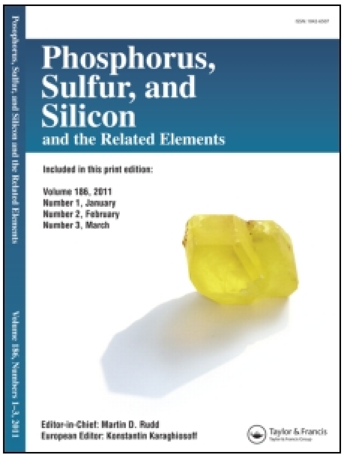

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A. S. Ionkin[a]; N. V. Nikolaeva[a]; V. M. Nekhoroshkov[a]; Yu. Ya. Efremov[a]; B. A. Arbuzov[a]
[a] A. E. Arbuzov Institute of Organic and Physical Chemistry of the Kazan Scientific Centre of the USSR Academy of Sciences, Kazan, USSR

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INTERACTION OF DISULFIDES AND SULFENYLCHLORIDES WITH C—N,N-DIALKYLAMINOSUBSTITUTED PHOSPHAALKENES

A. S. IONKIN,† N. V. NIKOLAEVA, V. M. NEKHOROSHKOV, YU. YA. EFREMOV and B. A. ARBUZOV

A. E. Arbuzov Institute of Organic and Physical Chemistry of the Kazan Scientific Centre of the USSR Academy of Sciences, 8, A. E. Arbuzov Street, Kazan 420083, USSR

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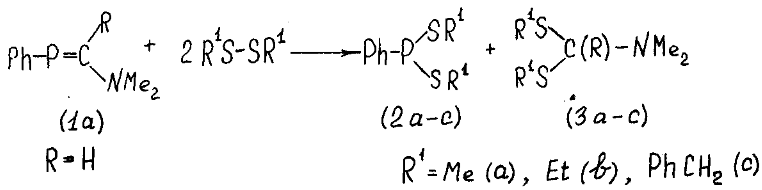
Interaction of dialkyl disulfides with C—N,N-dimethylaminomethylene-P-phenylphosphine **1a** results in the complete cleavage of the P=C double bond and formation of S,S-dialkylphenyldithiophosphonites. Ethyl sulfenylchlorides undergoes dehydrochlorination by **1a**, while phenyl sulfenylchloride cleaves the P=C bond in C—N,N-dialkylaminosubstituted phosphaalkenes with the predominant formation of either $PhP(SPh)_2$ **6** or PhP(SPh)Cl **7** depending on the phosphaalkene used and reaction conditions.

Key words: C-(N,N-dialkylamino) substituted phosphaalkenes; disulfides; sulfenylchlorides.

Disulfides were previously shown to be able of adding to double bonds between phosphorus and tin $\left(-\mathrm{P{=}Sn}\langle\right)^{1,2}$ as well as to those between phosphorus and germanium $\left(-\mathrm{P{=}Ge}\langle\right)^{2,3}$. However, even with a large excess of disulfides the complete cleavage of the $-\mathrm{P{=}Ge}\langle$/$-\mathrm{P{=}Sn}\langle$ bond was not observed. On the other hand dimethyldisulfide is known to undergo desulfurization by diphosphene (—P=P—).[4]

It seemed to be of interest to study the interaction of disulfides with C—N,N-dialkylaminosubstituted phosphaalkenes, which are different from other phosphaalkenes by specific reactivity.[5,6]

We have found that prolonged heating of disulfides with C—N,N-dimethylaminomethylene-P-phenylphosphine **1a** resulted in the complete cleavage of the P=C double bond and formation of S,S-dialkylphenyldithiophosphonites 2.[7]



(1a) R=H

(2a–c)

(3a–c)

R^1 = Me (a), Et (b), $PhCH_2$ (c)

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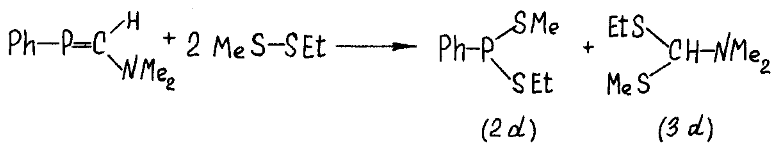
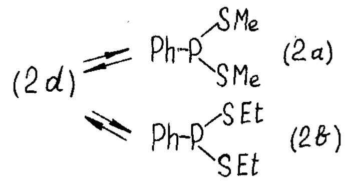
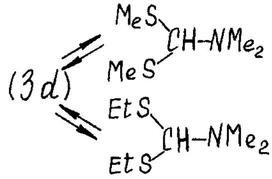
† To whom correspondence should be sent.

With asymmetrical methylethyldisulfide, an equilibrium mixture of S,S-dialkylphenyldithiophosphonites and amidacetals is formed.





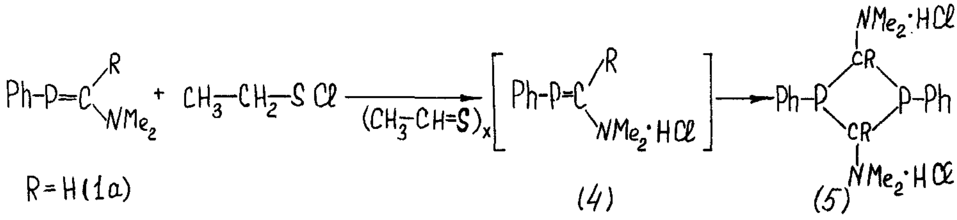


In ^{31}P-NMR spectra of **2a+b+d** signals of **2a** at 80.8 ppm, of **2d** at 7.64 ppm, and of **2b** at 73.6 ppm in ratio of 1:2:1 are observed. In the electron-impact mass spectra for **2a+b+d** there are peaks of the corresponding molecular ions with m/e 202, 216, and 230, respectively. In the mass spectrum of the reaction mixture of phosphaalkene **1a** and methyldisulfide peaks of molecular ions of all three isomeric amidacetals **3a, 3d**, and **3b** with m/e 151, 165, and 179, respectively, are present.

We failed, however, to detect the desulfurization products of disulfides by phosphaalkene **1a**. Therefore, the reaction of disulfides with C—N,N-dimethylaminomethylene-P-phenylphosphine **1a** seems to proceed with complete cleavage of the P=C double bond under such severe conditions.

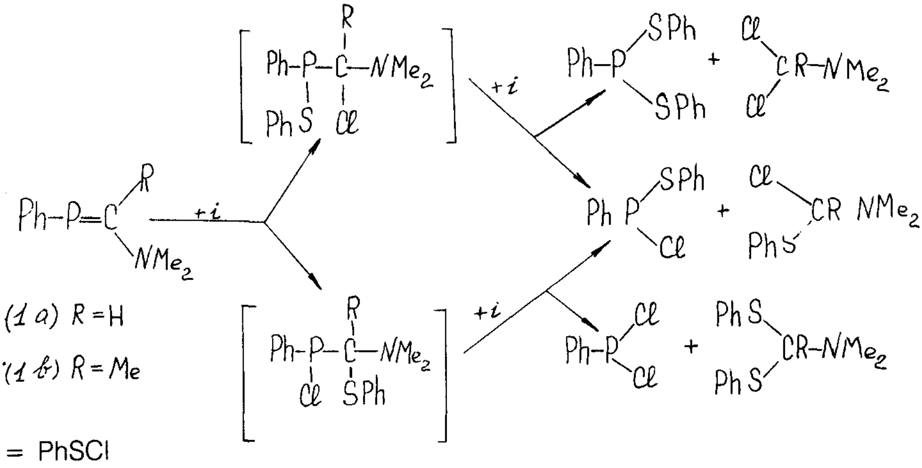
M. Regitz et al.[8] and A. Schmidpeter et al.[9] have shown that sulfenylchlorides are added to the P=C double bond of 1,2,3-diazaphospholes to form unstable adducts containing carbon-sulfur and chlorine-phosphorus bonds. Regiochemistry of addition of sulfenylchloride to such type of compounds with two-coordinated phosphorus is consistent with polarization of the P=C double bond according to the difference in electronegativities of participating atoms. On the other hand, C—N,N-dialkylaminosubstituted phosphaalkenes are known to have an alternative polarization of the P=C double bond.[10] Therefore one can expect the reverse order for adding sulfenylchlorides to these particular phosphaalkenes.

We carried out a reaction of ethyl sulfenylchloride with phosphaalkene **1a**. The reaction has led, however, to a dimer of **1a** in its bis(hydrochloride) form **5**.



Coordination of HCl with the nitrogen rather with the phosphorus atoms is verified by the absence of the direct coupling constant $^1J_{PH}$ (usually in the range of 200–1000 Hz) in the ^{31}P nmr spectrum of **5** along with the presence in its IR spectrum of the vibrational absorption of $R_3NH^+Cl^-$ in the region of 2250–2400 cm^{-1} with the maximum at 2380 cm^{-1}. In the mass spectrum of **5** there are molecular peaks both of the phosphaalkene **1a** with m/e 165 and of HCl with m/e 37, which are characteristic of the electron-impact spectra of the **1a** ammonium salts. All these facts allowed us to suggest that the reaction studied proceeds via dehydrochlorination of ethyl sulfenylchloride by the dimethylamino group of **1a** and transient formation of the corresponding ammonium salts **4**. Since the nitrogen atoms in **4** are unable to take part in conjugation with and, hence, in thermodynamical stabilization of the —P=C< fragment, the latter appears to be forced to dimerize to give **5**.

In order to avoid the processes of dehydrochlorination we replaced alkyl sulfenylchlorides by phenyl sulfenylchloride. The reaction proceeds exothermally to give a complex mixture of products and needs for its completion the molar ratio of phosphaalkene to sulfenylchloride as 1:2.



i = PhSCl

Similarly to reactions with disulfides this reaction is found to result in complete cleavage of the P=C double bond. The proportion of final products depends on the substituent R in phosphaalkene, the nature of solvent and reaction conditions. Thus, with **1a** R=H, S,S-diphenyl-P-phenyldithiophosphonite **6** is found to be the major phosphorus-containing reaction product, while S-phenyl-P-phenylthiophosphonous chloride **7** is formed in minor quantities. According to the ^{31}P NMR spectral data, the proportion of **6** to **7** in the reaction mixture varies from 6:1 to 7:1, with no phenyldichlorophosphine **8** being detected. In the case of **1b** R=Me, compound **7** becomes the major reaction product, while compound **6** turns into the minor one. The proportion of **7** to **6** varies from 28:1.5 (phosphaalkene is added to phenyl sulfenylchloride with ether—CH_3CN, 1:1, as solvent) to 3:2.4 (the reverse order of mixing reagents in CH_3CN); besides, phenyldichlorophosphine **8** appears in trace quantities. It can also be concluded from ^{31}P NMR spectra, that addition of PhSCl to **1b** proceeds rather stereospecifically since the compound **7** formed consists mainly (13:1) of one stereoisomer with the chemical shift δ ^{31}P = +138.8 ppm; the minor stereoisomer has a chemical shift δ ^{31}P = +137.8 ppm.

EXPERIMENTAL

^{31}P and ^{1}H NMR spectra were recorded on Bruker M-250 and on Varian T-60 spectrometers, respectively. The electron-impact mass spectra were measured with an MX-1310 mass-spectrometer, μ = 70 eV. IR spectra were measured on UR-20 spectrophotometer.

S,S-Dimethylphenyldithiophosphonite **2a**. A mixture of 2.0 g (0.012 mol) of **1a** and 2.28 g (0.024 mol) of dimethyldisulfide in 30 ml benzene was refluxed for 72 hours. After removing solvent and other low-boiling compounds under the ambient conditions, the residue was distilled in vacuum to give 1.4 g (53%) of **2a**, b.p. 72°C/10^{-2} mm. PMR spectrum (δ, TMS): δ 2.10 (doublet, $^{3}J_{PH}$ 9.6 Hz, 6H, SMe), δ 6.74–7.43 (multiplet, 5H, pH). ^{31}P NMR spectrum: +80.8 ppm. M/e 202. Found: P 14.7. $C_8H_{11}PS_2$. Calc.: P 15.34.

S,S-Diethylphenyldithiophosphonite **2b**. 3.5 (0.021 mol) of **1a** and 5.7 g (0.047 mol) of diethyldisulfides in 10 ml of benzene were refluxed for 84 hours. After removal of the volatile components in vacuum of the water-pump the residue was fractionated to give 2.78 g (57%) of **2b** with b.p. 95–97°C/10^{-2} mm. ^{31}P NMR spectrum: +73.6 ppm (lit. 75 ppm).[11] Found: P 12.90. $C_{10}H_{15}PS_2$. Calc.: P 13.47.

S,S-Dibenzylphenyldithiophosphonite **2c**. 2.5 g (0.015 mol) of **1a** and 8.20 g (0.033 mol) of dibenzyldisulfide in 10 ml benzene were refluxed for 84 hours. The precipitated crystals were filtered and washed with ether. Yield of **2c** is 1.8 g (34%), m.p. 63–65°C (lit., m.p. 65°C).[11] ^{31}P NMR spectrum: +74.11 ppm (lit., δ ^{31}P 76 ppm).[11]

Reaction of **1a** *with methylethyldisulfide* **2a+b+d**. 1.8 g (0.11 mol) of **1a** and 3.53 g (0.033 mol) of methylethyldisulfides in 10 ml of benzenes were refluxed for 72 hours. The solvent and low-boiling components were removed under vacuum of the water-pump, and the residue was fractionated to afford 1.46 g (62%) of **2d** with b.p. 85–89°C/10^{-2} mm. ^{31}P NMR spectrum: +80.8, 76.4, 73.6 ppm in the ratio of 1:2:1. Found: P 13.98. $C_9H_{13}PS_2$. Calc.: P 14.35.

2,4-Dimethylammonia-1,3-diphenyl-1,3-diphosphetane dihydrochloride **5**. 2.6 g (0.027 mol) of ethyl sulfenylchloride were added dropwise to 4.4 g (0.027 mol) of **1a** in 10 ml of benzene, with an exothermal reaction occurring. After removal of the low-boiling components under vacuum, the residue was recrystallised from CH_3CN-ether, 1:1, to give 2.3 g (42%) of **5**, m.p. 171–172°C. ^{31}P NMR spectrum: +3.8 ppm (DMSO). Found: N 6.9. $C_{16}H_{20}N_2Cl_2P_2$. Calc.: N 7.0.

Reaction of **1a** *with phenyl sulfenylchloride*. 2.2 g (0.012 mol) of **1a** were added dropwise to 6.4 g (0.052 mol) of phenyl sulfenylchloride in 15 ml CH_3CN at 0°C. After the exothermal reaction is completed, the precipitated crystals were filtered off and recrystallized from CH_3CN to afford 1.25 g (73%) of dimethylaminochloromethane, m.p. (in a sealed capillary) 140°C (lit., m.p. 140–145°C).[12] Found: N 11.23. $C_3H_7NCl_2$. Calc.: N 10.93. The combined filtrate was distilled to give 2.04 g (47%) of **6** with b.p. 146–147°C/10^{-2} mm (lit., b.p. 200–203°C/0.04 cm).[13] ^{31}P NMR spectrum: +90.0 ppm (lit., δ ^{31}P 90 ppm).[13] Found: P 8.80. $C_{18}H_{15}PS_2$. Calc.: P 9.52.

Reaction of **1b** *with phenyl sulfenylchlorides*. 3.55 g (0.024 mol) of phenyl sulfenylchloride were added dropwise to 2.2 g (0.012 mol) of **1b** in 10 ml of CH_3CN with an exothermal reaction being observed. The reaction mixture was then removed from the resin formed and fractionated to give 0.8 g (20%) of **6** with b.p. 146–147°C/10^{-2} mm (lit., 200–203°C/0.04 mm).[13] ^{31}P NMR spectrum: 90.0 ppm (lit., δ ^{31}P = 90 ppm).[13]

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