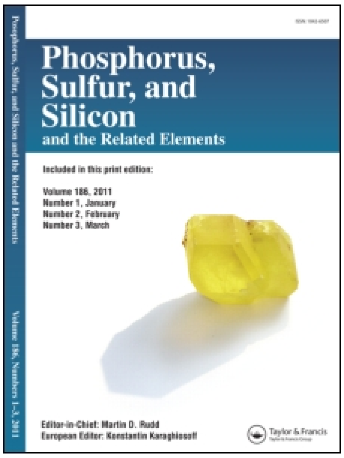


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Novel Approach to the Synthesis of Phosphorus Sulfur Organic Compounds and Their Metal Complexes

Elvira S. Batyeva[a]; Elena K. Badeeva[a]; Lidiya I. Kursheva[a]; Elena V. Platova[a]; Aidar T. Gubaidullin[a]; Igor A. Litvinov[a]; Oleg G. Sinyashin[a]
[a] A. E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences Kazan Scientific Center, Kazan, Russia

To cite this Article Batyeva, Elvira S. , Badeeva, Elena K. , Kursheva, Lidiya I. , Platova, Elena V. , Gubaidullin, Aidar T. , Litvinov, Igor A. and Sinyashin, Oleg G.(2005) 'Novel Approach to the Synthesis of Phosphorus Sulfur Organic Compounds and Their Metal Complexes', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 5, 1405 — 1409

To link to this Article: DOI: 10.1080/10426500590912736

URL: http://dx.doi.org/10.1080/10426500590912736

Phosphorus, Sulfur, and Silicon, 180:1405–1409, 2005
Copyright © Taylor & Francis Inc.
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500590912736

Taylor & Francis
Taylor & Francis Group

Novel Approach to the Synthesis of Phosphorus Sulfur Organic Compounds and Their Metal Complexes

Elvira S. Batyeva
Elena K. Badeeva
Lidiya I. Kursheva
Elena V. Platova
Aidar T. Gubaidullin
Igor A. Litvinov
Oleg G. Sinyashin
A. E. Arbuzov Institute of Organic and Physical Chemistry,
Russian Academy of Sciences Kazan Scientific Center, Kazan, Russia

The reaction of elemental phosphorus (P_4) and sulfur with protonodonor reagents (alcohols, phenols, and thiols) has been studied in the presence of amines and complexes based on trialkyltrithiophosphites and transition metal halides. A novel approach to the synthesis of phosphorus sulfur organic compounds has been proposed on the basis of these reactions.

Keywords Amines; complex; elemental phosphorus; sulphur; thiols

INTRODUCTION

Until recently the traditional techniques for the preparation of phosphorus and sulfur organic compounds have been based on phosphorus chlorides and phosphorus sulfides. This reaction was accompanied by the evolution of hydrogen chloride or hydrogen sulfide.[1] Therefore, one of the actual problems of chemistry is the development of new ecologically pure methods for their preparation.

Our investigations are based on the reaction of elemental phosphorus (P_4) and sulfur and their derivatives as well as on organic and inorganic reagents.

Received July 9, 2004; accepted October 5, 2004.

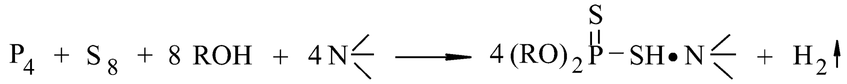
The authors express their sincere thanks to O. Kataeva and D. Krivolapov for X-ray investigations. The grants of the Russian Foundation of Basic Research and Program 7 of the Division of Chemistry and Material Science RAS are gratefully acknowledged.

Address correspondence to Elvira S. Batyeva, A. E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences Kazan Scientific Center, Arbuzov Str. 8, 420088 Kazan, Russia. E-mail: batyeva@iopc.knc.ru

The reaction of P_4 and sulfur with protonodonor reagents (alcohols, phenols, and thiols) has been studied in the presence of compounds of a bidentate character. We have suggested and used amines forming appropriate complexes on interaction with elemental sulfur or bidentate complexes based on trialkyltrithiophosphites and transition metal halides. These compounds are supposed to promote the phosphorus tetrahedron cleavage.

RESULTS AND DISCUSSION

It has been established that the reaction of elemental phosphorus and sulfur with alcohols and phenols in the presence of amines resulted in the formation of ammonium salts of O,O-dialkyldithiophosphoric acids.[2]



$$P_4 + S_8 + 8\,ROH + 4\,N\!\lessdot \longrightarrow 4\,(RO)_2\overset{S}{\overset{\|}{P}}-SH\bullet N\!\lessdot + H_2\uparrow$$

R: alkyl C_2 - C_{12}, aryl : phenyl, n-cresol, n-nonylphenol

$N\!\lessdot$: NH_3 ; H_2NR'; HNR'_2; NR'_3 (R' : alkyl C_2 - C_{12})
aromatic amines; heterocyclic amines; ethanolamines

We used either aliphatic alcohols or phenols, or a mixture of alcohol and substituted phenol and ammonia, aliphatic, aromatic and heterocyclic amines, and ethanolamines as amines.

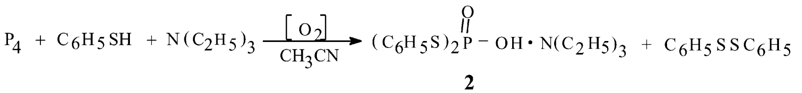
The reaction was followed by hydrogen evolution in contrast to the reaction of phosphorus sulfide (P_2S_5) with alcohols in which the evolution of hydrogen sulfide was observed. The use of amines makes the method more suitable and useful both for laboratory practice and industry.

It is well known that dialkyldithiophosphoric acids and their derivatives are used as lubricating oil additives.[1]

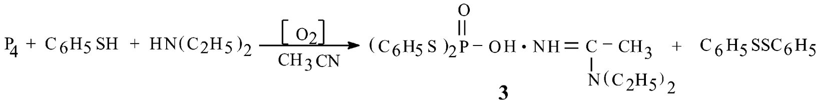
We applied amines for the cleavage of phosphorus tetrahedron in the reaction of P_4 with thiophenol and amines in acetonitrile when heated with the formation of ammonium salt **2** (62%) and acetamidine salt **3** (47%) of S,S-diphenyldithiophosphoric acid, depending on the nature of the amine used. (The reactions were carried out in the presence of oxygen from the air.)

The crystal structure of the obtained acetamidine salt of S,S-diphenyldithiophosphoric acid **3** was determinated by X-ray diffraction.

Diphenyldisulfide is the second product obtained by us in the presence of basic reagents.



$$P_4 + C_6H_5SH + N(C_2H_5)_3 \xrightarrow[CH_3CN]{[O_2]} \underset{\mathbf{2}}{(C_6H_5S)_2\overset{O}{\overset{\|}{P}}-OH \cdot N(C_2H_5)_3} + C_6H_5SSC_6H_5 \quad (1)$$

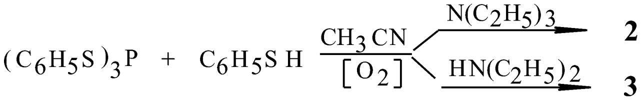


$$P_4 + C_6H_5SH + HN(C_2H_5)_2 \xrightarrow[CH_3CN]{[O_2]} \underset{\mathbf{3}}{(C_6H_5S)_2\overset{O}{\overset{\|}{P}}-OH \cdot NH{=}\underset{N(C_2H_5)_2}{\underset{|}{C}}-CH_3} + C_6H_5SSC_6H_5 \quad (2)$$

The degradation of the tetrahedron of elemental phosphorus in the interaction of P_4 with thiophenol proceeds identically with both the triethylamine and diethylamine. As a result, intermediate triphenyltrithiophosphite is formed. Indeed, the corresponding chemical shift at δ_p 130 ppm was observed in the NMR ^{31}P spectra of the reaction mixture.

Further, triphenyltrithiophosphite reacts with thiophenol and alkylamines to yield the final product—ammonium or acetamidine salts of S,S-diphenyldithiophosphoric acid.

That triphenyltrithiophosphite is involved in the interaction has been confirmed by model reactions. Thus, in the interaction of triphenyltrithiophosphite with thiophenol, triethylamine or diethylamine compounds **2**, **3** were isolated that were completely identical to the salts obtained as a result of the Equations (1) and (2).



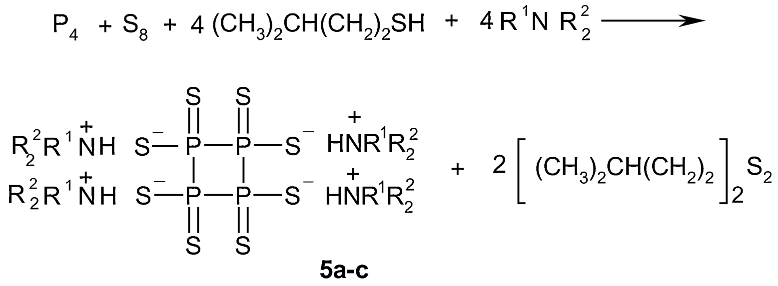
$$(C_6H_5S)_3P + C_6H_5SH \xrightarrow[[O_2]]{CH_3CN} \begin{cases} \xrightarrow{N(C_2H_5)_3} \mathbf{2} \\ \xrightarrow{HN(C_2H_5)_2} \mathbf{3} \end{cases}$$

It is interesting to note that the use of the catalytic quantity of alkylamines gives only triphenyltrithiophosphate in all the reactions.

The method of obtaining ammonium and acetamidine salts of S,S-diphenyldithiophosphoric acid suggested by us can be employed in biochemical synthesis.[3]

We have obtained some unexpected products (tetraphosphetane salts) from the reaction of elemental phosphorus with thiol and alkylamines in the presence of elemental sulfur (ratio 1:1:1:2) in contrast to a similar reaction of P_4 with alcohols and amines in the presence of sulfur, which leads to the formation of ammonium salts of dithiophoshoric acids.

Thus, we have found that, in the interaction of P_4 with sulfur, 3-methyl-1-butanethiol and alkylamines at 15–30°C for 1–1.5 h precipitates of tetra(alkylammonium) salts 1,2,3,4-tetramercapto-1,2,3,4-tetrathioxotetraphosphetanes **5a–c** are formed.



a $R^1 = R^2 = Et$; **b** $R^1 = H$, $R^2 = Et$; **c** $R^1 = H, R^2_2 = -(CH_2)_5-$

Previously unknown tetraphosphetane salts **5a–c** were light yellow crystalline compounds. The yields were 18 (**5a**), 20 (**5b**), and 22% (**5c**). ^{31}P signals were observed at 122, 125.1, and 123.4 ppm, respectively. The crystals are soluble in polar solvents. They are stable in the air and water at the temperatures up to 45°C. The crystal structure of the obtained tetrakis(triethylammonium) salt 1,2,3,4-tetramercapto-1,2,3,4-tetrathioxotetraphosphetane **5a** was determined by X-ray diffraction. The asymmetric part of the unit cell contains two triethylamine molecules and half of the tetraphosphetane moiety located in the center of symmetry (Figure 1). Selected bond lengths (Å) and angles(deg): P(1)-S(2) 1.969(1), P(1)-S(1) 1.990(1), P(1)-P(2) 2.305(1), P(1)-P(2)($-x + 2$, $-y - 1$, $-z + 1$) 2.311(1), P(2)-S(3)

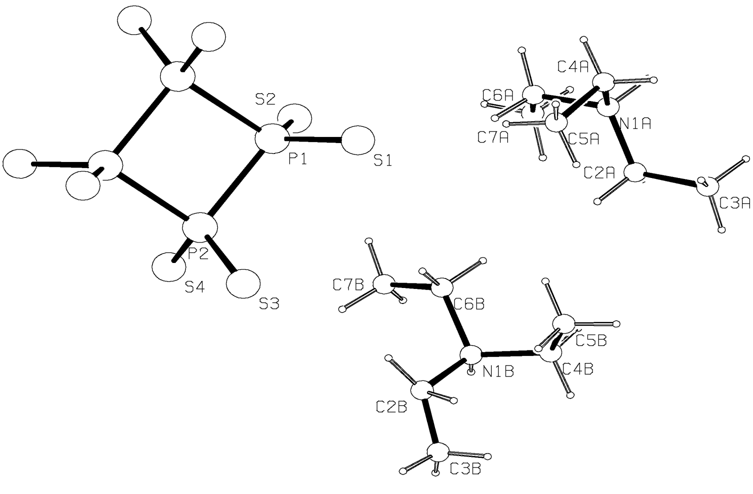


FIGURE 1 Crystal structure of compound **5a**.

1.978(1), P(2)-S(4) 1.993(1), N(1B)-C(2B) 1.473(8), N(1B)-C(4B) 1.490(6), N(1B)-C(6B) 1.533(7), N(1A)-C(2A) 1.477(7), N(1A)-C(4A) 1.493(7), N(1A)-C(6A) 1.539(7), S(2)P(1)S(1) 117.05(6), S(2)P(1)P(2) 114.53(5), S(1)P(1)P(2) 109.78(6), S(2)P(1)P(2) $(-x+2, -y-1, -z+1)$ 112.18(5), S(1)P(1)P(2)$(-x+2, -y-1, -z+1)$ 110.20(6), P(2)P(1)P(2)$(-x+2, -y-1, -z+1)$ 89.89(5), S(3)P(2)S(4) 117.42(6), S(3)P(2)P(1) 110.90(6), S(4)P(2)P(1) 112.77(5), S(3)P(2)P (1)$(-x+2, -y-1, -z+1)$ 111.98(6), S(4)P(2)P(1)$(-x+2, -y-1, -z+1)$ 110.45(6), P(1)P(2)P(1)$(-x+2, -y-1, -z+1)$ 90.11(5)

It is well known that reactions of P_4 with disulfides result in the formation of trialkyltrithiophosphites, which can be used as original materials for the synthesis of various organophosphorus compounds.[4,5]

Earlier we established[6] that trialkyltrithiophosphites, $(RS)_3P$, in which R = Et, Pr, Bu, react with Cu(I) and Cu(II) to form infinite polymeric chains of regular structure with the bidentate type of coordination phosphorus and sulfur atoms of trithiophosphite ligand.

Organic complexes have been studied as catalysts promoting the opening of the molecule of elemental phosphorus.

We have studied the reaction of P_4 with mercaptanes in the presence of metal complexes on the basis of thioesters phosphorus, $R'_2P\text{-}SR{\cdot}CuBr$, in which R = Et, Bu; R′ = Ph, SEt.

It has been established that the main products of the reaction of P_4 and sulfur with mercaptanes are the appropriate tetrathiophosphates.

Crystallographic data (excluding structure factors) for the structure **5a** reported in this paper have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 243023. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0) 1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

REFERENCES

[1] D. Corbridj, *Phosphor. Osnovy khimii, biokhimii, technologii, Moscow, "Mir," 2 izd, gl.* **7,** 436 (1982) (in Russian).

[2] E. S. Batyeva, E. K. Badeeva, E. V. Platova, L. I. Kursheva, and O. G. Sinyashin, Abstracts of the *XVII Mendeleev Congress on General and Applied Chemistry*. Applied Chemistry, Russia, Kazan (21–26 September 2003) p. 117.

[3] M. Sekine, K. Hamaoki, and T. Hata, *J. Org. Chem.*, **44,** 2325 (1979).

[4] D. R. Stevens and R. S. Spindt, U. S. Pat. 2,542,370, *Chem. Abstracts*, **45,** 5712 (1951).

[5] Ch. Wu, *J. Am. Chem. Soc.*, **87,** 2522 (1965).

[6] L. I. Kursheva, L. V. Frolova, E. S. Batyeva, and R. Schmutzler, *Zhurnal Obsch. Khimii* (Russian Ed.), **64,** 1613 (1994).