HYDROBORATION OF P-PHENYL-C, C-BIS(TRIMETHYLSILYLTHIO)METHYLENEPHOSPHINE

A. S. Ionkin, S. N. Ignat'eva,V. M. Nekhoroshkov, Yu. Ya. Efremov,and B. A. Arbuzov

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P-Phenyl-C,C-bis(trimethylsilylthio)methylenephosphine is hydroborated with dicyclohexylborane, with the hydroboration product undergoing spontaneous  $\beta$  elimination with the formation of trimethylsilylthio(dicyclohexyl)borane and P-phenyl-C-trimethylsilylthiomethylenephosphine.

Earlier we showed that dialkylamino and trimethylsiloxy groups at a carbon atom of phosphaalkenes exhibit a strong directional effect in the hydroboration reaction, causing the insertion of a boron atom in the  $\beta$  position (i.e., attack on the phosphorus atom of the phosphaalkene) [1, 2]. The products of hydroboration of C-heterosubstituted phosphaalakenes undergo  $\beta$  elimination, with the products obtained from C-dialkylamino-substituted phosphaalkenes being more stable than those obtained from C-trimethylsiloxy-substituted phosphaalkenes, which makes it possible to carry out certain reactions of insertion at the P-B bond [3, 4].

We have investigated the effect of the thio substituent on the carbon in a phosphaalkene on the direction of the hydroboration and ease of  $\beta$  elimination. For this purpose we chose P-phenyl-C,C-bis(trimethylsilylthio)methylenephosphine (I), which is stable at ~20°C [5]. However, during synthesis of (I) we found that (I) easily dimerizes at ~20°C with the formation of the corresponding 1,3-diphosphetane (chemical shift (CS)  $\delta^{31}$ P 102 ppm). The appearance of the CS of 1,3-diphosphetane in the low-field region is possible because of the effect of the four trimethylsilylthio groups in the ring. The analogous 1,3-dimethyl-2,2,4,4-tetrakis(trimethylsilylthio)-1,3-diphosphetane has CS  $\delta^{31}$ P = 106.4 ppm [6].

Dicyclohexylborane was selected as the hydroborating reagent, since it can react with unstable phosphaalkenes that are obtained in the process of  $\beta$  elimination of the products of hydroboration of C-(N,N-dialkylamino)- and C-trimethylsiloxy-substituted phosphaalkenes [1, 2].

For complete  $\beta$ -elimination ( $\beta$ -EL) of two trimethylsilylthic groups and trapping of the resulting P-phenylmethylphosphine we used a phosphaalkene:borohydride ratio of 1:3



The product of hydroboration of (II) could not be detected spectrally. It easily breaks down by  $\beta$ -elimination with the formation of trimethylsilylthio(dicyclohexyl)borane (III) and unstable P-phenyl-C-trimethylsilylthiomethylenephosphine (IV).

Trimethylsilylthio(dicyclohexyl)borane (III) was isolated by distilling the reaction mixture in the form of an easily hydrolyzed liquid with typical mercaptan odor. The mass spectrum of (III) upon electron impact (precision measurement of ion masses, elemental analysis) exhibits a peak of a molecular ion with m/z 282, and also peaks of the fragments  $C_6H_{11}B$ -S-SiMe<sub>3</sub>,  $C_6H_{11}$ , and  $C_6H_{10}$ . Because of the high sensitivity of analogous compounds

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. 9, pp. 2127-2129, September, 1990. Original article submitted July 28, 1989. to hydrolysis, (III) was hydrolyzed and characterized in the form of the dicyclohexylboric acid [7].

P-Phenyl-C-trimethylsilylthiomethylenephosphine (IV), because of insufficient steric capacity of the molecule, is unstable and polymerizes, and it cannot be caught by an excess of dicyclohexylborane. The <sup>31</sup>P NMR spectrum of the reaction mixture after completion of the reaction contains a group of signals from 78 to 54 ppm that relate to polymer (IV). The PMR spectrum of polymer (IV), which remains in the bottom part from distillation of the reaction mixture, contains besides the cyclohexyl protons from the excess dicyclohexylborane, signals of phenyl and trimethylsilylthio groups in a 5:9 ratio.

Since the <sup>31</sup>P NMR spectrum of the reaction mixture does not have any signals in the high field that might correspond to products with P-H bonds that are obtained as a result of the alternative direction of the hydroboration reaction, it can be concluded that the trimethylsilylthic groups direct the boron atom to the  $\beta$  position during hydroboration of (I).

## EXPERIMENTAL

The <sup>31</sup>P NMR spectra were recorded on a Bruker M-250 spectrometer, the PMR spectra were recorded on a Varian T-60 spectrometer. Mass spectra were obtained on an MX-1310 mass spectrometer. All operations were conducted in argon.

To 7.0 g (21.2 mmoles) P-phenyl-C,C-bis(trimethylsilylthio)methylenephosphine (I) in 10 ml THF was added 11.3 g (63.6 mmoles)dicyclohexylborane at 0°C. The reaction mixture was boiled for 6 h, in which time the dicyclohexylborane dissolved. Then the reaction mixture was distilled, collecting trimethylsilylthio(dicyclohexyl)borane (III), bp 86°C ( $10^{-3}$ mm Hg). Yield 4.3 g (72%). PMR spectrum ( $\delta$ , ppm, TMS): 0.37 s (9H, SiMe<sub>3</sub>), 1.2-2.1 m (22H, C<sub>6</sub>H<sub>11</sub>B). (III) was hydrolyzed to dicyclohexylboric acid with mp 54°C (see [7]).

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