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# Zwitterionic 1-Phosphonioalkyl Dithiophosphinates

Florian Breitsameter, Hans-Peter Schrödel, and Alfred Schmidpeter

*Institut für Anorganische Chemie der Universität München, Meiserstrasse 1, D-80333 München, Germany*

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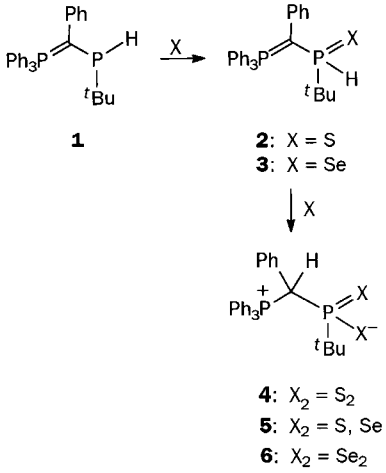
ABSTRACT: *The title compounds (and, in part, their seleno analogs) result from the oxidation of an ylidylphosphine and also from the addition of ylides to a perthiophosphonic anhydride. They can be deprotonated and alkylated to give anions or cations, respectively. The reaction with phenacyl bromide opens a way to 1,3,2-oxathiaphosphole sulfides.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:433–437, 1998

The oxidation of secondary phosphines by a two-step addition of elemental sulfur has long been known [1,2]. The second step leads to dithiophosphinic acids. In fact, this reaction was used for the first recorded preparation of a dithiophosphinic acid more than a hundred years ago. In the reaction of triphenylphosphoniumbenzylidyl-*t*-butylphosphine **1** [3] with excess sulfur or selenium, the first step leading to the phosphine sulfide **2** and selenide **3** is complete within a few minutes, while the second step is slow enough to enable us to observe **2** and **3** in the reaction mixture. Their $^{31}$P-NMR spectra, as compared to that of **1**, are characterized by a sharp decrease of $^{2}J_{PP}$ [4] and an increase of $^{1}J_{PH}$ [5].




**1**

**2**: X = S
**3**: X = Se

**4**: $X_2 = S_2$
**5**: $X_2$ = S, Se
**6**: $X_2 = Se_2$

From the second step, besides the dithio and diseleno compounds **4** and **6,** the mixed compound **5** can also be obtained if selenium and sulfur are added successively. In these products, the hydrogen atom is shifted from P to C resulting in a zwitterionic structure. With the loss of ylide character, $^{2}J_{PP}$ becomes so small that it is no longer detected. In compound **6,** the chiral nature of the carbon atom is furthermore reflected by the observation of diastereotopic selenium atoms (Table 1).

Betaines of type **4** are also accessible by the addition of an ylide [6], such as **7–9**, to a perthiophosphonic anhydride [7,8], such as **10.** The products **11–13** correspond in their $^{31}$P-NMR spectra to **4.** In accord with their zwitterionic nature, they may be converted to an anion as shown in **14** by deprotonation or to a cation as in **18** by methylation.

Dedicated to Prof. Heinrich Nöth on the occasion of his seventieth birthday.

*Correspondence to:* Alfred Schmidpeter.

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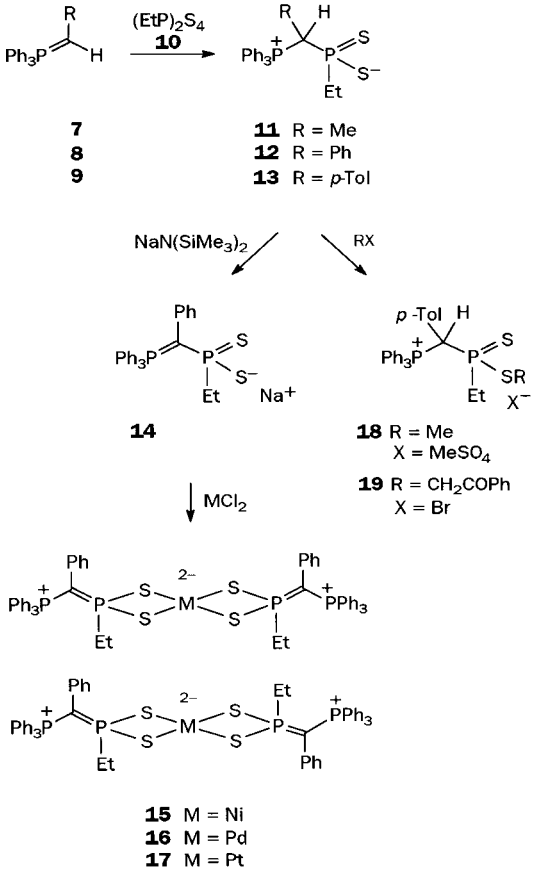
**TABLE 1** $^{31}$P NMR Data of 1-Phosphonioalkyl Thiophosphinite and Dithiophosphinate Derivatives and Some Seleno Analogs (in dichloromethane if not otherwise indicated); Coupling Constants *J* in Hz

| | *C-R* | *P-R* | *X* | $\delta(PPh_3)$ | $\delta(PX)$ | $^2J_{PP}$ | $^1J_{PH}$ | $^1J_{PSe}$ |
|---|---|---|---|---|---|---|---|---|
| **1** | Ph | *t*Bu | — | 21.5 | −33.2 | 154.9 | 207.1 | |
| **2** | Ph | *t*Bu | S | 18.8 | 43.3 | 40.5 | | |
| **3** | Ph | *t*Bu | Se | 18.2 | 25.3 | 36.3 | 427.7 | 644.7 |
| **11** | Me | Et | S | 26.3 | 97.3 | <1.5 | | |
| **12** | Ph | Et | S | 26.3 | 77.3 | <1.0 | | |
| **13** | *p*-Tol | Et | S | 26.5 | 78.0 | <1.0 | | |
| **4** | Ph | *t*Bu | S | 29.8 | 93.3 | <1.0 | | |
| **5**[a] | Ph | *t*Bu | S/Se | 29.0 | 81.8 | <1.0 | | 705.9 |
| **6** | Ph | *t*Bu | Se | 30.3 | 61.4 | <1.0 | | 636.3, 685.0[b] |
| **14** | Ph | Et | S | 16.6 | 66.6 | 49.8 | | |
| **15** | Ph | Et | S, Ni | 21.0 | 75.2 | 50.9 | | |
| | | | | 20.9 | 74.8 | 50.9 | | |
| **16** | Ph | Et | S, Pd | 21.1 | 95.7 | 47.7 | | |
| | | | | 21.1 | 94.1 | 46.7 | | |
| **17** | Ph | Et | S, Pt | 21.5 | 95.1 | 48.3 | | 303.1[c] |
| | | | | 21.5 | 93.0 | 46.7 | | 311.4[c] |
| **18** | *p*-Tol | Et | S | 24.9 | 81.5 | <2.0 | | |
| | | | | 24.3 | 80.7 | <2.0 | | |
| **19** | *p*-Tol | Et | S | 23.7 | 81.5 | <2.0 | | |
| | | | | 22.8 | 77.6 | <2.0 | | |
| **20** | *p*-Tol | Et | S | 20.5 | 76.4 | 54.5 | | |

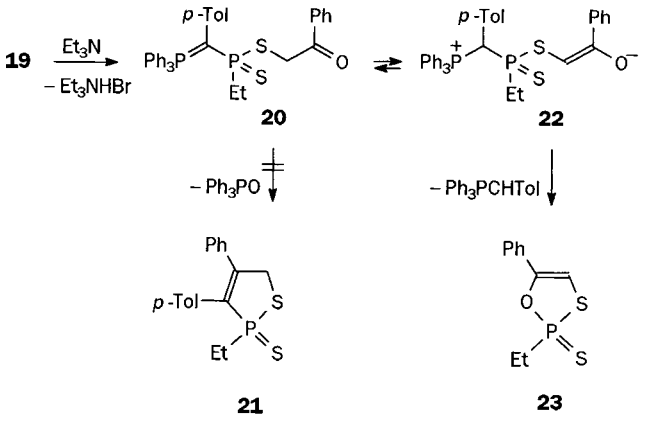
[a]In benzene.
[b]Two diastereomers; the one resulting in higher amount is given first.
[c]$^2J_{PtP}$




The ylide character of the anion of **14** becomes apparent in the large coupling $^2J_{PP}$ (Table 1). As it is well known for other dithiophosphinates [9], the anion forms chelates with $Ni^{2+}$, $Pd^{2+}$, and $Pt^{2+}$, which are obtained as mixtures of two diastereomers.

In the alkylation of **13,** the phosphorus atom becomes chiral and the products **18** and **19** consequently result as two diastereomers (in roughly equal amounts, Table 1). Phenacyl bromide was used for alkylation to give **19,** the precursor for a possible intramolecular Wittig reaction: Deprotonation of **19** could conceivably lead to the ylide **20** that, in a second step, could lose triphenylphosphine oxide to yield the 1,2-thiaphospholene sulfide **21.**

As a matter of fact, **19,** on the addition of triethylamine, underwent a clean decomposition into two phosphorus-containing products, with **20** as an observable intermediate (Table 1). The two products could be separated due to their high and low solubility in cyclohexane and identified as 4-methylbenzyl-triphenylphosphonium bromide and 2-ethyl-5-phenyl-1,3,2-oxathiaphosphole 2-sulfide **23** [10].




Thus, the ring closure is not initiated as expected via the nucleophilic attack of the ylidic carbon atom on the carbonyl group of **20** but probably starts from the enolic form **22** where an intramolecular substitution at the phosphorus atom, with the ylide **9** (R = **p**-Tol) as the leaving group, leads to **23** [11, 12]. The product is only made up from the perthiphosphonic anhydride **10** and phenacyl bromide. As the ylide **9** is not integrated into the product **23,** and in fact only acts as a base, a condensation of this type may perhaps be achieved by other bases as well.

## *EXPERIMENTAL*

All manipulations were carried out in flame-dried glassware under argon using the Schlenk technique. Dry dichloromethane, chloroform, and benzene were used as obtained (Fluka). Pentane was dried over molecular sieves (4 Å). Tetrahydrofuran was dried by refluxing with sodium/benzophenone and subsequent distillation. Melting points were determined in sealed capillaries—NMR: JEOL GSX 270 ($^{31}$P) and JEOL EX 400 ($^{1}$H, $^{13}$C) with $Me_4Si$ (int.) and 85% $H_3PO_4$ (ext.) as standards. The aromatic hydrogen atoms in *ortho, meta,* and *para* positions of *C*-Aryl are identified as 2,3,4-H, and those of $Ph_3P$, as *o,m,p*-H.

### *Reactions of* **1** *with Elemental Sulfur and Selenium*

The orange red solution of **1** (106 mg, 0.2 mmol) in 0.5 mL $CH_2Cl_2$, on addition of elemental sulfur (16 mg, 0.5 mmol), immediately turned yellow. The $^{31}$P-NMR spectrum, after 5 minutes, showed the signals of **2** and **4** (Table 1) in similar intensities, and after 30 minutes, only those of **4.**

After addition of gray selenium (62 mg, 0.8 mmol) to **1** (198 mg, 0.4 mmol) in 0.5 mL of $CH_2Cl_2$, a pale yellow solution formed. After 5 minutes, the $^{31}$P-NMR spectrum showed the signals (Table 1) of **3** (45%) and **6** (55%).

To a solution of **1** (127 mg, 0.3 mmol) in 0.5 mL $C_6H_6$, selenium (23 mg, 0.3 mmol), and after 10 minutes, sulfur (10 mg, 0.3 mmol) were added. After a further 30 minutes, the $^{31}$P-NMR spectrum showed the signals of **5** (Table 1) together with those of **4** in minor intensity.

### *Preparation of 1-Triphenylphosphonioalkyl-ethyl-dithiophosphinates* **11–13**

To a solution of the ylide **7** (7.18 g, 24.7 mmol) in 40 mL of tetrahydrofuran, the solution of ethylperthiophosphonic anhydride **10** (3.04 g, 12.2 mmol) was added dropwise. The adduct **11** immediately separated as a white precipitate ($^{31}$P-NMR data in Table 1).

In the same way, the ylide **8** (6.20 g, 17.6 mmol) and **10** (2.27 g, 9.1 mmol) gave colorless **12** · THF (8.87 g, 92%), mp 152–155°C. $^{1}$H NMR ($CDCl_3$): $\delta$ = 1.17 (dt, $^{3}J_{PH}$ = 22.1 Hz, $^{3}J_{HH}$ = 7.3 Hz, 3H, $CH_3$), 1.69–1.90 (m, 2H, $CH_2$), 1.82 (m, 4H, 3-H, THF), 3.71 (m, 4H, 2-H, THF), 5.17 (dd, $^{2}J_{PH}$ = 18.6 Hz, 12.3 Hz, 1H, CH), 6.94–7.22 (m, 3H, 3-H, 4-H), 7.43–7.49 (m, 6H, *m*-H), 7.58–7.65 (m, 3H, *p*-H), 7.75–7.81 (m, 8H, *o*-H, 2-H).

$^{13}$C{$^{1}$H} NMR ($CDCl_3$): $\delta$ = 7.4 (d, $^{2}J_{PC}$ = 4.0 Hz, $CH_3$), 25.6 (s, THF), 38.7 (dd, $^{1}J_{PC}$ = 59.5 Hz, $^{3}J_{PC}$ = 5.0 Hz, $CH_2$), 54.6 (dd, $^{1}J_{PC}$ = 43.9 Hz, 15.3 Hz, CH), 67.9 (s, THF), 120.1 (d, $^{1}J_{PC}$ = 85.8 Hz, *i*-C), 128.1 (broad, 4-C), 128.4 (t, $^{3}J_{PC}$ = 2.3 Hz, 2-C), 128.9 (d, $^{3}J_{PC}$ = 12.6 Hz, *m*-C), 131.1 (dd, $^{2}J_{PC}$ = 4.8 Hz, 3.4 Hz, 1-C), 132.4 (broad, 3-C), 133.9 (d, $^{4}J_{PC}$ = 3.1 Hz, *p*-C), 135.5 (d, $^{2}J_{PC}$ = 9.5 Hz, *o*-C). Anal. found: C, 66.99; H, 6.01; S, 12.49%; calcd. for $C_{31}H_{34}OP_2S_2$ (**12** · THF, 548.7): C, 67.86; H, 6.25; S, 11.69%.

In the same way, the ylide **9** (2.10 g, 6.26 mmol) and **10** (0.78 g, 3.13 mmol) gave **13** · THF (3.09 g, 88%). $^{1}$H NMR ($CDCl_3$): $\delta$ = 1.16 (dt, $^{3}J_{PH}$ = 21.9 Hz, $^{3}J_{HH}$ = 7.4 Hz, 3H, $CH_3$, Et), 1.77 (m, 2H, $CH_2$), 1.82 (m, 4H, 3-H, THF), 2.28 (s, 3H, $CH_3$, Tol), 3.71 (m, 4H, 2-H, THF), 5.15 (dd, $^{2}J_{PH}$ = 18.6, 12.6 Hz, 1H, CH), 6.91 (m, 4H, *o,m*-H), 7.46 (m, 6H, 1-H), 7.63 (m, 3H, 3-H), 7.79 (m, 6H, 2-H). Anal. found: C, 67.91; H, 6.08%; calcd. for $C_{32}H_{36}OP_2S_2$ (**13** · THF, 562.7): C, 68.30; H, 6.45%.

### *Preparation of* **14** *and Formation of Complexes* **15–17**

Compound **12** (4.50 g, 8.2 mmol) was added to a solution of $NaN(SiMe_3)_2$ (2.14 g, 11.7 mmol) in 40 mL of benzene, and the mixture was stirred for 3 days

at room temperature. Compound **14** resulted as yellow powder (3.41 g, 83%), mp 129–133°C. $^1$H NMR ($CD_2Cl_2$): $\delta$ = 1.10 (dt, $^3J_{PH}$ = 21.4 Hz, $^3J_{HH}$ = 7.3 Hz, 3H, $CH_3$), 1.91 (dq, $^2J_{PH}$ = 11.1 Hz, $^3J_{HH}$ = 7.3 Hz, 2H, $CH_2$), 6.76–6.89 (m, 3H, 2,4-H), 7.30–7.43 (m, 9H, *m,p*-H), 7.69–7.79 (m, 2H, 3-H), 7.81–7.86 (m, 6H, *o*-H).

$^{13}$C{$^1$H} NMR ($CD_2Cl_2$): $\delta$ = 7.8 (d, $^2J_{PC}$ = 4.6 Hz, $CH_3$), 22.0 (dd, $^1J_{PC}$ = 124.4 Hz, 84.7 Hz, C=$PPh_3$), 39.5 (d, $^1J_{PC}$ = 6.26 Hz, $CH_2$), 123.5 (s, broad, 2-C), 127.8 (d, $^3J_{PC}$ = 11.4 Hz, *m*-C), 128.4 (s, *p*-C), 128.7 (dd, $^1J_{PC}$ = 124.4 Hz, $^3J_{PC}$ = 13.0 Hz, *i*-C), 131.0 (s, 4-C), 134.5 (m, 3-C), 134.7 (d, $^2J_{PC}$ = 9.2 Hz, *o*-C), 135.6 (t, $^2J_{PC}$ = 8.4 Hz, 1-C). Anal. found: C, 58.50; H, 4.94; S, 10.74%; calcd. for $C_{27}H_{31}NaP_2S_2$ (**14** · $3H_2O$, 552.6): C, 58.68; H, 5.65; S, 11.61%.

A sample of **14** was dissolved in THF. Evaporation gave a dark yellow powder. Anal. found: C, 59.15; H, 6.00; S, 9.66%; calcd for $C_{31}H_{39}NaO_4P_2S_2$ (**14** · THF, 3 $H_2O$, 624.7): C, 59.60; H, 6.29; S, 10.27%.

A solution of **14** in $CH_2Cl_2$ was added each to $NiCl_2$, $PdCl_2$(cyclooctadiene) and to $PtCl_2(PhCN)_2$ in a 2:1 molar ratio. In the latter two cases, the solution immediately turned dark red, and the $^{31}$P-NMR spectrum (Table 1) indicated complete formation of **16** and **17.** With $NiCl_2$ after 1 day, **15** had formed only to 57% yield.

### *Methylation of* **13**

To a solution of **13** (61 mg, 0.1 mmol) in 0.5 mL of $CDCl_3$, dimethyl sulfate (19 mg, 0.15 mmol) was added. The NMR spectra recorded after 30 minutes showed the signals of the diastereomers **18** ($^{31}$P NMR: Table 1). $^1$H NMR ($CDCl_3$): $\delta$ = 0.86 (dt, $^3J_{PH}$ = 24.6 Hz, $^3J_{HH}$ = 7.3 Hz, 3H, $CH_3$, Et), 0.98 (dt, $^3J_{PH}$ = 24.7 Hz, $^3J_{HH}$ = 7.4 Hz, 3H, $CH_3$, Et), 1.68 (d, $^3J_{PH}$ = 14,8 Hz, *S*-$CH_3$), 1.99 (d, $^3J_{PH}$ = 15.0 Hz, 3H, *S*-$CH_3$), 2.05–2.45 (m, $CH_2$), 2.19 (s, 3H, $CH_3$, Tol), 2.20 (s, 3H, $CH_3$, Tol), 3.62 (s, 3H, $SO_4CH_3$), 6.40 (dd, $^2J_{PH}$ = 17.8, 14.1 Hz, 1H, CH), 6.51 (dd, $^2J_{PH}$ = 17.9, 14.2 Hz, 1H, CH), 7.01 (m, 4H, *o,m*-H), 7.53 (m, 6H, 1-H), 7.67 (m, 3H, 3-H), 7.85 (m, 6H, 2-H).

### *Preparation of* **19**

To a solution of **13** (339 mg, 0.61 mmol) in 5 mL of $CH_2Cl_2$ at 0°C, phenacyl bromide (199 mg, 0.61 mmol) in 2 mL of $CH_2Cl_2$ was added dropwise. After having been stirred for 30 minutes, the colorless solution was warmed to room temperature and reduced to one-third of its volume. After addition of cyclohexane, a white precipitate formed, which was filtered off, washed twice with 2 mL of cyclohexane, and dried in vacuo. The NMR spectra showed the signals of the diastereomers of **19** in similar intensity ($^{31}$P NMR: Table 1).

$^1$H NMR ($CD_2Cl_2$; the diastereomer resulting in slightly higher amount is given first; in each isomer, the *S*-$CH_2$ protons are diastereotopic): $\delta$ = 1.06 (dt, $^3J_{PH}$ = 25.1 Hz, $^3J_{HH}$ = 7.3 Hz, 3H, $CH_3$, Et), 0.96 (dt, $^3J_{PH}$ = 24.4 Hz, $^3J_{HH}$ = 7.3 Hz, 3H, $CH_3$, Et), 2.25 (s, 3H, $CH_3$, Tol), 2.32 (s, 3H, $CH_3$, Tol), 2.52–2.75 (m, both isomers 2H, $CH_2$, Et), 3.75 (dd, $^2J_{HH}$ = 16.5 Hz, $^3J_{PH}$ = 11.0 Hz, 1H, *S*-$CH_2$), 4.07 (dd, $^2J_{HH}$ = 16.5 Hz, $^3J_{PH}$ = 11.6 Hz, 1H, *S*-$CH_2$), 4.54 (dd, $^2J_{HH}$ = 17.1 Hz, $^3J_{PH}$ = 9.4 Hz, 1H, *S*-$CH_2$), 4.77 (dd, $^2J_{HH}$ = 17.1 Hz, $^3J_{PH}$ = 14.9 Hz, 1H, *S*-$CH_2$), 6.91–8.65 (m, both isomers 25H, aromatic H and CH). Anal. found: C, 62.14; H, 4.91%; calcd. for $C_{36}H_{35}BrOP_2S_2$ (689.7): C, 62.70; H, 5.12%.

### *Preparation of the 1,3,2-Oxathiaphosphole Sulfide* **23**

To a solution of **13** · THF (1.14 g, 2.03 mmol) in 10 mL of dichloromethane at 0°C, phenacyl bromide (0.41 g, 2.03 mmol) in 4 mL of dichloromethane was added dropwise. The NMR spectra recorded after 20 hours showed the signals of the diastereomers of **19** (Table 1). With the addition of $Et_3N$ (0.21 g, 2.03 mmol), the color of this solution immediately changed to yellow. After the mixture had been stirred for 2 days, the color of the solution faded, and all volatiles were removed in vacuo. The residue on extraction with 35 mL of cyclohexane left a white powder that was identified by $^1$H- and $^{31}$P-NMR spectroscopy as a mixture of 4-methylbenzyltriphenylphosphonium and triethylammonium salt (hydrobromides of **9** and triethylamine). From the filtrate, the solvent was removed in vacuo, and **23** was left as a soft crystalline mass.

$^1$H NMR ($C_6D_6$): $\delta$ = 7.29–6.96 (m, 5H, 2,3,4-H), 5.38 (d, 1H, $^3J_{PH}$ = 17.8 Hz), 2.00 (average of AB system, 2H, $^2J_{PH}$ = 14.9 Hz, $CH_2$; A: ddq, $^3J_{HH}$ = 7.5 Hz, $^2J_{PH}$ = 13.1 Hz; B: ddq, $^3J_{HH}$ = 7.5 Hz, $^2J_{PH}$ = 12.5 Hz), 1.34 (br, cyclohexane), 0.92 (dt, 3H, $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ = 25.2 Hz, $CH_3$).

$^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ = 149.3 (d, $^2J_{PC}$ = 3.8 Hz, C-5), 130.0 (d, $^3J_{PC}$ = 8.1 Hz, *i*-C), 128.6 (s, *o,m*-C), 124.4 (s, *p*-C), 97.6 (d, $^2J_{PC}$ = 1.9 Hz, C-4), 35.7 (d, $^1J_{PC}$ = 72.9 Hz, $CH_2$), 7.17 (d, $^2J_{PC}$ = 5.8 Hz, $CH_3$).

$^{13}$C NMR ($C_6D_6$): $\delta$ = 149.5 (ddq, $^2J_{CH}$ = 4.3 Hz, $^2J_{PC}$ = 4.0 Hz, $^3J_{CH}$ = 3.9 Hz, C-5), 130.2–127.5 (*i,o,m*-C), 124.7 (dm, $^1J_{CH}$ = 161.9 Hz, $^2J_{CH}$ = 6.4 Hz, $^3J_{CH}$ = 4.1 Hz, *p*-C), 97.9 (d, $^1J_{CH}$ = 188.0 Hz, C-4), 35.7 (dtq, $^1J_{PC}$ = 72.5 Hz, $^1J_{CH}$ = 131.2 Hz, $^2J_{CH}$ = 4.4 Hz, $CH_2$), 7.40 (dtq, $^1J_{CH}$ = 129.8 Hz, $^2J_{CH}$ = 4.5 Hz, $^2J_{PC}$ = 5.7 Hz, $CH_3$). $^{31}$P NMR ($CH_2Cl_2$): $\delta$ = 128.6.

Anal. found: C, 55.54; H, 5.86%; calcd. for $C_{10}H_{11}POS_2 \cdot 0.5\ C_6H_{12}$ (284.38): C, 54.91; H, 6.03%.

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[12] By a somewhat different mechanism, the reaction could give a 1,3,2-dithiaphosphole oxide in place of **23.** The two isomers are best distinguished by the chemical shifts of the two carbon ring members. These are found as $\delta$(C-4) = 98 and $\delta$(C-5) = 149 (see Experimental) and indicate a bonding to sulfur and oxygen, respectively. For comparison, the chemical shift of C-2 in thiophene is $\delta$ = 126, and in furan, $\delta$ = 144.