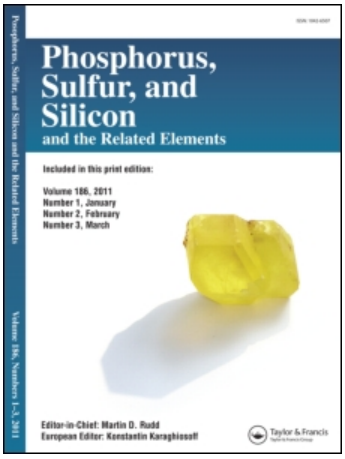


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Chemo- and Regiospecific Monoaddition of Secondary Phosphine Sulfides to 1-Acyl-2-phenylacetylenes

Tatyana E. Glotova[a]; Marina Yu. Dvorko[a]; Nina K. Gusarova[a]; Svetlana N. Arbuzova[a]; Igor A. Ushakov[a]; Tatyana I. Kazantseva[a]; Boris A. Trofimov[a]

[a] A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, Irkutsk, Russia

To cite this Article Glotova, Tatyana E. , Dvorko, Marina Yu. , Gusarova, Nina K. , Arbuzova, Svetlana N. , Ushakov, Igor A. , Kazantseva, Tatyana I. and Trofimov, Boris A.(2008) 'Chemo- and Regiospecific Monoaddition of Secondary Phosphine Sulfides to 1-Acyl-2-phenylacetylenes', Phosphorus, Sulfur, and Silicon and the Related Elements, 183: 6, 1396 — 1401

To link to this Article: DOI: 10.1080/10426500701648069

URL: http://dx.doi.org/10.1080/10426500701648069

Phosphorus, Sulfur, and Silicon, 183:1396–1401, 2008

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500701648069

Taylor & Francis
Taylor & Francis Group

Chemo- and Regiospecific Monoaddition of Secondary Phosphine Sulfides to 1-Acyl-2-phenylacetylenes

Tatyana E. Glotova, Marina Yu. Dvorko, Nina K. Gusarova, Svetlana N. Arbuzova, Igor A. Ushakov, Tatyana I. Kazantseva, and Boris A. Trofimov
A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, Irkutsk, Russia

Secondary phosphine sulfides react with 1-acyl-2-phenylacetylenes under mild conditions (KOH, THF, r.t.) to afford chemo- and regiospecifically 3-diorganophosphorothioyl-1-R-3-phenyl-2-propen-1-ones in high yield, with the E-isomers being formed exclusively (R = Ph and 2-thienyl) or predominantly (60%, R = Me).

Keywords 1-Acyl-2-phenylacetylenes; 3-(diphenethylphosphorothioyl)-1-*R*-3-phenyl-2-propen-1-one; bis(2-phenylethyl)phosphine sulfide; nucleophilic monoaddition

INTRODUCTION

The development of a convenient method for the preparation of secondary phosphines and phosphine chalcogenides from elemental phosphorus, organohalides[1] and aryl or hetarylalkenes,[2] in the presence of strong bases has opened new opportunities for atom-economic syntheses of tertiary phosphines and phosphine chalcogenides—including functionalized and unsaturated derivatives—based on the nucleophilic and radical addition of the PH-function to multiple C—C[3,4]and double C—O[5,6] bonds. At the same time, reactions of secondary phosphine sulfides with acetylenes have been poorly investigated.

To the best of our knowledge the only report in the literature describing a nucleophilic addition of secondary phosphine sulfides to a C≡C triple bond concerns the double α,β-addition of bis(2-phenylethyl)phosphine sulfide to 3-phenyl-2-propynenitrile in the

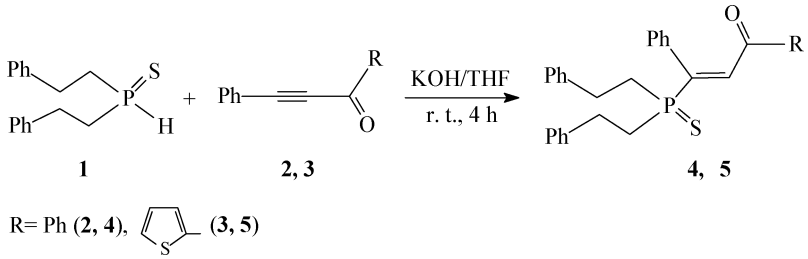
Received 27 April 2007; accepted 14 August 2007.
Address correspondence to Boris A. Trofimov, A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 1 Favorsky Street, 664033, Irkutsk, Russia. E-mail: glotova@irioch.irk.ru

presence of KOH to form 2,3-bis[bis(2-phenylethyl)phosphorothioyl]-3-phenylpropanenitriles.[7] 3-(Trialkylsilyl)- and 3-(trialkylgermyl)-2-propynals were also reported to react with secondary phosphine chalcogenides at the carbonyl group under catalyst-free conditions to give the corresponding tertiary phosphine chalcogenides with acetylenic and hydroxyl moieties in high yield.[6]

In order to extend the synthetic potential of the chemistry of secondary phosphine sulfides, acetylenes, and carbonyl compounds, and to synthesize new polyfunctional tertiary phosphine sulfides, we have investigated the reaction of bis(2-phenylethyl)phosphine sulfide **1** with 1-acyl-2-phenylacetylenes.

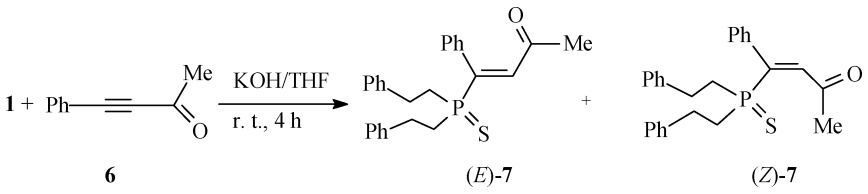
RESULTS AND DISCUSSION

We have found that the phosphine sulfide **1** reacts readily (KOH, THF, 20–22°C, 4 h) with 1,3-diphenyl-2-propyn-1-one **2** and 3-phenyl-1-(2-thienyl)-2-propyn-1-one **3** to give chemo-, regio-, and stereospecifically the *E*-isomers of the addition products **4**, **5** in 80–85% yield (Scheme 1). This contradicts the conventional *trans*-mode addition of nucleophiles to monosubstituted acetylenes, usually producing the *Z*-isomers.



SCHEME 1

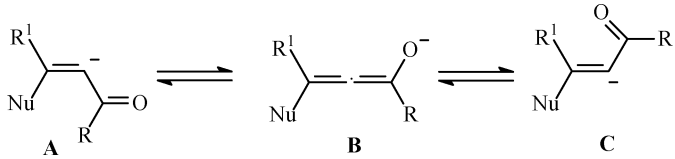
Under similar conditions, addition of the phosphine sulfide **1** to 4-phenyl-3-butyn-2-one **6** proceeds non-stereospecifically to give 4-(diphenethylphosphorothioyl)-4-phenyl-3-buten-2-one **7** in 67% yield as a 3 : 2 mixture of the *E*- and *Z*-isomer (Scheme 2).



SCHEME 2

It is unlikely that the *E*-isomer of the phosphine sulfide **7** is formed because of post-isomerization of the *Z*-isomer formed initially, since the ratio of these isomers remains practically unchanged upon prolonged heating (100°C, 8 h) in DMSO.

At the same time the violation of *trans*-mode addition in the above reactions agrees with the known data on the addition of nucleophiles to acylacetylenes[8] or methyl propiolate[9] to give the vinylic carbanions **A** and **C**, which readily isomerize to each other *via* the allenic intermediate **B** (Scheme 3). The formation of allenic intermediates of the type **B** was observed, for example, in the reaction of organocuprates with alkynyl carbonyl compounds.[10]



SCHEME 3

The preferred or exclusive formation of *E*-adducts in the reactions studied (Schemes 2 and 3) is likely to be influenced by steric effects.[3]

The configurations of the *E*- and *Z*-isomer of compound **7** were determined based on 1D and 2D homo- and heteronuclear ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. The positions of the thiophosphoryl and acyl groups relative to the double bond in compound **7** were established by comparison of the heteronuclear *trans* and *cis* coupling constants $^{3}J_{PH}$, $^{3}J_{PC=O}$ and $^{3}J_{CH}$ (C_{ipso} PhC=CH), which are known to be highly stereospecific. The data obtained allowed us to assign the *E*-configuration to compounds **4** and **5**.

Thus, the reaction of phosphine sulfides with acylacetylenes proves to be a general approach to the expedient atom-economic synthesis of polyfunctional tertiary phosphine sulfides, possible polydentate ("hemilabile") ligands for the design of metal complex catalysts,[11] intermediates and coordinating solvents for the preparation of conductive nanomaterials,[12] as well as reactive building blocks for organic synthesis.

EXPERIMENTAL

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with 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. The values of the coupling constants $^{3}J_{CH}$ were obtained

by the analysis of sections of the 2D HMBC NMR spectra. IR spectra were measured with a Bruker IFS 25 instrument in microlayer and as KBr pellets.

Synthesis of Bis(2-phenylethyl)-(1-phenyl-2-acylethenyl) phosphine Sulfides 4, 5, and 7—General Procedure

To a solution of bis(2-phenylethyl)phosphine sulfide (0.55 mmol) and 1-acyl-2-phenylacetylene (0.55 mmol) in 3 mL of THF, KOH 0.5 H_2O (15% water content) (0.11 mmol) was introduced. The suspension thus obtained was stirred at 20–22°C for 4 h. KOH was filtered off, and the solvent was removed from the filtrate under reduced pressure. The crude honey-like product was washed with a mixture of ether and petroleum ether (1 : 3) (2 mL). After drying under vacuum (1 Torr), the phosphine sulfides **4**,**5**, and **7** were obtained.

(E)-3-(Diphenethylphosphorothioyl)-1,3-diphenyl-2-propen-1-one (4)

Light-yellow powder, m.p. 94–96°C, 224 mg (85%) yield. ^{1}H NMR, δ (ppm), J (Hz): 2.15, 2.31 (br. m, 4H, CH_2P), 3.03, 3.19 (br. m, 4H, $\underline{CH}_2Ph$), 7.10–7.91 (m, 20H, Ph), 8.32 (d, $^3J_{P-C=C-H}$ 22.5, 1H, =CH). ^{13}C NMR, δ (ppm), J (Hz): 28.6 (d, $^2J_{PC}$ 2.0, $\underline{C}H_2Ph$), 31.5 (d, $^1J_{PC}$ 51.6, $\underline{C}H_2P$), 126.6, 128.2, 128.3, 128.6, 128.8, 128.9, 133.8 (C-*o*, C-*m*, C-*p* $PhCH_2$, PhC=C, PhC=O), 134.3 (d, $^2J_{PC}$ 7.4, $^3J_{CH}$ 9.4, C-*i* PhC=CH), 136.8 (C-*i* PhC=O), 140.6 (d, $^3J_{PC}$ 16.2, C-*i* $PhCH_2$), 144.0 (d, $^2J_{PC}$ 11.1, P–C=$\underline{C}$H), 144.8 (d, $^1J_{PC}$ 55.3, P–$\underline{C}$=CH), 192.0 (d, $^3J_{PC}$ 17.0, C=O). ^{31}P NMR, δ (ppm): 50.8. IR ν (cm^{-1}): 1660 (C=O), 680 (P=S). Anal. Calcd. for $C_{31}H_{29}OPS$: C, 77.47; H, 6.08; P, 6.44; S, 6.67. Found: C, 77.23; H, 6.28; P, 6.78; S, 6.38.

(E)-3-(Diphenethylphosphorothioyl)-3-phenyl-1-(2-thienyl)-2-propen-1-one (5)

Yellow oil, 214 mg (80%) yield. ^{1}H NMR, δ (ppm), J (Hz): 2.05, 2.19 (br. m, 4H, CH_2P), 2.92, 3.06 (br. m, 4H, $\underline{CH}_2Ph$), 7.11 (2H, *o*–H PhC=C), 7.16 (dd, $^3J_{H4-H3}$ 3.7, $^3J_{H4-H5}$ 4.9, 1H, H-4 thienyl), 7.18 (4H, *o*-H $PhCH_2$), 7.22 (2H, *p*-H $PhCH_2$), 7.28 (4H, *m*-H $PhCH_2$), 7.38 (3H, *m*-H, *p*-H PhC=C), 7.70 (m, 1H, H-5 thienyl), 7.86 (m, 1H, H-3 thienyl), 8.28 (d, $^3J_{P-C=C-H}$ 22.0, 1H, =CH). ^{13}C NMR, δ (ppm), J (Hz): 28.5 (d, $^2J_{PC}$ 2.0, $\underline{C}H_2Ph$), 31.4 (d, $^1J_{PC}$ 51.5, $\underline{C}H_2P$), 126.7 (C-*p* $PhCH_2$), 127.9 (d, $^3J_{PC}$ 3.2, C-*o* PhC–C), 128.3 (C-*o* $PhCH_2$), 128.5 (C-4 thienyl), 128.7 (C-*p* PhC=C), 128.8 (C-*m* $PhCH_2$), 128.9 (C-*m* PhC=C), 133.7 (C-3 thienyl), 134.5 (d, $^2J_{PC}$ 7.2, $^3J_{CH}$ 9.4, C-*i* PhC=CH), 135.2 (C-5 thienyl), 140.6 (d, $^3J_{PC}$ 15.0, C-*i* $PhCH_2$), 141.5 (d, $^2J_{PC}$ 12.0, P–C=$\underline{C}$H), 144.8 (C-2

thienyl), 146.3 (d, $^{1}J_{PC}$ 54.3, P–C=CH), 182.8 (d, $^{3}J_{PC}$ 18.0, C=O). ^{31}P NMR, δ (ppm): 50.7. IR ν (cm^{-1}): 1620 (C=O), 680 (P=S). Anal. Calcd. for $C_{29}H_{27}OPS_2$: C, 71.58; H, 5.59; P, 6.36; S, 13.18. Found: C, 71.76; H, 5.82; P, 6.52; S, 13.01.

4-(Diphenethylphosphorothioyl)-4-phenyl-3-buten-2-one (7)

Red oil, 154 mg (67%) yield. **(*E*)-isomer**: ^{1}H NMR, δ (ppm), J (Hz): 2.00 (s, 3H, Me), 2.00, 2.40 (br. m, 4H, CH_2P), 2.80, 3.10 (br. m, 4H, CH_2Ph), 7.04–7.45 (m, 15H, Ph), 7.54 (d, $^{3}J_{P-C=C-H}$ 22.3, 1H, =CH). ^{13}C NMR, δ (ppm), J (Hz): 28.5 (d, $^{2}J_{PC}$ 1.6, CH_2Ph), 30.9 (s, Me), 31.3 (d, $^{1}J_{PC}$ 52.0, CH_2P), 126.6, 128.1, 128.3, 128.6, 129.1 (C-*o*, C-*m*, C-*p* $PhCH_2$, PhC=C), 134.5 (d, $^{2}J_{PC}$ 7.2, $^{3}J_{CH}$ 9.9, C-*i* PhC=CH), 140.5 (d, $^{3}J_{PC}$ 15.5, C-*i* $PhCH_2$), 144.3 (d, $^{1}J_{PC}$ 54.7, P–C=CH), 144.5 (d, $^{2}J_{PC}$ 10.4, P–C=CH), 199.1 (d, $^{3}J_{PC}$ 17.6, C=O). ^{31}P NMR, δ (ppm): 50.4. **(*Z*)-isomer**: ^{1}H NMR, δ (ppm), J (Hz): 2.54 (s, 3H, Me), 2.00, 2.40 (m br., 4H, CH_2P), 2.80, 3.10 (m br., 4H, CH_2Ph), 7.04–7.45 (m, 15H, Ph), 6.74 (d, $^{3}J_{P-C=C-H}$ 33.8, 1H, –CH). ^{13}C NMR, δ (ppm), J (Hz): 28.7 (d, $^{2}J_{PC}$ 2.0, CH_2Ph), 31.7 (s, Me), 34.4 (d, $^{1}J_{PC}$ 50.3, CH_2P), 126.42, 128.1, 128.3, 128.6, 128.7, 129.0 (C-*o*, C-*m*, C-*p* $PhCH_2$, PhC=C), 138.8 (d, $^{2}J_{PC}$ 8.0, $^{3}J_{CH}$ 7.2, C-*i* PhC=CH), 140.8 (d, $^{3}J_{PC}$ 16.4, C-*i* $PhCH_2$), 144.0 (d, $^{1}J_{PC}$ 55.9, P–C=CH), 145.0 (d, $^{2}J_{PC}$ 7.6, P–C=CH), 200.8 (d, $^{3}J_{PC}$ 5.2, C=O). ^{31}P NMR, δ (ppm): 44.9. IR ν (cm^{-1}): 1675 (C=O), 1690 (C=O), 695 (P=S). Anal. Calcd. for $C_{26}H_{27}OPS$: C, 74.61; H, 6.50; P, 7.40; S, 7.66. Found: C, 74.33; H, 6.32; P, 7.77; S, 7.39.

REFERENCES

[1] (a) S. N. Arbuzova, L. Brandsma, N. K. Gusarova, and B. A. Trofimov, *Recl. Trav. Chim. Pays-Bas*., **113,** 575 (1994); (b) B. A. Trofimov, N. K. Gusarova, and L. Brandsma, *Main Group Chem. News*, **4,** 18 (1996).

[2] (a) B. A. Trofimov, L. Brandsma, S. N. Arbuzova, S. F Malysheva, and N. K. Gusarova, *Tetrahedron Lett*., **35,** 7647 (1994); (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); (c) 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] B. A. Trofimov, S. N. Arbuzova, A. G. Mal'kina, N. K. Gusarova, S. F. Malysheva, M. V. Nikitin, and T. I. Vakul'skaya, *Mendeleev Commun.*, 163 (1999).

[4] (a) N. K. Gusarova, S. I. Shaikhudinova, S. N. Arbuzova, T. I. Vakul'skaya, B. G. Sukhov, L. M. Sinegovskaya, M. V. Nikitin, A. G. Mal'kina, N. A. Chernysheva, and B. A. Trofimov, *Tetrahedron,* **59**,4789 (2003); (b) B. A. Trofimov, B. G. Sukhov, S. F. Malysheva, N. A. Belogorlova, A. P. Tantsirev, L. N. Parshina, L. A. Oparina, S. P. Tunik, and N. K. Gusarova, *Tetrahedron Lett.,* **45,** 9143 (2004); (c) T. Bunlaksananusorn and P. Knochel, *J. Org. Chem.*, **69,** 4595 (2004); (d) N. K. Gusarova, M. V. Bogdanova, N. I. Ivanova, N. A. Chernysheva, B. G. Sukhov, L. M. Sinegovskaya,

O. N. Kazheva, G. G. Alexandrov, O. A. D'yachenko, and B. A. Trofimov, *Synthesis*, 3103 (2005); (e) D. Leca, L. Fensterbank, E. Lacôte, and M. Malacria, *Chem. Soc. Rev.,* **34,** 858 (2005); (f) A. F. Parsons, D. J. Sharpe, and P. Taylor, *Synlett,* 2981 (2005); (g) S. N. Arbuzova, N. K. Gusarova, and B. A. Trofimov, *Arkivoc*, 12 (2006); (h) T. Hirai and L.-B. Han, *Org. Lett.,* **9,** 53 (2007).

[5] (a) R. K. Haynes, W. W.-L. Lam, and L.-L. Yeung, *Tetrahedron Lett*., **37,** 4729, (1996); (b) N. K. Gusarova, A. M. Reutskaya, N. I. Ivanova, A. S. Medvedeva, M. M. Demina, P. S. Novopashin, A. V. Afonin, A. I. Albanov, and B. A. Trofimov, *J. Organomet. Chem*., **659,** 172 (2002).

[6] N. K. Gusarova, N. I. Ivanova, N. A. Konovalova, B. G. Sukhov, L. V. Baikalova, L. M. Sinegovskaya, D. V. Pavlov, and B. A. Trofimov, *Synthesis,* 4159 (2006).

[7] S. N. Arbuzova, N. K. Gusarova, M. V. Bogdanova, N. I. Ivanova, I. A. Ushakov, A. G. Mal'kina, and B. A. Trofimov, *Mendeleev Commun*., 183, (2005).

[8] J. I. Dickstein and S. I. Miller, in *The Chemistry of the Carbon-Carbon Triple Bond,* S. Patai, Ed. (Wiley, Chichester, 1978), Chap. 19, pp. 813–955.

[9] Y. I. El'natanov and R. G. Kostyanovsky, *Izv. Akad. Nauk SSSR, Ser. Khim*., 382 (1988).

[10] S. Mori, E. Nakamura, and K. Morokuma, *Organometallics*, **23,** 1081 (2004).

[11] (a) *Asymmetric Catalysis in Organic Synthesis,* R. Noyori, Ed. (Wiley, New York, 1994); (b) *Comprehensive Asymmetric Catalysis,* E. N. Jacobsen, A. Pfaltz, H. Yamamoto, Eds.; Springer: Berlin, 1999; (c) *Catalytic Asymmetric Synthesis,* I. Ojima, Ed. (VCH, Weinheim, 2000), 2nd ed.; (d) M. Arisawa and M.Yamaguchi, *Adv. Synth. Catal.,* **343,** 27 (2001); (e) J. W. Faller, J. C. Wilt, and J. Parr, *Org. Lett.,* **6,** 1301 (2004); (f) D. Liu, Q. Dai, and X. Zhang, *Tetrahedron,* **61**, 6460 (2005); (g) G. C. Fu, *Acc. Chem. Res.,* **39,** 853 (2006); (h) Q. Dai, W. Gao, D. Liu, L. M. Kapes, and X. Zhang, *J. Org. Chem.,* **71,** 3928 (2006); (i) D. K. Whelligan and C. Bolm, *J. Org. Chem.,* **71,** 4609 (2006).

[12] (a) S. P. Gubin, N. A. Kataeva, and G. B. Khomutov, *Izv. Akad. Nauk. Ser. Khim.,* 811 (2005); (b) H. Liu, J. S. Owen, and A. P. Alivisatos, *J. Am. Chem. Soc.,* **129,** 305 (2007).