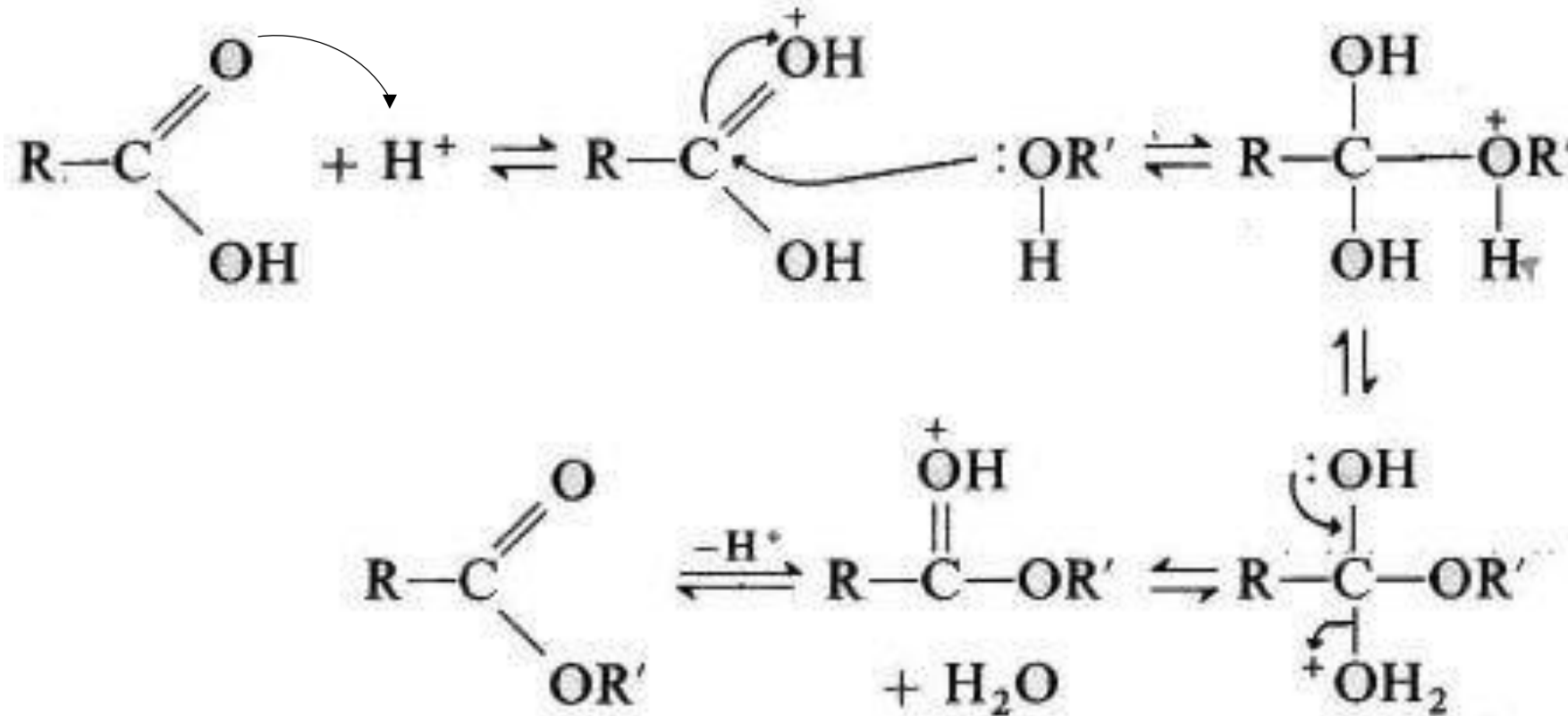
$\delta$ -lattoni

# Esterificazione di FISCHER

È una reazione di equilibrio che può essere spostata a destra usando un eccesso di alcol o rimuovendo l'acqua che si forma



# Meccanismo della esterificazione di Fischer



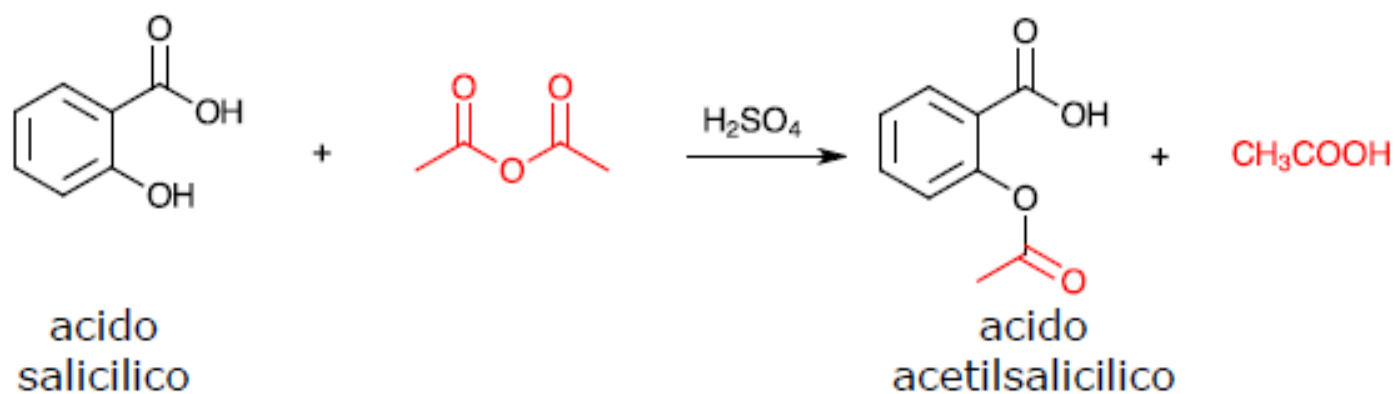
1) Addizione

Trasferimento protonico  
che porta alla formazione  
di un buon gruppo  
uscente

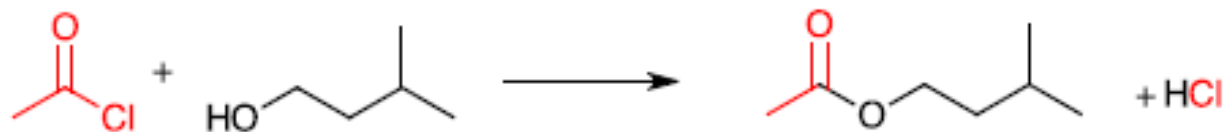
2) Eliminazione

# Sintesi di esteri

da anidridi (sintesi della aspirina della Bayer):



da cloruri acilici:

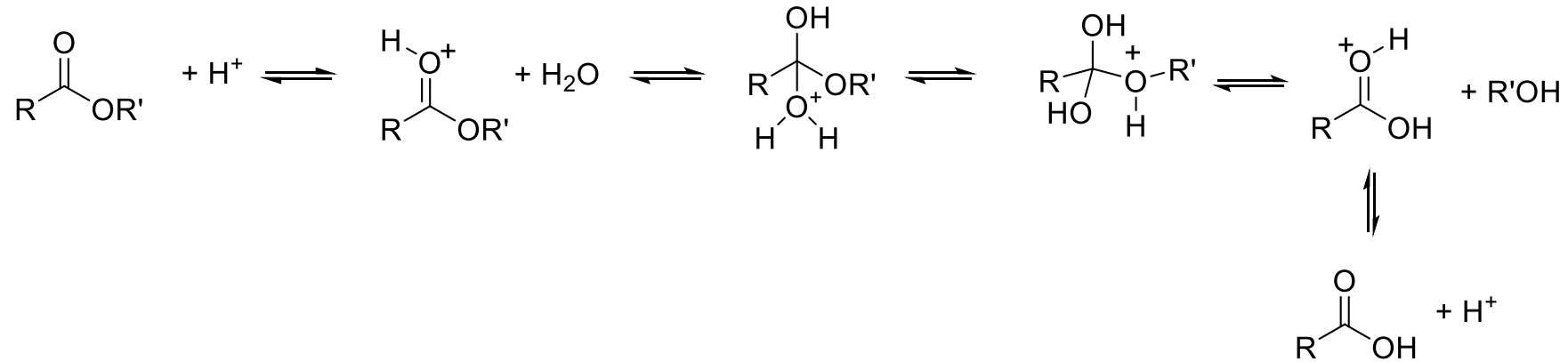




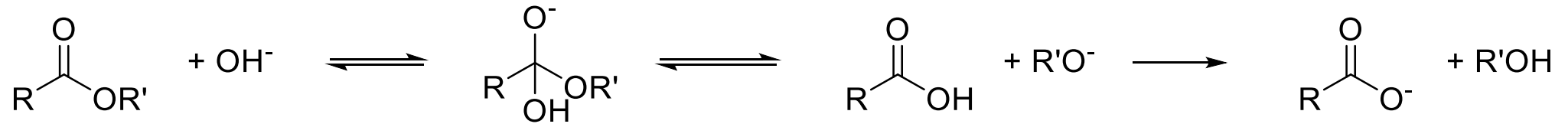
# Idrolisi di esteri

Completare con le opportune frecce

Acido catalizzata:



Idrolisi basica (saponificazione):

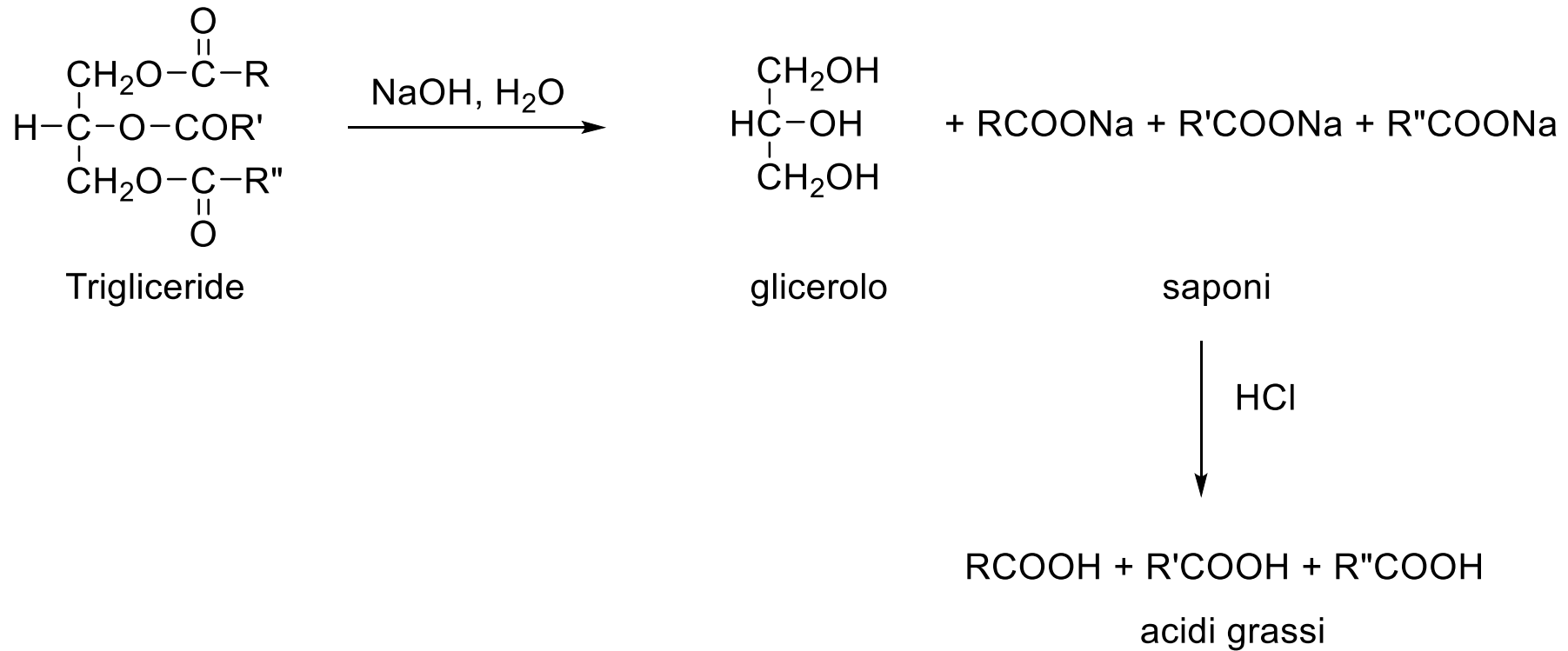


Ultimo passaggio  
irreversibile

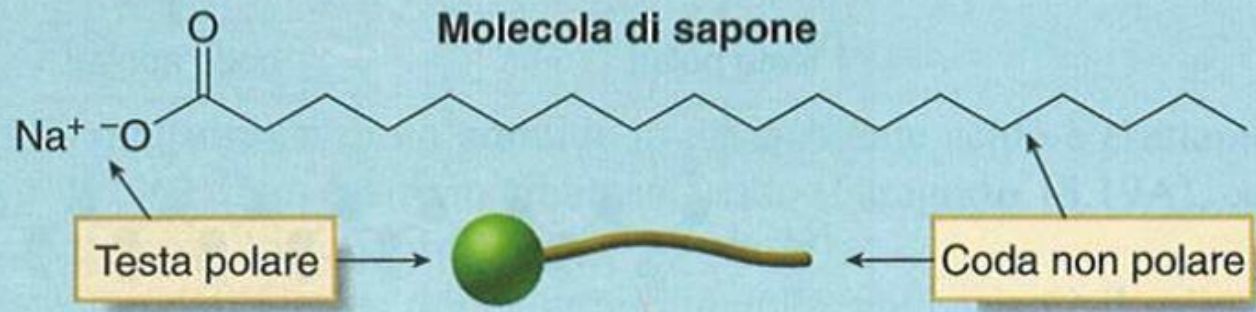
# Trigliceridi o triacilgliceroli

Triesteri del glicerolo con 3 acidi grassi

Saponificazione dei trigliceridi



Saponificazione: idrolisi basica dei trigliceridi



Sapone

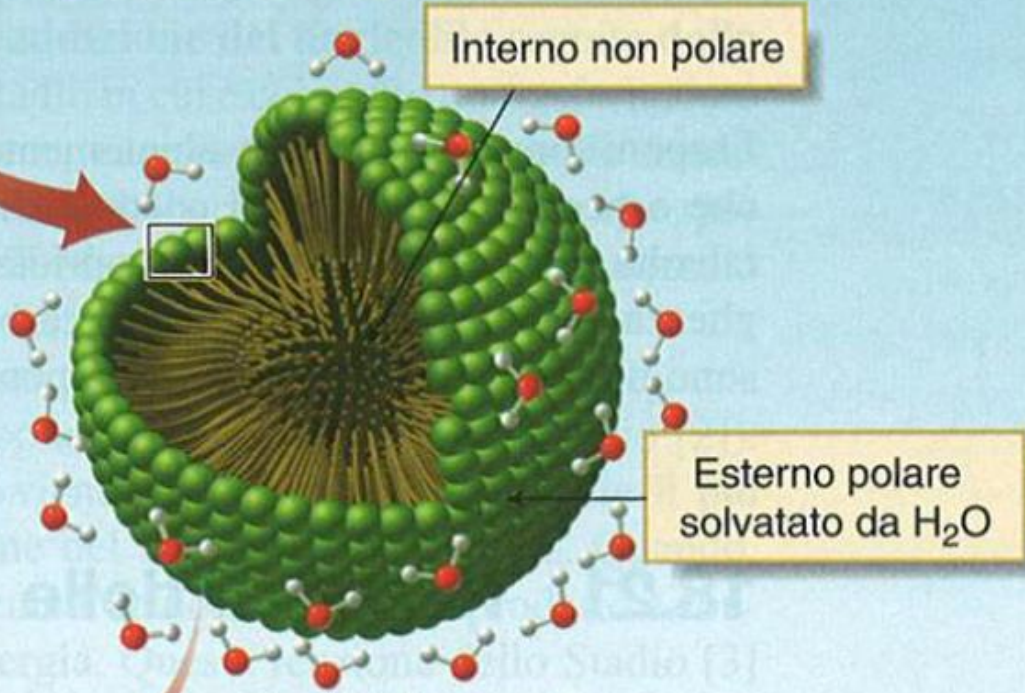
+



H<sub>2</sub>O

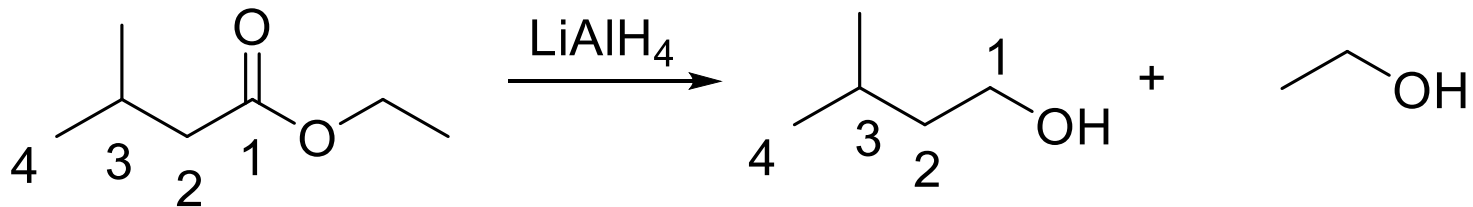


Micelle di sapone in H<sub>2</sub>O



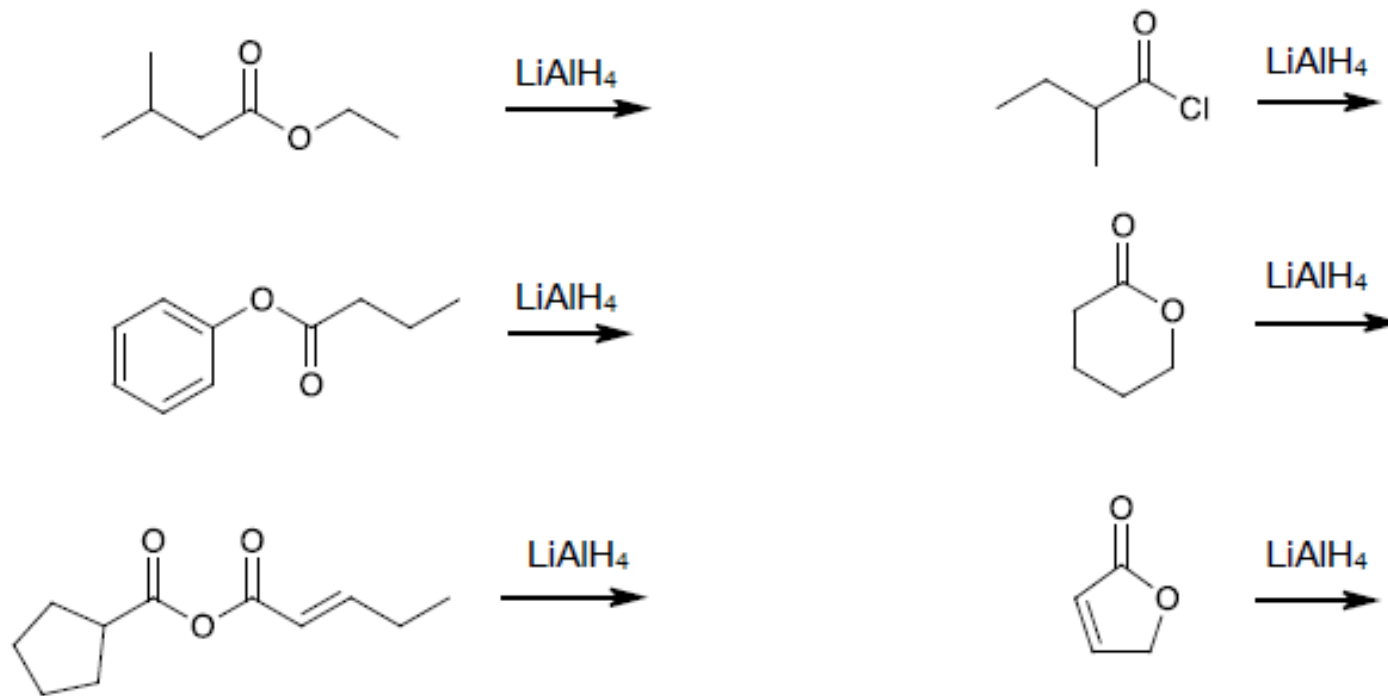
# Riduzione di alogenuri acilici, anidridi e esteri

- Gli alogenuri acilici, le anidridi e gli esteri vengono ridotti ad alcoli primari con Litio alluminio idruro ( $\text{LiAlH}_4$ )

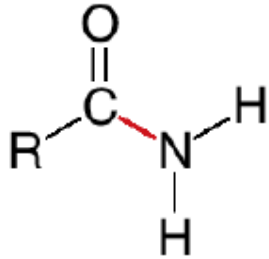


# Riduzione di alogenuri acilici, anidridi e esteri

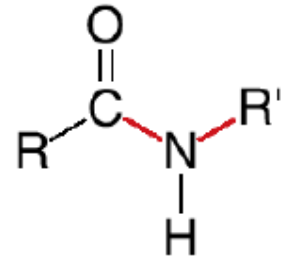
- Gli alogenuri acilici, le anidridi e gli esteri vengono ridotti ad alcoli primari con Litio alluminio idruro ( $\text{LiAlH}_4$ )



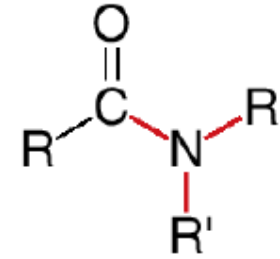
# Ammidi



Ammide primaria  
1 legame N-C

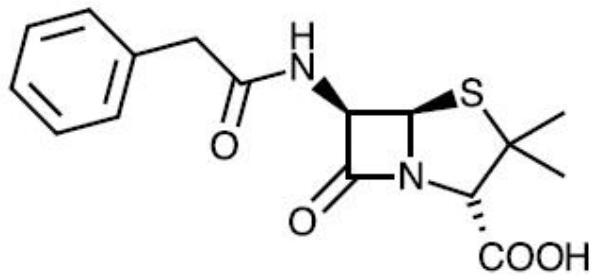


Ammide secondaria  
2 legami N-C

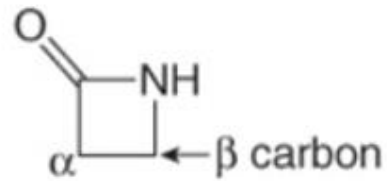


Ammide terziaria  
3 legami N-C

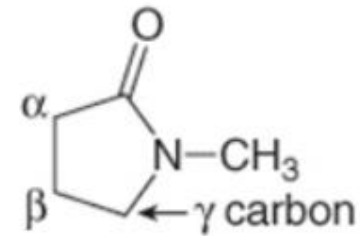
Lattami: ammidi cicliche



Benzil penicillina



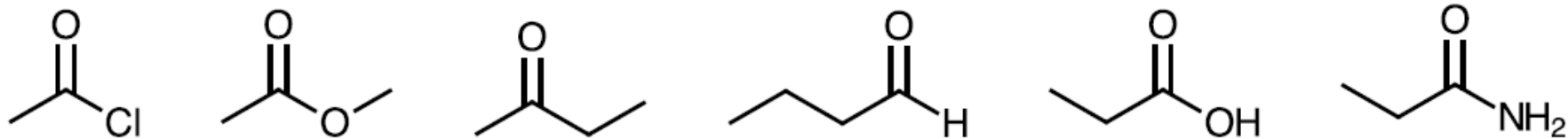
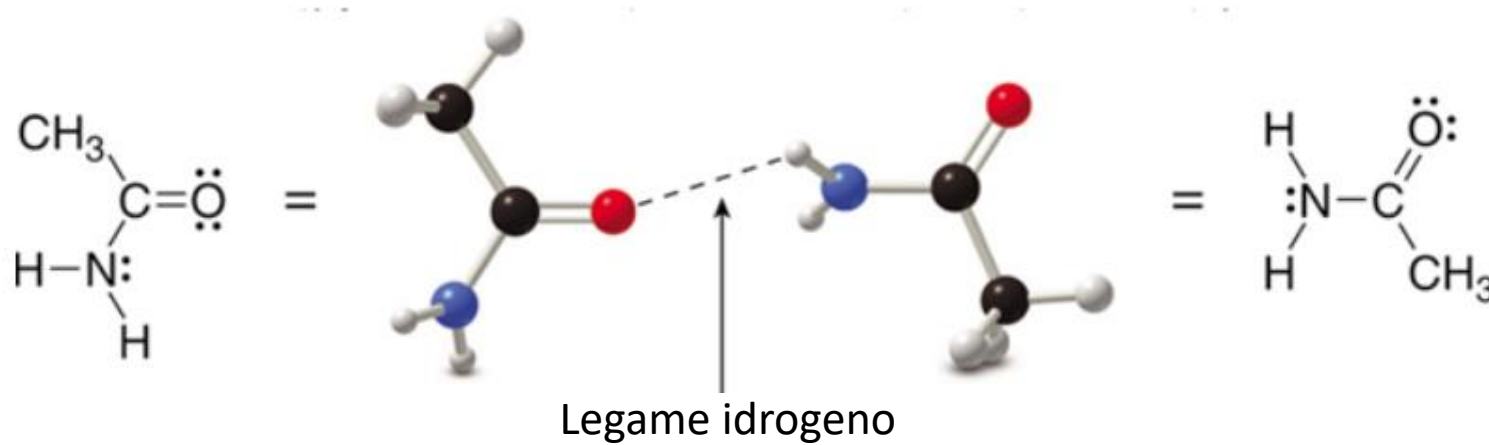
$\beta$ -lattame



$\gamma$ -lattame

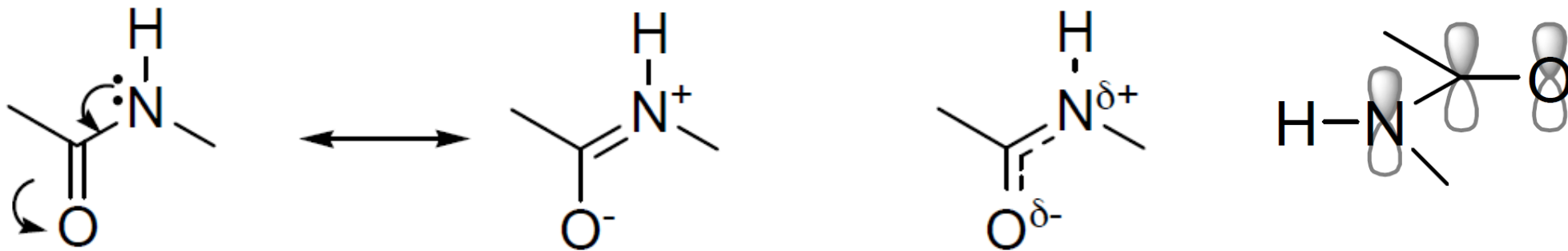
# Ammidi : proprietà fisiche

- Interazioni dipolo-dipolo e legami idrogeno

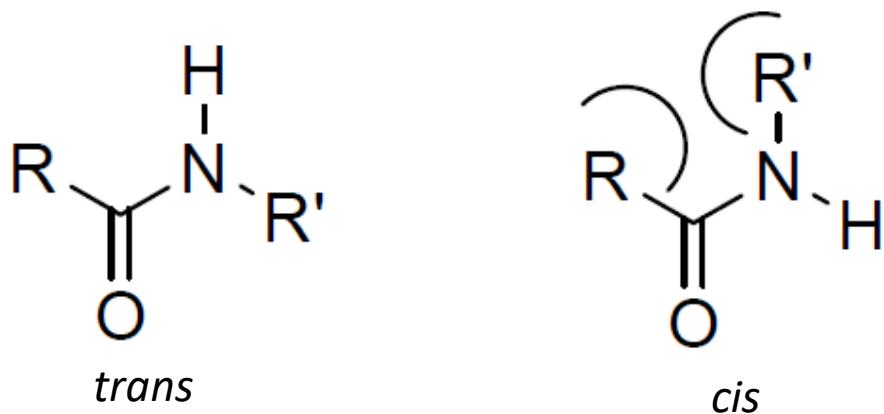


MW	78.5	74	72	72	74	73
b.p.	52 °C	58 °C	75 °C	80 °C	141 °C	213 °C

# Ammidi: struttura



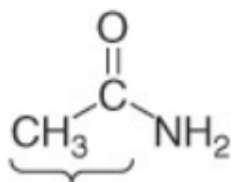
Non c'è libera rotazione attorno al legame N-CO



E' preferita la configurazione con i gruppi R e R' in *trans*  
Le ammidi **non** sono basiche

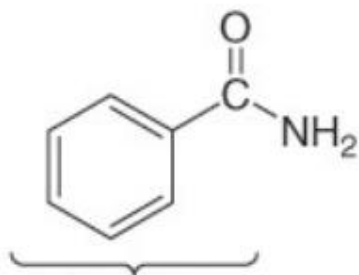


# Nomenclatura ammidi primarie



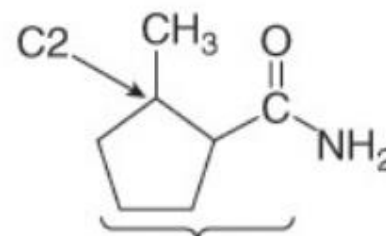
**acetammide**

Deriva  
dall'acido acetico



**benzammide**

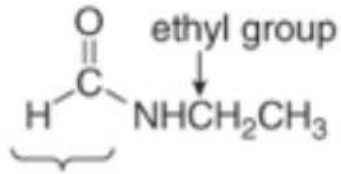
Deriva dall'acido benzoico



**2-metilciclopentancarbossammide**

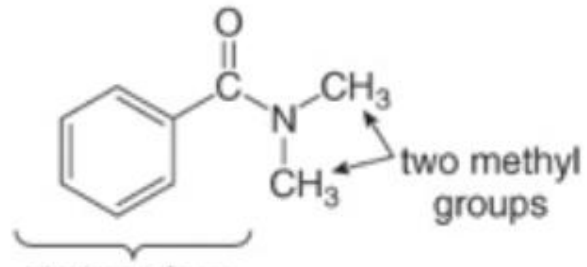
Deriva dall'acido 2-  
metilciclopentancarbossilico

# Nomenclatura ammidi secondarie e terziarie



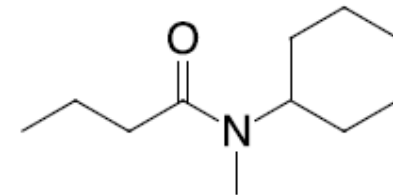
**N-etilformamide**

Deriva dall'acido formico



**N,N-dimetilbenzamide**

Deriva dall'acido benzoico

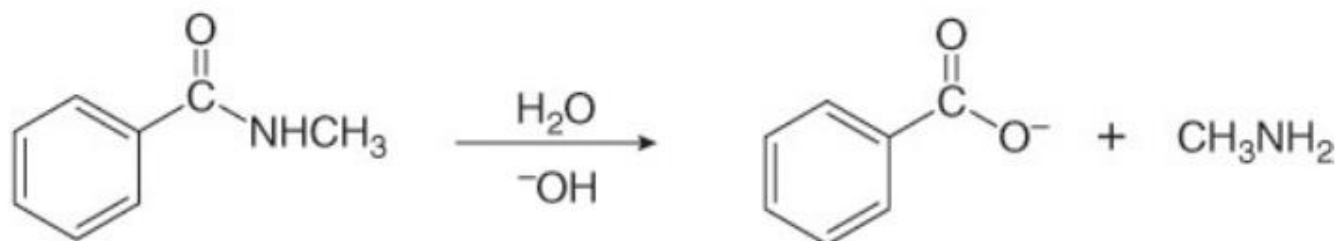
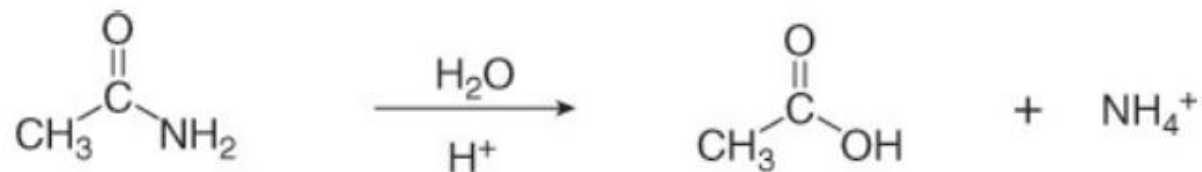


**N-cicloesil-N-metilbutanamide**

Deriva dall'acido butanoico

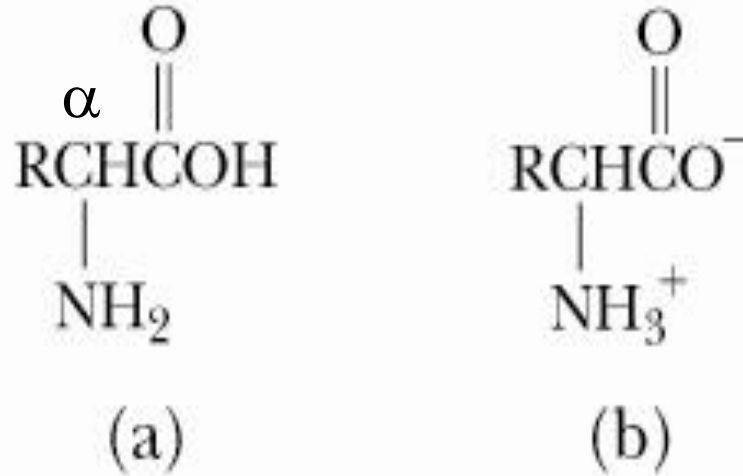


Idrolisi acida e basica difficile e necessita di riscaldamento



## $\alpha$ -Aminoacidi:

al carbonio in alfa al carbossile è legato un gruppo amminico



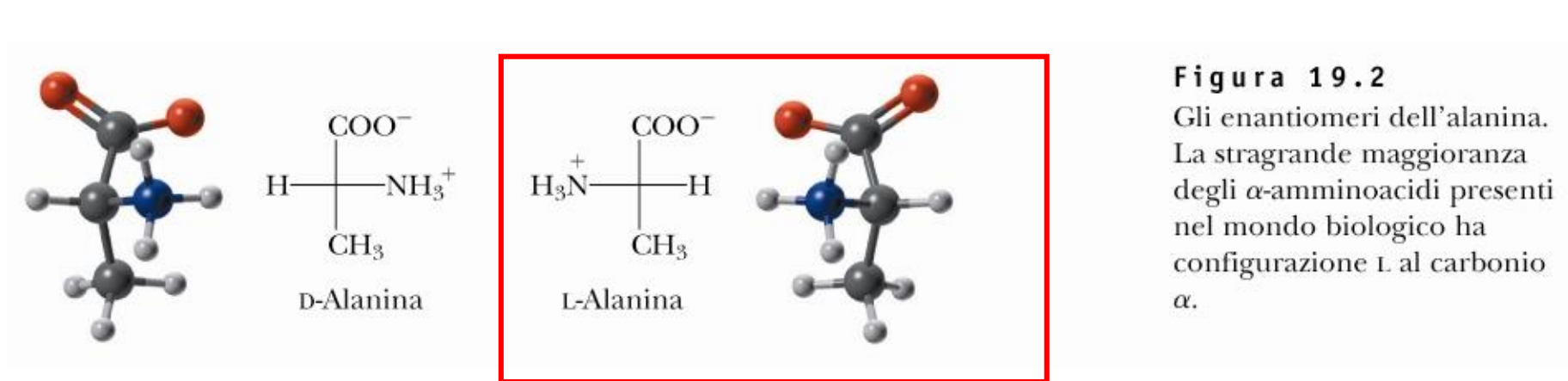
**Figura 19.1**

Un  $\alpha$ -amminoacido.

(a) Forma non ionizzata e

(b) sale interno (zwitterione).


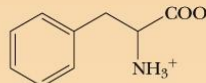
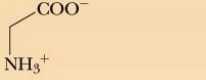
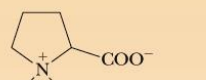
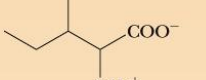

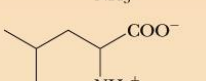
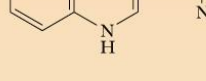
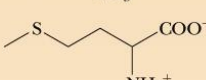
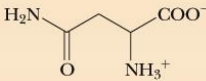
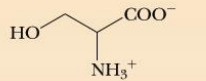
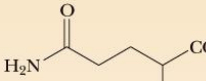
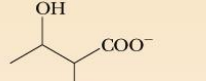
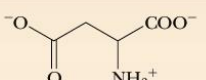
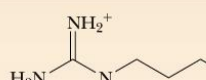

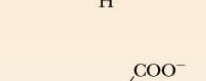
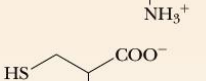
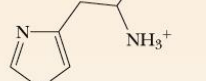
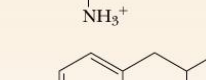
# $\alpha$ -Aminoacidi



**Figura 19.2**

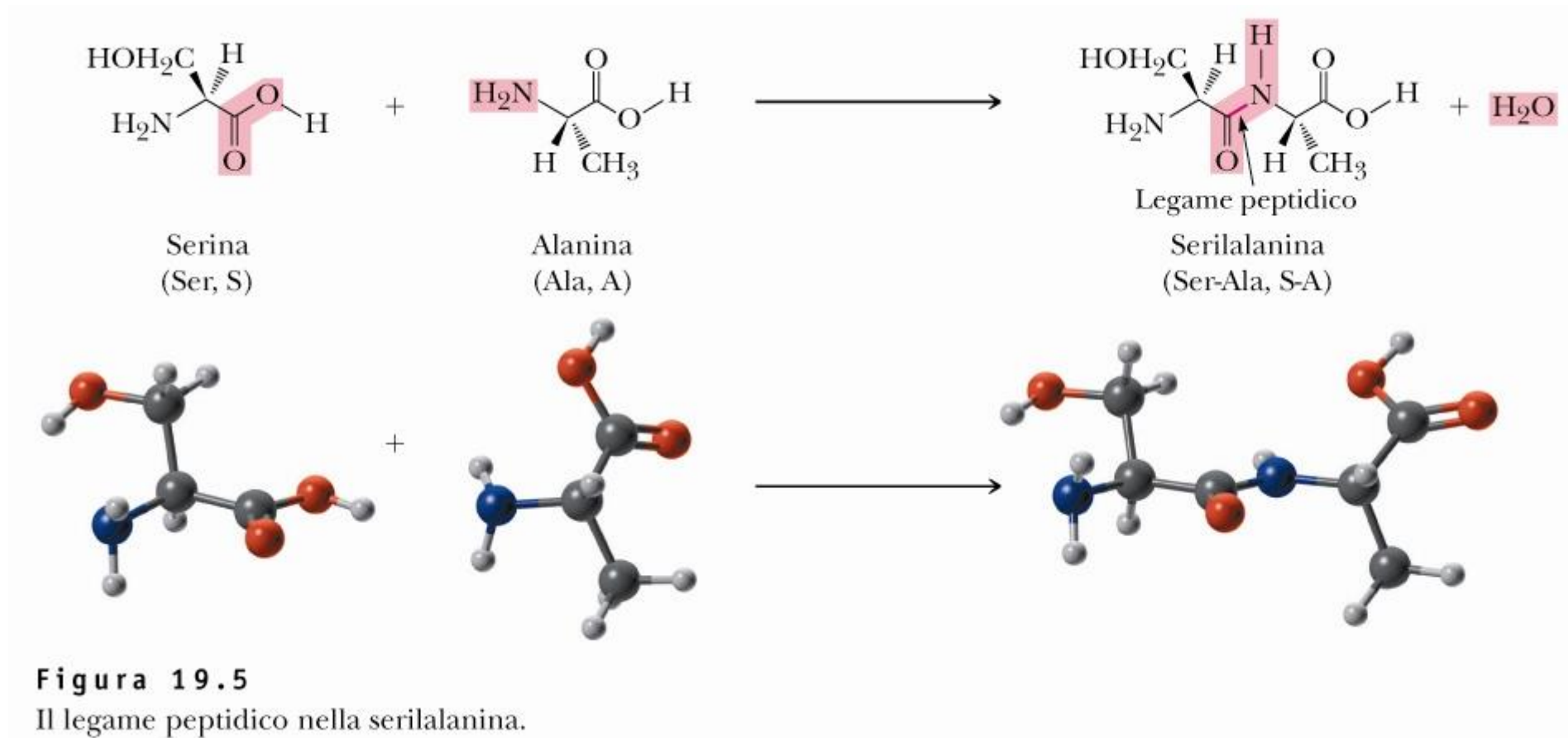
Gli enantiomeri dell'alanina. La stragrande maggioranza degli  $\alpha$ -amminoacidi presenti nel mondo biologico ha configurazione L al carbonio  $\alpha$ .

**TABELLA 19.1 I 20 amminoacidi comunemente presenti nelle proteine**

Catene laterali non polari			
	Alanina (Ala, A)		Fenilalanina (Phe, F)
	Glicina (Gly, G)		Prolina (Pro, P)
	Isoleucina (Ile, I)		Triptofano (Trp, W)
	Leucina (Leu, L)		Valina (Val, V)
	Metionina (Met, M)		
Catene laterali polari			
	Asparagina (Asn, N)		Serina (Ser, S)
	Glutammina (Gln, Q)		Treonina (Thr, T)
Catene laterali acide		Catene laterali basiche	
	Acido aspartico (Asp, D)		Arginina (Arg, R)
	Acido glutammico (Glu, E)		Istidina (His, H)
	Cisteina (Cys, C)		Lisina (Lys, K)
	Tirosina (Tyr, Y)		

Nota: Ciascuna funzione ionizzabile è mostrata nella forma presente in concentrazione maggiore a pH 7.0 in soluzione acquosa.

# Legame peptidico

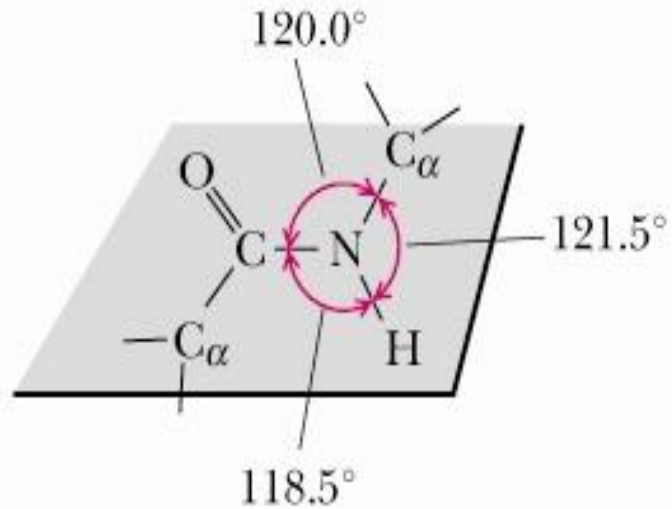


**Figura 19.5**

Il legame peptidico nella serilalanina.

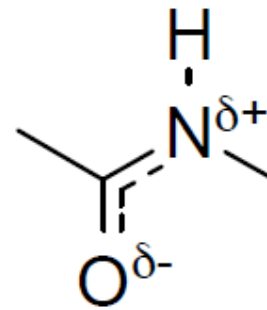
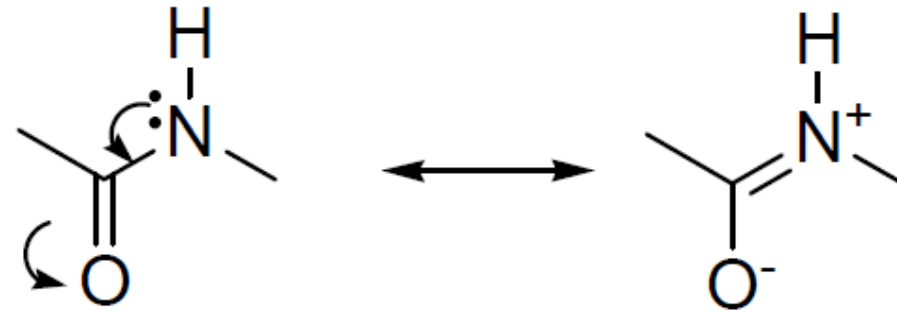


# Legame peptidico



**Figura 19.9**

Planarità del legame peptidico. Gli angoli di legame attorno al carbonio carbonilico e all'azoto ammidico sono approssimativamente di  $120^\circ$ .



# Tripeptide

