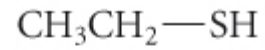
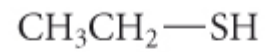


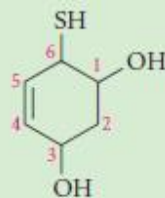
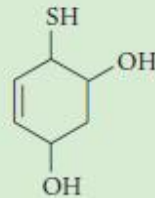
# TIOLI: Nomenclatura



etanolo + *tiolo* = **etantiolo**



**mercaptano di etile**



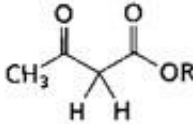
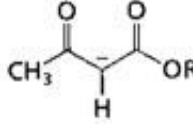
**6-mercapto-4-cicloesen-1,3-diolo**

# TIOLI: proprietà acido-base

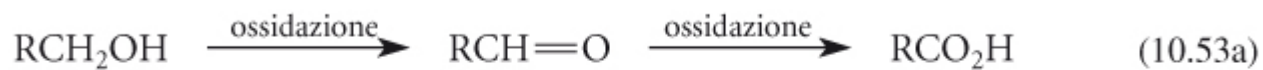


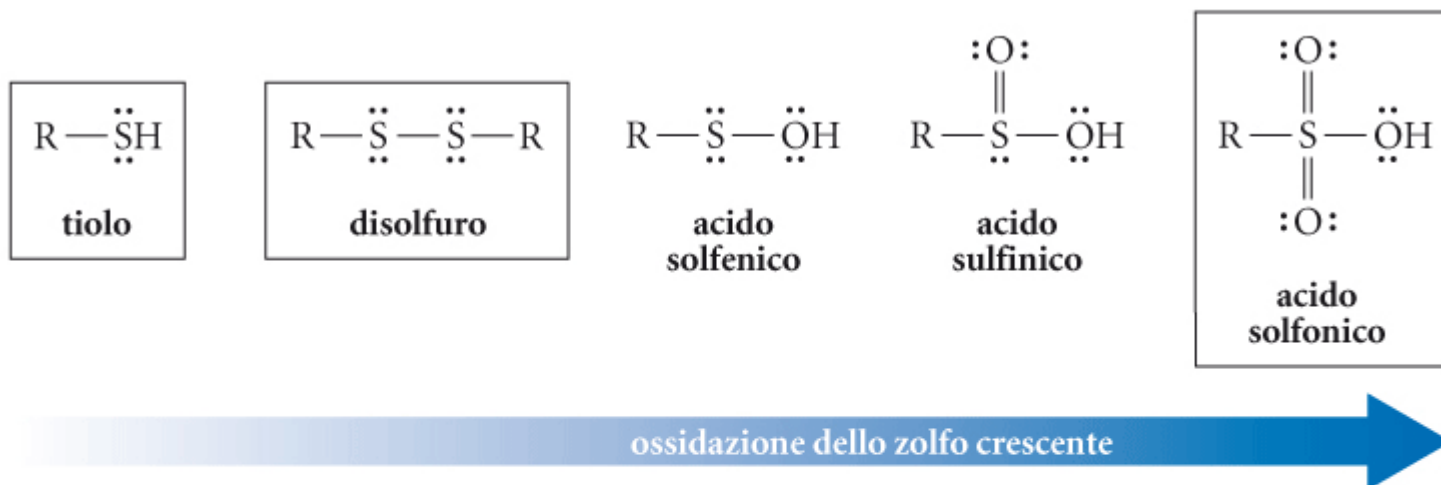
**Table 6.3**

Acidities of molecules and ions commonly encountered in organic chemistry.<sup>a</sup>

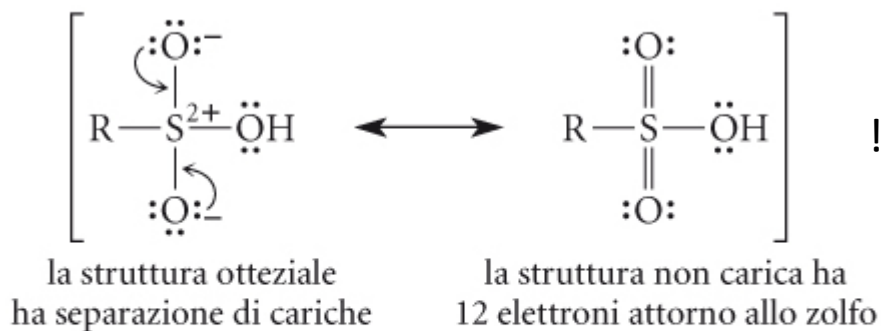
Acid	Conjugate base	$pK_a$	Acid	Conjugate base	$pK_a$
HClO <sub>4</sub>	ClO <sub>4</sub> <sup>-</sup>	-10	HCN	CN <sup>-</sup>	9.2
HI	I <sup>-</sup>	-10	NH <sub>4</sub> <sup>+</sup>	NH <sub>3</sub>	9.2
$\begin{array}{c} \text{+OH} \\ \parallel \\ \text{R}-\text{C}-\text{H} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{H} \end{array}$	-10	ArOH	ArO <sup>-</sup>	10
H <sub>2</sub> SO <sub>4</sub>	HSO <sub>4</sub> <sup>-</sup>	-10	R-CH <sub>2</sub> NO <sub>2</sub>	R- $\bar{\text{C}}\text{H}$ -NO <sub>2</sub>	10
HBr	Br <sup>-</sup>	-9	RNH <sub>3</sub> <sup>+</sup>	RNH <sub>2</sub>	11
HCl	Cl <sup>-</sup>	-7	RSH	RS <sup>-</sup>	11
$\begin{array}{c} \text{+OH} \\ \parallel \\ \text{R}-\text{C}-\text{R} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{R} \end{array}$	-7			11
ArSO <sub>3</sub> H	ArSO <sub>3</sub> <sup>-</sup>	-6.5	CH <sub>3</sub> OH	CH <sub>3</sub> O <sup>-</sup>	15.2
$\begin{array}{c} \text{+OH} \\ \parallel \\ \text{R}-\text{C}-\text{OR}' \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OR}' \end{array}$	-6	H <sub>2</sub> O	HO <sup>-</sup>	15.7
$\begin{array}{c} \text{H} \\   \\ \text{R}-\text{O}^+-\text{R}' \end{array}$	R-O-R'	-3.5	RCH <sub>2</sub> OH	RCH <sub>2</sub> O <sup>-</sup>	16
$\begin{array}{c} \text{H} \\   \\ \text{R}-\text{O}^+-\text{H} \end{array}$	R-O-H	-2	R <sub>2</sub> CH-OH	R <sub>2</sub> CH-O <sup>-</sup>	17
			R <sub>3</sub> C-OH	R <sub>3</sub> C-O <sup>-</sup>	17
			$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{NH}_2 \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{NH}^- \end{array}$	17
			$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{NH}_2 \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{NH}^- \end{array}$	20

# TIOLI: proprietà redox

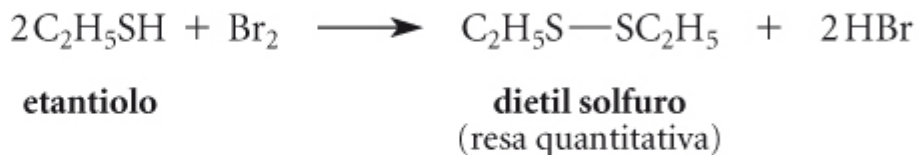
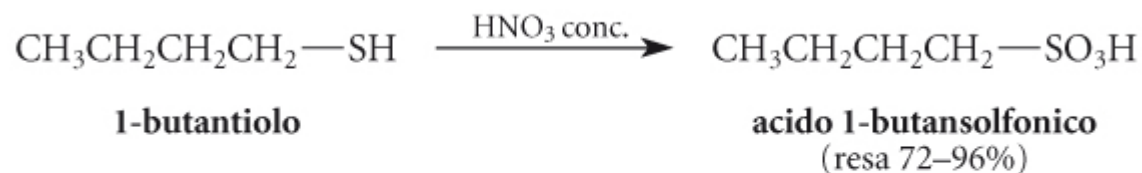


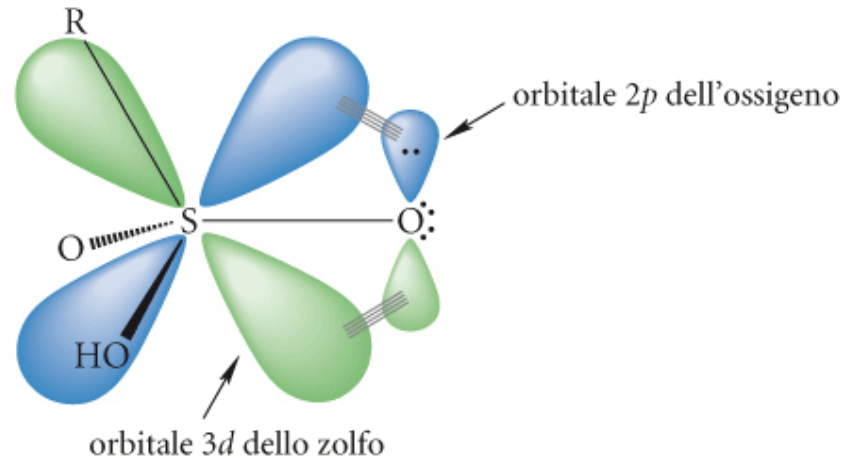


**Figura 10.3** L'ossidazione dei tioli può dare diversi prodotti di ossidazione. Fra questi, i disolfuri e gli acidi solfonici (nei riquadri) sono i prodotti più comuni.



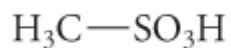
! Espansione dell'ottetto per lo zolfo !



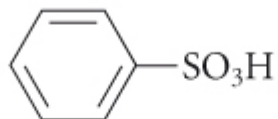


**Figura 10.4.** Il legame negli stati di ossidazione elevati dello zolfo coinvolge i suoi orbitali  $3d$ . I lobi positivi e negativi sono mostrati in blu e verde, rispettivamente. Nell'acido solfonico ( $\text{RSO}_3\text{H}$ , Eq. 10.54), una coppia elettronica di non legame sull'ossigeno si sovrappone ad uno dei numerosi orbitali  $3d$  dello zolfo. La sovrapposizione è indicata da linee colorate. Nota che questa sovrapposizione è poco efficiente, sia perché gli orbitali hanno dimensioni differenti, sia perché metà dell'orbitale  $3d$  dello zolfo punta in una direzione opposta al legame.

**! Meno efficiente ancora è la formazione del doppio legame  $\text{C}=\text{S}$  che NON può coinvolgere gli orbitali  $d$  vuoti dello zolfo !**



acido metansolfonico



acido benzensolfonico

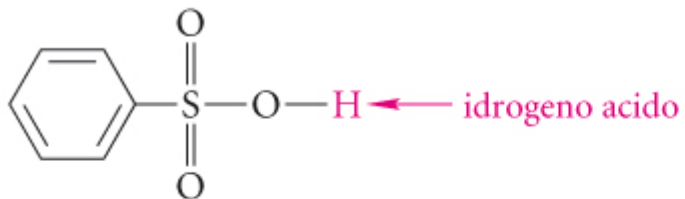


acido *p*-toluensolfonico

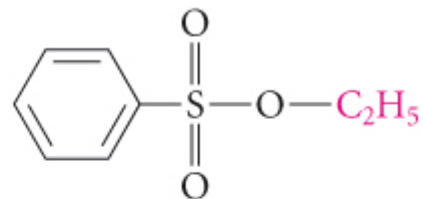


Loudon  
Chimica Organica  
EdiSES

N.B. protoni acidi!



acido benzensolfonico



benzensolfonato di etile  
(un estere solfonico)



Loudon  
Chimica Organica  
EdiSES



**metansolfonato di etile**

**mesilato di etile**



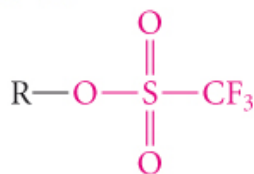
***p*-toluensolfonato di *sec*-butile**

**tosilato di *sec*-butile**



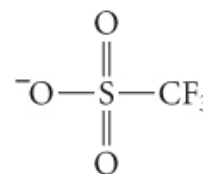
Loudon  
**Chimica Organica**  
**EdISES**

il gruppo triflato,  
un gruppo uscente molto reattivo



un estere triflato

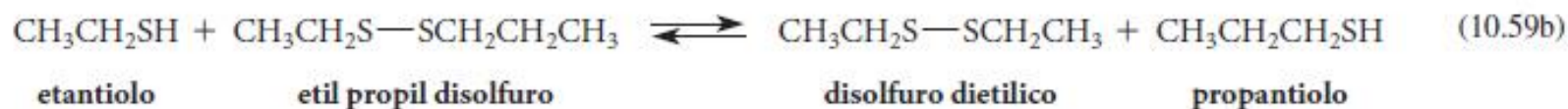
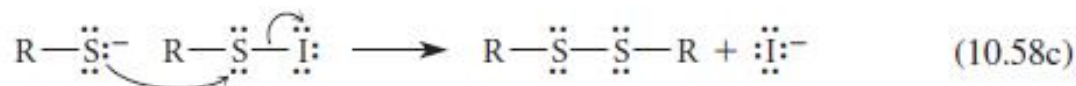
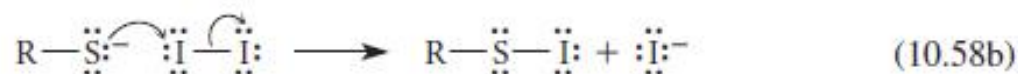
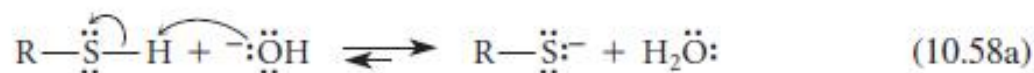
$\text{R}-\text{OTf}$   
abbreviazione per  
l'estere triflato



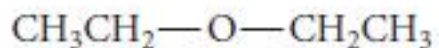
**anione triflato**  
una base molto debole



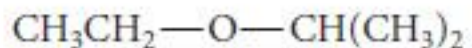




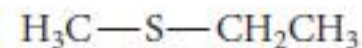
# SOLFURI: Nomenclatura



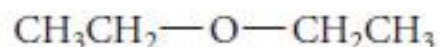
**dietil etere**



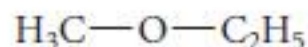
**etil isopropil etere**



**etil metil solfuro**



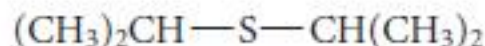
**dietil etere**  
(o anche etere etilico  
o semplicemente etere)



**etil metil etere**



**etil metil solfuro**  
(o anche etil metil tioetere)

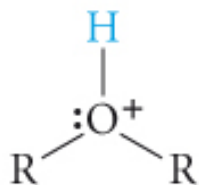


**diisopropil solfuro**

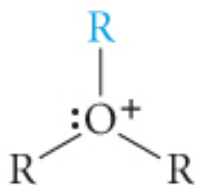


**2-etossi-5-metilesano**

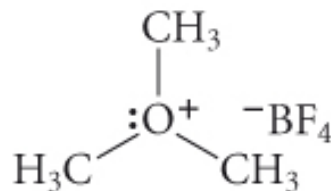
# I Sali di SOLFONIO in Biochimica



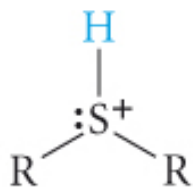
un etere  
protonato



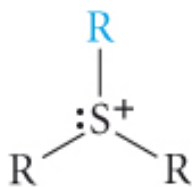
uno ione di  
trialchilossonio



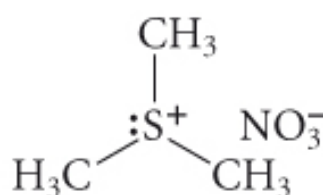
**tetrafluoroborato  
trimetilossonio**  
(un sale di ossonio)



un solfuro  
protonato

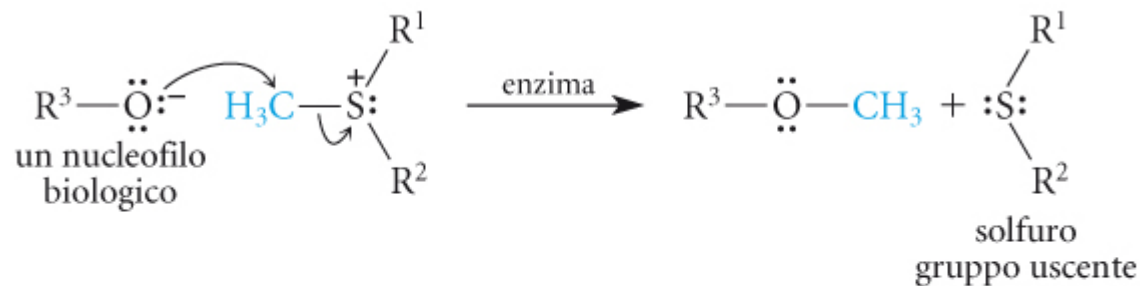
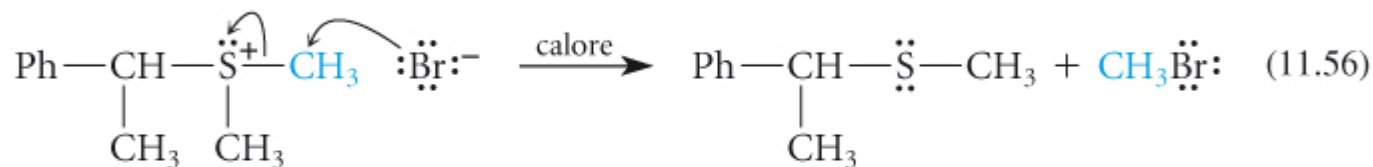


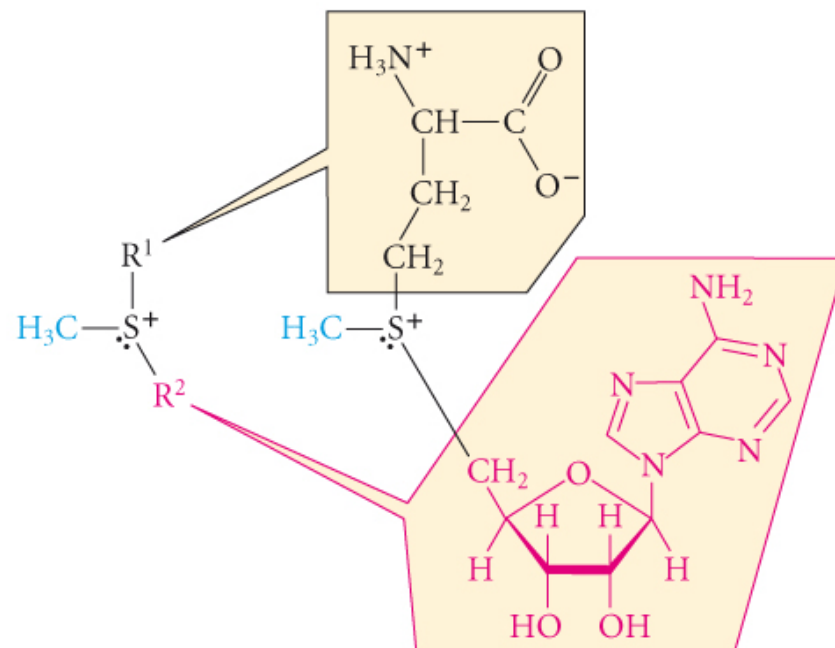
uno ione di  
trialchilsolfonio



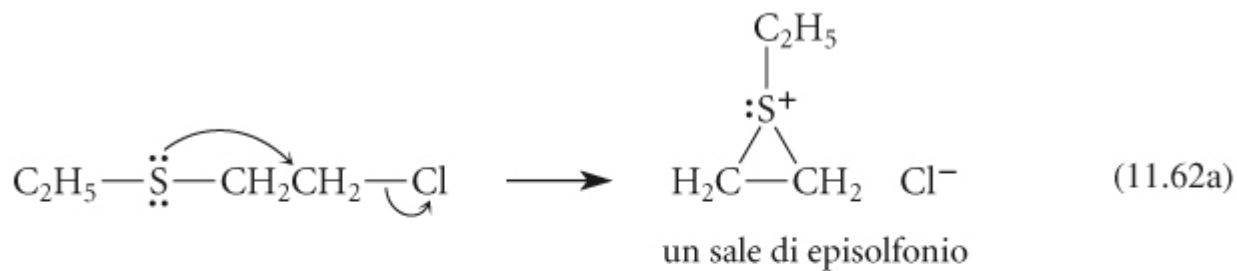
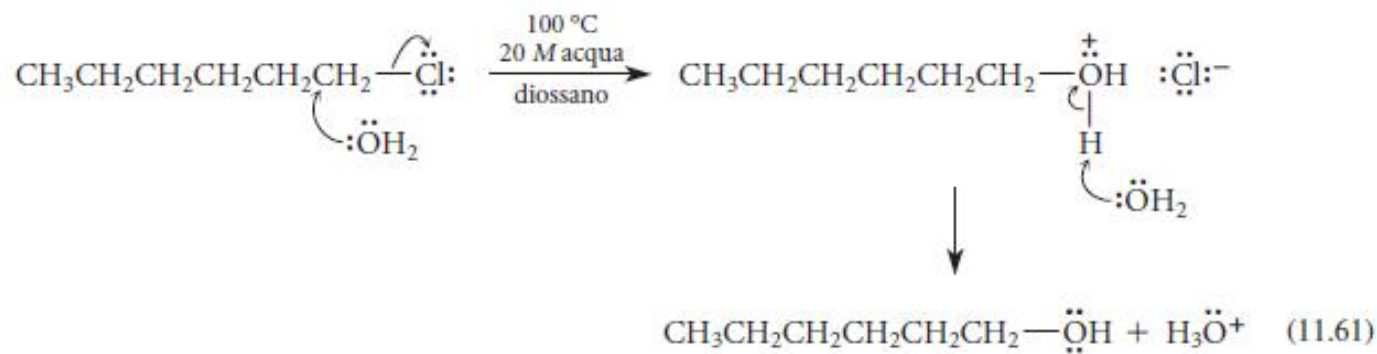
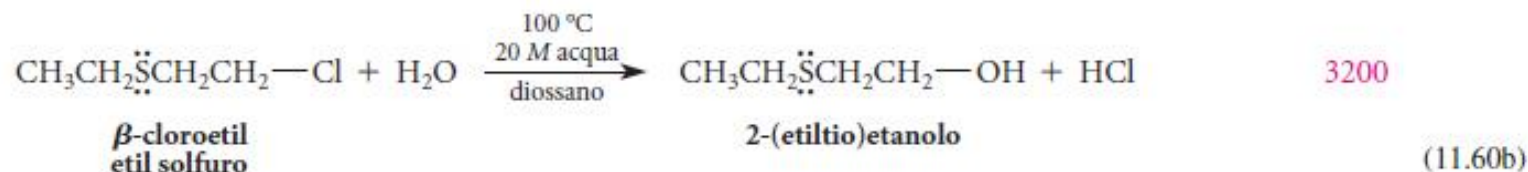
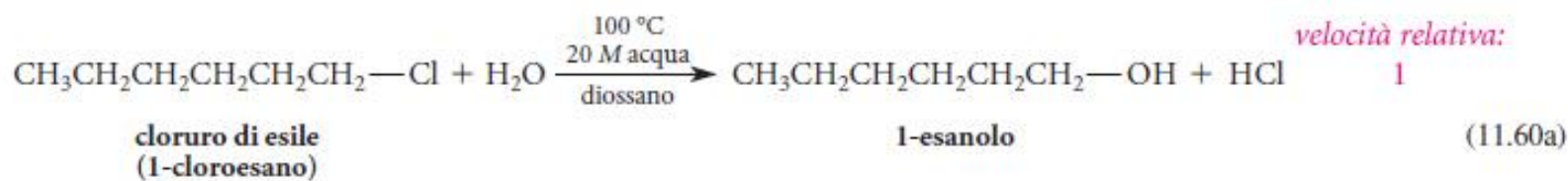
**nitrate di  
trimetilsolfonio**  
(un sale di solfonio)

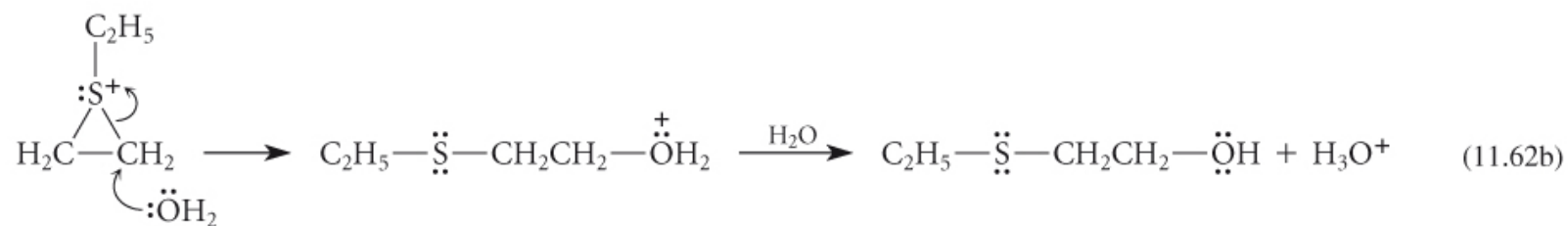






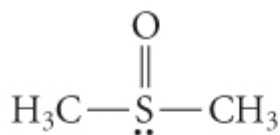
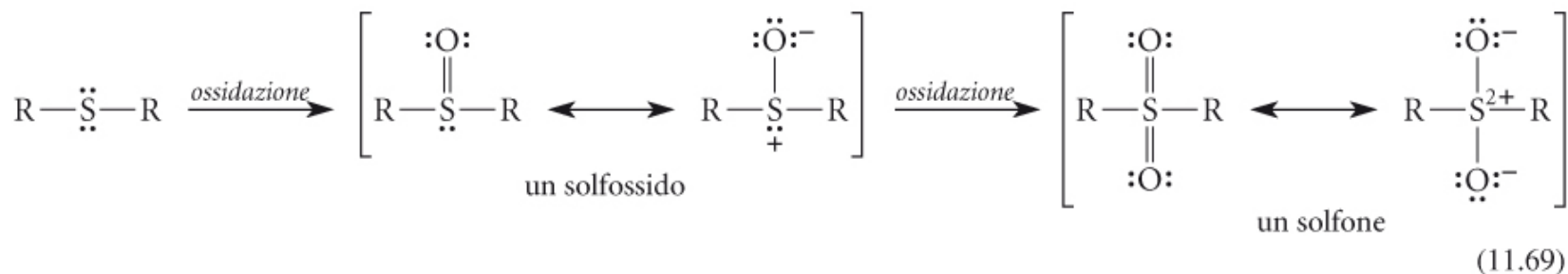
**Figura 11.1** S-Adenosilmetionina (SAM). Le parti della struttura racchiuse nei riquadri sono abbreviate con R<sup>1</sup> e con R<sup>2</sup> nel testo.



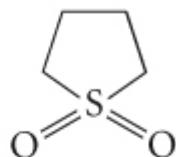


**Reazioni intramolecolari ed EFFETTO di PROSSIMITA'**

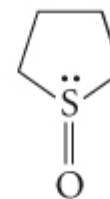
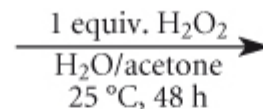
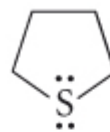
# SOLFURI: Reattività REDOX



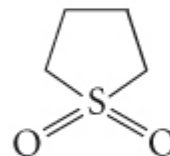
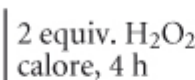
dimetilsolfossido  
(DMSO)



tetrametilensolfone,  
o solfolano



(resa 88%)



(resa 97%)



Loudon  
Chimica Organica  
EdISES



Loudon  
Chimica Organica  
EdISES