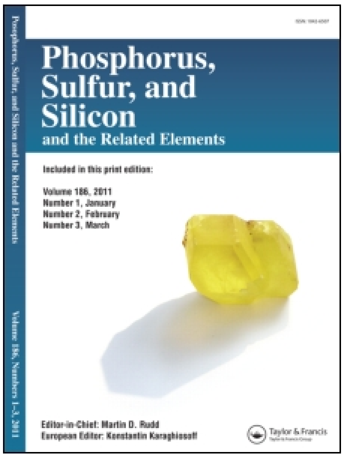

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Atom-Economic Synthesis of Tris[2-(organylthio)ethyl]phosphine Oxides from Phosphine and Vinyl Sulfides

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To cite this Article Gusarova, Nina K. , Ivanova, Nina I. , Bogdanova, Maria V. , Sinegovskaya, Lidiya M. , Gusarov, Alexander V. and Trofimov, Boris A.(2005) 'Atom-Economic Synthesis of Tris[2-(organylthio)ethyl]phosphine Oxides from Phosphine and Vinyl Sulfides', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 7, 1749 — 1754

To link to this Article: DOI: 10.1080/104265090885345

URL: http://dx.doi.org/10.1080/104265090885345

Phosphorus, Sulfur, and Silicon, 180:1749–1754, 2005
Copyright © Taylor & Francis Inc.
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/104265090885345

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Phosphine, generated from elemental phosphorus in the system KOH-toluene-H_2O, reacts with vinyl sulfides under free radical conditions (AIBN, dioxane, 65–70°C, atmospheric pressure) to form regiospecifically tris[2-(organylthio)ethyl]phosphines, which are readily oxidized in air to corresponding tris[2-(organylthio)ethyl]phosphine oxides.

Keywords Addition; phosphine; radical reactions; tris[2-(organylthio)ethyl]phosphine oxides; vinyl sulfides

The development of a convenient method for generation of phosphine from elemental phosphorus and potassium hydroxide in aqueous organic systems has opened new opportunities for synthetic utilization of this efficient phosphorylating agent[1] and allowed to carry out atom-economic syntheses of primary, secondary, and tertiary phosphines (including functional and unsaturated), based on the nucleophilic addition of phosphine to aryl[1,2] and hetarylalkenes[1,3] and acetylenes.[1,2a,b,4]

To expand the synthetic potential of phosphine and synthesize new prospective polyfunctional sulfur-containing organophosphorus

Received August 24, 2004; accepted August 26, 2004.

Financial support from the Ministry of Industry, Science and Technologies of Russian Federation (Grant No. NSH-2241.2003.3) and Russian Foundation for Basic Research (Grant No. 04-03-32045-a) is gratefully acknowledged.

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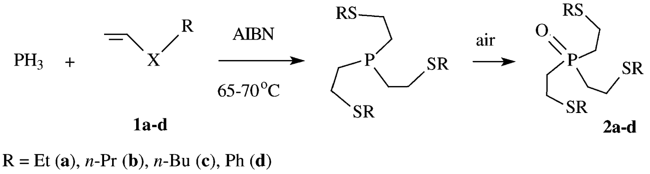
compounds based thereon, we have investigated the reaction of phosphine with available organyl vinyl sulfides.[5,6]

RESULTS AND DISCUSSION

We have found that phosphine reacts readily with vinyl sulfides **1a–d** under free-radical conditions to give regiospecifically anti-Markovnikov adducts. The reaction proceeds upon passing phosphine, generated as a phosphine-hydrogen mixture from red phosphorus and potassium hydroxide in aqueous toluene medium, through a solution of vinyl sulfide **1** in dioxane heated to 65–70°C in the presence of AIBN. To achieve the complete organylsulfenylethylation of phosphine, vinyl sulfide is introduced into the reaction vessel by two portions: the first one (three fourth) is placed into the flask at the initial reaction stage, while the remaining portion is added after the phosphine feeding is stopped. Under these conditions, the major reaction products are the corresponding tris[2-(organylthio)ethyl]phosphines (identified in the reaction mixture by ^{31}P NMR peaks at $-27 \div -28$ ppm), which are readily oxidized by air oxygen during their isolation and purification on Al_2O_3 to give tris[2-(organylthio)ethyl]phosphine oxides **2a–d** in 56–83% yield (Scheme 1).



SCHEME 1

The reaction mixture also contained trace amounts of the corresponding primary and secondary phosphines: peaks at $-138 \div -139$ ppm (J_{H-P-H}, ~ 192 Hz) and $-70 \div -71$ ppm (J_{H-P}, 194–195 Hz), respectively.

Moderate yield of phosphine oxides **2a**,**b** (56 and 61%, respectively) as compared to the yield of phosphine oxides **2c**,**d** (74–83%) can be accounted for by the higher volatility of the starting ethyl and *n*-propyl vinyl sulfides, which therefore may be carried out of the reaction mixture with the flow of phosphine.

Structures of the synthesized compounds **2** were confirmed by their NMR and IR spectral characteristics (Tables I and II).

Thus, the reaction of phosphine with vinyl sulfides represents a convenient approach to the atom-economic synthesis of tertiary phosphine oxides with a sulfide moiety, potentially capable of metal chelating and,

TABLE I NMR Spectral Data of Compounds 2a–d

		NMR ($CDCl_3$), δ (ppm), J (Hz)		
Compound	Formula	^1H	^{13}C	^{31}P
2a	$(C^1H_3C^2H_2SC^3H_2C^4H_2)_3P{=}O$	1.28 (t, 9H, C^1-H, $^3J_{HH}$ 7.3), 2.08 (m, 6H, C^4-H), 2.59 (q, 6H, C^2-H, $^3J_{HH}$ 7.3), 2.80 (q, 6H, C^3-H, $^3J_{HH}$ 8.6)	14.65 (C^1), 23.78 (C^3, J_{PC} 3.0), 26.27 (C^2), 29.34 (d, C^4, J_{PC} 59.9)	44.8
2b	$(C^1H_3C^2H_2C^3H_2SC^4H_2C^5H_2)_3P{=}O$	0.98 (t, 9H, C^1-H, $^3J_{HH}$ 7.5), 1.61 (q, 6H, C^2-H, $^3J_{HH}$ 7.5), 2.11 (m, 6H, C^5-H), 2.53 (t, 6H, C^3-H, $^3J_{HH}$ 7.5), 2.76 (m, 6H, C^4-H)	12.84 (C^1), 22.18 (C^2), 23.53 (C^4), 28.76 (d, C^5, J_{PC} 59.5), 33.81 (C^3)	44.4
2c	$(C^1H_3C^2H_2C^3H_2C^4H_2SC^5H_2C^6H_2)_3P{=}O$	0.84 (t, 9H, C^1-H, $^3J_{HH}$ 7.3), 1.33 (m, 6H, C^2-H), 1.54 (m, 6H, C^3-H), 2.09 (m, 6H, C^6-H), 2.48 (m, 6H, C^4-H, $^3J_{HH}$ 7.3), 2.73 (m, 6H, C^5-H)	13.60 (C^1), 21.89 (C^2), 24.11 (C^5), 29.71 (d, C^6, J_{PC} 60.0), 31.47 (C^4), 32.01 (C^3)	44.5
2d	$(PhSC^1H_2C^2H_2)_3P{=}O$	2.06 (m, 6H, C^2-H), 3.08 (m, 6H, C^1-H), 7.24 (m, 15H, Ph)	26.37 (d, C^1, J_{PC} 3.9), 28.88 (d, C^2, J_{PC} 59.9), 127.06 (C_p), 129.28 (C_o), 130.31 (C_m), 134.39 (C_{ipso})	42.4

MS (EI): *m/z* (%), for **2a**: 314 (0.16) [M^+], 197 (100) [$C_2H_5SCH_2CH_2P(OH)CH_2CH_2S$], 89 (85) [$C_2H_5SC_2H_4$], 75 (39) [$C_2H_5SCH_2$], 61 (56) [$C_2H_5S$], 29 (63) [$C_2H_5$].

TABLE II IR Spectra of Compounds 2a–d

Compound	Infrared Spectra (cm^{-1})[a]
2a	2965 ν_{as} (CH_3), 2925 ν (CH_2), 2870 ν_s (CH_3), 1452 δ_{as} (CH_3), 1424 δ (CH_2), 1375 δ_s (CH_3), 1293, 1263, 1211 sh, 1199 δ (CH_2), 1159 ν (P=O), 1053 δ (CH_3), 1008, 971, 916 δ (CH), 830 δ (CH_2), 785, 763 ν (C–S), 477 δ (OPC), 451 δ (PCC)
2b	2960 ν_{as} (CH_3), 2928 ν (CH_2), 2871 ν_s (CH_3), 1458 δ_{as} (CH_3), 1420 δ (CH_2), 1377 δ_s (CH_3), 1337, 1289, 1239, 1198 δ (CH_2), 1160 ν (P=O), 1050 δ (CH_3), 1011, 920, 896 δ (CH), 830 δ (CH_2), 783, 741 ν (C–S), 477 δ (OPC), 452 δ (PCC)
2c	2957 ν_{as} (CH_3), 2929 ν (CH_2), 2871 ν_s (CH_3), 1464 δ_{as} (CH_3), 1437, 1420 δ (CH_2), 1379 δ_s (CH_3), 1290, 1273, 1214, 1198 δ (CH_2), 1159 ν (P=O), 1055 δ (CH_3), 1034, 1011, 916, 896 δ (CH), 830, 814 δ (CH_2), 786, 745 ν (C–S), 474 δ (OPC), 449 δ (PCC)
2d	3073, 3054, 3018, 3000 ν (=CH), 2952, 2922, 2902, 2853 ν (CH_2), 1583, 1572 sh, 1480, 1438 ν (C=C), 1415, 1294, 1219, 1200 δ (CH_2), 1150 ν (P=O), 1095, 1023, 1009, 938, 890 δ (CH), 842 δ (CH_2), 780, 761 sh, 747 sh ν (C–S), 732, 690 δ (=CH), 493 δ (OPC), 465 δ (PCC)

[a] Spectra of compounds **2a–c** were taken in microlayer, spectra of products **2d** were run in KBr.

therefore, representing prospective polydentate (*hemilabile*) ligands for the design of metal complex catalysts.[7] These compounds are also reactive building blocks for organic synthesis and convenient models for solving important theoretical problems, for example: which one of two heteroatomic functions better stabilizes the carbanion generated in vicinal $R_2P(O)CH_2CH_2S$ moiety under the action of a strong base?[8]

Experimental

^{1}H, ^{13}C, and ^{31}P NMR spectra were taken on a Bruker DPX 400 (400.13, 101.61, and 161.98 MHz, respectively) spectrometer in $CDCl_3$ solutions and referenced to internal HMDS and external 85% H_3PO_4, respectively. IR spectra were measured on a Bruker IFS 25 instrument in microlayer and in KBr. Mass spectrum was obtained on a LKB-2091 GC/MS spectrometer at the ionizing voltage of 70 eV.

Synthesis of Tris[2-(organylthio)ethyl]phosphine Oxides 2c–d

General Procedure

A solution of AIBN (0.06 g) in dioxane (25 mL) was blown with argon and saturated with phosphine-hydrogen mixture, generated in a separate flask by addition of 50% aqueous solution of KOH (200 g) to a mixture of red phosphorus (20 g) in 70 mL of toluene at 70–75°C.

To the solution obtained, vinyl sulfide **1** (9.3 mmol) in 6 mL of dioxane was added dropwise over 1 h at 65–70°C, while bubbling phosphine at a rate of 45–50 bubbles/min, with the following heating of the reaction mixture for additional 2 h (65–70°C) upon vigorous passing phosphine. The phosphine feeding was then stopped, the system was blown with argon, and a solution of vinyl sulfide (3.2 mmol) in 3 mL of dioxane was introduced into the reaction mixture, which was then heated at 65–70°C for additional 1.5 h. The system was cooled and analyzed by ^{31}P NMR, δ, ppm. The major reaction products were tris[2-(organylthio)ethyl]phosphines (peaks at $-27 \div -28$ ppm). The reaction mixture also contained trace amounts of the tertiary phosphine oxide **2**, as well as the corresponding primary and secondary phosphines: peaks at $-138 \div -139$ ppm ($J_{\mathrm{H-P-H}}$, ~192 Hz) and $-70 \div -71$ ppm ($J_{\mathrm{H-P}}$, 194–195 Hz), respectively. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (Al_2O_3, activity level II, eluent: ethanol) to give phosphine oxides **2a–c**. Phosphine oxide **2d** was purified by recrystallization from hexane.

Tris[2-(ethylthio)ethyl]phosphine oxide (**2a**). Light-yellow oil, 56% yield.

Anal. Calcd. for $C_{12}H_{27}OPS_3$: C, 45.83; H, 8.65; P, 9.85; S, 30.59. Found: C, 45.48; H, 8.59; P, 9.46; S, 29.99.

Tris[2-(propylthio)ethyl]phosphine oxide (**2b**). Light-yellow oil, 61% yield.

Anal. Calcd. for $C_{15}H_{33}OPS_3$: C, 50.52; H, 9.33; P, 8.69; S, 26.98. Found: C, 50.39; H, 9.28; P, 7.99; S, 26.70.

Tris[2-(butylthio)ethyl]phosphine oxide (**2c**). Light-yellow oil, 74% yield.

Anal. Calcd. for $C_{18}H_{39}OPS_3$: C, 54.23; H, 9.86; P, 7.77; S, 24.13. Found: C, 54.39; H, 9.79; P, 7.68; S, 23.97.

Tris[2-(phenylthio)ethyl]phosphine oxide (**2d**). White powder, m.p. 84–86°C (from hexane), 83% yield.

Anal. Calcd. for $C_{24}H_{27}OPS_3$: C, 62.85; H, 5.93; P, 6.75; S, 20.97. Found: C, 62.58; H, 5.91; P, 6.79; S, 20.81.

REFERENCES

[1] B. A. Trofimov, S. N. Arbuzova, and N. K. Gusarova, *Russ. Chem. Rev.*, **68,** 215 (1999).

[2] a) B. A. Trofimov, N. K. Gusarova, and L. Brandsma, *Main Group Chem. News*, **4,** 18 (1996); b) N. K. Gusarova, S. F. Malysheva, S. N. Arbuzova, and B. A. Trofimov, *Russ. Chem. Bull.*, **47,** 1645 (1998); c) B. A. Trofimov, L. Brandsma, S. N. Arbuzova, S. F Malysheva, and N. K. Gusarova, *Tetrahedron Lett.*, **35,** 7647 (1994); d) B. A. Trofimov, L. Brandsma, S. N. Arbuzova, S. F. Malysheva, N. A. Belogorlova, and N. K. Gusarova, *Zh. Obshch. Khim.*, **67,** 695 (1997); e) N. K. Gusarova, S. I. Shaikhudinova,

T. I. Kazantseva, S. F. Malysheva, B. G. Sukhov, N. A. Belogorlova, V. I. Dmitriev, and B. A. Trofimov, *Zh. Obshch. Khim.*, **72,** 399 (2002).

[3] a) N. K. Gusarova, B. A. Trofimov, S. F. Malysheva, S. I. Shaikhudinova, N. A. Belogorlova, S. N. Arbuzova, K. V. Nepomnyashchikh, and V. I. Dmitriev, *Zh. Obshch. Khim.*, **67,** 70 (1997); b) B. A. Trofimov, S. I. Shaikhudinova, V. I. Dmitriev, K. V. Nepomnyashchikh, T. I. Kazantseva, and N. K. Gusarova, *Zh. Obshch. Khim.*, **70,** 43 (2000).

[4] a) N. K. Gusarova, S. F. Malysheva, S. N. Arbuzova, L. Brandsma, and B. A. Trofimov, *Zh. Obshch. Khim.*, **64,** 2062 (1994); b) B. A. Trofimov, N. K. Gusarova, S. N. Arbuzova, S. F. Malysheva, R. den Besten, and L. Brandsma, *Synthesis*, 387 (1995).

[5] B. A. Trofimov, *Sulfur Rep.*, 207 (1992).

[6] B. A. Trofimov and B. A. Shainyan. In *The Chemistry of Functional Groups. Supplement. S: The Chemistry of Sulfur-Containing Functional Groups*, edited by S. Patai and Z. Rappoport (Wiley, New York, 1993), chap. 14.

[7] a) C. S. Slone, D. A. Weinberger, and C. A. Mirkin, *Progr. Inorg. Chem.*, **48,** 233 (1999); b) C. Liek, R. Machnitzki, T. Nickel, S. Schenk, M. Tepper, and O. Stelzer, *Naturforsch.*, **54b,** 1532 (1999); c) M. Hingst, M. Tepper, and O. Stelzer, *Eur. J. Inorg. Chem.*, 73 (1998); d) O. Herd, A. Hebter, M. Hingst, R. Machnitzki, M. Tepper, and O. Stelzer, *Catal. Today*, **42,** 413 (1998); e) D. J. Brauer, K. W. Kottsieper, T. Nickel, and W. S. Sheldrick, *Eur. J. Inorg. Chem.*, 1251 (2001); f) A. Bader and E. Linder, *Coord. Chem. Rev.*, **108,** 27 (1991).

[8] a) T. Minami, T. Okauchi, H. Matsuki, M. Nakamura, J. Ichikawa, and M. Ishida, *J. Org. Chem.*, **61,** 8132 (1996); b) T. Minami, T. Okauchi, and R. Kouno, *Synthesis*, 349 (2001); c) B. A. Trofimov, N. K. Gusarova, S. F. Malysheva, N. I. Ivanova, B. G. Sukhov, N. A. Belogorlova, and V. A. Kuimov, *Synthesis*, 2207 (2002).