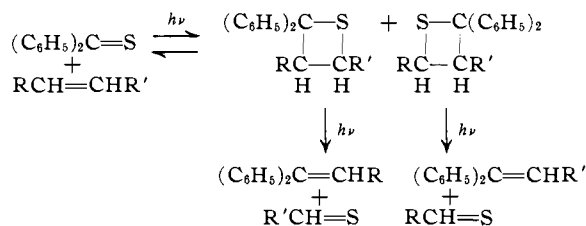


60 g. of Woelm Activity Grade 1 acid alumina gave 0.32 g. of an oil upon elution with 600 ml. of petroleum ether. Analysis of this oil by gas chromatography and n.m.r., and comparison with known mixtures, showed that it was composed of $60 \pm 3\%$ of 1,1-diphenyl-1-hexene⁹ and $40 \pm 3\%$ of 1,1-diphenylethylene. Hence, the more highly substituted olefinic product is formed in slight preference to the less highly substituted one, but it appears that thiobenzophenone is not very selective in its photochemical reaction with a simple terminal olefin.

We have succeeded in extending this reaction to other olefins. A possible mechanistic route which is in agreement with our observations involves the addition of thiobenzophenone to the olefin to give a cyclic sulfide, followed by the decomposition of the cyclic sulfide to the products.¹¹



Studies in our laboratory on the mechanism and scope of the photochemical reaction of thiobenzophenone with olefins and its extension to other thioiketones are being actively pursued.¹²

(11) This mechanism leads to several predictions which can be tested. Among these is the obvious requirement that the cyclic sulfides which have been postulated as intermediates should be capable of reacting in the manner indicated. Experiments on this fundamental point are in progress. Furthermore, since aliphatic thioiketones and thioaldehydes are generally unstable as monomers and tend to trimerize, it is quite likely that trimeric and other polymeric sulfur-containing compounds are produced from $\text{RCH}=\text{S}$ and $\text{R}'\text{CH}=\text{S}$ in our photolyses.

(12) This work was initiated while both authors were in the Department of Chemistry at Washington University, St. Louis. We wish to express our gratitude to Professor C. D. Gutsche for permission to use his photolytic equipment and Dr. G. L. Bachman for carrying out some of the exploratory experiments.

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Phosphonic Acids and Esters. VII.¹ Intramolecular Electrophilic Catalysis of Phosphonate Ester Hydrolysis by Neighboring Carboxyl

Sir:

The hydrolysis of dialkyl arylphosphonates to the corresponding phosphonic acids is well known to require pH extremes^{2,3} and vigorous conditions, e.g., refluxing concentrated hydrobromic acid for 24 hr. On the other hand, the hydrolysis of alkyl and aryl phosphates is much more facile,⁴ and numerous examples of intramolecular facilitation of phosphate hydrolyses have been reported.^{5,6} We have observed

(1) Part VI: D. J. Martin and C. E. Griffin, *J. Organometallic Chem.*, **1**, 292 (1964).

(2) Acidic hydrolyses: K. Sasse, "Methoden der Organischen Chemie," Vol. XII/1, E. Muller, Ed., Georg Thieme Verlag, Stuttgart, 1963, pp. 352-356; R. F. Hudson and L. Keay, *J. Chem. Soc.*, 2463 (1956).

(3) Basic hydrolyses: R. Rabinowitz, *J. Am. Chem. Soc.*, **82**, 4564 (1960).

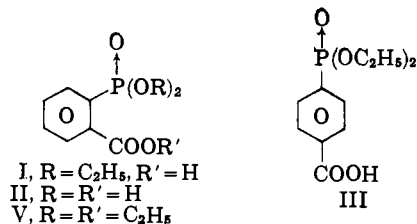
(4) G. S. Hartley, Special Publication No. 8, The Chemical Society, London, 1957, pp. 33-40.

(5) F. R. Atherton, *ibid.*, pp. 77-88.

(6) M. L. Bender and J. M. Lawlor, *J. Am. Chem. Soc.*, **85**, 3010 (1963), and references cited therein.

the occurrence of similar intramolecular assistance in a dialkyl arylphosphonate leading to hydrolysis under extremely mild conditions with an extraordinarily large enhancement of the rate of hydrolysis.

The initial observation of this rate enhancement was made during the attempted recrystallization of diethyl *o*-carboxyphenylphosphonate (I) from hot water; after a relatively short contact period, only the free acid (II) was recovered. Hydrolysis of I in DMSO-*d*₆ containing 2 molar equiv. of D₂O gave II and ethanol and was essentially complete after 7 hr. at 36°.⁷ In



30% aqueous DMSO at 36°, I underwent similar hydrolysis to II with a half-life of 15.0 min.; under identical conditions, the *para* isomer (III) underwent no detectable hydrolysis during a period of 77,960 min. Since a minimum of 0.4% of ethanol could be detected in this system, the rate of hydrolysis of I is at least 7.85×10^7 times greater (pseudo-first-order calculations) than that of the *para* isomer in which no intramolecular catalysis is possible. Further evidence for the intramolecular nature of the observed catalysis was provided by the failure of a 1:1 mixture of diethyl phenylphosphonate and benzoic acid to undergo hydrolysis under these conditions at a detectable rate.

The sodium salt (IV) of I underwent approximately 30% hydrolysis to a salt of II in D₂O at 36° during a period of 1 week; acidification of this solution of partially hydrolyzed sodium salt with 1:1 hydrochloric acid led to immediate hydrolysis at the rate observed for the hydrolysis of I. The ethyl ester (V) failed to undergo detectable hydrolysis under these conditions.⁸ Hydrolysis of I in wet benzene proceeded (with precipitation of II) at a rate comparable to that in aqueous DMSO, indicating that catalysis of hydrolysis by II is probably negligible.

These results indicate that the un-ionized carboxyl group is involved in the facilitation of hydrolysis, probably by assistance in removal of ethanol by a proton transfer to give the zwitterion VI in a manner analogous to that postulated by Bender and Lawlor in the hydrolysis of salicyl phosphate.⁶ Alternatively, proton transfer from carboxyl to phosphoryl giving zwitterion VII may be involved¹²; in either case, proton transfer

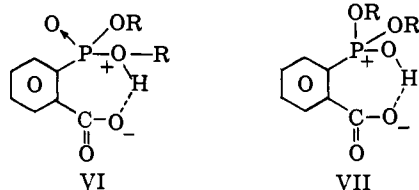
(7) Hydrolyses were conveniently followed by proton magnetic resonance spectra determinations. Quantitative determinations of the relative amounts of I and ethanol were obtained from integrals of methylene peaks [I, τ 5.83 (center of quintet); ethanol, τ 6.50 (center of quartet) in DMSO-*d*₆]; plots of the integrals gave good mirroring curves. All p.m.r. spectra were determined with a Varian Associates A-60 spectrometer; integrals were obtained at a sweep width of 250 c.p.s.

(8) Compounds I, V, and the ethyl ester of III were prepared by photolysis of the corresponding aryl iodide in the presence of triethyl phosphite.⁹ Compound III was prepared by partial saponification of its ethyl ester,¹⁰ III¹¹ was isolated by recrystallization of I from water, and IV was prepared by neutralization of I with sodium hydroxide in DMSO. All compounds gave satisfactory elemental analyses and their spectra (infrared, p.m.r., and ultraviolet) were consistent in all respects with assigned structures.

(9) J. B. Plumb and C. E. Griffin, *J. Org. Chem.*, **27**, 4711 (1962).

(10) L. D. Freedman and H. H. Jaffé, *J. Am. Chem. Soc.*, **77**, 920 (1955).

(11) L. D. Freedman, H. Tauber, G. O. Doak, and H. J. Magnuson, *ibid.*, **75**, 1379 (1953).



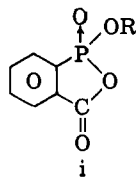
would render the phosphorus atom more amenable to attack by water leading to hydrolysis with a marked rate enhancement.¹³

To the best of our knowledge, the hydrolysis of I represents the first reported example of intramolecular electrophilic catalysis of an arylphosphonate hydrolysis and the most facile such hydrolysis reported. Further studies in this area are in progress.

Acknowledgment.—We thank the Petroleum Research Fund of the American Chemical Society for its support of this work and Dr. E. M. Arnett for several helpful discussions.

(12) The existence of a strong intramolecular hydrogen bond of this type is shown by the infrared spectra (KBr disks) of I ($\nu_{PO} = 1202 \text{ cm}^{-1}$, broad) and III ($\nu_{PO} = 1222 \text{ cm}^{-1}$, relatively sharp).

(13) Some assistance by the carboxylate anion may be involved in a manner analogous to that postulated by Chanley¹⁴ in the hydrolysis of *o*-carboxy-arylphosphates since IV does hydrolyze at a rate significantly greater than that of III. However, the great rapidity of the hydrolysis of I rules out such assistance as a major factor in rate enhancement. There is also apparently no intervention of intermediates such as i since the p.m.r. spectra



of hydrolyzing solutions of I shows peaks characteristic only of I, II, and ethanol (see ref. 6 for a discussion of similar cyclic intermediates in the corresponding phosphates). The possibility of a pentavalent phosphorus intermediate is believed to be unlikely but cannot be ruled out on the basis of available evidence.

(14) J. D. Chanley and E. Feageson, *J. Am. Chem. Soc.*, **77**, 4002 (1955).

(15) National Science Foundation Cooperative Fellow, 1963–1964.

(16) Fellow of the Petroleum Research Fund, 1961–1964.

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Transfer of Alkyl-Substituted Methylene from Sulfonium Alkylides to Carbonyl Groups

Sir:

The utility of dimethyloxosulfonium methylide (I)¹ and dimethylsulfonium methylide (II)² as reagents for selective methylene transfer in organic synthesis has prompted an investigation of the possibility of effecting analogous transfer reactions involving alkyl-substituted methylene (alkylidene) groups.^{3,4} In particular, we have been concerned with ylides derived from sulfonium salts of type III rather than the presently in-

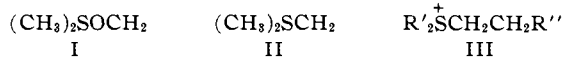
(1) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 867 (1962); *ibid.*, **86**, 1610 (1964).

(2) E. J. Corey and M. Chaykovsky, *ibid.*, **84**, 3782 (1962); *Tetrahedron Letters*, No. 4, 169 (1963).

(3) Studies with sulfonium methylides which parallel ours have been reported by V. Franzen and H.-E. Driessen, *ibid.*, No. 15, 661 (1962); *Chem. Ber.*, **96**, 1881 (1963).

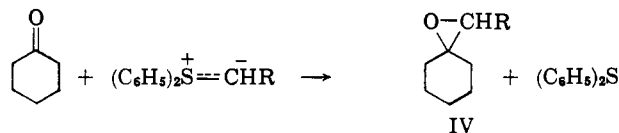
(4) For some recent applications of methylene transfer from sulfur ylides to organic synthesis see (a) P. T. Izzo, *J. Org. Chem.*, **28**, 1713 (1963); (b) R. K. Bly and R. S. Bly, *ibid.*, **28**, 3165 (1963); (c) E. J. Corey and S. Nozoe, *J. Am. Chem. Soc.*, **85**, 3527 (1963).

accessible oxosulfonium analogs. Because of the known susceptibility of sulfonium salts such as III, R''



= H and R' = C₂H₅, to base-catalyzed β -elimination^{5,6} and the probable instability of the corresponding ylides after formation due to α,β' -elimination^{5,6} as well as loss of alkylidene,^{2,3,7} it was clear that the generation of the ylides would have to be carried out at low temperatures using strong, soluble bases. Despite these and other complications, a straightforward and effective procedure has been found for the generation of ylides from sulfonium ions of type III, and the conditions have been defined for efficient alkylidene transfer to the carbonyl group of various aldehydes and ketones to form oxiranes.

For our initial studies on ylide formation diphenylethyl sulfonium fluoroborate⁷ was selected as the substrate in order to avoid the complication of α,β' -elimination,^{5,6} and a vigorously agitated suspension of this salt in tetrahydrofuran at -76° (under N₂) was treated with solutions of various lithium alkyls. Interaction of phenyllithium with 1.1 equiv. of the sulfonium salt for *ca.* 30 min. under these conditions and subsequent addition of 0.9 equiv. of cyclohexanone afforded a mixture of the oxirane IV, R = CH₃⁸ (50% yield),



diphenyl sulfide, diphenyl, ethylphenyl sulfide (36% yield), and other minor products. Similarly, with *n*-butyllithium and with methyllithium much by-product, including ethyl phenyl sulfide, was formed and only low yields (30–50%) of oxirane were obtained. With *t*-butyllithium as base, however, diphenylsulfonium ethylide was generated much more efficiently; the oxirane IV, R = CH₃, was produced from cyclohexanone in 92% yield (v.p.c. analysis) and isolated (distillation) in 74% yield; ethyl phenyl sulfide became a very minor by-product (6% yield).⁹ This example typifies our results and so the detailed procedure is given here.

To a vigorously stirred suspension of 1.81 g. (6.0 mmoles) of ethyldiphenylsulfonium fluoroborate⁷ (finely ground) in 30 ml. of dry tetrahydrofuran under nitrogen at -76° was added (dropwise) 2.2 ml. of 2.5 *N* *t*-butyllithium solution in pentane.¹⁰ After 30 min. at -76° cyclohexanone, 0.490 g. (5 mmoles) in 2 ml. of tetrahydrofuran, was added (the yellow solution faded immediately) and the mixture was stirred for an additional hour at -76° . The reaction mixture was

(5) V. Franzen and Ch. Mertz, *Chem. Ber.*, **93**, 2819 (1960).

(6) V. Franzen and H. J. Schmidt, *ibid.*, **94**, 2937 (1961).

(7) V. Franzen, H. J. Schmidt, and C. Mertz, *ibid.*, **94**, 2942 (1961).

(8) Satisfactory microanalytical, infrared, and n.m.r. data were obtained for all new compounds reported herein.

(9) In this work the oxiranes were generally separated from diphenyl sulfide by distillation, liquid chromatography on neutral alumina, or preparative vapor phase chromatography (p.v.p.c.).

(10) All the reactions of ylides were performed under nitrogen with rigorously dried solvent and glassware. The organolithium reagents were commercial products (Lithium Corp. of America) except for lithium diethylamide which was prepared from methyllithium and diethylamine in ether. The relative amounts of base, sulfonium salt, and carbonyl compound (in equivalents) were 1.0, 1.1, and 0.9, respectively.