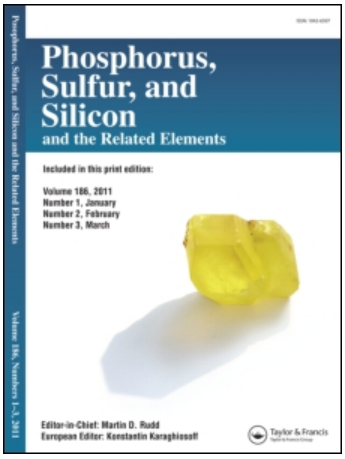

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Shabana, R.(1987) 'STUDIES ON ORGANOPHOSPHORUS COMPOUNDS. PART VI.† THE REACTION OF ALKOXIDES WITH 2,4-BIS(4-METHOXYPHENYL)-1,3,2,4-DITHIADIPHOSPHETANE 2,4-DISULFIDE (LR). A NEW APPROACH FOR THIO-INEZIN', Phosphorus, Sulfur, and Silicon and the Related Elements, 29: 2, 293 — 296
To link to this Article: DOI: 10.1080/03086648708080516
URL: http://dx.doi.org/10.1080/03086648708080516

Phosphorus and Sulfur, 1987, Vol. 29, pp. 293-296
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STUDIES ON ORGANOPHOSPHORUS COMPOUNDS. PART VI.† THE REACTION OF ALKOXIDES WITH 2,4-BIS(4-METHOXYPHENYL)-1,3,2,4-DITHIADIPHOSPHETANE 2,4-DISULFIDE (LR). A NEW APPROACH FOR THIO-INEZIN.

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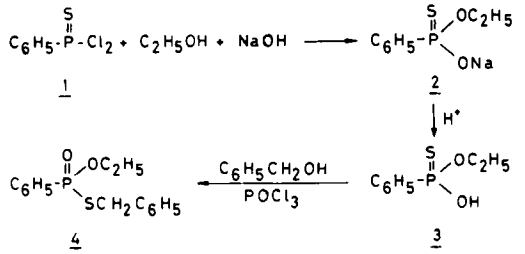
(This paper is dedicated to the memory of the late Prof. Dr. S.-O. Lawesson, Chemistry Department, University of Aarhus, Denmark).

(*Received February 17, 1986; in final form May 5, 1986*)

Sodium alkoxide, a hard nucleophile, reacts with 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide (LR) on phosphorus to give O-alkyl S-sodium-(4-methoxyphenyl) phosphonothiolothionate **5** as an intermediate. Compound **5** reacts with benzyl (or benzoyl) chloride to give good yields of O-alkyl S-benzyl (benzoyl) (4-methoxy-phenyl)phosphonothiolothionate (**6a–e**).

INTRODUCTION

Almost all industrial phosphorus-containing fungicides which are being manufactured in Japan belong to the group of phosphorothiolic and phosphorodithiolic acids[1] as e.g. O,O-diethyl S-benzyl phosphorothiolate (Kitazin), O,O-diisopropyl S-benzyl phosphorothioate (Kitazin *p*) and O-ethyl S-benzyl phenylphosphonothioate (Inezin) (review 2). In the manufacture of inezin,[3–5] the dichloride of phenylphosphonothioic acid, **1**, is treated with NaOH in alcohol to give **2**, which on acidification affords **3**, Treatment of **3** with benzyl alcohol in presence of phosphoryl chloride gives inezin **4**. **4** can also be prepared by high temperature S-benzylation of O,O-diethyl phenylphosphonothioate by Pishchimuka's



† For part V, R. Shabana, M. T. M. El-Wassimy and A. B. A. G. Ghattas Chemistry & Industry, 140 (1986).

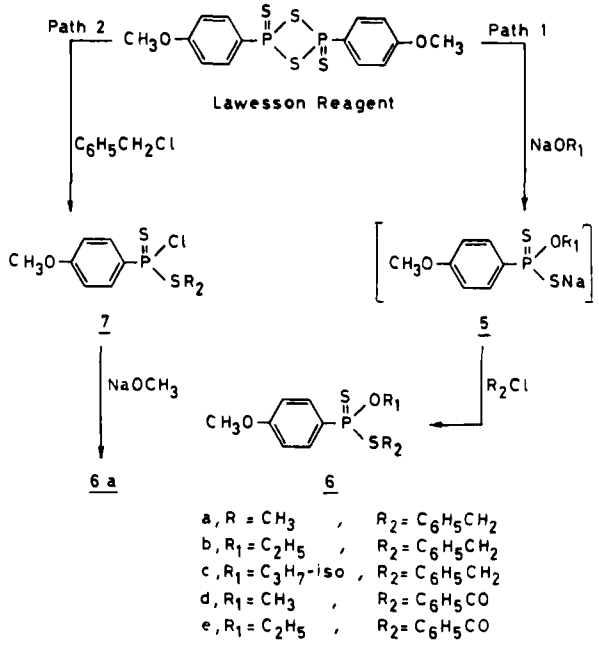
method.[6] Also it is known that hard nucleophiles attack 2,4-bis (4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide, LR, (Lawesson's Reagent) on phosphorus.[7] In continuation of our work on amines,[8,9] alcohols,[10] thiols,[10] oximes[11] and benzene sulfenyl chloride[12] (soft electrophile), we report now on the reaction of alkoxides with LR and subsequently with benzyl chloride to give thio-inezin. This is a versatile method for the preparation of this class of compounds.

RESULTS AND DISCUSSION

LR reacts with sodium alkoxide like other $(RPS_2)_2$-compounds[13] (for a review see reference 14) in anhydrous benzene at 80°C to give O-alkyl S-sodium (4-methoxyphenyl)phosphonothiolothionate (5), which subsequently react with benzyl (benzoyl) chloride to give O-alkyl S-benzyl (benzoyl) (4-methoxyphenyl)phosphonothiolothionate (**6a–e**) after refluxing for 1 hr. (Scheme 1, path 1). The structure of **6a–e** has been established by microanalyses, NMR (^1H, ^{13}C, ^{31}P) and precise mass measurements (see Table I).

Compound **6a** has also been prepared by another route (path 2)[14,15] by reacting LR with benzyl chloride to give **7**, which on subsequent reaction with sodium methoxide produces **6a**, which in all respects (spectra, physical data) is identical with the product prepared by path 1.

As to the formation of compound 6 (path 1) it is suggested that the hard nucleophile (NaOR) will attack LR on phosphorus to afford the intermediate 5



a, $R = CH_3$, $R_2 = C_6H_5CH_2$
b, $R_1 = C_2H_5$, $R_2 = C_6H_5CH_2$
c, $R_1 = C_3H_7$-iso , $R_2 = C_6H_5CH_2$
d, $R_1 = CH_3$, $R_2 = C_6H_5CO$
e, $R_1 = C_2H_5$, $R_2 = C_6H_5CO$

Scheme 1

TABLE I

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

Compound	^1H NMR (ppm) ($CDCl_3$)	^{31}P	MS	Yield
6a	3.40 and 3.70 (d, 3H, J_{PH} 15 Hz P-OCH_3), 3.75 (s, O$\underline{CH_3}$), 3.70 and 3.90 (d, 2H, J_{PH} 15 Hz, P-S$\underline{CH_2}$) 6.70–6.90 (d, 2H, J_{PH} 4 Hz, J_{HH} 9 Hz aromatic P-), 7.10 (s, 5H, aromatic) 7.50–8.00 (dd, 2H, J_{PH} 15 Hz, J_{HH} 9 Hz, m-protons)	97.68	324 (M^+), 232 M^+-(CH_3 + Ph) 202 ($\frac{1}{2}$ LR), 170 (M^+-(SCH_2Ph + OCH_3) 139 (M^+-(SCH_2Ph + 2OCH_3)	85
6b	1.05–1.35 (3H, t, $OCH_2\underline{CH_3}$), 3.75 (s, 3H, OCH_3), 3.85–4.00 (d, 2H, S$\underline{CH_2}$), 3.80–4.20 (q, 2H, $\underline{CH_2}CH_3$) and then the same aromatic part.	94.79	338 (M^+), 246 (M^+-CH_2Ph) 215 (M^+-SCH_2Ph) 186 (M^+-(SCH_2Ph + C_2H_5) 170 (M^+-(SCH_2Ph + OC_2H_5) 139 (M^+-(SCH_2Ph + 2 OC_2H_5)	90
6c	L.20–1.40 (d, 6H, $CH\langle^{CH_3}_{CH_3}$), 3.75 (s, 3H, OCH_3), 3.75–4.05 (d, 2H, SCH_2), 4.50–5.20 (m, 1H, $\underline{CH}$) and then the same aromatic part.	93.13	352 (M^+), 187 M^+-(SCH_2Ph + C_3H_7) 155 (M^+-(SCH_2Ph + C_3H_7 + OCH_3) 139 M^+-(SCH_2Ph + OC_3H_7 + OCH_3)	78
6d	3.80 (s, 3H, OCH_3), 3.80–3.95 (d, 3H, P-OCH_3), 6.70–8.20 the aromatic protons	88.12	338 (M^+), 202 ($\frac{1}{2}$ LR) 139 (M^+-SCOPh + 2 OCH_3)	75
6e	1.15–1.45 (t, 3H, OCH_2CH_3), 3.80 (s, 3H, OCH_3) 4.00–4.50 (m, 2H, OCH_2CH_3), 6.70–8.20 the aromatic part as multiplets.	84.90	352 (M^+), 215 (M^+-SCOPh) 199 M^+-(SCOPh + CH_3), 187 M^+-(SCOPh + C_2H_5) 139 M^+-(SCOPh + OC_2H_5 + OCH_3)	82

Notes: 1—All the products are oils. 2—Sufficiently correct microanalyses or precise mass measurements have been obtained for all the products.

which could not be isolated. Subsequent reaction of 5 with benzyl (benzoyl) chloride gave 6 in good overall yields.

EXPERIMENTAL

^1H NMR spectra were recorded at 60 MHz with a Varian EM-360 spectrometer. ^{13}C NMR spectra were recorded at 20 MHz on Varian CFT-20 spectrometer. $SiMe_4$ was used as internal standard and chemical shifts are expressed in δ-values. $CDCl_3$ was used as a solvent. Mass spectra were recorded on a Micromass 7070 f Spectrometer operating at 70 ev using direct inlet. Microanalyses were carried out by Lovens Kemiske Fabrik, DK-2750, Ballerup (Microanalytical lab.)

Starting Materials: Compound 1 (LR) is commercially available now and can also be prepared as described earlier.[16]

General Procedure for the Reaction of LR with Sodium Alkoxide (*Path* 1): 2.02 gr of Lawesson Reagent (0.005 mole) were suspended in dry benzene (25 ml) and 0.01 mole of sodium alkoxide (prepared by reacting 0.23 gr Na with 6 ml absolute alcohol) was added at room temperature, and then the reaction mixture was heated under reflux for 15 min. whereby a clear solution was obtained. After addition of 0.01 mole of benzyl chloride (or benzoyl chloride) the reaction mixture was heated for one hr. at reflux, cooled, poured into cold H_2O and extracted with ether three times. The combined extracts were purified on a Silica gel column (type 60 Merck) using 50% ether-light petroleum as an eluent.

Preparation of 6*a* (*Path* 2): To a suspension of LR (0.005 mole) in benzene was added 0.01 mole of benzyl chloride and the reaction mixture was heated in an oil bath for 20 minutes at 50°C whereby the reaction mixture became a clear solution. After cooling to room temperature 0.01 mole of sodium methoxide was added and then the mixture refluxed for one hr. The product was purified as above to give compound **6a** (comparative IR, NMR and Ms).

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