BRIEF COMMUNICATIONS

[1 + 2] ADDITION OF DISULFIDES TO PHOSPHAALKENES

A. S. Ionkin, N. V. Nikolaeva, V. M. Nekhoroshkov, UDC 542.955:547.279.3:547.1'118 Yu. Ya. Efremov, and B. A. Arbuzov

We are the first to report the [1 + 2] addition of disulfides to phosphaalkenes in the case of C-(N,N-dimethylaminomethylene)-P-phenylphosphine (I) and dimethyl disulfide (II). This reaction proceeds with the complete cleavage of the P-C double bond and the addition of two equivalents of the disulfide.

Halogens [1] and acids [2] undergo [1 + 2] addition to the P-C double bond of phosphaalkenes. In the reaction of disulfides with phosphaalkenes, we would expect desulfurization reactions, which are common in the reactions of trivalent phosphorus compounds with disulfides [3]. We are the first to report the reaction of disulfides with phosphaalkenes in the case of C-(N,N-dimethylaminomethylene)-P-phenylphosphine (I) and dimethyl disulfide (II).

$$\begin{array}{c|c} Ph-P=CH-NMe_{2}+MeS-SMe \\ \hline (I) & (II) \end{array} \xrightarrow[\left(\begin{array}{c} Ph-P-CH-NMe_{2}\\ I \\ MeS \\ (III) \end{array}\right) \xrightarrow[\left(\begin{array}{c} Ph-P-CH-NMe_{2}\\ I \\ MeS \\ (III) \end{array}\right) \xrightarrow[\left(\begin{array}{c} Ph-P-CH-NMe_{2}\\ I \\ MeS \\ (IV) \\ (IV) \\ (V) \end{array}\right) \xrightarrow[\left(\begin{array}{c} SMe \\ MeS \\ MeS \\ (V) \\ ($$

A (I):(II) ratio equal to 2:1 and prolonged heating are required for completion of this reaction. Desulfurization does not proceed under these conditions and disulfide (II) undergoes [1 + 2] addition to the P=C double bond. The specific characteristics of C-(N,N-dialkylamino)phosphaalkenes are also evident. The reaction does not stop upon the addition of one equivalent of disulfide, but rather proceeds with complete cleavage of the P=C double bond and formation of bis(methylthio)phosphite (IV) and bis(methylthio)dimethyl-aminomethane (V). The electron impact mass spectrum of the reaction mixture shows molecular ion peaks for (IV) with m/z 202 and (V) with m/z 151. The ³¹P NMR spectrum of the reaction mixture shows a peak for (IV) at 81.2 ppm. Intermediate (III) could not be detected. The addition of the first equivalent of disulfide is apparently the rate-limiting step of this reaction.

EXPERIMENTAL

The ³¹P NMR spectra were taken on a Bruker 250 spectrometer, while the PMR spectra were taken on a Varian T-60 spectrometer at 34.6°C. The mass spectra were taken on an MKh-1310 spectrometer with precision measurement of the ion masses and their elemental analysis, $\mu = 60$ V. All the operations were carried out in an argon atmosphere.

A mixture of 2.0 g (0.012 mole) (I) and 2.28 g (0.024 mole) (II) in 30 ml benzene was heated at reflux for 72 h. The solvent and other volatile components were removed under atmospheric pressure and the residue was distilled, collecting the fraction with bp 72°C (0.01 mm). The yield of (IV) was 1.4 g (53%). PMR spectrum relative to TMS (δ , ppm): 2.10 d (6H, S-CH₃, ³J_{PH} = 9.6 Hz), 6.74-7.43 m (5H, Ph). The ³¹P NMR spectrum of this fraction displays a signal at 81.2 ppm, while the electron impact mass spectrum features a molecular ion peak with m/z 202. Found: P, 17.1%. Calculated for C₈H₁₁PS₂: P, 17.4%.

LITERATURE CITED

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A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 186-187, January, 1991. Original article submitted February 5, 1990.