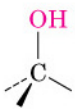
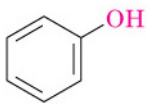
# Alcoli, fenoli ed eteri

Alcoli:
gruppo ossidrilico legato ad un carbonio saturo




Alcol



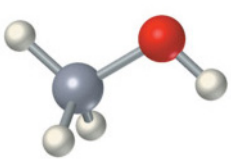

Fenolo

Fenoli:
gruppo ossidrilico legato ad un anello aromatico

**Metanolo**

$$CO + 2\,H_2 \xrightarrow[\text{Zinco ossido/cromo ossido}]{400^\circ C} CH_3OH$$

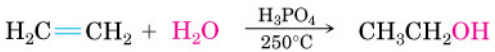
Sintesi industriale

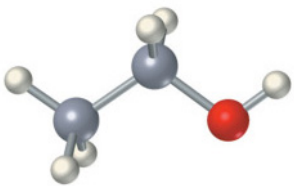


Tossico per l'uomo (<15mL cecità; 100-250mL morte)

Usato come solvente e materiale di partenza per numerosi composti

**Etanolo**: produzione per fermentazione di cereali e zuccheri e purificazione per distillazione

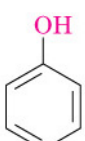


Sintesi industriale

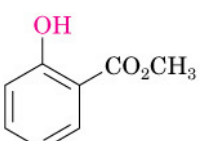
Usato come solvente o intermedio in reazioni chimiche

**Fenoli**: diffusi in natura e usati a livello industriale



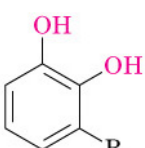

**Fenolo**
**(noto anche come acido carbolico)**

disinfettante




**Metil salicilato**

aromatizzante

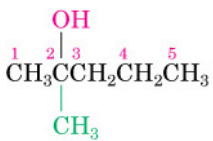



**Urushioli**
**(R = differenti catene alchiliche ed alcheniliche $C_{15}$)**

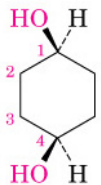
allergeni in piante velenose

# Alcoli: nomenclatura

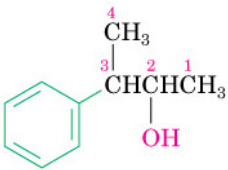
alcano -> alcanolo



**2-Metil-2-pentanolo**

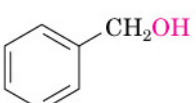


***cis*-1,4-Cicloesandiolo**



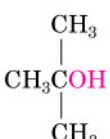
**3-Fenil-2-butanolo**

Nomi comuni di alcoli semplici



**Alcol benzilico (Fenil metanolo)**

**Alcol allilico (2-Propen-1-olo)**



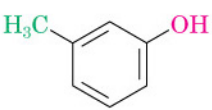
**Alcol *tert*-butilico (2-Metil-2-propanolo)**

**Glicole etilenico (1,2-Etandiolo)**

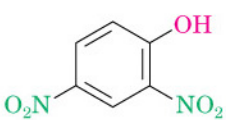
**Glicerolo (1,2,3-Propantriolo)**

# Fenoli: nomenclatura

Termine fenolo: usato sia per il singolo composto che per l'intera classe

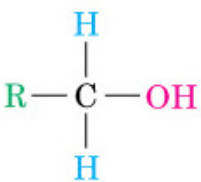



*m*-Metilfenolo
(*m*-Cresolo)

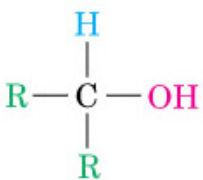



2,4-Dinitrofenolo

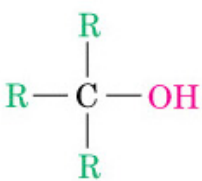
qui il composto base è fenolo, non benzene




**Alcol primario (1°)**

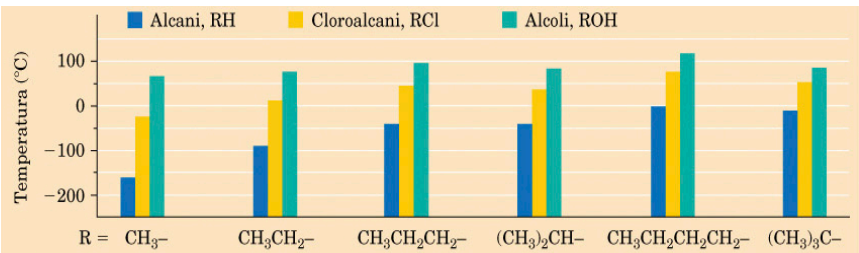


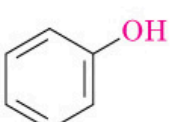

**Alcol secondario (2°)**



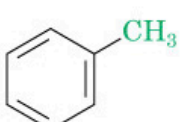

**Alcol terziario (3°)**

Confronto dei punti di ebollizione di alcuni alcani, cloroalcani ed alcoli. Gli alcoli mostrano generalmente i punti di ebollizione più alti.



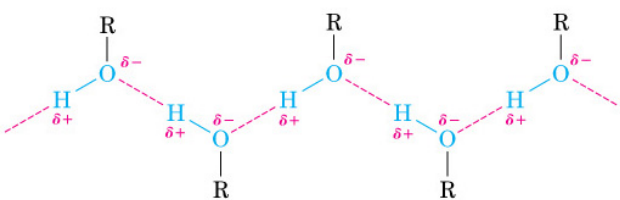



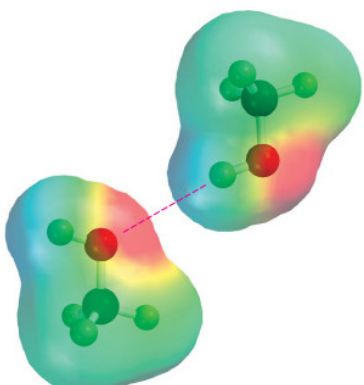

**Fenolo: p.e. = 181.7°C**

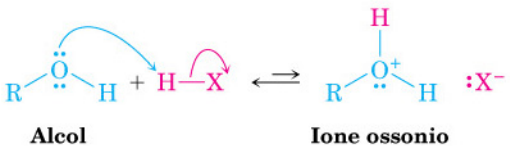



**Toluene: p.e. = 110.6°C**

Il legame a idrogeno negli alcoli e nei fenoli. Le molecole sono tenute unite da una debole attrazione che si instaura tra un idrogeno polarizzato positivamente di un gruppo OH e l'ossigeno polarizzato negativamente di un altro gruppo OH.
La mappa di potenziale elettrostatico del metanolo mostra chiaramente l'idrogeno del legame O-H polarizzato positivamente (zona blu) e l'ossigeno polarizzato negativamente (zona rossa).

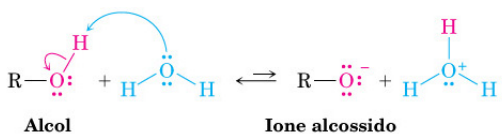


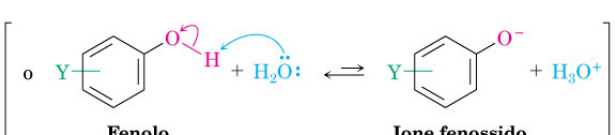






$$\left[\text{o} \quad \text{ArOH} + \text{HX} \rightleftharpoons \text{ArO}^{+}\text{H}_2 \quad \text{X}^-\right]$$

Basi deboli

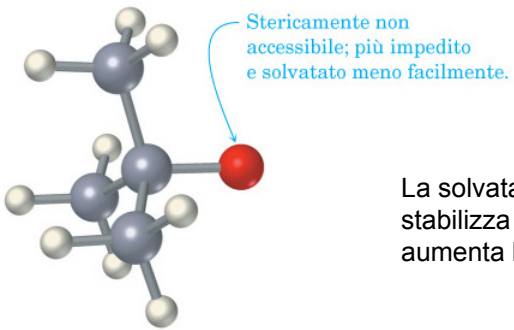



Acidi deboli

Fattori che influenzano l'acidità

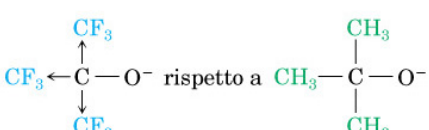
**Ione metossido, $CH_3O^-$**
**($pK_a$ = 15.54)**




**Ione *tert*-butossido, $(CH_3)_3CO^-$**
**($pK_a$ = 18.00)**

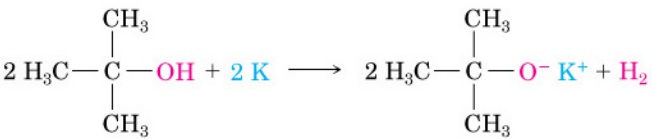
La solvatazione stabilizza gli anioni e aumenta l'acidictà

**I gruppi elettron-attrattori stabilizzano lo ione alcossido ed abbassano il $pK_a$**




**$pK_a$ = 5.4** **$pK_a$ = 18**

Essendo acidi deboli, reagiscono solo con basi forti



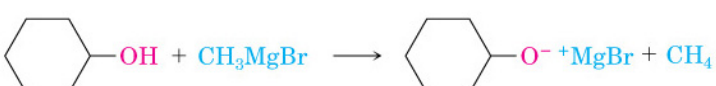
**Alcol *tert*-butilico** — **Potassio *tert*-butossido**

$$CH_3OH + NaH \longrightarrow CH_3O^- Na^+ + H_2$$

**Metanolo** — **Sodio metossido**

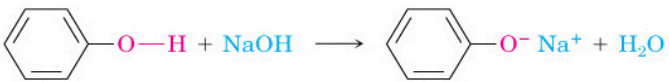
$$CH_3CH_2OH + NaNH_2 \longrightarrow CH_3CH_2O^- Na^+ + NH_3$$

**Etanolo** — **Sodio etossido**



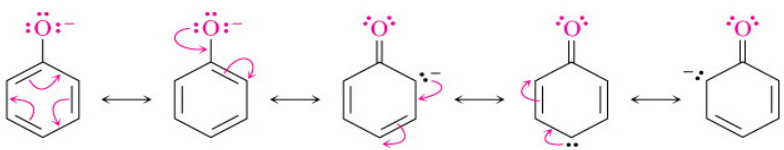
**Cicloesanolo** — **Bromomagnesio cicloesossido**

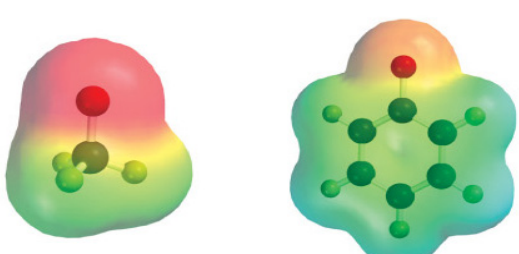
I fenoli sono molto più acidi degli alcoli e reagiscono bene con NaOH
sono solubili in soluzioni alcaline diluite



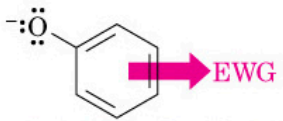

**Fenolo** **Sodio fenossido**

Lo ione fenossido, stabilizzato per risonanza, è più stabile di uno ione alcossido. Le mappe di potenziale elettrostatico mostrano come la carica negativa sia concentrata sull'ossigeno nello ione metossido, mentre sia delocalizzata sull'anello aromatico nel caso dello ione fenossido.

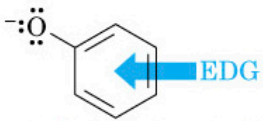




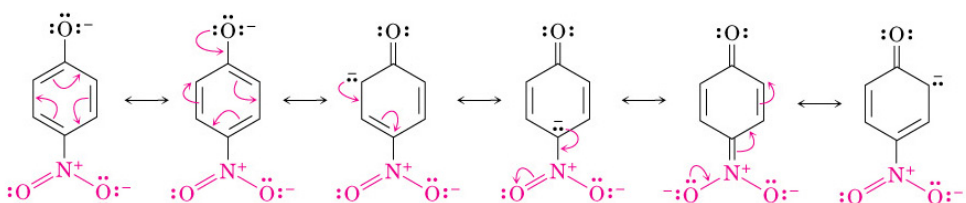
$CH_3O^-$ $C_6H_5O^-$



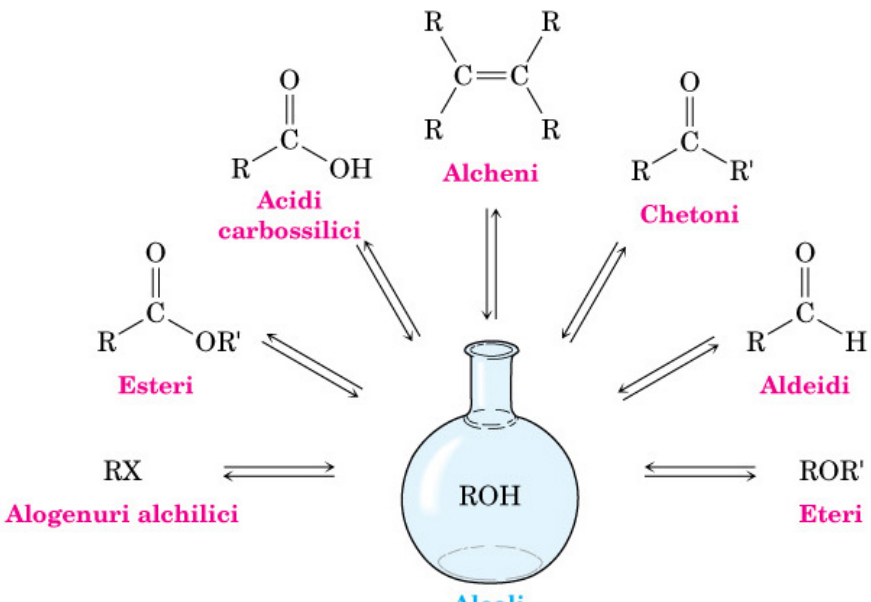

**I gruppi elettron-attrattori (EWG) stabilizzano lo ione fenossido, determinando così un aumento dell'acidità del fenolo**




**I gruppi elettron-donatori (EDG) destabilizzano lo ione fenossido, determinando così una diminuzione dell'acidità del fenolo**

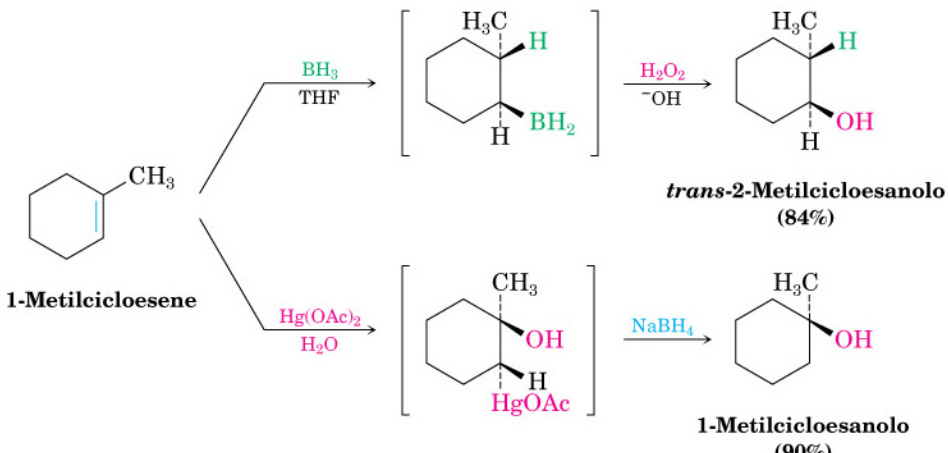


Il ruolo centrale degli alcoli nella chimica organica. Gli alcoli possono essere preparati da, e trasformati in molti composti organici.

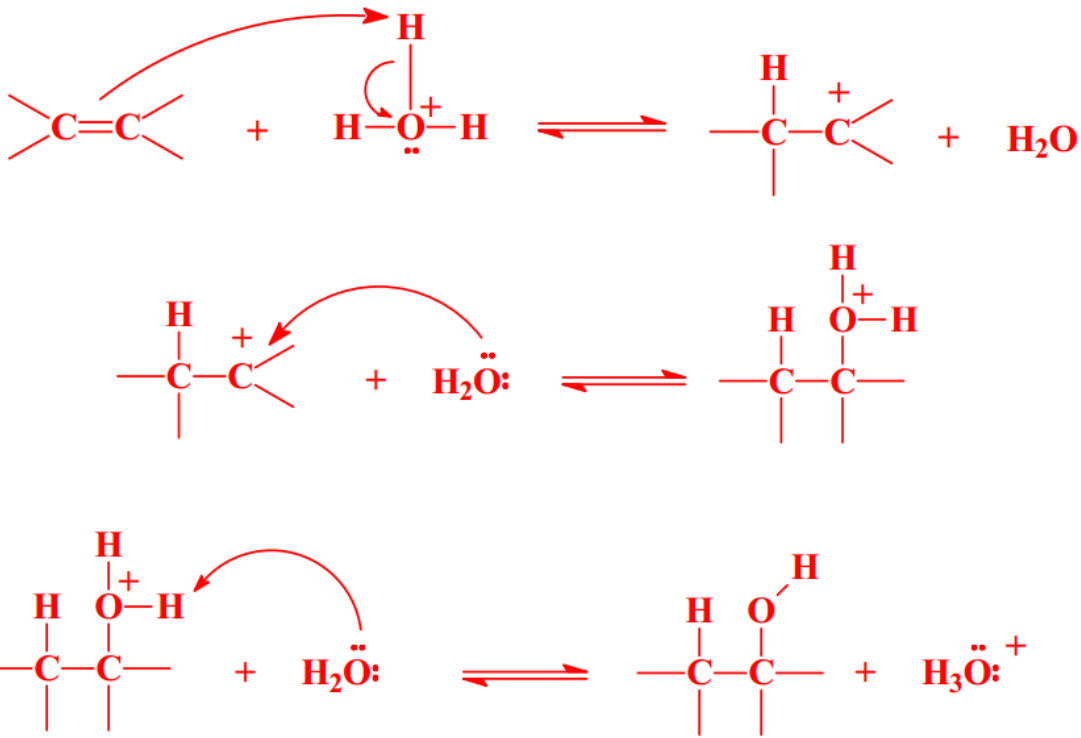


Idratazione degli alcheni

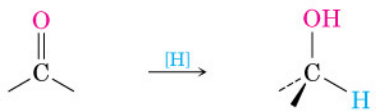
Idratazione diretta con acidi acquosi
oppure con metodi indiretti più blandi:



Meccanismo di idratazione



Riduzione di composti carbonilici

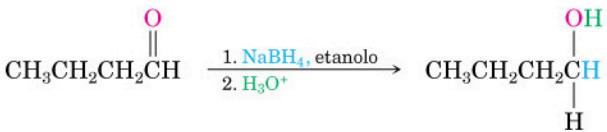



dove [H] indica un generico agente riducente

**Composto carbonilico** **Alcol**

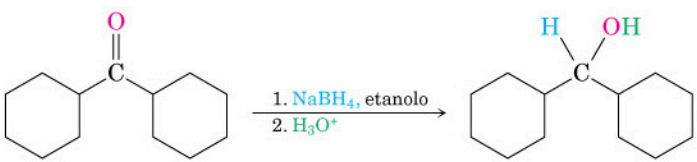
**Aldeide** **Alcol primario** **Chetone** **Alcol secondario**

**Riduzione di una aldeide**



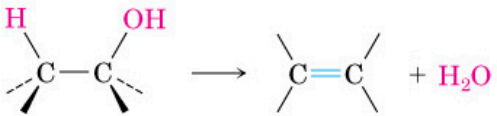

**Butanale** — **1-Butanolo (85%) (alcol 1°)**

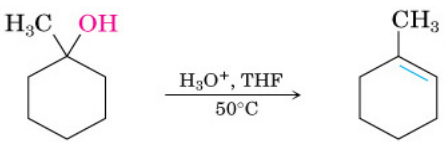
**Riduzione di un chetone**



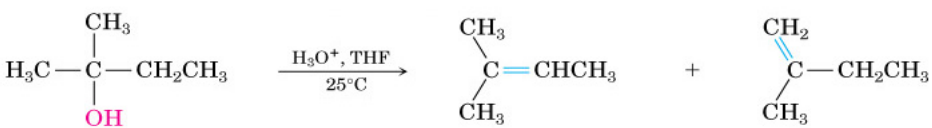

**Dicicloesilchetone** — **Dicicloesilmetanolo (88%) (alcol 2°)**

**Reazione di disidratazione**




**1-Metilcicloesanolo** **1-Metilcicloesene (91%)**




**2-Metil-2-butanolo**

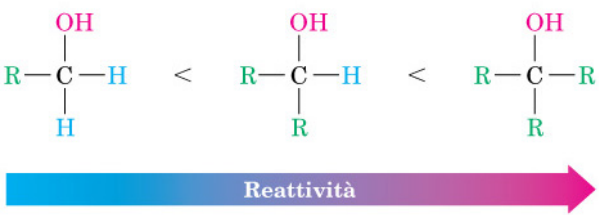
**2-Metil-2-butene (alchene trisostituito)**

**Prodotto principale**

**2-Metil-1-butene (alchene disostituito)**

**Prodotto secondario**

# Alcoli: disidratazione



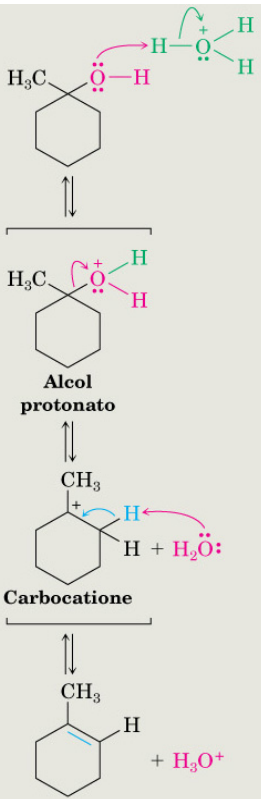

Alcoli secondari e primari richiedono condizioni più drastiche

**MECCANISMO:**
Disidratazione acido-catalizzata di un alcol per formare un alchene. Il processo coinvolto è una reazione di tipo E1 e prevede l'intervento di un carbocatione intermedio.

Due elettroni dell'atomo di ossigeno si legano all'$H^+$, a dare un alcol protonato.

Il legame carbonio-ossigeno si rompe ed i due elettroni del legame rimangono sull'ossigeno, generando un carbocatione intermedio.

I due elettroni appartenenti ad un legame carbonio-idrogeno adiacente danno luogo al legame $\pi$ dell'alchene, con eliminazione di un $H^+$ (un protone).

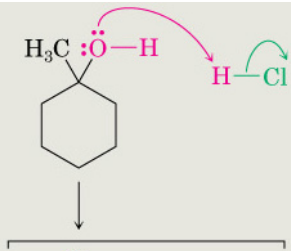


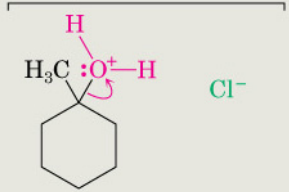

Si forma l'alchene più stabile ovvero più sostituito

**MECCANISMO:**
La reazione di un alcol terziario con HCl per dare un cloruro alchilico terziario. Inizialmente l'alcol viene protonato a dare uno ione ossonio che dà luogo ad una reazione di tipo $S_N1$.

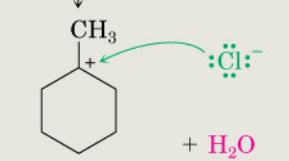
Terziari più reattivi

La protonazione dell'ossigeno alcolico per reazione con HCl genera uno ione ossonio che dà quindi luogo ad una reazione $S_N1$.

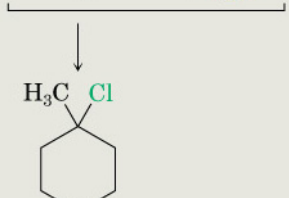


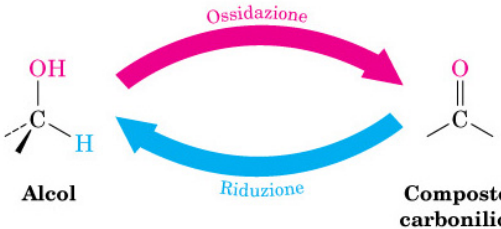




La perdita spontanea di acqua conduce ad un carbocatione intermedio...

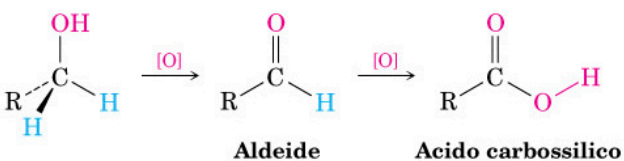



...che reagisce con lo ione cloruro per dare il cloruro alchilico quale prodotto della reazione.

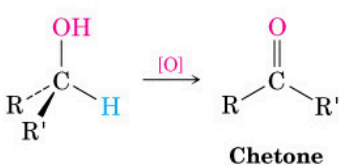




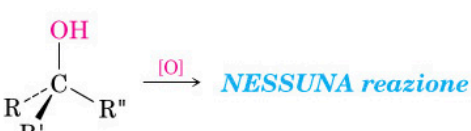

**Alcol primario**

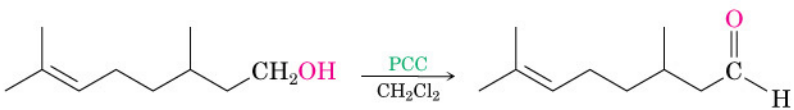



**Alcol secondario**

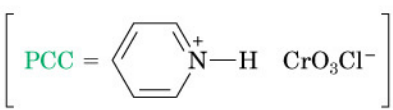



**Alcol terziario**

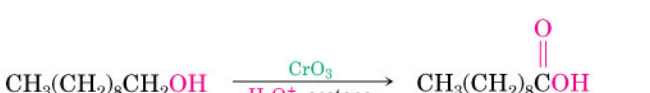





**Citronellolo (dall'olio di rose)** **Citronellale (82%)**



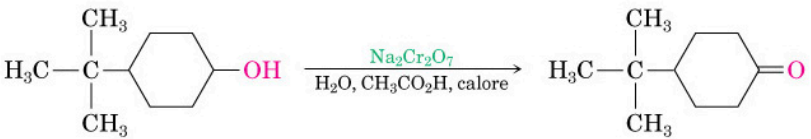

ossidante blando




**1-Decanolo** **Acido decanoico (93%)**

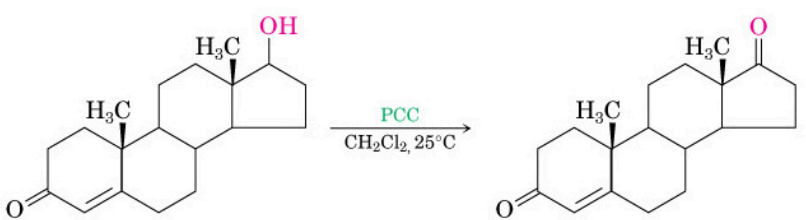
ossidante forte

Facile ossidazione di alcoli secondari a chetoni




**4-*tert*-Butilcicloesanolo** **4-*tert*-Butilcicloesanone (91%)**

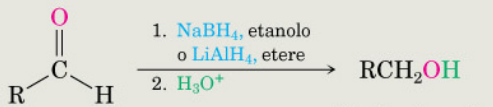
Se l'alcol è più delicato occorrono condizioni blande




**Testosterone**
**(ormone steroideo sessuale maschile)**

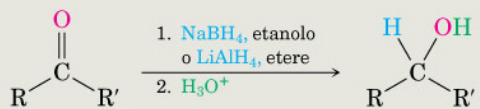
**4-Androsten-3,17-dione (82%)**

1. Sintesi degli alcoli
   (a) Riduzione dei composti carbonilici (Paragrafo 17.5)
      (1) Aldeidi



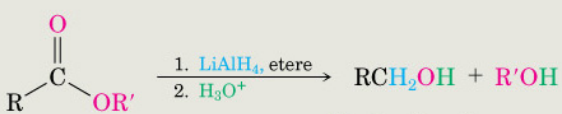

**Alcol primario**

      (2) Chetoni



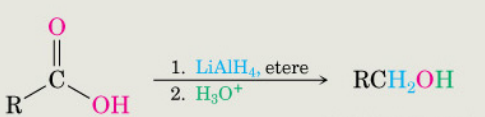

**Alcol secondario**

      (3) Esteri




**Alcol primario**

      (4) Acidi carbossilici




**Alcol primario**

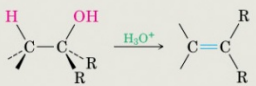
2. Reazioni degli alcoli

(a) Acidità (Paragrafo 17.3)

$$ROH + NaH \longrightarrow RO^- Na^+ + H_2$$
$$2\,ROH + 2\,Na \longrightarrow 2\,RO^- Na^+ + H_2$$

(b) Disidratazione (paragrafo 17.7)

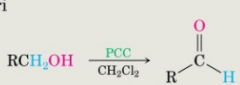
(1) Alcoli terziari



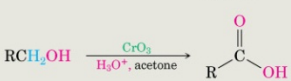

(2) Alcoli secondari e terziari

(c) Ossidazione (Paragrafo 17.8)

(1) Alcoli primari

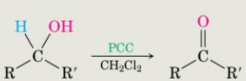



**Aldeide**

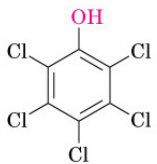



**Acido carbossilico**

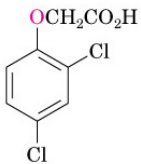
(2) Alcoli secondari



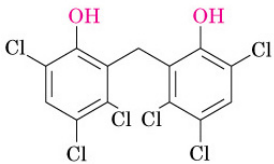

**Chetone**



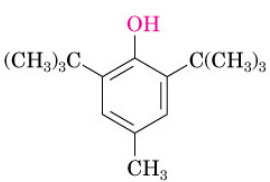

**Pentaclorofenolo**
**(conservante del legno)**



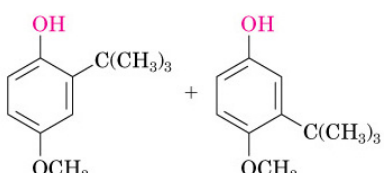

**Acido 2,4-diclorofenossiacetico,**
**2,4-D (erbicida)**




**Esaclorofene**
**(antisettico)**




**BHT**



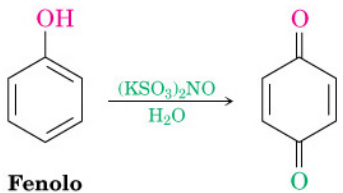

**BHA**

Idrossitoluene butilato

Idrossianisolo butilato

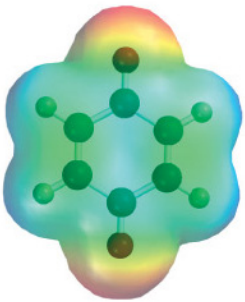
Conservanti per alimenti

Ossidazione avviene con meccanismo radicalico



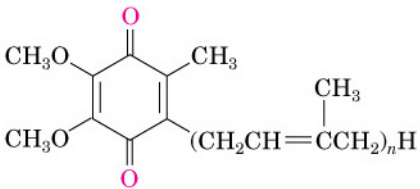

**Fenolo**

**Benzochinone (79%)**



Composti usati come agenti redox: facilmente ossidabili e riducibili

**Benzochinone** **Idrochinone**

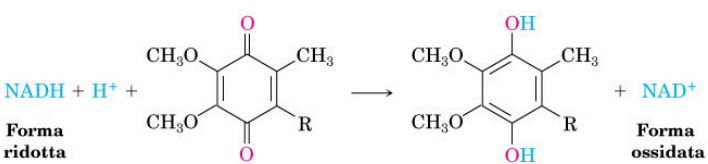


**Ubichinoni ($n$ = 1–10)**

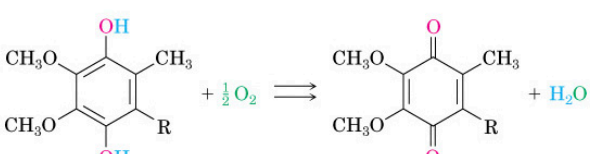
Coenzimi Q: ossidanti biologici

Importanti per il funzionamento delle cellule

**STADIO 1**




**STADIO 2**

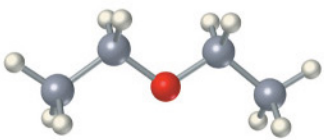



NADH: riducente biologico

**Reazione complessiva:** $NADH + \frac{1}{2} O_2 + H^+ \longrightarrow NAD^+ + H_2O$

Reazione che libera energia

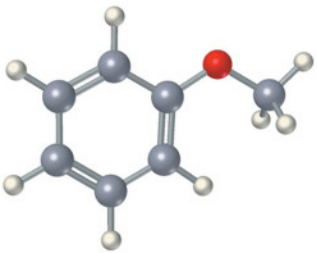
Eteri: due gruppi organici legati allo stesso atomo di ossigeno

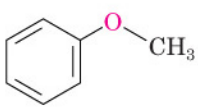


$CH_3CH_2—O—CH_2CH_3$

**Dietil etere**

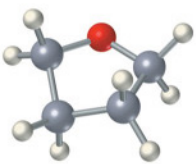
Anestetico
e solvente






**Anisolo**
**(Fenil metil etere)**

Industria profumi

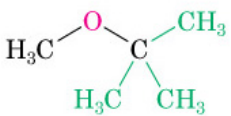


**Tetraidrofurano**
**(etere ciclico)**

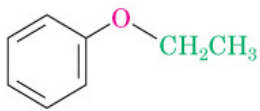
solvente

Stabili, poco reattivi, ma possono dar luogo a perossidi che sono esplosivi

Composti semplici: alchil1-alchil2-etere

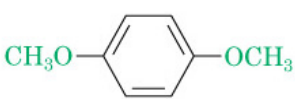


***tert*-Butil metil etere**

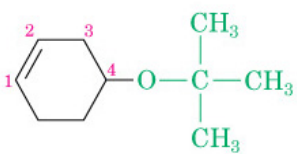


**Etil fenil etere**

In presenza di altri gruppi funzionali si denominano come sostituenti alcossilici

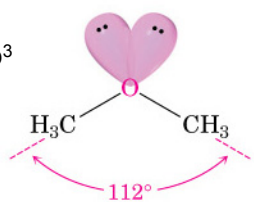


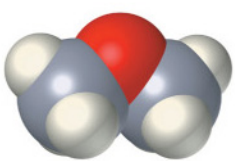
***p*-Dimetossi benzene**

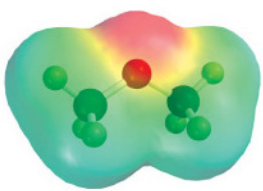


**4-*tert*-Butossi-1-cicloesene**

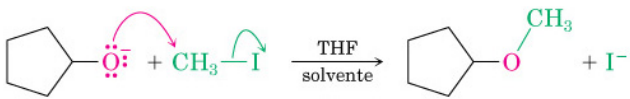
sp$^3$



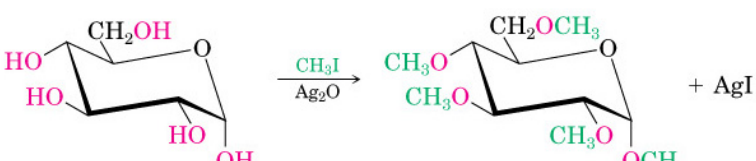


Hanno momento dipolare e perciò punti di ebollizione più alti dei rispettivi alcani




**Ione ciclopentossido**

**Ciclopentil metil etere**
**(74%)**

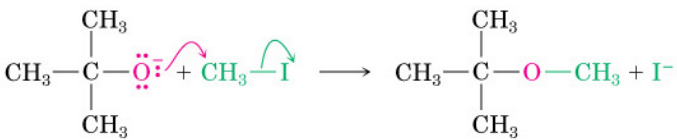



**α-D-Glucosio**

**α-D-Glucosio pentametil etere**
**(85%)**

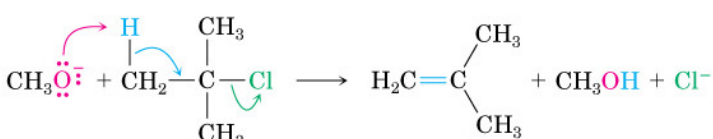
Alcossido sostituito con alogenuro poco sostituito

**Reazione $S_N2$**



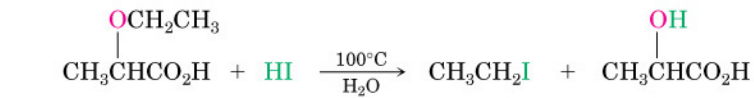
**Ione *tert*-butossido** **Iodometano** ***tert*-Butil metil etere**

**Reazione E2**

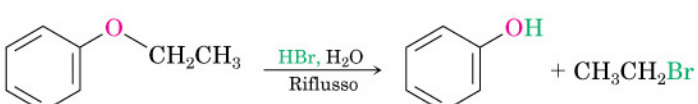


**Ione metossido** **2-Cloro-2-metilpropano** **2-Metilpropene**

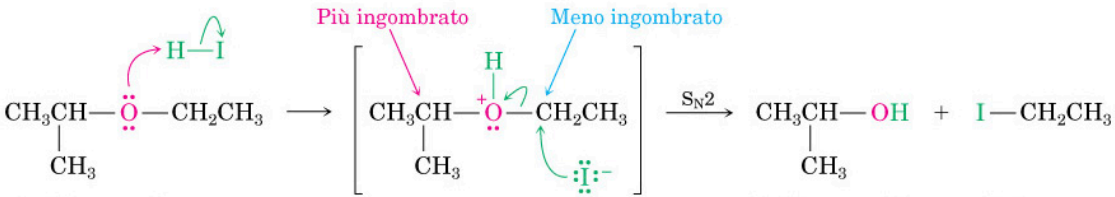
Subiscono scissione ad opera di acidi forti



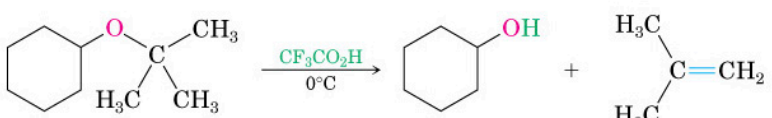

**Acido 2-etossipropanoico** **Iodoetano** **Acido lattico**




**Etil fenil etere** **Fenolo** **Bromoetano**

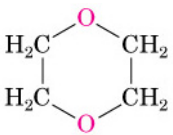



**Etil isopropil etere** — **Alcol isopropilico** — **Iodoetano**

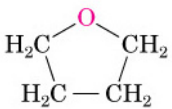



***tert*-Butil ciloesil etere** — **Cicloesanolo (90%)** — **2-Metilpropene**

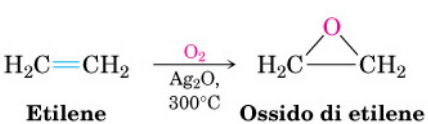
# Eteri ciclici: epossidi



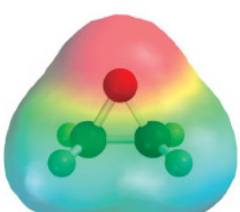

**1,4-Diossano**



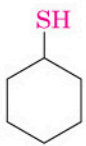

**Tetraidrofurano**



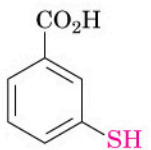

**Etilene** **Ossido di etilene**



**Etan**tiolo

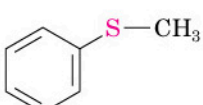



**Cicloesan**tiolo

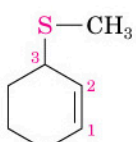



Acido *m*-mercapto**benzoico**

**Dimetil solfuro**




**Metil fenil solfuro**




**3-(Metiltio)cicloesene**