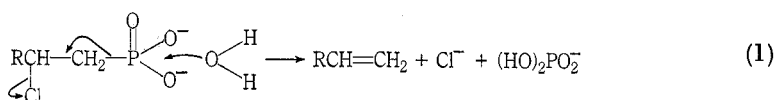


## ORGANOPHOSPHORUS COMPOUNDS\*

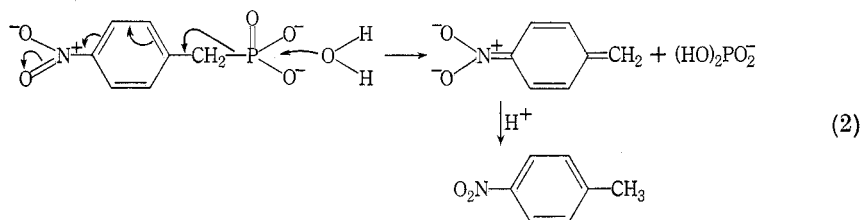
### III. THE DECOMPOSITION OF *p*-NITROBENZYLPHOSPHONIC ACID IN ALKALI†

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In Part I of this series,<sup>1</sup> it was shown that 2-chloroalkylphosphonic acids decompose rapidly in neutral or alkaline solution giving an alk-1-ene and chloride and phosphate ions, and the mechanism shown in equation (1) was suggested.



On the basis of this mode of decomposition, the 2-chloroalkylphosphonic acids were developed as phosphorylating agents for alcohols and phenols.<sup>1</sup> It seemed possible that *p*-nitrobenzylphosphonic acid<sup>2</sup> might also decompose in alkali with fission of a carbon-phosphorus bond (eqn. (2)) and might likewise be a potential phosphorylating agent.



The expected decomposition was in fact observed, but occurred only at a slow rate. When the acid was heated at 72°C in a five-fold excess of 0.002*N* sodium hydroxide, the extent of decomposition was 25% after 3 hr and around 90% after 72 hr. A similar rate was observed for decomposition by 0.1*N* sodium hydroxide. *p*-Nitrotoluene was isolated from the reaction, together with traces of 1,2-di(*p*-nitrophenyl)ethane, probably formed by aerial oxidation of *p*-nitrotoluene.<sup>3-5</sup>

\* Manuscript received March 14, 1963.

† For Part II of this series see reference 6.

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<sup>1</sup> Maynard, Judith A., and Swan, J. M. (1963).—*Aust. J. Chem.* **16**: 596.

<sup>2</sup> Kosolapoff, G. M. (1949).—*J. Amer. Chem. Soc.* **71**: 1876.

<sup>3</sup> Fuson, R. C., and House, H. O. (1953).—*J. Amer. Chem. Soc.* **75**: 1325.

<sup>4</sup> Yohe, G. R., Hill, D. R., Dunbar, J. E., and Scheidt, F. M. (1953).—*J. Amer. Chem. Soc.* **75**: 2688.

<sup>5</sup> Tsuruta, T., Nagatomi, R., and Furukawa, J. (1952).—*Bull. Inst. Chem. Res. Kyoto Univ.* **30**: 47.

Both ethyl hydrogen *p*-nitrobenzylphosphonate, prepared by alkaline hydrolysis of the diethyl ester, and *p*'-chlorophenyl hydrogen *p*-nitrobenzylphosphonate, prepared from the acid by the dicyclohexylcarbodi-imide method<sup>6</sup> were found to be stable to prolonged heating in alkali. An attempt to phosphorylate ethanol by heating a solution of *p*-nitrobenzylphosphonic acid in ethanol containing cyclohexylamine was unsuccessful, the acid being precipitated as its sparingly soluble cyclohexylammonium salt.

### Experimental

*p*-Nitrobenzylphosphonic acid, m.p. 223–226°C, was prepared according to Kosolapoff<sup>2</sup> by nitration of diethyl benzylphosphonate followed by acid hydrolysis of the ethyl ester groups. Hydrolysis of the diester in ethanolic KOH gave *ethyl hydrogen p*-nitrobenzylphosphonate, m.p. 157.5–158.5°C (Found: C, 44.2; H, 5.0; N, 5.7; P, 12.6%. Calc. for C<sub>9</sub>H<sub>12</sub>NO<sub>5</sub>P: C, 44.1; H, 4.9; N, 5.7; P, 12.6%). Addition of cyclohexylamine to a solution of *p*-nitrobenzylphosphonic acid in ethanol gave an immediate precipitate of *cyclohexylammonium hydrogen p*-nitrobenzylphosphonate, m.p. 260°C (decomp.) (Found: C, 49.3; H, 6.8; N, 8.7%. Calc. for C<sub>13</sub>H<sub>21</sub>N<sub>2</sub>O<sub>5</sub>P: C, 49.4; H, 6.7; N, 8.9%). The salt was sparingly soluble in ethanol and dissolved slowly in hot 5*N* H<sub>2</sub>SO<sub>4</sub> to regenerate the free acid.

*p*'-Chlorophenyl Hydrogen *p*-Nitrobenzylphosphonate.—*p*-Chlorophenol (0.64 g; 5 mmoles), *NN*'-dicyclohexylcarbodi-imide (4.12 g; 20 mmoles) and *p*-nitrobenzylphosphonic acid (1.08 g; 5 mmoles) were dissolved in anhydrous pyridine (10 ml). The mixture became warm and *NN*'-dicyclohexylurea began to separate. The mixture was allowed to stand overnight and was then diluted with water and allowed to stand for a further 24 hr. The urea was filtered off and the filtrate was acidified giving 1.6 g of *p*'-chlorophenyl hydrogen *p*-nitrobenzylphosphonate, m.p. 174–176°C, after recrystallization from benzene–light petroleum or from acetone (Found: C, 47.5; H, 3.4; Cl, 11.0; N, 4.3%. Calc. for C<sub>13</sub>H<sub>11</sub>ClNO<sub>5</sub>P: C, 47.6; H, 3.4; Cl, 10.8; N, 4.3%). The infrared spectrum in Nujol showed a broad and shallow peak at 2400–2600 cm<sup>-1</sup> (POH), and characteristic bands at 1545m (NO<sub>2</sub>), 1355s (NO<sub>2</sub>), 1230m (PO), and 1195m cm<sup>-1</sup> (POC aromatic).

*Decomposition by Alkali*.—A typical experiment was carried out as follows: the phosphonic acid or half-ester (0.02 mmole) was dissolved in 0.002*N* NaOH (100 ml) and the solution was heated at 72°C. Aliquots were removed at various times, cooled, extracted with iso-octane, and the extracts analysed spectroscopically. In iso-octane, *p*-nitrotoluene has λ<sub>max</sub> 264 mμ, ε = 12,250. Concentration of appropriate extracts gave *p*-nitrotoluene, m.p. 50–51°C (lit.<sup>7</sup> 51.4). In larger-scale experiments the aqueous phase became cloudy due to formation of small amounts of 1,2-di(*p*-nitrophenyl)ethane, identified by m.p. 178–181°C; (lit.<sup>4</sup> gives m.p. 181–182°C) and by infrared spectrum.

<sup>6</sup> Maynard, Judith A., and Swan, J. M. (1963).—*Aust. J. Chem.* **16**: 609.

<sup>7</sup> Holleman, A. F., Vermeulen, J., and De Moody, W. J. (1914).—*Rec. Trav. Chim. Pays-Bas*