- 2. S. Forsen, F. Mereniy, and M. Nilsson, Acta Chem. Scand., 18, 1208 (1964).
- A. K. Grinval'de, É. Ya. Gren, and Ya. P. Stradyn', Izv. Akad. Nauk Latv. SSR, Ser. Khim., 311 (1971).
- 4. M. J. S. Dewar, E. G. Zoebisch, and J. J. R. Stewart, J. Am. Chem. Soc., <u>107</u>, 3902 (1985) and references therein.
- S. L. Baughcum, Z. Smith, E. B. Milson, and R. M. Duerst, J. Am. Chem. Soc., <u>103</u>, 6296 (1981); <u>106</u>, 2260 (1984).
- J. Bicerano, H. F. Schaefer, III, and W. H. Miller, J. Am. Chem. Soc., <u>105</u>, 2550 (1983).
- 7. A. V. Iogansen, in: The Hydrogen Bond [in Russian], Nauka, Moscow (1981), p. 149.
- V. V. Gromak, V. Z. Kurbako, and N. I. Garbuz, Abstracts of the 20th Spectroscopy Conference [in Russian], Part 1, Kiev (1988), p. 433.
- 9. V. A. Shagun, V. F. Sidorkin, V. A. Usov, and M. G. Voronkov, Izv. Akad. Nauk SSSR, Ser. Khim., 1747 (1981).

## REACTION OF PHENYL AZIDE WITH N, N-DIMETHYL-

## AMINOMETHYLENEPHENYLPHOSPHINES

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Phenyl azide reacts with N,N-dimethylamino-P-phenylmethylenephosphines with cleavage of the phosphorus-carbon double bond and formation of the dimer of diiminophosphorane and amidines.

Azides undergo the Staudinger reaction with dicoordinated phosphorus compounds with the formation of iminophosphoranes and [3 + 2]-cycloaddition products [1]. We studied the reaction of N,N-dimethylamino-P-phenylmethylenephosphine (Ia) and N,N-dimethylamino-P-phenyl-C-methylmethylenephosphine (Ib) with phenyl azide. The reaction of (Ia) with phenyl azide was carried out with mole ratios of 1:1, 1:2, and 1:3. The reaction was monitored by electron impact mass spectrometry.



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. 10, pp. 2381-2382, October, 1989. Original article submitted March 10. 1989. When the (Ia): phenyl azide ratio was 1:1 and 1:2, the mass spectra showed molecular peaks for N,N-dimethyl-N'-phenylformamidine (m/z 148) and molecular peak of unreacted (Ia) (m/z 165). Intermediates (II) and (III) could not be detected. Apparently, (II) and (III) are more reactive in the reaction with phenyl azide than starting (Ia).

When the (Ia):phenyl azide mole ratio is 1:3, the reaction led only to (V) and 1,3-diphenyl-2,4-di(phenylimino)-1,3-diaza-2,4-diphosphetidine (VI), which is formed due to dimerization of unstable diminophosphorane (IV). Reaction (Ib) with phenyl azide was carried out only with 1:3 mole ratio and led to analogous results.

## EXPERIMENTAL

The <sup>31</sup>P NMR spectra were measured on KGU-4 and Bruker WM-250 spectrometers. The IR spectra were taken on a UR-20 spectrometer. The mass spectra were taken on an MKh-1310 mass spectrometer with precision determination of the ion masses,  $\mu$  60 V.

Reaction of Phenyl Azide with (Ia). A solution of 8.69 g (73 mmoles) PhN<sub>3</sub> in 10 ml absolute ether was added dropwise with stirring and ice cooling to a solution of 4.02 g (24.3 mmoles) (Ia) in 10 ml absolute ether. The reaction mixture was then heated for 2 h. The crystalline precipitate was filtered off and washed with ether to give 3.5 g (50%) (VI), mp 233°C,  $\delta$  <sup>31</sup>P 17 ppm (DMF). Found: C, 74.59; H, 5.60; N, 9.59; P, 10.51%. Calculated for C<sub>18</sub>H<sub>15</sub>PN<sub>2</sub>: C, 74.48; H 5.17; N 9.65; P 10.68%. The molecular weight determined ebullioscopically in benzene was 597 (calc. 580). After separation of the crystals, the filtrate was distilled in vacuum, collecting the fraction with bp 78-80°C (0.1 mm). The yield of (Va) was 2.8 g (78%), n<sub>D</sub><sup>20</sup> 1.5942 (see the work of Bredereck [2]). Found: N, 18.91%. Calculated for C<sub>g</sub>H<sub>12</sub>N<sub>2</sub>: N, 18.9%.

Reaction of Phenyl Azide with (Ib). A solution of 6.38 g (53.6 mmoles) PhN<sub>3</sub> in 10 ml ether was added dropwise with stirring and ice cooling to a solution of 3.2 g (17.8 mmoles) (Ib) in 8 ml absolute ether. The reaction mixture was heated on a water bath at reflux for 4 h. The crystalline precipitate was filtered off and washed with ether to give 2 g (40%) (VI), mp 233°C,  $\delta$  <sup>31</sup>P 17 ppm (DMF). IR and PMR spectral analysis indicated that this sample was identical to that obtained in the previous experiment. After separation of the crystals, the filtrate was distilled in vacuum, collecting the fraction with bp 80°C (10<sup>-3</sup> mm). The yield of (Vb) was 2.5 g (85%),  $n_D^{20}$  1.5772 (see the work of Bredereck [2]).

## LITERATURE CITED

- T. A. Vonderknaap, T. C. Klebach, E. Visser, et al., Tetrahedron, <u>40</u>, No. 6, 991 (1984).
- 2. H. Bredereck, R. Gompper, K. Klemm, and H. Rempfer, Chem. Ber., 92, 837 (1959).