CHEMISTRY LETTERS, pp. 2091 - 2092, 1984. © The Chemical Society of Japan 1984

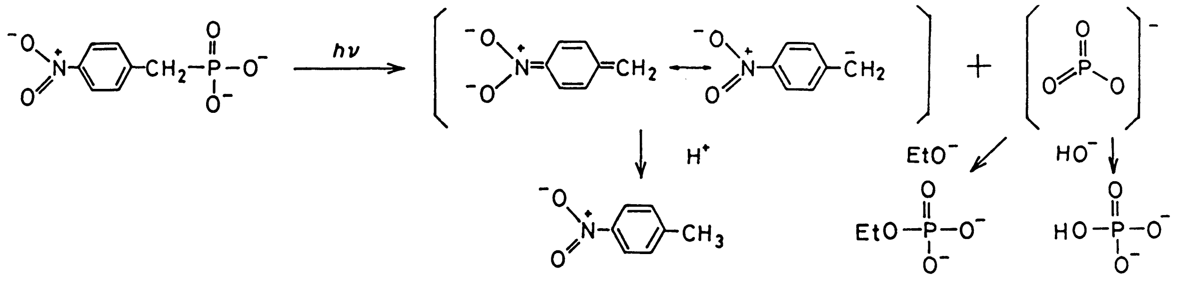
PHOTOCHEMICAL C-P BOND CLEAVAGE OF (p-NITOROPHENYL)METHYLPHOSPHONIC ACID

Yoshiki OKAMOTO,* Narimasa IWAMOTO, and Setsuo TAKAMUKU
The Institute of Scientific and Industrial Research, Osaka University,
8-1 Mihogaoka, Ibaragi, Osaka 567

(p-Nitrophenyl)methylphosphonic acid underwent easily photochemical C-P bond cleavage in alkaline 80% ethanol solution, resulting in the formation of p-nitrotoluene, orthophosphate, and ethyl phophate. In acidic solution, the phosphonic acid was stable on irradiation.

The chemical and thermal stability of C-P bond in free phosphonic acid is well known,$^{1)}$ and chemical reaction involving cleavage of the C-P bond are not commom.$^{2)}$ One of the examples is the decomposition of 2-haloalkylphoshonic acid, whose C-P bond is easily cleaved into the fragments, alkene and monomeric metaphosphate, in basic aqueous solution (Conant-Swan reaction).$^{3)}$ Recently, the photochemical C-P bond homolysis of dialkyl (trichloromethyl)phosphonates, has been reported.$^{4)}$ But, the photochemical C-P bond cleavage of free phosphonic acid has not yet been reported.$^{5)}$ In this communication, we wish to report the results of some preliminary experiments which indicate that the C-P bond cleavage of (p-nitrophenyl)methylphosphonic acid (**1**)$^{6)}$ is remarkably accelerated by light.

In the absence of light, the decomposition of **1** occurred only at slow rate in alkaline solution at room temperature, and trace amounts of p-nitrotoluene could be detected after several weeks. When an aqueous solution of **1** was heated at 72 ^{o}C in large excess of sodium hydroxide, the extent of demcomposition was around 90% after 72 h.$^{7)}$ When the 80% ethanol solution$^{8)}$ of **1** (10 mmol dm^{-3}), adjusted to pH 12 with 10% aqueous solution of sodium hydroxide, was irradiated in nitrogen atmosphere at room temperature through a Pyrex filter, using a 350 W high pressure mercury lamp, the photolysis of 1 was completed within 20 min to afford p-nitrotoluene, orthophosphate, and ethyl phosphate nearly quantitativly. The progress of photolysis of **1** was followed by the determination of amounts of p-nitrotoluene with GC analysis (5% of Silicone OV-17 Chromosorb W, 1 m X 3 mm, 180 ^{o}C). Analysis of phosphorus compounds was directly carried out by ^{31}P nmr spectrometry.$^{9)}$ The signal of phosphorus of dianion of **1** appeared at δ =15.2 ppm as a triplet (J=20 Hz). The signals of phosphorus of the dianions of orthophosphate and ethyl



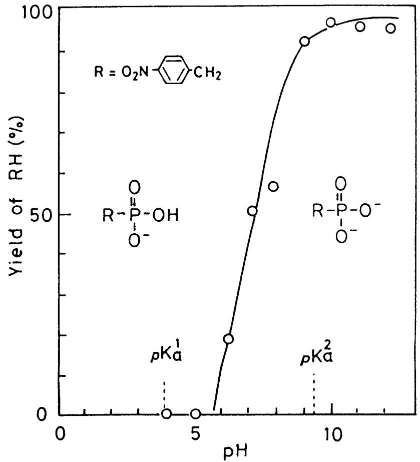


Fig. 1. Effect of pH on the photolysis of 1 in 80% ethanol.

phosphate appeared at δ = 2.5 and 3.5 ppm (triplet J=9,0 Hz), respectively. The ratio of ethyl phosphate/orthophosphate was 0.2. The effect of pH on photolysis of **1** is shown in Fig. 1. In acidic solution, **1** was quite stable on irradiation. This result indicates that the formation of dianion of **1** is necessary for the C-P bond cleavage. We suggest that this process involves probably an unimolecular elimination of the (p-nitrophenyl)methanid via intramolecular electron-transfer from PO_3^{2-} to (p-nitrophenyl)methyl group in the photo-excited state to give monomeric metaphosphate anion. This high reactive metaphosphate anion is immediately captured by nucleophiles to yield orthophosphate or ethyl phosphate. On irradiation, the acid (**1**) behaves as a source of monomeric metaphosphate anion at ambient temperature, and it may be used as a new phosphorylating method.$^{10)}$

References

1) K. Sasse, "Organische Phosphorverbindungen Teil 1," in "Methoden der Organischen Chemie Band XII/1," ed by E. Müller, Georg Thieme, Verlag. Stuttgart (1963), p. 85; L. D. Freedman and G. O. Doak, Chem. Rev., 57, 489 (1957); T. Hori, M. Horiguchi, and A. Hayashi, "Biochemistry of Natural C-P Compounds," Japanese Association for Research on the Biochemistry of C-P Compounds, Otsu (1984), p. 14.

2) Wittig-Horner-Emmons olefination involving cleavage of C-P bond of phosphonic acid dialkyl ester having an adjacent stabilized carbanion are well known; B. J. Walker, "Transformation via Phosphorus-stabilized Anions 2: PO-activated Olefinations," in Organophosphorus Reagents in Organic Synthesis," ed by J. I. G. Cadogan (1979), p. 155.

3) J. A. Mayard and J. M. Swann, Aust. J. Chem., 16, 596 (1963).

4) H. Suzuki, T. Kawai, S. Inoue, N. Sano, and Y. Izawa, Bull. Chem. Soc. Jpn., 53, 1421 (1980).

5) The photochemical reaction involving the cleavage of the P-O bond of 2,4- or 3,5-dinitrophenyl phosphate have been reported; A. J. Kirby and A. G. Vorogilis, J. Chem. Soc., Chem. Commun., 1967, 405.

6) The acid (**1**) was prepared by nitration of (phenylmethyl)phosphonic acid; F. Kagan, R. D. Birkenmeyer, and R. E. Strube, J. Am. Chem. Soc., 81, 3026 (1959): UV_{max} (80% C_2H_5OH, pH 12) 305 nm (ε 10,500), pK^1_a 3.9, pK^2_a 9.3 (80% C_2H_5OH)

7) A. Meistere and J. M. Swan, Aust. J. Chem., 16, 725 (1963).

8) Disodium salt of **1** was hardly soluble in pure ethanol.

9) Phosphorus 31 chemical shifts are expressed in ppm from 85% H_3PO_4, more positive values reflecting lower shildings. Quantitative messurments were carried out on a JNM FX 100 Fourier Transform spectrometer (40.25 MHz), under the conditions of proton decoupling with taking into account the differences in T_1 and nuclear Overhauser effects.

10) F. H. Westheimer, Chem. Rev., 81, 313 (1981).

(Received September 14, 1984)