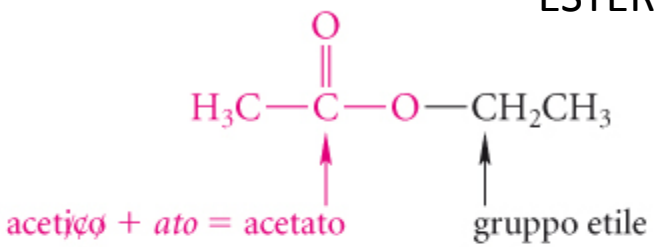
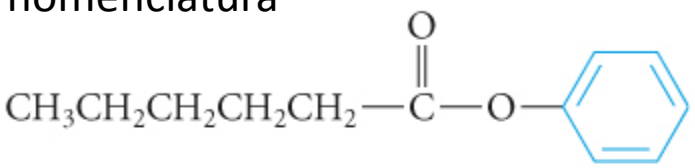
DERIVATI degli ACIDI CARBOSSILICI

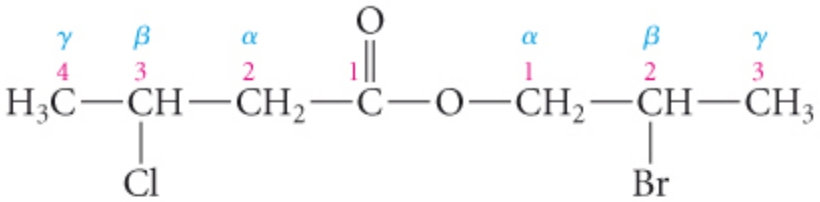
ESTERI: nomenclatura



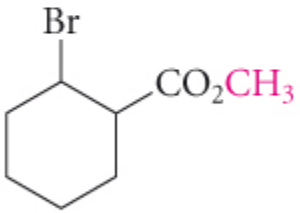
acetato di etile
(nome d'uso)



esanoato di fenile
(nome sostitutivo)

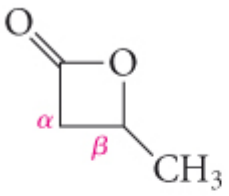


nome d'uso: **β-clorobutirrato di β-bromopropile**
nome sostitutivo: **3-clorobutanoato di 2-bromopropile**

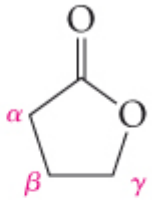


2-bromocicloesancarbossilato di metile

succinato di diisopropile



β-butirrolattone
(un β-lattone)



γ-butirrolattone
(un γ-lattone)

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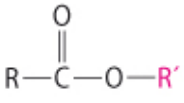
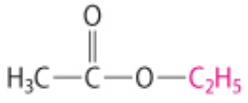
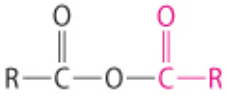
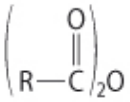
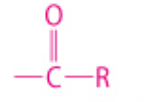
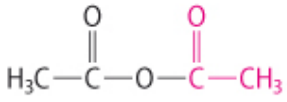
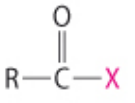
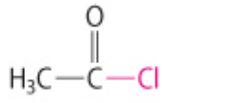
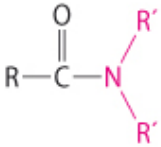
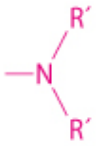
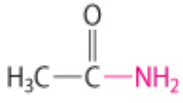
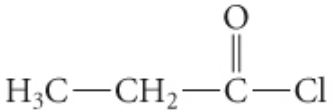
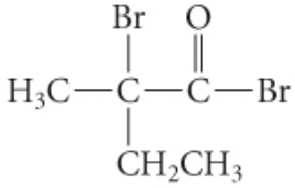
TABELLA 21.1 Strutture dei derivati degli acidi carbossilici

Struttura generale, nome del derivato	Struttura condensata	Derivazione*		Esempio
		Sostituisci—	Con—	
 estere	$R-CO_2R'$	—H	—R′	 **acetato di etile**
 anidride		—H	 (gruppo acilico)	 **anidride acetica**
 alogenuro acilico	$R-CO-X$	—OH	—X (alogeno)	 **cloruro di acetile**
 ammide	$R-CO-NR'_2$	—OH		 **acetammide**
 nitrile	$R-CN$	$-CO_2H$	—CN (gruppo ciano)	 **acetonitrile**

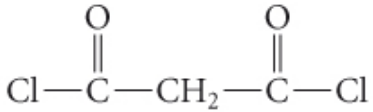
*Sostituisci il gruppo nella colonna 3 con il gruppo nella colonna 4 nella struttura dell'acido carbossilico  e ottieni il derivato. (Nota che questa tabella indica solo la relazione tra le varie strutture, ma non necessariamente come si possono trasformare l'una nell'altra attraverso reazioni chimiche.)



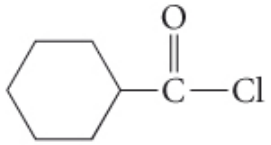
propionico + *ile* =
cloruro di propionile o propionil cloruro (nome d'uso)
cloruro di propanoile o propanoil cloruro (nome sostitutivo)



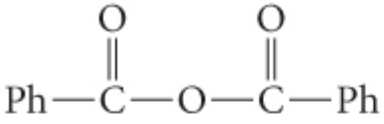
bromuro di α-bromo-α-metilbutirrile (nome d'uso)
2-bromo-2-metilbutanoil bromuro (nome sostitutivo)



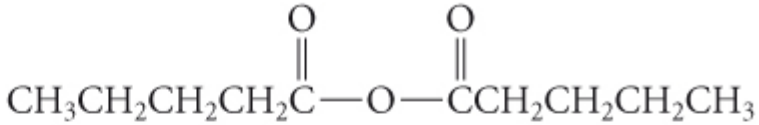
dicloruro di malonile o malonil dicloruro



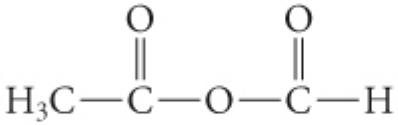
cloruro di cicloesancarbonile o cicloesancarbonil cloruro



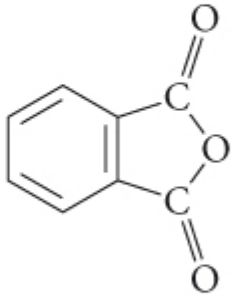
anidride benzoica



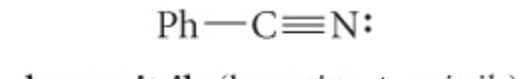
anidride valerica (nome d'uso)
anidride pentanoica (nome sostitutivo)



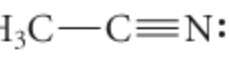
anidride acetica formica
(un'anidride mista)



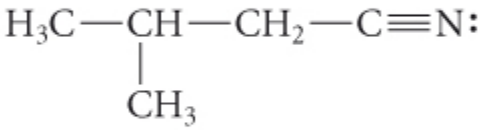
anidride ftalica
(un'anidride ciclica)



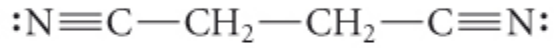
benzonitrile (benzoico + *onitrile*)



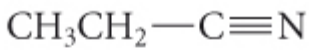
acetonitrile (acetico + *onitrile*)



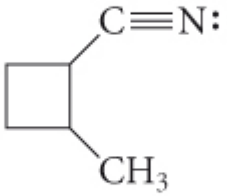
isovaleronitrile (nome d'uso)
3-metilbutanonitrile (nome sostitutivo)



succinonitrile (nome d'uso)
butanonitrile (nome sostitutivo)



propionitrile (*non* propiononitrile)



2-metilciclobutancarbonitrile

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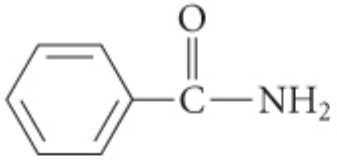
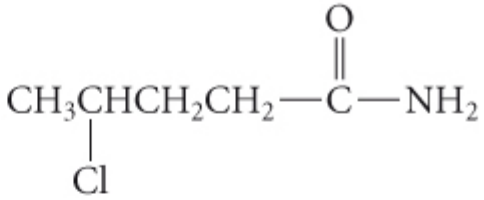
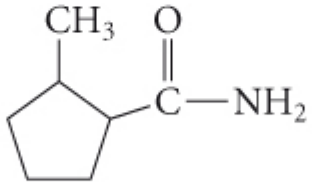


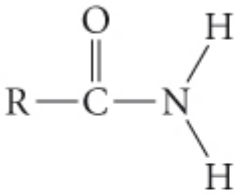
benzammide (benzoi¢¢ø + *ammide*)



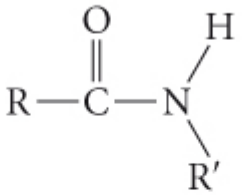
γ-clorovalerammide (nome d'uso)
4-cloropentanammide (nome sostitutivo)



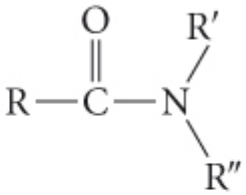
2-metilciclopentancarbossiammide



ammide primaria



ammide secondaria



ammide terziaria

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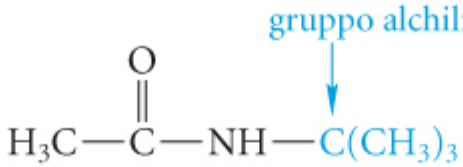
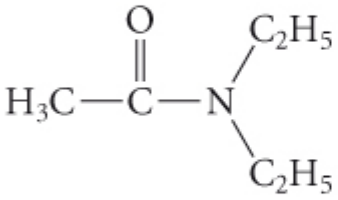
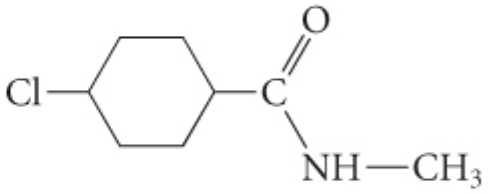


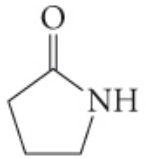
un'ammide secondaria



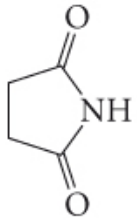
***N,N*-dietilacetammide**
(la doppia *N* sta a significare che entrambi i gruppi etilici sono sull'azoto)



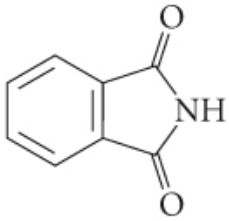
4-cloro-*N*-metilcicloesancarbossiammide



γ-butirrolattame
(un γ-lattame)



succinimmide



ftalimmide

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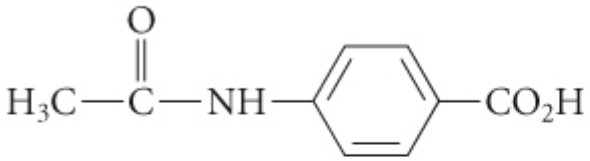
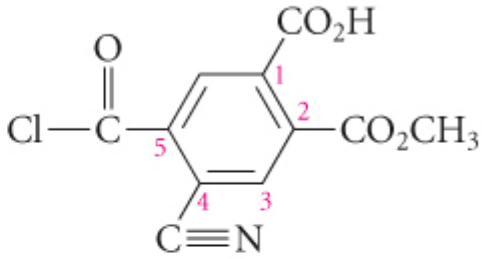


acido *p*-acetammidobenzoico
acido 4-(acetilammino)benzoico



acido 5-cloroformil-4-ciano-2-metossicarbonilbenzoico

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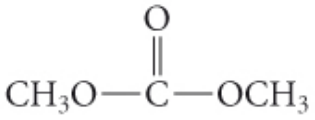
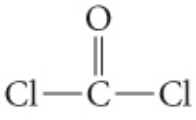
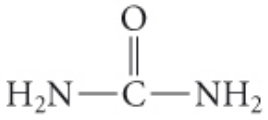
DERIVATI dell'ACIDO CARBONICO



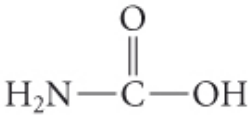
carbonato dimetilico



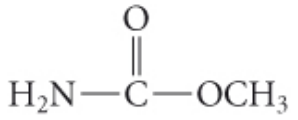
fosgene



urea



acido carbammico
(instabile, ma molti suoi derivati sono stabili)



carbammato di metile
(un derivato stabile dell'acido carbammico)

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STRUTTURA AMMIDI

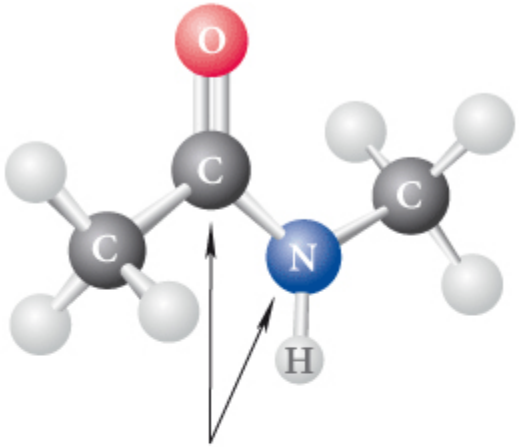
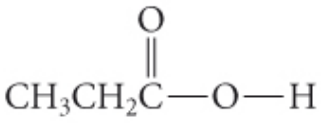
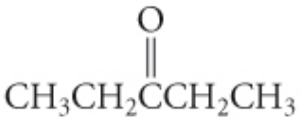
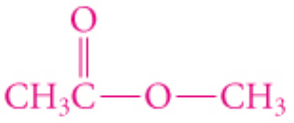
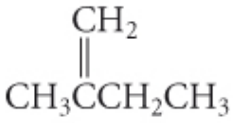


Figura 21.1 Modello a sfere e bastoncini della *N*-metilacetammide. La geometria trigonale planare del carbonio carbonilico e dell'azoto fa in modo che gli atomi contrassegnati dal loro simbolo giacciano tutti nello stesso piano.

Parziale carattere di doppio legame C=N, possibile isomeria Z/E delle ammidi secondarie e terziarie (isomero Z predominante).

Rotazione C-C butano ha una frequenza di 10^{11} volte al secondo, attorno al legame C=O-N solo 10 volte al secondo.

PROPRIETA' FISICHE

				
	acido propionico	**2-butanone**	**acetato di metile**	**2-metil-1-butene**
punto di ebollizione	141°C	80°C	57°C	31.2°C

	$H_3C-C\equiv N:$	$CH_3CH_2-C\equiv N:$	$H_3C-C\equiv C-H$
	acetonitrile	**propionitrile**	**propino**
punto di ebollizione	81.6°C	97.4°C	−23.3°C

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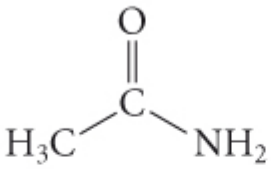
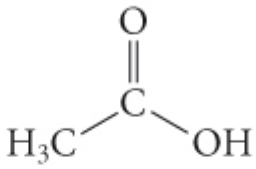
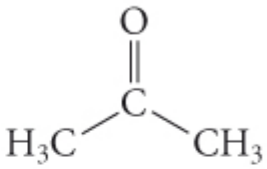
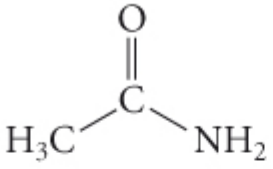
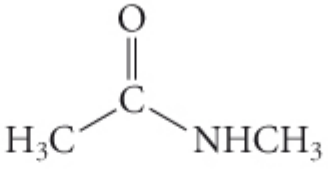


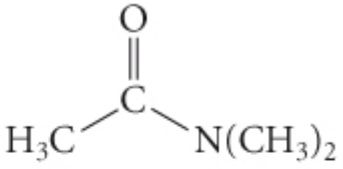




	acetammide	**acido acetico**	**acetone**
punto di ebollizione	221.2°C	117.9°C	56.5°C
punto di fusione	82.3°C	16.7°C	−94°C



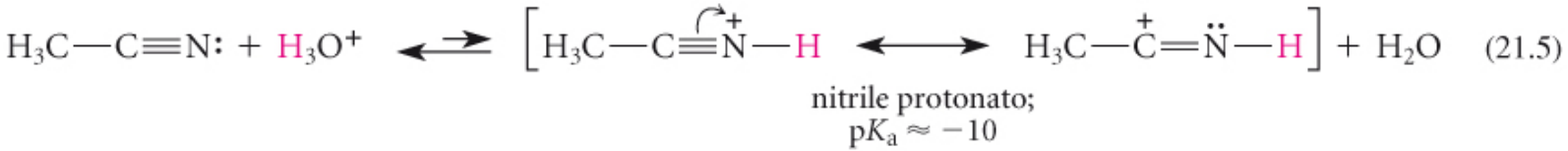




	acetammide	***N*-metilacetammide**	***N*,*N*-dimetilacetammide**
punto di ebollizione	221.2°C	204–206°C	166.1°C
punto di fusione	82.3°C	28°C	−20°C

BASICITA’

pKa (estere protonato) = -6 pKa (ammide protonata) = -1



(21.5)

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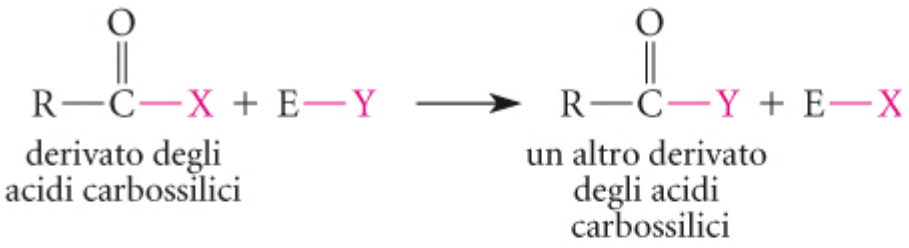
Ammide è la più basica: minore elettronegatività dell’azoto

SOSTITUZIONE NUCLEOFILA ACILICA

Sostituzione al C=O = addizione al C=O + eliminazione



(21.6)

(21.25)

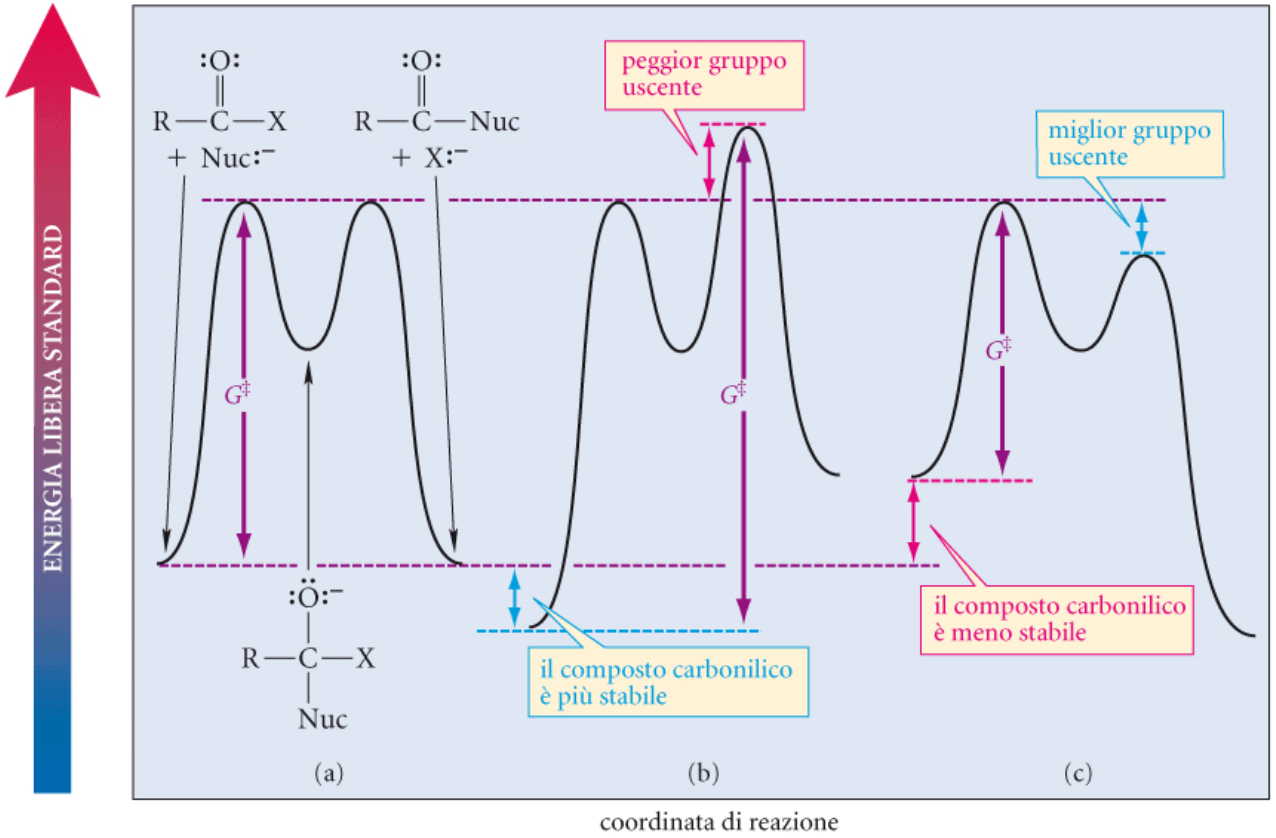
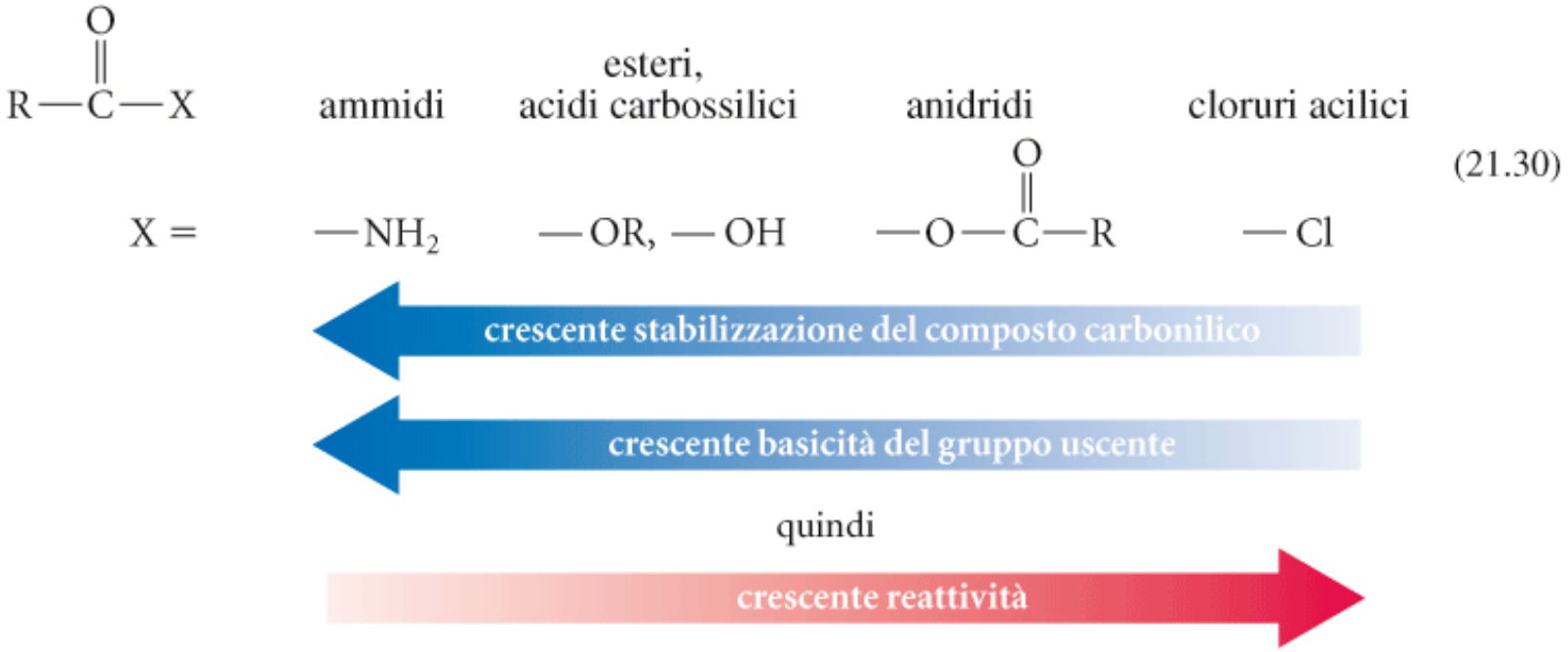


Figura 21.6 Effetto della struttura di un composto carbonilico sulla velocità delle sue reazioni di sostituzione nucleofila. In ogni caso, l'intermedio reattivo è l'intermedio tetraedrico di addizione (Vedi Eq. 21.25). Lo stato di transizione della reazione del nucleofilo è indicato allo stesso livello di energia in tutti e tre i diagrammi per avere un riferimento. (a) Diagramma di energia libera di reazione per una generica reazione in cui i reagenti e i prodotti hanno la stessa energia libera standard e i gli stati di transizione dei due stadi riportati nell'Eq. 21.25 hanno anch'essi la stessa energia libera standard. (b) Quando un composto carbonilico (ad esempio, un'ammide) è stabilizzato per risonanza e contiene un cattivo gruppo uscente, sia la velocità di formazione, sia quella di rottura dell'intermedio tetraedrico di addizione, sono più basse e la sostituzione nucleofilica è più lenta. Un aumento della stabilità del composto carbonilico determina la diminuzione della velocità poiché fa aumentare la *differenza* di energia libera tra composto di partenza e stato di transizione. (c) Quando un composto carbonilico (ad esempio, un cloruro acilico) è destabilizzato e contiene un ottimo gruppo uscente, sia la velocità di formazione, sia quella di rottura dell'intermedio tetraedrico di addizione sono più alte e la sostiuzione nucleofila è più veloce.

nitrili < ammidi < esteri, acidi << anidridi < cloruri acilici

reattività crescente

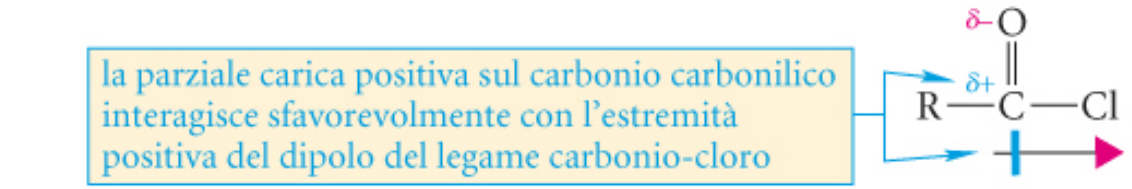
(21.24)

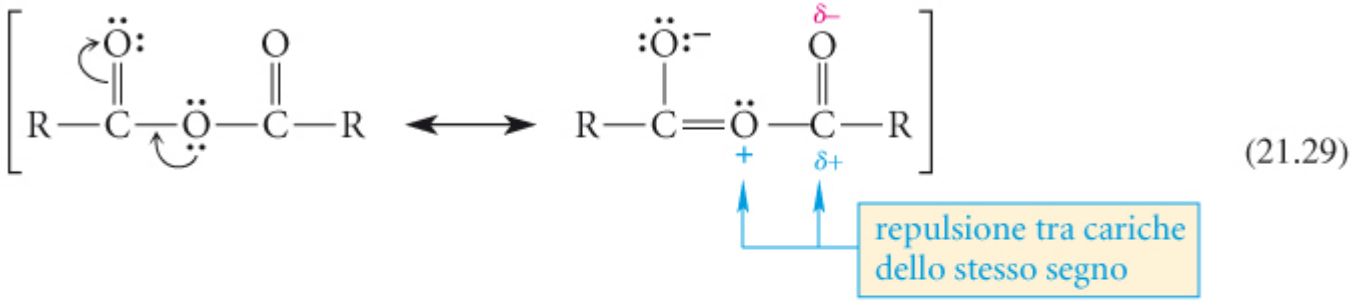


(21.30)

STABILITA' COMPOSTO CARBONILICO

la parziale carica positiva sul carbonio carbonilico interagisce sfavorevolmente con l'estremità positiva del dipolo del legame carbonio-cloro



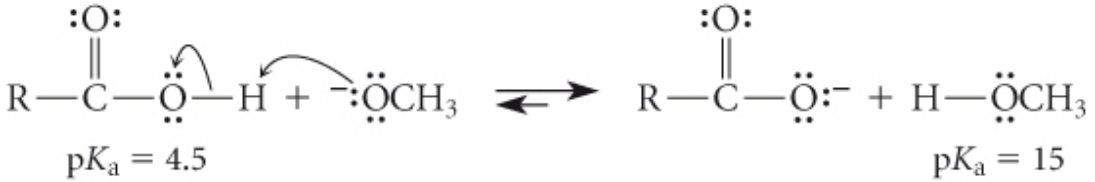


repulsione tra cariche dello stesso segno

(21.29)

IDROLISI BASICA ESTERI

(21.9a)



(21.9b)

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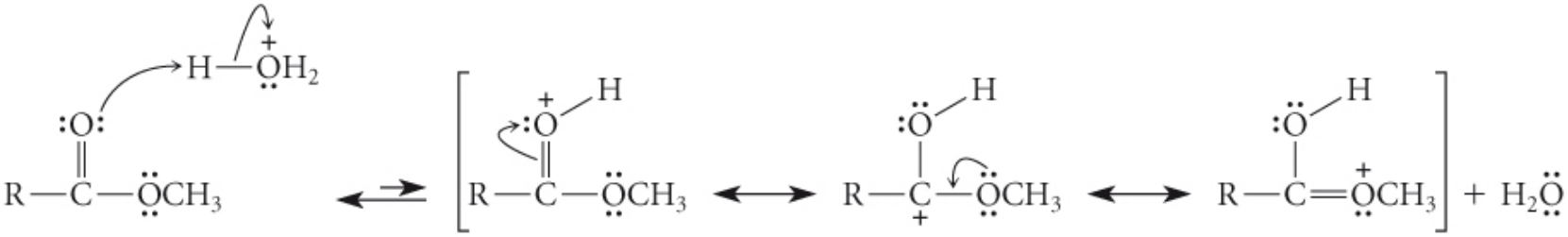
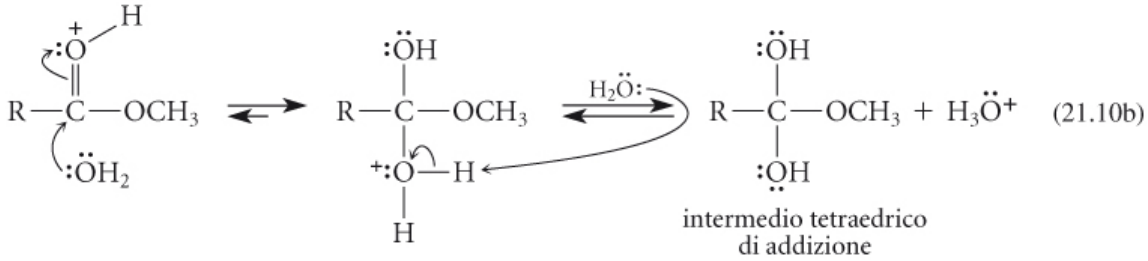
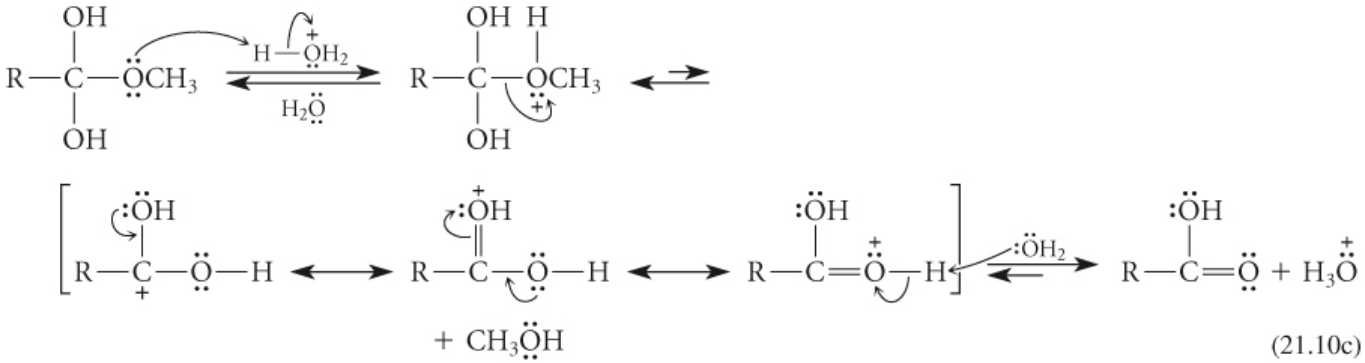
IDROLISI ESTERI CATALIZZATA da ACIDI



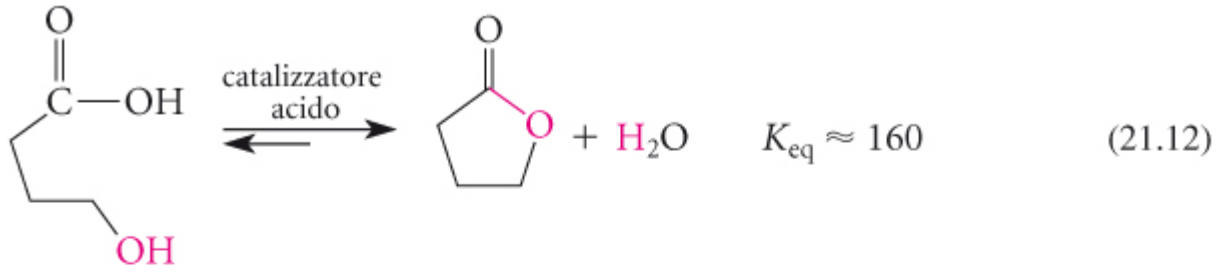
(21.10a)

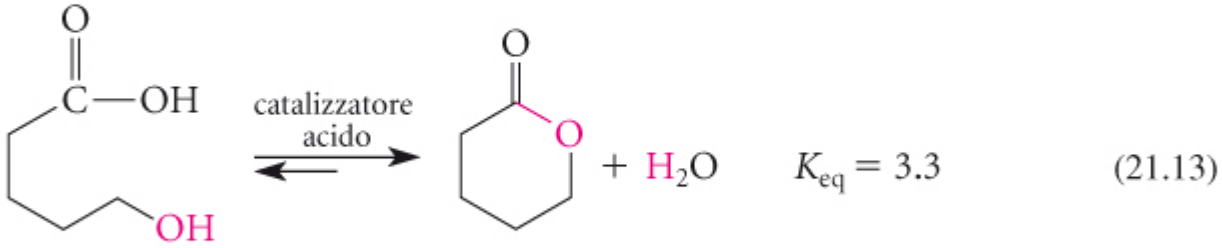


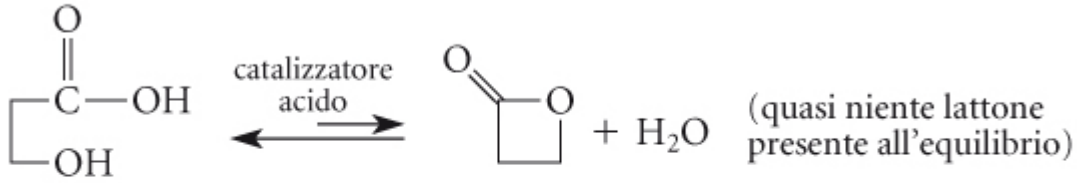
(21.10b)



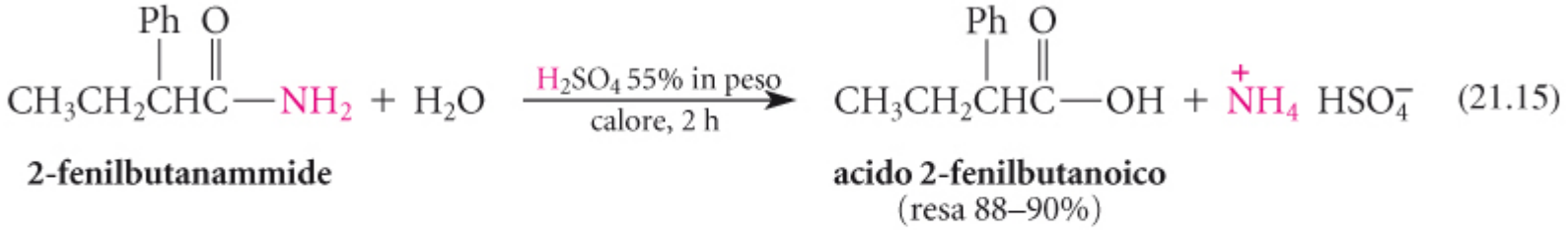
(21.10c)


O
C—OH
OH
catalizzatore
acido
O
O
+ H2O
Keq ≈ 160
(21.12)


O
C—OH
OH
catalizzatore
acido
O
O
+ H2O
Keq = 3.3
(21.13)

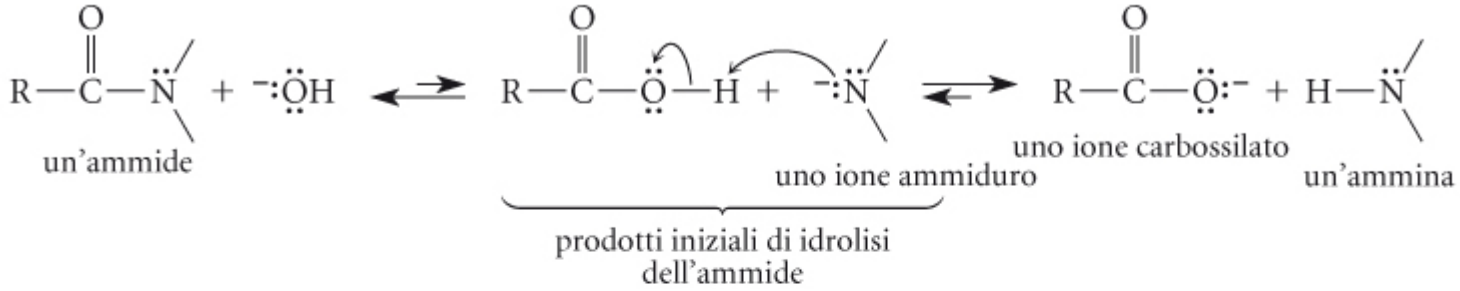

O
C—OH
OH
catalizzatore
acido
O
O
+ H2O
(quasi niente lattone
presente all'equilibrio)

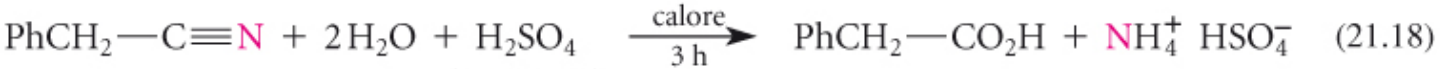
IDROLISI AMMIDI e NITRILI



2-fenilbutanammide

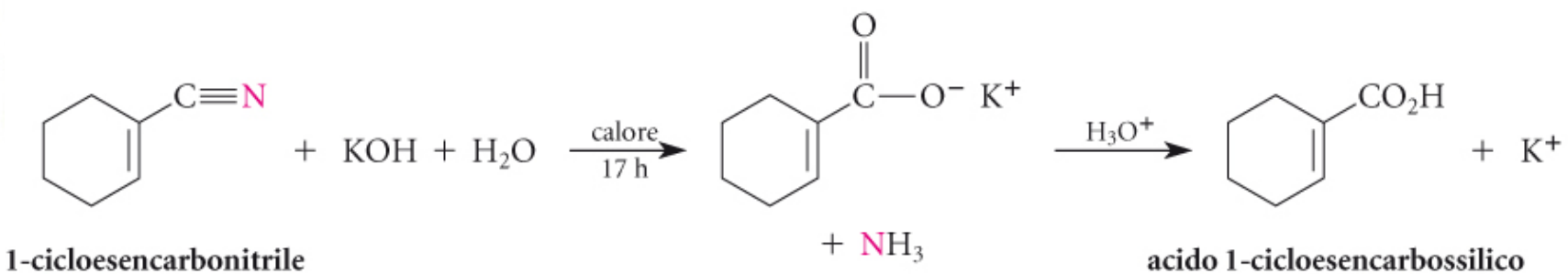
acido 2-fenilbutanoico
(resa 88–90%)





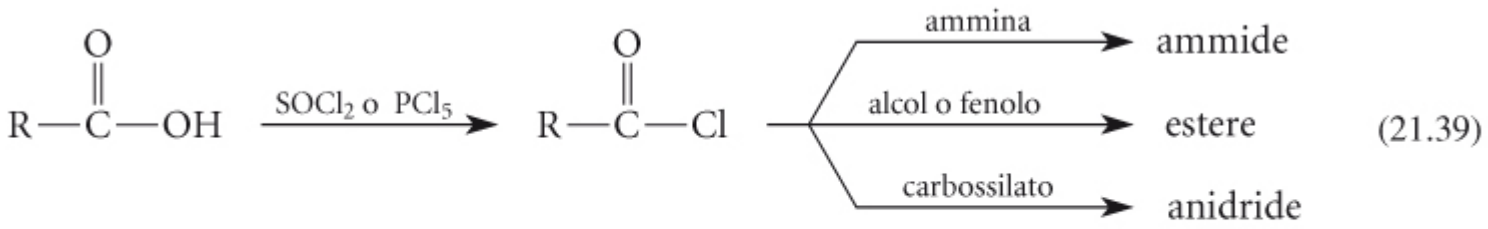
fenilacetonitrile

acido fenilacetico
(resa 78%)



1-cicloesencarbonitrile

acido 1-cicloesencarbossilico
(resa 79%)



(21.39)

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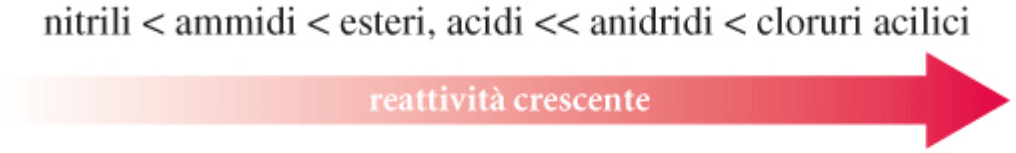
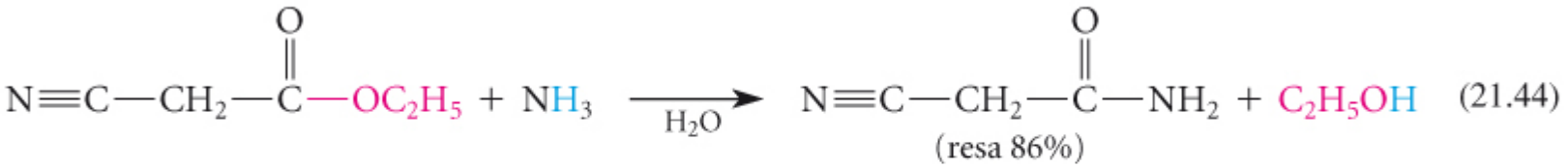
Il derivato dell'acido che si vuole produrre si può ottenere da qualunque derivato più reattivo di quello da ottenere…
Anidride da cloruro, estere da anidride o cloruro, ammide da estere, anidride o cloruro.

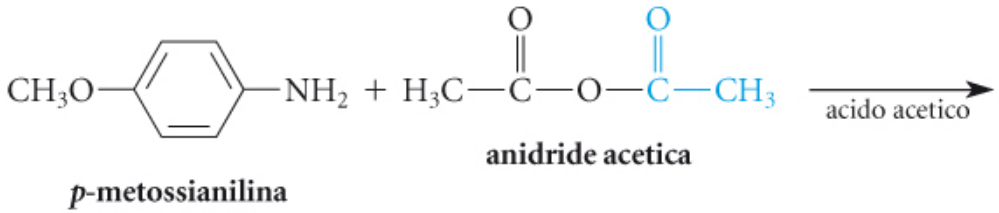


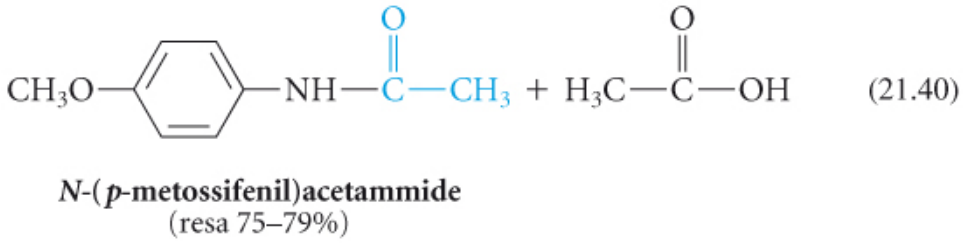
(21.24)

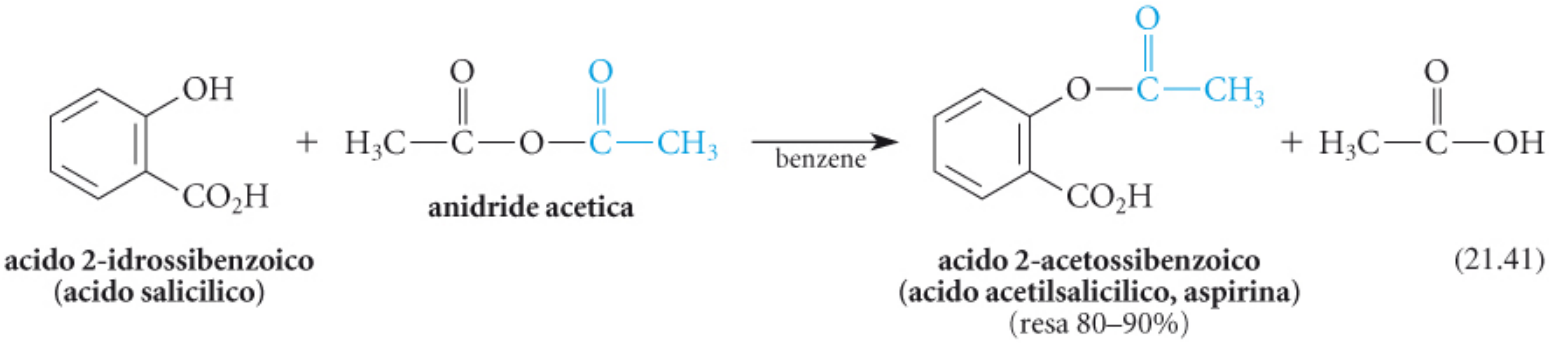
Ammide da estere



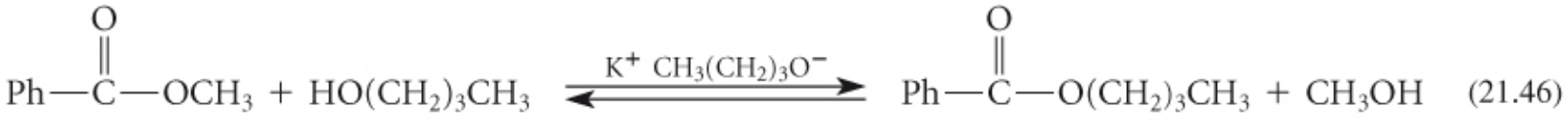
Estere ed ammide da anidride







TRANSESTERIFICAZIONE



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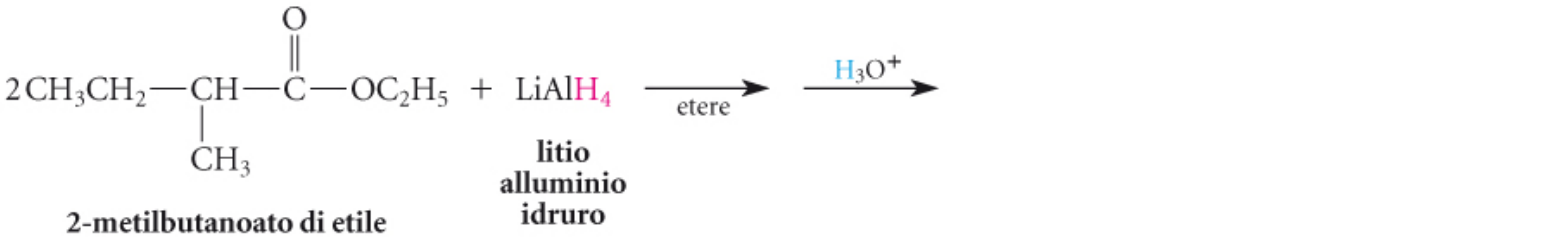
REAZIONE di RIDUZIONE



2-metilbutanoato di etile

litio alluminio idruro

etanolo

2-metil-1-butanolo
(resa 91%)

(21.47)

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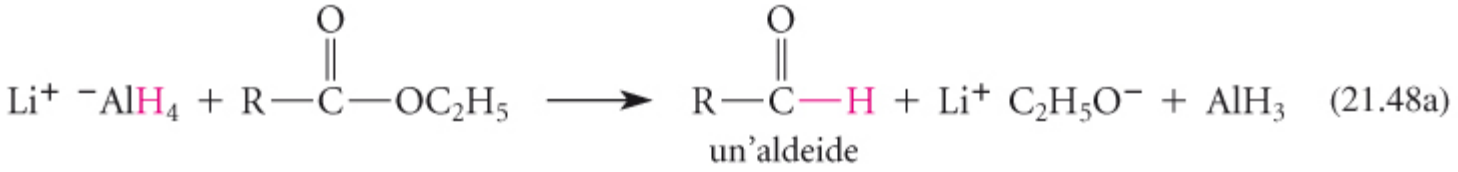
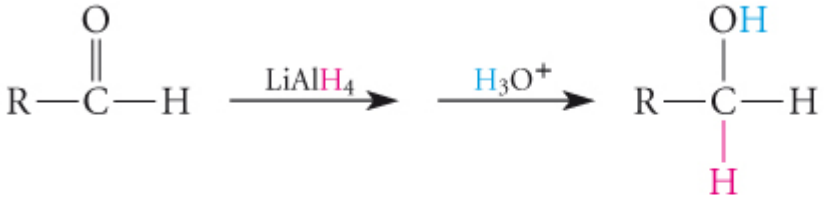
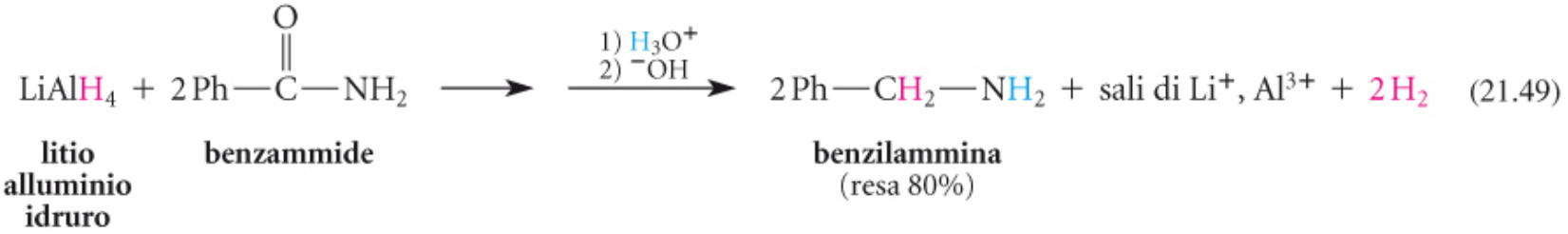


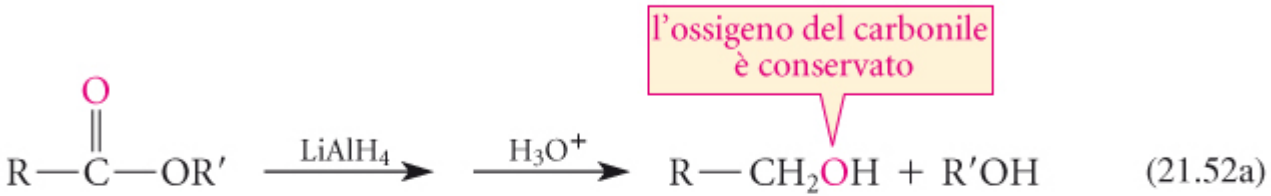
un'aldeide

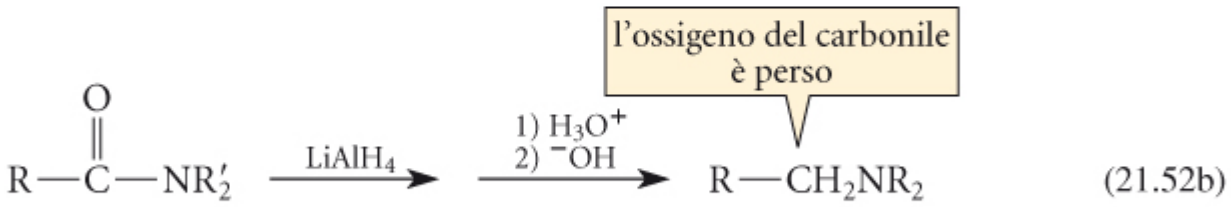
(21.48a)



(21.48b)







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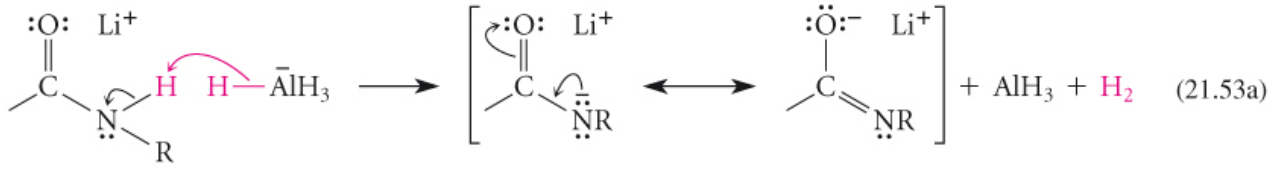
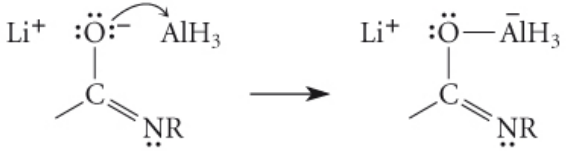
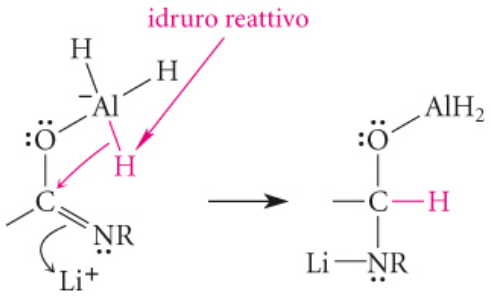


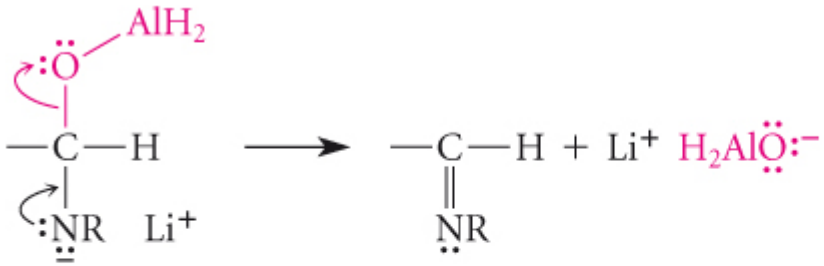
(21.53a)



(21.53b)

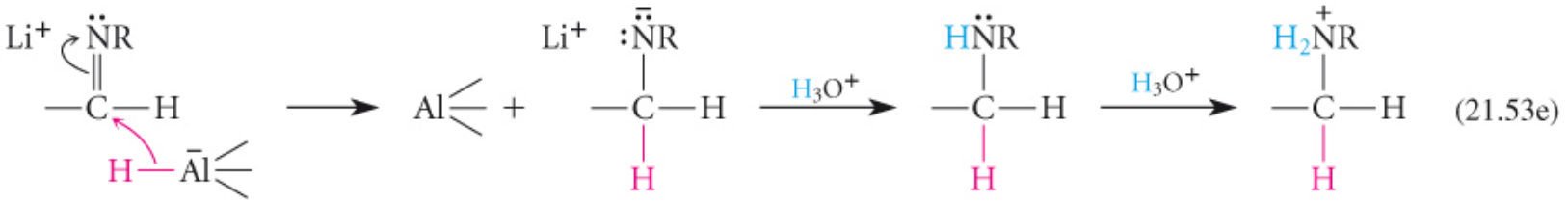


(21.53c)



un'immina

(21.53d)



(21.53e)

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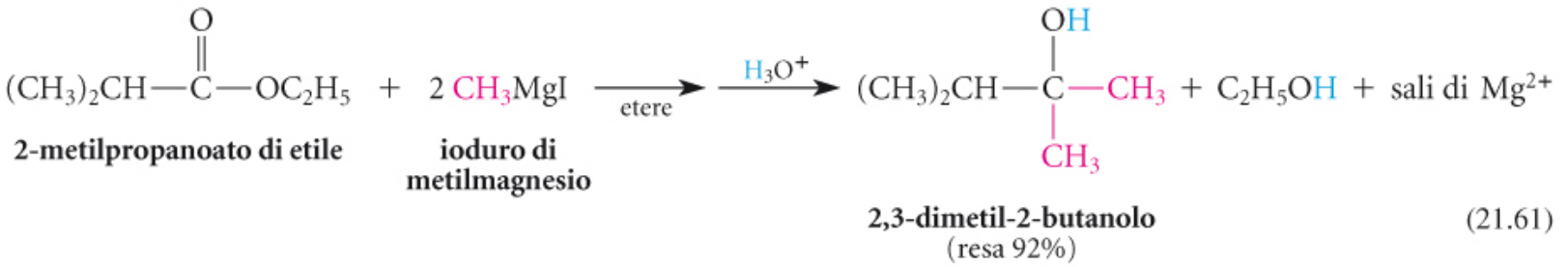
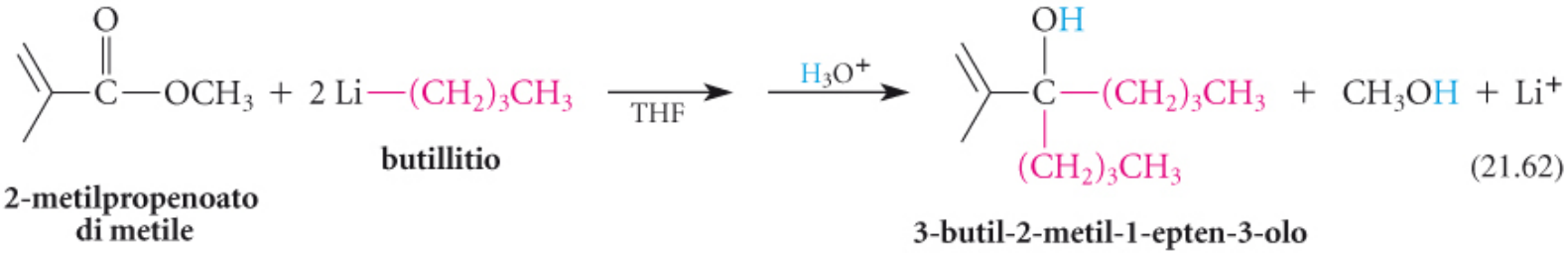
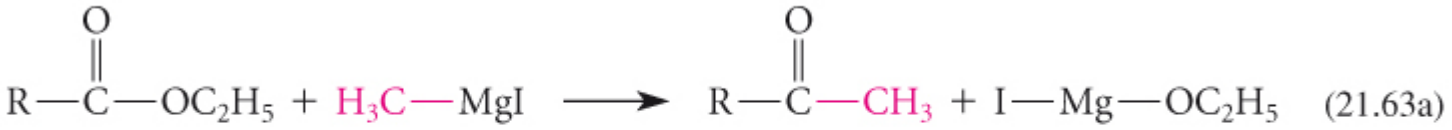
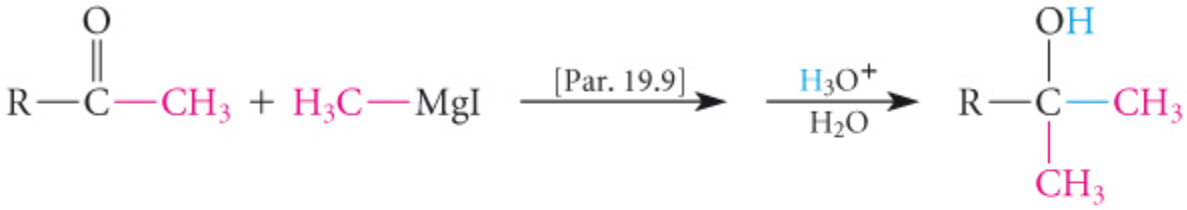
REAZIONE con REAGENTI ORGANOMETALLICI



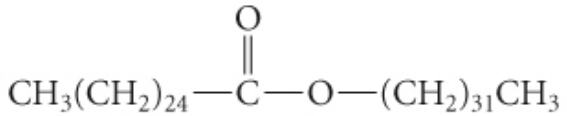




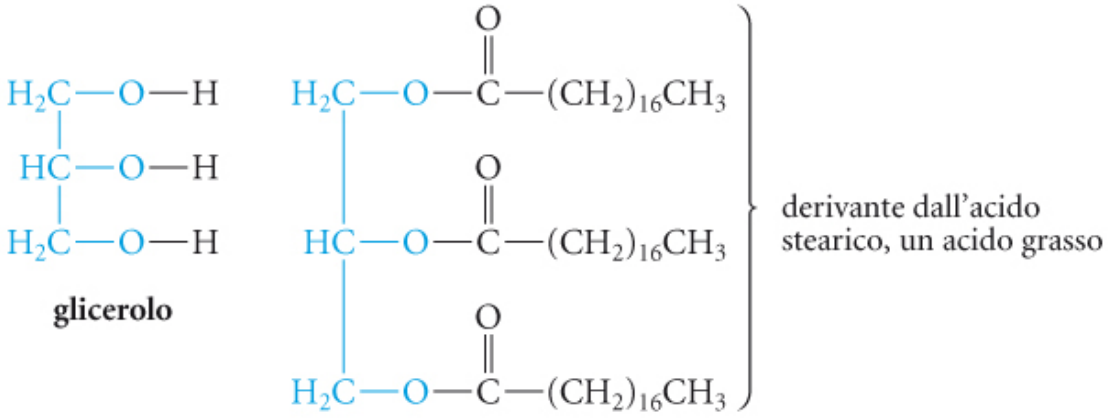


(21.63b)

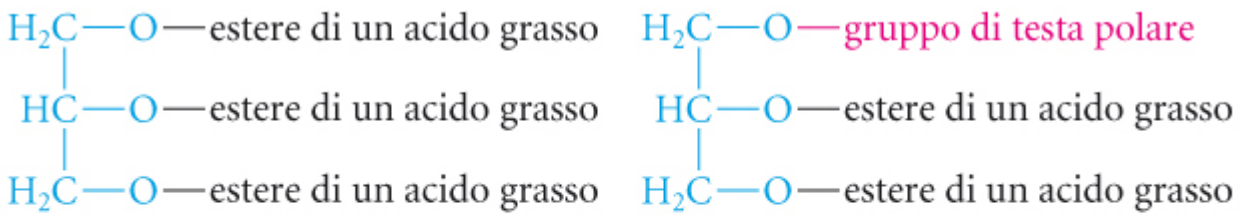
CERE, GRASSI e FOSFOLIPIDI

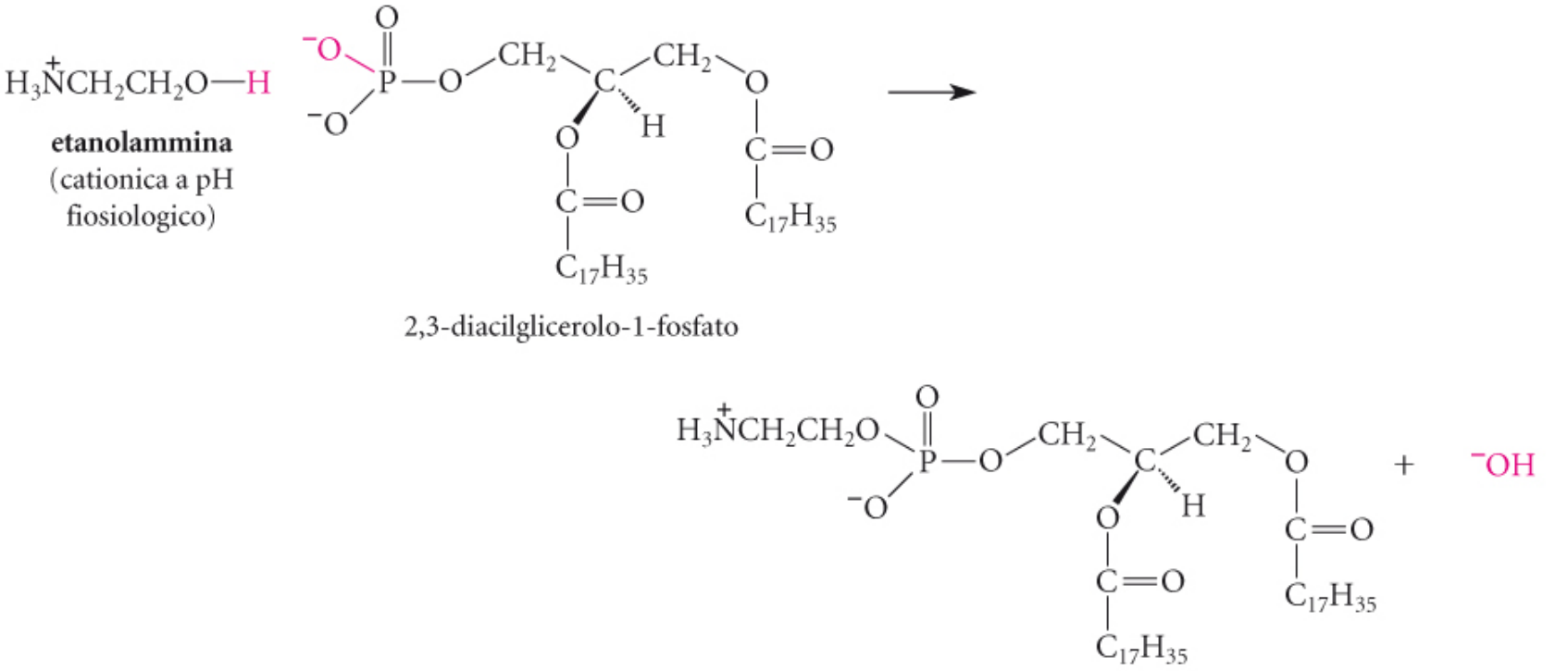


un componente della cera carnauba



tristearato di glicerile
(un tipico grasso)





(8.7)