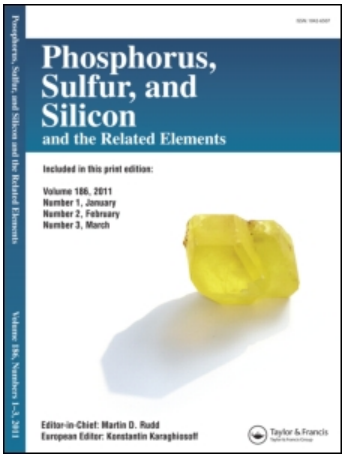

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

STUDY ON THE SYNTHESIS AND STEREOCHEMISTRY OF *α*-ARYL-*β*-NITROALKYL PHENYL PHOSPHINOTHIONATES

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To cite this Article Zhou, Han-Jie , Zhang, Yong-Qiang , Li, Yu-Gui , Wang, Jin-Ling , Liu, Xiao-Lan , Miao, Fang-Ming , Yang, Song-Cheng , Jiang, Xiao-Chun , Feng, Rui and Yan, Zhong-Xian(1995) 'STUDY ON THE SYNTHESIS AND STEREOCHEMISTRY OF *α*-ARYL-*β*-NITROALKYL PHENYL PHOSPHINOTHIONATES', Phosphorus, Sulfur, and Silicon and the Related Elements, 102: 1, 185 — 193
To link to this Article: DOI: 10.1080/10426509508042556
URL: http://dx.doi.org/10.1080/10426509508042556

Phosphorus, Sulfur, and Silicon, 1995, Vol. 102, pp. 185–193
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STUDY ON THE SYNTHESIS AND STEREOCHEMISTRY OF α-ARYL-β-NITROALKYL PHENYL PHOSPHINOTHIONATES

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(Received December 15, 1994; in final form January 10, 1995)

In this paper the synthetic methods of α-aryl-β-nitroalkyl phenyl phosphinothionates **4** which were unknown were studied in detail and it was found that only when using Lawesson's reagent (**LR**) as thionating agent these compounds were obtained in high yields. The configuration of **4** was determined through the analysis of high resolution ^1H, $^{31}PNMR$ and X-ray diffraction. With the help of investigation of plausible mechanism, the stereochemistry of **LR** thionating the P=O group was studied. So far this is the first detailed report as to the mechanism and stereochemistry of sulfurization of compounds involving the P=O group with **LR**.

Key words: Phosphinothionate, Lawesson's Reagent, configuration, single crystal, stereochemistry.

INTRODUCTION

It was reported[1] that phenenylamine is an insect neuro toxin and β-aminophosphinates are animal metabolites. β-Nitro phosphinates and phosphinothionates could be thought as their predecessors or analogues. In order to investigate the role of phosphorus-chemistry in the activities of live and find new biorational pesticides, study on the synthesis of these compounds is very interesting.

The synthesis of β-nitrophosphinates has attracted attention for a long time,[2] but the progress is slow. Under strong base condition, the reaction of phosphonite with derivatives of β-nitrostyrene is affected by many factors and is therefore of little value in the synthesis. Recently, a new method was discovered which is based

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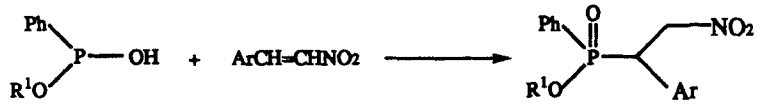
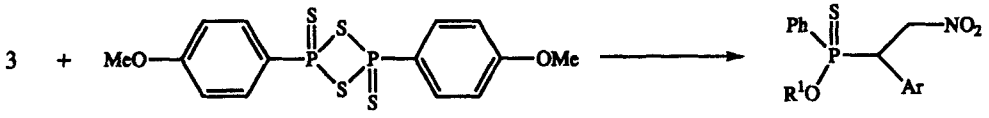
on the use of silyphosphonites. We have reported the following reaction for the preparation of compounds **3** in a previous paper.[3]



1 **2** **3a-m**

To convert phosphinates **3** into phosphinothionates **4**, Lawesson's Reagent, 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide, was selected as thionating agent. Thirteen title compounds **4** were thus obtained in high yields.



LR **4a-m**

RESULTS AND DISCUSSION

1. Selection of Synthetic Methods

Up to now there is no report that thiophosphonites can be silylated. This is probably due to the fact that the S—Si bond is much weaker than the O—Si bond. Furthermore thiophosphonites are not easily prepared and are unstable. A method, in which compounds **3** were prepared and then converted into the corresponding thionated products **4**, is discussed below.

At present hydrogen sulfide,[4] borontrisulfide,[5] thiophosphoryl bromide,[6] phosphorus pentasulfide[7] and sulfur[8] are known as thionating agents. However, there is almost no reaction between phosphorus pentasulfide or sulfur and compounds **3**. Surprisingly, compounds **4** were obtained in high yields when **LR** was used. The attractiveness of **LR** is associated with its ready availability, simplicity and convenience of use, especially its ideal effectivity.[9]

2. Stereochemistry of Compounds **4**

Obviously there should be two pairs of racemic isomers because of two chiral centres, P and C atoms, in compounds **4**. It has been determined that compounds **3** consist of two pairs of racemic isomers with difference in contents, in which (RPRC + SPSC) racemate is the main product. What attracted our attention is the exact configuration of compounds **4** after sulfurization with **LR**.

There are few speculations on the mechanism and stereochemistry of sulfurization of compounds involving the P=O group with **LR**.[10,11] It was known that the con-

TABLE I

Physical and spectral data of compounds 4[a]

No.	R^1	R^2	Yield (%)	m.p. (°C)	Element Anal.(%)[b] C	H	N	IR γ (cm-1) NO_2	P-Ph	P-O	P-C	P=S	m/z(%)[c] B.P.[d]	M	^{1}HNMR (CDCl3, TMS) ppm P-OCH-R		R^2	P-CH / P-OCH	CH_2NO_2	R^2- C_6H_4		P-C_6H_5
4a	n-Bu	p-MeO	76.0	99.5-100.5	57.95	6.18	3.63	1548.5	1436.3	1028.7	989.6	636.3	134	393	0.84-0.98	1.10-1.84	3.68	3.95-4.46		4.90-5.20	6.54-6.64	6.80-6.95	7.16-7.70
					(58.00)	(6.15)	(3.56)	1371.2		857.1				(4.86)	(t, 3H)	(m, 4H)	(s, 3H)	(m, 3H)		(m, 2H)	(d, 2H)	(dd, 2H)	(m, 5H)
4b	n-Pr	p-Me_2N	81.0	117.0-118.5	58.36	6.40	7.00	1517.2	1433.7	1028.7	980.3	637.3	147	392	0.80-0.96	1.44-1.80	2.80	3.50-3.85	3.90-4.36	4.84-5.08	6.31-6.40	6.62-6.80	7.18-7.62
					(58.15)	(6.42)	(7.14)	1369.1		849.1				(15.54)	(t, 3H)	(m, 2H)	(s, 6H)	(m, 1H)	(m, 2H)	(m, 2H)	(d, 2H)	(dd, 2H)	(m, 5H)
4c	n-Pr	H	83.5	112.0-113.0	58.20	5.79	4.26	1540.6	1450.1	1050.8	970.1	634.0	157	349	0.88-1.05	1.52-1.90		3.55-3.88	3.90-4.52	4.88-5.28	6.82-7.20		7.20-7.66
					(58.44)	(5.77)	(4.01)	1368.6		850.1				(5.09)	(t, 3H)	(m, 2H)		(m, 1H)	(m, 2H)	(m, 2H)	(m, 5H)		(m, 5H)
4d	i-Pr	m-PhO	82.5	94.5-95.5	62.15	5.56	3.16	1539.3	1478.5	1069.4	968.3	638.7	157	441	1.12-1.44		6.90-7.75	4.04-4.42	4.64-4.90	4.95-5.12	6.55-6.90		6.90-7.75
					(62.37)	(5.48)	(3.17)	1365.6		884.2				(13.55)	(dd, 6H)		(m, 5H)	(m, 1H)	(m, 1H)	(m, 2H)	(m, 4H)		(m, 5H)
4e	n-Pr	m-PhO	85.5	100.5-101.5	62.31	5.54	3.35	1541.1	1430.3	1020.3	971.0	631.0	157	441	0.88-1.04	1.52-1.82	6.92-7.78	3.58-3.92	3.98-4.48	4.88-5.24	6.52-6.90		6.92-7.78
					(62.37)	(5.48)	(3.17)	1363.6		887.1				(10.69)	(t, 3H)	(m, 2H)	(m, 5H)	(m, 1H)	(m, 2H)	(m, 2H)	(m, 4H)		(m, 5H)
4f	Et	p-Me_2N	76.5	142.5-144.0	56.84	6.14	7.44	1548.1	1433.0	1031.8	951.9	632.0	147	378	1.29-1.41		2.90	3.82-4.42		4.90-5.20	6.40-6.50	6.76-6.90	7.30-7.70
					(57.13)	(6.13)	(7.40)	1357.0		846.0				(17.41)	(t, 3H)		(s, 6H)	(m, 3H)		(m, 2H)	(d, 2H)	(dd, 2H)	(m, 5H)
4g	i-Pr	H	79.0	90.5-93.0	58.52	5.78	3.89	1544.1	1430.6	1099.7	971.6	648.2	157	349	1.10-1.44			4.04-4.44	4.60-4.92	4.92-5.16	6.88-7.16		7.16-7.70
					(58.44)	(5.77)	(4.01)	1370.6		849.0				(3.91)	(dd, 6H)			(m, 1H)	(m, 1H)	(m, 2H)	(m, 5H)		(m, 5H)
4h	Et	H	81.0	132.5-133.5	57.11	5.46	4.35	1544.6	1435.4	1022.1	953.7	634.8	157	335	1.17-1.42			3.75-3.98	4.00-4.45	4.98-5.20	6.90-7.16		7.20-7.66
					(57.30)	(5.41)	(4.18)	1369.3		842.1				(3.85)	(t, 3H)			(m, 1H)	(m, 2H)	(m, 2H)	(m, 5H)		(m, 5H)
4i	i-Pr	p-MeO	88.0	120.5-122.0	56.50	5.84	3.65						134	379	1.00-1.37		3.58	3.94-4.32	4.46-4.80	4.84-5.01	6.41-6.51	6.70-6.82	7.08-7.60
					(56.98)	(5.84)	(3.69)							(6.07)	(dd, 6H)		(s, 3H)	(m, 1H)	(m, 1H)	(m, 2H)	(d, 2H)	(dd, 2H)	(m, 5H)
4j	Et	p-MeO	84.5	87.5-89.0	55.75	5.50	3.89						134	365	1.15-1.41		3.72	3.70-4.00	4.04-4.44	4.90-5.15	6.55-6.65	6.83-6.95	7.20-7.70
					(55.88)	(5.52)	(3.83)							(5.07)	(t, 3H)		(s, 3H)	(m, 1H)	(m, 2H)	(m, 2H)	(d, 2H)	(dd, 2H)	(m, 5H)
4k	n-Pr	p-MeO	85.0	83.0-85.0	56.48	5.76	4.20	1547.8	1435.8	1028.1	981.5	638.0			0.82-0.98	1.44-1.84	3.64	3.80-4.40		4.80-5.18	6.48-6.58	6.76-6.88	7.16-7.60
					(56.98)	(5.84)	(3.69)	370.6		858.5					(t, 3H)	(m, 2H)	(s, 3H)	(m, 3H)		(m, 2H)	(d, 2H)	(dd, 2H)	(m, 5H)
4l	i-Pr	p-Me_2N	83.0	136.5-138.0	58.10	6.48	7.16						147	392	0.99-1.33		2.76	3.90-4.28	4.40-4.76	4.80-5.02	6.28-6.38	6.64-6.76	7.04-7.64
					(58.15)	(6.42)	(7.14)							(11.06)	(dd, 6H)		(s, 6H)	(m, 1H)	(m, 1H)	(m, 2H)	(d, 2H)	(dd, 2H)	(m, 5H)
4m	Et	m-PhO	77.5	122.5-124.0	61.35	5.26	3.32						157	427	1.16-1.31		6.84-7.60	3.60-4.36		4.85-5.14	6.42-6.80		6.84-7.00
					(61.82)	(5.19)	(3.28)							(9.21)	(t, 3H)		(m, 5H)	(m, 3H)		(m, 2H)	(m, 4H)		(m, 5H)

[a] Ar = R^2-C_6H_4, [b] Found(Calcd.), [c] Related contents, [d] Base Peak

figuration of the chiral atoms adjacent to the reaction center isn't affected by **LR**.[12] That was to say the configuration of the chiral carbon in compounds **4** is retained.

In order to clarify the stereochemistry of sulfurization, the high resolution ^{1}H and $^{31}PNMR$ spectra were studied. As a result, it was found that two peaks with different intensities appear in the $^{31}PNMR$ spectra, as shown in Table II. Furthermore, in the $^{1}HNMR$ (400.13 mHz) "abnormal" peaks appear likewise. The investigation of $^{1}HNMR$, shown in Figure 1, shows that two groups of slightly different chemical shifts with different integration constants are present. Table III summarizes the $^{1}HNMR$ data of selected compounds **4**.

In general, under non-chiral condition the behavior of nuclear magnetic resonance of racemic isomers is the same, but different between diastereoisomers. Furthermore, it was noteworthy that the intensities of signals are almost the same according to the integration constants of $^{31}PNMR$ and $^{1}HNMR$ spectra. So this result indicates the existence of two pairs of racemic isomers in different amounts.

TABLE II

$^{31}PNMR$ data of selected compounds **4***

No.	ppm	Δ δ (ppm)	Intensity(%)	Content(%)
4g	88.569 (A)	4.123	15.686 (A)	86.47 (A)
	84.446 (B)		2.454 (B)	13.53 (B)
4i	88.704 (A)	4.586	100.00 (A)	91.10 (A)
	84.118 (B)		9.766 (B)	8.90 (B)
4k	88.568 (A)	4.053	19.663 (A)	91.75 (A)
	84.516 (B)		1.768 (B)	8.25 (B)

* Solvent: $CDCl_3$, External Standard: 85% H_3PO_4

TABLE III

Contents and $^{1}HNMR$ data (400.13 mHz) of selected compounds **4**‡

No.	Content (%)	$^{1}HNMR$ (ppm) OCH(CH3)2	OCH2CH2CH3	OCH2CH2CH3	P-OCHn†	P-CH
4c	(A) 94.29		0.951-0.988 (t, 3H)	1.693-1.764 (m, 2H)	3.712-3.755 (m, 1H) 4.077-4.141 (m, 1H)	4.310-4.396 (m, 1H)
	(B) 5.71		0.829-0.866 (t, 3H)	1.540-1.595 (m, 2H)	3.635-3.695 (m, 1H) 3.770-3.815 (m, 1H)	4.158-4.200 (m, 1H)
4d	(A) 96.24	1.127-1.143 (d, 3H) 1.388-1.402 (d, 3H)			4.762-4.821 (m, 1H)	4.220-4.291 (m, 1H)
	(B) 8.86	1.097-1.254 (dd, 6H)			4.645-4.700 (m, 1H)	4.095-4.164 (m, 1H)
4e	(A) 91.14		0.936-0.973 (t, 3H)	1.654-1.743 (m, 2H)	3.682-3.758 (m, 2H)	4.255-4.329 (m, 1H)
	(B) 8.86		0.844-0.896 (t, 3H)	1.548-1.488 (m, 2H)	4.055-4.136 (m, 2H)	4.109-4.195 (m, 1H)
4g	(A) 85.34	1.114-1.146 (d,3 H) 1.387-1.418 (d, 3H)			4.763-4.817 (m, 1H)	4.270-4.363 (m, 1H)
	(B) 14.64	1.041-1.114 (dd, 6H)			4.456-4.688 (m, 1H)	4.226-4.237 (m, 1H)
4i	(A) 91.80	0.821-0.836 (d, 3H) 1.185-1.201 (d, 3H)			4.661-4.718 (m, 1H)	4.296-4.379 (m, 1H)
	(B) 8.20	0.768-0.783 (d, 3H) 0.903-0.917 (d, 3H)			4.522-4.611 (m, 1H)	4.163-4.242 (m, 1H)

‡ Solvent: $CDCl_3$, Internal Standard: TMS. † n=1,2.

With the help of the analysis of X-ray diffraction of crystal **4e**, it was determined that the configuration is RPRC + SPSC (shown in Figure 2). So by the sulfurization with **LR**, the configuration of the chiral P atom is retained and compounds **4** consist

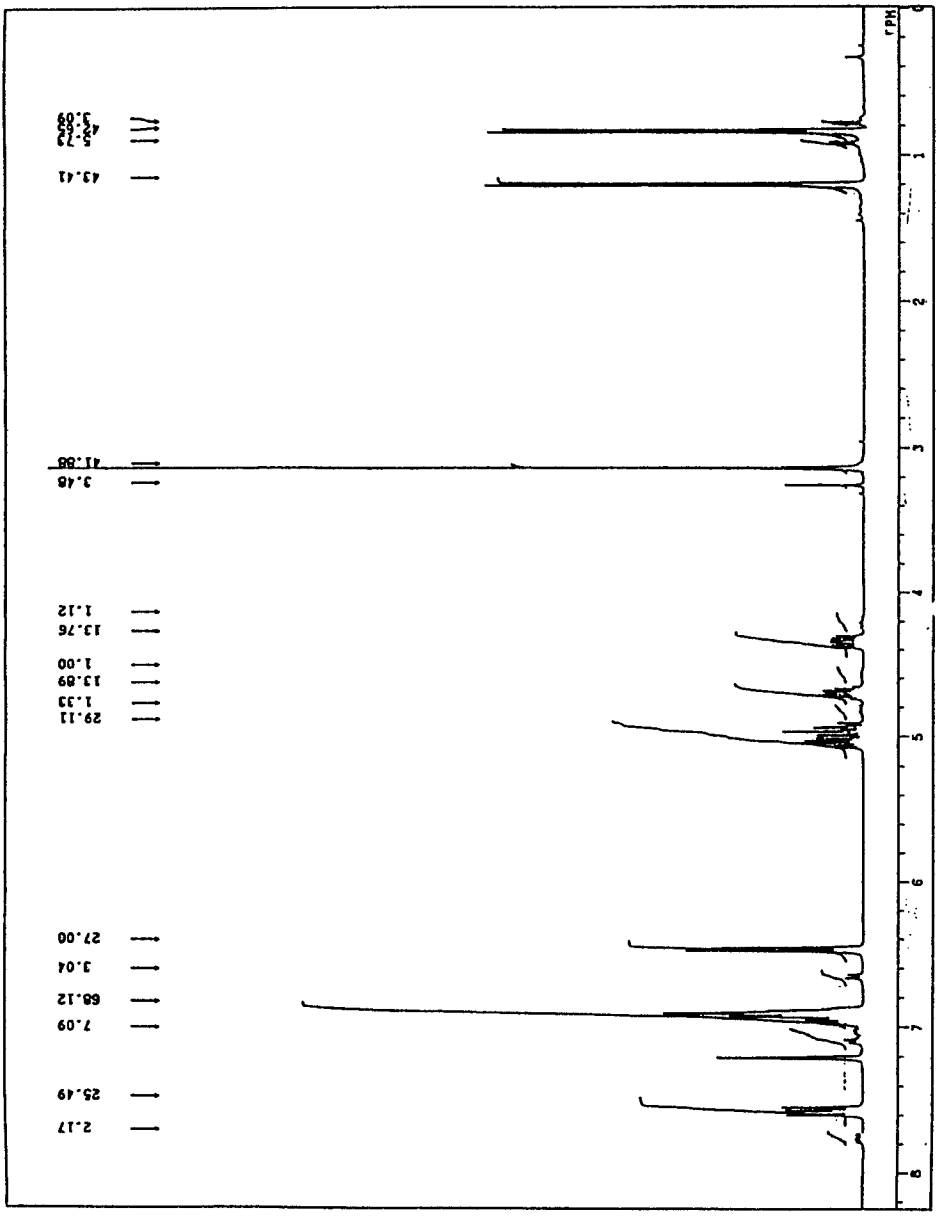
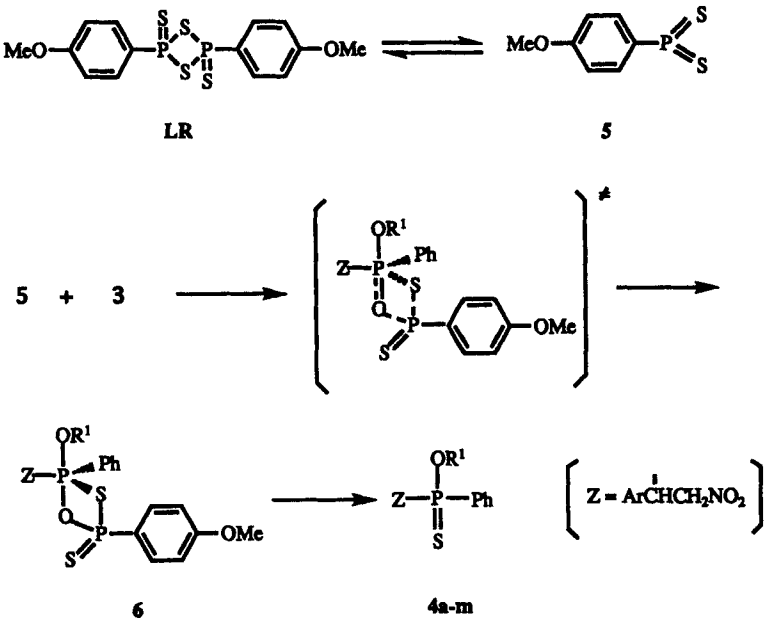


FIGURE 1 ^{1}HNMR spectrum (400.13mHz) of **4i**.

mainly of racemic isomers (RPRC + SPSC). The isolation and resolution will be studied further.

3. *Mechanism Discussion*

According to the results of experiments, the following plausible mechanism may be envisioned:



SCHEME I

It seems likely that the highly reactive intermediate **5**, rather than **LR** itself, is the active thionating agent and then a pentacoordinated phosphorus intermediate **6** is formed. The whole process may be summarized as cis-syn addition-elimination. Thus, the configuration of the chiral P atom is retained. To our knowledge, this is the first report as to mechanism and stereochemistry of sulfurization of compounds involving the P=O group with **LR**.

4. *Determination of X-Ray Crystal Structure of Compound* **4e**

Diffraction experiment was performed on Enraf-Nonius CAD4, 4-circle diffractometer, using Mo-Kα radiation. The single crystal is orthorhombic, space group is $Pna2_1$ (No. 33), with a = 18.046(2) Å, b = 20.406(4) Å, c = 6.145(2) Å, α = β = γ = 90.00(2)°, V = 2262.9 Å^3, Dcal. = 1.296 g·cm^{-3}, Z = 4, 1° < 2θ < 25° and F(000) = 928. The structure was solved by direct methods and refined to

final reliability indices R = 0.047, R_W = 0.051.[13] The bond angles and bond distances are given in Tables IV and V.

The perspective view of the molecular structure of **4e** with numbering is shown in Figure 2. Obviously, the configuration shown is RPRC, but the synthesis were carried out under non-chiral condition. So the crystal **4e** consists of, in fact, two enatiomers (RPRC + SPSC) with identical amounts. Besides, it is noteworthy that the three benzene rings are non-coparallel with dihedral angles of 60.06, 47.17 and 103.84°, respectively.

TABLE IV

Bond angles (°) of crystal **4e**#

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
S1	P1	O1	114.6(6)	C13	C14	C15	123.(2)
S1	P1	C10	114.7(6)	C14	C15	C16	118.(2)
S1	P1	C31	115.3(7)	C11	C16	C15	120.(2)
O1	P1	C10	98.5(7)	O2	C21	C22	113.(2)
O1	P1	C31	105.0(8)	O2	C21	C26	127.(3)
C10	P1	C31	107.0(7)	C22	C21	C26	119.(3)
P1	O1	C1	120.(2)	C21	C22	C23	119.(2)
C13	O2	C21	117.(2)	C22	C23	C24	124.(3)
O11	N1	O12	126.(2)	C23	C24	C25	114.(3)
O11	N1	C01	118.(2)	C24	C25	C26	125.(2)
O12	N1	C01	116.(2)	C21	C26	C25	118.(3)
P1	C10	C01	109.(1)	P1	C31	C32	121.(2)
P1	C10	C11	111.(1)	P1	C31	C36	119.(2)
C01	C10	C11	113.(1)	C32	C31	C36	120.(2)
N1	C01	C10	112.(2)	C31	C32	C33	119.(2)
C10	C11	C12	117.(2)	C32	C33	C34	119.(2)
C10	C11	C16	121.(2)	C33	C34	C35	121.(2)
C12	C11	C16	122.(2)	C34	C35	C36	122.(3)
C11	C12	C13	119.(2)	C31	C36	C35	120.(2)
O2	C13	C12	126.(3)	O1	C1	C2	113.(2)
O2	C13	C14	115.(2)	C1	C2	C3	127.(4)
C12	C13	C14	118.(2)				

Numbers in parentheses are estimated standard deviations in the least signifcant digits.

TABLE V

Bond distances in angstroms of crystal **4e***

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
P1	S1	1.932(7)	C14	C15	1.33(3)
P1	O1	1.57(1)	C15	C16	1.40(3)
P1	C10	1.82(2)	C21	C22	1.40(3)
P1	C31	1.77(2)	C21	C26	1.36(3)
O1	C1	1.42(3)	C22	C23	1.35(4)
O2	C13	1.37(3)	C23	C24	1.35(4)
O2	C21	1.37(3)	C24	C25	1.39(3)
O11	N1	1.21(2)	C25	C26	1.35(3)
O12	N1	1.17(2)	C31	C32	1.36(3)
N1	C01	1.51(2)	C31	C36	1.38(3)
C10	C01	1.50(2)	C32	C33	1.40(3)
C10	C11	1.54(2)	C33	C34	1.38(3)
C11	C12	1.37(2)	C34	C35	1.30(3)
C11	C16	1.34(3)	C35	C36	1.36(3)
C12	C13	1.38(3)	C1	C2	1.36(4)
C13	C14	1.38(3)	C2	C3	1.23(4)

*Numbers in parentheses are estimated standard deviations in the least significant digits.

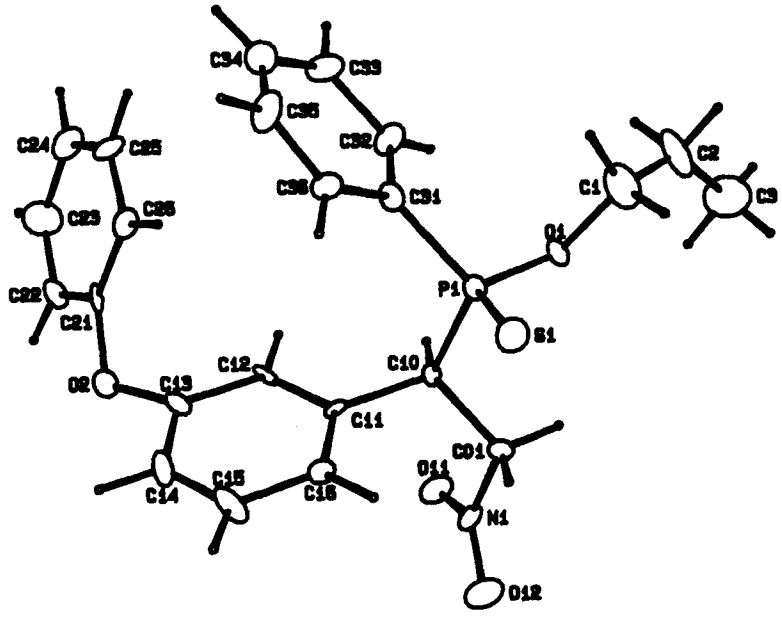


FIGURE 2 X-Ray crystal structure of **4e**.

5. *Analysis of Spectral Data*

(1) IR: In all products the characteristic absorbance of the P=O group disappears and the absorbance of the P=S group is seen at the range of 640–680 cm^{-1}. The absorbance of the NO_2 group is characteristic and still shows at the range of 1545 and 1360 cm^{-1}, respectively.

(2) MS: It was observed that all compounds **4** exhibit normal molecular ion peaks. Usually they have fragment ions $Ph(O)SH^{+\cdot}$,m/z:157 and $ArCH{=}CH^{+\cdot}$, the former comes from a McLafferty rearrangement and the latter from a heterolysis of the P—C bond.

(3) NMR: All ^1H chemical shifts corresponding to the structures were assigned. The isopropoxy group linked directly with the P atom shows long-distant double-double peaks due to the slightly difference of chemical environment of two methyl groups. The $^{13}CNMR$ shift signals were assigned on the basis of the analysis of substituent effects and coupling constants.

EXPERIMENTAL

Melting points were uncorrected. IR spectra were recorded on a JSCODS-405IR spectrometer (KBr). NMR spectra were obtained on JEDLFX-90QNMR and JEDL-GX NMR spectrometers. MS spectra were taken on a MAT-711 MASS spectrometer.

α-Aryl-β-nitroalkyl phenyl phosphinates **3** were prepared by the methods described before.[3]

LR was prepared according to the literature.[9]

The reactions of compounds **3** with phosphorus pentasulfide and sulfur were performed according to References 7 and 8 respectively. The results monitored by TLC indicated that no reaction occurred at all.

O-ethyl, α-phenyl-β-nitroethyl phenyl phosphinothionate **4h**: To a 50 ml four-necked flask equipped with a condensor ($CaCl_2$ dry tube) were added successively 3.20 g (10 mmol) **3h**, 2.22 g (5.5 mmol) **LR** and 40 ml of anhydrous toluene. The mixture was heated, with stirring, to 95°C and became homogenous. It was kept for 15 hours until **3h** almost disappeared, monitored by means of TLC. After removing toluene, the residue was chromatographed using a solvent mixture, petrolumn ether/ethyl acetate (5:1), as eluting agent. 2.7 g white solid were isolated, yield 81%. Recrystallization from petrolumn ether/ethyl acetate (2:1) gave colorless crystals of m.p.132–133.5°C.

In a similar procedure other compounds **4** were obtained.

ACKNOWLEDGEMENT

This work was financially supported by the National Natural Science Foundation of China.

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