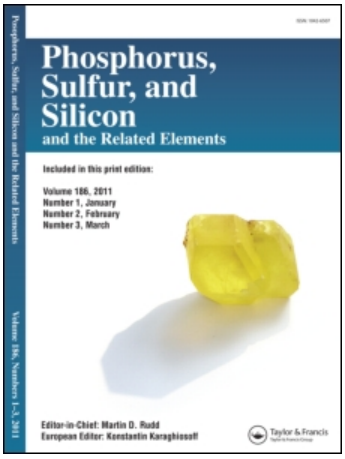

Phosphorus, Sulfur, and Silicon and the Related Elements

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 Robert, D. , Curci, M. , Chantar, H. , Seddiki, Es. , Born, M. , Mieloszynski, J. L. and Paquer, D.(1994) 'Synthesis of Phospho-Sulfurated Compounds Derived from Sulfurated Alcohols', Phosphorus, Sulfur, and Silicon and the Related Elements, 89: 1, 145 — 150
To link to this Article: DOI: 10.1080/10426509408020443
URL: http://dx.doi.org/10.1080/10426509408020443

Phosphorus, Sulfur, and Silicon, 1994, Vol. 89, pp. 145–150
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SYNTHESIS OF PHOSPHO-SULFURATED COMPOUNDS DERIVED FROM SULFURATED ALCOHOLS

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(Received February 22, 1994; in final form March 21, 1994)

Preparation of sulfurated phosphoro-compounds are presented; ^{13}C and ^{31}P chemical shifts of these compounds have been recorded.

Key words: Sulfide; phosphodithioic acids; phosphates; ^{1}H NMR; ^{13}C NMR; ^{31}P NMR.

INTRODUCTION

We have recently reported our results concerning the synthesis of sulfurated compounds.[1] In that report we propose the use of these compounds for the synthesis of particular O,O-dialkyldithiophosphoric acids $(RO)_2$—P(S)—SH, (thio)phosphoryl chlorides $(RO)_2$—P(Y)—Cl(Y = O, S) and phosphates $(RO)_3$—P(O) in which R contains at least one sulfur atom.[2]

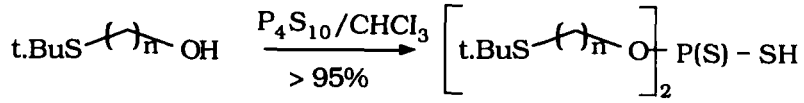
The first two types of products can be used to obtain other phosphorylated derivatives, especially zinc derivatives.

The products mentioned in this report are new. Some of the intermediates have obtained a registry number.[3]

RESULTS

1) Synthesis of Dithiophosphoric Acids

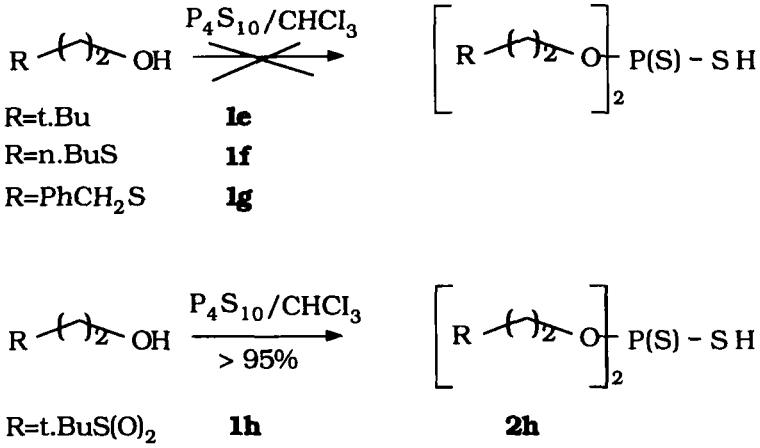
The synthesis of dithiophosphoric acids is well documented.[4–7] It consists in reacting an alcohol with P_4S_{10} together or without a solvent. The temperature depends on the alcohol and varies from 60°C up to 120°C (to prevent decomposition of the acid, elevated temperatures are avoided). The same reaction applied to the sulfurated alcohols[1] [t.Bu—S—$(CH_2)_n$—OH] with n = 2–6 leads to two results. First when n = 3, 5, 6 the reaction is effective and the corresponding dithiophophoric acids are obtained (yield = 95%) (Scheme I):



n = 3	**1a**	**2a**
n = 4	**1b**	**2b**
n = 5	**1c**	**2c**
n = 6	**1d**	**2d**

SCHEME I

However, with n = 2 another reaction takes place and the acid can't be isolated. Consequently we have replaced the t-butyl group by various alkyl groups. Alcohols **1e–g** gave the same result whereas alcohol **1h** gave the desired acid (yield = 90%) (Scheme II):

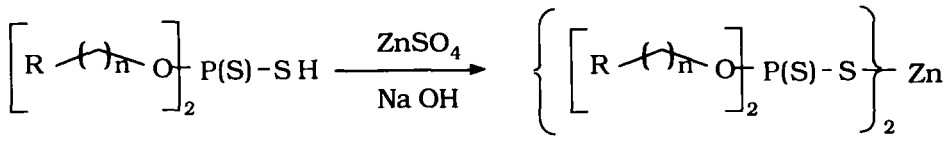


SCHEME II

Thus, when n is higher than 2 the **1a–d** alcohols act like normal alcohols, leading to the corresponding dithiophosphoric acids. On the other hand, with n = 2, the free electron doublet of the sulfur atom intervenes leading to a complex mixture, which is confirmed by making P_4S_{10} to react with the sulfone **1h**. In this case, the reaction leads to the dithiophosphoric acid **2h**.

2) Synthesis of Zinc Derivatives

Zinc dialkyldithiophosphates are well known for their extreme-pressure, anti-wear and anti-oxydation properties.[5,8-12] They are easily obtained by reacting the corresponding dithiophosphoric acid with zinc sulfate in the presence of an aquous base[13] as shown below (Scheme III):



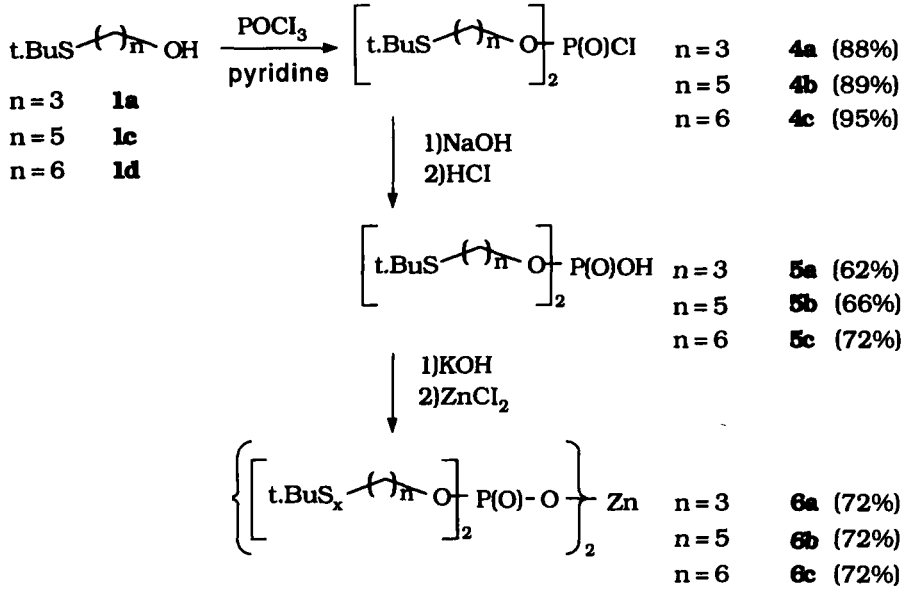
R=t. BuS	n = 3	**2a**	**3a**	(60%)
R=t. BuS	n = 5	**2b**	**3b**	(73%)
R=t. BuS	n = 6	**2c**	**3c**	(80%)

SCHEME III

3) Synthesis of Zinc Dialkylphosphates

These compounds have received little attention and few papers appeared in literature compared to the zinc dialkyldithiophosphates. Nevertheless, Dorinson[14] had synthetized the zinc di-n.butylphosphate and shown that it exhibited similar additive properties than the corresponding dithiophosphate.

The reaction proceeds in three steps. First the phosphorylchlorides **4a–c** are obtained from sulfurated alcohols and phosphorus oxychloride in the presence of pyridine. Then these derivatives are hydrolysed with successive basic and acidic treatment leading to compounds **5a–c**. Finally the corresponding potassium salt, treated with zinc dichloride, furnished the zinc dialkylphosphates **6a–c** (Scheme IV):

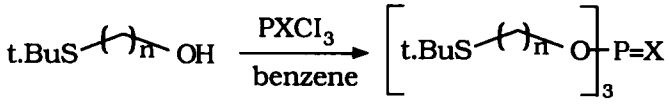


SCHEME IV

4) Synthesis of (Thio)phosphates

These compounds are frequently used in lubricants due to their good additive properties.[15–17] So we have envisaged to enhance the latters by incorporating a

sulfur atom in the alkyl groups. These compounds are accessible by reacting sulfurated alcohols with phosphorus oxychloride or thiochloride (Scheme V):



n = 3 **1a**
n = 6 **1d**

X = O n = 3 **7a** (67%)
n = 6 **7b** (40%)
X = S n = 3 **7c** (50%)

SCHEME V

In this reaction the formation of pyrophosphates (easily separated on silica chromatography), detected at −31 ppm in ^{31}P NMR, always occurs contributing to a loss of yield.

EXPERIMENTAL

^{13}C NMR and ^{1}H NMR spectra were recorded on a BRUKER AM-400 spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal standard. ^{31}P NMR spectra were recorded on a BRUCKER AM-400 spectrometer in $CDCl_3$ using H_3PO_4 as external standard.

For the attribution of various carbons we used a spin echo and/or a polarization transfer. All the compounds presented have not been analysed by ^{13}C NMR. Those that were analysed are presented in tables. Chemical shifts are in ppm units (abbreviations: s (singulet), d (doublet), t (triplet), m (multiplet). The presence and position of OH function are checked after a D_2O treatment. For that function the signal obtained is often of "a wide singulet" type.

Liquid products are not distilled. Effectively, a decomposition can appear during this procedure.

Preparation of dithiophosphoric acids (**2a–d, 2h**): To a solution of $CHCl_3$ (40 ml) and sulfurated alcohol (8 mmoles), P_4S_{10} (2 mmoles) is added portionwise at 60°C. The mixture is stirred at this temperature for 1 hour and then cooled. The solvent is evaporated under reduced pressure and a yellow liquid is obtained. The crude yields are quantitative: the compound is utilized without purification for the next steps.

Compound (**2a**). ^{31}P NMR: 85.9. ^{1}H NMR: ∂ = 4.2 (m, CH_2O); 2.6 (t, CH_2S); 2.0 (m, CH_2); 3.4 (s, SH); 1.3 (s, CH_3). ^{13}C NMR: ∂ = 66.5 (d, J_{CP} = 6.1, C—O); 42.1 (C of t.Bu); 30.9 (CH_3 of t.Bu); 30.2 (d, J_{CP} = 8.5, CH_2); 24.3 (C—S).

Compound (**2b**). ^{31}P NMR: 85.6. ^{1}H NMR: ∂ = 4.2 (m, CH_2O); 2.6 (t, CH_2S); 1.7 (m, CH_2); 3.1 (s, SH); 1.3 (s, CH_3). ^{13}C NMR: ∂ = 67.1 (d, J_{CP} = 6.0, C—O); 41.8 (C of t.Bu); 30.9 (CH_3 of t.Bu); 31.6 (CH_2); 27.6 (CH_2); 25.8 (C—S).

Compound (**2c**). ^{31}P NMR: 85.6. ^{1}H NMR: ∂ = 4.2 (m, CH_2O); 2.6 (m, CH_2S); 1.5 (m, CH_2); 3.6 (s, SH); 1.3 (s, CH_3). ^{13}C NMR: ∂ = 67.9 (d, J_{CP} = 6.0, C—O); 41.7 (C of t.Bu); 30.9 (CH_3 of t.Bu); 29.6 (CH_2); 29.2 (CH_2); 27.9 (CH_2); 25.0 (C—S).

Compound (**2d**). ^{31}P NMR: 85.6 ^{1}H NMR: ∂ = 4.2 (m, CH_2O); 2.5 (m, CH_2S); 1.5 (m, CH_2); 2.8 (s, SH); 1.3 (s, CH_3). ^{13}C NMR: ∂ = 68.0 (d, J_{CP} = 6.1, C—O); 41.6 (C of t.Bu); 30.9 (CH_3 of t.Bu); 29.8 (CH_2); 29.5 (CH_2); 28.5 (CH_2); 28.0 (CH_2); 25.1 (C—S).

Compound (**2h**). ^{31}P NMR: 86.9. ^{1}H NMR: ∂ = 4.6 (m, CH_2O); 3.4 (t, CH_2S); 3.0 (s, SH); 1.4 (s, CH_3). ^{13}C NMR: ∂ = 66.0 (d, J_{CP} = 6.5, C—O); 48.0 (C of t.Bu); 39.3 (d, J_{CP} = 6.2, C—S); 29.8 (CH_3 of t.Bu).

Preparation of zinc dialkyldithiophosphates (**3a–c**): To a solution of NaOH (7 mmoles) and water (10 ml) is added dithiophosphoric acid (6 mmoles). The mixture is stirred at 40°C for 30 minutes; then zinc sulfate (3.3 mmoles) dissolved in water (10 ml) is added. Vigorous stirring is continued for 30 minutes. After extraction (chloroform) and elimination of the solvent a viscous soil is isolated.

Compound (**3a**). ^{31}P NMR: 97.9. ^{1}H NMR: ∂ = 4.1 (m, CH_2O); 2.6 (m, CH_2S); 1.9 (m, CH_2); 1.3 (s, CH_3). ^{13}C NMR: ∂ = 66.8 (d, J_{CP} = 6.0, C—O); 42.2 (C of t.Bu); 31.0 (CH_3 of t.Bu); 30.5 (d, J_{CP} = 8.1, CH_2); 24.6 (C—S).

Anal.: Calcd. C: 39.81; H: 7.16; S: 30.37; P: 7.33; Zn: 7.74
Found: C: 37.57; H: 6.93; S:28.65; P: 6.75; Zn: 8.61

Compound (**3b**). ^{31} NMR: 98.1. ^{1}H NMR: ∂ = 4.1 (m, CH_2O); 2.5 (m, CH_2S); 1.5 (m, CH_2); 1.3 (s, CH_3). ^{13}C NMR: ∂ = 68.0 (d, J_{CP} = 6.0, C—O); 41.6 (C of t.Bu); 31.0 (CH_3 of t.Bu); 29.8 (CH_2); 29.4 (CH_2); 28.1 (CH_2); 25.1 (C—S).

Compound (**3c**). ^{31}P NMR: 98.1. ^{1}H NMR: ∂ = 4.0 (m, CH_2O); 2.5 (m, CH_2S); 1.5 (m, CH_2); 1.3 (s, CH_3). ^{13}C NMR: ∂ = 66.1 (d, J_{CP} = 6.0, C—O); 41.4 (C of t.Bu); 30.7 (CH_3 of t.Bu); 29.7 (CH_2); 29.4 (CH_2); 28.4 (CH_2); 27.9 (CH_2); 24.9 (C—S).

Preparation of zinc dialkylphosphates (**6a–c**). To phosphorus oxychloride (13 mmoles) in benzene (10 ml) is added dropwise a mixture of the corresponding alcohol (26 mmoles) and pyridine (26 mmoles) in benzene (10 ml). The solution is stirred at 20°C for one hour, then filtered. Standard work-up gave a yellow syrup which is utilized without further purification.

To a solution of the precedent phosphoryl chloride (10 mmoles) is added 2N NaOH (12 mmoles). The mixture, after stirring for 30 minutes, is washed with hexane and the aquous layer is acidified with 2N HCl, then extracted with hexane. The organic phase is washed, dried over Na_2SO_4 and the solvent evaporated under reduce pressure. The yellow oil is utilized without further purification.

To the precedent dialkylphosphate (6.6 mmoles) is added KOH (6.6 mmoles) dissolved in methanol (10 ml). Stirring is continued 30 minutes and a solution of $ZnCl_2$ (6.6 mmoles) in water (5 ml) is added dropwise. The mixture is stirred one hour and extracted with Et_2O. The organic phase is separated, washed with water and dried over Na_2SO_4. The solvent is evaporated and a white syrup is isolated.

For these kinds of compounds, the ^{31}P NMR is the only way to identify them.

Compound (**5a**). ^{31}P NMR: 1.0. ^{1}H NMR: ∂ = 7.3 (s, OH); 4.1 (m, CH_2O); 2.6 (m, CH_2S); 1.9 (m, CH_2); 1.3 (s, CH_3).

Compound (**5b**). ^{31}P NMR: 1.0. ^{1}H NMR: ∂ = 7.1 (s, OH); 4.1 (m, CH_2O); 2.5 (m, CH_2S); 1.6 (m, CH_2); 1.3 (s, CH_3).

Compound (**5c**). ^{31}P NMR: 1.2. ^{1}H NMR: ∂ = 7.1 (s, OH); 4.1 (m, CH_2O); 2.5 (m, CH_2S); 1.6 (m, CH_2); 1.4 (m, CH_2); 1.3 (s, CH_3).

Compound (**6a**). ^{31}P NMR: −1.1. ^{1}H NMR: ∂ = 4.0 (m, CH_2O); 2.6 (m, CH_2S); 1.8 (m, CH_2); 1.3 (s, CH_3).

Compound (**6b**). ^{31}P NMR: −1.5. ^{1}H NMR: ∂ = 3.9 (m, CH_2O); 2.5 (m, CH_2S); 1.6 (m, CH_2); 1.3 (s, CH_3).

Compound (**6c**). ^{31}P NMR: −1.8. ^{1}H NMR: ∂ = 3.9 (m, CH_2O); 2.5 (m, CH_2S); 1.6 (m, CH_2); 1.4 (m, CH_2); 1.3 (s, CH_3).

Preparation of trialkyl(thio)phosphates (**7a–c**). To phosphorus oxychloride or thiochloride (13 mmoles) in benzene (10 ml) is added dropwise a mixture of the corresponding alcohol (26 mmoles) and pyridine (26 mmoles) in benzene (10 ml). The solution is stirred at 5°C for 15 minutes, then refluxed 2 hours. After cooling the mixture is filtered and the organic phase is washed and dried over magnesium sulfate. The solvent is removed under reduced pressure and a yellow liquid is isolated.

For these kinds of compounds, the ^{31}P NMR is the only way to identify them.

Note: pyrophosphates (15%) are obtained as impurities and characterised in ^{31}P NMR (−13.0 ppm).

Compound (**7a**). ^{31}P NMR: −1.0. ^{1}H NMR: ∂ = 4.1 (m, CH_2O); 2.6 (m, CH_2S); 1.9 (m, CH_2); 1.3 (s, CH_3).

Compound (**7b**). ^{31}P NMR: −0.8. ^{1}H NMR: ∂ = 4.1 (m, CH_2O); 2.5 (m, CH_2S); 1.5 (m, CH_2); 1.4 (m, CH_2); 1.3 (s, CH_3).

Compound (**7c**). ^{31}P NMR: 69.0. ^{1}H NMR: ∂ = 4.1 (m, CH_2O); 2.6 (m, CH_2S); 2.0 (m, CH_2); 1.3 (s, CH_3).

ACKNOWLEDGEMENTS

This work was made with the constant collaboration of IFP (Institut Français du Pétrole), particularly the Direction of Search "Materials and Applied Chemistry." We wish here to thank all the members of this department.

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