VI   VII

would render the phosphor s 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 (ν_{PO} = 1202 cm.$^{-1}$, broad) and III (ν_{PO} = 1222 cm.$^{-1}$, relatively sharp).

(13) Some assistance by the carboxylate anion may be involved in a manner analogous to that postulated by Chanley[14] in the hydrolysis of o-carboxyarylphosphates 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

i
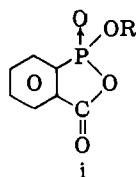
of hydrolyzing solutions of I shows peaks characteristic only of I, II, and ethanol (see ref. 6 for a discussion of similar cyclic intermediates in the corresponding phosphates). The possibility of a pentacovalent phosphorus intermediate is believed to be unlikely but cannot be ruled out on the basis 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 Methylenes 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**, 1640 (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., **86**, 3527 (1963).

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

$$(CH_3)_2SOCH_2 \qquad (CH_3)_2\overset{+}{S}CH_2 \qquad R'_2\overset{+}{S}CH_2CH_2R''$$
I   II   III
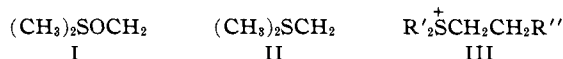
= H and R' = C_2H_5, to base-catalyzed β-elimination[5,6] and the probable instability of the corresponding ylides after formation due to α,β'-elimination[5,6] as well as loss of alkylidene,[2,3,7] it was clear that the generation of the ylides would have to be carried out at low temperatures using strong, 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 fluoroborate[7] 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 N_2) 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 = CH_3[8] (50% yield),

IV
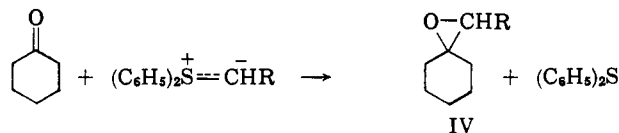
diphenyl sulfide, diphenyl, ethylphenyl sulfide (36% yield), and other minor products. Similarly, with *n*-butyllithium and with methyllithium much by-product, including ethyl phenyl sulfide, was formed and only low yields (30–50%) of oxirane were obtained. With *t*-butyllithium as base, however, diphenylsulfonium ethylide was generated much more efficiently; the oxirane IV, R = CH_3, 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 fluoroborate[7] (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 mmole.) 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.

poured into water and the products were isolated by extraction and concentration to remove the solvent. The oxirane was separated from the higher-boiling diphenyl sulfide by careful distillation (at 24 mm., 100° bath temperature).

Using the above procedure the following carbonyl compounds were converted to oxiranes by diphenylsulfonium ethylide: cyclopentanone, 80% analytical yield, 65% isolated yield (p.v.p.c.); benzaldehyde, 90% analytical yield, 85% isolated yield (distillation), as a 1:1 mixture of cis and trans isomers (analyzed both by v.p.c. and n.m.r.); benzophenone, 85% analytical yield, 74% isolated[11] yield.

Lithium diethylamide and lithium diisopropylamide are also very useful reagents for the efficient generation of sulfonium ylides. The former when used in the experiment detailed above (allowing 1 hr. for ylide formation) afforded the oxirane IV, R = CH₃, from diphenylethylsulfonium fluoroborate and cyclohexanone in 71% isolated yield.

The transfer of larger alkyl groups has also been realized experimentally. For example, diphenylsulfonium butylide, prepared from n-butyldiphenylsulfonium fluoroborate[7] and lithium diisopropylamide, afforded the oxirane IV, R = n-C₃H₇, with cyclohexanone in 88% analytical yield, 81% isolated yield (chromatography and distillation); with benzaldehyde a mixture of trans- and cis-oxiranes (ratio ca. 1.5:1) was isolated in 61% yield (chromatography and distillation).[12]

Solutions of diphenylsulfonium ethylide (0.2 M) in tetrahydrofuran (under nitrogen) decompose at −20° with a half-life of ca. 5 hr. and at +20° with a half-life of ca. 5 min.; at −76° they are stable at least for several hours.

The scope of these alkylidene transfer reactions remains to be determined. However, there does seem to be an important steric limitation. The reaction of diphenylsulfonium ethylide with 17-keto-5α-androstan-3β-ol benzoate (V), of interest as a route to the pregnan-20-one series, did not afford oxirane but, surprisingly, the pseudo-steroid VI.[13] This observation suggests that hindered ketones (and also highly substituted ylides) are deserving of further study.

Finally, it should be mentioned that the abundantly available triethylsulfonium iodide has been converted to the corresponding ylide (with lithium diethylamide),

V → VI
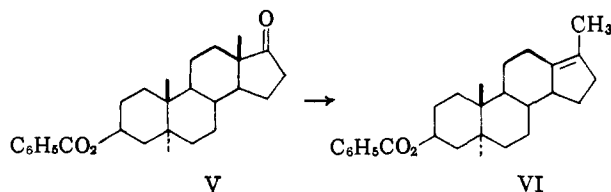
(11) In this instance the separation of oxirane from diphenyl sulfide was accomplished by oxidation of the latter to sulfone by permanganate in acetone with a stoichiometric amount of acetic acid followed by extraction of the semisolid reaction product with pentane and distillation. The oxiranes from benzaldehyde and benzophenone are readily isomerized by acids to phenylacetone and unsym-diphenylacetone, respectively.

(12) In a recent paper there is reported the generation of diphenylsulfonium butylide using n-butyllithium and the subsequent reaction with p-nitrobenzaldehyde to form an oxirane in 40% yield (only example given): A. W. Johnson, V. J. Hruby, and J. L. Williams, J. Am. Chem. Soc., 86, 918 (1964). These authors maintain that oxirane formation is stereospecific, in contrast to our results.

(13) Identified by mass spectrum (found m/e = 378, courtesy of Prof. K. Biemann), n.m.r. and infrared spectra, microanalysis, and conversion to the known 3β-hydroxy derivative; see K. Miescher and H. Kagi, Helv. Chim. Acta, 32, 761 (1949).

which is fairly stable at −76° and which affords the oxirane IV, = CH₃, with cyclohexanone; evidently β-elimination can be largely circumvented in this case. Further studies are under way on the chemistry of this class of sulfonium ylides.[14]

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Isotope Effects for Solvolysis of t-Butyl Chloride and t-Butyl-d₉ Chloride in Solvent Mixtures of Constant Ionizing Power[1]

Sir:

We have determined isotope effects for the solvolysis at 25° of (CH₃)₃CCl and (CD₃)₃CCl in six solvent mixtures each having the same Y-value,[2] i.e. (by definition), the same reaction rate for (CH₃)₃CCl. Average rate constants and isotope effects are given in Table I. The rate constants were determined by gas chromatographic analysis for unreacted t-butyl chloride.[3] The relative amounts of most products can also be determined by gas chromatography, and we are currently studying these, along with other solvent mixtures.

The mean of the isotope effects, 2.39, is almost within experimental error of all of our observed results. However, the isotope effects for ethanol–water and acetic–formic acids differ by experimentally significant, although small, amounts from that for pyridine–water. It may be that a small amount of bimolecular elimination occurs in the presence of large amounts of pyridine, increasing the observed isotope effect; however, bimolecular elimination is thought to be generally unimportant in solvolysis of t-butyl chloride.[2]

The reaction of t-butyl chloride was chosen for study because it was known to exhibit a large isotope effect, 2.3271 in 60:40 ethanol–water at 25°[4] and ca. 2.39 in water at 25°.[5] Specific effects of different solvents on the nature of the transition state should change the isotope effect by especially large amounts because of the cumulative effect on nine deuterium atoms.

It can be seen that the isotope effects are hardly solvent-dependent at all. We conclude that the structural features of the transition states for solvolysis of t-butyl chloride in the various solvents studied are very similar. Three hypotheses which explain these observations occur to us.

First, it may be that the ionization of the substrate is truly unimolecular, with practically no participation by solvent. This mechanism is almost like a gas-phase ionization except that the ions are formed in a medium

(1) Supported in part by the Air Force Office of Scientific Research.

(2) S. Winstein, E. Grunwald, and H. W. Jones, J. Am. Chem. Soc., 73, 2700 (1951); E. Grunwald and S. Winstein, ibid., 70, 846 (1948).

(3) Ten-microliter aliquots of solutions initially ca. 0.02 M in t-butyl chloride were analyzed in a 12-ft. column at 60° using a nonreacting standard, carbon tetrachloride, in about the same concentration as the substrate. The temperature was 25.00 ± 0.01°, standardized with an N.B.S. calibrated platinum resistance thermometer. After analysis of each aliquot, the solvent was removed from the column by back-flushing.

(4) V. J. Shiner, Jr., B. L. Murr, and G. Heinemann, J. Am. Chem. Soc., 85, 2413 (1963).

(5) Corrected from the value of 2.568 at 2° [K. T. Leffek, J. A. Llewellyn, and R. E. Robertson, Can. J. Chem., 38, 2171 (1960)] by assuming the isotopic effect occurs entirely in the enthalpy of activation.