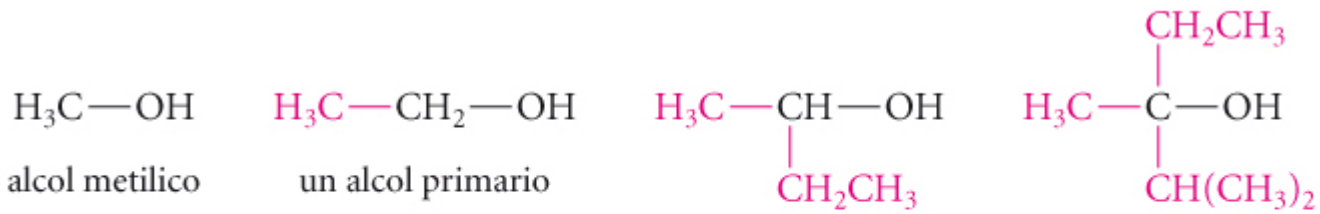
ALCOLI: Nomenclatura



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Idrocarburo di origine + desinenza *olo*

$CH_3CH_2—OH$

etanǿ + *olo* = **etanolo**

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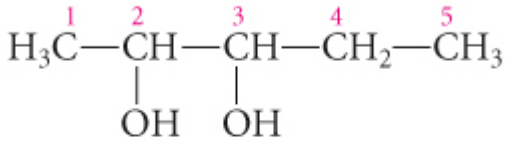
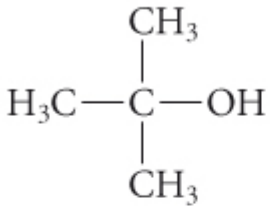
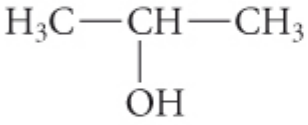


2,3-pentandiolo

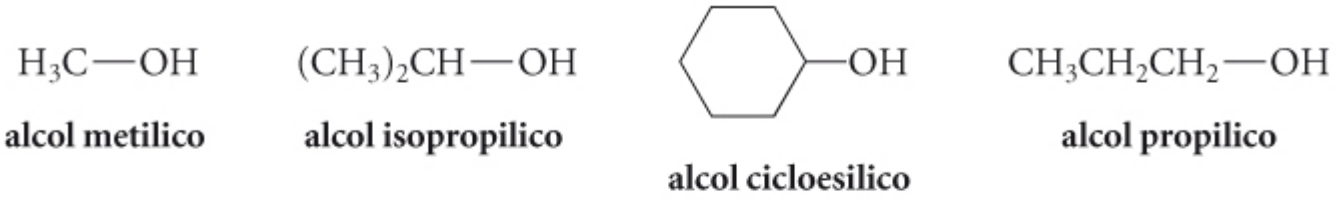


d'uso: alcol *terz*-butilico
sostitutiva: 2-metil-2-propanolo
errata: *terz*-butanolo oppure *t*-butanolo

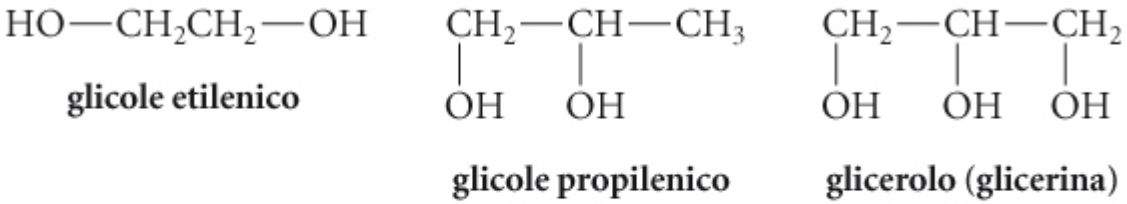


d'uso: alcol isopropilico
sostitutiva: 2-propanolo
errata: isopropanolo

ALCOLI di uso comune



I GLICOLI



ALCOLI: proprietà fisiche

	$CH_3CH_2—OH$	$CH_3CH_2CH_3$	$H_3C—O—CH_3$	$CH_3CH_2—F$
	etanolo	**propano**	**dimetil etere**	**fluoruro di etile**
di ebollizione	78 °C	−42 °C	−24 °C	−38 °C
nto dipolare	1.7 D	0 D	1.3 D	1.8 D

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	$CH_3CH_2—OH$	$H_3C—OH$	$H—OH$
	etanolo	**metanolo**	**acqua**
punto di ebollizione	78 °C	65 °C	100 °C

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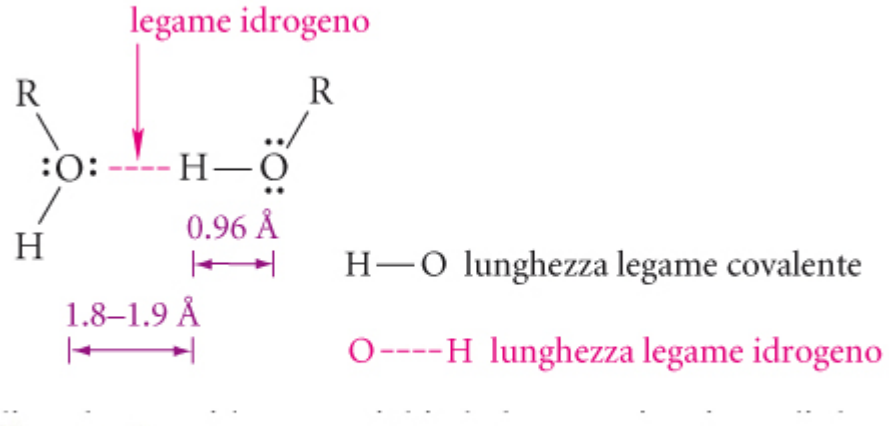

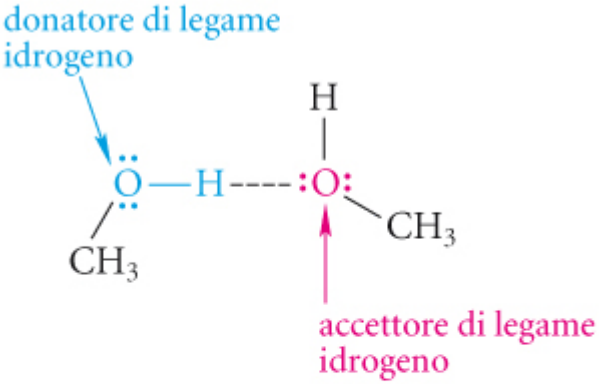

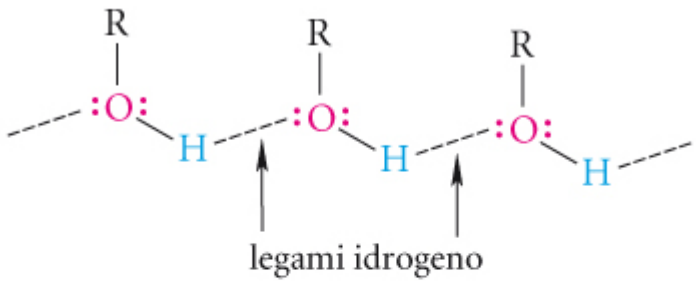

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Solubilità in acqua

	$CH_3CH_2CH_2CH_3$	CH_3CH_2Cl	$CH_3CH_2—O—CH_3$	$CH_3CH_2CH_2—OH$
solubilità in acqua:	virtualmente insolubile		solubile	miscibile

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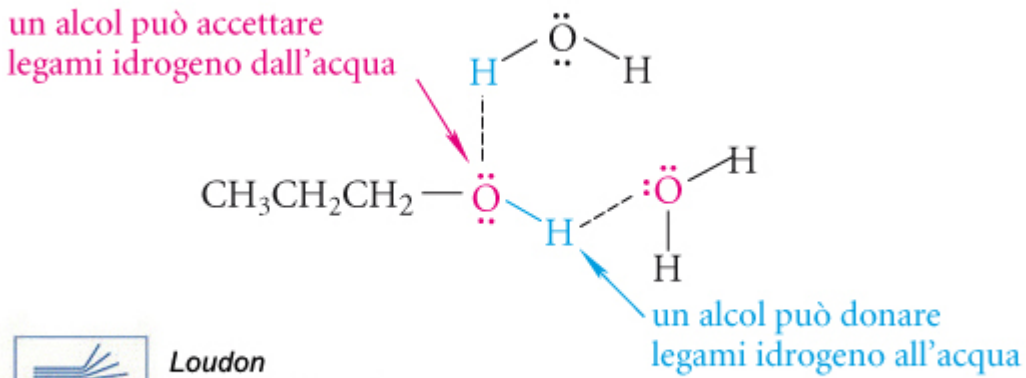
	CH_3OH	CH_3CH_2OH	$CH_3CH_2CH_2OH$	$CH_3CH_2CH_2CH_2OH$	$CH_3CH_2CH_2CH_2CH_2CH_2OH$
solubilità in acqua:	miscibile			7.7%	0.58%



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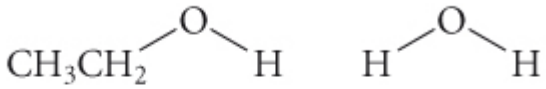
ALCOLI: proprietà acido-base



pK_a	15.9	15.7

pK_a	15.9	12.4

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pK_a	15.4	14.6	12.4

TABELLA 8.3 Acidità degli alcoli in soluzione acquosa

Alcol	pK_a	Alcol	pK_a
CH_3OH	15.1	$(CH_3)_2CHOH$	17.1
CH_3CH_2OH	15.9	$(CH_3)_3COH$	19.2

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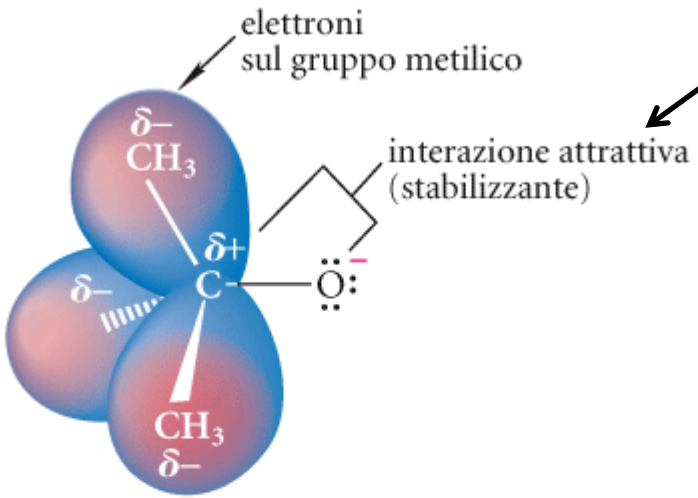
SOFFOCATA!



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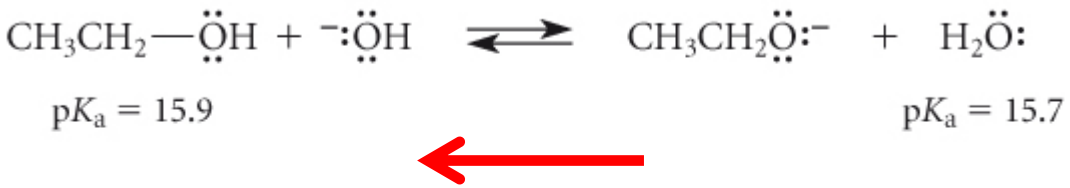
Acido 1 | Base coniugata 2 | Base coniugata 1 | Acido 2



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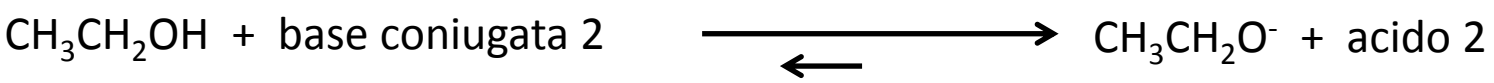
Come deprotonare quantitativamente un alcol

Acido 1

Base coniugata 1

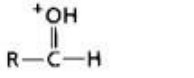
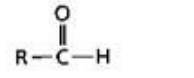
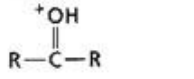
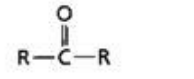
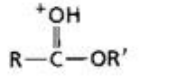
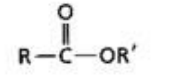
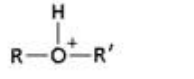
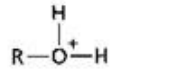
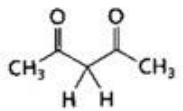
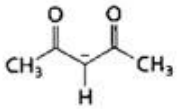


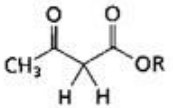
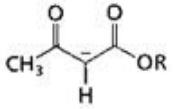
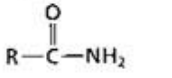
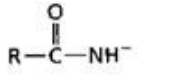
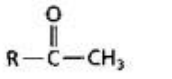
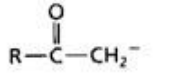
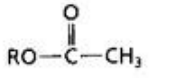
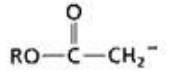
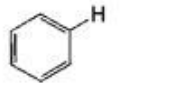
Se pKa (acido 2) è > pKa (acido 1)

[pKa (acido 2)/pKa (acido 1) ≥ 10^3]

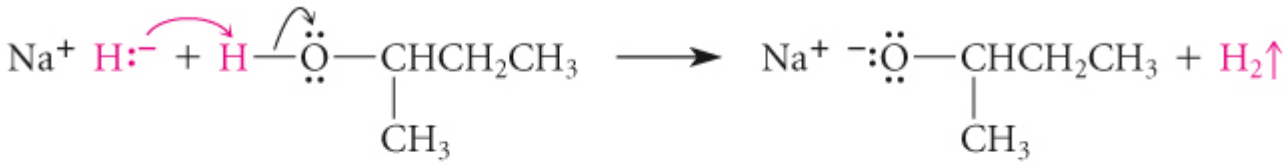
La base coniugata 2 deprotona quantitativamente l'alcol

Table 6.3
Acidities of molecules and ions commonly encountered in organic chemistry.[a]

Acid	Conjugate base	pK_a
$HClO_4$	ClO_4^-	−10
HI	I^-	−10
		−10
H_2SO_4	HSO_4^-	−10
HBr	Br^-	−9
HCl	Cl^-	−7
		−7
$ArSO_3H$	$ArSO_3^-$	−6.5
		−6
	$R-O-R'$	−3.5
	$R-O-H$	−2
H_3O^+	H_2O	−1.7
HNO_3	NO_3^-	−1.4
HSO_4^-	SO_4^{2-}	2
HF	F^-	3.1
$ArNH_3^+$	$ArNH_2$	4
RCOOH	$RCOO^-$	5
H_2CO_3	HCO_3^-	6.4
H_2S	HS^-	7
ArSH	ArS^-	7
		9

Acid	Conjugate base	pK_a
HCN	CN^-	9.2
NH_4^+	NH_3	9.2
ArOH	ArO^-	10
$R-CH_2NO_2$	$R-\bar{C}H-NO_2$	10
RNH_3^+	RNH_2	11
RSH	RS^-	11
		11
CH_3OH	CH_3O^-	15.2
H_2O	HO^-	15.7
RCH_2OH	RCH_2O^-	16
R_2CH-OH	R_2CH-O^-	17
R_3C-OH	R_3C-O^-	17
		17
		20
		24
$R-CH_2CN$	$R-\bar{C}H-CN$	25
$H-C\equiv C-H$	$H-C\equiv C^-$	25
H_2	H^-	35
NH_3	NH_2^-	38
$Ph-CH_3$	$Ph-CH_2^-$	40
		43
$CH_2=CH_2$	$CH_2=CH^-$	44
CH_4	CH_3^-	48

[a] pK_a values from J. March, *Advanced Organic Chemistry*, 4th ed., John Wiley & Sons, New York, 1992, pp. 250–252. Abbreviations: Ar = aryl; Ph = phenyl; R = alkyl.



resa quantitativa

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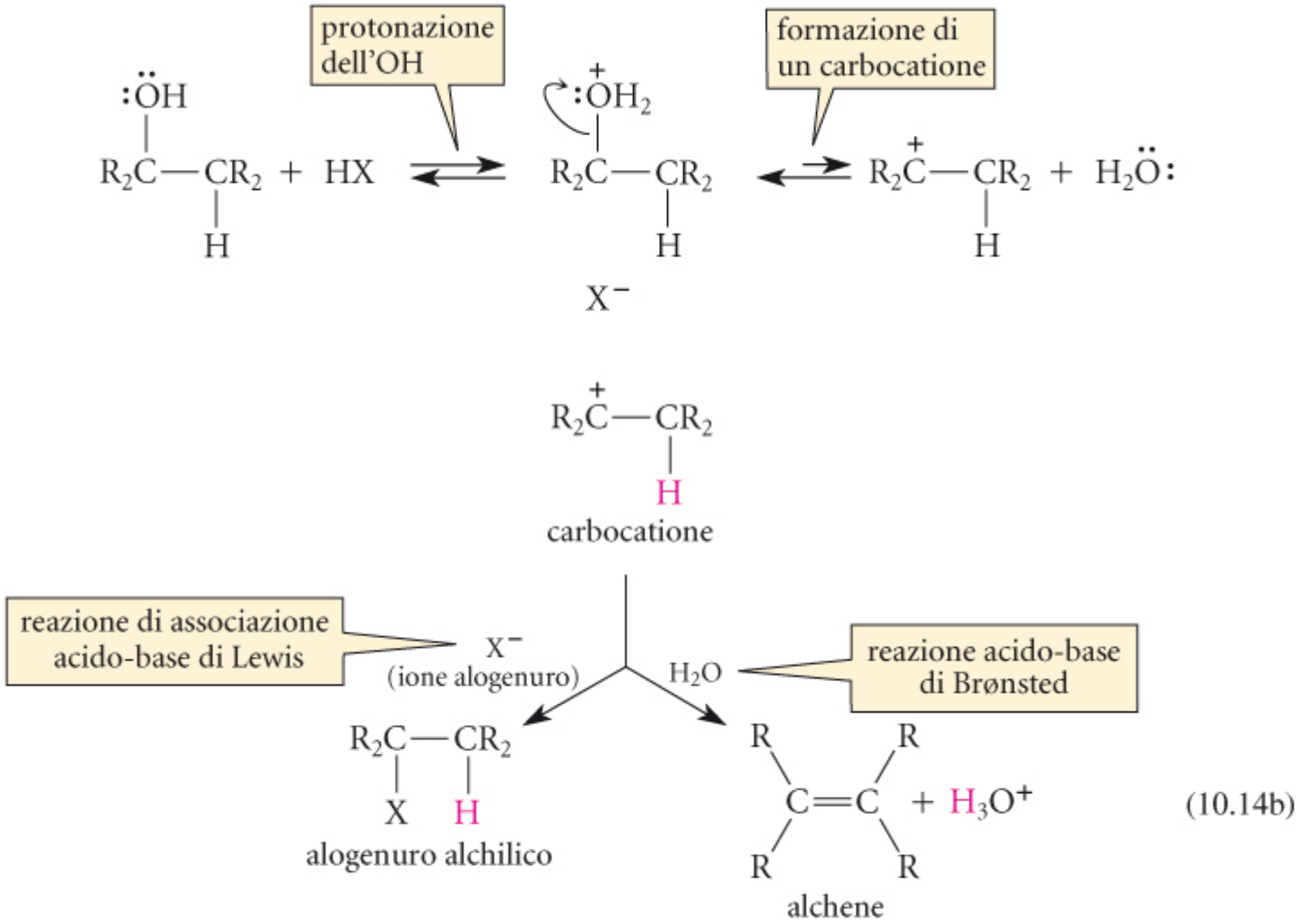
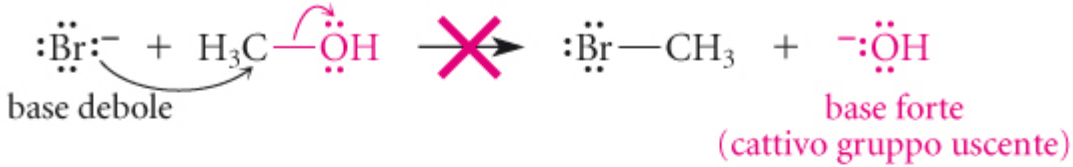
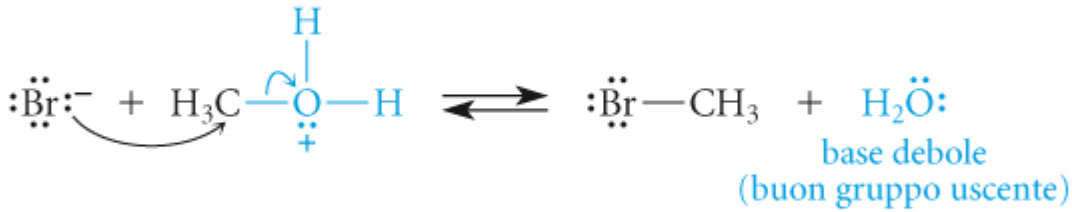
ALCOLI: reattività

Disidratazione *vs* SN







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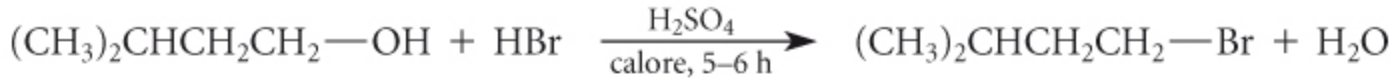
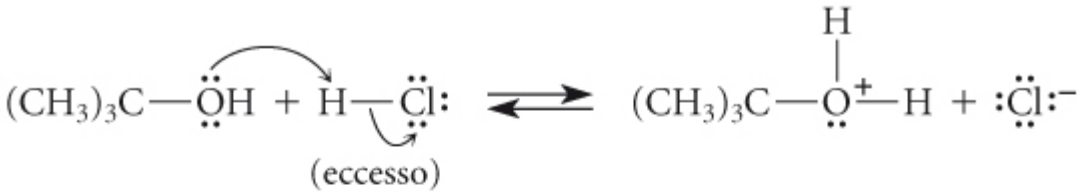
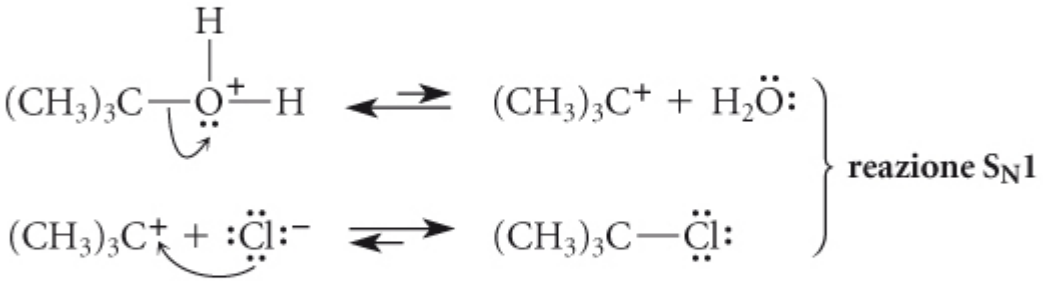
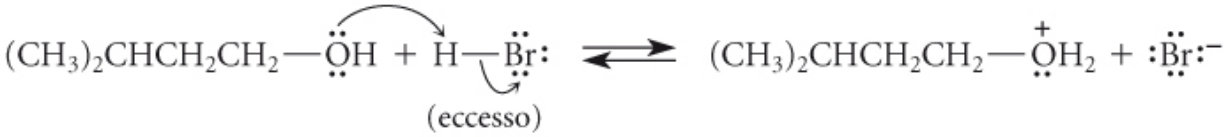


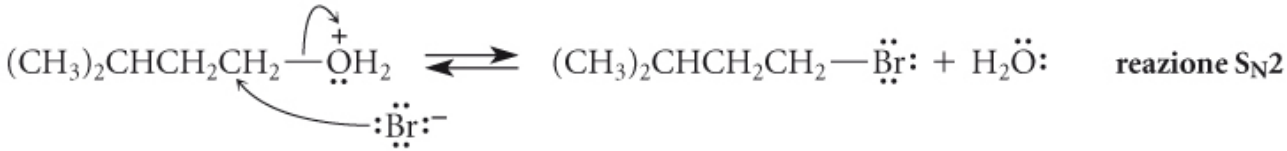
3-metil-1-butanolo — **1-bromo-3-metilbutano** (93% resa) (10.8)

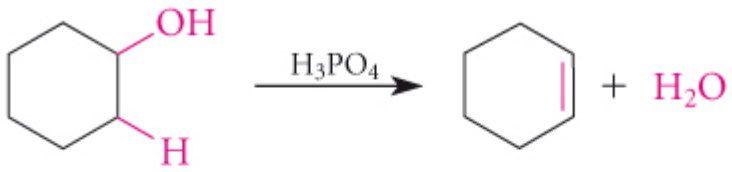
alcol *terz*-butilico — **cloruro di *terz*-butile** (resa quantitativa) (10.9)



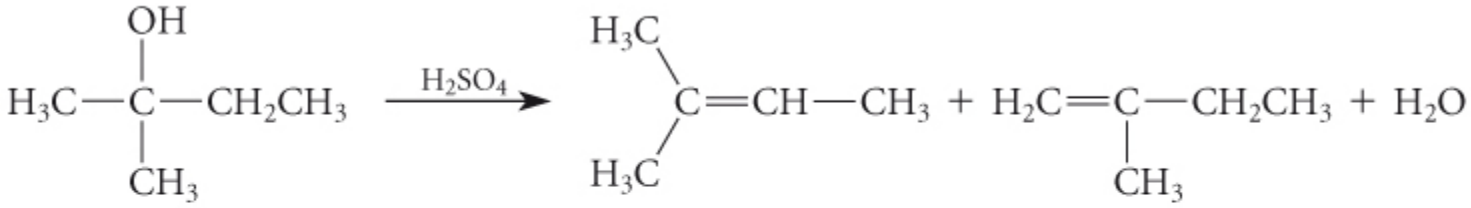








cicloesanolo **cicloesene** (resa 79–84%)



2-metil-2-butanolo **2-metil-2-butene** prodotto principale **2-metil-1-butene** prodotto secondario

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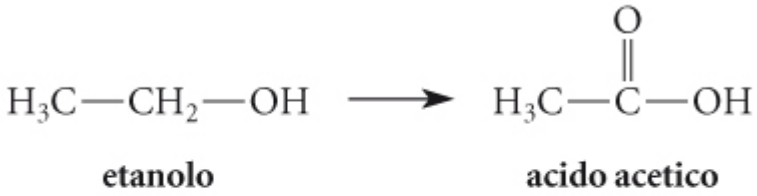
Reazione redox



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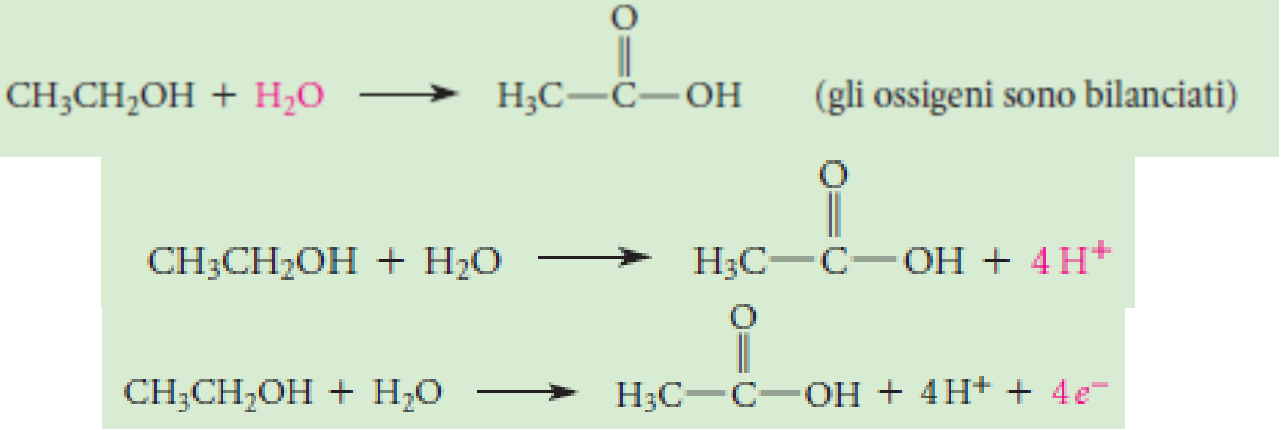
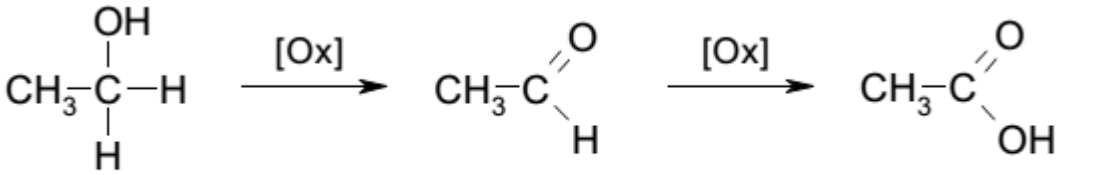
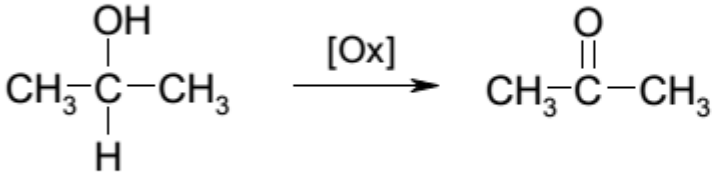


Ossidare un alcol significa ossidare il carbonio che regge l'ossidrile strappandogli un idrogeno e creando un doppio legame carbonio ossigeno, un carbonile.
L'ossidazione può avvenire **due volte sull'alcol primario** che possiede due idrogeni sul carbonio alfa (quello che regge l'OH) formando l'acido carbossilico.



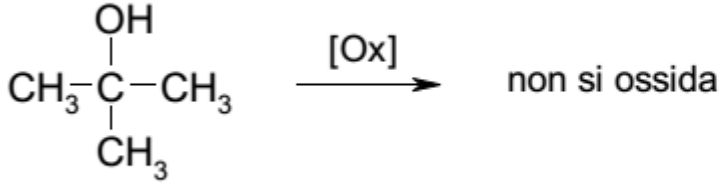
alcol primario aldeide acido carbossilico

L'ossidazione può avvenire **una sola volta sull'alcol secondario** che ha un solo idrogeno sul carbonio alfa.



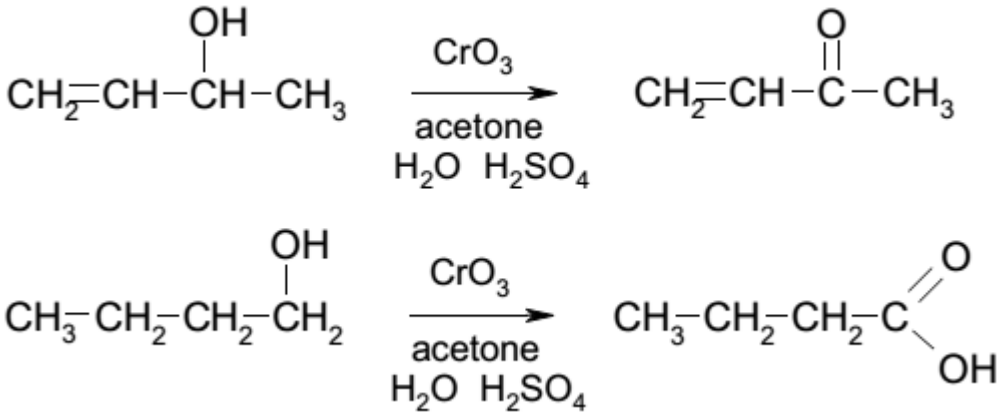
alcol secondario chetone

L'alcol terziario non si ossida in queste condizioni poichè non ha idrogeni sul carbonio alfa.



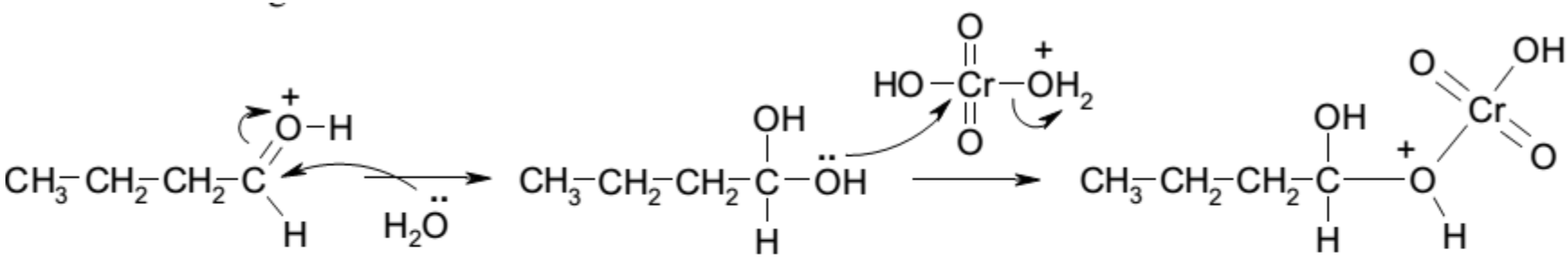
alcol terziario

Il reagente ossidante più utilizzato è il Cr^{6+} perché ossida solo l'ossidrile e lascia inalterati i doppi legami. Col Cr^{6+} è possibile ossidare in modo selettivo l'ossidrile di un alcol insaturo. Se l'alcol è solubile in acqua il reattivo può essere **bicromato di sodio, acqua, acido solforico**. Invece, se l'alcol è poco solubile in acqua, si usa: **anidride cromica, acetone, acqua, acido solforico** (reattivo di Jones)

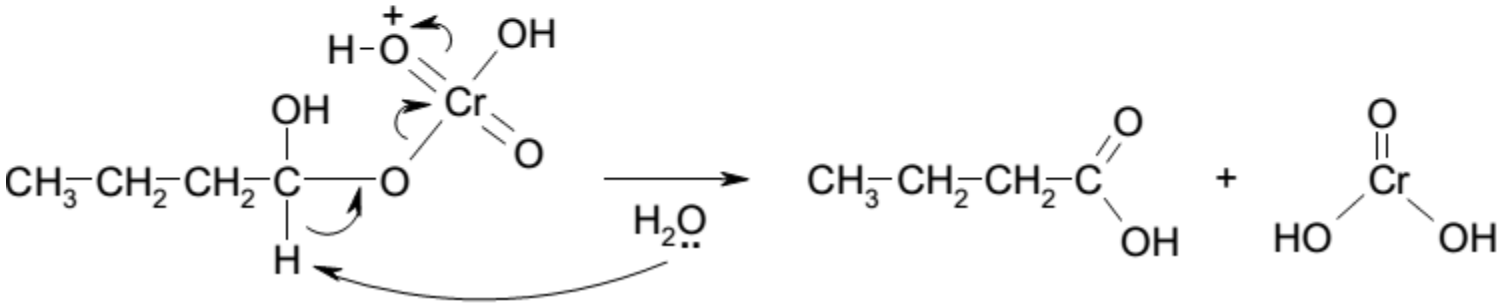


Uso alternativo del **$KMnO_4$**: 1) non selettivo

2) non possibile fermarsi ad aldeide

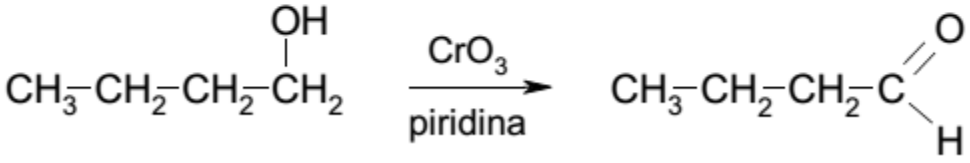


aldeide diolo geminale



Se si vuole **ossidare l'alcol solo fino ad aldeide** è necessario impedire che questa venga ossidata ad acido carbossilico nella seconda parte della reazione. Per ottenere questo risultato, si deve impedire che l'aldeide venga trasformata in diolo geminale per razione con acqua, in modo che non si possa generare l'estere dell'acido cromico.

Il reattivo per questa reazione deve essere rigorosamente **anidro**, si utilizza **anidride cromica in piridina**.

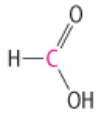


aldeide

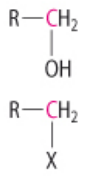
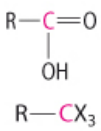
TABELLA 10.1 Confronto degli stati di ossidazione dei differenti gruppi funzionali

Tutte le molecole in un riquadro hanno lo stesso numero di ossidazione.
X = gruppo elettronegativo come un alogeno

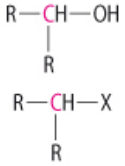
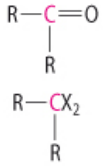
Metano ——— **numero di ossidazione crescente** ———→

CH_4	$H_3C—OH$ $H_3C—X$	$H_2C=O$ H_2CX_2	 H— C	$O=C=O$ CX_4

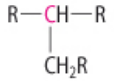
Carbonio primario ——— **numero di ossidazione crescente** ———→

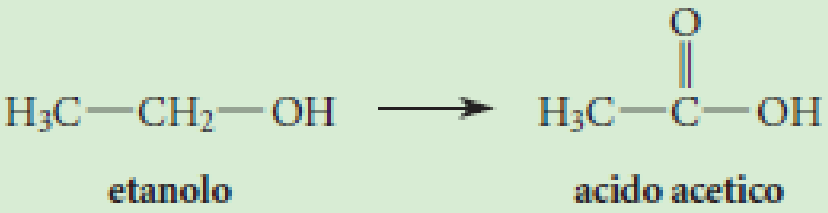
$R—CH_3$		$R—CH=O$ $R—CHX_2$	 $R—CX_3$

Carbonio secondario ——— **numero di ossidazione crescente** ———→

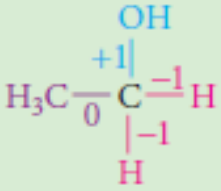
		

Carbonio terziario ——— **numero di ossidazione crescente** ———→

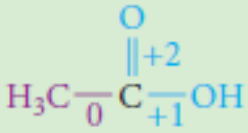


Reagente:

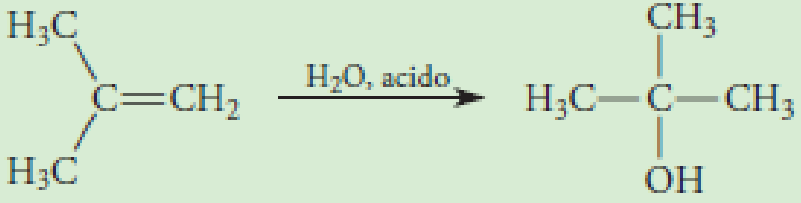


Somma: (+1) + 0 + (−1) + (−1) = −1

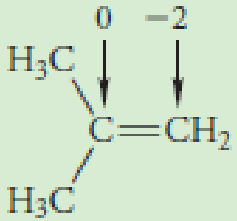
Prodotto:



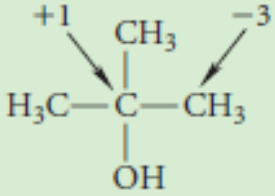
Somma: 0 + (+1) + (+2) = +3



2-metilpropene **alcol *terz*-butilico**



$N_{ox} = 0 + (-2) = -2$



$N_{ox} = +1 + (-3) = -2$