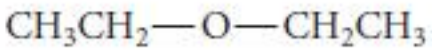
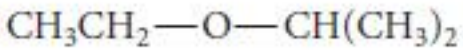
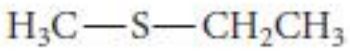
ETERI ed EPOSSIDI: Nomenclatura



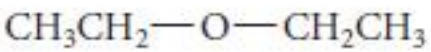
dietil etere



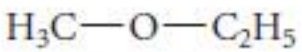
etil isopropil etere



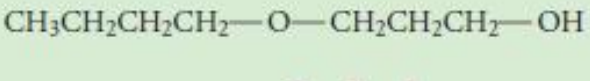
etil metil solfuro

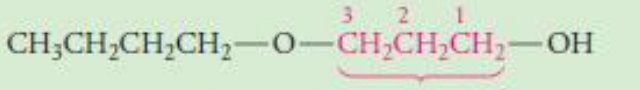


dietil etere
(o anche etere etilico
o semplicemente etere)

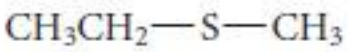


etil metil etere

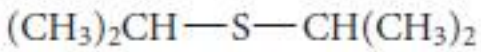




3-butossi-1-propanolo



etil metil solfuro
(o anche etil metil tioetere)



diisopropil solfuro

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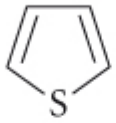
2-etossi-5-metilesano

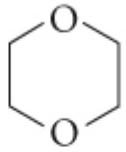
ETERI ciclici (ed epossidi)

furano

tetraidrofurano
(spesso indicato come THF)

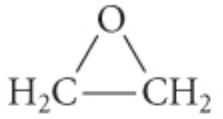


tiofene



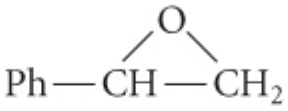
1,4-diossano
(semplicemente definito diossano)

ossirano
(ossido di etilene)

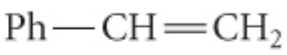


ossido di etilene

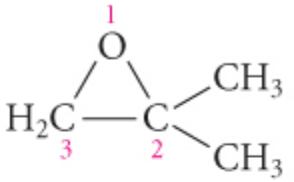
etilene



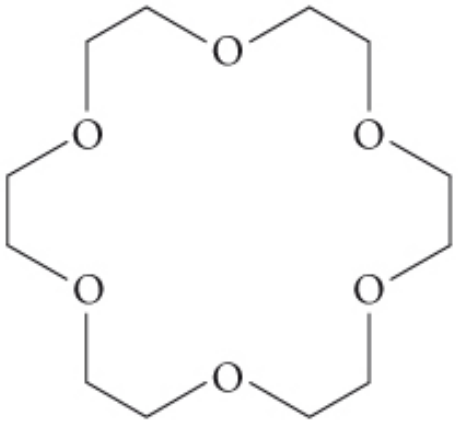
ossido di stirene



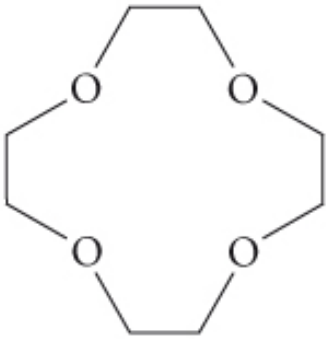
stirene



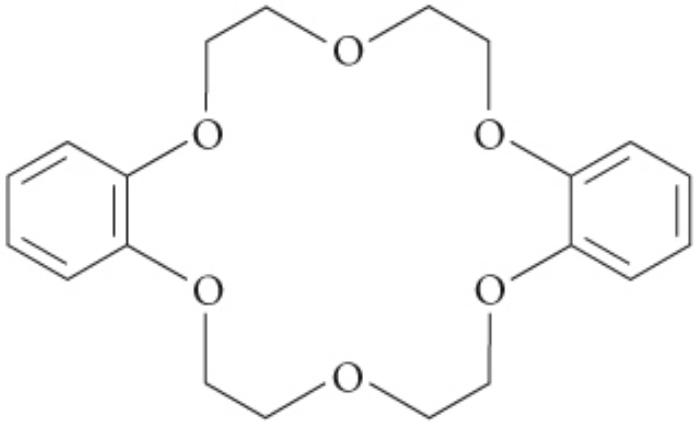
2,2-dimetilossirano



[18]-corona-6



[12]-corona-4



dibenzo[18]-corona-6

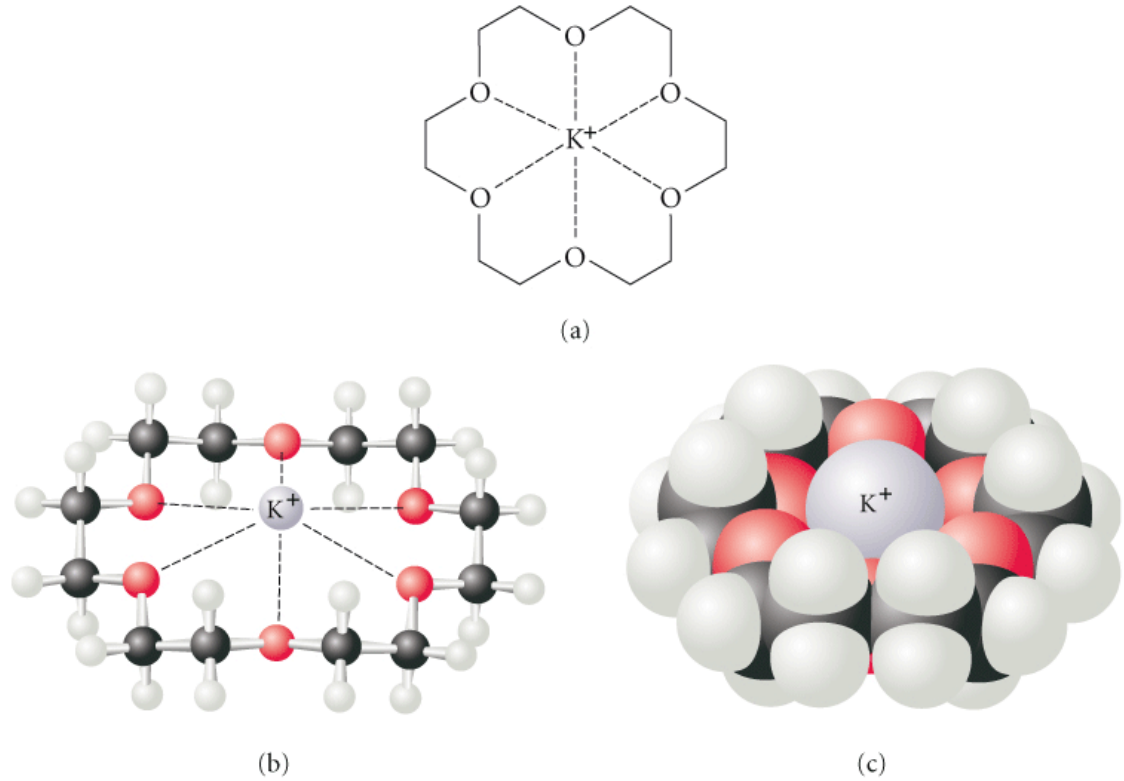


Figura 8.6 Struttura del complesso del [18]-corona-6 con lo ione potassio K^+. (a) Struttura di Lewis; (b) modello a sfere e bastoncini; (c) modello space filling. In (b) e (c) gli atomi di ossigeno sono in rosso. Poiché la parte superficiale del complesso è essenzialmente di natura idrocarburica, gli eteri corona e i loro complessi sono solubili in solventi idrocarburici.

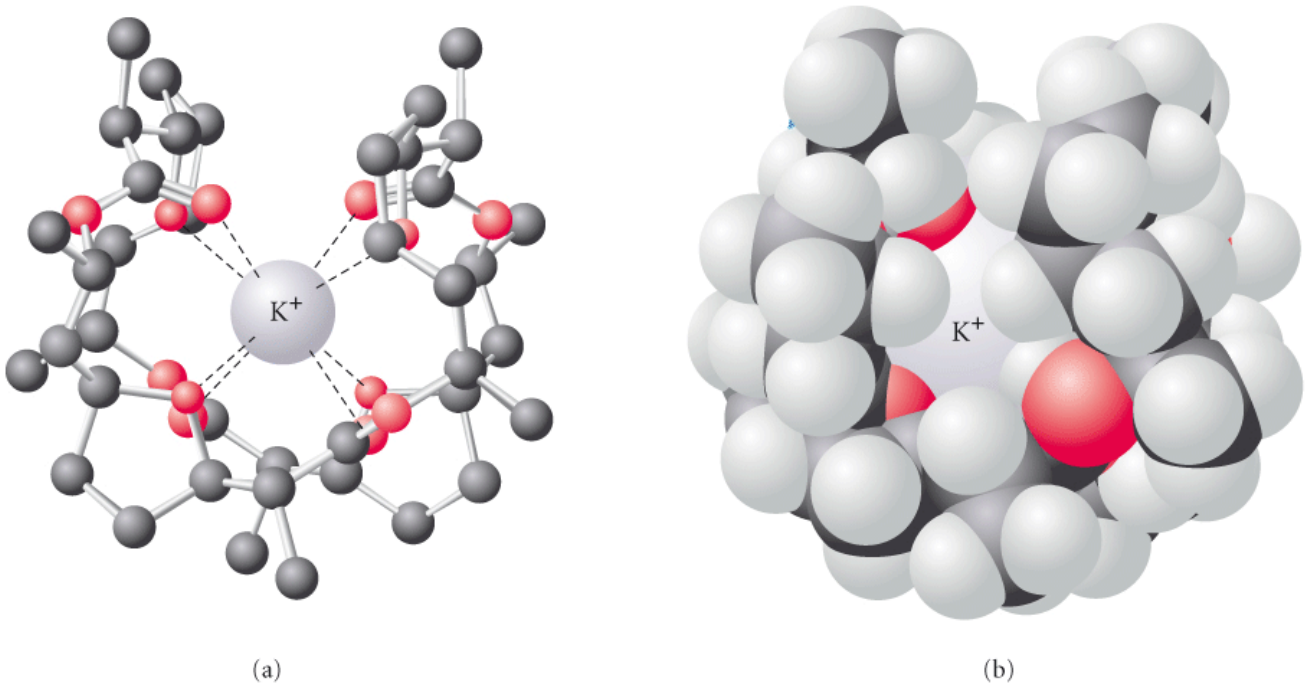
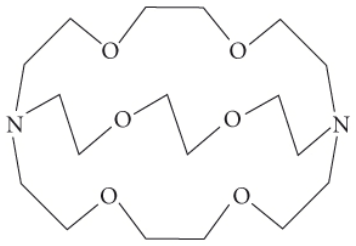
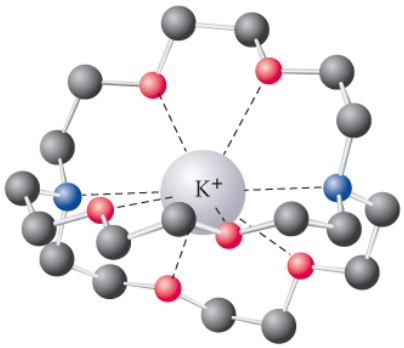


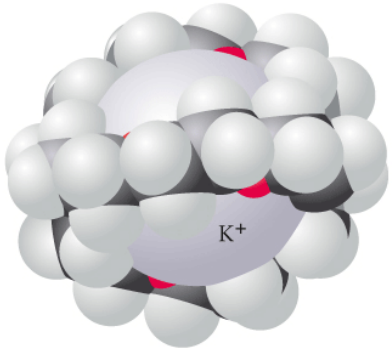
Figura 8.8 Modelli del complesso tra l'antibiotico nonactina e lo ione potassio. (a) Modello a sfere e bastoncini (gli idrogeni sono omessi). Le linee tratteggiate indicano le interazioni tra gli atomi di ossigeno (in *rosso*) e lo ione potassio. (b) Modello space filling, dove sono mostrati gli idrogeni. La nonactina circonda lo ione potassio . Poiché la superficie esterna del complesso è essenzialmente a carattere idrocarburico, il complesso, al pari di quelli eteri corona-metalli (Fig. 8.6), è solubile in solventi non polari aprotici.



(a)

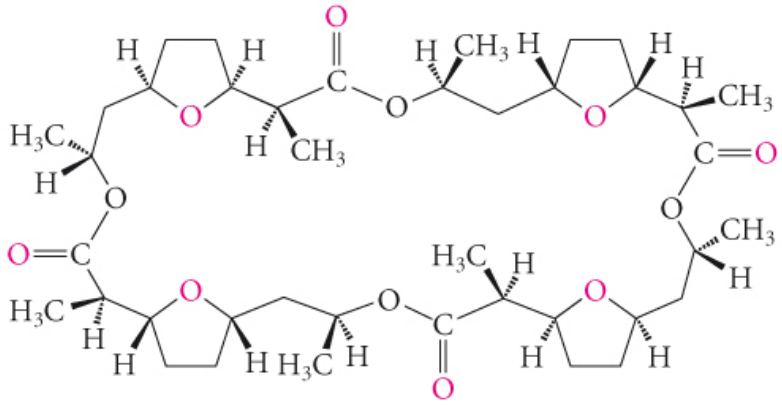


(b)



(c)

Figura 8.7 (a) Struttura del [2.2.2]-criptante. (I numeri in parentesi si riferiscono agli atomi di ossigeno presenti in ciascuna delle tre catene). (b) Modello a sfere e bastoncini di un criptato, il [2.2.2]-criptante con uno ione potassio complessato. (c) Modello space filling della struttura (b) con gli idrogeni evidenziati.



nonactina

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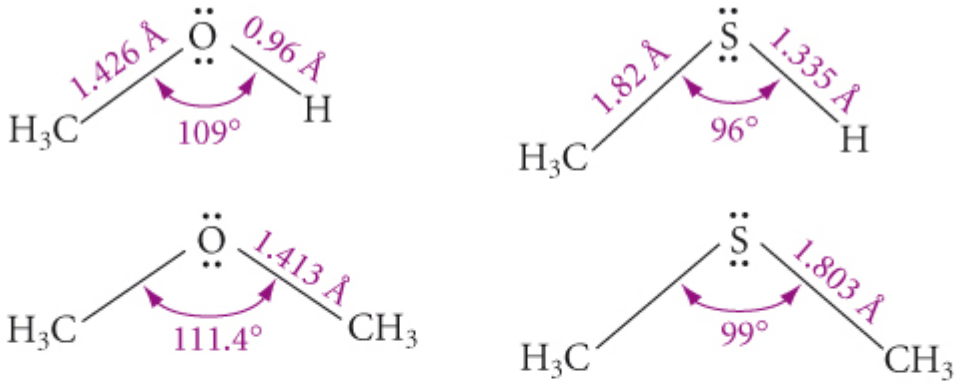
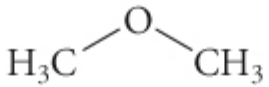
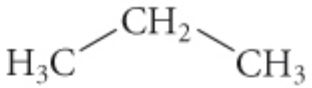
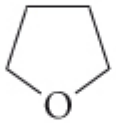


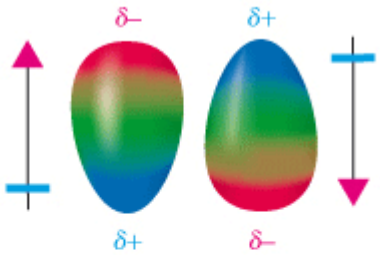
Figura 8.1 Lunghezze e angoli di legame in alcoli, tioli, eteri e solfuri semplici. Gli angoli di legame allo zolfo sono più piccoli di quelli all'ossigeno, mentre i legami allo zolfo sono più lunghi dei corrispondenti legami all'ossigeno.

Proprietà fisiche…

	$H_3C—F$ **fluoruro di metile**	$H_3C—Cl$ **cloruro di metile**	$H_3C—OH$ **metanolo**	$H_3C—O—CH_3$ **dimetil etere**	$H_3C—CH_2—CH_3$ **propano**
momento dipolare	1.82 D	1.94 D	1.7 D	1.31 D	0.08 D

	 **dimetil etere**	 **propano**
momento dipolare	1.31 D	0.08 D
punto di ebollizione	−23.7 °C	−42.1 °C

	 **tetraidrofurano (THF)**	 **ciclopentano**
momento dipolare	1.7 D	0 D
punto di ebollizione	66 °C	49.3 °C



MPE di due molecole polari
allineate per attrazione

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	$CH_3CH_2—OH$	$CH_3CH_2CH_3$	$H_3C—O—CH_3$	$CH_3CH_2—F$
	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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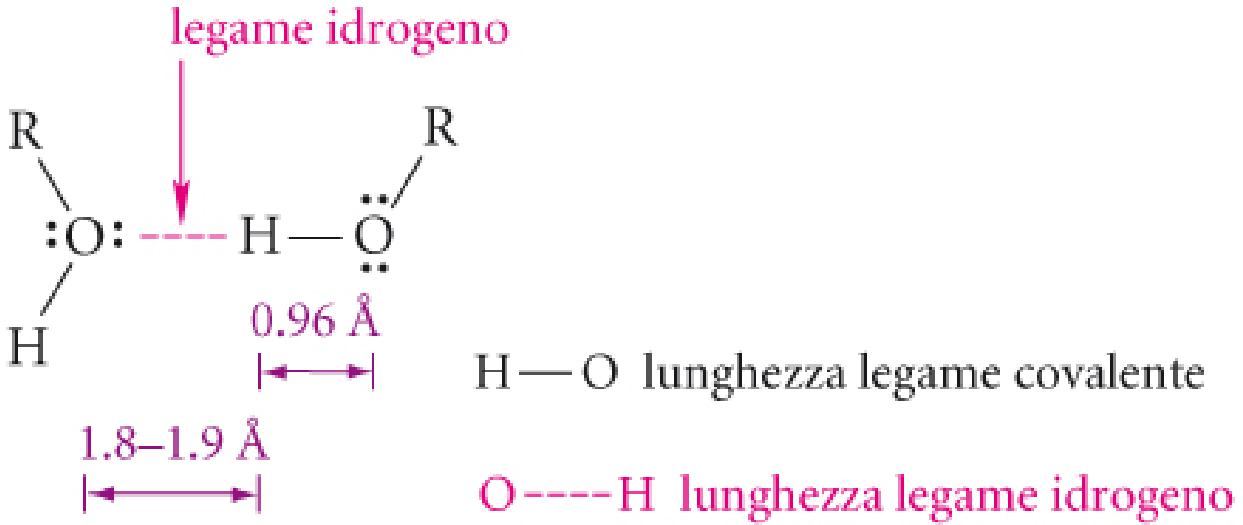
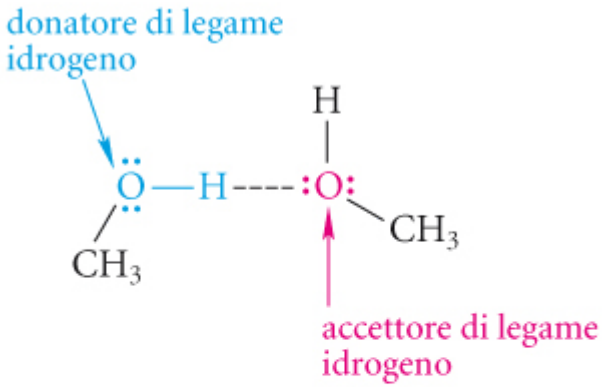

legame idrogeno
R
R
:O:
H—O
H
0.96 Å
1.8–1.9 Å
H—O lunghezza legame covalente
O----H lunghezza legame idrogeno


donatore di legame idrogeno
H
O—H----:O:
CH3
CH3
accettore di legame idrogeno

Solubilità?

	$CH_3CH_2CH_2CH_3$	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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un alcol può accettare legami idrogeno dall'acqua

un alcol può donare legami idrogeno all'acqua

un etere può accettare legami idrogeno dall'acqua

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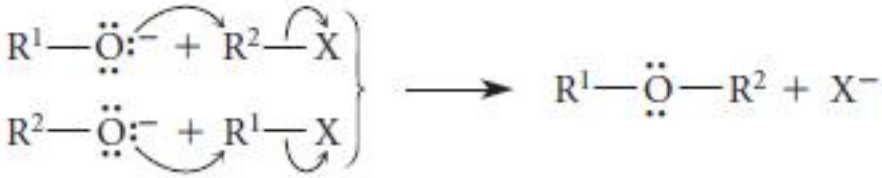
Come si sintetizzano gli eteri?

(11.3)



(11.4)

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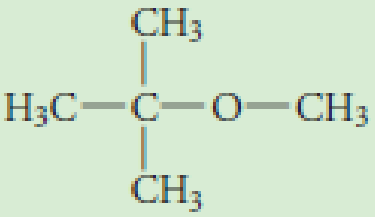
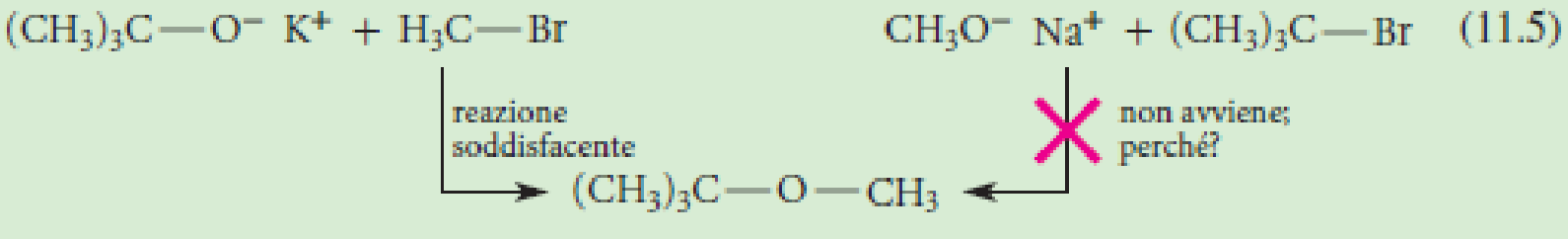


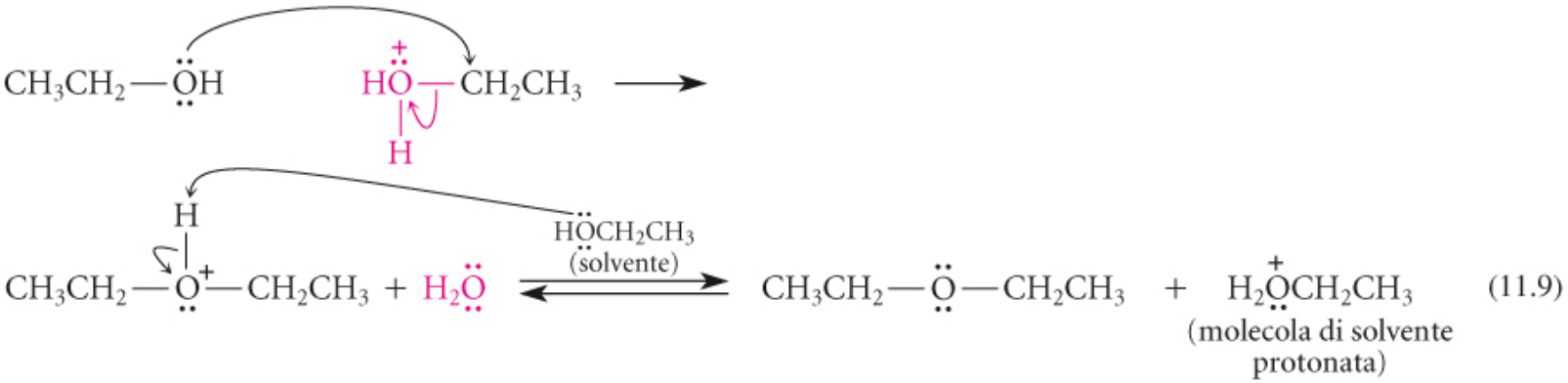
terz-butil metil etere



(11.5)

$$2\,CH_3CH_2{-}OH \xrightarrow[140\ ^\circ C]{H_2SO_4} CH_3CH_2{-}O{-}CH_2CH_3 + H_2O \qquad (11.8)$$

etanolo **etere dietilico**



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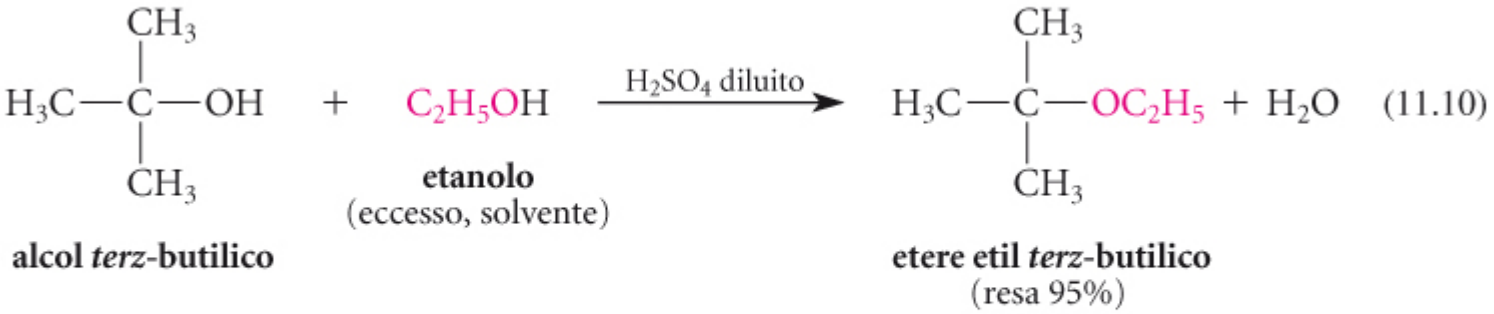
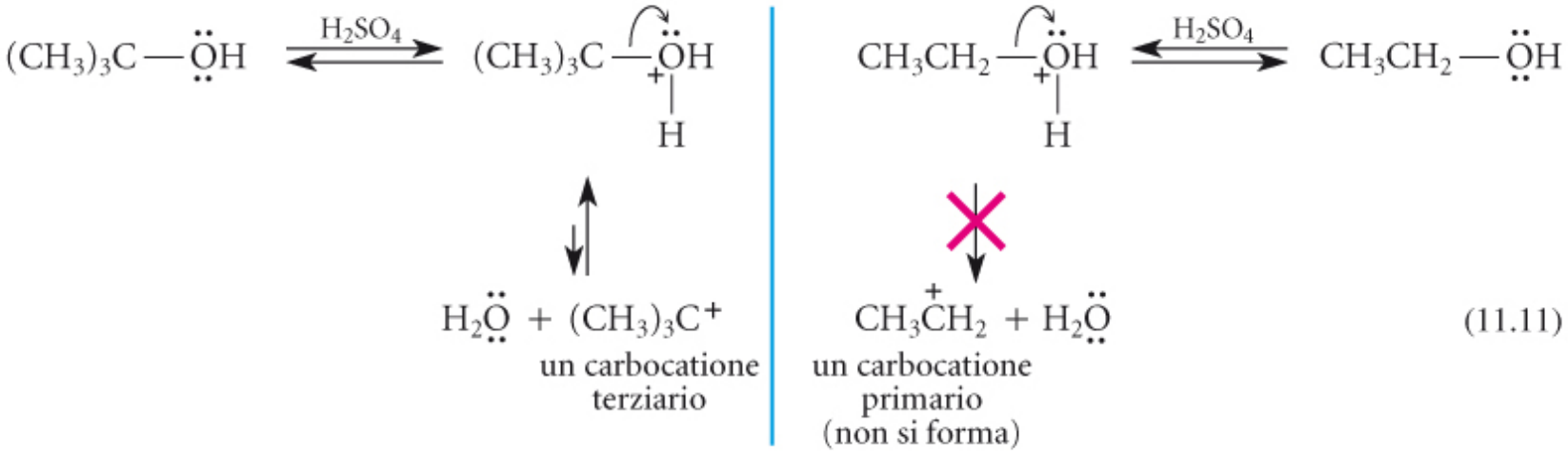
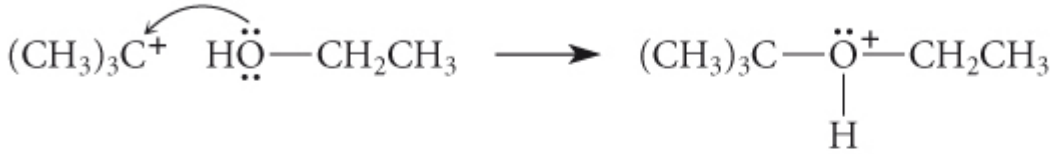

CH3
H3C—C—OH
CH3
+
C2H5OH
etanolo
(eccesso, solvente)
H2SO4 diluito
CH3
H3C—C—OC2H5
CH3
+ H2O
(11.10)
alcol terz-butilico
etere etil terz-butilico
(resa 95%)


(CH3)3C—OH
H2SO4
(CH3)3C—OH
H
H2O + (CH3)3C+
un carbocatione terziario
CH3CH2—OH
H2SO4
CH3CH2—OH
H
CH3CH2 + H2O
un carbocatione primario
(non si forma)
(11.11)



(11.12)

(dona un protone al solvente per dare il prodotto)

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Chimica Organica
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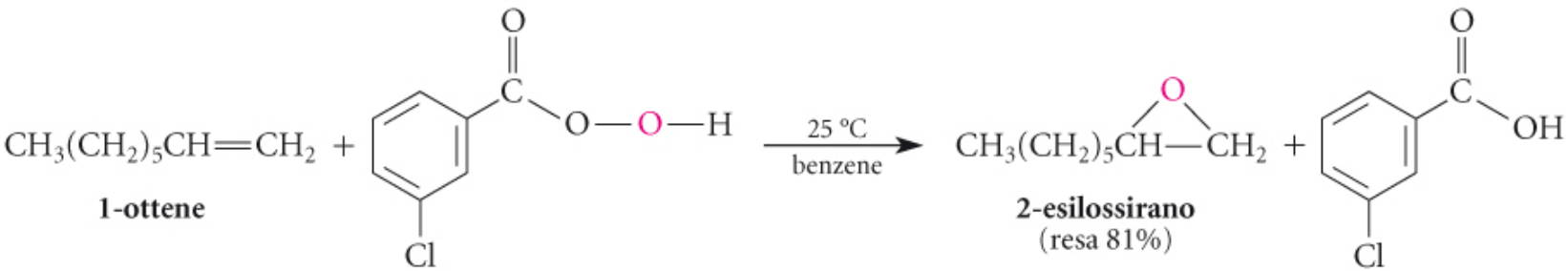
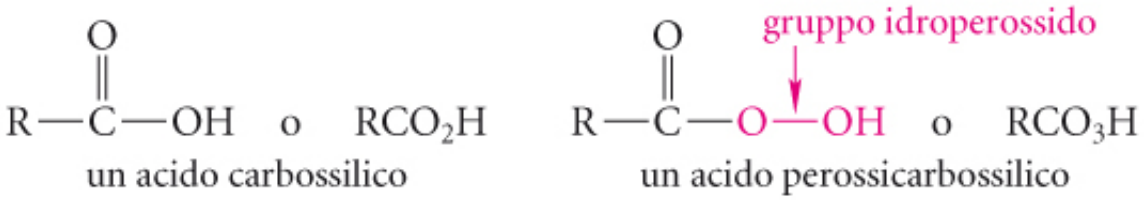
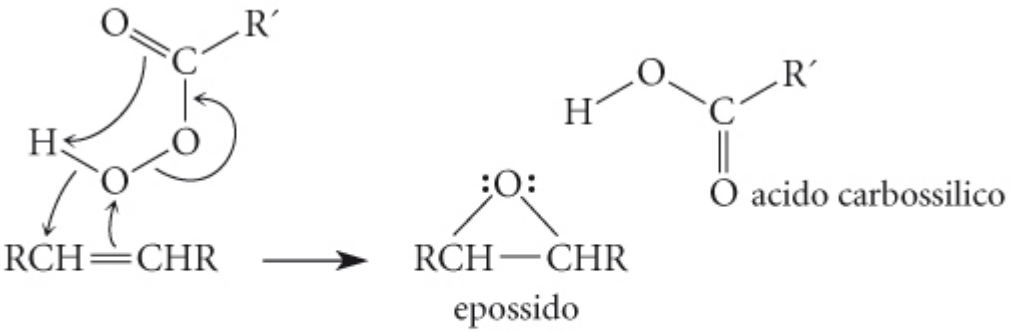
Come si sintetizzano gli epossidi?

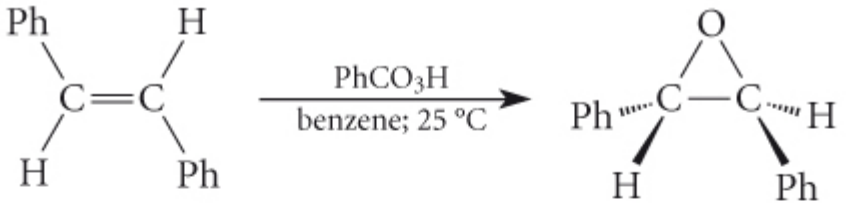


(11.15)



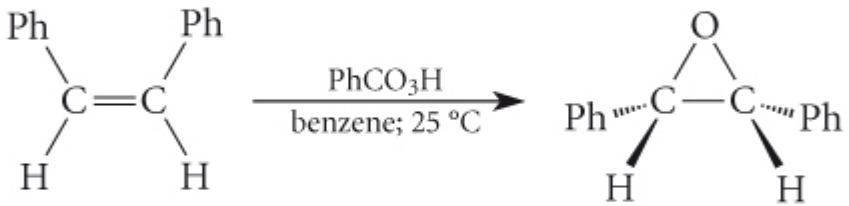
Meccanismo concertato





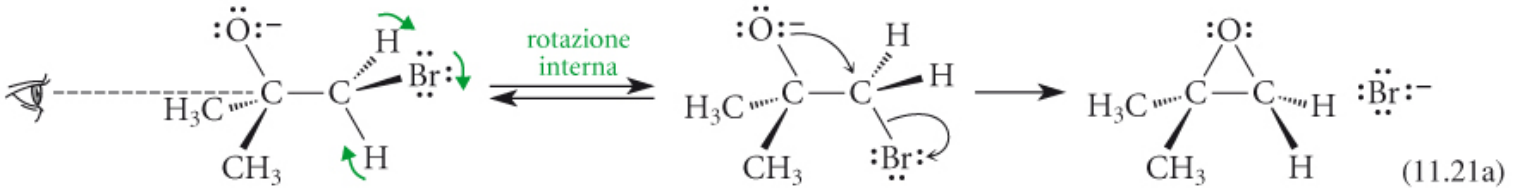
***trans*-stilbene**

***trans*-stilbene ossido**
(resa 55%)



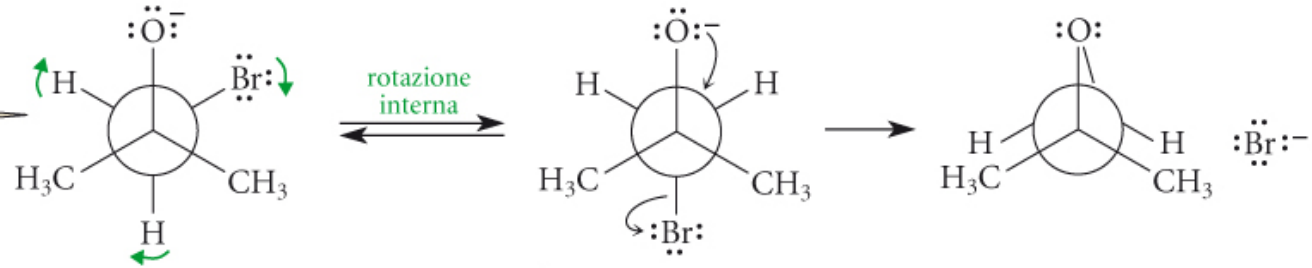
***cis*-stilbene**

***cis*-stilbene ossido**
(resa 52%)



(11.21a)

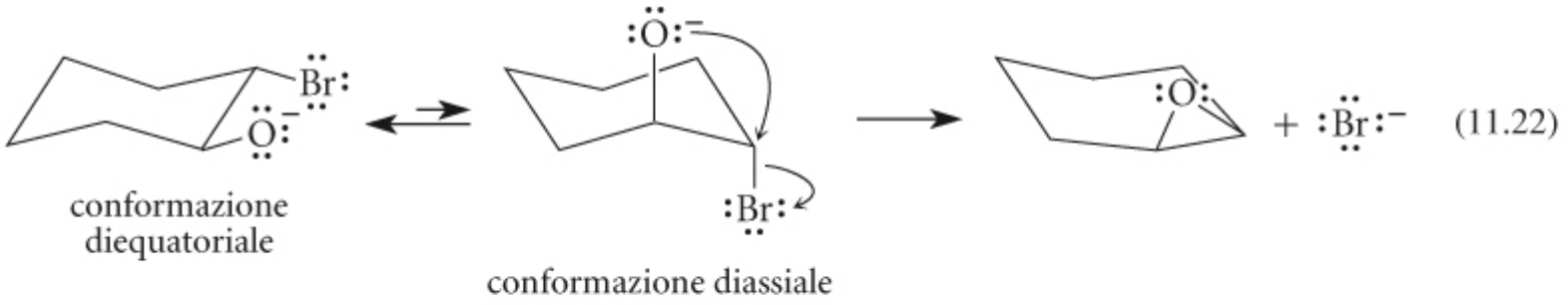
corrispondenti proiezioni di Newman



legami C—O e C—Br sono gauche; la sostituzione dal retro non è possibile

legami C—O e C—Br sono anti; la sostituzione dal retro è possibile

(11.21b)



(11.22)

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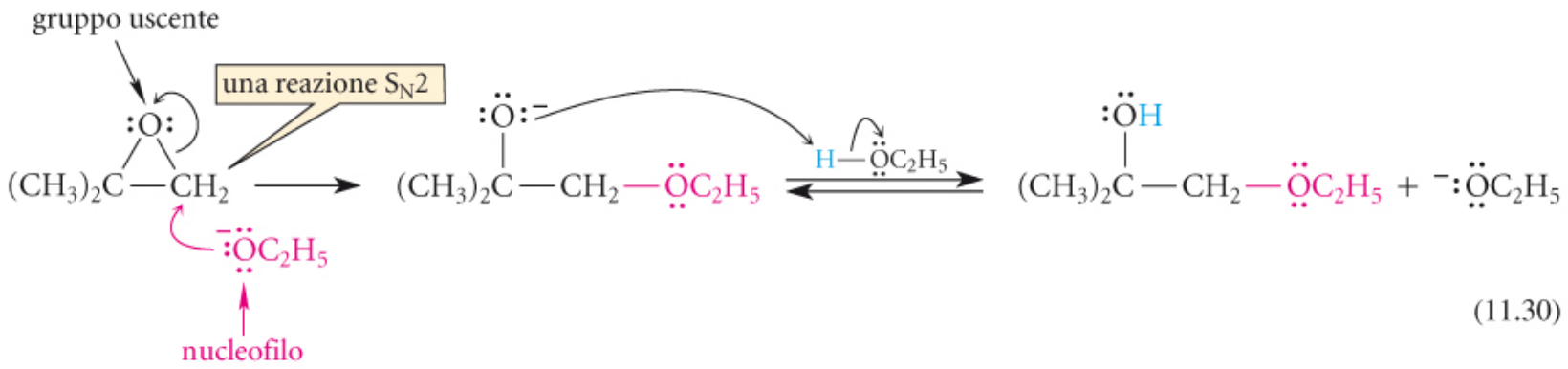
Reattività epossidi



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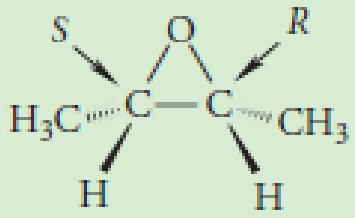
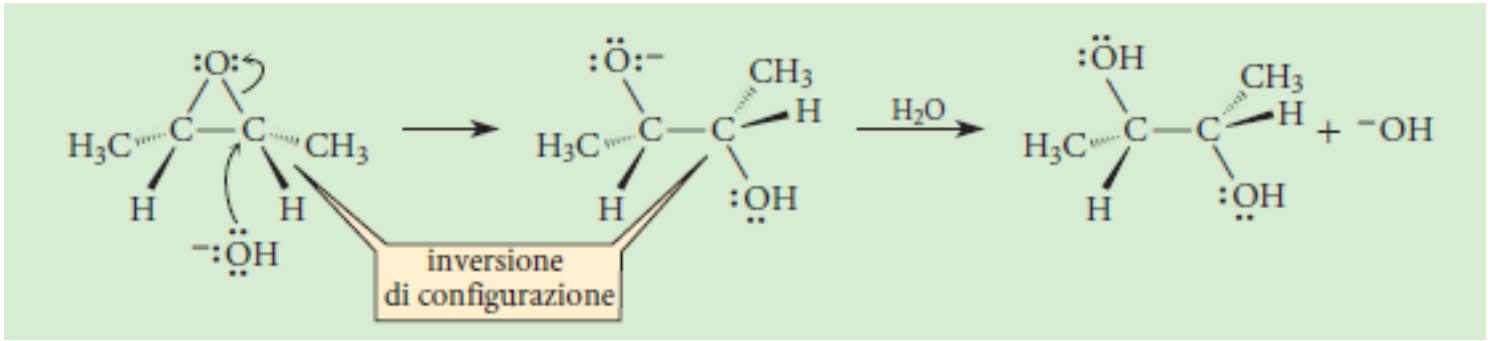
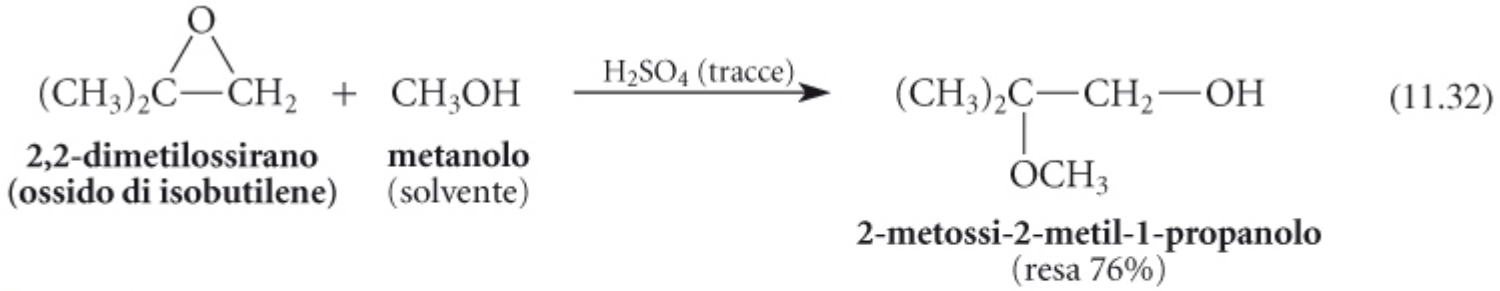


***meso*-2,3-dimetilossirano**

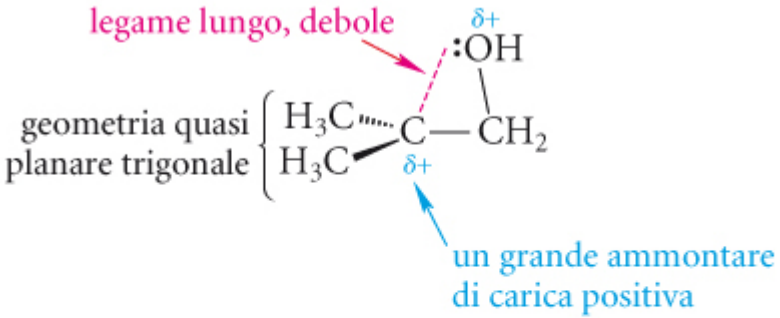




2,2-dimetilossirano (ossido di isobutilene) **metanolo** (solvente)

2-metossi-2-metil-1-propanolo (resa 76%)

(11.32)



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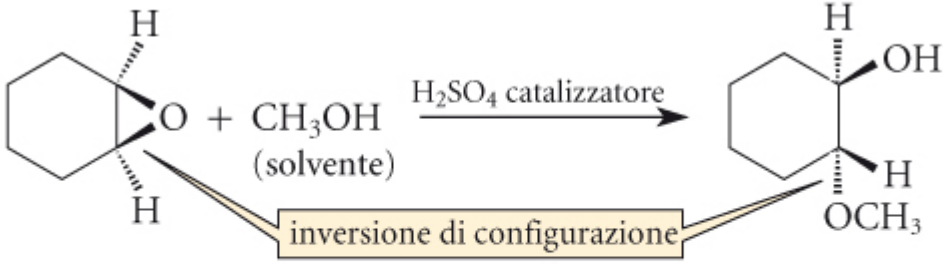

ossido di cicloesene

(±)-*trans*-2-metossicicloesanolo
(resa 82%)

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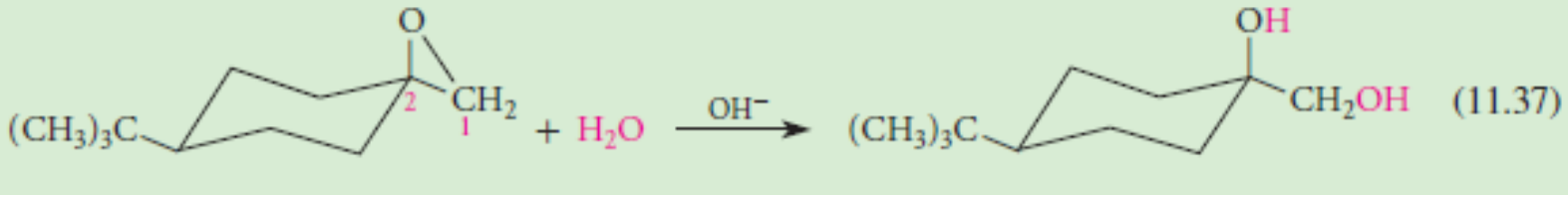
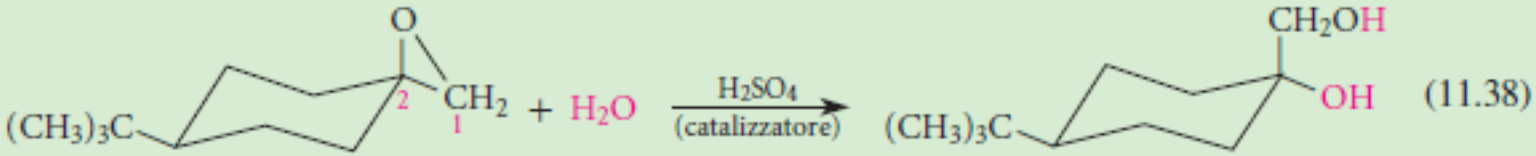
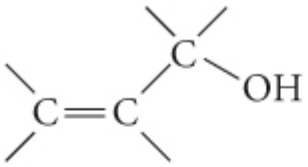


(11.37)

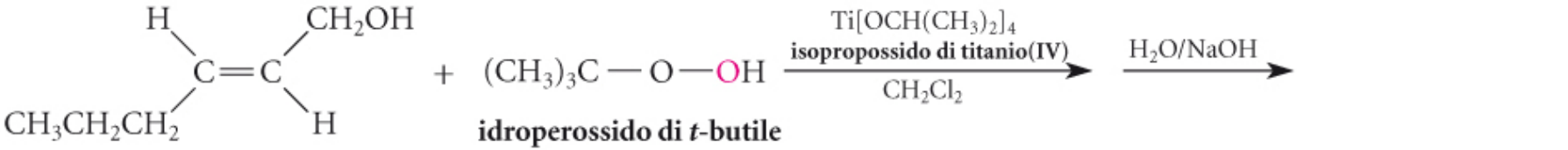


(11.38)



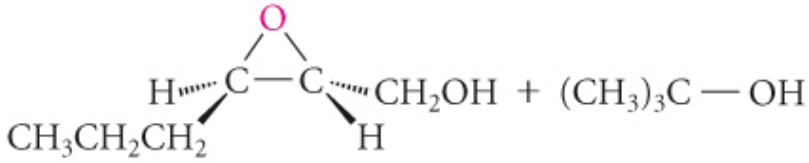
struttura generale di un alcol allilico

2-propen-1-olo
(alcol allilico)



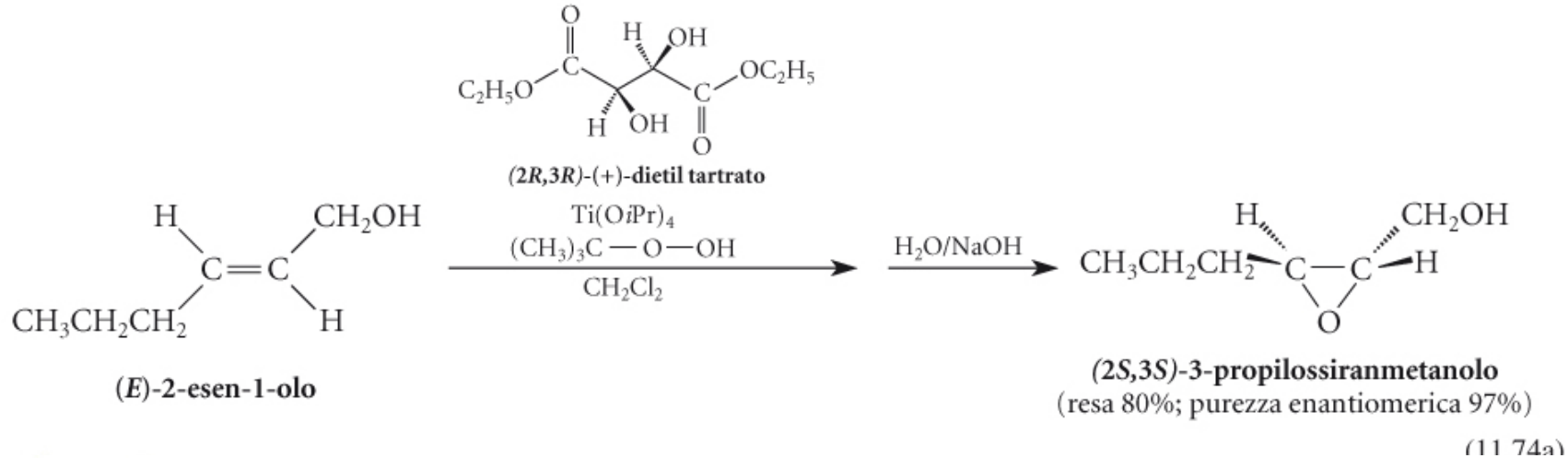
(*E*)-2-esen-1-olo

idroperossido di *t*-butile

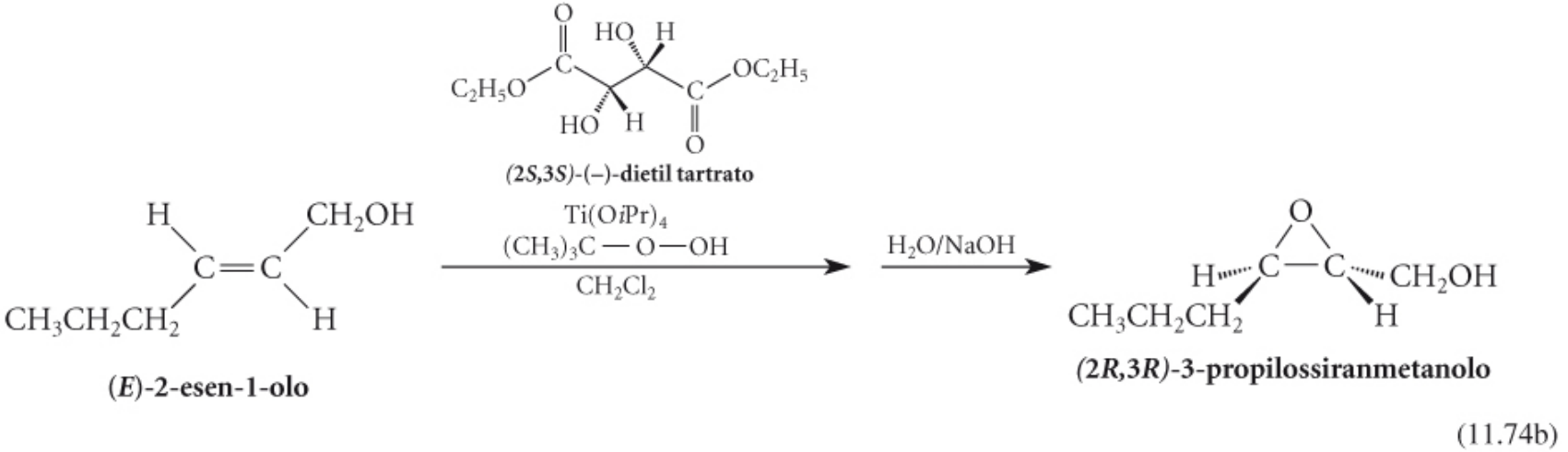


***trans*-3-propilossiranmetanolo**
(racemico)

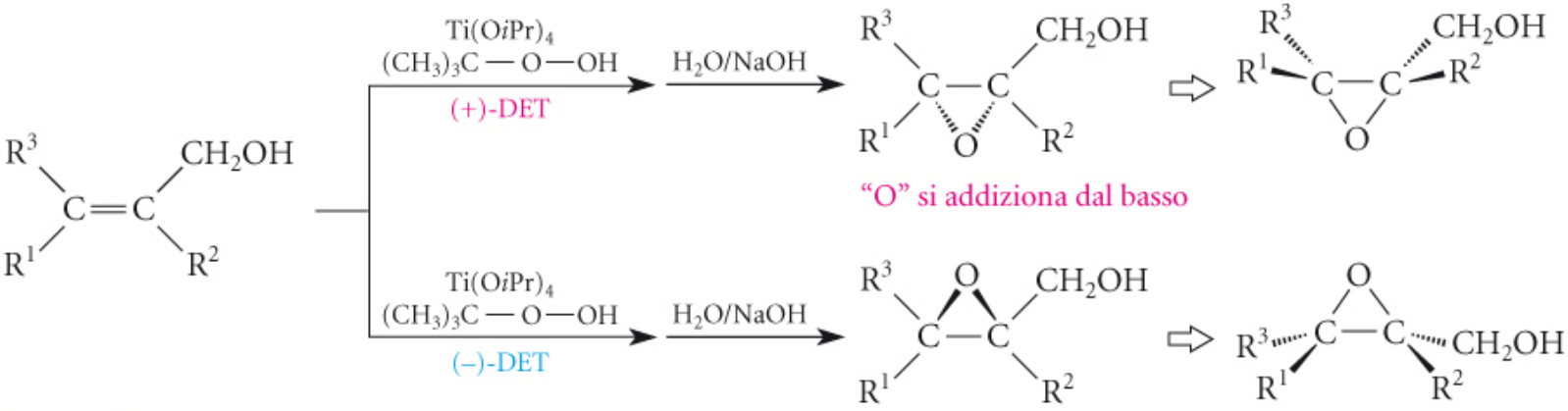
(11.73)



(11.74a)



(11.74b)



(11.75)

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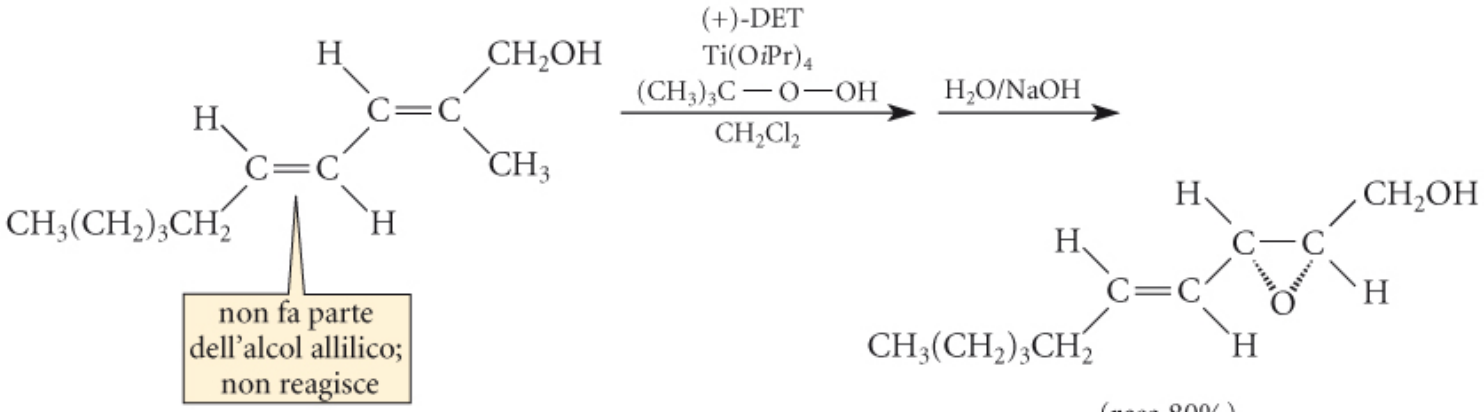

(resa 80%)

(11.76)