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Substituent Effects on Photochemical Extrusion of Phosphorus Group from 3-Phospholene System

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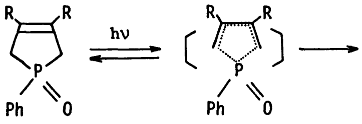
Synopsis. The rate of photo-extrusion of phenylphosphinidene oxide from 1-phenyl-3-phospholene 1-oxide was enhanced by β-methylation. It was found that the photo-extrusion can be extended to the generation of phenylphosphinidene, but attempts to generate other phosphorus intermediates *i.e.*, metaphosphite and methylphosphinidene oxide, were unsuccessful.

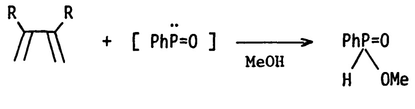
During the course of a study of the photochemical reactions of phosphorus heterocycles,$^{1)}$ it was found$^{2)}$ that 1-phenyl-3-phospholene 1-oxide upon UV irradiation efficiently cleaves to diene and phenylphosphinidene oxide (**3**) which is trapped by alcohol to give phosphinates (**4**). The reaction was shown$^{3)}$ to proceed *via* excited singlet state of **1a**. In view of an increasing interest in the reactive phosphorus intermediate,$^{4)}$ analog of carbene and nitrene, we have examined the substituent effects on the present reaction in an attempt to extend it to the generation of other important phosphorus intermediates, *e.g.*, metaphosphite and phosphinidenes.

Photolysis of a methanol solution of **1a** in a quartz tube was monitored by GLPC, which revealed a gradual disappearance of the starting material along with the formation of butadiene and methyl phenylphosphinate (**4**). The reaction was incomplete, more than 70% of starting material being recovered after 3 h irradiation.



1 a R=H 2

b R=Me



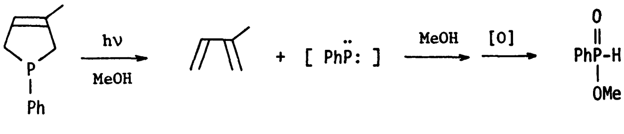
3 4

In contrast, a similar irradiation of 3,4-dimethyl derivative (**1b**) resulted in almost complete consumption of the starting material within *ca.* 1 h, being accompanied by efficient formation of 3,4-dimethylbutadiene and phosphinate (**4**) in nearly quantitative yields. Since apparent rates of disappearance are not always an indication of relative rates, the relative rates (k_r/k_{r_0}) of the photo-extrusion were calculated using quantum yields of the reaction (ϕ_r) and fluorescence (ϕ_f) and absorption spectrum according to the following equation:$^{5)}$

$$k_r/k_{r_0} = \phi_r\phi_{f_0}k_f/\phi_{r_0}\phi_f k_{f_0}$$

where k_f = rate constant for fluorescence calculated from the absorption spectrum. This gives the value k_r/k_{r_0} = 467. Alkylation in the β-position reduces the rate of thermal sulfur dioxide extrusion from sulfolene system by stabilizing the starting sulfolene.$^{6)}$ Thus a large rate enhancement by β-methylation in the present photo-extrusion reaction is especially noteworthy in this connection. An explanation of the result should include, at least in part, the stabilization of incipient diene by β-methyl group in the transition state (**2**) of the cleavage.

The photo-extrusion reaction was found to occur also in 1-phenyl-3-phospholene (**5**). Thus, irradiation of **5** in methanol under nitrogen gave isoprene as the sole low-boiling product detectable with GLPC. Evidence for the intervention of phenylphosphinidene (**6**) was provided by the formation of phosphinate (**4**) (20%) in the reaction mixture after oxidation. A possible formation of **4** should also be considered by the photolysis of phospholene 1-oxide resulting from the oxidation of **5** during the course of irradiation. However, this was ruled out since **4** could not be detected before oxidation. The reaction was much more complicated than that of the oxide, being accompanied by the formation of more than fourteen by-products which were detected by GLPC but not further characterized.



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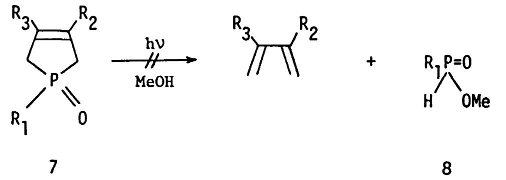
In order to examine whether the reaction can be applied to the generation of other phosphorus intermediates, the photochemical behavior of other 3-phospholene systems in alcohol was investigated. Irradiation of 1-ethoxy derivative (**7a**) in ethanol, however, gave no detectable amounts of diene and diethyl phosphite (**8a**) by GLPC. Introduction of phenyl group as a chromophor on ring carbon (**7b**) or oxygen atom (**7c**)



7 8

a R_1=OEt, R_2=R_3=Me

b R_1=OEt, R_2=R_3=Ph

c R_1=OPh, R_2=Me, R_3=H

d R_1=R_2=Me, R_3=H

also did not lead to the extrusion reaction, while these compounds were gradually photolyzed to give mainly intractable oil. Methyl derivative (**7d**) was recovered unchanged even after prolonged irradiation.

It can be concluded that the presence of the phenyl group on phosphorus atom is required for photochemical extrusion of the phosphorus group from the 3-phospholene system, indicating that the stabilization of incipient unshared electrons on phosphorus in the transition state of the cleavage is so stringent as to allow the present reaction to be utilized in general for the generation of phosphorus intermediates.

Experimental

GLPC analysis were performed on a Yanagimoto instrument, Model G-80. GLPC column A was prepared from 10% β,β'-dioxypropionitrile on Diasolid L (5.0 mm × 2.0 m); column B consisted of 10% SE-30 on Diasolid L (5.0 mm × 2.0 m).

H^1 NMR spectra were determined on a JEOL JNM-MH-100 NMR spectrometer. UV and fluorescence spectra were measured with Shimadzu UV 250 recording spectrometer and Hitachi MPF-2A spectrofluorometer, respectively.

Materials. All the 3-phospholene 1-oxides were prepared by cyclo-addition of dienes with phosphonous dihalides, followed by hydrolysis of the resulting adducts.[7] 3-Phospholene (**5**) was prepared[8] by trichlorosilane reduction of the corresponding phospholene 1-oxide.

Irradiations. All the irradiations were carried out using a Halos 300 W high-pressure mercury lamp unless otherwise stated. For analytical purposes, solutions (5.0 ml) of 3-phospholene 1-oxide (50 mg) in methanol were sealed in quartz tubes and irradiated at room temperature. The analyses of the reaction mixture were done by means of GLPC using column A for low-boiling products and column B for high-boiling one. Quantum yields were determined with 254 nm light from the monochrometer using potassium ferrioxalate solution as an actinometer.

Irradiation of 1-Phenyl-3-phospholene (5) in Methanol. To 250 ml of methanol which had been rigorously degassed by bubbling nitrogen was added 2.0 g of freshly distilled 3-phospholene (**5**) under nitrogen and the solution was irradiated using a water-cooled quartz immersion well under nitrogen. The reaction monitored by GLPC revealed a buildup of complex product mixtures as well as isoprene. The irradiation was interrupted when approximately 80% of the starting material had disappeared (*ca.* 6 h). No methyl phosphinate (**4**) was detected. Oxygen was bubbled through the resulting solution under vigorous stirring in the dark until all phosphines were oxidized to oxides. Evaporation of volatile components under reduced pressure at 30 °C gave viscous oil which was chromatographed on silica gel (Woelm Activity II) and eluted with ethyl ether. The foreband gave methyl phenylphosphinate (**4**) (210 mg, 20%), identical with an authentic sample as confirmed by NMR and IR.

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