using hexane as the solvent. Under a $CaCl_2$ drying tube, 85.0 g (0.64 mol) of anhydrous aluminum chloride was added to a solution of 54.0 g (0.50 mol) of anisole in 140 ml of hexane over a period of 12 min with mechanical stirring. To this was added a solution of 8.22 g (0.10 mol) of cyclohexene (1) in 10.0 ml of hexane over a period of 67 min with stirring. The resulting mixture was stirred at room temperature for 3 hr, then decomposed with 100 g of ice. The organic layer was separated, washed five times with 100-ml portions of water, and dried over anhydrous $MgSO_4$. The solution was concentrated *in vacuo* and the residue was fractionated through a 10-cm Vigreux column to give 11.98 g (63%) of cyclohexylanisole, bp 108.5–117.0° (2.5 mm). Integration of the nmr singlets at δ 3.68 and 3.63 indicated a 66:34 mixture of ortho and para isomers.

The major isomer, *o*-cyclohexylanisole (**2**), was isolated from the product of an analogous reaction by preparative gas chromatography[21] as a colorless liquid, ir (neat) 760 cm^{-1} (aromatic CH). The minor isomer, *p*-cyclohexylanisole (**3**), was obtained in similar fashion as a white solid, mp 55–56° (lit.[22] mp 57–58°), ir (KBr) 824 cm^{-1} (aromatic CH).

Ethyl [2-(Methoxyphenyl)propyl]malonate.—The minor (35%) isomer, ethyl [2-(*p*-methoxyphenyl)propyl]malonate (**6a**), produced on monoalkylation of anisole with ethyl allylmalonate (**4a**) in excess anisole, was isolated after preparative gas chromatography[21] and short path distillation (0.5 mm and 160° bath) as a colorless liquid: ir (neat) 1748, 1732 (ester C=O), and 836 cm^{-1} (aromatic CH); nmr (CCl_4) δ 1.18 (3 H, t, J = 7 Hz, CH_2CH_3), 1.24 (3 H, t, J = 7 Hz, CH_2CH_3), 1.24 (3 H, d, J = 7 Hz, $CHCH_3$), 3.71 (3 H, s, OCH_3), 4.04 (2 H, q, J = 7 Hz, OCH_2CH_2), 4.12 (2 H, q, J = 7 Hz, OCH_2CH_3), and 6.60–7.15 (4 H, symmetrical A_2B_2 m, aromatic CH).

Anal. Calcd for $C_{17}H_{24}O_5$: C, 66.21; H, 7.85. Found: C, 66.57; H, 7.86.

The major (65%) isomer, ethyl [2-(*o*-methoxyphenyl)propyl]malonate (**5a**), was also isolated by preparative gas chromatography[21] as a colorless liquid: ir (neat) 1750, 1734 (ester C=O), and 760 cm^{-1} (aromatic CH); nmr (CCl_4) δ 1.14 (3 H, t, J = 7 Hz, CH_2CH_3), 1.18 (3 H, t, J = 7 Hz, CH_2CH_3), 1.22 (3 H, d, J = 7 Hz, $CHCH_3$), 3.73 (3 H, s, OCH_3), 4.02 (2 H, q, J = 7 Hz, OCH_2CH_2), 4.11 (2 H, q, J = 7 Hz, OCH_2CH_3), and 6.67–7.30 (4 H, complex m, aromatic CH). Characterization was accomplished by saponification to [2-(*o*-methoxyphenyl)propyl]malonic acid (**5b**), mp 148.0–149.5° dec (lit.[4] mp 143–144°).

Registry No.—**1**, 110-83-8; **4a**, 2049-80-1; **4b**, 109-49-9; **4c**, 1968-40-7; **5a**, 34399-51-4; **5c**, 34399-52-5; **5d**, 34399-53-6; **6a**, 34399-54-7; **6b**, 34399-55-8; **6c**, 34399-56-9; **7**, 108-29-2; **10**, 3153-44-4; $AlCl_3$, 7446-70-0; anisole, 100-66-3.

(21) A 5 ft × 0.25 in. column packed with 15% silicone SF-96 on Chromosorb P was employed.

(22) D. Bodroux, *Ann. Chim. (Paris)*, **11**, 511 (1929).

General Acid Catalysis of Ortho Ester Hydrolysis

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The rates of hydrolysis of diethylphenyl orthoformate, diphenylethyl orthoformate, and diphenylethyl orthoacetate have been determined in 50% dioxane–H_2O (v/v) at 25 and 45°. A pronounced general acid catalysis is observed in the hydrolysis of these compounds. The value of the Brønsted coefficient α is 0.47, 0.68, and 0.49, respectively. Thus, general acid catalysis is more favorable with very weak acids in the case of diethylphenyl orthoformate in comparison with diphenylethyl orthoformate even though the latter compound is of lower basicity. This is due to the more stable oxocarbonium ion produced from diethylphenyl orthoformate which causes the bond-breaking process to be more facile.

It has long been known that certain types of ortho esters are subject to general acid catalyzed hydrolysis in aqueous solution.[2] The pseudo-first-order rate constants for hydrolysis of ethyl orthocarbonate, ethyl orthoacetate, and ethyl orthopropionate are dependent on buffer acid concentration at constant pH.[2] The hydrolysis of methyl orthobenzoate was reported to be catalyzed by general acids in aqueous methanol,[3] and general acid catalysis was claimed for hydrolysis of triethyl orthoformate in 70% dioxane–H_2O but not in H_2O.[4] However, it has recently been shown that this result was possibly due to specific salt effects in aqueous dioxane.[5] Bunton and DeWolfe[6] stressed relatively low basicity of ortho esters as a feature responsible for general acid catalysis. The Brønsted coefficient α for general acid catalyzed hydrolysis of ethyl orthocarbonate[2,7] and also methyl orthobenzoate[3] is approximately 0.7. It has been considered that ortho ester hydrolysis will generally be characterized by high α values.[8]

General acid catalysis has also been observed in acetal and ketal hydrolysis with 2-(substituted phenoxy)-tetrahydropyrans,[9] tropone diethyl ketal,[10] and benzaldehyde di-*tert*-butyl acetals.[11] Electron withdrawal in the leaving group of a phenoxytetrahydropyran will both lower basicity and increase the ease of C–O bond breaking. With tropone diethyl ketal[10] the leaving group is poor, but the great stability of the intermediate carbonium ion makes C–O bond breaking relatively easy. In the case of the benzaldehyde di-*tert*-butyl acetals[11] the bond breaking process is facilitated by relief of ground state strain during the hydrolytic reaction. With all of these compounds, ease of bond breaking is most likely the predominant feature giving rise to general acid catalysis.[9-12]

Triphenyl orthoformate, an ortho ester with which basicity would be very low and with which the leaving group would be reasonably good, has been studied.[13]

(1) Postdoctoral Fellow, Department of Biochemistry, University of Southern California.

(2) J. N. Brønsted and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929).

(3) H. Kwart and M. B. Price, *J. Amer. Chem. Soc.*, **82**, 5123 (1960).

(4) R. H. DeWolfe and R. M. Roberts, *ibid.*, **76**, 4379 (1954).

(5) M. Lahti and A. Kankaanpera, *Acta Chem. Scand.*, **24**, 706 (1970).

(6) C. A. Bunton and R. H. DeWolfe, *J. Org. Chem.*, **30**, 1371 (1965).

(7) A. J. Kresge and R. J. Preto, *J. Amer. Chem. Soc.*, **87**, 4593 (1965).

(8) E. H. Cordes, *Progr. Phys. Org. Chem.*, **4**, 1 (1967).

(9) T. H. Fife and L. K. Jao, *J. Amer. Chem. Soc.*, **90**, 4081 (1968).

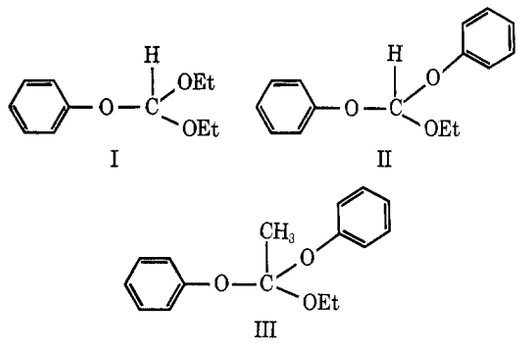
(10) E. Anderson and T. H. Fife, *ibid.*, **91**, 7163 (1969).

(11) E. Anderson and T. H. Fife, *ibid.*, **93**, 1701 (1971).

(12) T. H. Fife and L. H. Brod, *ibid.*, **92**, 1681 (1970).

(13) M. Price, J. Adams, C. Lagenaur, and E. H. Cordes, *J. Org. Chem.*, **34**, 22 (1969).

The rates of hydrolysis of that compound are quite slow, and a search for general acid catalysis by buffer acids was not reported.[13] In that case the intermediate carbonium ion would not be highly stabilized by the adjoining phenoxy groups with the result that the bond-breaking process would still be difficult. Ortho esters possessing both a good leaving group and a reasonably stable carbonium ion intermediate have not been studied. It was felt that, in view of the results obtained in acetal hydrolysis reactions,[9-12] such an ortho ester should show a pronounced general acid catalysis with a relatively low Brønsted coefficient. We have therefore studied the hydrolysis of diethylphenyl orthoformate (I), and, for comparison purposes, diphenylethyl orthoformate (II) and diphenylethyl orthoacetate (III).



I II III

Experimental Section

Materials.—Diethylphenyl orthoformate was obtained commercially from Aldrich Chemical Co. and distilled before use, boiling at 75° (0.1 mm), $n^{23}D$ 1.4813. Diphenylethyl orthoformate was prepared by the method of Stetter and Reske[14] and boiled at 154° (0.3 mm), $n^{23}D$ 1.5391. Diphenylethyl orthoacetate was prepared by the method of Smith,[15] except that a molar ratio of phenol to ethyl orthoacetate of 3:1 was used and the forerun of diethylphenyl orthoacetate was rejected. The product boiled at 140° (0.3 mm), $n^{23}D$ 1.5323.

Dioxane was purified by the method of Fieser[16] and was stored frozen in brown bottles. Deuterium oxide (99.8%) was obtained from Bio-Rad Laboratories. Standard HCl solutions were made from "Dilut-it" concentrated analytical reagent by dilution with boiled deionized water. Other chemicals were A. R. grade materials.

Kinetic Measurements.—Fresh stock solutions of ortho ester in acetonitrile were made up before each series of kinetic runs. The rates of hydrolysis were determined at 25 and 45° with a Gilford 2000 recording spectrophotometer by following the increase in absorbance at 272.3 mμ due to the phenol product. The solvent was 50% dioxane–H_2O (v/v) and ionic strength was maintained at 0.1 with KCl. To initiate the reactions 7 μl of stock solution was added to 3 ml of buffer solution in the cuvette. The reactions were followed to completion, and pseudo-first-order rate constants were calculated by a rigorous least-squares procedure with an IBM 360-40 computer. In the cases of II and III, 2 equiv of phenol was released. The pH of each solution was measured with a Model 22 Radiometer pH meter. The glass electrode gives the correct pH reading in dioxane–H_2O mixtures.[17]

Product Analysis.—The appropriate ortho ester was added from a microsyringe to 1 ml of the appropriate 50% dioxane buffer (0.01 N HCl or 0.1 M CH_3CO_2H–0.1 M $CH_3CO_2^-$) to form a 0.01 M solution. After hydrolysis was complete, 1 μl of the solution was chromatographed on a Hewlett-Packard flame ionization chromatograph equipped with a Hewlett-Packard digital integrator. Flow rates were, He, 25 cc/min; H_2, 15 cc/min; air, 150 cc/min. Temperatures were, injection block, 55°; detector, 250°; oven, 100–150° at 10°/min. The column was 6-ft OV 17 on Chromosorb P. Retention times (min) were, ethyl acetate, 0.79; dioxane, 1.20; phenol, 3.58; ethyl formate, 0.64. The observed retention times were the same to ±0.02 min as obtained with authentic samples, and addition of the authentic materials to the solutions gave no further peaks. In the case of I, the products were solely ethanol, phenol, and ethyl formate. With II and III, the products were solely phenol and either ethyl formate or ethyl acetate in a molar ratio of 1.8 ± 0.3/1.

(14) H. Stetter and E. Reske, *Chem. Ber.*, **103**, 643 (1970).
(15) B. Smith, *Acta Chem. Scand.*, **10**, 1006 (1956).
(16) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath, Boston, Mass., 1956, p 284.
(17) H. P. Marshall and E. Grunwald, *J. Chem. Phys.*, **21**, 2143 (1953).

Results

It would be expected that the initial C–O bond broken in hydrolysis would be that involving the phenoxyl group, since that would result in a good leaving group and formation of the most stable carbonium ion. That phenol is the leaving group is easily demonstrated for the present compounds. Product analysis after the hydrolysis of II and III under actual hydrolytic conditions (excepting a tenfold increase in concentration) by glc shows the products to be solely phenol and either ethyl formate or ethyl acetate. Initial ethoxyl cleavage would require the products to be ethanol, phenol, and phenyl formate or phenyl acetate. Product analysis shows the products of the hydrolysis of I to be ethanol, phenol, and ethyl formate. This is, however, not conclusive evidence for phenoxyl cleavage with I. Therefore, the acetic acid catalyzed methanolysis of I and the dimethyl analog, dimethylphenyl orthoformate, prepared by the method of Smith,[15] was studied. In 0.1 M acetic acid in absolute methanol, I solvolyzes four times faster than dimethylphenyl orthoformate, excluding the latter as an intermediate. Pseudo-first-order kinetics were obeyed to 7 half-lives, making the intercession of a stable intermediate highly unlikely. Furthermore, the rate constant for solvolysis of I in methanol is close to that for catalysis by 0.1 M acetic acid in water, 5.8×10^{-3} sec^{-1} *vs.* 1.63×10^{-2} sec^{-1}, indicating that the mechanism is very likely the same.

A very large general acid catalysis is observed in the hydrolysis of the ortho esters I, II, and III. For example, in acetic acid buffers at HA = A^-/2 (pH 6.38), 0.05 M acetic acid produced a 12.7-fold enhancement in the pseudo-first-order rate constant for hydrolysis of diethylphenyl orthoformate in comparison with the intercept value. Catalysis is by the acid species of the buffer since identical second-order rate constants were obtained from plots of k_{obsd} *vs.* buffer acid concentration at three different acetic acid/acetate buffer ratios and at two different formic acid/formate buffer ratios. A plot is shown in Figure 1 of k_{obsd} for hydrolysis of diethylphenyl orthoformate *vs.* total acetate buffer concentration. Values of the second-order rate constants for general acid catalysis are given in Table I. In Figure 2 a plot is shown of log k_{HA} *vs.* the pK_a of the catalyzing acid in the hydrolysis of diethylphenyl orthoformate. The slope of this plot is −0.47 with a correlation coefficient of 0.993. In this correlation cacadylic acid was included with the six carboxylic acids. The slopes of plots of log k_{HA} *vs.* pK_a for hydrolysis of diphenylethyl orthoformate and diphenylethyl orthoacetate were −0.68 (r = 0.997) and −0.49 (r = 0.981), respectively.

Rate constants for hydronium ion catalysis were determined in HCl solutions and are reported in Table I. The point for hydronium ion in Figure 2 falls con-

TABLE I

RATE CONSTANTS k_{HA} (M^{-1} sec^{-1}) FOR GENERAL ACID CATALYZED HYDROLYSIS OF DIETHYLPHENYL ORTHOFORMATE, DIPHENYLETHYL ORTHOFORMATE, AND DIPHENYLETHYL ORTHOACETATE IN 50% DIOXANE–H_2O (v/v) WITH μ = 0.1, MAINTAINED WITH KCl

Acid	pK_a[a]	Diethylphenyl orthoformate[b]	Diphenylethyl orthoformate[c]	Diphenylethyl orthoacetate[b]
H_3O^+		74.0[d]	1.35[d]	35.3[d]
D_3O^+		64.6	1.48	30.9
Dichloroacetic	2.60		0.085	
Cyanoacetic	3.74	2.29	0.0195	0.68
Chloroacetic	4.00	1.57	0.0103	0.367
Formic	4.80	0.535	0.00299	0.171
Formic (D_2O)			0.0014	
Glycolic	4.95	0.388	0.0023	0.108
Acetic	6.06	0.154		0.0497
Acetic (D_2O)		0.073		0.0214
Succinic	6.90	0.078		
Cacadylic	7.50	0.03		

[a] Determined by half-neutralization at 25°. [b] At 25°. [c] At 45°. [d] The second-order constant is k_{obsd}/a_H.

siderably below the line and was omitted from the correlation. This was also the case in the similar plots of log k_{HA} *vs.* pK_a for hydrolysis of diphenylethyl orthoformate and diphenylethyl orthoacetate.

Rate constants were also determined in 50% dioxane–D_2O in these reactions and are reported in Table I. It will be noted that second-order rate constants for buffer acid catalysis are approximately twofold less in 50% dioxane–D_2O. The rate constants for hydronium ion catalysis show a slight change when the solvent is changed from 50% dioxane–H_2O to 50% dioxane–D_2O, the ratio $k_{D_3O^+}/k_{H_3O^+}$ being 0.87, 1.10, and 0.88 for hydrolysis of I, II, and III.

Salt and ionic strength effects are reasonably small in the hydrolysis of these orthoesters. The second-order rate constant for acetic acid catalyzed hydrolysis of diphenylethyl orthoacetate at 25° is 0.06 M^{-1} sec^{-1} when ionic strength is held constant at 0.5 M with KCl, approximately 20% greater than the rate constant obtained when ionic strength is 0.1. Likewise, the rate constant for acetic acid catalyzed hydrolysis of diethylphenyl orthoformate is only slightly greater when ionic strength is held constant at 0.5 M with $NaClO_4$, being 0.214 M^{-1} sec^{-1}.

Discussion

It has been observed that some of the reports of general acid catalysis in ortho ester hydrolysis reactions are possibly due to specific salt effects.[5,18] It would be expected that such effects would be most pronounced in media with a high percentage of organic solvent. The rate enhancements produced by small concentrations of buffer acids in the present study are certainly much too large to be attributable to specific salt effects. Furthermore, it was ascertained that greatly increasing the ionic strength to 0.5 M, held constant with KCl or with $NaClO_4$, gave rise to small increases in the second-order rate constants for buffer catalysis. At such high ionic strengths the contribution of the buffer anion to the total ionic strength is quite small. The

(18) P. Salomaa, A. Kankaanpera, and M. Lahti, *J. Amer. Chem. Soc.*, **93**, 2084 (1971).

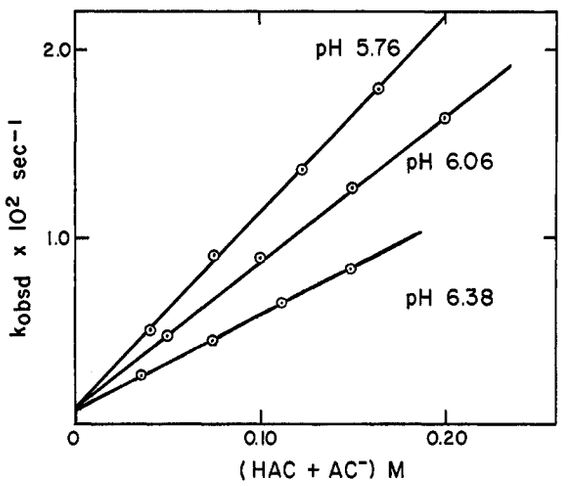


Figure 1.—Plots of k_{obsd} for hydrolysis of diethylphenyl orthoformate *vs.* total acetate buffer concentration in 50% dioxane–H_2O at 25° (μ = 0.1).

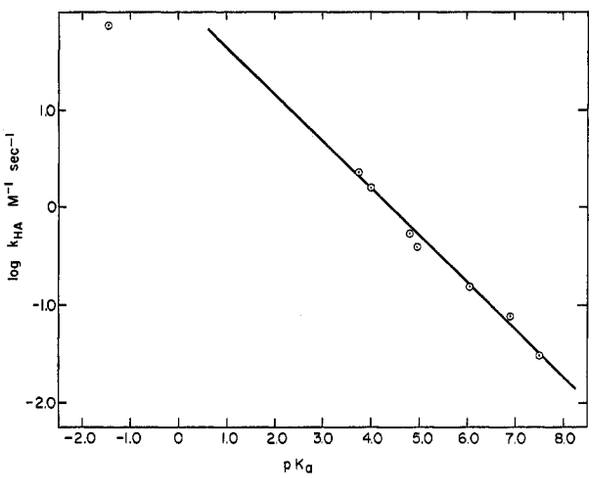


Figure 2.—Plot of log k_{HA} for general acid catalyzed hydrolysis of diethylphenyl orthoformate *vs.* the pK_a of the catalyzing acid in 50% dioxane–H_2O at 25° (μ = 0.1).

observed rate enhancements produced by increasing the buffer concentration at constant ionic strength and pH are then due to genuine general acid catalysis.

The Brønsted coefficient α of 0.47 for diethylphenyl orthoformate is considerably less than previously observed values of ~0.7 in ortho ester hydrolysis.[2,3,7] It is also less than observed in hydrolysis of the acetal 2-(*p*-nitrophenoxy)tetrahydropyran in 50% dioxane–H_2O (0.69).[12] The relatively fast rates of hydrolysis of diethylphenyl orthoformate in comparison with triphenyl orthoformate[13,19] and the pronounced general acid catalysis in comparison with the lack of general acid catalysis in the hydrolysis of triethyl orthoformate[4] must be due in part to the fact that with diethylphenyl orthoformate the leaving group is good and the intermediate carbonium ion is well stabilized by the adjoining ethoxy groups. Thus, as with acetals[9-12] ease of bond breaking appears to be a key factor in facilitating general acid catalysis.

This interpretation is strongly supported by the data for hydrolysis of diphenylethyl orthoformate with which

(19) The value of k_{obsd} for hydrolysis of triphenyl orthoformate in 40% dioxane–H_2O at 25° with 1 M HCl is 7.8 × 10^{-4} sec^{-1}. Therefore, although experimental conditions are different, the hydronium ion catalyzed hydrolysis of diethylphenyl orthoformate must proceed approximately 10^5 times more rapidly.

the leaving group is the same as with diethylphenyl orthoformate but where the intermediate carbonium ion should be less stable and where basicity will be considerably less because of the electron-withdrawing ability of the phenoxy group relative to ethoxy.[20] This ortho ester is also subject to general acid catalysis, but it will be noted in Table I that the magnitude of the rate constants is much less at 45° than in the case of diethylphenyl orthoformate at 25°. The rate constant for hydronium ion catalysis is 55-fold less. Of critical importance is the fact that the slope of the Brønsted plot of log k_{HA} *vs.* pK_a is much greater (−0.68). Thus, proton transfer is very likely occurring to a considerably greater extent in the transition state. General acid catalysis is therefore much less favorable with weak acid catalysts even though basicity is less.

Greatly increasing the stability of the oxocarbonium ion intermediate in the diphenylethyl system by employing diphenylethyl orthoacetate as the substrate led to a large reduction in the magnitude of the Brønsted coefficient (0.49). This again illustrates the importance of oxocarbonium ion stability and the ease of bond breaking in facilitating general acid catalysis in these reactions. From knowledge of the structural features leading to general acid catalysis in acetal and ketal hydrolysis,[9-12] it has therefore been possible to predict what types of ortho esters would show pronounced general acid catalysis and also the relative magnitudes of the Brønsted coefficients. Thus, the conclusion that ease of bond breaking is the critical feature in these reactions in regard to general acid catalysis would appear to be well established and general in application.

(20) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 556.

Registry No.—I, 14444-77-0; II, 25801-57-4; III, 33712-25-3.

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Acetolysis of 1-Tosyloxy-2,2-dideuteriobicyclopropyl

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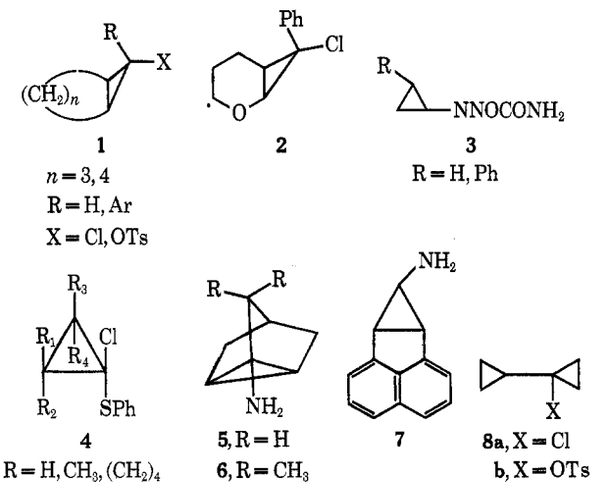
Acetolysis of 1-tosyloxy-2,2-dideuteriobicyclopropyl at 25° for 120 hr in the presence of sodium acetate produced a mixture of acetates **13** and **16** in which the position of the deuterium atoms eliminated the possibility of any of the degenerate rearrangements shown in Scheme I.

Examples of cyclopropyl derivatives that form stabilized cyclopropyl cations in solvolytic reactions and do not entirely undergo ring cleavage to allylic products are few. Unrearranged products have been obtaned in the solvolysis of exo-substituted bicyclo[*n*.1.0]-derivatives **1**, **2**,[1] cyclopropyl-*N*-nitrosoureas **3**,[2] cyclopropyl thioethers **4**,[3] the nitrous acid deamination of apotricyclyamine (**5**),[4a] 1-aminonortricyclene (**6**),[4b] and 3-amino-1,2-cyclopropanoacenaphthene (**7**),[4c] and solvolysis of bicyclopropyl derivatives **8**.[5]

Steric prohibition of the favored electrocyclic transformation[6] to an allylic system is justification[1c,d,6b] for the nonrearranged products of the solvolysis of compounds **1**, **2**, **5**, **6**, and **7**; however, a free-radical mechanism has been suggested[7] for compounds **5**, **6**, and **7**, and, although it might be extended to **3**, a carbonium ion mechanism has also been invoked for the latter.[2] Of all of the aforementioned systems, bicyclopropyl derivatives remain among the most interesting because substantial amounts of both ring-opened and ring-closed products are found.



Although acetolysis of **8a** in the presence of silver ion produced a mixture of **9**, **10**, and **11**,[5b,8] the use of **8b** with acetic acid and sodium acetate resulted in a mixture of **9** and **12** in addition to several minor products.[5c]

(1) (a) U. Schöllkopf, K. Fellenberger, M. Patsch, P. v. R. Schleyer, T. Su, and G. W. Van Dine, *Tetrahedron Lett.*, 3639 (1967); (b) U. Schollköpf, *Angew. Chem., Int. Ed. Engl.*, **7**, 588 (1968); (c) D. B. Ledlie and E. A. Nelson, *Tetrahedron Lett.*, 1175 (1969); (d) D. T. Clark and G. Smale, *Chem. Commun.*, 868, 1050 (1969); (e) D. B. Ledlie and W. H. Hearne, *Tetrahedron Lett.*, 4837 (1969).

(2) (a) W. Kirmse and H. Schütte, *Chem. Ber.*, **101**, 1674 (1968); (b) W. Kirmse and H. Schütte, *J. Amer. Chem. Soc.*, **89**, 1284 (1967).

(3) U. Schöllkopf, E. Ruban, P. Tonne, and K. Riedel, *Tetrahedron Lett.*, 5077 (1970).

(4) (a) P. Lippe and C. Padberg, *Chem. Ber.*, **54**, 1316 (1921); (b) H. Hart and R. A. Martin, *J. Amer. Chem. Soc.*, **82**, 6362 (1960); (c) R. Petit, *ibid.*, **82**, 1972 (1960).

(5) (a) J. A. Landgrebe and L. W. Becker, *ibid.*, **89**, 2505 (1967); (b) J. A. Landgrebe and L. W. Becker, *ibid.*, **90**, 395 (1968); (c) B. A. Howell and J. C. Jewett, *ibid.*, **93**, 798 (1971).

(6) (a) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965); (b) C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *ibid.*, **87**, 4006 (1965).

(7) K. V. Scherer, Jr., and R. S. Lunt, III, *ibid.*, **88**, 2860 (1966).

(8) An error in our original report[5b] resulted in enol acetate structures in which methyl and acetoxy groups were interchanged. However, the nmr spectra clearly establish the structures shown for **10** and **11**.