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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>

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To cite this Article Moedritzer, Kurt and Miller, R. E.(1981) '1-PHENOXYPHOSPHOLENE 1-OXIDES', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 9: 3, 293 — 297

To link to this Article: DOI: 10.1080/03086648108078253

URL: <http://dx.doi.org/10.1080/03086648108078253>

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1-PHENOXYPHOSPHOLENE 1-OXIDES

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(Received April 14, 1980; in final form May 30, 1980)

Isomerically pure samples of the two isomers of 1-phenoxyphospholene 1-oxide were prepared and exhaustively characterized by ^1H , ^{31}P and ^{13}C nmr, IR and mass spectrometry.

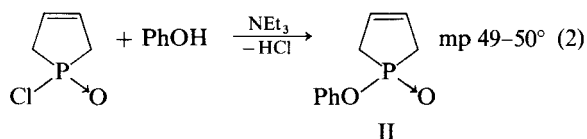
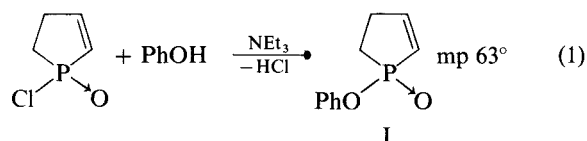
INTRODUCTION

In the course of studies of derivatives of phospholene 1-oxides we were interested in the two isomeric 1-phenoxyphospholene 1-oxides. Although these compounds have been discussed previously in the literature,¹⁻⁶ there are discrepancies in the reported characterization data of these compounds and the isomeric purity of the samples investigated is questionable. In one publication the 3-isomer is reported¹ to melt at 60-62°, in another communication a mixture of the two isomers is reported⁴ to melt at 49-50°, in a third communication⁵ a melting point of 48-49° is listed for the 3-isomer and several other authors^{2,6} do not give any melting point at all. The 2-isomer has been reported to catalyze the conversion of isocyanates to carbodiimides, however, data characterizing this compound have not been disclosed.³

RESULTS AND DISCUSSION

The purpose of the present paper is to clear up the above discrepancies and to prepare and characterize unequivocally pure samples of the two isomers of 1-phenoxyphospholene 1-oxide analytically and spectroscopically.

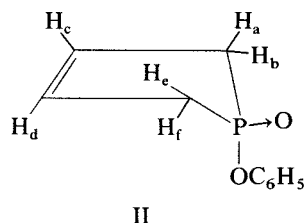
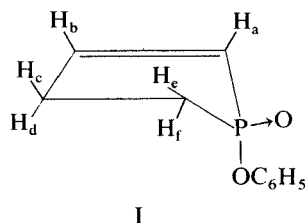
Each of the two isomers of 1-phenoxyphospholene 1-oxide was prepared in high yield by reacting the respective isomerically pure 1-chlorophospholene 1-oxide⁷ with phenol in the presence of triethylamine ($\text{Ph}=\text{C}_6\text{H}_5$).



The resulting compounds, after work-up consisting of vacuum distillation followed by crystallization, were obtained in high purity. Both isomers under the above conditions were found to be stable and no double bond isomerization was observed.

Proton Nmr Spectra

In discussing the proton nmr spectra of the two isomers of 1-phenoxyphospholene-1-oxide it is helpful to visualize the various proton environments of the 5-ring system as shown below.



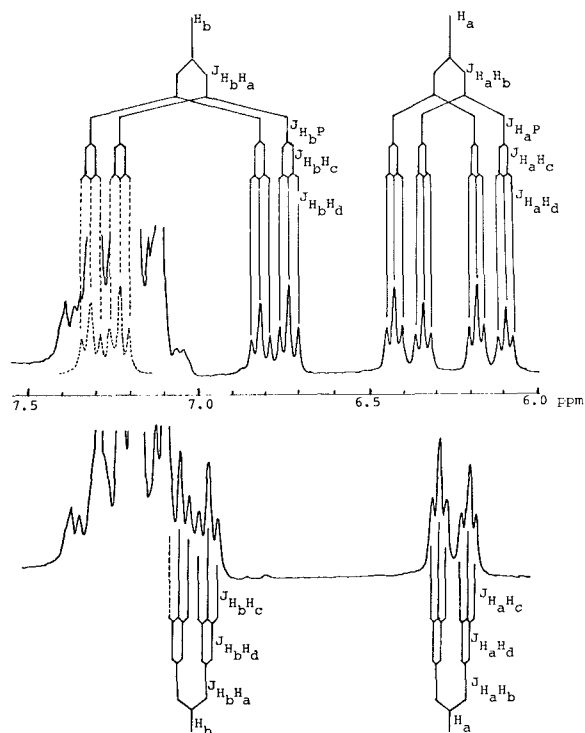


FIGURE 1 Coupled (top) and ^{31}P -decoupled (bottom) Proton Nmr Spectra of the Olefinic Protons of 1-Phenoxy-2-phospholene 1-Oxide in CDCl_3 at 100 MHz. (JOEL FX-100 FT).

The 2-isomer is a seven spin system (disregarding the aromatic protons) with the proton nmr spectrum of the olefinic protons shown in Figure 1. Each olefinic proton, H_a and H_b , results in a set of four triplets due to coupling to P, H_a or H_b , H_c and H_d .

For the low-field olefinic proton two of the triplets overlap with the aromatic protons and in Figure 1 are represented by broken lines. These were extrapolated from the ^{31}P -decoupled spectrum shown at the bottom of Figure 1. The ^{31}P -decoupled proton nmr spectrum indicates that the two olefinic protons display different ^{31}P coupling constants, $^3J_{\text{HP}} = 22.0$ and 49.8 Hz. Based on assignments made for 1-phenyl-2-phospholene 1-oxide⁸ the proton having the smaller coupling constant and being at higher field is assigned to H_a and the other to H_b . The coupling constants $^3J_{\text{H}_a\text{H}_b} = 8.6$ Hz, $^4J_{\text{H}_a\text{H}_c} = ^4J_{\text{H}_a\text{H}_d} = 2.2$ Hz, $^3J_{\text{H}_b\text{H}_c} = ^3J_{\text{H}_b\text{H}_d} = 2.2$ Hz.

The ^1H nmr resonances of the methylene protons of the 2-isomer are shown in Figure 2 indicating a high degree of coupling. The two sets of

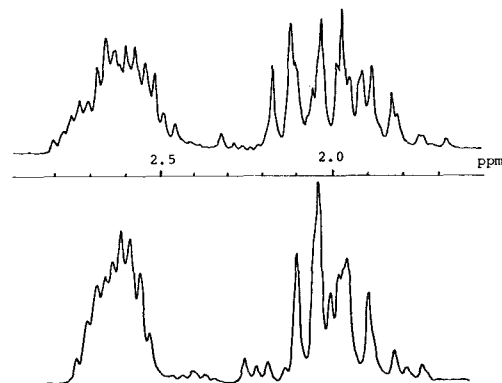


FIGURE 2 Proton Nmr Spectra (100 MHz) of the CH_2 protons of 1-Phenoxy-2-phospholene 1-Oxide; top: normal spectrum; bottom: ^{31}P -decoupled (JOEL FX-100 FT).

multiplets, each representing two protons, are well separated, however, ^{31}P -decoupling does not simplify the spectrum.

The ^1H nmr spectrum of the 3-isomer is significantly simpler than that of the 2-isomer. The olefinic protons are represented by a doublet ($^3J_{\text{HP}} = 34$ Hz) at 5.43 ppm which collapses to a singlet upon ^{31}P -decoupling. The CH_2 protons are represented by the rather simple peak system shown in Figure 3, an apparent doublet seen at 60 MHz which turns into a doublet and singlet at 100 MHz. A similar effect, although more pronounced, has been observed earlier in the spectra of 1-phenyl-3-phospholene 1-oxide⁸ and 1-methyl-3-phospholene 1-oxide,⁹ where the corresponding methylene protons also are non-equivalent and consequently were expected to give an $\text{A}_2\text{B}_2\text{X}$ spectrum instead

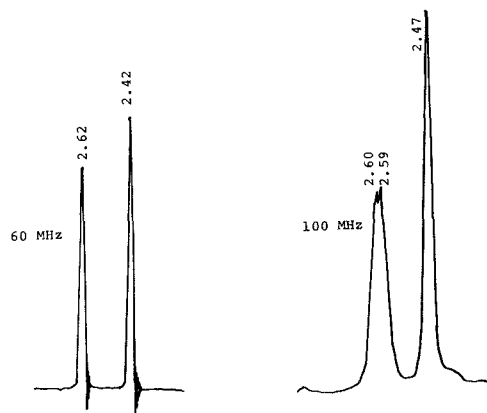


FIGURE 3 Proton Nmr Spectra of the CH_2 Protons (shifts in ppm) in 1-Phenoxyphospholene 1-Oxide at Various Magnetic Fields.

of the doublet seen at low magnetic field. Only at higher magnetic field strengths the expected multiplet was seen in agreement with the anticipated A_2B_2X pattern. This effect, also in the present case, may be explained in terms of an accidental, deceptive simplification of an actual A_2B_2X spectrum at these particular magnetic field strengths.

^{31}P Nmr Data



The ^{31}P nmr chemical shifts of the 1-phenoxyphospholene 1-oxides, 2-isomer: 73.2 ppm and 3-isomer: 72.2 ppm, are downfield of the range normally observed¹⁰ for phosphinate esters and in agreement with ^{31}P nmr shifts found for other phospholene derivatives. The shifts of the 1-phenoxyphospholene 1-oxides are similar to those of the corresponding 1-hydroxy derivatives,⁷ (2-isomer: 76.8 ppm, 3-isomer: 75.1 ppm).

^{13}C Nmr Spectra

The ^{13}C nmr data of the two isomers of 1-phenoxyphospholene 1-oxide are tabulated in Table I. All nmr peaks of the phospholene ring carbon atoms are doublets due to ^{13}C - ^{31}P nuclear spin coupling. The olefinic carbon atoms (sp^2) in the five-membered ring are easily identified by their downfield shifts (low shielding) relative to the sp^3 carbon atoms.

TABLE I

^{13}C Nmr chemical shifts^a (in ppm) and ^{13}C - ^{31}P spin coupling constants (in Hz) of the two isomeric 1-phenoxyphospholene 1-oxides and the precursor 1-chlorophospholene 1-oxides

				
	X = OPh	X = Cl	X = OPh	X = Cl
C-1	122.78(94.5)	126.68(108.4)	29.06(91.6)	36.43(76.2)
C-2	152.74(33.0)	151.53(36.1)	120.31(4.4)	126.2(17.6)
C-3	27.26(16.4)	28.30(16.6)	—	—
C-4	20.40(96.0)	28.28(82.0)	—	—

^a Spectra were recorded at 25.05 MHz on a Joel FX-100 FT Nmr Spectrometer (X = OPh) and at 15.09 MHz on a Bruker WH-60 FT-Nmr Spectrometer (X = Cl) in CDCl_3 solution; peaks are references versus TMS with downfield shifts being positive; resonances for the aromatic protons are not shown. Coupling constants are listed in parentheses.

In the 2-isomer the assignment of the olefinic resonances to C-1 and C-2 was based on the expected larger ^{13}C - ^{31}P coupling constant for C-1 than for C-2. The two sets of resonances in the sp^3 carbon region were again assigned on the basis of the ^{13}C - ^{31}P coupling constants.

The assignment of the resonances in the 3-isomer was based on similar reasoning with the assignment simplified by the presence of only two ring carbon environments.

The ^{13}C chemical shifts and ^{13}C - ^{31}P coupling constants observed in these compounds are similar to those observed in the corresponding isomers of 1-phenylphospholene 1-oxide⁸ with only minor differences in the chemical shift values and somewhat more significant differences in the values of the coupling constants.

Mass Spectra

The fragmentation patterns in Figure 4 show that the molecular ion is seen for both isomers (m/e 194), with the base peak being at m/e 47 for the

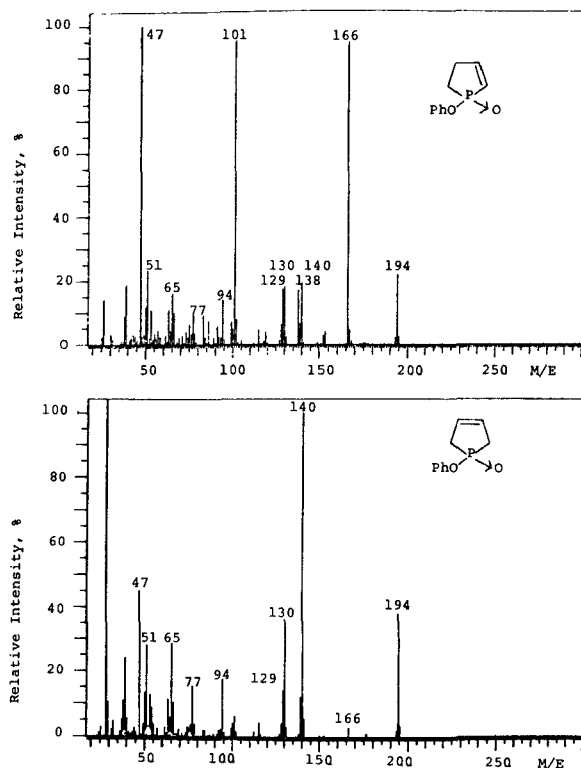


FIGURE 4 Mass Spectra (Varian-MAT 311A) of the Two Isomers of 1-Phenoxyphospholene 1-Oxide at 70 eV (Probe Temperature: 25°, Source Temperature: 205°).

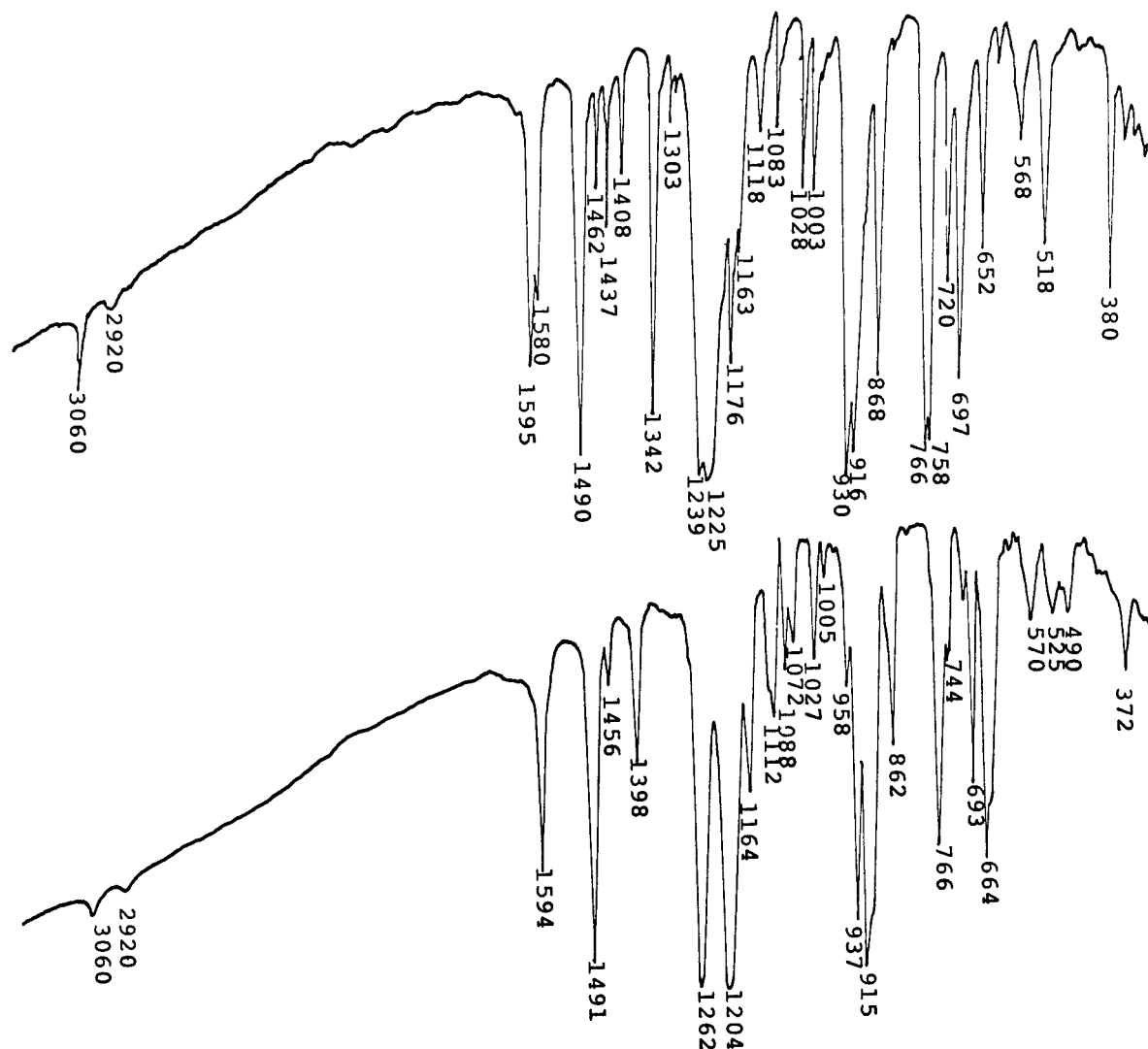


FIGURE 5 IR Spectra (Beckman IR-12 Spectrometer, KBr pellet) of the 2-isomer (top) and 3-isomer (bottom) of 1-Phenoxypospholene 1-Oxide.

2-isomer and at m/e 140 for the 3-isomer. Although the same ions appear in both isomers their intensities differ significantly suggesting different cracking mechanisms upon electron impact. For the 2-isomer the major ions correspond to m/e 166 ($M^+ - CH_2CH_2$), 101 ($M^+ - C_6H_5O$) and 47 (PO^+) with the primary cracking processes being loss of ethylene and loss of a phenoxy group. For the 3-isomer there is only one ion of comparable intensity, the one corresponding to the base peak at m/e 140 ($M^+ - C_4H_6$) with loss of butadiene as the major process.

Infra-red Spectra

The infra-red data in Figure 5 clearly demonstrate significant differences in the two spectra. However, the olefinic stretching vibration, generally a good diagnostic absorption to be used for distinction between 2- and 3-isomers of phospholenes, in the present case overlaps with the group of four bands generally seen in the range $1450-1650\text{ cm}^{-1}$ and associated with skeletal stretching modes of the benzene ring system. Therefore, an unambiguous assignment of the phospholene olefinic

stretching vibrations in the present case cannot be made. The phosphoryl stretching vibration may be assigned to the absorption at 1225 cm^{-1} in the 2-isomer and at 1204 cm^{-1} in the 3-isomer, which agrees with the calculated values (using phosphorus inductive constants¹¹) of 1202 cm^{-1} for the 2-isomer and 1210 cm^{-1} for the 3-isomer.

EXPERIMENTAL

Materials and Instrumentation

Pure isomers of 1-chlorophospholene 1-oxide were prepared as described⁷ previously, phenol (Mallinckrodt, Inc.) and triethylamine (Eastman Kodak Company) were used as received. ^{31}P nmr spectra were recorded on a Varian HR-100 spectrometer operating at 40.5 MHz and referenced versus external 85% H_3PO_4 .

1-Phenoxy-2-phospholene 1-Oxide

To a solution of 80.5 g (0.85 mol) of phenol and 90.3 g (0.89 mole of triethylamine in 1L of benzene kept at 0° was added dropwise a solution of 116.7 g (0.85 mol) of 1-chloro-2-phospholene 1-oxide in 100 mL of benzene. After completed addition the resulting slurry was kept at room temperature overnight and then filtered. The filtrate was evaporated on a rotary evaporator resulting in 163 g of a brown liquid which upon distillation *in vacuo*, bp $150-5^\circ/0.3\text{ mm}$, resulted in 143 g (0.74 mol) of product, 86.6% yield. $\delta^{31}\text{P}$ (CDCl_3): 73.2 ppm. Upon standing the liquid crystallized, mp $60-61^\circ$. The analytical sample was recrystallized from toluene, mp 63° .

Anal. Calcd for $\text{C}_{10}\text{H}_{11}\text{O}_2\text{P}$: C, 61.85; H, 5.71. Found: C, 61.72; H, 5.73.

1-Phenoxy-3-phospholene 1-Oxide

This compound was prepared by the same procedure as above from 117.4 g (0.86 mol) of 1-chloro-3-phospholene 1-oxide, 80.9 g (0.86 mol) of phenol and 91.37 g (0.90 mol) of triethylamine. Work-up of the reaction solution resulted in 167 g of a brown liquid which upon distillation *in vacuo*, bp $110^\circ/0.1$

mm, yielded 148.6 g (0.77 mol) of product, 89.0% yield, which crystallized (mp $47-48^\circ$) upon storage in a refrigerator, $\delta^{31}\text{P}$ (CDCl_3): 72.2 ppm. The analytical sample was recrystallized from methylcyclohexane, mp $49-50^\circ$.

Anal. Calcd for $\text{C}_{10}\text{H}_{11}\text{O}_2\text{P}$: C, 61.85; H, 5.71. Found: C, 61.64; H, 5.68.

ACKNOWLEDGMENT

We wish to thank K. E. Zwikelmaier for obtaining the mass spectra and Mark L. Bowers for some of the experimental work.

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