

OXIDATION OF SULFIDES TO SULFOXIDES BY OPTICALLY ACTIVE
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A study was carried out on the oxidation of dialkyl and aryl alkyl sulfides by optically active phosphite ozonides in the case of the oxidation of methyl phenyl sulfide, methyl decyl sulfide, and benzyl octyl sulfide by the ozonides of L-(-)-menthyl o-phenylene phosphite, L-(-)-menthyl (2,2'-methylene-bis(4-methyl-6-tert-butylphenyl) phosphite, and L-(-)-bornyl (2,2'-methylene-bis(4-methyl-6-tert-butylphenyl) phosphite. These ozonides oxidize the indicated sulfides to the corresponding sulfoxides at -80°C . Partial asymmetric oxidation is possible. The addition of $\text{Ti}(\text{OC}_3\text{H}_7)_4$ increases the asymmetric control of the reaction.

The oxidation of sulfides to the corresponding sulfoxides by peroxide compounds such as hydrogen peroxide, peracids, and hydroperoxides is well known [1]. Phosphite ozonides, which are obtained in the low-temperature ozonization of phosphites, are efficient oxidizing agents for sulfides [2,3]. The partial asymmetric oxidation of prochiral sulfides to sulfoxides has been found for optically active peracids and hydroperoxides (the optical yields were 0.3-5% and 4-27%, respectively) [4,5]. The use of optically active phosphite ozonides for this purpose has not been described. In the present communication, we discuss the possibility of the use of the ozonides of optically active phosphites for the asymmetric oxidation of sulfides.

The oxidation of methyl phenyl sulfide (I), methyl decyl sulfide (II), and benzyl octyl sulfide (III) by the ozonides of L-(-)-menthyl o-phenylene phosphite (IV), L-(-)-menthyl (2,2'-methylene-bis(4-methyl-6-tert-butylphenyl) phosphite (V), and L-(-)-bornyl (2,2'-methylene-bis(4-methyl-6-tert-butylphenyl) phosphite (VI) was studied at -80°C in CH_2Cl_2 . Under these conditions, ozonides (IV)-(VI) are thermally stable [6,7]. The rapid oxidation of (I)-(III) to sulfoxides was observed in all cases.

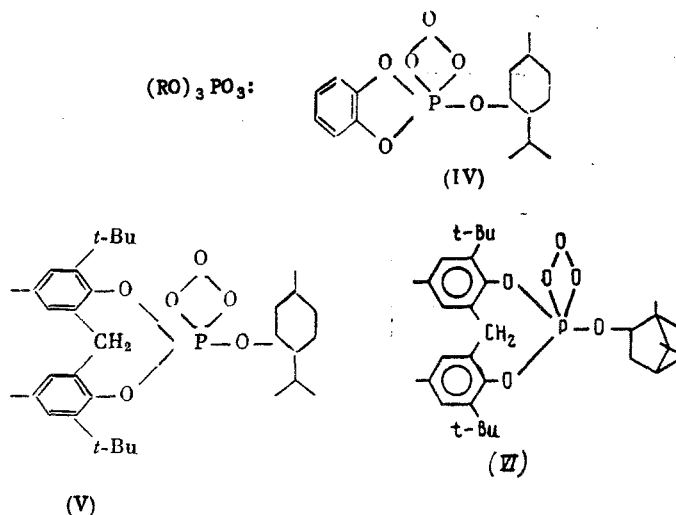
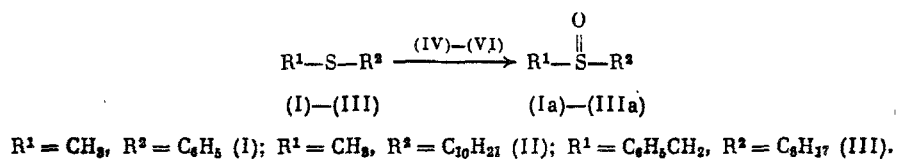


TABLE 1. Asymmetric Oxidation of Sulfides by the Ozonides of Optically Active Phosphites at -80°C in CH_2Cl_2

No.	Ozonide	Sulfide	Sulfoxide yield, mole/mole*	Absolute configuration***	Specific rotation	Optical yield, % (e. e.)****
1	(IV)	(I)	1.05	(-)-S	-4.33°	2.43
2	(V)	(I)	1.23	(-)-S	-2.79°	1.56
3	(V)+Ti(OC ₃ H ₇ -i) ₄	(I)	0.74	(-)-S	-6.76°	3.79
4	(VI)	(I)	0.77	-	0	0
5****	(VI)	(I)	0.70	-	0	0
6	(VI)+Ti(OC ₃ H ₇ -i) ₄	(I)	0.15	(+)-R	$+5.92^{\circ}$	3.32
7	(V)	(II)	1.20	-	-0.38°	-
8	(V)	(III)	1.09	-	0	0

*Yield of sulfoxide relative to converted ozonide $\Delta[\text{R}^1\text{R}^2\text{SO}]/\Delta(\text{RO})_3\text{PO}$, mole/mole.

**According to Folli et al. [8], (-)-methyl phenyl sulfoxide has S configuration.

***Calculated from the specific rotation of the sulfoxide obtained and specific rotation of R-(+)-methyl phenyl sulfoxide $[\alpha]_D^{20} = 178.3^{\circ}$ (in CHCl_3).

****Temperature -25°C .

The chemical yield of sulfoxides (Ia)-(IIIa) is 0.7-1.2 mole/mole converted ozonide (Table 1). Partial asymmetric oxidation is observed. The optical yield (enantiomer excess, e. e.) was about 2%. This is less than in the case of the oxidation of optically active hydroperoxides but comparable to the optical purity achieved using optically active peracids.

The structure of the chiral ozonide has a relatively slight effect on the asymmetric control of the reaction (compare experiment nos. 1, 2, and 4 with nos. 3 and 6). The addition of $\text{Ti}(\text{OC}_3\text{H}_7\text{-i})_4$ permits an increase in the optical yield to 4% (see experiment nos. 3 and 6). We note a similar effect of $\text{Ti}(\text{OC}_3\text{H}_7\text{-i})_4$ in the oxidation of sulfides by optically active hydroperoxides [3]. The results obtained in the oxidation of sulfides (II) and (III) using reagent (V) (experiment nos. 7 and 8) show that if the α -substituents in $\text{R}^1\text{R}^2\text{S}$ have similar asymmetric bulk, the asymmetrical control of the reaction is either slight or completely absent.

EXPERIMENTAL

The ^{31}P NMR spectra were taken in CH_2Cl_2 at -80°C relative to H_3PO_4 on a Bruker CXP-100 spectrometer. The mass spectra were taken on an MKh-1320 mass spectrometer. The rotation angles α were determined on a Perkin-Elmer 241 MC polarimeter in a 1-dm thermostatted cell.

L-(-)-Menthol, $[\alpha]_D^{22} -40^{\circ}$ (in CH_2Cl_2), was separated from menthol oil [9] and distilled twice in vacuum. L-(-)-borneol, $[\alpha]_D^{22} -33^{\circ}$ (in toluene), was obtained from bornyl acetate according to Lazur'evskii et al. [9] and distilled in vacuum.

L-(-)-Menthyl (2,2'-methylene-bis(4-methyl-6-tert-butylphenyl) phosphite was obtained from (2,2'-methylene-bis(4-methyl-6-tert-butylphenyl) chlorophosphite and L-(-)-menthol. A sample of 10 g (24.7 mmol) acid chloride in 100 ml benzene was added to a three-necked flask equipped with a mechanical stirrer, reflux condenser, and dropping funnel. The mixture was warmed to $30-40^{\circ}\text{C}$ with stirring. Then, a mixture of 3.86 g (24.7 mmol) menthol and 1.95 g (24.7 mmol) pyridine in benzene was added dropwise over 1 h. The solution was heated to 80°C and stirred for 5-6 h. The salt precipitate was filtered off and the solvent was distilled off at reduced pressure. The reaction mixture crystallized and the crystalline mass was reprecipitated from acetone to give 7 g (54%) phosphite, $[\alpha]_D^{20} -40^{\circ}$ (CH_2Cl_2), mp 183°C , ^{31}P NMR spectrum (δ , ppm): +135. Mass spectrum: 524 M^+ . Found: C, 76.64; H 9.41; O, 7.99; P, 5.96%. Calculated: C, 75.57; H, 9.35; O, 9.16; P, 5.92%.

L-(-)-Bornyl (2,2'-methylene-bis(4-methyl-6-tert-butylphenyl) phosphite was obtained in 66% yield by an analogous procedure. ^{31}P NMR spectrum (δ , ppm): +133.5, $[\alpha]_D^{20} -21.68^{\circ}$ (CH_2Cl_2). Found: C, 74.90; H, 9.04; O, 10.62; P, 5.44%. Calculated: C, 75.86; H, 9.00; O, 9.20; P, 5.94%.

The synthesis of L-(-)-menthyl o-phenylene phosphite was described in our previous work [7].

Phosphite ozonides (IV)-(VI) were obtained by the ozonization of the corresponding phosphites at -80°C in CH_2Cl_2 according to previous procedures [4,6]. The content of these ozonides in the reaction mixture was determined by ^{31}P NMR spectroscopy.

Oxidation of Sulfides to Sulfoxides. A sample of 4-10 mmoles sulfide (I)-(III) in 2 ml CH_2Cl_2 was added to 2-4 mmoles freshly prepared ozonide (IV)-(VI) in 10 ml CH_2Cl_2 in an argon atmosphere at -80°C . The reaction mixture was stirred with argon bubbling and maintained for 2 h at from -80 to -60°C . The mixture was then brought to about 20°C . The sulfoxide was isolated by distilling off the solvent and passing the reaction mass through a column packed with L 40/100 silica gel (30 g silica gel per g reaction mass) using 20:4:1 benzene-ethyl acetate-ethanol as the eluent. The products were eluted in the following sequence: unreacted sulfide, phosphate, sulfoxide. The sulfoxide was further purified by repeated chromatography. For the oxidation of the sulfides in the presence of $\text{Ti}(\text{OC}_3\text{H}_7\text{-i})_4$, an equimolar amount of $\text{Ti}(\text{OC}_3\text{H}_7\text{-i})_4$ and 8-20 mmoles sulfide were added consecutively to 10 ml of a solution of 4-10 mmoles ozonide at -80°C . The reaction mass was stirred with argon bubbling for 2 h at -80°C and thawed. The mixture was washed with three 15-ml portions of 5% aq. sodium sulfite and three 15-ml portions of saturated aq. sodium chloride. The organic layer was dried over MgSO_4 . The solvent was distilled off at reduced pressure and the sulfoxide was subjected to chromatography as described above.

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