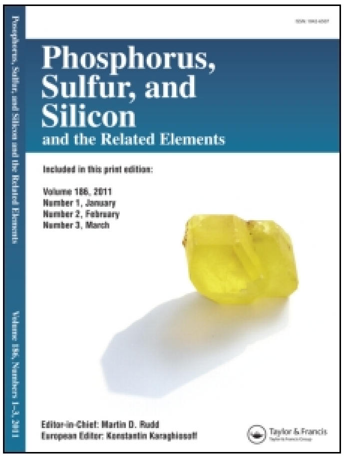

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# STUDIES ON ORGANOPHOSPHORUS COMPOUNDS. PART 52. THE REACTION OF BENZENESULFENYL CHLORIDE WITH 2,4-BIS (4-METHOXYPHENYL)-1,3,2,4-DITHIADIPHOSPHETANE 2,4-DISULFIDE

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# STUDIES ON ORGANOPHOSPHORUS COMPOUNDS. PART 52.* THE REACTION OF BENZENESULFENYL CHLORIDE WITH 2,4-BIS (4-METHOXY-PHENYL)-1,3,2,4-DITHIADIPHOSPHETANE 2,4-DISULFIDE

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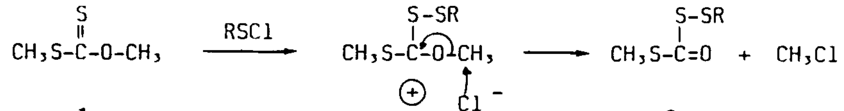
Benzenesulfenyl chloride, a soft electrophile, reacts with 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide (LR) on sulfur to give *S,S*-phenyl (4-methoxyphenyl) phosphonochloridothiolothionate (**3**) as an intermediate. Compound **3** reacts with nucleophiles as sodium alkoxides or amines to give good yields of *S,S*-phenyl *O*-alkyl(4-methoxyphenyl) phosphonothiolothionate (**4**) and *S,S*-phenyl (4-methoxyphenyl) phosphonopyrrolidinothiolothionate (**6**), respectively.

## INTRODUCTION

Benzenesulfenyl chloride reacts with thiocarbonyl compounds and *S,S*-acetals and gives after hydrolysis the corresponding carbonyl synthons.[1] Triphenylphosphine sulfide reacts similarly to give triphenylphosphine oxide.[1] Douglass and Evers[2] have shown that benzene and/or methanesulfenyl chloride reacts with *O,S*-dimethyl xanthate (**1**) by a mechanism which is an electrophilic attack at the thiocarbonyl sulfur atom to form 1-phenyl(methyl)-1,2,4-trithiapentanone-3 (**2**) and methyl chloride.



$$CH_3S\text{-}\overset{S}{\overset{\|}{C}}\text{-}O\text{-}CH_3 \xrightarrow{RSCl} CH_3S\text{-}\overset{S\text{-}SR}{\overset{|}{C}}\text{-}O\text{-}CH_3 \longrightarrow CH_3S\text{-}\overset{S\text{-}SR}{\overset{|}{C}}{=}O + CH_3Cl$$

**1** **2**

Also it is known that hard nucleophiles attack 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide, LR (Lawesson's Reagent) on phosphorous.[3] In continuation of our work on amines,[4,5] alchols,[6] thiols,[6] oximes[7] and their reactions with LR, we report now on the reaction of benzenesulfenyl chloride with LR.

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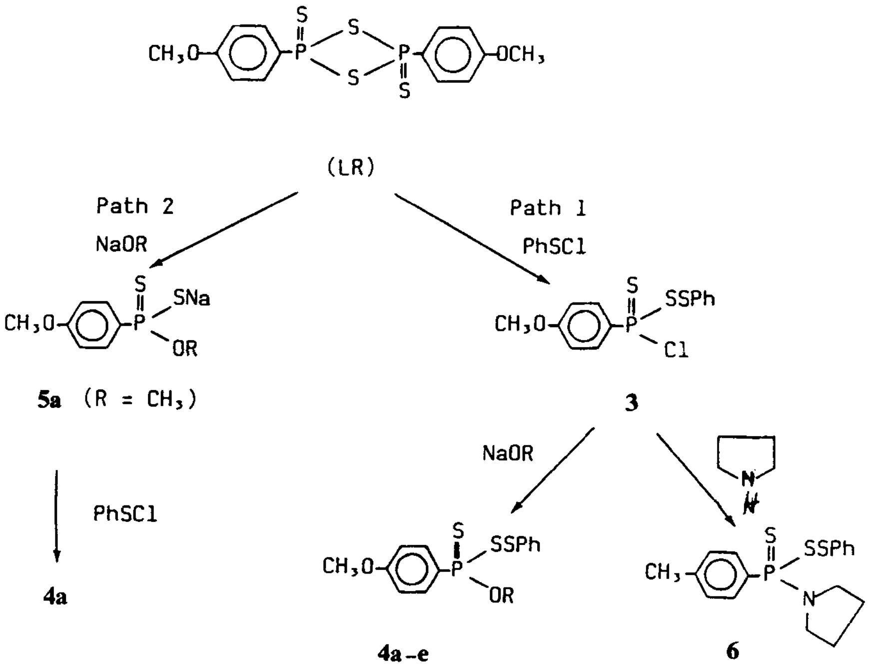
## RESULTS AND DISCUSSION

Benzenesulfenyl chloride reacts with LR in anhydrous benzene at 50°C to give *S,S*-phenyl (4-methoxyphenyl) phosphonochloridothiolothionate (**3**) which subsequently reacts with sodium alkoxides to give *S,S*-phenyl *O*-alkyl-(4-methoxyphenyl) phosphonothiolothionate (**4a–e**) after refluxing for 1 hr (Scheme 1, Table I) (Path 1).

The structure **4a–d** has been established by microanalyses, NMR ($^1H$, $^{13}C$, $^{31}P$) and precise mass measurements (Table I). In the $^1H$ NMR of **4a**, $POCH_3$ hydrogens appear as a doublet in the region 3.33–3.63 ppm with $^3J_{PH}$ 15–16 Hz (coupling to P), while the $CH_2$ hydrogens in **4b, c, e** appear as multiplet in the region 3.8–4.4 ppm and the $>CH$ hydrogen in **4d** as multiplet in the region of 4.5–5.1 ppm. The $^{31}P$ NMR spectra of **4a–e** show resonances in the region 88.37–90.30 in accordance with earlier findings.[8] The mass spectra of **4a–d** showed molecular ion ($M^+$), $M^+$–OR, [$M^+$–(OR + S)], $M^+$–SPh), and ($M^+$–SSPh) (Table I).

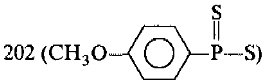
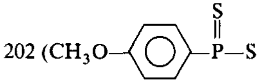
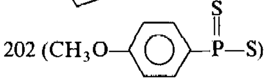


a, R = $CH_3$
b, R = $C_2H_5$
c, R = n-$C_3H_7$
d, R = i-$C_3H_7$
e, R = n-$C_4H_9$

SCHEME 1

TABLE I

NMR ($^1$H, $^{31}$P) and mass spectra of compounds **4a–e** and **6**

| Compound | $^1$H NMR (ppm) (CHCl$_3$) | $^{31}$P (ppm) | MS | Yield (%) |
|---|---|---|---|---|
| **4a** | 3.35 and 3.55 (d, 3 H, $J_{PH}$, 15 Hz, $p$-OCH$_3$), 3.75 (s, 3 H, OCH$_3$), 6.7 (dd, 2 H, $J_{PH}$, 4 Hz, $J_{HH}$, 9 Hz), 7.05 (m, 5 H, aromatic), 770 (dd, 2 H, $J_{PH}$ 15, $J_{HH}$ 9 Hz,-m-protons) | 90.30 | 342 (M$^+$), 311 (M$^+$-OCH$_3$), 289 [M$^+$–(OCH$_3$ + S)], 248 [M$^+$–(2-OCH$_3$ + S] 233 (M$^+$-SPh),<br>202  | 85 |
| **4b** | 1.2 (t, 3 H, CH$_3$), 3.7 (s, 3 H, OCH$_3$), 4.1 (m, 2 H, OC$\underline{H}_2$), the aromatic part as **4a** | 90.27 | 356 (M$^+$), 311 (M$^+$-OC$_2$H$_5$), 289 [M$^+$–(OC$_2$H$_5$ + S)], 247 (M$^+$–SPh), 215 (M$^+$-SSPh),<br>202  | 81 |
| **4c** | 0.8 (t, 3 H, —$\underline{CH_3}$), 1.6 (m, 2 H, $\underline{CH_2}$CH$_3$), 3.8 (s, 3 H, O$\underline{CH_3}$), 4.1 (m, 2 H, O$\underline{CH_2}$), then the same aromatic part as **4a** | 90.11 | 370 (M$^+$), 311 (M$^+$-OC$_3$H$_7$), 261 (M$^+$-SPh), 229 (M$^+$-SSPh) | 85 |
| **4d** | 1.3 (2d (6 H, CH$\langle^{\underline{CH_3}}_{\underline{CH_3}}$), 3.75 (s, 3 H, OCH$_3$) 4.9 (m, 1 H, —$\underline{C}$H$\langle$), then the aromatic part as **4a** | 88.27 | The same fragmentation pattern as **4c** | 84 |
| 4e | 0.85 (m, 3 H, $\underline{CH_3}$), 1.4 (m, 4 H, 2 $\underline{CH_2}$), 3.8 (s, 3 H, O$\overline{CH_3}$), 4.1 (m, 2 H, O $\overline{CH_2}$) and then the same aromatic part | 90.20 | 384 (M$^+$), 323 (M$^+$-OC$_4$H$_9$), 291 [M$^+$–(OC$_4$H$_9$ + S], 243 (M$^+$–SSPh) | 72 |
| **6** | 1.6–1.9 (m, 4 H, meta to N), 2.7–3.5 (m, 4 H ortho to N), 3.8 (s, 3 H, O$\underline{CH_3}$), and then the same aromatic part as in **4a** | 78.16 | 279 M$^+$–(N  + S), 241 (M$^+$–SSPh),<br>118, 202  | 69 |

*Notes*: 1. All the products are oils except **4d** which is solid with m.p. 65 °C.
2. Sufficiently correct microanalyses or precise mass measurements have been obtained for all the new products.

Compound **4a** has also been prepared by another route (Path 2) by reacting LR with sodium methoxide to give **5** which on subsequent reaction with benzenesulfenyl chloride produces **4a**, which in all respects (spectra, physical data) is identical with the product prepared by Path 1.

As to the formation of compound **4** (Path 1) it is suggested that the soft electrophile PhScl will attack LR on the soft sulfur to afford the intermediate **3**, which could not be isolated (it decomposes on attempting distillation or on silica gel column). Subsequent reaction of **3** with sodium alkoxides gave **4** in good overall yields.

Similarly, the intermediate **3** reacts with 2 moles of pyrrolidine to afford *S*,*S*-phenyl(4-methoxphenyl) phosphonopyrrolidinothiolothionate (**6**) in good yields.

Path 2 is an example of a hard nucleophile ($CH_3O^-Na^+$) attacking LR on the hard P to give **5**, which on subsequent reaction with benzene–sulfenyl chloride undergoes a soft-soft interaction to give **4**.

## EXPERIMENTAL

$^1$H NMR spectra were recorded at 60 MHz with a Varian EM-360 spectrometer. $^{13}$C NMR spectra were recorded at 20 MHz on a Varian CFT-20 spectrometer. $SiMe_4$ was used as internal standard and chemical shifts are expressed in $\delta$-values. $CDCl_3$ was used as a solvent. Mass spectra were recorded on a Micromass 7070F spectrometer operating at 70 eV using direct inlet.

*Starting Materials.* Compound **1** (LR) is commercially available now and can also be prepared as described earlier.[10] Benzenesulfenyl chloride was prepared according to a known procedure.[11]

*General Procedure for the Reaction of Benzenesulfenyl Chloride with LR.* 1.44 g of benzenesulfenyl chloride (0.01 mole) were added portionwise to a suspension of 2.02 g (0.005 mole) of LR in 25 ml anhydrous benzene under nitrogen at room temperature. The reaction mixture was heated in an oil bath at 50°C for 20 min, whereby the reaction mixture forms a clear solution. After cooling to room temperature, addition of 0.01 mole of sodium alkoxide and refluxing for 1 hr, the reaction mixture was poured into cold water. The water layer was extracted with ether (3 times). The combined extracts were washed with $NaHCO_3$ and dried with $MgSO_4$. The product was purified on silica gel column using a mixture of ether/light petroleum as eluent.

In the case of pyrrolidine 2 moles were used and the product was purified as above.

*Preparation of* **4a** *(Path 2).* To a suspension of 2.02 g (0.005 mole) of LR in benzene (25 ml) was added 0.01 mole of sodium methoxide (prepared by reacting 0.01 mole of Na in 5 ml methanol) and the reaction mixture was stirred at 50°C for 1/2 h whereby the reaction mixture becomes clear. Addition of 0.01 mole of benzenesulfenyl chloride portionwise at room temperature and heating for another 1 h at reflux temperature completed the reaction. (The reaction was followed by TLC). The reaction mixture is worked up as above.

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