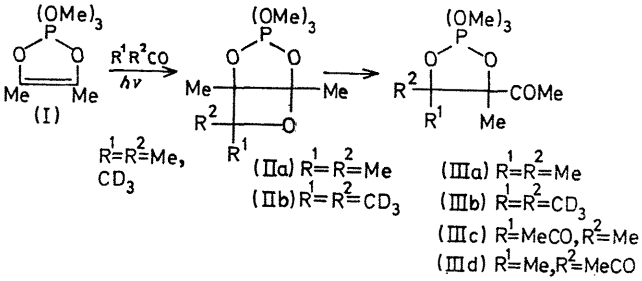
Oxetan Intermediate in the Photocondensation of Acetone with 2,2,2-Trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholen

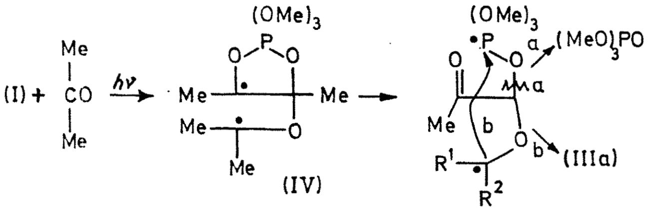
By WESLEY G. BENTRUDE* and K. R. DARNALL

(*Department of Chemistry, University of Utah, Salt Lake City, Utah* 84112)

IT was shown[1] recently that irradiation of solutions of 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholen (I) in acetone gives the condensation product (IIIa), a dioxaphospholan in 54% yield. We now have direct n.m.r. evidence that the reaction proceeds *via* initial formation of an oxetan (II) rather than by rearrangement of the initially formed diradical adduct (IV).[2] Although oxetan formation in photoreactions of ketones in the presence of olefins is well known,[2] condensations with cyclic phospholans, as shown above, and the subsequent rearrangement are new processes.



Irradiation of a 0·1 M-solution of (I) in $(CD_3)_2CO$ in a Pyrex n.m.r. tube for 70 min. at −75° gave a solution, the low-temperature n.m.r. spectrum of which is shown in the Figure (a). Unreacted phospholen (I) is responsible for the doublet at τ 6·40 and singlet at τ 8·15. The remaining peaks are those expected of an intermediate of structure



(IIb); 9H doublet, J 13 Hz., at τ 6·35 (CH_3OP); 3H singlets at τ 8·45 and 8·66 (bridgehead methyls). [By way of comparison, the ring methyl peaks in (IIIa) appear at τ 8·89, 8·76 and 8·70.] The Figure, (b) and (c) shows the effect on the n.m.r. spectrum of warming this solution to room temperature for periods of 6 and 45 min., respectively.

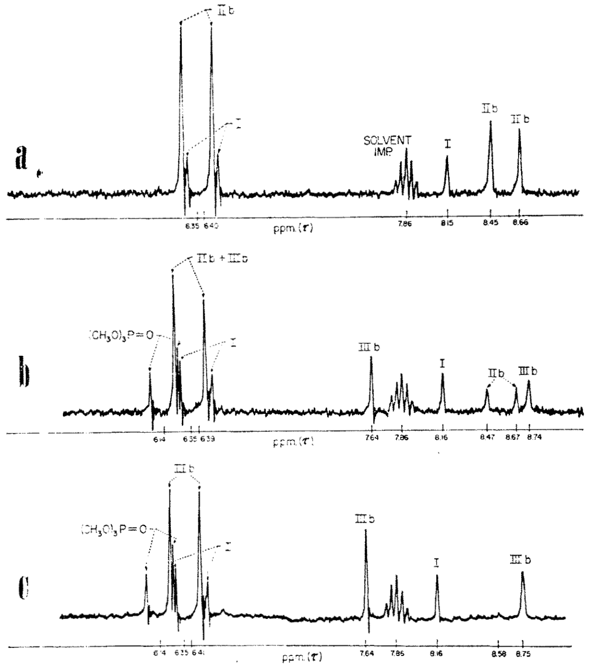
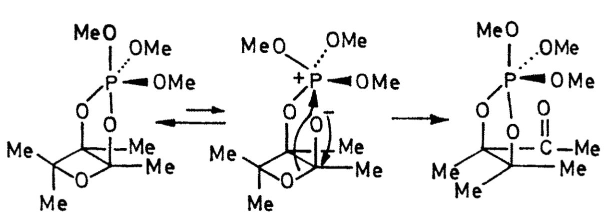


FIGURE. *N.m.r. spectra* (−50°) *of irradiated* $(CD_3)_2CO$ *solution of* (I).

Peaks in spectra (b) and (c) readily assigned† to (IIIb) are: the doublet at τ 6·35, methoxy; and the singlets at τ 7·64 (CH_3CO) and 8·75 (ring CH_3). The formation of trimethyl phosphate (25%), which always accompanies the reaction, is indicated by the doublet at τ 6·14† It should be noted that the phosphate arises from (IIb) and that its formation is competitive with rearrangement of (IIb) to (IIIb). Evidence in the n.m.r. spectrum for the other fragment(s) which should be formed in the reaction giving phosphate is not seen.

We envisage that the rearrangement probably involves a 1,3-oxygen shift in one or more steps as shown below.



The *cis*-ring fusion orients the oxetan oxygen in position reasonably favourable to migration.

A significant stereochemical contrast between the thermal oxaphospholen condensation studied by Ramirez[3] and the photochemical reactions is seen in the reaction of *biacetyl* with (I). A benzene solution, 0·4 M in biacetyl and 0·11 M in (I), was kept at room temperature, and the thermal condensation to give the *cis*- and *trans*-products (IIIc) and (IIId) was monitored by v.p.c. The ratio, *cis* : *trans*, was invariant in the thermal reaction at 6 : 1 over the range 0—40% conversion (120 hr.). When an identical mixture was irradiated ($\lambda > 365$ nm.) at room temperature, the *cis* : *trans* ratio increased progressively from 13 : 1 at 15% conversion (135 min.) to 19 : 1 at 75% conversion (615 min.). This stereochemical difference is consistent with the idea that the photo- and thermal oxaphospholan condensations proceed by different mechanisms. The predominantly *cis*-product formation in the oxaphospholane photocondensation is readily explained if an initial diradical adduct[2] closes to give oxetan (assumed) in a stereospecific manner. We are presently attempting to determine whether or not an oxetan intermediate is involved in the oxaphospholan photocondensation of biacetyl.

The photochemical formation of (IIIc) and (IIId) is completely quenched by addition of *trans*-stilbene under conditions in which light is absorbed only by biacetyl [solutions 0·1 M in (I), 0·4 M in biacetyl, and 0·3 M in *trans*-stilbene, $\lambda > 365$ nm.]. The observed conversion of *trans*-stilbene into the *cis*- isomer is further evidence that reactive biacetyl triplets are being quenched by *trans*-stilbene, a process known to be diffusion controlled.[4] For reasons not understood at present, the formation of phosphate is only partly quenched.

This research was supported by a grant from the National Science Foundation.

(*Received, May 23rd,* 1969; *Com.* 726.)

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† These spectral assignments were confirmed by comparison with spectra of solutions of (IIa) and trimethyl phosphate in $(CD_3)_2CO$.

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