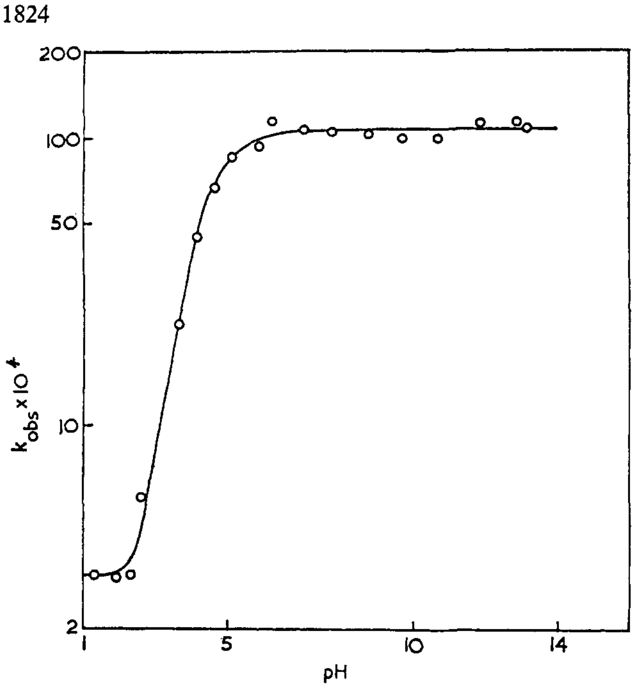
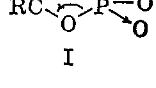


Figure 1. pH-rate profile for the hydrolysis of 2,4-dinitrophenyl phosphate in aqueous solution of ionic strength 1.0, at 39°.

stituted benzoyl phosphate dianions[4] *vs.* the pK_a of the leaving group gives a straight line on which the value for the dianion of *p*-nitrophenyl phosphate also falls. The dianion of 2,4-dinitrophenyl phosphate is hydrolyzed just twice as fast as predicted from this plot, with a half-life of 66 min at 39° and ionic strength 1.0.

The monoanion is hydrolyzed at less than $^1/_{30}$ this rate (Figure 1). This reversal of the usual relative reactivities of mono- and dianion has been observed with certain acyl phosphates,[4,5] but not previously with a phosphate ester. It is a consequence of the much greater sensitivity of the rate of hydrolysis of the dianionic species to the pK_a of the leaving group.[6]

The ratio of the hydrolysis rates of dianion and monoanion is some 20 times larger than that observed for benzoyl phosphates with leaving groups with pK_a comparable to that of 2,4-dinitrophenol. This factor may be a measure of the efficiency of the special mechanism available to the monoanions of acyl phosphates suggested by Jencks;[4] this mechanism involves intramolecular protonation of the leaving group in a six-membered cyclic transition state, I.



I

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[4] G. Di Sabato and W. P. Jencks, *J. Am. Chem. Soc.*, **83**, 4400 (1961).

[5] A. Marcus and W. B. Elliott, *ibid.*, **80**, 4287 (1958).

[6] The plot of log k_{hyd} against pK_a of the leaving group for the dianions of acyl and monoaryl phosphates has a slope of 1.2 at 39°. The slope of the corresponding plot for the monoanions of a wide range of monoalkyl and monoaryl phosphates at 100° is 0.27.[7]

[7] A. J. Kirby and A. G. Varvoglis, to be published.

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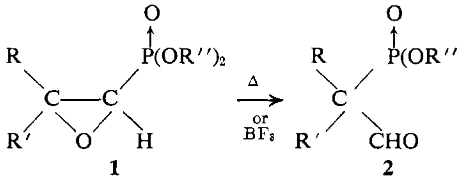
1,2 Shifts of Dialkoxyphosphono Groups in Skeletal Rearrangements of α,β-Epoxyvinylphosphonates[1]

Sir:

A variety of rearrangements of organophosphorus compounds involving migration of a phosphorus substituent from carbon to oxygen,[2a] oxygen to carbon,[2b] nitrogen to oxygen,[2c] and oxygen to oxygen[2d] have been characterized. However, no comparable shifts from carbon to carbon paralleling the well-known skeletal rearrangements of organic compounds have been reported. We have observed what we believe to be the first example of such a rearrangement, namely, the thermal and acid-catalyzed rearrangement of α,β-epoxyvinylphosphonates (**1**) to α-formylalkylphosphonates (**2**).



a, R = C_6H_5; R′ = CH_3; R″ = C_2H_5
b, R = R′ = CH_3; R″ = CH_3
c, R = R′ = C_6H_5; R″ = C_2H_5
d, R = R′ = C_6H_5; R″ = CH_3
e, R = R′ = $-(CH_2)_5-$; R″ = C_2H_5
f, R = C_6H_5; R′ = H; R″ = C_2H_5

Distillation of diethyl α,β-epoxy-β-methyl-β-phenylvinylphosphonate[3] [**1a**, bp 97–100° (0.05 mm)] at 170° (0.7 mm) led to the isolation of the product of diethoxyphosphono group migration, diethyl α-formyl-α-phenylethylphosphonate [**2a**, bp 131–133° (0.7 mm), ν_{CO} 1724 cm^{-1}],[4] in 86% yield.[5] Trace amounts of atropaldehyde (**3**) and diethyl phosphite (**4**) were also isolated. It was shown in a separate experiment that **3** and **4** represent thermal decomposition products of **2a** and not primary products from **1a**. Analogous rearrangements were observed for the epoxides **1b**–**1d** at 200–300° (0.6–0.7 mm). The rearranged products (**2e**, **2f**) of epoxides **1e** and **1f** are apparently unstable at the temperatures (270–300°) required for rearrangement and only the dephosphonated aldehydes are isolated, *e.g.*, cyclohexene-1-carboxaldehyde and **4** are formed from **1e**. However, rearrangement of **1e**

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[1] Phosphonic Acids and Esters. XIV. Part XIII: M. Gordon and C. E. Griffin, *J. Org. Chem.*, **31**, 333 (1966).

[2] (a) K. Sasse, "Methoden der Organischen Chemie," Vol. 12, Part I, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, Germany, 1963, pp 432, 489–495, 523; H. Machleidt and G. U. Strehlke, *Angew. Chem. Intern. Ed. Engl.*, **3**, 443 (1964); (b) V. Mark, *Tetrahedron Letters*, 281 (1962); A. P. Boisselle and N. A. Meinhardt, *J. Org. Chem.*, **27**, 1828 (1962); (c) K. Sasse, "Methoden der Organischen Chemie," Vol. 12, Part II, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, Germany, 1964, p 441; (d) A. M. Michelson, "The Chemistry of Nucleosides and Nucleotides," Academic Press Inc., New York, N. Y., 1963, pp 108, 125, 142–146.

[3] The epoxides (**1**) were prepared in acceptable yield by the Darzens condensation of the dialkyl chloromethylphosphonate with the appropriate aldehyde or ketone; sodium hydride in dimethyl sulfoxide proved to be the most effective condensation agent. The only previous report of the preparation of an epoxyphosphonate by the Darzens route is that of V. F. Martynov and V. E. Timofeev [*J. Gen. Chem. USSR*, **32**, 3383 (1962)]; these workers obtained **1e** by condensation with cyclohexanone in the presence of sodium ethoxide.

[4] The product of hydrogen migration, $C_6H_5(CH_3)CHCOP(O)(OC_2H_5)_2$, would be expected to show ν_{CO} of a lower frequency, *e.g.*, $CH_3COP(O)(OC_2H_5)_2$, ν_{CO} 1695 cm^{-1}.

[5] The infrared and pmr spectra and elemental analyses of **1** and **2** were in complete accord with the postulated structures. The unsaturated aldehydes (*e.g.*, **3**) were characterized as their 2,4-dinitrophenylhydrazones.

and **1f** to **2e** and **2f** was achieved by treatment with boron trifluoride etherate at room temperature; rearrangements were complete in 10 min. In every instance only the carbonyl compound was isolated which necessarily involved migration of the phosphonate function; no evidence for the presence of the products of hydrogen migration, RR'CHCOP(O)(OR'')$_2$, was obtained.[6]

The preferential migration of the phosphono substituent observed in this study indicates that the group possesses a previously unrecognized high migratory aptitude.[8] The most closely related cases are those involving preferential migration of benzoyl[9] and chloride[10] substituents. Further studies of the mechanism and stereochemistry of this rearrangement and of rearrangements of phosphorus substituents in other systems are in progress.

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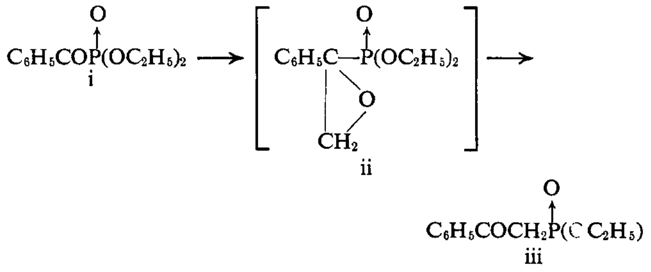
(6) Arbuzov, *et al.*,[7] recently reported that the reaction of diethyl benzoylphosphonate (i) with diazomethane failed to yield the anticipated epoxide (ii); the product isolated by distillation of the reaction mixture was diethyl phenacylphosphonate (iii). It is quite probable that this reaction also represents a case of phosphonate migration similar to that cited above.



(7) B. A. Arbuzov, V. S. Vinogradova, N. A. Polezhaeva, and A. K. Shamsutdinova, *Bull. Acad. Sci. USSR*, 604 (1963).

(8) For a review of the rearrangement of epoxides, see R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).

(9) H. O. House, *J. Am. Chem. Soc.*, **76**, 1235 (1954); H. O. House and D. J. Reif, *ibid.*, **79**, 6491 (1957).

(10) R. N. McDonald and P. A. Schwab, *ibid.*, **85**, 4004 (1963); *J. Org. Chem.*, **29**, 2459 (1964).

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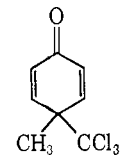
Stereospecificity and Solvent Control of Lumiproduct Formation *vs.* Fragmentation in Dienone Photochemistry[1,2]

Sir:

Recently, we postulated and provided evidence for a primary process, termed the radical fragmentation route, in the photochemistry of cross-conjugated cyclohexadienones.[3] That this reaction competes directly with the often-observed route to (so-called) lumiproduct[4] and that both reactions seem to proceed *via* a common triplet excited state is indicated by the following observations.

Irradiation (n → π^* band) of dienone I in a variety of solvents gives, in addition to *p*-cresol (II),[3] a new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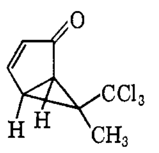
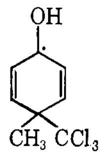

III


IV

ketone III which was isolated by repeated column chromatography from reactions in hexane. More conveniently, III was isolated by precipitation of polymer from the crude benzene photolysate upon addition of hexane, followed by recrystallization and vacuum sublimation of the residue, to give a white solid, mp 62–64°. Elemental analysis and mass spectroscopy gave a molecular formula of $C_8H_7Cl_3O$, while the mass spectrum indicated fragments from loss of from one to three chlorines along with loss of CO. A fragment of mass 144, corresponding to $C_3H_3Cl_3$, established that the methyl and trichloromethyl groups were attached to the same carbon. The chromophore is established by the ultraviolet spectrum ($\lambda_{\max}^{\text{dioxane}}$ 226 mμ (ϵ 7200) and 334 mμ (ϵ 29)) and infrared peaks at 1740, 1585, 1040, and 690 cm^{-1}. The nmr spectrum (parts per million relative to tetramethylsilane) shows a singlet (3 H) at 2.01, a doublet (J = 6 cps) at 3.15 (1 H), a symmetrical eight-line spectrum (J = 6, J' = 4, J'' = 1.5 cps) at 4.00 (1 H), a pair of doublets (J'' = 1.5, J''' = 6 cps) at 6.40 (1 H), and another pair of doublets (J' = 4, J''' = 6 cps) at 7.66 (1 H). The chemical shifts and magnitude of the coupling constants[5] are consistent with the proposed structure III. One equivalent of hydrogen was rapidly taken up over Pd–C to give a saturated ketone (no vinyl H in nmr; no infrared peaks at 1585 and 690 cm^{-1}) with a carbonyl band at 1755 cm^{-1}. The unusual high-frequency carbonyl band in III (bicyclo[3.1.0]hex-3-en-2-ones usually absorb at 1700–1710 cm^{-1})[4] is attributable to dipole interactions between the carbonyl and neighboring CCl_3 groups, requiring the stereochemistry shown in III. It is significant that the nmr spectrum of the crude benzene photolysate was identical in detail with that of purified III except for two broad peaks attributed to the polymer. The epimer of III would be expected to have much different nmr and infrared spectra and, if formed, would easily have been detected and should have survived the mild isolation procedure.

III is stable to further photolysis in benzene, while in ether it leads to a new photoketone; no cresols are formed in these reactions.

The formation of only one isomer of the lumiproduct is unexpected, and the generality of this observation remains to be shown. In this case, 3,5-bond formation from the excited state Ia would be expected to favor formation of Ib over Ib' so as to minimize nonbonded and dipolar interactions with the CCl_3 group. Concerted rearrangement by pivoting around the 5–6 bond, perhaps after electron demotion to the zwitterion,[4] would account for formation of III with the observed stereochemistry. The other alternative, that III

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(1) Part VII of a series on the photochemistry of unsaturated ketones in solution. Part VI: D. I. Schuster and C. J. Polowczyk, *J. Am. Chem. Soc.*, **88**, 1722 (1966).

(2) Supported in part by a grant from the U. S. Army Research Office (Durham), No. DA-ARO(D)-31-124-G425.

(3) D. I. Schuster and D. J. Patel, *J. Am. Chem. Soc.*, **87**, 2515 (1965).

(4) For recent reviews, see (a) H. E. Zimmerman and D. I. Schuster, *ibid.*, **84**, 4527 (1962); (b) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963); (c) O. L. Chapman, *ibid.*, **1**, 323 (1963); (d) H. E. Zimmerman, *Tetrahedron Suppl.*, **2**, 393 (1963); (e) P. J. Kropp, *J. Am. Chem. Soc.*, **86**, 4053 (1964).

(5) O. L. Chapman, *ibid.*, **85**, 2014 (1963); P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2017 (1963); G. V. Smith and H. Kreloff, *ibid.*, **85**, 2016 (1963).