## NITRATION OF ALKENYLPHOSPHONATES WITH NITROGEN TETRAOXIDE

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The nitration of alkenylphosphonates with various nitrating agents can be considered to be the most promising method for the synthesis of phosphorus-containing nitro compounds. The only methods known up to now are the nitration of aromatic phosphorus-containing compounds with nitric acid [1-6] and the addition of cyanogen chloride to alkenylphosphonates [7]. We were able to synthesize some O,O-dialkyl 1-hydroxy-2-nitroethylphosphonates by the nitration of alkenylphosphonates with N<sub>2</sub>O<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature.

 $\begin{array}{c} R'CH=CHP\;(OR)_2+N_2O_4\rightarrow R'CH-CH-P-(OR)_2\\ \parallel\\ O\\ R'=H,\;R=\mathit{i-C_3H_7}(I);\;R'=H,\;R=CH_2CH_2CI\;(II);\;R'=C_6H_5,\;R=CH_3\;(III) \end{array}$ 

After removal of the solvent, the reaction mixture, except the crystalline organophosphorus nitro alcohols, contained a tarry colored product that could not be removed from the pure compound even by column chromatography. The IR spectra of the obtained nitro alcohols resembled those of the adducts that were synthesized previously from nitroalkanes and acylphosphonates [8].

## EXPERIMENTAL

<u>O,O-Diisopropyl 1-Hydroxy-2-nitroethylphosphonate (I).</u> To 5.7 g of diisopropyl vinylphosphonate in 15 ml of dry CH<sub>2</sub>Cl<sub>2</sub> at 0°C was added in drops a solution of 2.8 g of N<sub>2</sub>O<sub>4</sub> in 10 ml of dry CH<sub>2</sub>Cl<sub>2</sub>. The mixture was held at ~ 20° for 3-5 h and then 5 ml of methanol was added. The reaction mixture was washed in succession with 3% Na<sub>2</sub>CO<sub>3</sub> solution and water, and then dried over MgSO<sub>4</sub>. Removal of the solvent gave 3.8 g (50%) of (I) with mp 94-95° (from a 2:1 CCl<sub>4</sub>-hexane mixture). Found: C 37. 8; H 7.2; N 5.7; P 12.2%. C<sub>8</sub>H<sub>18</sub>NO<sub>6</sub>P. Calculated: C 37.6; H 7.1; N 5.5; P 12.1%. Infrared spectrum ( $\nu$ , cm<sup>-1</sup>): 990 (P-O-C), 1243 (P=O), 1380 and 1565 (NO<sub>2</sub>), 3260 very broad (OH).

O,O-Di( $\beta$ -chloroethyl) 1-Hydroxy-2-nitroethylphosphate (II). The same as the preceding, from 23.3 g of O,O-di( $\beta$ -chloroethyl) vinylphosphonate and 9.2 g of N<sub>2</sub>O<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> we obtained 11.8 g (40%) of (II), mp 87-88° (from a 2:1 CHCl<sub>3</sub>-hexane mixture). Found: C 24.4; H 4.0; N 4.9; P 10.6%. C<sub>6</sub>H<sub>12</sub>Cl<sub>2</sub>NO<sub>6</sub>P. Calculated: C 24.4; H 4.1; N 4.8; P 10.4%. Infrared spectrum ( $\nu$ , cm<sup>-1</sup>): 1032 (P-O-C), 1275 (P=O), 1375 and 1560 (NO<sub>2</sub>), 3250 v. br. (OH).

<u>O,O-Dimethyl 1-Hydroxy-2-nitro-2-phenylethylphosphonate (III)</u>. From 13.7 g of O,O-dimethyl 2-phenylvinylphosphonate and 4.6 g of N<sub>2</sub>O<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> we obtained 5.4 g (30%) of (III), mp 104-105° (from a 2:1 CHCl<sub>3</sub>hexane mixture). The product was isolated by column chromatography on silicic acid. Found: C 43.6; H 5.1; N 5.1; P 11.4%. C<sub>10</sub>H<sub>14</sub>NO<sub>6</sub>P. Calculated: C 43.6; H 5.1; N 5.1; P 11.3%. Infrared spectrum ( $\nu$ , cm<sup>-1</sup>): 1045 (P-O-C), 1260 (P=O), 1370 and 1560 (NO<sub>2</sub>), 3350 v. br. (OH).

## CONCLUSIONS

A new method was developed for the synthesis of organophosphorus nitro compounds, which consists in the direct nitration of alkenylphosphonates with  $N_2O_4$ .

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- 1. A. Michaelis and E. Benzinger, Ber., 8, 500 (1873).
- 2. L. D. Freedman and G. O. Doak, J. Am. Chem. Soc., 77, 6221 (1955).
- 3. L. D. Freedman and G. O. Doak, Chem. Rev., 57, 479 (1957).
- 4. A. Michaelis, Ann. Chem., 293, 193 (1896).
- 5. C. Dörker, Ber., 21, 1505 (1888).
- 6. L. A. Rapp, Ann. Chem., 224, 156 (1884).
- 7. S. Z. Ivin and V. K. Promonenkov, Zh. Obshch. Khim., Supplement "Chemistry of Organophosphorus Compounds" [in Russian], Nauka, Leningrad (1967), p. 142.
- 8. T. A. Mastryukova, G. M. Baranov, V. V. Perekalin, and M. I. Kabachnik, Dokl. Akad. Nauk SSSR, 171, 1341 (1966).

BENZOPHENONE-SENSITIZED PHOTOREDUCTION OF METAL IONS AND OXIDATION OF ALCOHOLS TO GIVE MOLECULAR HYDROGEN

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The photochemical preparation of hydrogen offers much promise from the standpoint of converting light energy into chemical energy. The continuous photoformation of hydrogen in protic solvents can be achieved by photogeneration in a system where the reducing agent has a quite low redox potential [1].

In the present paper it was shown that the benzophenone-sensitized photoliberation of hydrogen is possible, which occurs as the result of the photoreduction of transition metal ions ( $V^{3+}$ ,  $Cr^{3+}$ ,  $Eu^{3+}$ ), whose oxidation-reduction potential is more negative than that of hydrogen ( $E^0 = -0.255$ , -0.41, and -0.43 respectively) [1]. Benzophenone, which is used as the sensitizer, in the electron-excited triplet state is easily reduced in alcohol solutions, where it dehydrogenates the solvent and forms ketyl radicals in a high quantum yield [3]. It may be assumed that the ketyl radicals are characterized by a high reduction capacity, since the polarographic reduction of benzophenone in the dark proceeds at a quite negative potential ( $E_{1/2}$  satd. calomel electrode = -1.3 V at pH 7 [4]).

Actually, the irradiation of ethanol and isopropanol solutions of benzophenone that contain VCl<sub>3</sub> at the absorption band of benzophenone ( $\lambda$  365 nm) leads to a change in the absorption spectrum of the solution in the region of the d<sup>-d</sup> transitions of the V<sup>3+</sup> ions, which indicates their reduction [1]. The irradiation of these solutions in the presence of small amounts of Adams Pt results in the continuous liberation of H<sub>2</sub>. The kinetic curves for the accumulation of H<sub>2</sub> in the reaction vessel are given in Fig. 1. The induction period can be explained by the activation of the catalyst (PtO<sub>2</sub>). The photoformation of hydrogen is also observed when alcohol solutions of benzophenone, containing CrCl<sub>3</sub> or EuCl<sub>3</sub>, are illuminated. In the absence of Pt catalyst the H<sub>2</sub> liberation is comparatively slight and is caused by the light-initiated reaction of the divalent ions with the protons of the medium [1]. The measured quantum yields of H<sub>2</sub> in alcohol solutions of benzophenone under continuous photolysis conditions are given in Table 1. Chromatographic analysis of the irradiated ethanol and isopropanol solutions disclosed the respective accumulation of acetaldehyde and acetone during photore-action. Starting with the obtained data, the following sequence of reactions can be proposed:

 $\begin{array}{l} (C_{6}H_{5})_{2}C=O\xrightarrow{h^{\nu}}(C_{6}H_{5})_{2}C=O^{*}\\ (C_{6}H_{5})_{2}C=O^{*}+CH_{3}RCHOH\rightarrow(C_{6}H_{5})_{2}COH+CH_{3}RCOH\\ (C_{6}H_{5})_{2}COH+M^{3+}\rightarrow(C_{6}H_{5})_{2}C=O+M^{2+}+H^{+}\\ CH_{3}RCOH+M^{3+}\rightarrow CH_{3}RCO+M^{2+}+H^{+}\\ 2M^{2+}+2H^{+\frac{PtO_{2}}{2}}2M^{3+}+H_{2}\\ M=V,\ Cr,\ Eu;\ R=H,\ CH_{3}\end{array}$ 

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