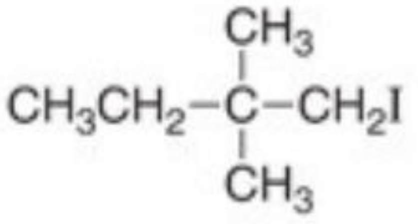
Gruppi funzionali

Alogenuri alchilici o Alogenoalcani

Alogenoalcani

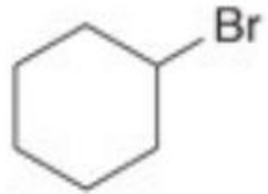
- Sono composti contenenti un atomo di alogeno legato covalentemente ad un atomo di carbonio ibridato sp^3
- Hanno formula generale R-X (X = F, Cl, Br, I)
- Sono importanti perché spesso utilizzati quali substrati di partenza per la sintesi di alcoli, eteri, ammine ed alcheni.
- Le principali reazioni di questi composti sono reazioni di:
  - **sostituzione nucleofila**
  - **β-eliminazione**

Alogenoalcani o alogenuri alchilici

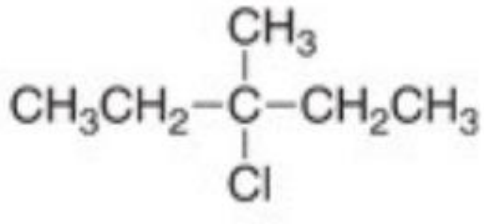


$$\begin{array}{ccc} & CH_3 & \\ & | & \\ CH_3CH_2- & C & -CH_2I \\ & | & \\ & CH_3 & \end{array}$$

1-Iodo-2,2-dimetilbutano
Alogenuro alchilico primario



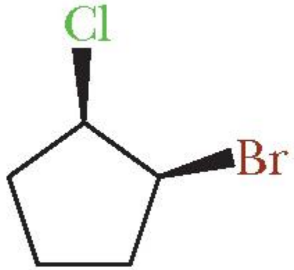
Bromocicloesano
(Cicloesil bromuro)
secondario



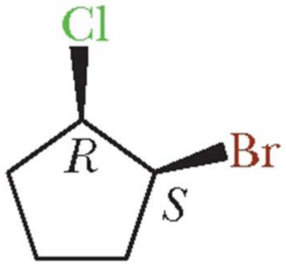
$$\begin{array}{ccc} & CH_3 & \\ & | & \\ CH_3CH_2- & C & -CH_2CH_3 \\ & | & \\ & Cl & \end{array}$$

3-cloro-3-metilpentano
terziario

negli anelli, più alogeni sono elencati e numerati in ordine alfabetico



1-Bromo-2-clorociclopentano



(1*S*,2*R*)-1-Bromo-2-clorociclopentano

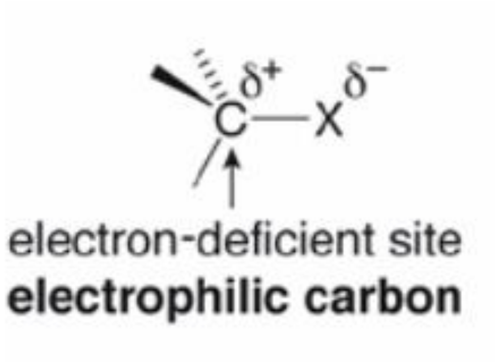
oppure

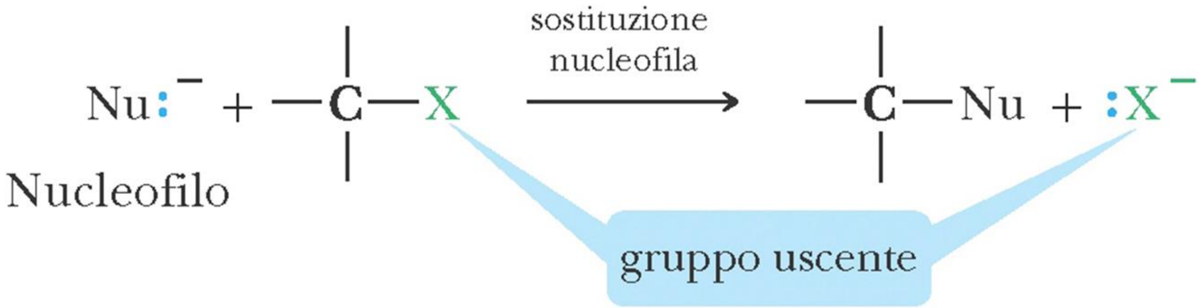
cis-1-bromo-2-clorociclopentano

Alogenoalcani o alogenuri alchilici

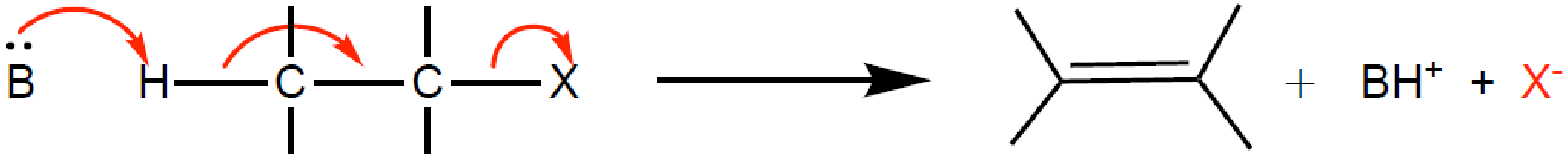
- CH_3Cl clorometano o metil cloruro (gas)
- CH_2Cl_2 diclorometano o metilencloruro o cloruro di metilene
  - Solvente clorurato più denso dell’acqua (1,33 g/mL)
- $CHCl_3$ cloroformio (o triclorometano)
  - Solvente clorurato più denso dell’acqua (1,49 g/mL)
- CCl_4 tetracloruro di carbonio
  - Solvente clorurato più denso dell’acqua (1,59 g/mL)

Polarità del legame C-X

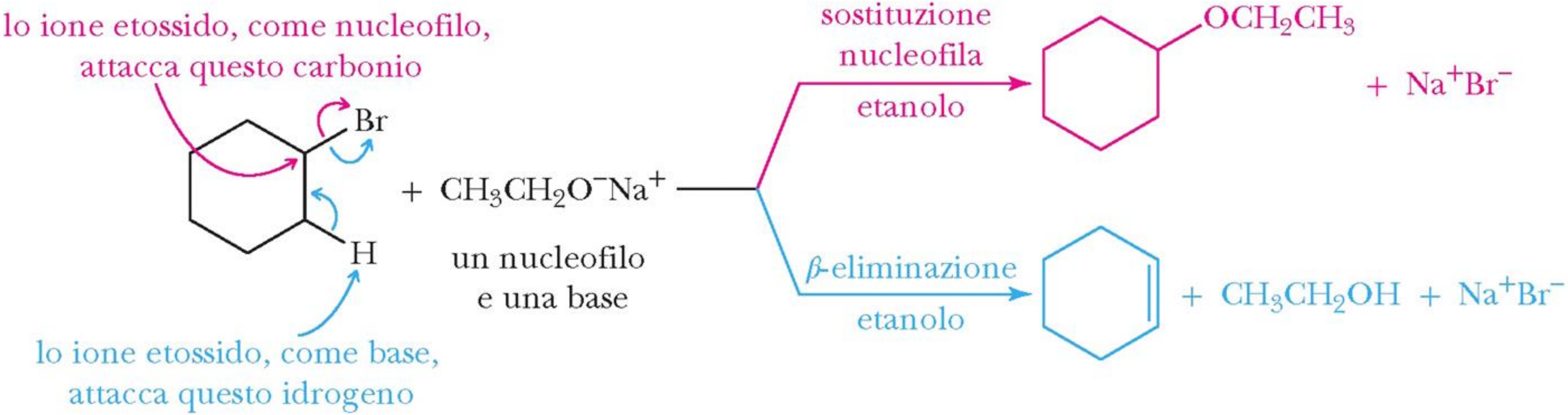




Gli alogenuri alchilici reagiscono con i nucleofili: **sostituzione nucleofila**



Gli alogenuri alchilici reagiscono con le basi di Bronsted-Lowry: **eliminazione**

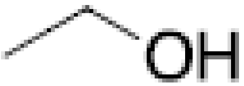


lo ione etossido, come nucleofilo, attacca questo carbonio

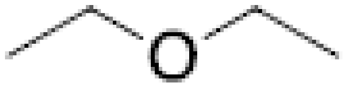
lo ione etossido, come base, attacca questo idrogeno

Alcoli, Eteri e Tioli

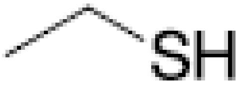
Struttura di Alcoli, Eteri e Tioli



etanolo



dietiletere



etantiolo

"tio" viene dal greco θεῖον che vuol dire zolfo

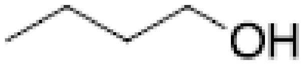
Nomenclatura degli Alcoli

CH_3-OH

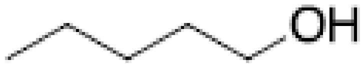
metanolo

etanolo

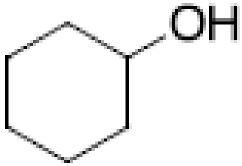
1-propanolo



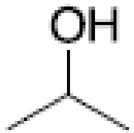
1-butanolo



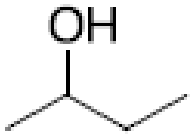
1-pentanolo



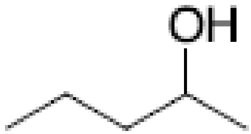
cicloesanolo



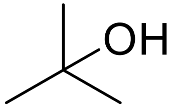
2-propanolo
(isopropanolo)



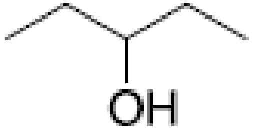
2-butanolo



2-pentanolo

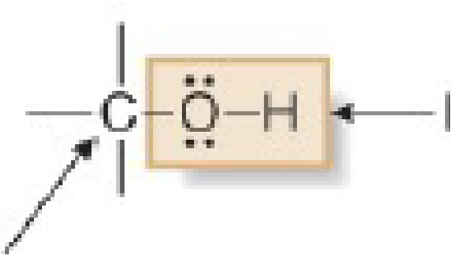


tert-butanolo
2-metil-2-propanolo



3-pentanolo

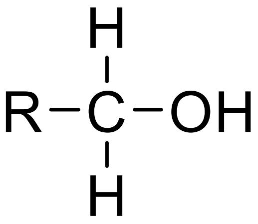
Alcoli



Gruppo ossidrilico

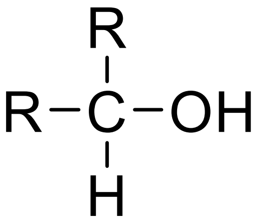
Carbonio ibridato sp^3

Classificazione degli alcoli



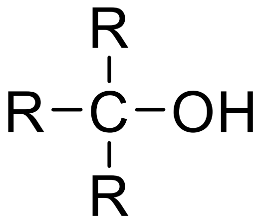
$$\mathrm{R-\overset{H}{\underset{H}{C}}-OH}$$

alcol primario
un gruppo R



$$\mathrm{R-\overset{R}{\underset{H}{C}}-OH}$$

alcol secondario
due gruppi R

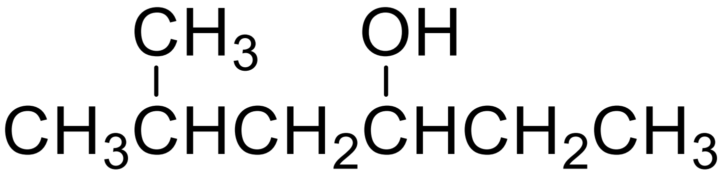


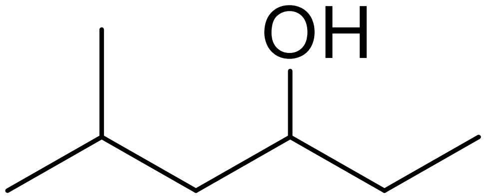
$$\mathrm{R-\overset{R}{\underset{R}{C}}-OH}$$

alcol terziario
tre gruppi R

Alcoli primari, secondari e terziari

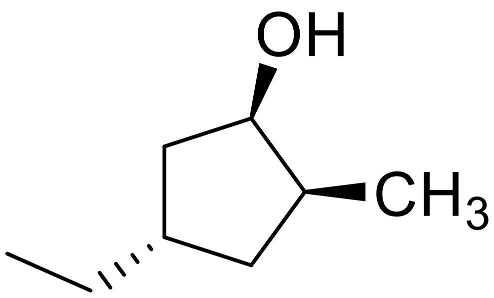
Nomenclatura degli alcoli

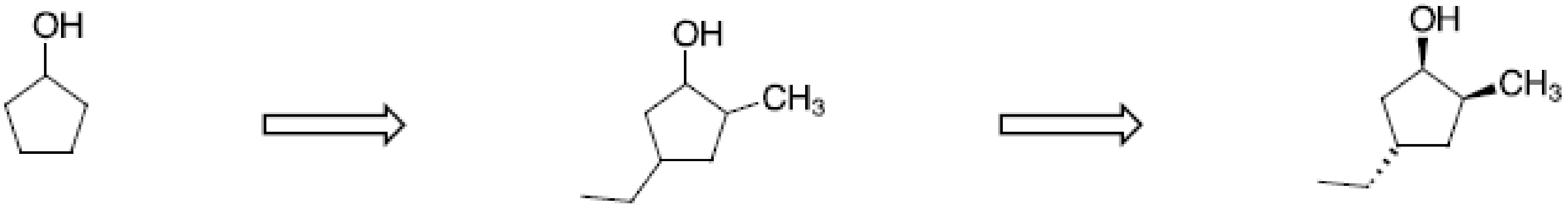

$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2\overset{\overset{OH}{|}}{C}HCH_2CH_3$



1) Trovare la catena carboniosa più lunga che contenga il gruppo ossidrilico: esano
2) Cambiare la desinenza in olo: esanolo
3) Numerare la catena in modo da assegnare al gruppo ossidrilico il numero più basso
4) Applicare le altre regole della nomenclatura

5-metil-3-esanolo





ciclopentanolo

4-etil-2-metilciclopentanolo

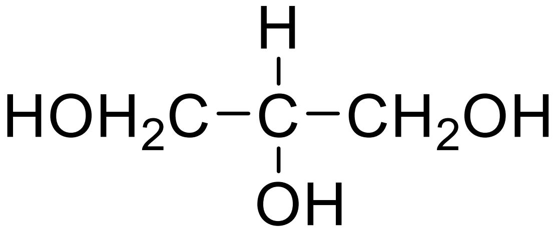
(1*R*,2*S*,4*S*)-4-etil-2-metilciclopentanolo

Nomenclatura degli alcoli

Composti con due gruppi ossidrilici sono detti dioli o glicoli.
Composti con tre gruppi ossidrilici sono detti trioli

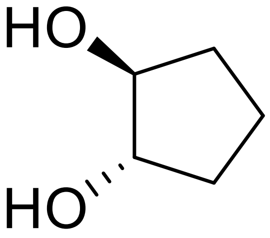
$HOCH_2CH_2OH$

Glicol etilenico
1,2-etandiolo



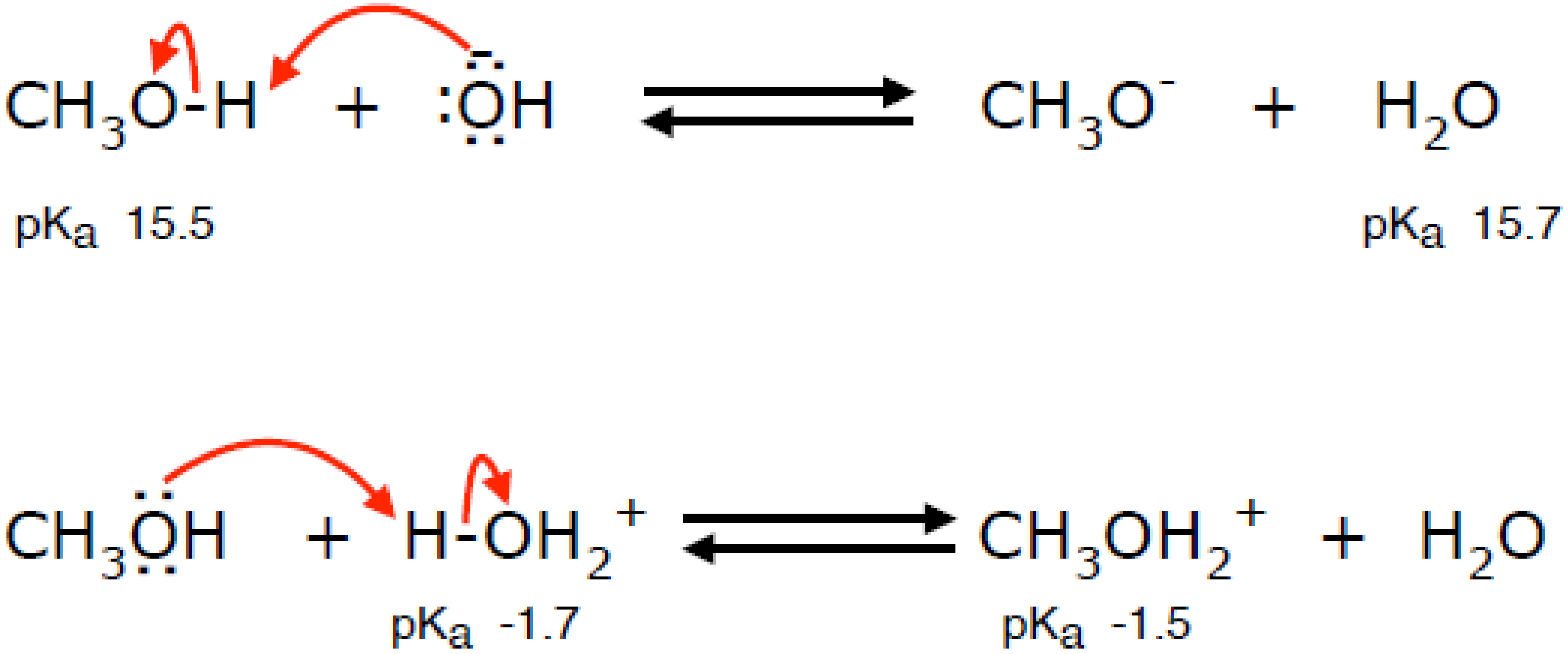
$$HOH_2C-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-CH_2OH$$

Glicerolo o glicerina
1,2,3-propantriolo



trans 1,2-ciclopentandiolo

Acidità e Basicità



$$CH_3O\text{-}H + {:}\ddot{O}H^- \rightleftharpoons CH_3O^- + H_2O$$

pKa 15.5

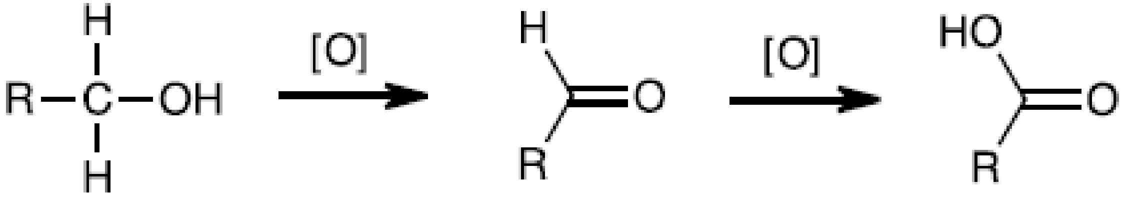
pKa 15.7

$$CH_3\ddot{O}H + H\text{-}OH_2^+ \rightleftharpoons CH_3OH_2^+ + H_2O$$

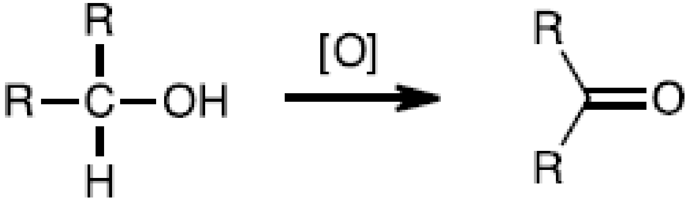
pKa -1.7

pKa -1.5

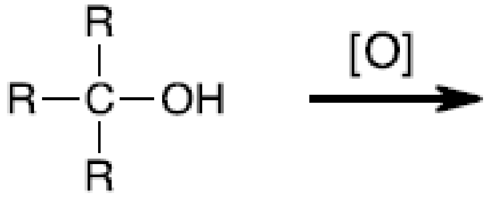
Ossidazione degli alcoli



Alcol primario viene ossidato ad aldeide e poi ad acido carbossilico

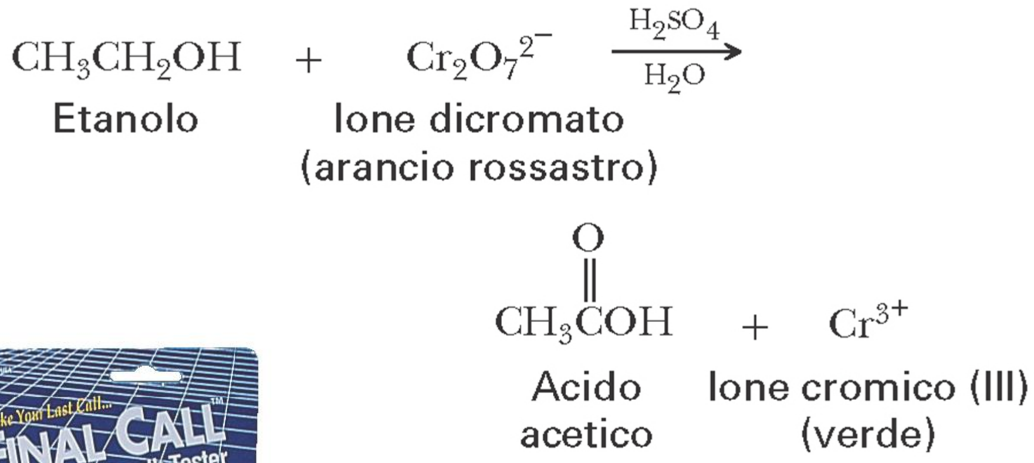


Alcol secondario viene ossidato a chetone



Alcol terziario non dà nessuna reazione

Alcol test



$$CH_3CH_2OH + Cr_2O_7^{2-} \xrightarrow[H_2O]{H_2SO_4} CH_3\overset{\overset{\Large O}{\|}}{C}OH + Cr^{3+}$$

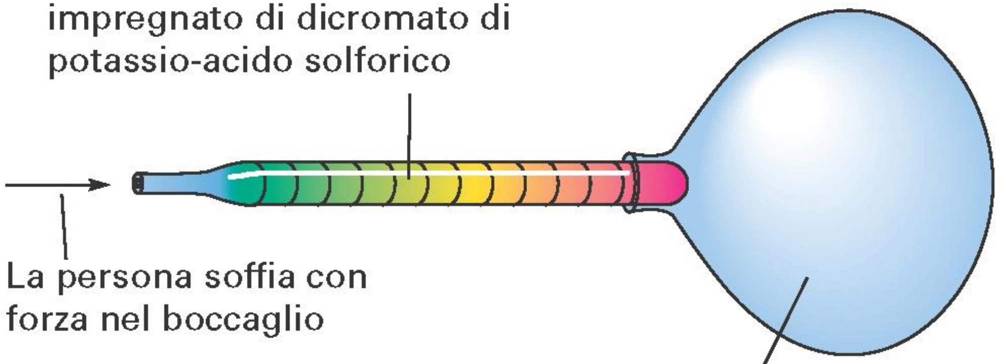
Etanolo

Ione dicromato
(arancio rossastro)

Acido
acetico

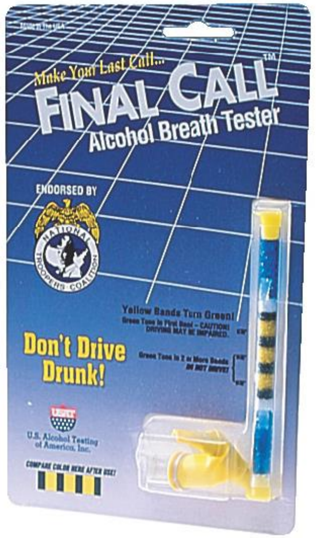
Ione cromico (III)
(verde)

Tubo di vetro contenente gel di silice
impregnato di dicromato di
potassio-acido solforico



La persona soffia con
forza nel boccaglio

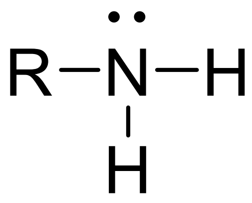
Nel momento in cui la persona
soffia, il palloncino si gonfia



Charles D. Winters

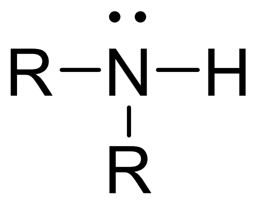
Ammine

Introduzione



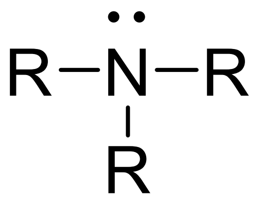
$\mathrm{R-\underset{\underset{H}{|}}{\ddot{N}}-H}$

ammina primaria



$\mathrm{R-\underset{\underset{R}{|}}{\ddot{N}}-H}$

ammina secondaria



$\mathrm{R-\underset{\underset{R}{|}}{\ddot{N}}-R}$

ammina terziaria

Azoto legato ad un solo gruppo alchilico

Azoto legato due gruppi alchilici

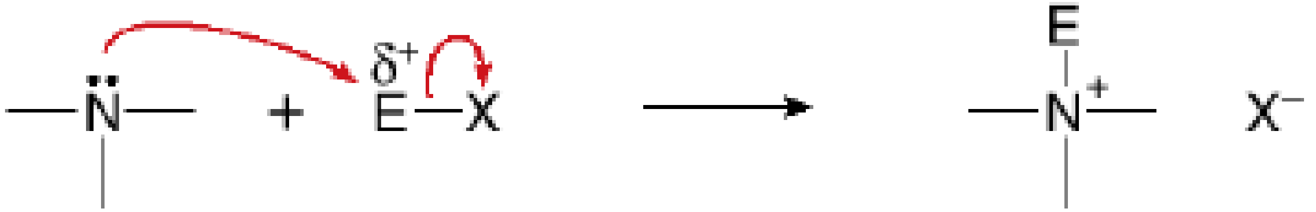
Azoto legato a tre gruppi alchilici

Ammine

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

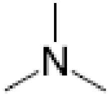
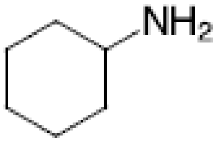
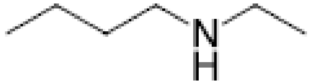
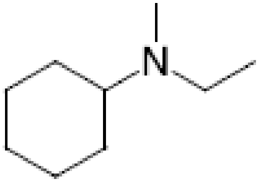
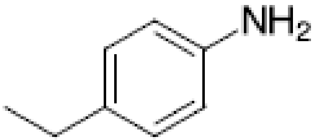
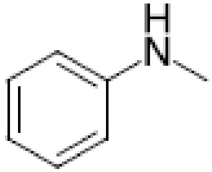
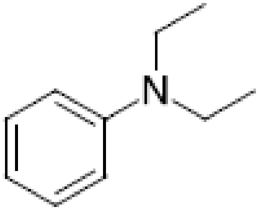
Reazione come base

Reazione come nucleofilo

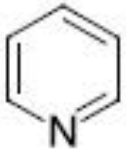


La chimica delle ammine si basa sulla presenza del doppietto non condiviso sull’azoto

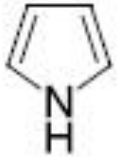
Nomenclatura

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

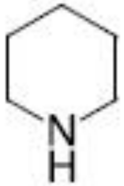
Ammine eterocicliche



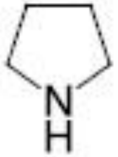
piridina



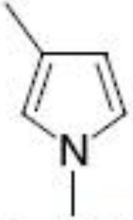
pirrolo



piperidina

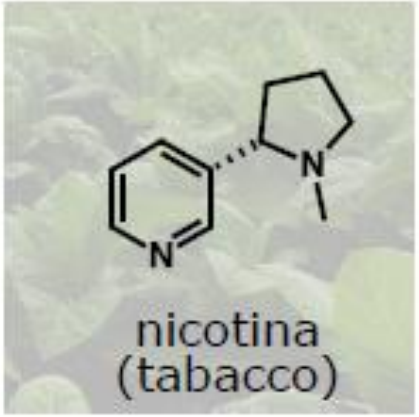


pirrolidina

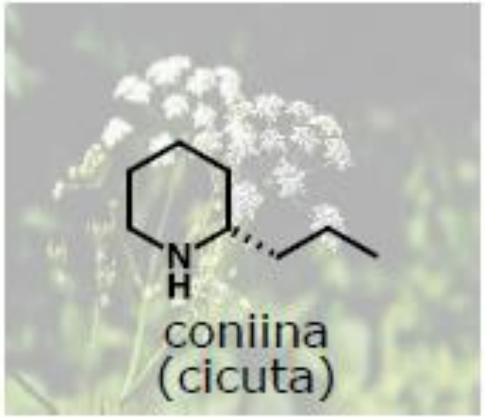


1,3-dimetilpirrolo

alcaloidi

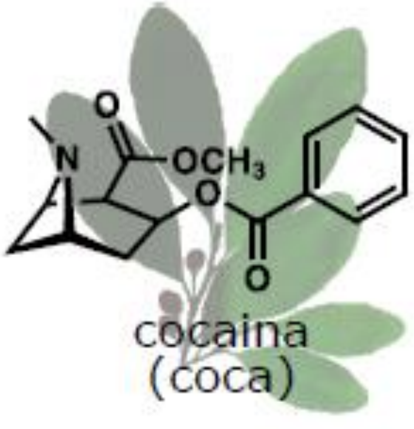


nicotina
(tabacco)



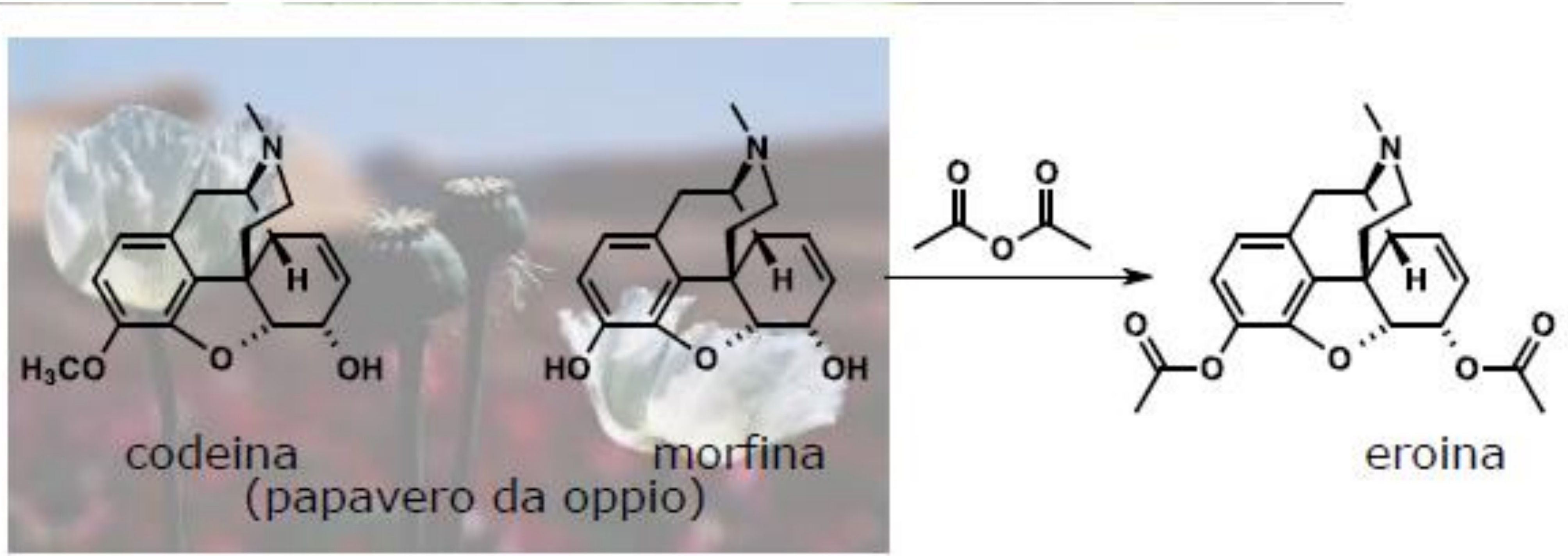
coniina
(cicuta)

stricnina
(noce vomica)



cocaina
(coca)

Ammine eterocicliche

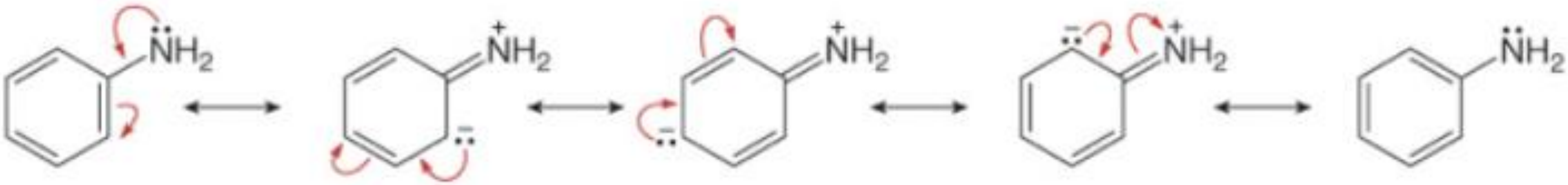


Basicità delle ammine

- 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

$CH_3CH_2-\ddot{N}H_2$ ← **The electron pair is localized on the N atom.**

$CH_3CH_2NH_3^+$: pK_a 10.8



The electron pair is delocalized on the benzene ring.

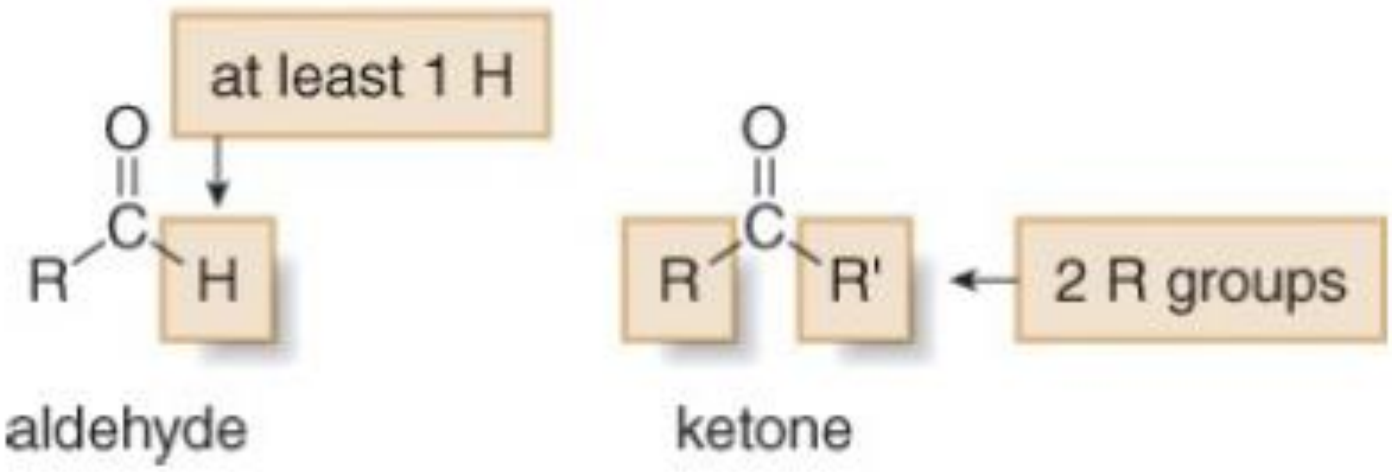
$C_6H_5NH_3^+$: pK_a 4.6

Le ammine in presenza di un acido si protonano

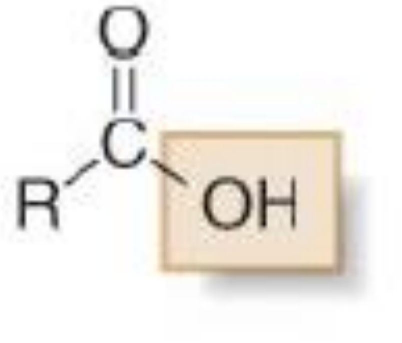
Aldeidi e chetoni

Introduzione

- Contengono il gruppo carbonilico come gruppo funzionale
- Aldeidi: hanno un idrogeno legato al gruppo carbonilico
- Chetoni: hanno due gruppi alchilici legati al carbonile

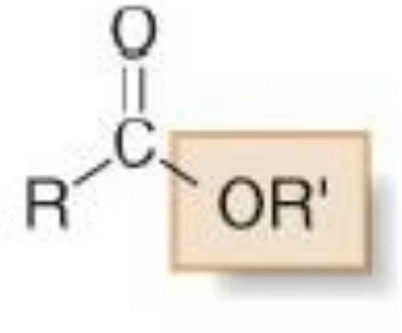


Altri gruppi funzionali che contengono il gruppo carbonilico

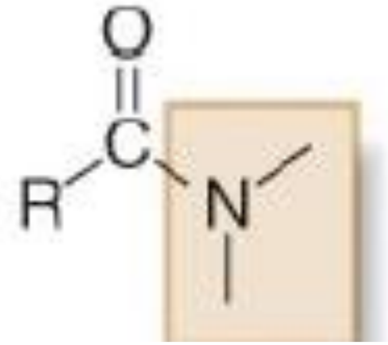


Acidi carbossilici

Alogenuri acilici

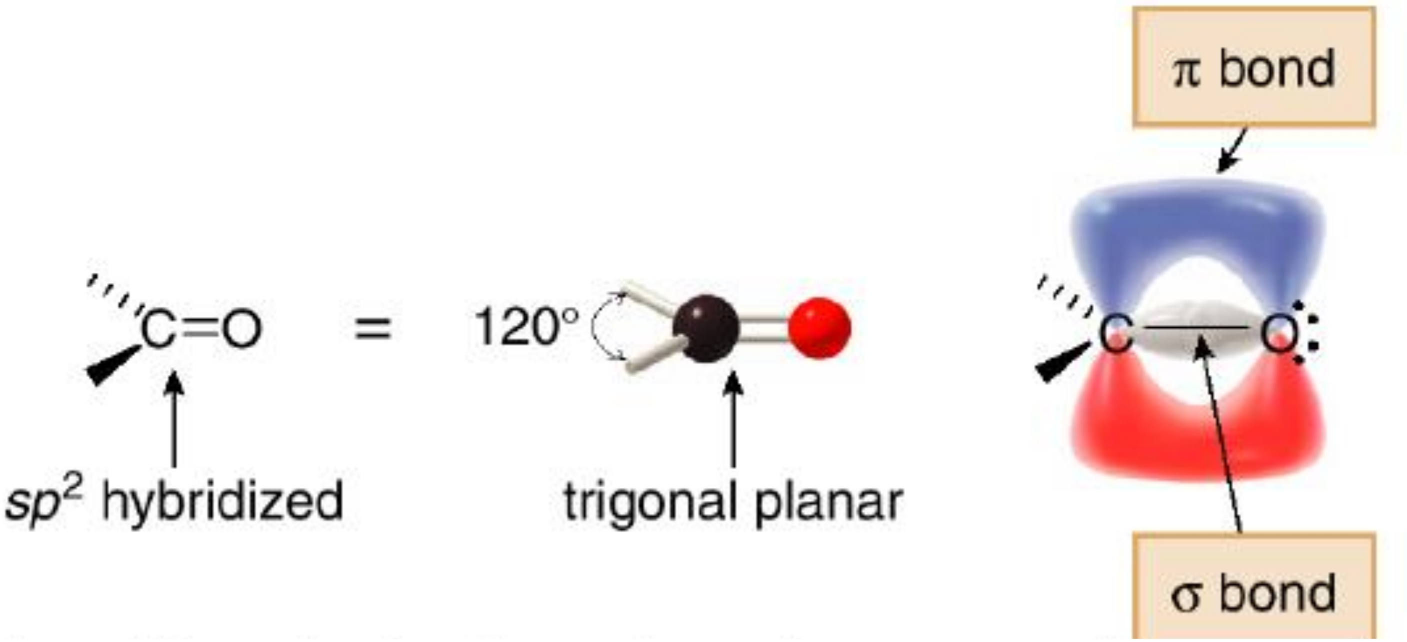


Esteri

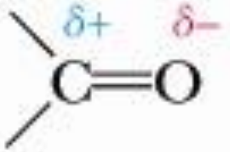


Ammidi

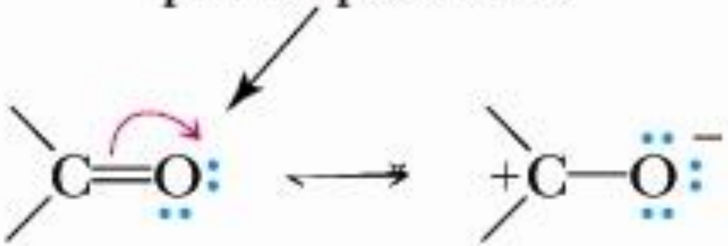
Struttura del gruppo carbonilico



Struttura del gruppo carbonilico



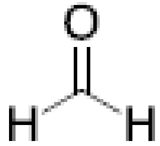
Polarità del gruppo carbonilico


la struttura limite più importante

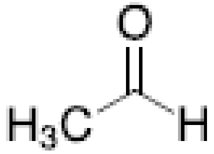
Un gruppo carbonilico come ibrido di risonanza

Nomenclatura delle aldeidi

- Trova la catena più lunga contenente il gruppo CHO
- Cambia la *-o* finale del nome dell’alcano con il suffisso *-ale*
- Se il gruppo CHO è legato ad un anello, nomina l’anello e aggiungi il suffisso *-carbaldeide*

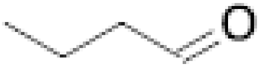


Metanale
formaldeide

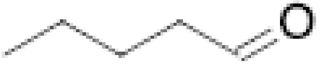


Etanale
acetaldeide

propanale
propionaldeide

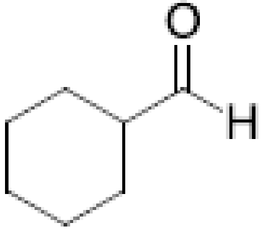


Butanale
butirraldeide

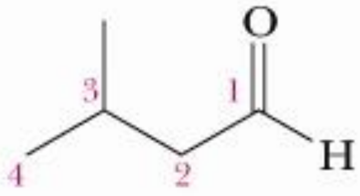


Pentanale
valeraldeide

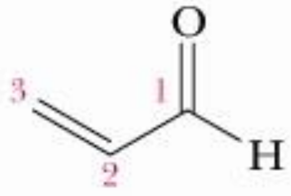
Esanale



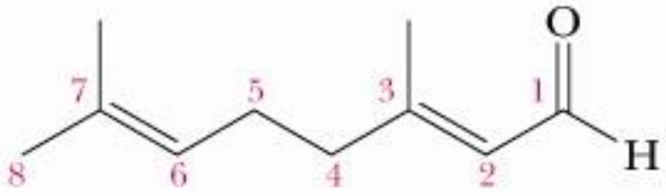
cicloesancarbaldeide



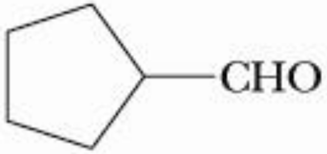
3-Metilbutanale



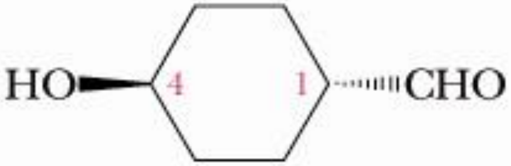
2-Propenale
(Acroleina)



(2E)-3,7-Dimetil-2,6-ottadienale
(Geraniale)



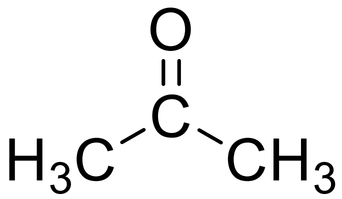
Ciclopentancarbaldeide



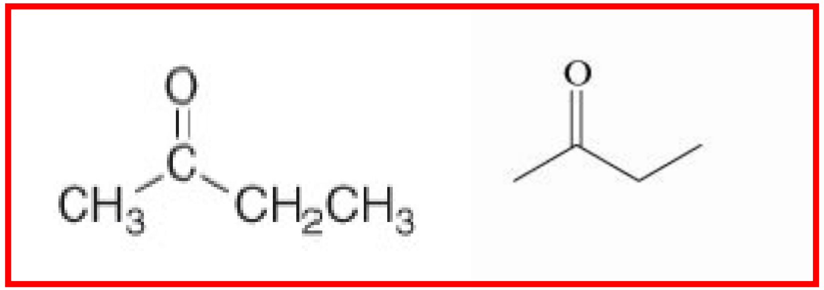
trans-4-Idrossicicloesancarbaldeide

Nomenclature dei chetoni

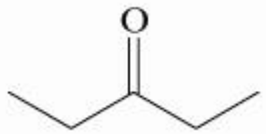
- Trova la catena più lunga contenente il gruppo -CO
- Cambia la *-o* finale del nome dell’alcano con il suffisso *–one* e aggiungi davanti al nome il numero (più basso possibile) del carbonio che porta il doppio legame con l’ossigeno.



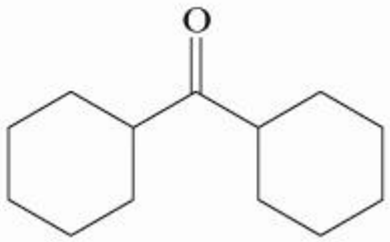
Acetone



2-butanone
metiletilchetone

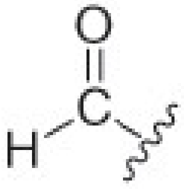


3-pentanone
dietilchetone

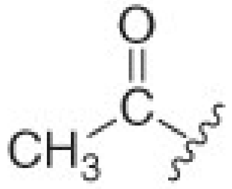


dicicloesilchetone

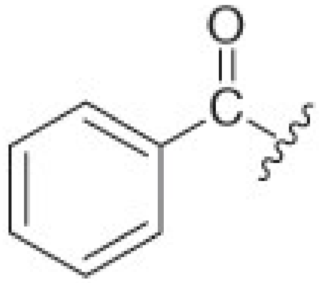
Residui contenenti il C=O



formile

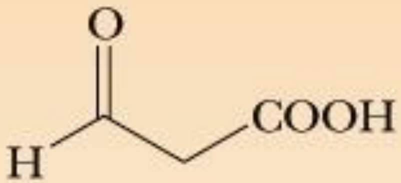
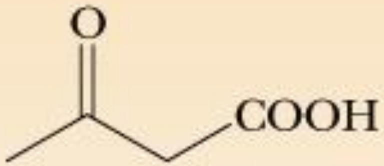
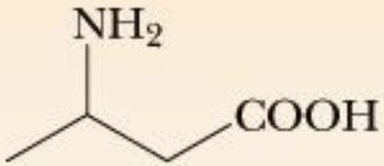


acetile



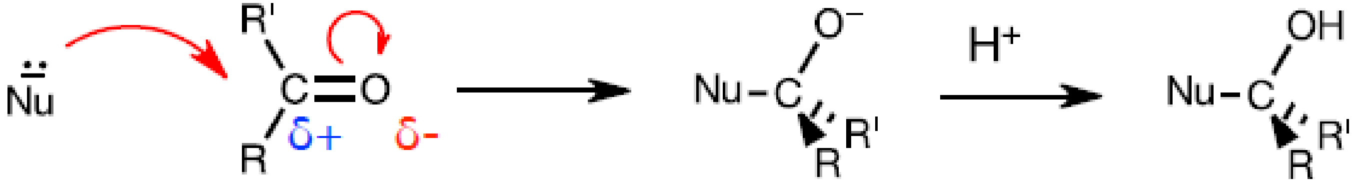
benzoile

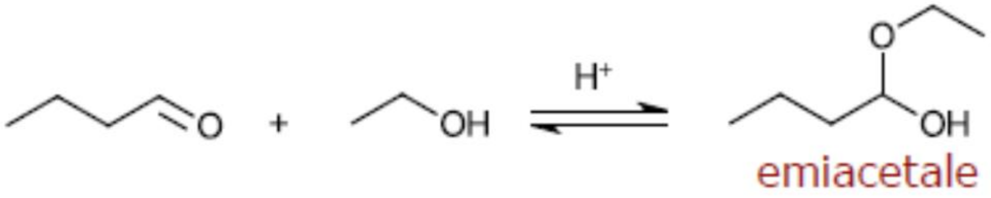
TABELLA 13.1 Ordine di precedenza di sei gruppi funzionali

Gruppo funzionale	Suffisso	Prefisso	Esempio di quando il gruppo funzionale ha una priorità più bassa	
Gruppo carbossilico	acido -oico	—		
Gruppo aldeidico	-ale	osso-	Acido 3-ossopropanoico	
Gruppo chetonico	-one	osso-	Acido 3-ossobutanoico	
Gruppo alcolico	-olo	idrossi-	Acido 4-idrossibutanoico	
Gruppo amminico	-ammina	ammino-	Acido 3-amminobutanoico	
Gruppo solfidrilico	-tiolo	mercapto-	2-Mercaptoetanolo	

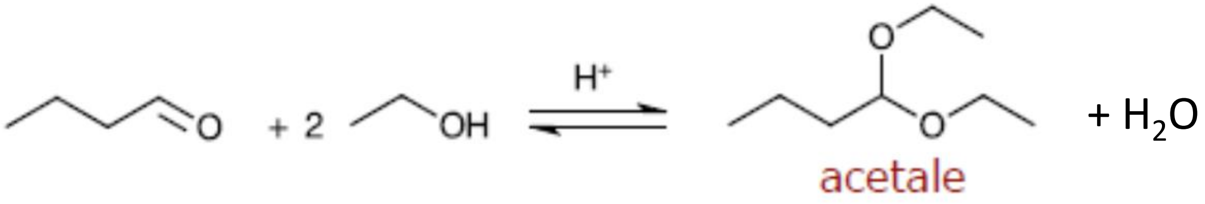
Addizione Nucleofila al Carbonile

buoni nucleofili:



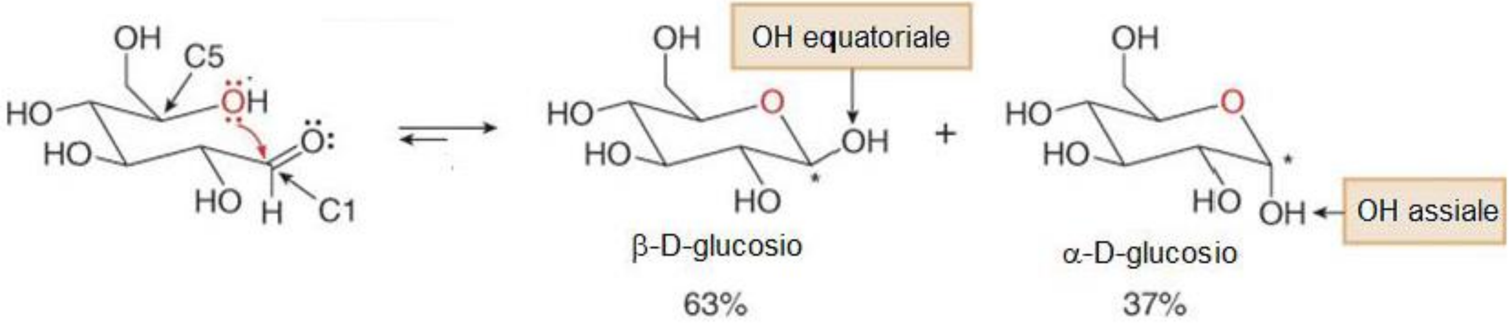


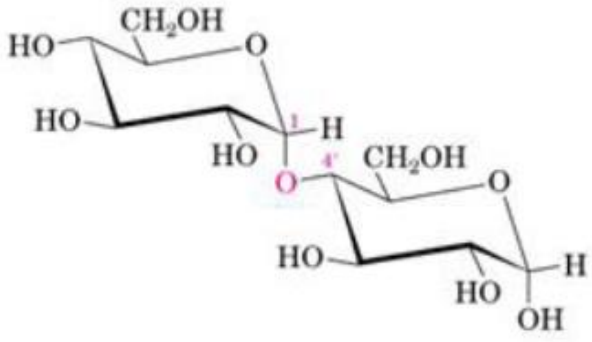
da aldeidi:



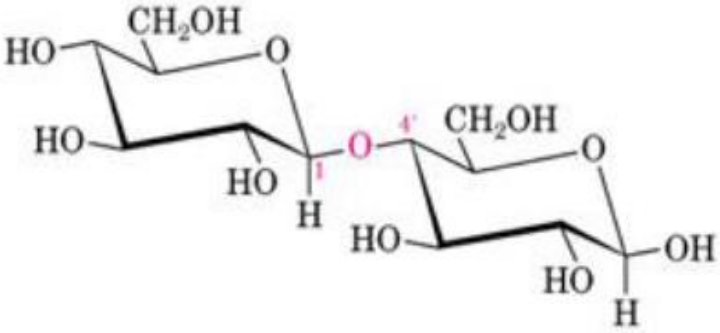
Carboidrati (Zuccheri)

- I carboidrati, comunemente chiamati zuccheri, sono poliidrossi aldeidi e chetoni
- Molti carboidrati contengono acetali ciclici o emiacetali. Esempi sono il glucosio, il maltosio e il cellobiosio.





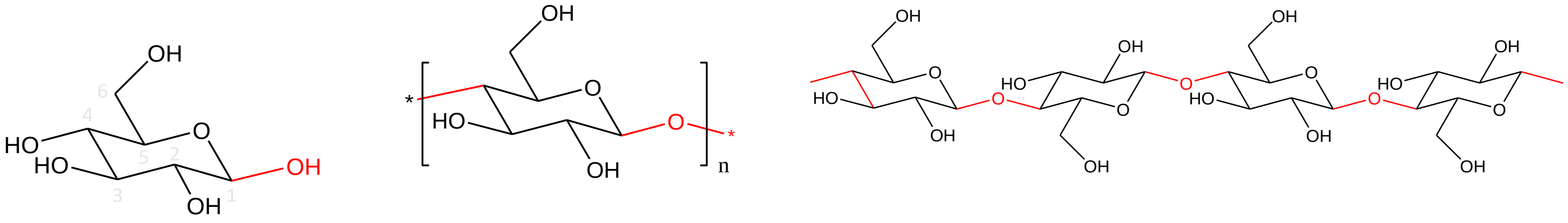
Maltosio, un 1,4′-α-glicoside
[4-*O*-(α-D-glucopiranosil)-α-D-glucopiranosio]



Cellobiosio, un 1,4′-β-glicoside
[4-*O*-(β-D-glucopiranosil)-β-D-glucopiranosio]

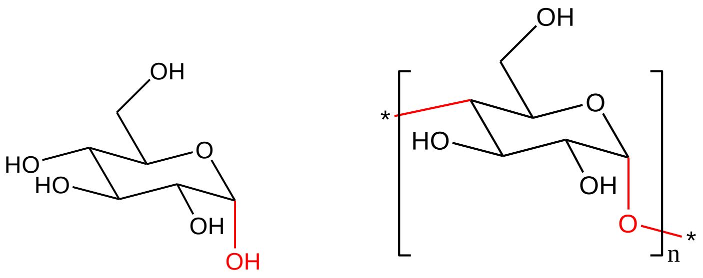
Polisaccaridi

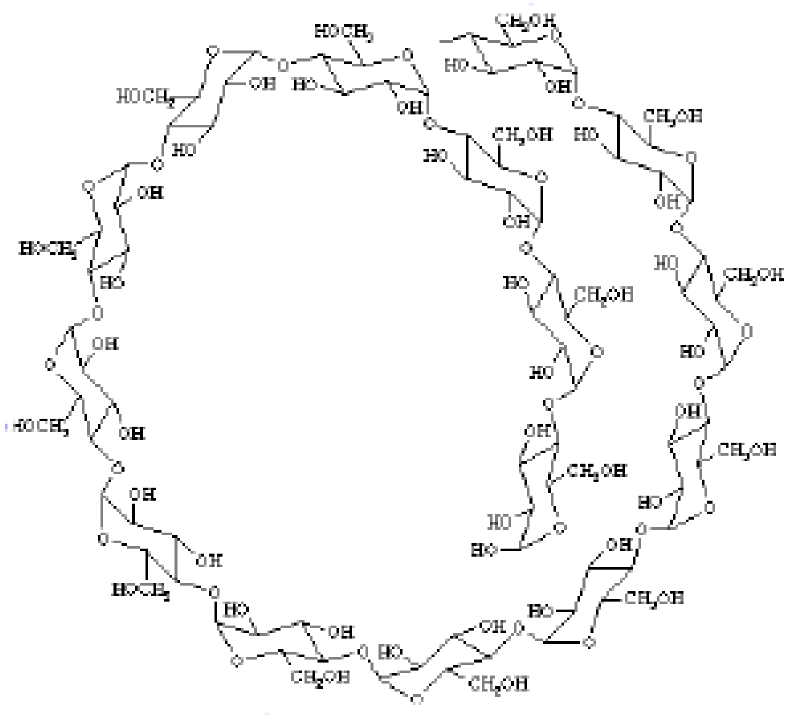
Cellulosa



Polimero del β-D-glucosio

Amido

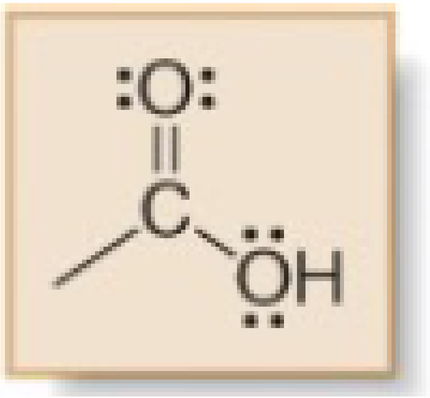


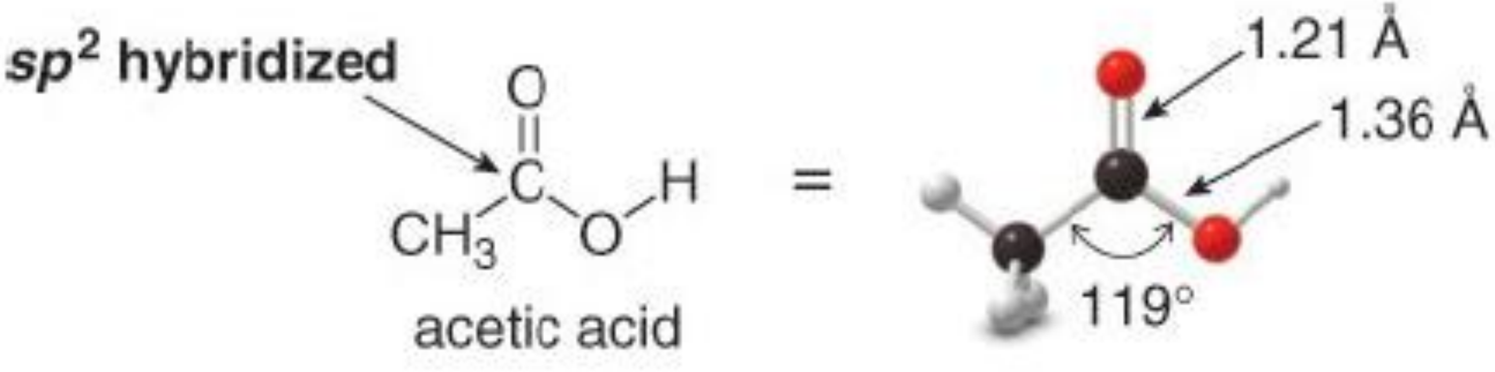


Polimero dell’α-D-glucosio

Acidi Carbossilici e Derivati

Gruppo carbossilico



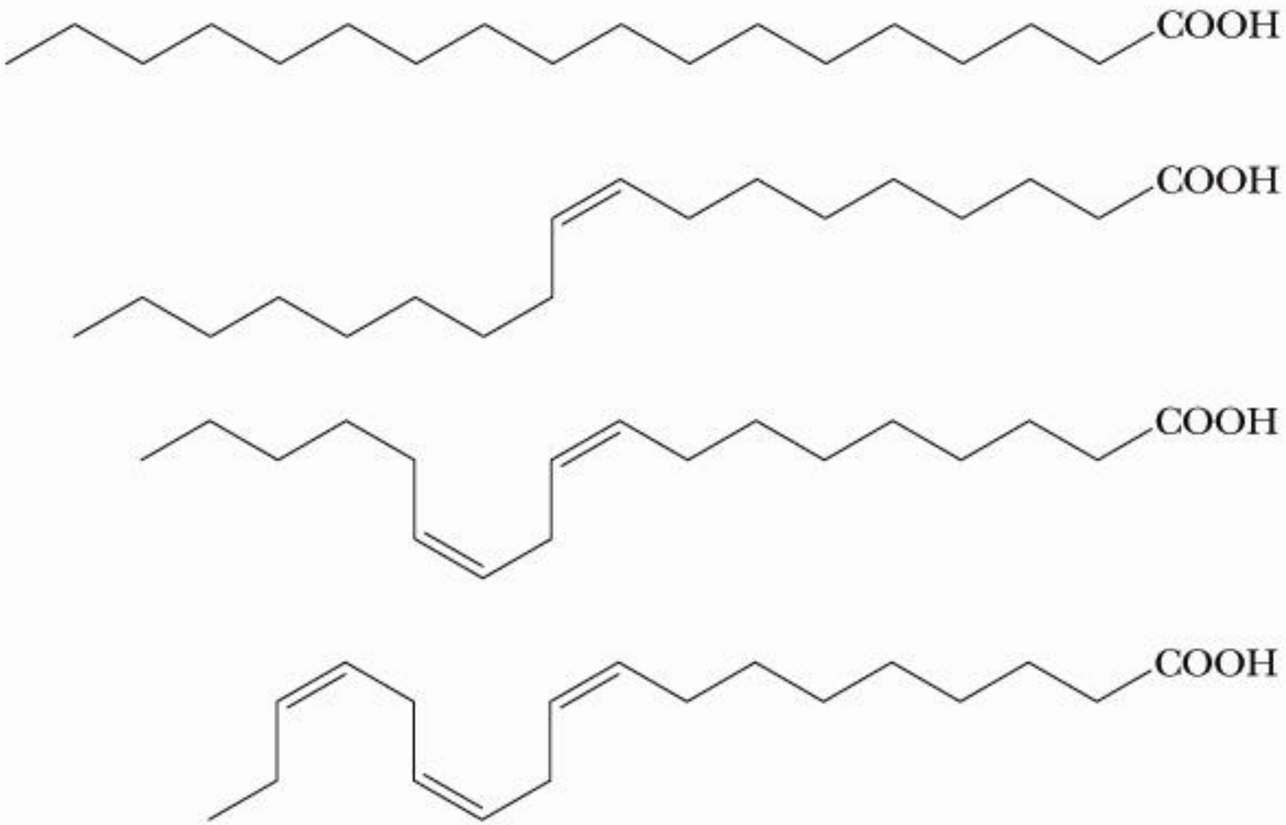


acetic acid

TABELLA 14.1 Alcuni acidi carbossilici alifatici e i loro nomi comuni

Struttura	Nome IUPAC	Nome comune	Derivazione
$HCOOH$	acido metanoico	acido formico	Latino: *formica*, formica
CH_3COOH	acido etanoico	acido acetico	Latino: *acetum*, aceto
CH_3CH_2COOH	acido propanoico	acido propionico	Greco: *propion*, primo grasso
$CH_3(CH_2)_2COOH$	acido butanoico	acido butirrico	Latino: *butyrum*, burro
$CH_3(CH_2)_3COOH$	acido pentanoico	acido valerianico	Latino: *valere*, esser forte
$CH_3(CH_2)_4COOH$	acido esanoico	acido caproico	Latino: *caper*, capra
$CH_3(CH_2)_6COOH$	acido ottanoico	acido caprilico	Latino: *caper*, capra
$CH_3(CH_2)_8COOH$	acido decanoico	acido caprico	Latino: *caper*, capra
$CH_3(CH_2)_{10}COOH$	acido dodecanoico	acido laurico	Latino: *laurus*, lauro
$CH_3(CH_2)_{12}COOH$	acido tetradecanoico	acido miristico	Greco: *myristikos*, fragrante
$CH_3(CH_2)_{14}COOH$	acido esadecanoico	acido palmitico	Latino: *palma*, albero di palma
$CH_3(CH_2)_{16}COOH$	acido ottadecanoico	acido stearico	Greco: *stear*, grasso solido
$CH_3(CH_2)_{18}COOH$	acido eicosanoico	acido arachidico	Greco: *arachis*, arachide

Negli acidi grassi insaturi il doppio legame ha geometria ***cis***.
All’aumentare del numero dei doppi legami si ha un abbassamento del punto di fusione



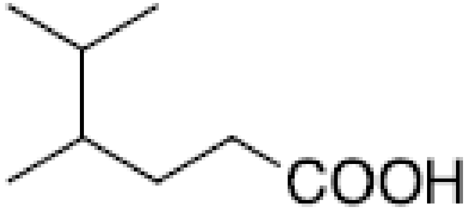
Acido stearico (18 : 0)
(p.f. 70°C)

Acido oleico (18 : 1)
(p.f. 16°C)

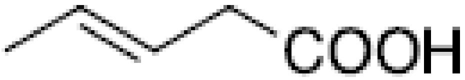
Acido linoleico (18 : 2)
(p.f. –5°C)

Acido linolenico (18 : 3)
(p.f. –11°C)

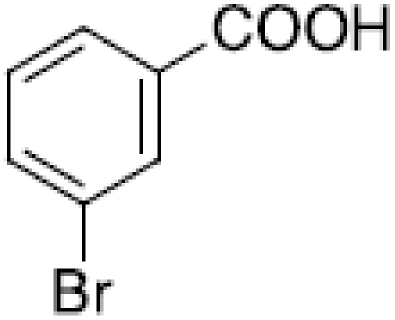
Nomenclatura degli acidi carbossilici



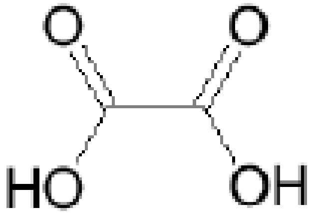
Acido 4,5-dimetilesanoico



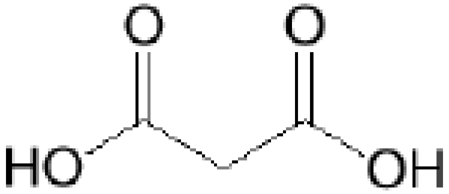
Acido 3-pentenoico



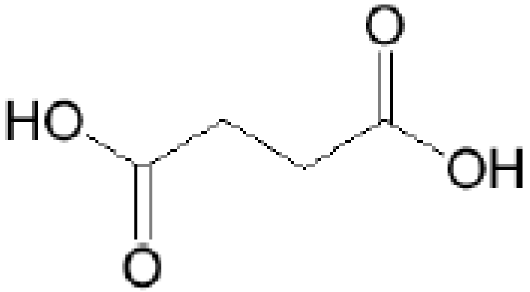
Acido 3-bromobenzoico



Acido ossalico
Acido etandioico

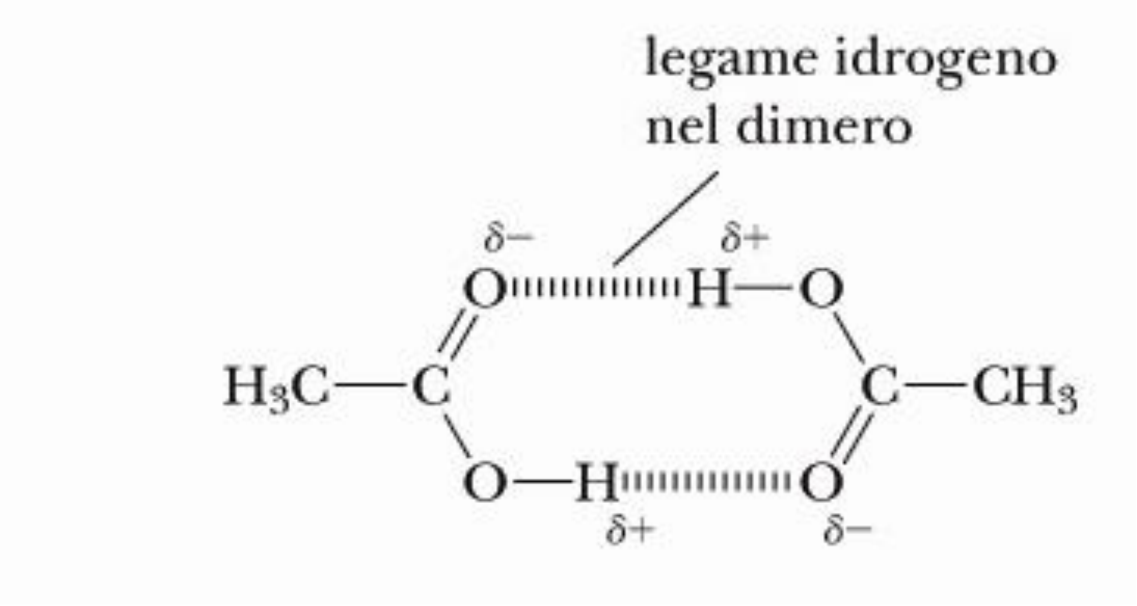


Acido malonico
Acido propandioico



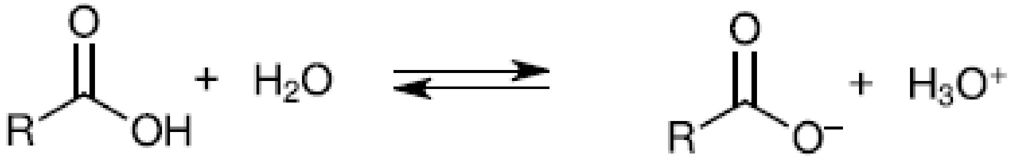
Acido succinico
Acido butandioico

Proprietà fisiche



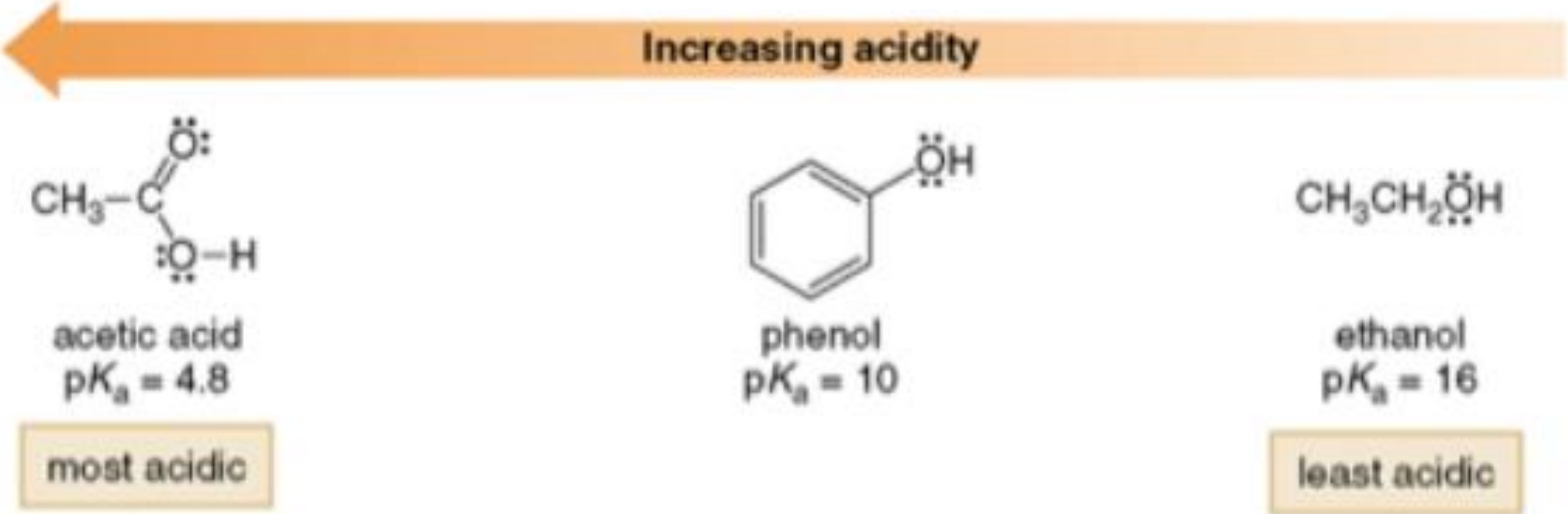
Gli acidi carbossilici si associano in dimeri tramite legami idrogeno intermolecolari

Acidità degli acidi carbossilici

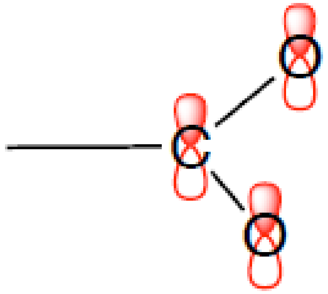


$$K_a = \frac{[RCOO^-][H_3O^+]}{[RCOOH]} = 10^{-4} \div 10^{-5}$$

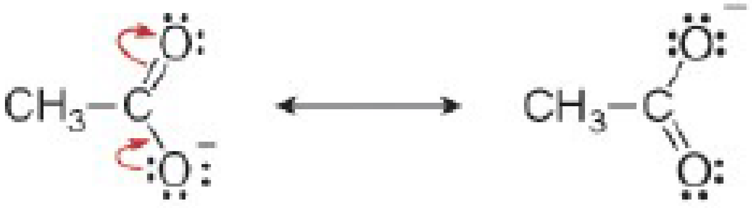
pKa = 4 ÷ 5

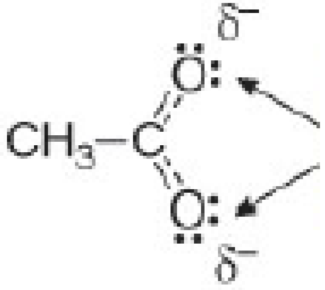


Struttura dell’anione carbossilato

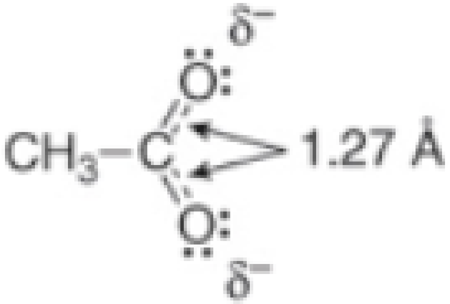


4 elettroni π delocalizzati in 3 orbitali 2p





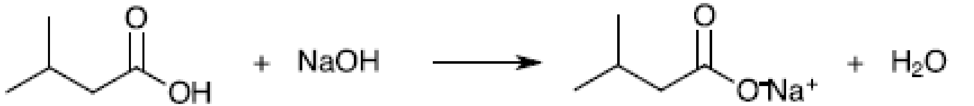
La carica
negativa è
delocalizzata
sui due
ossigeni



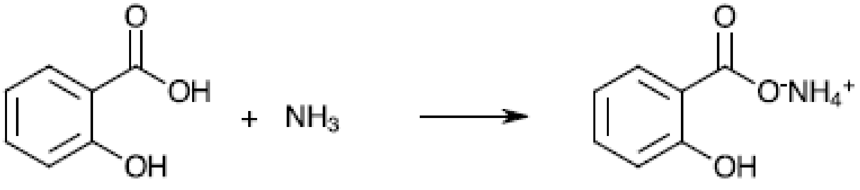
Ibrido di risonanza

REAZIONI CON BASI

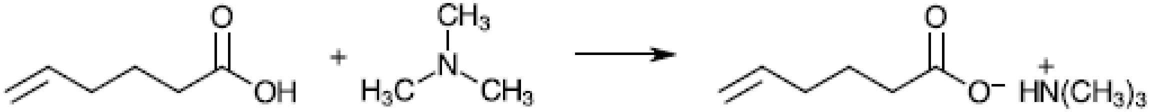
- Gli acidi carbossilici reagiscono irreversibilmente con le basi per dare i corrispondenti sali



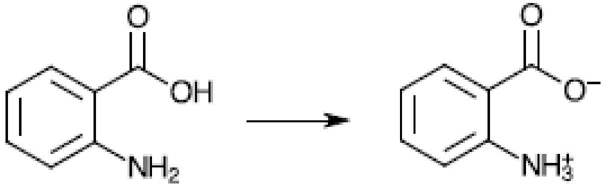
3-metilbutanoato di sodio



o-idrossibenzoato di ammonio
(salicilato di ammonio)

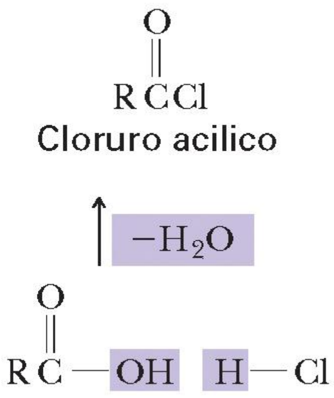


5-esenoato di trimetilammonio



sale interno

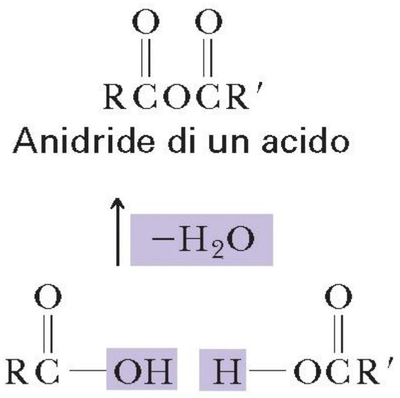
DERIVATI DEGLI ACIDI CARBOSSILICI



$$R\overset{O}{\overset{\|}{C}}Cl$$

Cloruro acilico

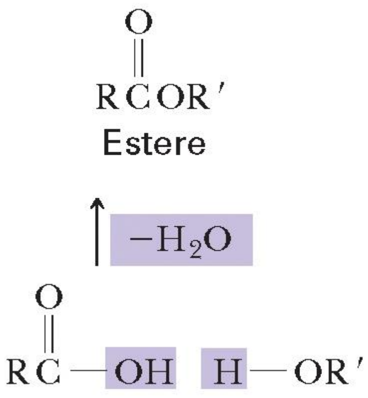
$$R\overset{O}{\overset{\|}{C}}-OH \quad H-Cl \xrightarrow{-H_2O} R\overset{O}{\overset{\|}{C}}Cl$$



$$R\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}R'$$

Anidride di un acido

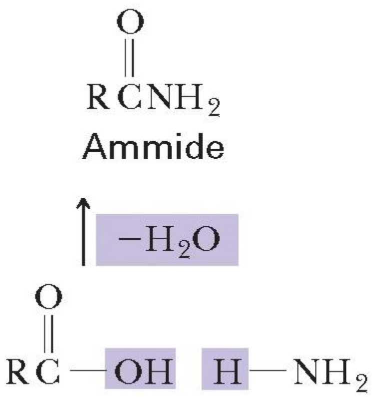
$$R\overset{O}{\overset{\|}{C}}-OH \quad H-O\overset{O}{\overset{\|}{C}}R' \xrightarrow{-H_2O} R\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}R'$$



$$R\overset{O}{\overset{\|}{C}}OR'$$

Estere

$$R\overset{O}{\overset{\|}{C}}-OH \quad H-OR' \xrightarrow{-H_2O} R\overset{O}{\overset{\|}{C}}OR'$$

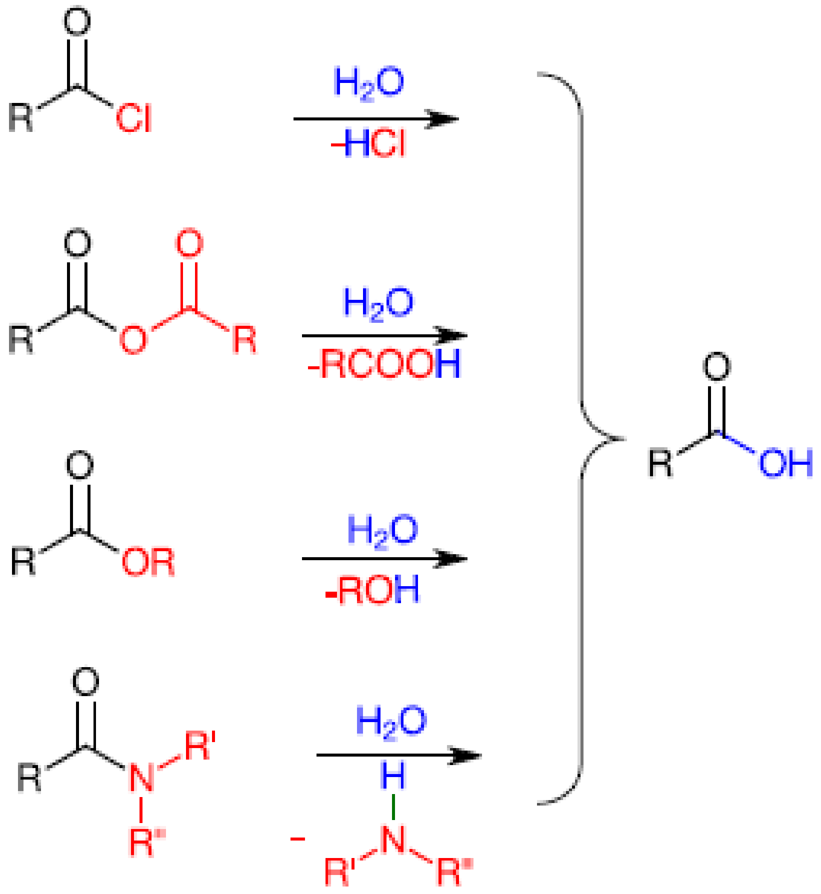


$$R\overset{O}{\overset{\|}{C}}NH_2$$

Ammide

$$R\overset{O}{\overset{\|}{C}}-OH \quad H-NH_2 \xrightarrow{-H_2O} R\overset{O}{\overset{\|}{C}}NH_2$$

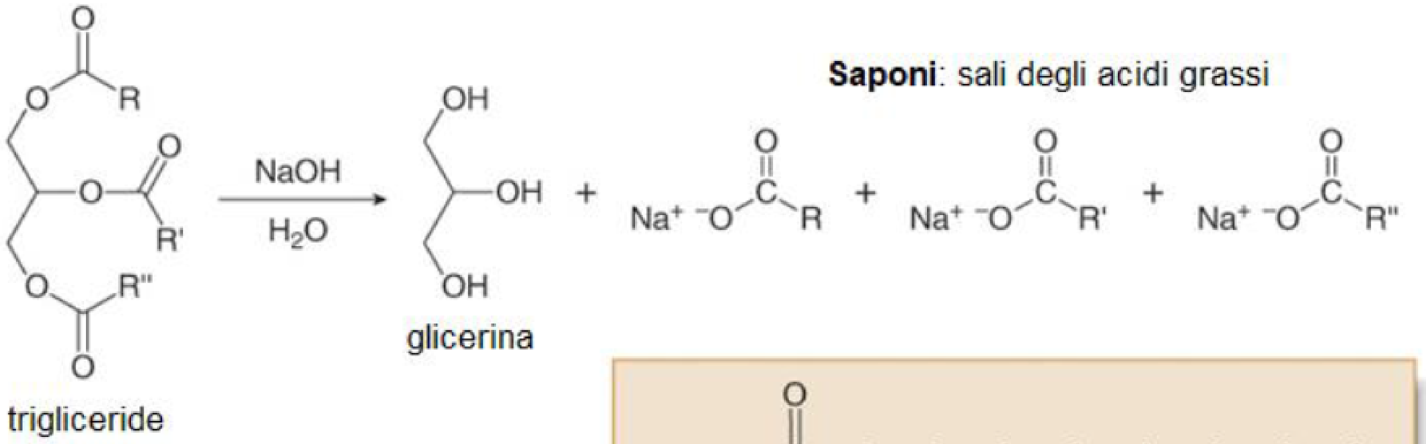
REAZIONI DI ACIDI CARBOSSILICI E DERIVATI: IDROLISI

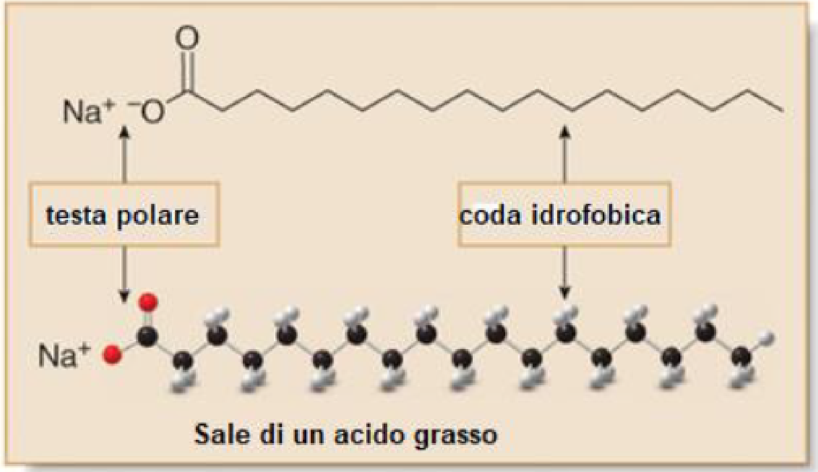


Grassi e oli

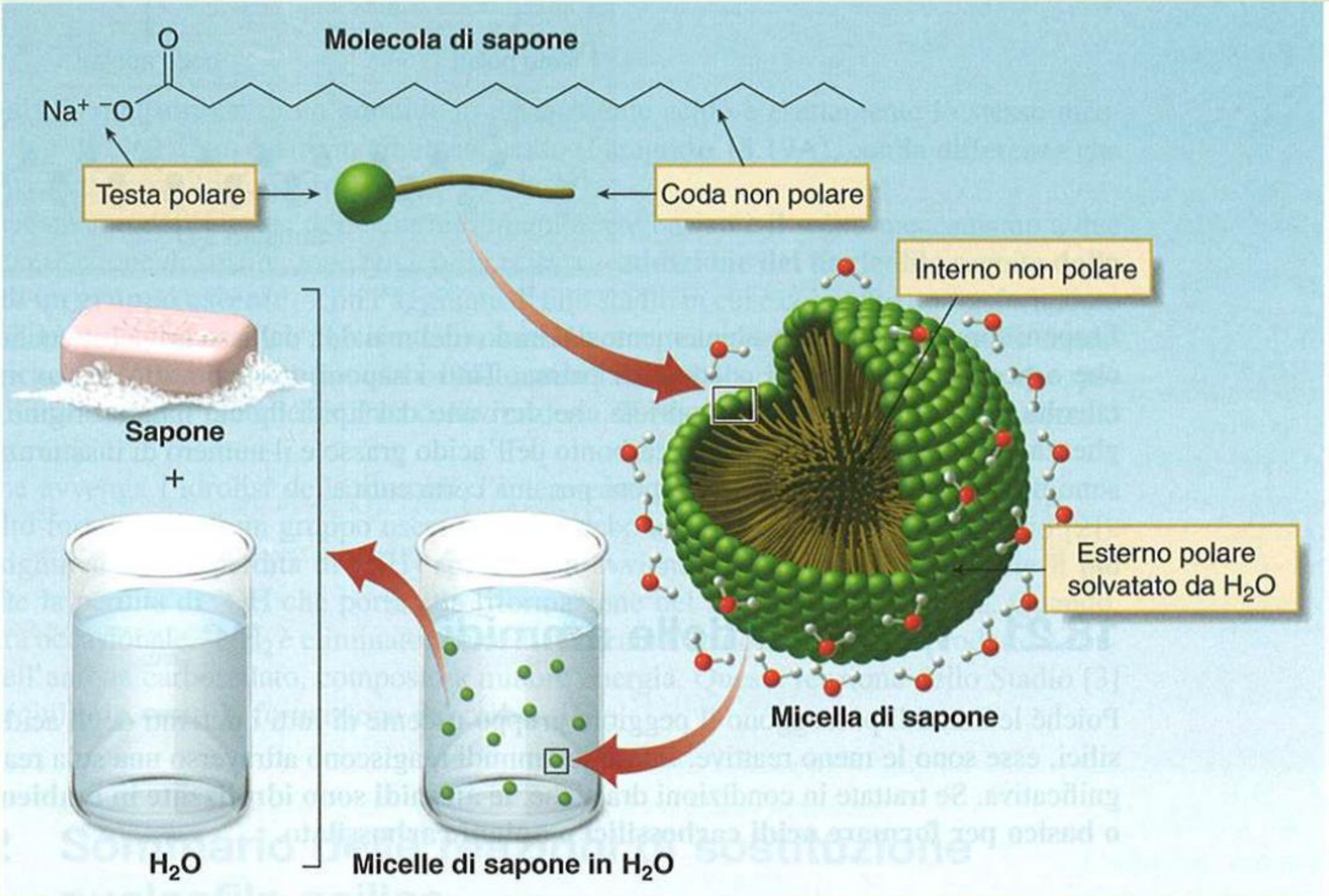
I *grassi animali* e gli *oli vegetali* sono triesteri del glicerolo con tre acidi carbossilici lineari a catena lunga. Vengono anche chiamati *trigliceridi*. Gli acidi contenuti nei trigliceridi sono detti *acidi grassi*, hanno un numero di atomi di carbonio compreso tra 12 e 20 e possono contenere una o più insaturazioni di solito con geometria cis.

L'idrolisi basica dei grassi (*saponificazione*) porta ad una miscela di sali di acidi grassi e glicerolo. Tradizionalmente la reazione veniva condotta utilizzando grassi animali e cenere (lisciva) che contiene sali alcalini di sodio e potassio. Questa miscela purificata per ebollizione in acqua e precipitazione dei sali degli acidi grassi per aggiunta di NaCl o KCl fornisce il *sapone*.

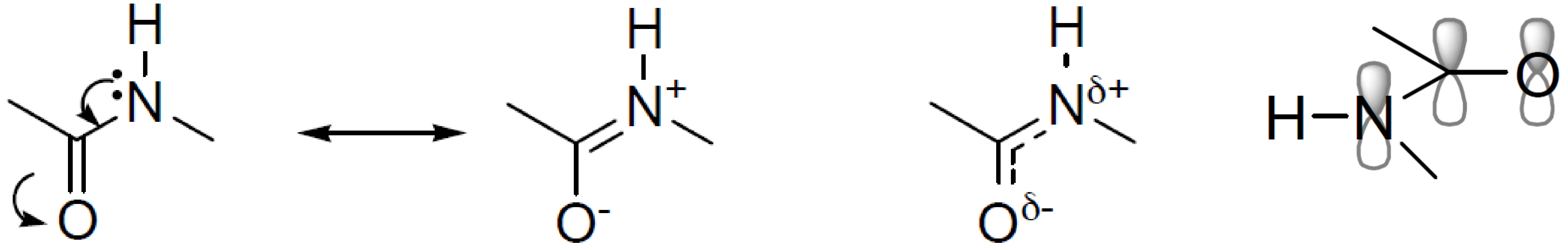




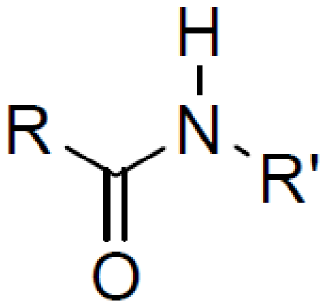
Sale di un acido grasso


Molecola di sapone
Na+ −O
O
Testa polare
Coda non polare
Interno non polare
Esterno polare solvatato da H2O
Sapone
+
H2O
Micelle di sapone in H2O
Micella di sapone

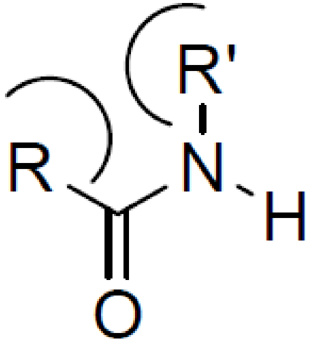
Ammidi: struttura



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



trans

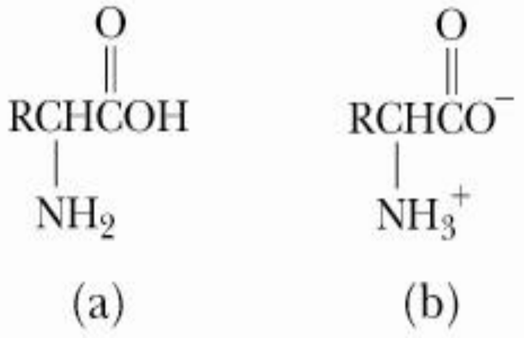


cis

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

Amminoacidi e proteine

- Gli α-amminoacidi sono molecole che che portano legati allo stesso atomo di carbonio (C-α) sia un gruppo acido che un gruppo amminico



$\mathrm{RCH(NH_2)C(=O)OH}$ (a) $\quad$ $\mathrm{RCH(NH_3^+)C(=O)O^-}$ (b)

Figura 19.1

Un *α*-amminoacido.
(a) Forma non ionizzata e
(b) sale interno (zwitterione).

Legame peptidico

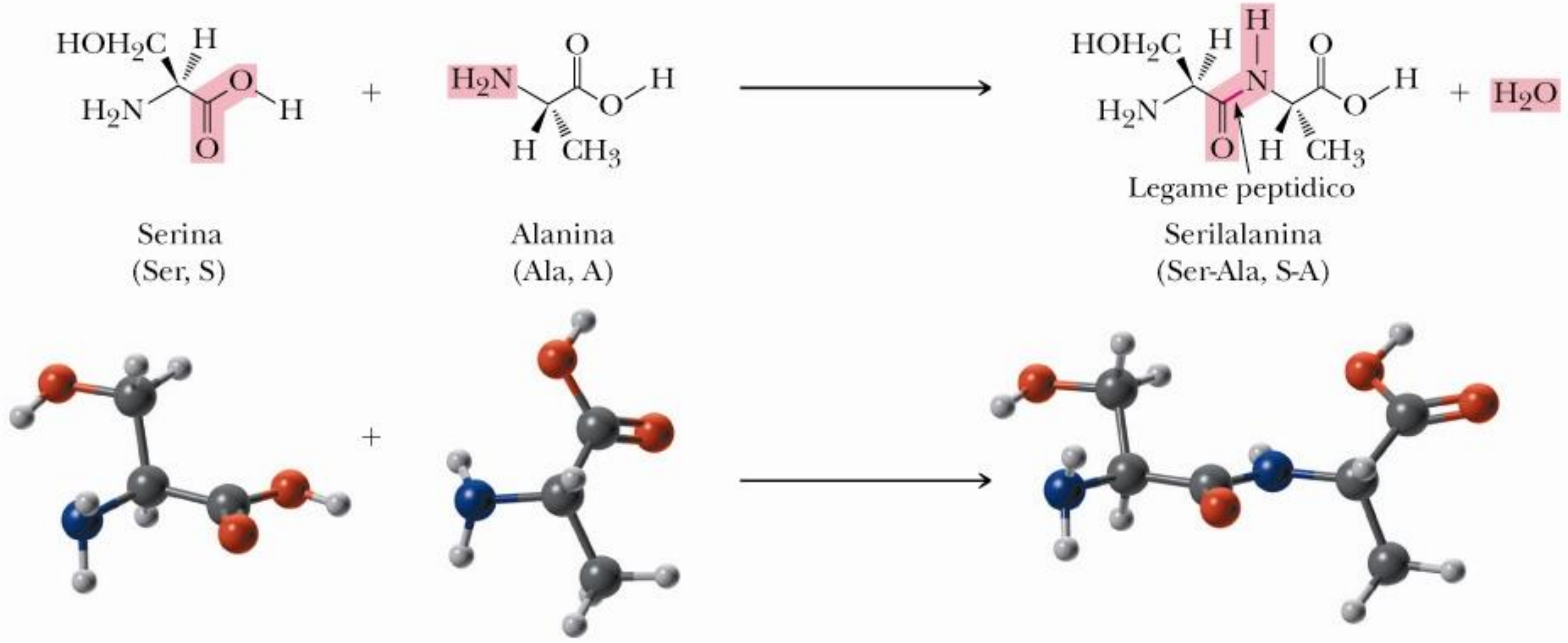


Figura 19.5
Il legame peptidico nella serilalanina.