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α -PHOSPHORYL SULFOXIDES 7.¹ CHIROPTICAL PROPERTIES OF α -PHOSPHORYL SULFOXIDES

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α -PHOSPHORYL SULFOXIDES 7.¹ CHIROPTICAL PROPERTIES OF α -PHOSPHORYL SULFOXIDES

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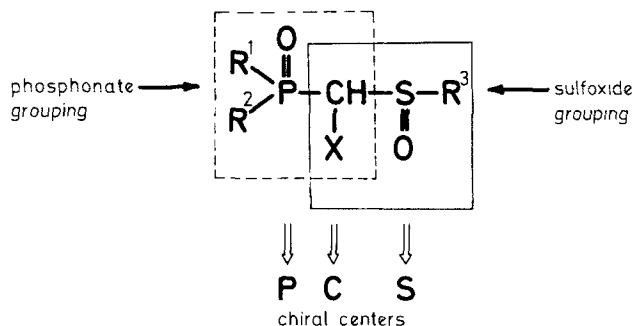
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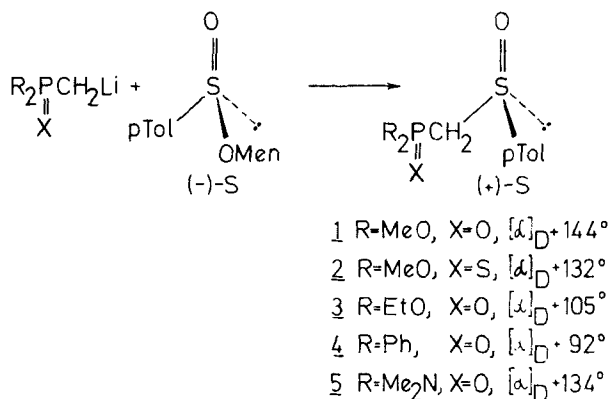
The paper describes the synthesis and chiroptical properties of (+)- α -phosphoryl sulfoxides of general formulae, $R^1_2P(X)CHR^2S(O)Tol-p$ (where $R^1 = MeO, EtO, Ph, Me_2N$, $X = O, S$, $R^2 = H, Me, Cl$) obtained from (–)-(S)-menthyl p-toluenesulfinate and the corresponding α -phosphonate, α -thiophosphonate and α -phosphinoxide anions. The CD curves of (+)- α -phosphoryl sulfoxides are of the same shape with two Cotton effects of opposite sign. At 240–245 nm one observes the positive Cotton effect while that at 220 nm is negative. The CD spectra of all (+)- α -phosphoryl sulfoxides measured are almost identical with that of (+)-(R)-methyl p-tolyl sulfoxide indicating that they have the S-chirality at sulfur. The change of ethanol for isooctane as a solvent does not influence the UV and CD spectra.

Among α -substituted sulfoxides, α -phosphoryl sulfoxides² deserve special attention as synthetic reagents and model compounds in stereochemical studies. Owing to the presence of the phosphonate moiety, α -phosphoryl sulfoxides are key substrates in the synthesis of α, β -unsaturated sulfoxides based on the Horner-Wittig reaction.^{3–5} From the stereochemical viewpoint it is interesting that besides the chiral sulfinyl center the phosphonate moiety may also be chiral provided that two different substituents (R^1 and R^2) at phosphorus are present. Moreover, substitution of one of the two α -methylene hydrogens by another substituent leads to creation of a third chiral center at the α -carbon atom. Such a situation is shown below.

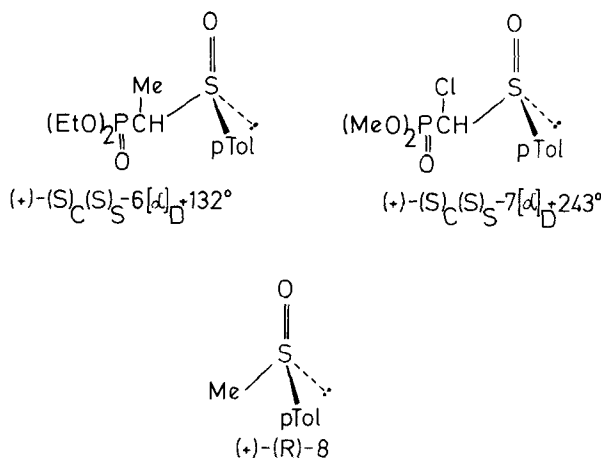


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The first example of the optically active (at the sulfinyl center) α -phosphoryl sulfoxide i.e. α -dimethylphosphorylmethyl p-tolyl sulfoxide (**1**) was obtained in this laboratory⁴ via the optical resolution utilizing a phosphonic acid moiety as the resolving "handle" or in a stereoselective way by treatment of (–)-(S)-menthyl p-toluenesulfinate with dimethylphosphorylmethyl lithium (Equation 1). The latter approach has a general character and allowed us to synthesize other optically active α -phosphoryl sulfoxides and their structural analogues, **2–5**, shown below.



(eq. 1)



The configuration at sulfur in (+)-**1** has been assigned as S based on the reasonable assumption that replacement of the menthoxy-group by the α -phosphonate carbanion occurs with inversion of the configuration at sulfur. However, since the nucleophilic substitution reactions at chiral sulfur may also occur with retention of configuration,⁶ we decided to investigate chiroptical properties of α -phosphoryl and α -thiophosphoryl sulfoxides **1–5** as well as **6**¹ and **7**⁷ in order to find another, more reliable method for the determination of absolute configuration at sulfur in this class of compounds. Previous ORD and CD studies⁸ of chiral sulfoxides have demonstrated that there is a rather clear relationship between the sign of the Cotton effect and the absolute configuration of chiral dialkyl and alkyl aryl sulfoxides with the except of benzyl alkyl and allyl

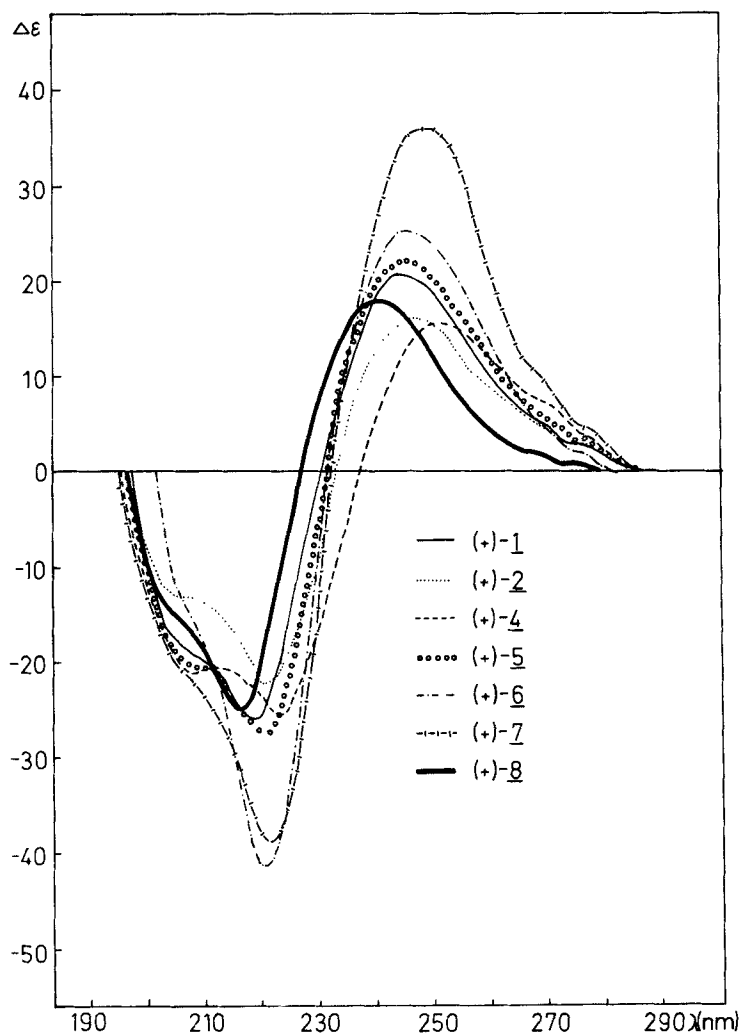


FIGURE 1 CD curves of (+)- α -phosphoryl sulfoxides (**1–7**) and (+)-*R*-methyl *p*-tolyl sulfoxide (**8**) in ethanol c , 10^{-3} mol/L.

alkyl sulfoxides where the electronic, steric and solvent effects influence the chiroptical phenomena in a hardly predictable way. In this context, one should note that the effect of the α -phosphorylmethyl group on chiroptical properties of sulfoxides is unknown.

The absorption spectra of sulfoxides **1–7** consist of two bands: the intense primary band near 240–255 nm which is probably due to a strong coupling between the benzene $\pi \rightarrow \pi^*$ and the sulfoxide $n - \pi^*$ transition and the second band centered at about 220 nm. The CD-curves (see Figure 1) of all the sulfoxides investigated here are of the same shape and show in ethanol two Cotton effects of opposite sign: the positive Cotton effect in the region of the primary band (ca 250 nm) and the negative one at 220 nm. Moreover, the CD-curves of the

dextrorotatory sulfoxides **1–7** are almost identical with that of (+)-(R)-methyl p-tolyl sulfoxide (**8**).¹⁰ These observations provide evidence not only that the sulfoxides (+)-**1–7** have the same absolute configuration but also that they are homochiral with (+)-(R)-**8**. Therefore, the chirality at sulfur in (+)-sulfoxides **1–7**, after taking into account the Cahn–Ingol–Prelog rules,¹¹ should be established as S. In this way, the CD measurements confirmed the correctness of our preliminary assignment of the (S)-chirality to (+)-**1**. Moreover, they indicate that the phosphorylmethyl moiety, in contrast to the benzyl or allyl group, has no significant influence on the chiroptical properties of sulfoxides.

Molecules having methylene groups between an asymmetric center and a chromophore often show special chiroptical properties.¹¹ Thus, ORD and CD curves of benzyl alkyl sulfoxides and other sulfoxides structurally related to them have been shown to be strongly dependent on the polarity of solvent.¹² The observed variations in the amplitude and sign of the Cotton effects were rationalized in terms of a conformational equilibrium change and/or asymmetric solvation of the aromatic chromophore. This prompted us to measure the UV and

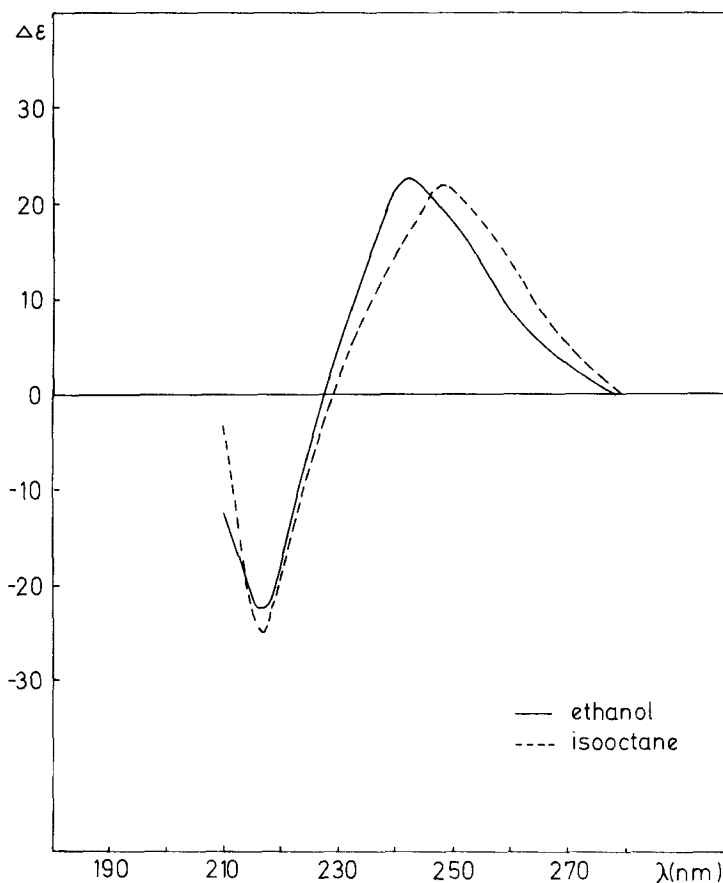
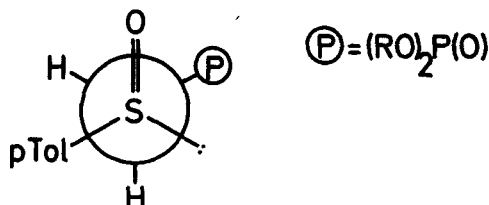


FIGURE 2 CD curves of (+)-diethylphosphorylmethyl p-tolyl sulfoxide (**3**) in ethanol and isooctane c, 10^{-4} mol/L.

CD spectra of (+)-S- α -diethylphosphorylmethyl p-tolyl sulfoxide (**3**) in isooctane. The absorption spectra of (+)-(S)-**3** in both solvents (ethanol, isooctane) contain two bands of the same shape with the same amplitude of the Cotton effect (see Figure 2). Such behaviour strongly suggests that α -phosphoryl sulfoxides exist predominantly in a conformation in which the bulky phosphoryl group at carbon and the p-tolyl group at sulfur are in an antiperiplanar orientation. This conformation has been found by X-ray analysis for α -diphenylphosphorylmethyl phenyl sulfoxide¹³ as well as for sulfoxides (+)-**6**¹ and (+)-**7**.⁷



EXPERIMENTAL

Circular dichroism spectra were determined by means of a Roussel-Jouan Dichrographe III in 1 mm quartz cells at room temperature. ¹H-NMR spectra were recorded at 60 MHz with a R12B Perkin-Elmer spectrometer and at 90 MHz with a Bruker HX 90 spectrometer and ³¹P-NMR spectra were obtained on a Jeol JNM-C-60 H1 spectrometer with internal Me₄Si and external H₃PO₄ as the standards, respectively. Column chromatography was done on Merck silica gel, 100–200 mesh. Optical activity measurements were made with a Perkin-Elmer 241 MC photopolarimeter.

Synthesis of Optically Active α -Phosphoryl Sulfoxides 2–5. All the sulfoxides **2–5** were obtained according to the procedure for preparation of α -phosphoryl sulfoxide (+)-(S)-**1** from (–)-(S)-menthyl p-toluenesulfonate, $[\alpha]_D^{20} -202^0$, described previously.⁴ The isolation procedure as well as the physical and spectral data of sulfoxides **2–5** follow.

(+)-(S)-**2** ($R = MeO$, $X = S$). Column chromatography (benzene/pentane 2:1) of the crude product obtained from dimethyl methanethiophosphonate and (–)-(S)-menthyl p-toluenesulfonate, gave 83.5% yield of sulfoxide (+)-**2** $[\alpha]_D + 132.4^0$ (c, 1.5 acetone) $n_D^{20} 1.5750$, $\delta_{31P}(CHCl_3)$ 84.8 ppm. ¹H-NMR (CDCl₃) δ : 2.42 (s, 3H), 3.44 (m, 2H, AB part of ABX system), 3.73 (d, $J_{PH} = 13.4$ Hz, 3H), 3.79 (d, 13.7 Hz, 3H), 7.55 (A₂B₂ system, 4H, aromatic). Anal. Calcd. for C₁₀H₁₅O₃PS₂: C, 43.13; H, 5.43; P, 11.13. Found: C, 42.95; H, 5.57; P, 10.86.

(+)-(S)-**3** ($R = EtO$, $X = O$). Column chromatography (benzene/acetone 10:1) of the crude product obtained from diethyl methanephosphonate and (–)-(S)-menthyl p-toluenesulfonate, gave (+)-(S)-**3** in 68% yield, $[\alpha]_D + 105^0$ (c, 3.0 acetone), $n_D^{20} 1.5202$, $\delta_{31P}(CHCl_3)$ 16.8 ppm. ¹H-NMR (CDCl₃) δ : 1.22 (dt, $J_{HH} = 7.0$ Hz, $J_{PH} = 1.67$ Hz, 6H), 2.3 (s, 3H), 3.30 and 3.34 (AB part of ABX system, $J_{AB} = 14.93$, $J_{AX} = 13.88$, $J_{BX} = 15.99$ Hz, 2H), 4.01 (m, 4H), 7.73 (A₂B₂, 4H aromatic). Anal. Calcd. for C₁₂H₁₉O₄PS: C, 49.65; H, 6.60; P, 10.67. Found: C, 49.37; H, 6.69; P, 10.85.

(+)-(S)-**4** ($R = Ph$, $X = O$). Diphenylmethyl phosphine oxide and (–)-(S)-menthyl p-toluenesulfonate gave, after the usual work-up, the crude sulfoxide (+)-**4**. Column chromatography (benzene/acetone 20:1) and crystallization (pentane/benzene 1:1) afforded pure compound in 63% yield, $[\alpha]_D + 92^0$ (c, 2.2 acetone); m.p. 134–5°, $\delta_{31P}(CHCl_3)$ 23.8 ppm. ¹H-NMR (CDCl₃) δ : 2.25 (s, 3H), 3.46 and 4.07 (AB part of ABX system, $J_{AB} = 14.35$ Hz, $J_{AX} = 11.99$ Hz, $J_{BX} = 8.2$ Hz, 2H), 6.89–8.00 (m, 14H aromatic). Anal. Calcd. for C₂₀H₁₅O₂PS: C, 67.78; H, 5.40; P, 8.75. Found: C, 68.09; H, 5.53; P, 9.01.

(+)-(S)-**5** ($R = Me_2N$, $X = O$). Column chromatography (benzene/acetone 20:1) of the crude product afforded the pure sulfoxide (+)-**5** in 78% yield, $[\alpha]_D + 134^0$ (c, 2.5 acetone) $n_D^{20} 1.5473$, $\delta_{31P}(CHCl_3)$ 25.4 ppm. ¹H-NMR (CDCl₃) δ : 2.41 (s, 3H), 2.55 (s, $J_{PH} = 10.27$ Hz, 3H), 2.75 (d, $J_{PH} = 9.98$ Hz, 3H), 3.20, 3.36 (AB part of ABX system, $J_{AB} = 14.5$ Hz, $J_{AX} = 14.9$ Hz, $J_{BX} = 8.1$ Hz,

2H), 7.49 (A₂B₂, 4H aromatic). Anal. Calcd. for C₁₂H₂₁O₂N₂PS: C, 49.98; H, 7.34; P, 10.74. Found: C, 50.20; H, 7.40; P, 10.99.

Synthesis and physical properties of (+)-(S)-diethylphosphorylethyl p-tolyl sulfoxide **6** and (+)-(S)- α -chloro- α -(dimethylphosphoryl)methyl p-tolyl sulfoxide **7** are described in references 1 and 7, respectively.

REFERENCES

1. Part XLV of the series: Organosulfur Compounds; Part XLIV: M. Mikołajczyk, W. Midura, A. Miller and M. Wieczorek, *Tetrahedron*, **43**, 2967, (1987).
2. M. Mikołajczyk, A. Zatorski, *Synthesis*, 669 (1973). M. Mikołajczyk, S. Grzejszczak and A. Zatorski, in "Organic Sulphur Chemistry", C. J. M. Stirling, Ed. Butterworths, London, 413, 1975.
3. M. Mikołajczyk, S. Grzejszczak and A. Zatorski, *J. Org. Chem.* **40**, 1979, (1975).
4. M. Mikołajczyk, W. Midura, S. Grzejszczak, A. Zatorski and A. Chefczyńska, *J. Org. Chem.*, **43**, 473 (1978).
5. R. W. Hoffmann and N. Maak, *Tetrahedron Lett.*, 2237, (1976); G. Solladie and G. Moine., *J. Am. Chem. Soc.*, **106**, 6097 (1984); C. Maignan, A. Guessons and F. Rouessac, *Tetrahedron Lett.*, **25**, 1727 (1984); R. A. Holton, Kim Hyeong-Baik, *Tetrahedron Lett.*, **27**, 2191 (1986).
6. M. Mikołajczyk, J. Drabowicz and B. Bujnicki, *Tetrahedron Lett.*, **26**, 5699 (1985); S. Colonna, G. Germinario and C. J. M. Stirling, *Gaz. Chim. Italiana*, **117**, 67 (1987) and references cited therein.
7. M. Mikołajczyk, S. Grzejszczak, W. Midura, F. Montanari, M. Cinquini and M. Wieczorek, paper in preparation.
8. M. Legrand and M. J. Rongier, in "Stereochemistry. Fundamentals and Methods". Ed. H. Kagan, Georg Thieme Publishers Stuttgart 1977, vol. 2 pp 166–168.
9. K. Mislow, M. M. Green, P. P. Laur, J. T. Melilo, T. Simmons and A. L. Ternay, *J. Am. Chem. Soc.*, **87**, 1958 (1965).
10. S. R. Cahn, C. K. Ingold and V. Prelog, *Experientia*, **12**, 81, (1956), *Angew. Chem.; Int. Ed. Engl.* **5**, 385 (1966).
11. P. Crabbe, in Topics in Stereochemistry, N. L. Allinger, E. L. Eliel; Ed. Interscience, New York, vol. I p. 154.
12. U. Folli, F. Montanari and G. Torre, *Tetrahedron Lett.* 5037, (1966); D. N. Jones and W. Higgins; *J. Chem. Soc.*, (C) 2159 (1969).
13. M. Mikołajczyk, W. Midura, M. Wieczorek and G. Bujacz, *Phosphorus Sulfur*, **31**, 19 (1987).