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α-PHOSPHORYL SULPHOXIDES.VI[1,2]
SYNTHESIS OF α-PHOSPHORYLETHYL p-TOLYL SULPHOXIDE AND ASYMMETRIC INDUCTION ON THE α-CARBON ATOM

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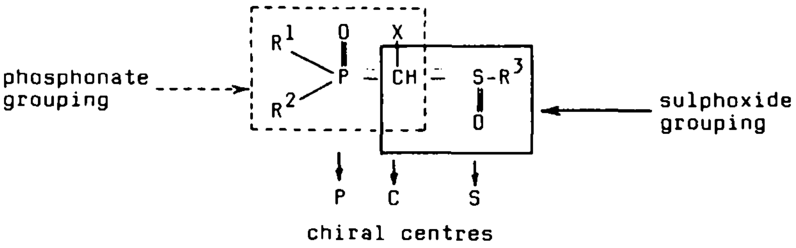
Abstract - Optically active α-dimethylphosphorylethyl p-tolyl sulphoxide (2a) was prepared by methylation of optically active (+)-(S)-α-dimethylphosphorylmethyl p-tolyl sulphoxide and by treatment of (-)-(S)-menthyl p-toluenesulphinate with dimethylphosphorylethyllithium. In both reactions a substantial asymmetric induction at the α-carbon atom was observed and rationalized. The structure of the major diastereoisomer of the sulphoxide 2a, $[\alpha]_D$+157°, m.p. 98-99°C, having the $(S)_C(S)_S$-configuration was determined by X-ray analysis. $C_{11}H_{17}O_4SP$, orthorombic, space group $P2_12_12_1$, a=24.080(3), b=7.239(1), c=7.754(1)Å, V=1351.64 $Å^3$, Z=4, D_m=1.35 $Mg \cdot m^{-3}$, D_c=1.357 $Mg \cdot m^{-3}$, F(000)=584.0, $\mu(CuK_\alpha)$=3.13 mm^{-1}. The structure was solved by direct methods and refined to R=0.085. Racemic α-diethylphosphorylethyl p-tolyl sulphoxide (2b) was obtained by oxidation of the corresponding sulphide. The diastereoselectivity observed in this reaction was rationalized based on the adapted Felkin's model.

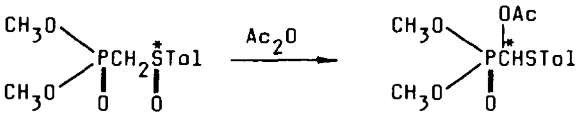
INTRODUCTION

α-Phosphoryl sulphoxides[3-6] are an interesting class of compounds useful in synthetic and stereochemical studies. Owing to the presence of the phosphonate moiety, α-phosphoryl sulphoxides undergo the Wittig-Horner reaction with carbonyl compounds affording vinyl sulphoxides[4]. The use of optically active α-dimethylphosphorylmethyl p-tolyl sulphoxide (1) in the Wittig-Horner reaction leads to optically active vinyl sulphoxides[5]. This reaction is general in scope and some interesting applications for it have recently been found[7].

From the stereochemical viewpoint it is obvious that α-phosphoryl sulphoxides are chiral since they contain the chiral sulphoxide moiety. Moreover, in the case of two different substituents at phosphorus and three different substituents at the α-carbon atom (as shown below) two additional asymmetric centres at P and C are present.

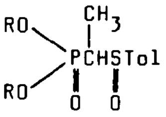


This particular situation offers many possibilities for studies of asymmetric induction, especially on the α-carbon atom. In fact, a substantial extent of asymmetric induction was observed[6] in the Pummerer reaction of optically active sulphoxide 1 which resulted in the formation of the corresponding α-acetoxy α-phosphoryl sulphide with 24 to 45% of optical purity. In this case, a new chiral centre on the α-carbon atom is created, while the chirality at sulphur disappears.



1

*denotes optically active centre



2

a, R = CH_3

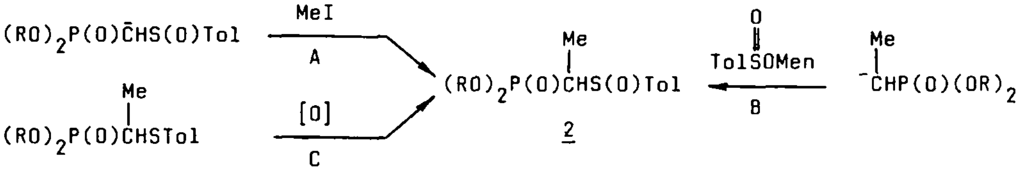
b, R = C_2H_5

In this paper, we wish to report the synthesis of α-phosphorylethyl p-tolyl sulphoxide (2) containing two chiral centres on the sulphur and α-carbon atoms and to discuss some aspects of asymmetric induction observed in the reactions leading to 2.

RESULTS

Synthesis of α-Phosphorylethyl p-Tolyl Sulphoxide (2)

The title sulphoxide 2 was prepared by three different reactions A,B and C shown below.



The first approach to 2 involves methylation of the α-carbanion derived from α-unsubstituted α-phosphoryl sulphoxide. In the second approach, we took advantage of the fact that α-phosphonate carbanions react with sulphinic acid esters to give α-phosphoryl sulphoxides[5]. Finally, the sulphoxide 2 was obtained by the oxidation of the corresponding α-phosphoryl sulphide.

In order to better elucidate the structure of the sulphoxides 2 formed, as well as to determine stereochemistry of the reactions A and B, we used optically active (+)-(S)-α-dimethylphosphorylmethyl p-tolyl sulphoxide (1)[5] and (-)-(S)-menthyl p-toluenesulphinate (3)[8] as the reaction substrates. Thus, quenching the lithium salt of (+)-(S)-1 (generated from 1 in THF at -78°C) with methyl iodide gave sulphoxide 2a as a mixture of two diastereoisomers. Since they show different chemical shifts in $^{31}P\{^1H\}$ NMR spectrum, it was possible to determine easily the diastereoisomeric ratio. The major diastereoisomer of 2a, $[\alpha]_D$+157°, mp. 98-99°C, was isolated from the mixture by preparative chromatography and crystallization from hexane. Its configuration was established by X-ray analysis (see the next section) as $(S)_C(S)_S$.

Treatment of (-)-(S)-menthyl p-toluenesulphinate (3) with the lithium salt of dimethyl ethanephosphonate (4) affords a mixture of the same diastereoisomeric sulphoxides $(S)_C(S)_S$-2a and $(R)_C(S)_S$-2a. Similar reaction between (-)-(S)-3 and the lithium salt of diethyl ethanephosphonate (5) resulted in the formation of the diastereoisomeric sulphoxides 2b. Based on the spectral data, it is quite reasonable to assume that the predominant diastereoisomer of 2b, $[\alpha]_D +132^0$, mp. 79-80^{0}C, isolated from the mixture has also the $(S)_C(S)_S$-configuration.

The third synthetic approach to 2 involved oxidation of α-diethylphosphorylethyl p-tolyl sulphide (6) to the corresponding sulphoxide 2b. In this case, however, we used racemic sulphide 6. It was oxidized by hydrogen peroxide in methanol and by sodium metaperiodate in acetone. Both oxidizing agents gave a mixture of racemic, diastereoisomeric sulphoxides 2b. Some experimental details concerning the synthesis of 2 are collected in Table 1.

Table 1. Synthesis of α-phosphorylethyl p-tolyl sulphoxides 2

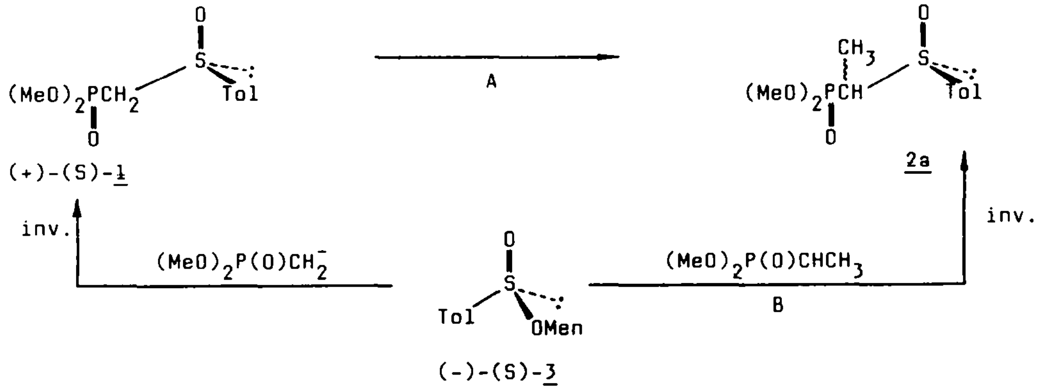
Method/Substrate	Product			Isomeric ratio
	No	Yield	Predominant isomer (δ_{31P}ppm)	
A, (+)-(S)-1	2a	70	$(S)_C(S)_S$-2a, 24.7	3:1
B, (-)-(S)-3	2a	85	$(S)_C(S)_S$-2a, 24.7	2.4:1
B, (-)-(S)-3	2b	92	$(S)_C(S)_S$-2b, 22.1	2.45:1
C, (±)-6	2b	95	$(R)_C(R)_S/(S)_C(S)_S$-2b, 22.1	2.5:1[a]

[a] using H_2O_2/MeOH; 3.1:1 ratio was observed using $NaIO_4$

Determination of the Crystal and Molecular Structure of $(S)_C(S)_S$-α-Dimethylphosphorylmethyl p-Tolyl Sulphoxide (2a)

In order to explain the steric course of the reactions A,B and C it was desirable to know the absolute configurations at sulphur and α-carbon in the formed diastereoisomeric sulphoxides 2. Since the methylation reaction (A) of (+)-(S)-1 occurs without bond breaking at the chiral sulphinyl centre, it is obvious that in both diastereoisomeric sulphoxides 2a the chirality at sulphur is the same as that of (+)-(S)-1 i.e. S.

In this context, we should note that the reaction B leads also to the sulphoxides 2a with the S-configuration at sulphur as a result of inversion at the sulphinyl centre in (-)-(S)-3[5].



Therefore, the absolute configuration at the α-carbon atom in 2a could be easily deduced from a simple X-ray analysis by internal comparison of two chiral centres. With this end in mind, we determined the crystal and molecular structure of the major diastereoisomer of the sulphoxide 2a, $[\alpha]_D$+157°, mp. 98-99°C $_P$ 24.7 ppm by X-ray diffractometric technique. The structure has been solved by direct methods and refined by full-matrix least-squares to the final value R = = 0.085.

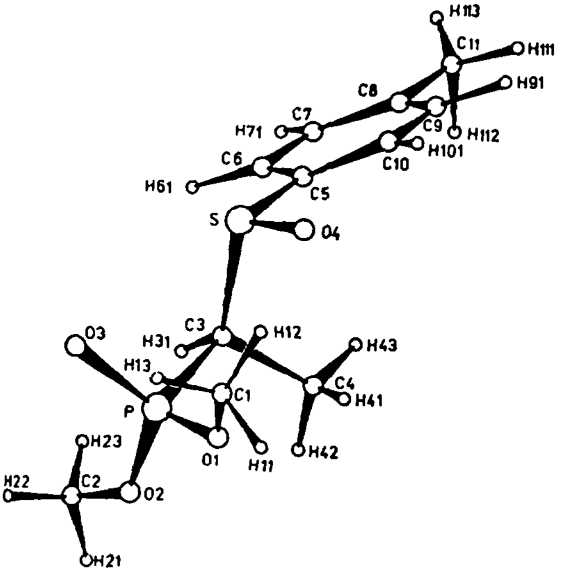


Fig.1. Three-dimensional view of (+)-$(S)_C(S)_S$-2a

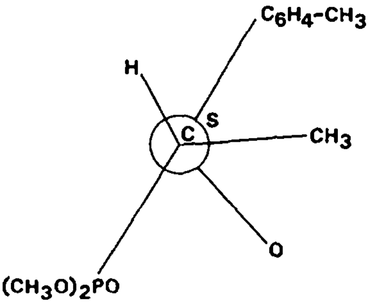


Fig.2. Newman projection around the C(3)-S b

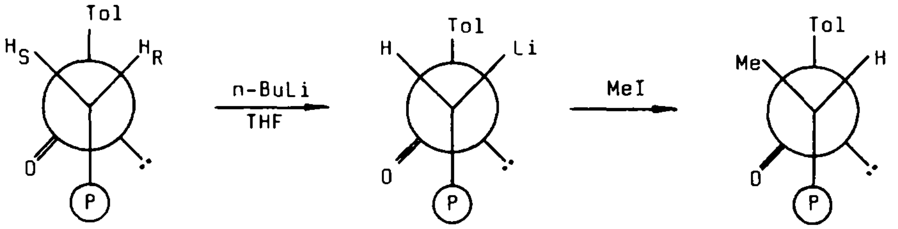
The molecular structure of the sulphoxide 2a investigated with the numbering system is shown in Fig.1. As it is seen from Fig.1, the absolute configuration at the α-carbon atom is S. Thus, the major diastereoisomer of 2a obtained in both reactions A and B has the $(S)_C(S)_S$-configuration. Fig.2 shows the Newman projection around the C(3)-S bond which clearly reveals that the sulphoxide 2a adopts the conformation with the antiperiplanar arrangement of the dimethoxyphosphoryl group at C(3) and p-tolyl group at S.

The geometry at phosphorus and sulphur is close to tetrahedral and bond distances and angles show no significant variations from the expected values[9].

DISCUSSION

The results presented above show that in all of the three reactions affording the sulphoxide 2, a great extent of asymmetric induction is observed. However, whereas the reactions A and B involve asymmetric formation of a new chiral carbon centre under the steric control of the chiral sulphinyl group, in the reaction C asymmetric induction, which occurs during the oxidation reaction at sulphur, is controlled by a chiral α-carbon centre.

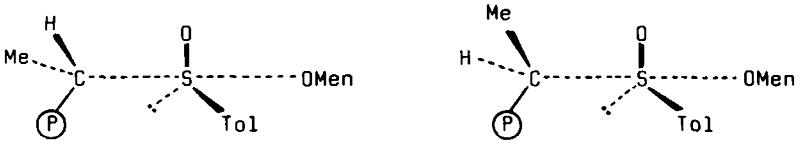
It is generally accepted that the stereochemistry of the reactions of α-lithiosulphoxides with various electrophilic agents depends upon the nature of the latter. Thus, protonation of α-lithiosulphoxides occurs with retention, while methylation with methyl iodide occurs with inversion of configuration at the α-carbon atom[10]. Assuming the same steric course of methylation in our case and taking into account the fact that the sulphoxide $(S)_C(S)_S$-2a is preferentially produced in the reaction A, the following rationale may be proposed. The sulphoxide (+)-(S)-1 exists most probably in a favourable conformation in which the bulky dimethoxyphosphoryl group at carbon and the p-tolyl group at sulphur in an antiperiplanar orientation. This conformation has been found by X-ray analysis for a closely related α-diphenylphosphorylmethyl phenyl sulphoxide[2]. Moreover, an analogous conformation has also been assumed for t-butyl benzyl sulphoxide for which a very high stereoselectivity of the formation of α-lithioderivative and its reactions with electrophiles was observed. In full analogy with the latter case, the abstraction of the pro-R hydrogen atom in (+)-(S)-1 should be favoured for stereoelectronic reasons leading to the $(R)_C(S)_S$-lithioderivative of 1. Its subsequent reaction with methyl iodide takes place with inversion at carbon giving $(S)_C(S)_S$-2a as shown below.



(+)-(S)-1 $(R)_C(S)_S$ $(S)_C(S)_S$-2a

(P)= $(MeO)_2P(O)$

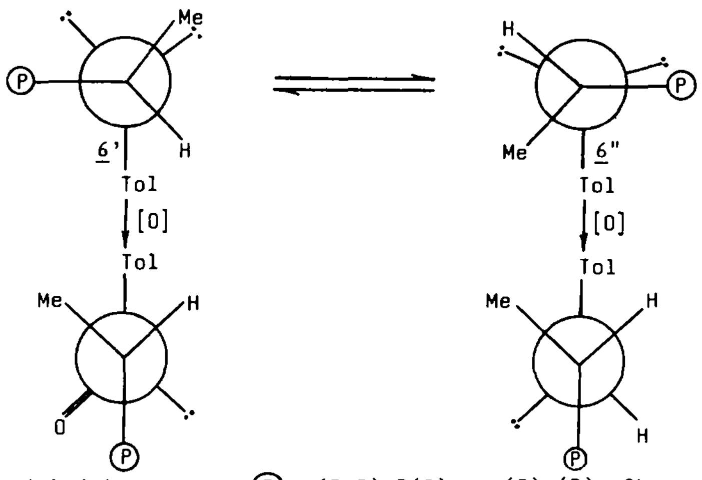
In contrast to the reaction A discussed above, the formation of a new chiral α-carbon in the reaction B takes place during a typical nucleophilic substitution at sulphur in (-)-(S)-3 by the α-phosphonate carbanion. The diastereoselectivity observed in this reaction may be explained in terms of diastereoisomeric transition states I and II (or sulphurane intermediates if the addition-elimination mechanism is operating) with different free energies. Most probably, the formation of the transition state I leading to the sulphoxide $(S)_C(S)_S$-2a, is energetically favoured since the non-bonding repulsive intereactions between the substituents on two reacting centres (carbon and sulphur) are smaller as compared with those in II.



I II

(P) = $(MeO)_2P(O)$

Finally, we would like to comment briefly the stereochemical aspects of the reaction C involving the conversion of sulphide 6 to diastereoisomeric sulphoxides 2b. Asymmetric oxidation of sulphides to sulphoxides has a long history[11]. However, the most relevant results to our work are reported by Nishihata and Nishio[12] who investigated the oxidation of optically active α-phenylethyl p-tolyl sulphide to the corresponding diastereoisomeric sulphoxides. In accord with the results of the above-mentioned authors, our results cannot also be explained in terms of Cram's principles of steric control of asymmetric induction[13]. However, adaptation of the Felkin's model[14] to the reaction investigated allowed us to explain reasonably the predominant formation of the (RR/SS)-isomer of 2b (Scheme shows the oxidation of one enantiomer of 6 only). Thus, oxidation of the conformer 6' is preferred and leads to $(S)_C(S)_S$-2b.



$(S)_C(S)_S$-2b   P = $(EtO)_2P(O)$ $(S)_C(R)_S$-2b

EXPERIMENTAL SECTION

Methylation of (+)-(S)-Dimethylphosphorylmethyl p-Tolyl Sulphoxide (1)

To a solution of (+)-(S)-α-phosphoryl sulphoxide (1), $[\alpha]_D$+144, (1.31 g, 0.005 mol) in tetrahydrofuran (10 ml) a solution of n-butyllithium (4 ml, 0.0055 mol) in hexane was added at -78° under nitrogen atmosphere. The reaction mixture was stirred at this temperature for 15 min and then a solution of methyl iodide (2.84 g, 0.02 mol) in THF (3 ml) was added. The mixture was warmed slowly to room temperature and quenched with aqueous ammonium chloride. The aqueous layer was extracted with chloroform (3 x 10 ml). The chloroform solution was dried and evaporated to give a crude product (2a) in 70% yield. According to ^{31}P NMR it consists of two diastereoisomers with ^{31}P 24.7 and 23.4 ppm in a ratio 3:1. Purification by preparative chromatography (eluent CCl_4/methanol 3.5:1) and crystallization from hexane afforded one pure diastereoisomer of (2a), $\delta^{31}P$ 24.7 ppm, $[\alpha]_D$+157° (c,1.7 acetone), m.p. 98-99°C.
^1H-NMR ($CDCl_3$) 1.32 (dd,3,CH_3-CHP, J_{HH} 7.0 Hz, J_{PH} 15.0 Hz); 2.42 (s,3,$CH_3C_6H_4$); 2.8 (m,1,CH_3-CH); 3.76 (d,3,CH_3OP, J_{PH} 11.30 Hz); 3.81 (d,3,CH_3OP, J_{PH} 10.85 Hz) 7.35 (A_2B_2,4,aromatic). Anal.Calcd. for $C_{11}H_{17}O_4PS$ C, 47.82 H, 7.20 P, 11.21 Found C, 48.03 H, 6.12 P, 11.32.

Preparation of α-Phosphorylethyl p-Tolyl Sulphoxides (2) from (-)-(S)-Menthyl p-Toluenesulphinate (3)

To a solution of the lithium derivative of ethylphosphonate (0.01 mol) prepared as above, a solution of (-)-(S) menthyl p-toluenesulphinate (3) (1.47 g, 0.005 mol) $[\alpha]_D$-202° (c,1.2 acetone) in 10 ml of THF was added at -78°. After 15 min the reaction mixture was warmed to -20°C and quenched with ammonium chloride. After the usual work-up the crude product was purified by chromatography.

(+)-$(S)_C(S)_S$-Dimethylphosphorylethyl p-Tolyl Sulphoxide (2a)

Crude product was obtained in 85% yield, as a mixture of diastereoisomers in a 2.37:1 ratio and pure major diastereoisomer (^{31}P 24.7 ppm) was isolated.

(+)-$(S)_C(S)_S$-Diethylphosphorylethyl p-Tolyl Sulphoxide (2b)

Crude product as a mixture of diastereoisomers in a ratio 2.45:1 was obtained in 82% yield. The ratio was determined the intergration of signals in ^{31}P NMR spectra 22.1 (major) and 20.4 ppm.

^1H NMR ($CDCl_3$) 1.04-1.49 (m,9,$C\underline{H}_3$-CH_2O and $C\underline{H}_3$-CH); 2.41 (s,3,$C\underline{H}_3$-C_6H_4); 2.90 and 3.31 (2xdq,1,C$\underline{H}$-P, J_{PH} 17.61 Hz, J_{HH} 7.33 Hz and J_{PH} 18.48 Hz, J_{HH} 7.33 Hz); 4.04 (m,4,$C\underline{H}_2OP$); 7.31 (A_2B_2,4,aromatic).

After column chromatography (eluent benzene/acetone 10:1) pure major diastereoisomer of (2b) was obtained, m.p. 79-80°C(after crystallization from ethyl ether). $[\alpha]_D$+132° (c,2.4 acetone) ^{31}P NMR ($CHCl_3$) 22.1 ppm; ^1H NMR$\{^{31}P\}$ ($CDCl_3$) 1.31 (d,3,$C\underline{H}_3$-CHP(O), J_{HH} 7.04 Hz); 1.33 and 1.35 (dt,6,$C\underline{H}_3$-CH_2O J_{HH} 7.04 Hz); 2.41 (s,3,$C\underline{H}_3$-C_6H_4); 2.89 (q,1,CH_3-C$\underline{H}$, J_{HH} 7.33 Hz) 4.17 and 4.22 (dq,4, $CH_3C\underline{H}_2O$, J_{HH} 7.04 Hz); 7.41 (A_2B_2,4,aromatic). Anal.Calcd. for $C_{13}H_{21}O_4PS$ C,51.30; H, 6.95; P, 10.18; Found C, 51.43; H,7.01 P,10.32.

Oxidation of (±)-Dimethylphosphorylethyl p-Tolyl Sulphide (6)

To a solution of sulphide (6) (0.57 g, 0.002 m) in 3 ml of acetone and 1 ml of water a solution of sodium metaperiodate (0.45 g, 0.0021 m) in water was added within 1h at -5 to 0°C. The reaction mixture was stirred at 0° for 4h and allowed to stand at 5°C for 3 days. The precipitated sodium iodate was filtered off. After removal of acetone the water solution was extracted with chloroform. Chloroform extract was dried over anhydrous $MgSO_4$ and evaporated to give the sulphoxide (2b) as a mixture of two diastereoisomers (^{31}P 22.1 and 20.4 ppm) formed in a 3.1:1 ratio.

To a stirred mixture of sulphide (6) (0.57 g, 0.002 mol) in methanol (10 ml) and optically active amyl alcohol (200 mg), hydrogen peroxide was added at once. Progress of the oxidation was controlled by ^{31}P NMR spectra. When the reaction was complete, water (50 ml) was added to the reaction mixture. The aqueous phase was extracted with chloroform (3 x 20 ml) and organic extract was dried over magnesium sulphate. Evaporation of chloroform afforded pure sulphoxide (2b) as a diastereoisomeric mixture in a 2.5:1 ratio.

X-Ray Analysis of the Sulphoxide $(S)_S(S)_C$-2a

Preliminary unit cell parameters were obtained from Weissenberg photographs and were refined from diffractometric measurements. The intensity data were collected on a SYNTEX $P2_1$ four-circle diffractometer (CuK_α radiation, graphite monochromator). Measurements were carried out in the θ-2θ scan mode for $2\theta \leq 115°$. 932 independent reflections were collected and 928 of them were considered to be observed $|I \geq 3\sigma|$ and included in the refinement. The intensity data were reduced to structure factors by the application of Lorentz and polarization factors, no correction for absorption was applied. The structure was determined by direct methods with SHELX 76 (Sheldrik 1976) and refined by full-matrix least-squares method with anisotropic temperature factors for all non-hydrogen atoms. The H positions were refined with a group isotropic temperature factors. The final R value was 0.085. The positional parameters and anisotropic temperature factors for non-hydrogen atoms are given in Table 2, and in Table 3 hydrogen atoms positional parameters with isotropic temperature factors are given. Bond diastances and angles with their standard deviations are given in Table 4 and 5.

Table 2. Positional parameters (x10^4) and temperature parameters for non-hydrogen atoms, $B_{eq} = 8\,^2\,(U_{11} \cdot U_{12} \cdot U_{13})^{1/3}$

Atom	X	Y	Z	B_{eq}(A^2)
P	1957(1)	3356(4)	3676(3)	2.47(12)
S	1485(1)	7036(5)	2966(4)	3.28(14)
O1	1562(4)	2620(15)	5133(11)	4.19(44)
O2	2070(4)	1474(14)	2773(10)	4.00(44)
O3	2449(3)	4383(14)	4258(9)	3.08(37)
O4	1085(5)	6913(18)	4438(10)	5.46(58)
C1	1551(7)	3546(23)	6782(13)	4.20(56)
C2	2430(7)	1361(26)	1311(18)	5.62(80)
C3	1543(5)	4715(18)	2139(14)	3.05(54)
C4	998(5)	3787(18)	1677(14)	3.40(55)
C5	1112(5)	7987(18)	1173(12)	2.78(52)
C6	1351(4)	8117(22)	-435(12)	2.77(56)
C7	1056(5)	8862(22)	-1794(15)	4.14(69)
C8	524(5)	9544(17)	-1566(12)	2.61(53)
C9	297(5)	9512(19)	78(14)	3.20(62)
C10	587(5)	8746(19)	1483(16)	3.64(63)
C11	212(6)	10352(24)	-3052(17)	5.05(74)

Table 3. Positional parameters (x10^4) and temperature parameters for hydrogen atoms

Atom				
H11	1305(7)	2408(23)	7257(13)	9.7(16)
H12	1328(7)	4824(23)	6976(13)	9.7(16)
H13	1949(7)	3597(23)	7473(13)	9.7(16)
H21	2305(7)	-27(26)	980(18)	9.7(16)
H22	2868(7)	1381(26)	1600(18)	9.7(16)
H23	2347(7)	2272(26)	238(18)	9.7(16)
H31	1750(5)	4798(18)	906(14)	8.8(52)
H41	730(5)	4783(18)	1060(14)	9.7(16)
H42	806(5)	3305(18)	2852(14)	9.7(16)
H43	1066(5)	2633(18)	820(14)	9.7(16)
H61	1770(4)	7634(22)	-633(12)	5.1(17)
H71	1244(5)	8918(22)	-3058(15)	5.1(17)
H91	-110(5)	10094(19)	285(14)	5.1(17)
H101	408(5)	8739(19)	2761(16)	5.1(17)
	-192(6)	10685(24)	-2533(17)	9.7(16)
H112	177(6)	9183(24)	-3910(17)	9.7(16)
H113	372(6)	11525(24)	-3755(17)	9.7(16)

Lists of structure factors and anisotropic thermal parameters and bond lengths involving H-atoms are available from the Cambridge Crystallographic Data Centre

Table 4. Bond lengths (Å)

P - O(1)	1.570(10)	C(3) - C(4)	1.517(18)
P - O(2)	1.556(10)	C(5) - C(6)	1.376(14)
P - O(3)	1.469(9)	C(8) - C(7)	1.385(17)
P - C(3)	1.838(12)	C(6) - C(7)	1.381(17)
S - C(3)	1.804(13)	C(8) - C(9)	1.387(15)
S - O(4)	1.496(11)	C(9) - C(10)	1.407(17)
S - C(5)	1.793(11)	C(5) - C(10)	1.400(16)
O(1) - C(1)	1.444(15)	C(8) - C(11)	1.494(18)
O(2) - C(2)	1.429(17)		

Table 5. Bond angles ($^{\circ}$)

O(2) - P - O(1)	97.6(5)	C(4) - C(3) - P	112.6(9)
O(3) - P - O(1)	116.1(5)	C(4) - C(3) - S	115.4(9)
O(3) - P - O(2)	116.1(5)	C(6) - C(5) - S	121.3(9)
C(13) - P - O(1)	108.7(5)	C(10) - C(5) - S	118.1(8)
C(3) - P - O(2)	105.7(5)	C(10) - C(5) - C(6)	120.4(10)
C(3) - P - O(3)	111.4(6)	C(9) - C(8) - C(7)	118.4(10)
C(3) - S - O(4)	105.4(7)	C(11) - C(8) - C(7)	120.4(10)
C(5) - S - O(4)	107.0(6)	C(11) - C(8) - C(9)	121.2(11)
C(5) - S - C(3)	96.9(6)	C(7) - C(6) - C(5)	120.2(10)
C(1) - O(1) - P	119.4(9)	C(6) - C(7) - C(8)	121.2(10)
C(2) - O(2) - P	120.8(10)	C(10) - C(9) - C(8)	121.6(11)
S - C(3) - P	108.0(6)	C(9) - C(10) - C(5)	118.0(10)

ACKNOWLEDGEMENTS

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