Tetrahedron Letters No.26, pp. 2511-2513, 1967. Pergamon Press Ltd. Printed in Great Britain.

PHOTOCONDENSATION OF ACETONE WITH 2,2,2-TRIMETHOXY-4,5-DIMETHYL-1,3,2-DIOXAPHOSPHOLENE

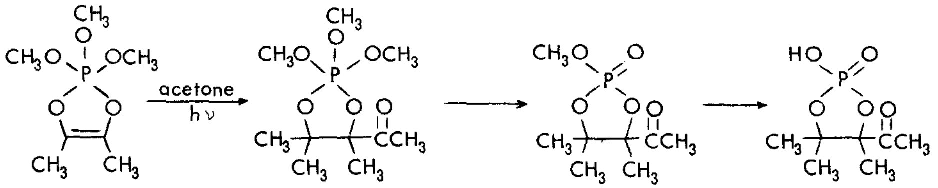
Wesley G. Bentrude and K. R. Darnall

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

(Received 6 April 1967)

We recently reported[1] the photolysis of 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene (I) in cyclohexane to biacetyl, trimethyl phosphite and trimethyl phosphate. Attempts to photosensitize the reactions using acetone and acetophenone also resulted in formation of trimethyl phosphate, but the phosphite could not be detected (v.p.c.). The formation of considerable quantities of a high boiling products in the ketone-sensitized reactions, but not in cyclohexane without added ketone, suggested the possibility that I might be undergoing a direct chemical reaction with the electronically excited ketone carbonyl. We now wish to report that a photocondensation does indeed occur.

The irradiation* of a 0.15 M solution of I in dry acetone for 12 hours yielded oxaphospholane II as the only high-boiling product detectable by v.p.c. [yield, 54%; b.p. 46-47° at 0.1 Hg; m.p. 26-28°]. Use of slightly damp acetone gave cyclic phosphate III as a result of the very facile hydrolysis of II.** The n.m.r. spectrum of II had peaks of appropriate areas at: τ 6.48, J_{HP} = 12.5 cps (CH_3O); τ 7.70 (CH_3CO-); τ 8.70, 8.77, 8.92 (CH_3 groups). The infrared spectrum of II was grossly similar to that of I with important new absorptions at 1718 cm.$^{-1}$ and 1380 cm.$^{-1}$ (doublet). The structure of II is also supported



I II III IV

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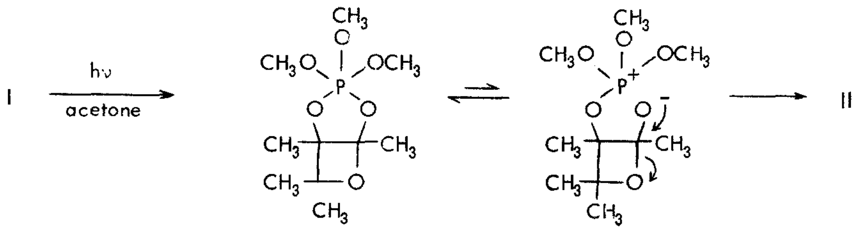
* All irradiations were carried out with a broad spectrum UV source and a Vycor filter. A flow of nitrogen gas through the photolysis mixture provided an inert atmosphere and a means of stirring.

** Rapid hydrolysis of phosphoranes analogous to II is well established.[2]

by the results of hydrolysis and methanolysis. Phospholane II itself is photolyzed slowly on further irradiation in acetone or benzene to give trimethyl phosphate among other products. N.m.r. shows III to be a mixture of two diastereomers. Exposure of III to the atmosphere (H_2O?) affords a quantitative yield of IV, a crystalline white solid, [m.p. 131-3°, n.m.r. absorption at τ - 1.86 (1H), τ 7.66 (3H), τ 8.48 (6H) and τ 8.60 (3H)]. This type of hydrolysis has previously been shown to be rapid.[3] Acid IV also results, in quantitative amounts, on exposure of II to air. Satisfactory P analyses were obtained for II and IV.

We feel that the formation of II in this manner constitutes a rather novel photocondensation of a carbonyl group with a carbon-carbon unsaturated derivative. It is particularly interesting since the Ramirez group has recently reported[4] the exactly analogous *thermal* reaction of I with a variety of aldehydes, and α-diketones, with certain cyclic aliphatic monoketones, and with acetophenone, p-nitroacetophenone and hexafluoroacetone. However, *aliphatic acyclic ketones and benzophenone were notably unreactive thermally.* Acetone, for example, failed to react in 3 months at 20°, and butanone gave no oxyphospholane in 48 hours at 80°. Although we have investigated in detail only the photoreaction of acetone, benzophenone and acetophenone were also consumed along with I under conditions in which most of the light is absorbed by the ketone. If subsequent photolysis of the product oxyphospholanes is slow, as it is with II, the photocondensation may prove to be more generally applicable to ketones than the thermal reaction. The photocondensation may have a further advantage in that it can be carried out at room temperature. Ramirez *et al.*[4] found the yields from the thermal reactions to be somewhat limited, in some instances, by thermal decomposition of the product oxaphospholanes. The scope of the photocondensation reactions is under investigation. Since the photocondensation occurs on irradiation with Pyrex- or Corex- filtered light, we assume that reaction of an excited, presumably triplet, carbonyl function is involved. One intriguing mechanistic possibility is that an oxetane is formed initially and subsequently undergoes rearrangement to II. We are attempting to trap such an intermediate in irradiation experiments at low temperatures.



Acknowledgement. This work was supported by the Petroleum Research Fund (2439-A4).

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