

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

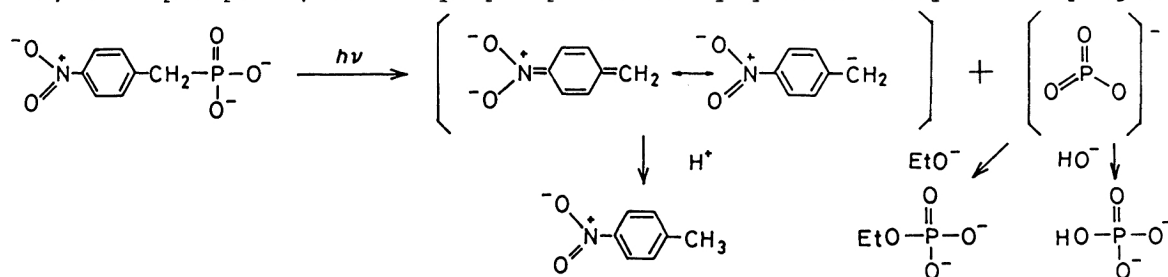
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(p-Nitrophenyl)methylphosphonic acid underwent easily photochemical C-P bond cleavage in alkaline 80% ethanol solution, resulting in the formation of p-nitrotoluene, orthophosphate, and ethyl phosphate. In acidic solution, the phosphonic acid was stable 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 common.²⁾ One of the examples is the decomposition of 2-haloalkylphosphonic 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 °C in large excess of sodium hydroxide, the extent of decomposition was around 90% after 72 h.⁷⁾ When the 80% ethanol solution⁸⁾ 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 quantitatively. 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 °C). Analysis of phosphorus compounds was directly carried out by ³¹P 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

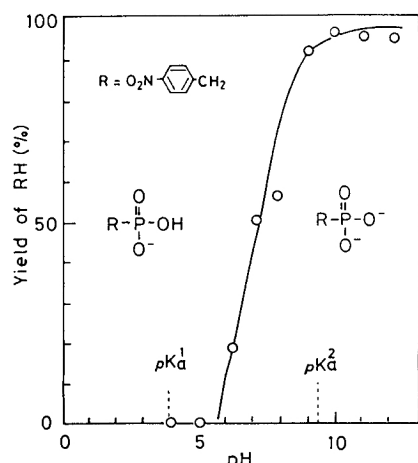


Fig. 1. Effect of pH on the photolysis of **1** in 80% ethanol.

phosphate appeared at $\delta = 2.5$ 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

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