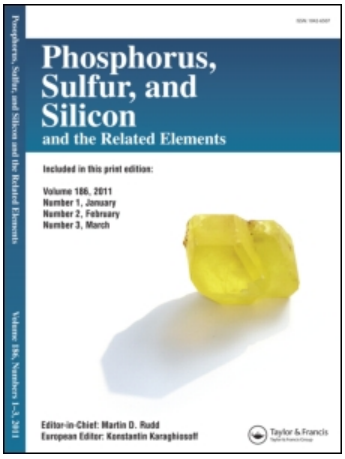


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# α-PHOSPHORYL SULFOXIDES.V.[1,2] SYNTHESIS AND CRYSTAL AND MOLECULAR STRUCTURE OF O,O-DIPHENYLPHOSPHORYL-METHYL PHENYL SULFOXIDE

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# α-PHOSPHORYL SULFOXIDES.V.[1,2] SYNTHESIS AND CRYSTAL AND MOLECULAR STRUCTURE OF O,O-DIPHENYLPHOSPHORYL-METHYL PHENYL SULFOXIDE

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*(Received May 26, 1986; in final form July 29, 1986)*

The crystal structure of the title compound (**1**) was determined by X-ray diffraction technique from diffractometer intensity measurements; $C_{19}H_{17}O_4PS$, triclinic space group $P\bar{1}$, $a = 9.4630(6)$, $b = 9.8814(6)$, $c = 10.2977(5)$Å, $\alpha = 84.37(4)$, $\beta = 84.59(5)$, $\gamma = 70.40(4)^0$, 2998 reflections, $R = 0.0402$. The molecule of **1** adopts a conformation in which the diphenoxyphosphoryl and phenyl groups are in antiperiplanar orientation around the sulfur-methylene carbon bond.



α-Phosphoryl sulfoxides, $(RO)_2P(O)CH_2S(O)R'$, first synthesized in racemic[3] and optically active[4] forms in our Laboratory, are interesting compounds from both synthetic and stereochemical points of view. Owing to the presence of the phosphonate moiety, α-phosphoryl sulfoxides are useful substrates in the synthesis of α,β-unsaturated sulfoxides via their Horner–Wittig reaction with carbonyl compounds.[5] It is interesting to point out that optically active O,O-dimethylphosphorylmethyl *p*-tolyl sulfoxide, $(MeO)_2P(O)CH_2S(O)Tol\text{-}p$, has been used by us[4] and recently also by other groups[6] as a reagent of choice for the synthesis of the variously substituted chiral vinyl sulfoxides.

In the course of our further studies on the chemistry and stereochemistry of α-phosphoryl sulfoxides, we became interested in the asymmetric chlorination and methylation of chiral O,O-dimethylphosphorylmethyl *p*-tolyl sulfoxide. These reactions take place at the α-carbon atom and lead to the generation of the second chirality center as a result of the replacement of one of the two prochiral methylene hydrogen atoms by chlorine and methyl group, respectively. To

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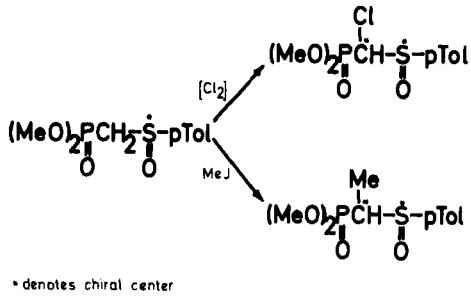
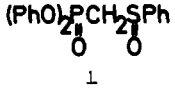
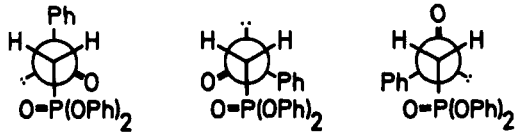
explain the steric course and mechanism of these two processes it was desirable to know the conformation of the starting $\alpha$-phosphoryl sulfoxide.




The purpose of the present investigation was to establish the solid state conformation of O,O-diphenylphosphorylmethyl phenyl sulfoxide (**1**) as a model compound.



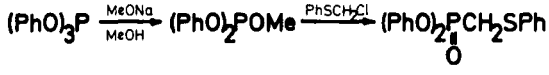

1



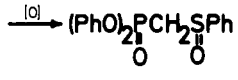

1-A 1-B 1-C

Theoretically, the sulfoxide **1** can exist in three conformations (**A**, **B** and **C**) shown above. Although it could be expected that the conformation **1-A** should be most favourable for steric reasons (antiperiplanar orientation of the bulky diphenylphosphoryl group at carbon with respect to the phenyl group at sulfur) it was necessary to confirm this view experimentally.

The synthesis of the title sulfoxide (**1**) has been accomplished as follows:




2 3




1

Triphenyl phosphite was converted selectively into diphenyl methyl phosphite (**2**) by treatment with stoichiometric amount of sodium methoxide in methanol essentially according to the procedure described by Russian workers.[7] The

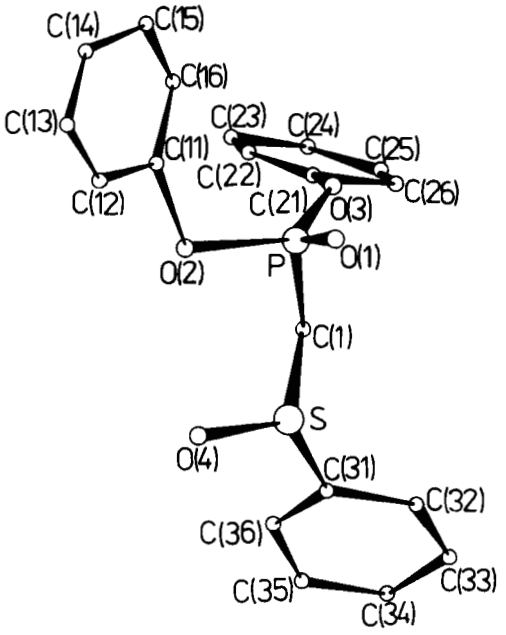



FIGURE 1 Three-dimensional view of O,O-diphenylphosphorylmethyl phenyl sulfoxide (**1**) with atom numbering.

Arbuzov reaction of the phosphite **2** with chloromethyl phenyl sulfide gave O,O-diphenylphosphorylmethyl phenyl sulfide (**3**). The latter was oxidized selectively by hydrogen peroxide in the presence of optically active amyl alcohol[8] to give the desired sulfoxide **1**. The suitable crystals of **1** (m.p. 75–76°C) for X-ray analysis were obtained by slow crystallization from acetone.

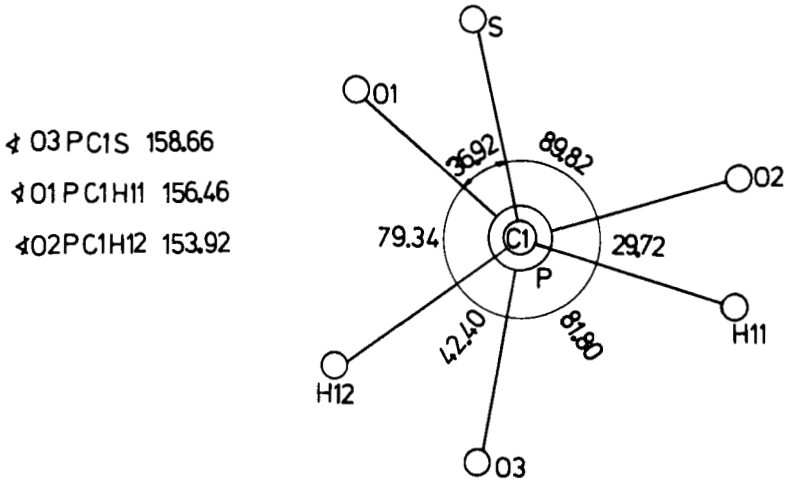



FIGURE 2 Newman projection around the C(1)-P bond showing the relevant torsion angles (°) in **1**.

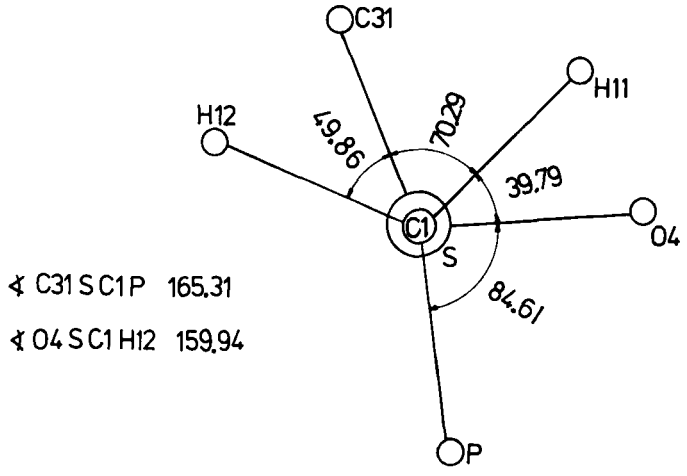



FIGURE 3 Newman projection around the C(1)-S bond showing the relevant torsion angles (°) in **1**.

The structure of **1** has been determined by the direct method and refined by least-squares to the final value $R = 0.0402$.

A three dimensional view of the molecule of **1** and the atom numbering are shown in Figure 1. Figure 2 and Figure 3 show the Newman projections around the C(1)-P and C(1)-S bond, respectively, together with the corresponding torsion angles. With regard to the main question in this work, Figure 3 reveals clearly

TABLE I

Positional parameters ($\times 10^4$) for non-hydrogen atoms

| | *x* | *y* | *z* |
|---|---|---|---|
| P | 5495(1) | 7785(1) | 5528(1) |
| S | 5739(1) | 8070(1) | 2592(1) |
| O1 | 6645(2) | 8474(2) | 5505(2) |
| O2 | 6091(2) | 6083(2) | 5800(2) |
| O3 | 4229(2) | 8387(2) | 6636(2) |
| O4 | 6499(3) | 6555(3) | 2290(3) |
| C1 | 4519(3) | 8053(3) | 4060(3) |
| C31 | 4232(3) | 8824(3) | 1523(2) |
| C32 | 3708(3) | 10305(3) | 1289(3) |
| C33 | 2580(4) | 10935(4) | 439(3) |
| C34 | 1996(4) | 10078(5) | −160(3) |
| C35 | 2509(5) | 8620(5) | 60(3) |
| C26 | 3662(4) | 7958(4) | 912(3) |
| C11 | 7144(3) | 5428(3) | 6749(3) |
| C12 | 8489(5) | 4453(4) | 6316(4) |
| C13 | 9544(5) | 3770(4) | 7284(7) |
| C14 | 9215(6) | 4093(5) | 8546(6) |
| C15 | 7881(6) | 5051(4) | 8939(4) |
| C16 | 6818(4) | 5730(3) | 8029(3) |
| C21 | 2808(3) | 8196(3) | 6707(2) |
| C22 | 2686(3) | 6858(3) | 7026(3) |
| C23 | 1260(4) | 6729(5) | 7136(4) |
| C24 | 20(4) | 7925(6) | 6927(4) |
| C25 | 171(4) | 9252(5) | 6627(4) |
| C26 | 1595(4) | 9416(4) | 6504(3) |

TABLE II

Hydrogen atom positional parameters ($\times 10^3$)

| | *x* | *y* | *z* |
|---|---|---|---|
| H11 | 404(3) | 723(2) | 395(3) |
| H12 | 370(3) | 910(2) | 409(3) |
| H321 | 416(3) | 1093(3) | 183(3) |
| H331 | 230(5) | 1206(2) | 13(4) |
| H341 | 111(3) | 1051(4) | −83(3) |
| H351 | 217(4) | 783(3) | −39(3) |
| H361 | 420(4) | 681(1) | 99(3) |
| H121 | 873(4) | 435(4) | 528(1) |
| H131 | 1049(4) | 317(4) | 669(4) |
| H141 | 1013(4) | 345(4) | 912(4) |
| H151 | 755(5) | 523(5) | 996(2) |
| H161 | 574(2) | 647(3) | 834(3) |
| H221 | 371(2) | 596(2) | 704(3) |
| H231 | 106(4) | 575(2) | 752(4) |
| H241 | −104(2) | 776(4) | 716(4) |
| H251 | −76(3) | 1022(2) | 651(4) |
| H261 | 180(3) | 1041(2) | 618(3) |



that the sulfoxide **1** adopts the conformation **1-A** with the antiperiplanar arrangement of the diphenoxyphosphoryl group at C(1) and phenyl group at S. The angle formed between these two substituents i.e. the torsion angle between C(31)-S and C(1)-P is 165.31°.

The final positional parameters with isotropic temperature factors for non-hydrogen atoms are listed in Table I and for hydrogen in Table II. Tables III and IV contain bond distances and angles.

TABLE III

Bond lengths (Å)

| | | | |
|---|---|---|---|
| O1-P | 1.462(2) | C35-C34 | 1.360(6) |
| O2-P | 1.589(2) | C36-C35 | 1.407(5) |
| O3-P | 1.578(2) | C12-C11 | 1.378(4) |
| C1-P | 1.798(3) | C16-C11 | 1.365(5) |
| O4-S | 1.477(2) | C13-C12 | 1.431(7) |
| C1-S | 1.816(3) | C14-C13 | 1.351(9) |
| C31-S | 1.795(3) | C15-C14 | 1.353(6) |
| C11-02 | 1.413(3) | C16-C15 | 1.393(6) |
| C21-03 | 1.413(4) | C22-C21 | 1.371(5) |
| C32-C31 | 1.380(4) | C26-C21 | 1.372(4) |
| C36-C31 | 1.380(5) | C23-C22 | 1.390(6) |
| C33-C32 | 1.384(4) | C24-C23 | 1.374(5) |
| C34-C33 | 1.373(6) | C25-C24 | 1.369(8) |
| | | C26-C25 | 1.402(6) |

## EXPERIMENTAL

M.ps and bps are uncorrected. Solvents and reactants were of reagent grade. $^{31}P$ NMR spectra were obtained with a JEOL-JNM-C-60HL spectrometer using 85% phosphoric acid as an external standard; positive $\delta_{^{31}P}$ values refer to down-field shifts from $H_3PO_4$.

TABLE IV

Bond angles(°)

| | | | |
|---|---|---|---|
| O2-P-O1 | 114.8(1) | C36-C35-C34 | 120.2(4) |
| O3-P-O1 | 110.0(1) | C35-C36-C31 | 118.2(3) |
| O3-P-O2 | 106.5(1) | C12-C11-02 | 116.6(3) |
| C1-P-O1 | 116.1(1) | C16-C11-02 | 121.1(2) |
| C1-P-O2 | 103.5(1) | C16-C11-C12 | 122.4(3) |
| C1-P-O3 | 105.1(1) | C13-C12-C11 | 116.5(4) |
| C1-S-O4 | 107.0(1) | C14-C13-C12 | 120.6(4) |
| C31-S-O4 | 107.6(2) | C15-C14-C13 | 121.5(5) |
| C31-S-C1 | 95.0(1) | C16-C15-C14 | 119.7(4) |
| C11-O2-P | 120.5(2) | C15-C16-C11 | 119.4(3) |
| C21-O3-P | 123.1(2) | C22-C21-03 | 120.2(2) |
| S-C1-P | 112.4(2) | C26-C21-03 | 116.4(3) |
| C32-C31-S | 117.7(3) | C26-C21-C22 | 123.3(3) |
| C36-C31-S | 121.2(3) | C23-C22-C21 | 118.3(3) |
| C36-C31-C32 | 121.1(3) | C24-C23-C22 | 120.0(4) |
| C33-C32-C31 | 119.8(3) | C25-C24-C23 | 120.5(4) |
| C34-C33-C32 | 119.4(3) | C26-C25-C24 | 120.8(3) |
| C35-C34-C33 | 121.3(3) | C25-C26-C21 | 117.1(3) |



Diphenyl methyl phosphite (**2**) was obtained according to Shakirova and Imaev[7] by transesterification of triphenyl phosphite with stoichiometric amounts of sodium methoxide in methanol at 100°C. The reaction progress was monitored by $^{31}$P NMR. The phosphite **2** was isolated by fractional distillation: b.p. 168–179°C/10 mmHg (lit.[9] 169–170.5°C/11 mmHg); $\delta_{^{31}P}$ 128.2 ppm (benzene).

*Diphenylphosphorylmethyl phenyl sulfide* (**3**). A mixture of the phosphite **2** (24.8 g, 0.1 mol) and chloromethyl phenyl sulfide (15.8 g, 0.1 mol) was heated at 150–160°C for 10 h to afford the crude sulfide **3** which was purified by column chromatography; 34.9 g (70%), m.p. 55–56°C; $^{31}$P NMR (benzene): 16.0 ppm; $^{1}$H NMR ($CDCl_3$): $\delta$ ppm 3.40 (d, 2H, $J_{PH} = 13.3$ Hz), 7.1–7.7 (15H, aromatic), (Found: C, 64.32, H, 4.90; P, 8.78. Calc for $C_{19}H_{17}O_3PS$: C, 64.03; H, 4.81; P. 8.69%).

*Diphenylphosphorylmethyl phenyl sufoxide* (1). To a solution of the sulfide **3** (1.78 g, 0.005 mol) and optically active amyl alcohol (0.5 g) in methanol (25 ml) a hydrogen peroxide (0.51 ml) was added at once. The progress of the oxidation was controlled by TLC. When the reaction was complete, water (150 ml) was added to the reaction mixture. Aqueous phase was extracted with chloroform (3 × 50 ml). The chloroform extracts were dried over anhydrous magnesium sulfate and evaporated to give 1.62 g (87%) of the sulfoxide **1**. Analytically pure sample of **1** was obtained by crystallization from acetone, m.p. 75–76°C; $^{31}$P NMR (benzene): 11.2. $^{1}$H NMR ($CDCl_3$): $\delta$ ppm 3.09–4.18 (m, 2H, ABX system), 6.45–7.68 (15H, aromatic) (Found: C, 61.22; H, 4.75; P, 8.36. Calc. for $C_{19}H_{17}O_4PS$: C, 61.28; H, 4.6=; P, 8.32).

*Structure determination of* **1**. A suitable crystal was grown from acetone solution. The cell parameters were determined from oscillation and rotation photographs using $CuK_\alpha$ radiation. These parameters were redetermined on the

Synthex $P2_1$ diffractometer using $MoK_\alpha$ radiation. The space group was found to be $P\bar{1}$. The intensity data were collected in the $\theta$-$2\theta$ mode ($3.0 \leq 2\theta \leq 50°$). Of 2998 reflections measured, 2720 were classifiying as observed i.e. $F > 4\sigma(F)$. Only Lorentz-polarization corrections were applied. The structure was solved by direct methods (SHELX 76) and refined by blocked full matrix least-squares techniques with anisotropic temperature factors for all non-hydrogen atoms. The remaining H atoms were refined with group istropic temperature factors. Convergence was reached at $R = 0.0402$.

*Crystal data.* $C_{19}H_{17}O_4PS$. $M = 372.38$. Triclinic space group $P\bar{1}$, $a = 9.4630(6)$, $b = 9.8814(6)$, $c = 10.2977(5)$Å, $\alpha = 84.37(4)$, $\beta = 84.59(5)$, $\gamma = 70.40(4)°$, $V = 900.80(20)$Å$^3$, $Z = 2$, $\mu[MoK_\alpha] = 2.40\ cm^{-1}$ $F(000) = 388$ $\lambda = 0.71069$Å.

*Note.* Anisotropic thermal parameters are deposited with the Cambridge Crystallographic Data Center (CCDC) U.K.



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