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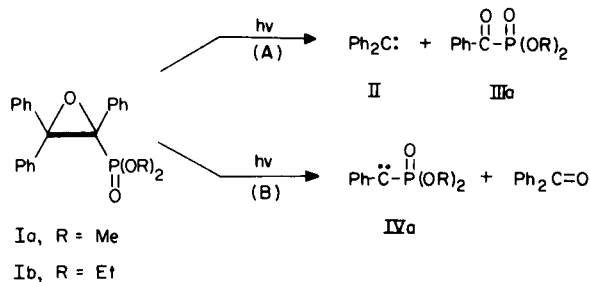
An alternative source to phosphonocarbenes is described using phosphorus substituted oxiranes as precursors which compliments the conventional diazo route to these transient species. The results are in accord with previous theories advanced to rationalize the mode of photocyclo-elimination of a variety of other unsymmetrically substituted oxiranes.

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Sir:

The photoinduced reactions of a variety of symmetrically and unsymmetrically substituted oxiranes have been investigated in detail (2-3), but no studies of the photolyses of oxiranes bearing stabilizing substituents containing phosphorus have been reported. The demonstration that vicinal diaryloxiranes undergo efficient cycloelimination to give arylcarbenes and carbonyl compounds (2a) suggested that comparable photocleavage of phosphorus-substituted oxiranes might be anticipated. Successful achievement of the goal could conceivably provide an alternative to the more conventional (diazoalkane) approaches to phosphorus-substituted carbenes developed by Seyferth (4) and Regitz (5).

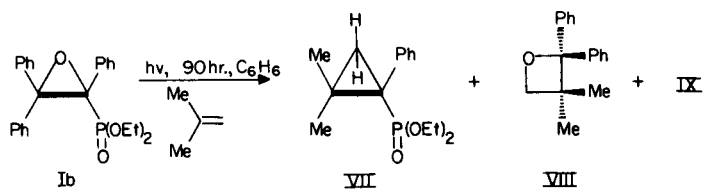
*A priori*, 1-dimethylphosphonyl-1,2,2-triphenyl oxirane (1a) (6) could photofragment in either of two competitive pathways to yield either (A) diphenylcarbene (II) and



PhCOP(O)(OCH<sub>3</sub>)<sub>2</sub> (IIIa), or (B) PhĊP(O)(OCH<sub>3</sub>)<sub>2</sub> (IVa) and benzophenone. Photolysis (254 nm) (7) of Ia (λ<sub>max</sub> = 260 nm, ε<sub>max</sub> = 697) in methanol for 72 hours resulted in 50% consumption of Ia and the formation of benzhydryl methyl ether (V, 1.8%) and dimethyl α-methoxybenzylphosphonate [VIa (8) 17.4%], the methanolysis products of carbenes II and IVa, respectively (2). Benzophenone and its photoreduction products, benzhydrol and benzpinacol, were also detected. The by-product, IIIa, anticipated in cleavage pathway A, was not detected, but methyl benzoate and dimethyl phosphonate were observed as secondary photoproducts. In a control experiment it was demonstrated that these products arise by ground

state methanolysis of IIIa (quantitative conversion in 40 hours). These results indicate that although Ia undergoes photocycloelimination by both of the possible cleavage pathways (A and B) I can serve as an efficient photoprecursor of carbene IVa. The relative yields of V and VIa indicate that the photocleavage is selective and pathway B is favored by an order of magnitude. Control photolyses (254 nm) (7) performed on V and VIa in methanol confirmed that these materials are photolabile; 45% of V and 27% of VIa were consumed in 30 hours. To obtain a more meaningful estimate of the degree of selectivity in the photolysis of Ia, a study of the dependence of the yield ratio V:VIa with time was conducted. Extrapolation to zero time showed that pathway B, the formation of the phosphonocarbene IVa, is favored by a factor of 4.1:1 over diphenylcarbene (II).

Confirmatory evidence that phosphono-substituted carbenes are indeed produced upon photolysis of oxiranyl phosphonates such as I was obtained by experiments performed with isobutylene as a trapping agent. The diethyl phosphonate (Ib) (0.55 g., 1.3 mmoles), a more soluble substrate prepared in the same manner as Ia (9), was dissolved in a 1:1 solution (by volume) of isobutylene in benzene. The resulting solution was irradiated (254 nm) (7) in a quartz vessel for a period of 90 hours and separation and purification of the photoproducts VII (0.17 g., 45%), VIII (0.10 g., 30%) and an unidentified material IX (a photooxidation product of Ib; m/e 406; 0.08 g., 14%) was achieved by preparative thick-layer chromatography on silica gel PF<sub>254</sub>.

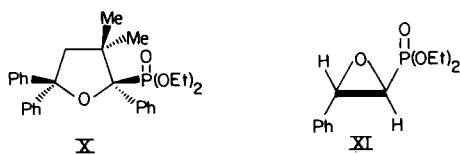


The structure of the cyclopropane VII [100 MHz, pmr; δ (deuteriochloroform): 0.72 (s, 3H, CH<sub>3</sub>), 1.07

(t of d, 3H,  $\text{OCH}_2\text{CH}_3$ ;  $^3\text{J} = 7$  Hz and  $^4\text{J}_{\text{POCCH}} = 1$  Hz), 1.18 (t of d, 3H,  $\text{OCH}_2\text{CH}_3$ ;  $^3\text{J} = 7$  Hz and  $^4\text{J}_{\text{POCCH}} = 1$  Hz), 1.53 (d, 3H,  $\text{CH}_3$ ;  $^4\text{J}_{\text{PCCCH}} = 1$  Hz), 3.89 (octet, 2H,  $\text{OCH}_2\text{CH}_3$ ;  $^3\text{J} = 7$  Hz and  $^3\text{J}_{\text{POCH}} = 2.5$  Hz), 3.96 (octet, 2H,  $\text{OCH}_2\text{CH}_3$ ;  $^3\text{J} = 7$  Hz and  $^3\text{J}_{\text{POCH}} = 2.5$  Hz), 7.10-7.40 (m, 5H, aromatic); 40.25 MHz,  $^{31}\text{P}$  (deuteriochloroform) + 27.9 ppm (phosphoric acid);  $m/e$  282] established by independent synthesis from diethyl  $\alpha$ -diazobenzylphosphonate (5) and isobutylene (in benzene) (0.2 g., 0.8 mmole) by photolysis (350 nm) (7) in a Pyrex test tube (15 hours; 0.19 g., 86%). Separation and purification in this case was conveniently accomplished by glc at  $190^\circ$  on a preparative column (2 m x 5 mm) packed with 10% DC-550 Chromosorb P. Similarly, the oxetane was synthesized by photocycloaddition (350 nm) (7) of benzophenone to isobutylene in benzene.

The mode of photocleavage observed upon irradiations of Ia and Ib is consistent with results previously observed for a variety of unsymmetrically substituted vicinal diaryloxiranes (2,3). The preferential cleavage by pathway B to give the carbene IVa incorporating that center bearing the more electron-negative group is in accord with expectations based on the two-step carbonyl ylide mechanism for these reactions postulated by Griffin and co-workers (2,3). The lower degree of selectivity (4.1:1) observed for pathway B, as compared to the 14.2:1 preference for the formation of phenylcyanocarbene in the photolysis of triphenylcyanooxirane (10a) reflects the relative electron acceptor capabilities of the phosphono and cyano groups (12).

While photochromism is a phenomenon characteristic of vicinal diaryloxiranes associated with carbonyl ylide formation (10b) irradiation (7) of Ib (254 nm) in a rigid matrix of 2-methyltetrahydrofuran at  $77^\circ\text{K}$  leads only to development of a faint pink color which fades rapidly on warming or exposure to visible light. The instability of the ylide precludes characterization by ultraviolet spectroscopy (3,11b) and may explain the absence of formation of detectable amounts of the 3+2 adduct X derived from addition of the dipolarophilic ylide derived from photolysis of Ib (3); however, more extensive screening of



dipolarophiles is required to confirm that such ylides cannot be intercepted since only isobutylene, an electron-rich alkene was utilized. This dipolarophile was selected since other such vicinal diaryloxiranes are known to undergo HOMO rather than LUMO controlled cycloadditions (13).

In contrast to the behavior of vicinal diaryloxiranes, in which carbon-carbon bond cleavage to ylides precedes

or competes efficiently with fragmentation to carbenes, simple monoaryloxiranes in general undergo photolysis by initial carbon-oxygen bond scission, followed by rearrangement of the resulting diradical (10b). Thus, photolysis of styrene oxide results in the formation of phenylacetaldehyde as a major product (11b). Analogous results were obtained with the monoaryloxirane XI bearing a phosphono group. Photolysis of diethyl 2-phenyl-3-epoxyethylphosphonyl oxirane (14) ( $\lambda_{\text{max}} = 258$  nm,  $\epsilon_{\text{max}} = 436$ ) in cyclohexene, methanol, and *n*-hexane for 45-50 hours resulted in 52%, 87%, and 50% consumption, of XI, respectively. No trace of such adducts as norcaranes or methyl ethers expected to result if 3 $\rightarrow$ 2+1 cycloelimination of XI were occurring in cyclohexene or methanol could be detected. Aside from extensive amounts of polymeric material, the sole products isolated were diethyl benzylphosphonate (XII, 3.2%) and methyl phenylacetate (XIII, 2.1%) from the reaction in methanol and XII (34.5%) from the reaction in *n*-hexane.

These studies indicate that the photochemistry of I parallels that of related substrates studied to date, and that the photolysis of such suitably substituted oxiranes provides an alternative route to phosphorus substituted carbenes. Further studies of the effects of structural variations on the course of the photocycloelimination reactions as a route to phosphonocarbenes are in progress.

Acknowledgment.

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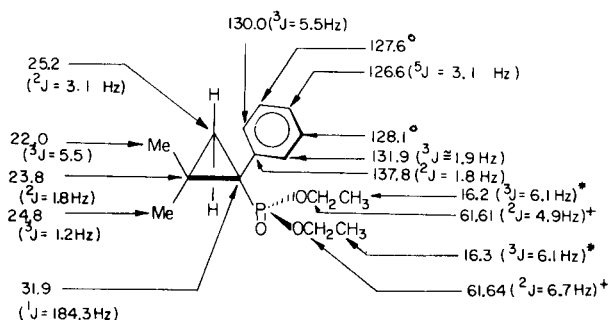
(7) Irradiations were conducted in serum-capped Vycor and/or quartz test tubes employing a Rayonet Chamber Reactor (The Southern New England Co., Middletown, CT) equipped with 16 8-W 254 or 350 nm lamps as specified unless otherwise indicated.

(8) Prepared by the photolysis (7) of dimethyl  $\alpha$ -diazobenzylphosphonate (9) in methanol.

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(10a) The cyclopropyl proton signals in the pmr spectrum of VII are obscured by the absorptions due to the ester methyl multiplets as well as the singlets assigned to the methyl groups bonded to the cyclopropane ring. Additional structural information, however, was obtained from an examination of the proton noise decoupled carbon-13 (25.1 MHz) spectrum of VII. The indicated assignments together with the measured phosphorus-31-carbon-13 coupling constants were substantiated by information gained from (1) single frequency off-resonance decoupling experiments as well as (2) single frequency selective heteronuclear decoupling and are consistent with the available carbon-13 data on structurally related cyclopropyl phosphonates (10b). The cyclopropyl carbon at 25.2 ppm appears as a triplet ( $^1J_{C-H} = 160$  Hz) (10c) in the coupled carbon-13 spectrum, and thus confirms the presence of the cyclopropane methylene in VII. The phosphonate VII possesses an added complicating structural feature,

#### CARBON-13 DATA



VII

<sup>o</sup>, <sup>+</sup>, \* Assignments may be reversed.

that of the chiral cyclopropane carbon atom. It is the presence of this chiral center which renders all six of the aromatic ring atoms as well as the methyl and methylene carbons of the ester residues bonded to phosphorus chemically non-equivalent (10d, 10e); (b) G. W. Buchanan and C. Benezra, *Can. J. Chem.*, **50**, 1078 (1972); (c) Cyclopropane, for example, displays  $^1J_{C-H} = 161$  Hz. See, for instance, "Interpretation of Carbon-13 NMR Spectra", F. W. Wehrli and T. Wirthin, Heyden and Son, Ltd. (London), 1976, p. 52; (d) For a recent discussion of chiral recognition see A. J. Jones and P. J. Stiles, *Tetrahedron Letters*, 1965 (1977) and P. J. Stiles, *Chem. Phys. Letters*, **43**, 23 (1976); (e) Because of the unusual nature of the cmr spectra of VII and related cyclopropyl phosphonates, a more detailed analysis of the spectra will appear elsewhere.

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