Photolyses of 1,3,2-Dioxaphosph(V)oles

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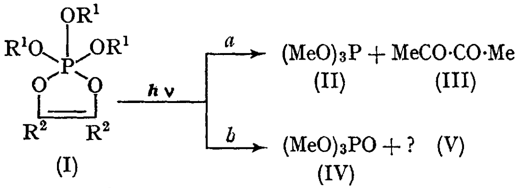
THE photochemistry of organophosphorus derivatives has received only a little attention.[1] This Communication reports preliminary results of a study of the photolyses of a novel class of organophosphorus compounds, the 1,3,2-dioxaphosph(V)oles (I). Results are compared with those recently reported for the pyrolytic[2] and copper-catalyzed[3] decompositions of such compounds. Preliminary inferences are drawn as to the nature of the excited state(s) involved.

A general scheme for these photolyses is shown below:



a; $R^1 = R^2 = Me$
b; $R^1 = Me$; $R^2 = Ph$

The distributions of products (II) and (IV) from photolysis of (Ia) under various conditions are recorded in the Table.

The reactions were carefully monitored throughout by v.p.c. analysis which showed consumption of (Ia) and formation of products (II) and (IV) to be reasonably linear functions of time during about the first 60% of reaction. Products (II) and (IV) were stable to reaction conditions. Yields in the Table are reported at 30% reaction except in expt. 5 in which acetophenone had retention time coincident with that of (Ia) and in expt. 6 in which difficulty was encountered in analysis for (Ia). Results in these cases are at 100% reaction. Although (III) is itself readily photolyzed, it was shown by v.p.c. in expt. 3 to build up to about 5 mole % of the original concentration of (Ia). Although (III) was not separated in the v.p.c. column normally used (footnote c, Table) it was detected on an SE-30 column in photolyses of 0·4 M-(Ia) in cyclohexane with Vycor-filtered light and by its characteristic yellow colour at 0·4M concentration in other solvents in which cases (II) was also formed. It seems consistent to suggest that *a* constitutes one photochemical pathway. Vapour-phase chromatograms in expts. 1—4 are remarkably free of products other than (II) and (IV).

A striking contrast was noted on photolysis of (Ib) in cyclohexane (Vycor) in that only the phosphate, (IV), was formed. This result may be compared with the report[2] of Mukaiyama, Nambu, and Kumato that *pyrolysis* of an analogous phosphorane [R^1 = Et; R^2 = Ph] under N_2 at 215° gives an 81% yield of triethyl phosphate along with about 11% of diphenylketen. An 81% yield of phosphate along with 41% of dibenzoylstilbene was also reported[3] in the copper-catalyzed decomposition in boiling toluene. No mention was made of any phosphite formation. We have confirmed these findings in the pyrolysis of (Ib). However, when we heated (Ia) under N_2 at 170—200° both (II) and (IV) were distilled from the reaction flask in about 1 : 1 molar ratio along with a considerable

TABLE

Photolysis of (Ia)[a b]

Expt.	Conditions	% Yields[c] $(MeO)_3PO$	% Yields[c] $(MeO)_3P$	$\frac{(MeO)_3P^c}{(MeO)_3PO}$
1	Cyclohexane	20	80	4
2	Cyclohexane, Corex	50	35	0·7
3	Ether	25, 35	60, 55	$\simeq 2$
4	Benzene, Pyrex	55	0	—
5	Cyclohexane, 0·4 M in acetophenone, Corex	55	0	—
6	Acetone, Corex	15	0	—

[a] The u.v. spectrum of (Ia) shows intense end-absorption indicating a maximum below 200 mμ.

[b] Photolyses with 200 w Hanovia Lamp, Model 654A-36 with Vycor filter unless otherwise noted. Solutions, 0·04M in (Ia), were swept with purified nitrogen before irradiation.

[c] V.p.c. analysis on 2-ft. column, 20% Celanese Ester No. 9 on Chromosorb W, bicyclohexyl internal standard. Yields reported to nearest 5%.

amount of (III). Thus, a parallel in the distribution of products (II) and (IV) between the photochemical and thermal reactions of (Ia) and (Ib) is noted. Evidence concerning the likely formation of a second product, (V) in the photolyses of (Ia) is at present lacking. The obvious possibility, by analogy with the pyrolysis,[2] is the keto-carbene $\mathrm{MeCO{\cdot}\ddot{C}Me}$.

Expt. 2 shows that the (II)/(IV) ratio is strongly wavelength-dependent and shifts in favour of (IV) at longer wavelengths. The effect in ether (u.v. cut-off at longer wavelength than cyclohexane) is as predicted by the wavelength effect. A true solvent effect may also be operative in these reactions as preliminary studies show a sharp reduction in proportion of (II) formed in acetonitrile.

With Pyrex-filtered light, photolysis of (Ia) in benzene (expt. 4) proceeds several times faster than in cyclohexane and gives only phosphate. This result suggests that benzene photosensitizes this reaction and that (IV) can arise *via* a triplet process. Compound (IV) was formed to the exclusion of (II) in expts. 5 and 6 using potential ketones as potential sensitizers [(II) was stable to all reaction conditions]. In the latter cases we are hesitant to assign with certainty the formation of (IV) to triplet chemistry since high yields of (IV) are not found, and in both instances a new, high-boiling product is formed in amounts greater than (IV). Compound (IV) may then arise as a secondary product of direct chemical reaction of excited carbonyl* group with (Ia). Resolution of this problem awaits completion of quencher and product studies now in progress.

(*Received, December 29th,* 1966; *Com.* 1033.)

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* Oxetan formation has been shown to be a very common process (ref. 4). We find that not only $\mathrm{Cl_3C{\cdot}}$ addition (ref. 5) but also t-butoxy-radical addition proceeds readily with (Ia) (unpublished result).

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