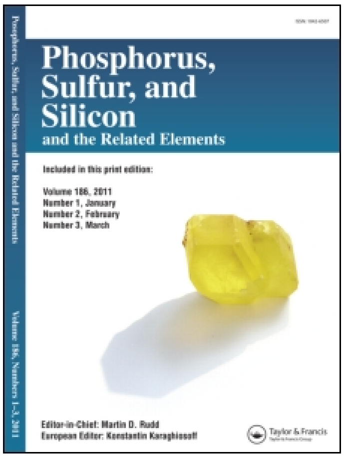

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Yousif, N. M. , Gadalla, K. Z. and Yassin, S. M.(1991) 'SYNTHESIS OF O,O-DIALKYL S-PHENYL PHOSPHOROTHIOLATES- AND DITHIOLATES', Phosphorus, Sulfur, and Silicon and the Related Elements, 60: 3, 261 — 263

To link to this Article: DOI: 10.1080/10426509108036789

URL: http://dx.doi.org/10.1080/10426509108036789

Phosphorus, Sulfur, and Silicon, 1991, Vol. 60, pp. 261–263

SYNTHESIS OF O,O-DIALKYL S-PHENYL PHOSPHOROTHIOLATES- AND DITHIOLATES

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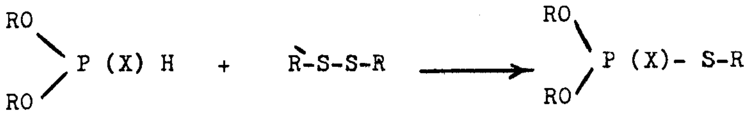
(Received June 1, 1990; in final form November 3, 1990)

Benzenesulfenyl chloride reacts with trialkylphosphite to give O,O-dialkyl S-phenyl phosphorothiolates **3** in high yield. Compounds **3** are thiated using 1,3-dithia 2,4-diphosphetane 2,4-disulfides **6** to produce O,O-dialkyl S-phenyl phosphorodithiolates **7** in nearly quantitative yield. Mechanistic consideration on the formation of the products are discussed.

Key words: Phosphorothiolates, dithiolates.

INTRODUCTION

O,O-Dialkyl S-phenyl phosphorothiolates- and dithiolates are of interest as effective pesticides and insecticides, and a variety of synthetic procedures have been investigated by the reaction of dialkyl phosphites **1** with sulfenyl chlorides,[1] disulfides,[2] sulfur,[3] and by other reactions.[4–8] We report here a new method for the preparation of O,O-dialkyl S-phenyl phosphorothiolates- and dithiolates.



1

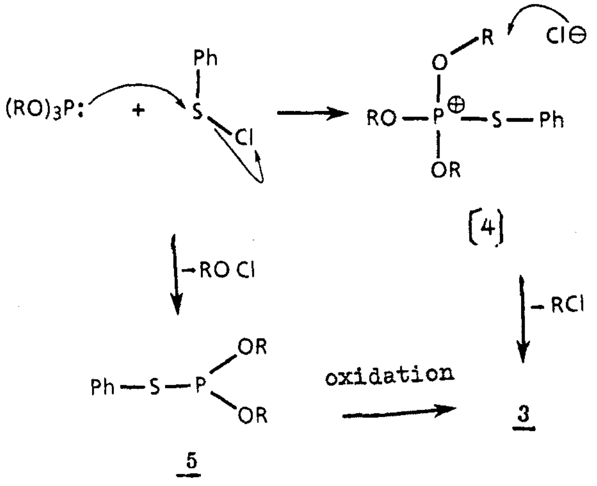
2, X = O
X = S

RESULTS AND DISCUSSION

Benzenesulfenyl chloride reacts with trialkyl phosphite in anhydrous benzene at 0°C to give O,O-dialkyl S-phenyl phosphorothiolates **3a, b** in high yield.

3a, $R= CH_3$
b, $R= C_2H_5$

Compounds **3a**, **b** are known and identified from microanalysis, and I R. ^{1}H NMR spectrum for compound **3a**, $POCH_3$ hydrogens appear as a doublet centered at 3.7 ppm ($^3J_{PH}$ = 12 Hz); and for compound **3b** $POCH_2$ hydrogens appear as a multiplets at 3.8–4.4 ppm. ^{13}C NMR ($CDCl_3$) for compound **3a** shows the methyl carbon at 54.2 ($^2J_{pc}$ = 8 Hz), C_4 at 126.1 ($^4J_{pc}$ = 7.4 Hz), C_2 at 129.2, C_3 at 129.4 and C_1 at 134.6 ($^2J_{pc}$ = 5 Hz). As to the formation of O,O-dialkyl S-phenyl phosphorothiolate **3** from compound **5** by oxidation,[9] it is suggested that electrophilic attack by the phosphorus of the trialkylphosphite on sulfur of the sulfenyl chloride either to form the phosphonium ion (**4**) or to give the intermediate **5**, which gets oxidized to the product **3** using ROCl.

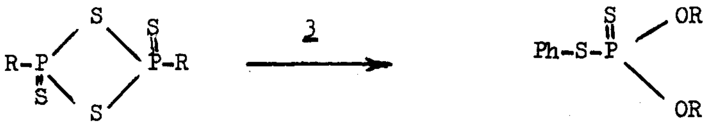


O,O-Dialkyl S-phenyl Phosphorothiolates **3a**, **b** reacted with 1,3-dithia-2,4-diphosphetane-2,4-disulfides **6a**, **b** to give O,O-dialkyl S-phenyl phosphorodithiolates **7a**, **b** in nearly quantitative yield (Table I).

TABLE I

Experimental data for the reaction of O,O-dialkyl S-phenyl phosphorothiolate **3** with **6a**, **b**

product	reagent	time h	temp. °C	yield %
7a	6a	2	140	92
7a	6b	3	80	90
7b	6a	3	140	93
7b	6b	4	80	89



6a, R= C_6H_4-OCH_3-p (LR) 7a, R= CH_3

b, R= -S-CH_3 b, R= C_2H_5

Compounds **7a**, **b** are known and identified from microanalysis and ^{1}H NMR. In the ^{1}H NMR for compound **7a**, $POCH_3$ hydrogens appear as a doublet in the region 3.4–3.7 ppm with $^3J_{PH}$ = 15–16 Hz (coupling to P).

EXPERIMENTAL

^{1}H NMR spectra are recorded at 60 MHz on a varian A-60 spectrometer. ^{13}C NMR spectra are recorded at 20 MHz on a varian CFT-20 spectrometer. TMS is used as internal standered, and chemical shifts are expressed in δ values.

Starting Material. Benzensulfenyl chloride is prepared according to a known procedure.[10] Compounds **6a**, **b** can be prepared as described earlier.[11,12]

General procedure for the reaction of benzenesulfenyl chloride with trialkylphosphite. 1.44 g of benzenesulfenyl chloride (0.01 mol) is added portionwise to 0.01 mol of trialkylphosphite in 10 ml dry benzene at 0°C with stirring. The reaction mixture is left at 0°C for one hour and then at room temperature for another one hour. Compounds **3a**, **b** are isolated by distillation under reduced pressure as follow: **3a** (0.18 m Hg) at 106–125°C (yield = 80%); **3b** (0.2 m Hg) at 120–135°C (yield = 94%).

General procedure for the synthesis of O,O-dialkyl S-phenyl phosphorodithiolates **7a**, **b**. A mixture of compound **6a**, **b** (0.01 mol) in 10 ml xylene or benzene and 0.01 mol of O,O-dialkyl S-phenyl phosphorothiolate **3a**, **b** are heated under reflux. The solvent is stripped off and the residue is placed on a silica gel column. Compounds **7a**, **b** are eluted with dichloromethane/P.E. (1:4) (Table I).

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