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.

Acknowledgment.—This work was supported by research grants from the National Science Foundation and the National Institutes of Health.

Acetolysis of 1-Tosyloxy-2,2-dideuteriobicyclopropyl

RONALD A. MARTIN AND JOHN A. LANDGREBE*

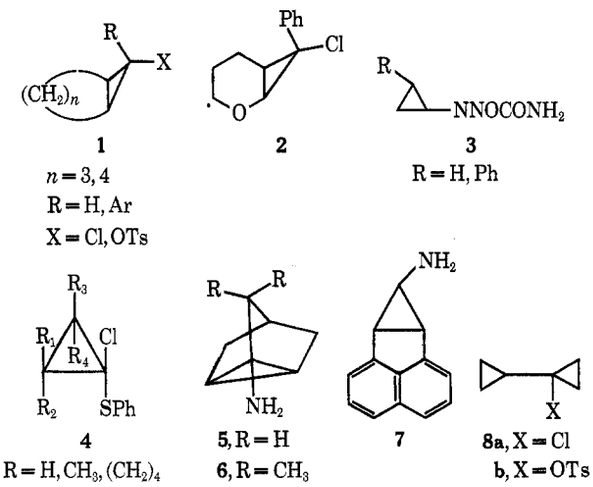
Department of Chemistry, University of Kansas, Lawrence, Kansas 66044

Received November 2, 1971

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).

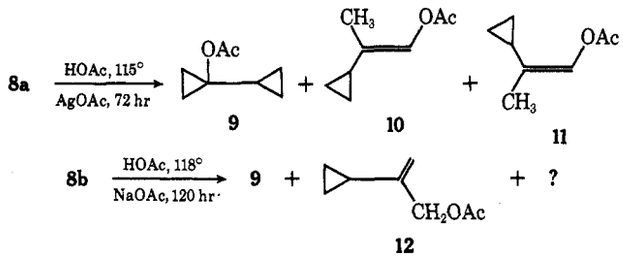
(4) (a) P. Lippe and C. Padberg, *Chem. Ber.*, **54**, 1316 (1921); (b) H. Hart and R. A. Martin, *J. Amer. Chem. Soc.*, **82**, 6362 (1960); (c) R. Petit, *ibid.*, **82**, 1972 (1960).

(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).

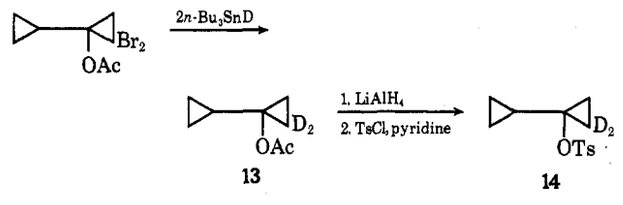
(8) An error in our original report[5b] resulted in enol acetate structures in which methyl and acetoxy groups were interchanged. However, the nmr spectra clearly establish the structures shown for **10** and **11**.



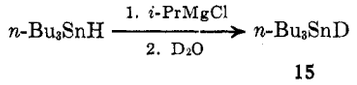
In the present study attention is focused on establishing whether or not there are degenerate rearrangements occurring during the solvolysis of **8b**.

Results and Discussion

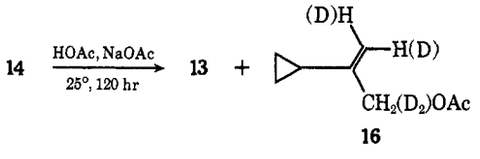
2,2-Dideuteriobicyclopropyl tosylate (**14**) was synthesized by a variation of the method previously described for the preparation of the undeuterated compound.[5a,b]



The reducing agent, tri-*n*-butyltin deuteride (**15**), was prepared by the deuterolysis of tri-*n*-butyltinmagnesium chloride,[9] which resulted in a product of *ca.* 99.8% deuterium content.



Acetolysis of deuterated tosylate **14** at 25° for 120 hr in the presence of sodium acetate produced a 1:2.5 mixture of bicyclopropyl acetate (**13**) and deuterated 2-cyclopropylallyl acetate (**16**) in comparable yield to

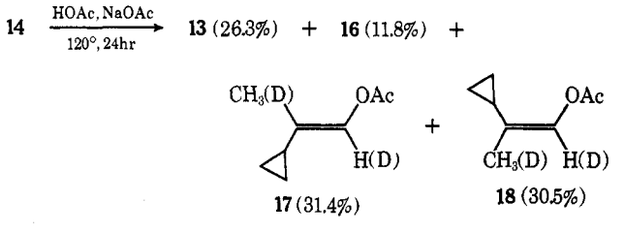


that reported by Howell and Jewett.[5c] Whether **16** forms directly from **14** or from the solvolysis of 2-cyclopropylallyl tosylate was not ascertained.

The location of the deuterium atoms in allyl acetate **16** was determined from an nmr spectrum of a sample isolated by preparative vapor phase chromatography. Chemical shift values agreed with those for undeuterated 2-cyclopropylallyl acetate.[10] Comparison of the integrated area for each type of proton with the acetate methyl as a three-proton internal standard revealed that the vinyl- and acetoxy-substituted carbon atoms contained all the deuterium atoms of the molecule about equally distributed between the two possible locations.

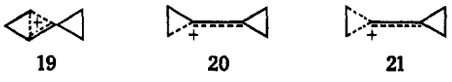
Analysis of the deuterium location in a collected sample of bicyclopropyl acetate (**13**) was accomplished by the use of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctan-4,6-dionatoeuropium.[11] The cis and trans protons (relative to acetoxy) at C-2 and C-3 appeared as two distinct AX doublets sufficiently removed from the multiplet assigned to the protons of the other cyclopropyl ring to allow a quantitative integration of the nmr spectrum and comparison with the acetate methyl. Proton assignments were confirmed by comparison with the nmr spectra of authentic **13** and undeuterated acetate **9** in the presence of the shift reagent. In the latter example, the cis and trans protons of C-2 and C-3 appeared as a pair of symmetrical multiplets containing four protons. Solvolysis product **13** had 95–100% of the deuterium atoms in the acetoxy-substituted ring, the small uncertainty being the result of an impurity and some line broadening caused by the nmr shift reagent.

The acetolysis of **14** in the presence of sodium acetate at 120° for 24 hr produced a mixture of **13**, **16**, *trans*-2-cyclopropylpropenyl acetate (**17**), and *cis*-2-cyclopropylpropenyl acetate (**18**) as well as three unidentified products which comprised no more than 3–5% of the total yield. Although the enol acetates **17** and **18**



were not individually isolated, an nmr spectrum of the product mixture indicated the presence of two deuterium atoms distributed between the allylic methyl group and the vinyl position. 2-Cyclopropylallyl acetate has been suggested as a precursor to the observed enol acetates[5c] but was never detected in their presence until shorter reaction times were used. In our work it has been observed that **16** readily formed a mixture of **17** and **18** on vapor phase chromatographic columns unless precautions were taken.

Although the observed lack of deuterium scrambling does not clearly distinguish between possible cationic intermediates such as **19**,[12] **20**,[13] or **21**,[14] it



does eliminate symmetrical species such as **22** and further indicates the lack of degenerate rearrangements represented by path a and path bcde of Scheme I. Evidence against path b (and e) is consistent with the observations of Wiberg[15] for the solvolysis of 4-tosyloxyspirohexane (**23**), which gives a variety of products,

(9) (a) J.-C. Lahournere and J. Valade, *J. Organometal. Chem.*, **22**, C3 (1970).

(10) The spectrum was kindly supplied by Professor J. Jewett, Ohio University.

(11) (a) C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969); (b) J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, 422 (1970); (c) R. E. Sievers and R. Rondeau, ARL Report 70-0285, 1970, Twelfth Experimental Nmr Conference, Gainesville, Fla., Feb 18, 1971.

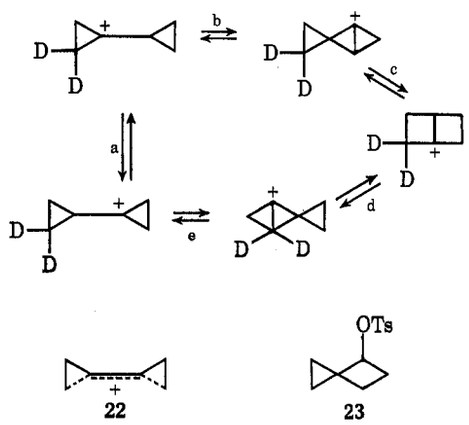
(12) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *J. Amer. Chem. Soc.*, **81**, 4399 (1959).

(13) S. Winstein and E. M. Kosower, *ibid.*, **81**, 4399 (1959).

(14) (a) C. U. Pittman, Jr., and G. A. Olah, *ibid.*, **87**, 5123 (1965); (b) H. G. Richey, Jr., and J. M. Richey, *ibid.*, **88**, 4971 (1966); (c) P. v. R. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2321 (1966).

(15) K. B. Wiberg and J. E. Hiatt, *ibid.*, **90**, 6495 (1968); see also D. E. Applequist and W. A. Bernett, *Tetrahedron Lett.*, 3005 (1968), and K. B. Wiberg and J. E. Hiatt, *ibid.*, 3009 (1968).

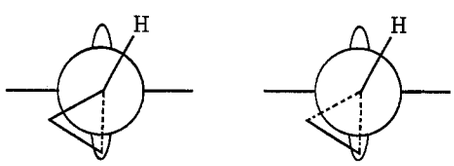
SCHEME I



22 23

none of which correspond structurally to those observed for the solvolysis of tosylate **14** under mild conditions.[16] It remains to be shown why the interconversion represented by path b is so energetically unfavorable.

In view of the ease of hydride migrations in various carbonium ions,[17a-c] the lack of an observable 1,2-hydride shift (path a) in the cation presumed to form during the solvolysis of **14** is significant. One possible explanation is that the preferred conformations for ions such as **20** and **21** (depected in structures **24** and **25**, respectively) result in dihedral angles between the methine C–H bond and the adjacent vacant orbital substantially different from the angle of 0° which is favored for hydride migration.



24 25

Experimental Section[18]

Tri-*n*-butyltin Deuteride (**15**).—This reagent was prepared by the method of Lahournere and Valade.[9a] To a stirred solution of isopropylmagnesium chloride (0.15 mol) in ether was added dropwise tri-*n*-butyltin hydride (10.0 g, 0.034 mol). The mixture was stirred at room temperature for 2.5 hr and then brought to reflux for 20 min. The contents were hydrolyzed with deuterium oxide and the resultant gel was slowly filtered and washed with ether. The ethereal solution was dried (Na_2SO_4), concentrated, and distilled to give 6.8 g (0.023 mol, 68%) of tri-*n*-butyltin deuteride, bp 78–70° (0.6 mm). The infrared spectrum (film) contained a Sn–D absorption at 1805 cm^{-1}.

2,2-Dideuteriobicyclopropyl Acetate (**13**).—The compound was obtained by a modification of the method described for the synthesis of bicyclopropyl acetate.[5b] Crude 2,2-dibromobicyclopropyl acetate was reduced by stirring it with tri-*n*-butyltin deuteride for 72–90 hr at 25° or overnight at 85° to give acetate **13** in 50% yield. The nmr spectrum (CCl_4) displays a complex multiplet at τ 9.2–9.85 (6 H) consistent with the introduction of two deuterium atoms and the nmr spectrum previously reported for bicyclopropyl acetate. More detailed nmr assignments are given in the description of the acetolysis.

2,2-Dideuteriobicyclopropyl Tosylate (**14**).—Acetate **13** (1.42 g, 0.010 mol) in ether (15 ml) was reduced with lithium aluminum hydride (0.95 g, 0.025 mol) in ether (50 ml) in a manner reported[5b] for the preparation of 1-hydroxybicyclopropyl to give 0.92 g (91.5%) of 1-hydroxy-2,2-dideuteriobicyclopropyl. The alcohol (0.92 g, 0.009 mol) and dry pyridine (18 ml) were chilled and tosyl chloride (3.43 g, 0.018 mol) was added; after dissolution, the mixture was stored at −20° for 5 days. Crystalline, long, white needles of tosylate **14** (1.28 g, 55.9%), mp 40.8–41.8°, were obtained from a work-up suggested by Fieser and Fieser.[19] The nmr spectrum (CCl_4) had absorptions at τ 2.23–2.7 (4 H, A_2B_2, para-substituted phenyl), 7.57 (3 H, singlet, tolyl methyl), and 8.13–9.95 (7 H, multiplet, cyclopropyl). An undeuterated sample of the tosylate was analyzed.

Anal. Calcd for $C_{13}H_{16}SO_3$: 61.88; H, 6.39. Found: C, 61.93; H, 6.38.

Acetolysis of 2,2-Dideuteriobicyclopropyl Tosylate (**14**) **at 25°.**—A mixture of tosylate **14** (1.017 g, 0.004 mol), anhydrous sodium acetate (0.492 g, 0.006 mol), and glacial acetic acid (180 ml) was stirred at 25° for 5 days. The solution was diluted with water (180 ml) and extracted with pentane (5 × 40 ml). The combined pentane solutions were washed with saturated aqueous sodium bicarbinate solution and concentrated to give 0.810 g of an oil which contained two components in a ratio of 1:2.5 by vpc analysis with a 5 ft, 10% OV-101 on 60/80 Gas-Chrom Q column at 100°. The two products were collected individually with a 6 ft, 10% OV-210 on 100/120 Gas-Chrom Q glass column at 75°. The product of shorter retention time and lower yield proved indistinguishable from authentic acetate **13** with both of the above columns. The nmr spectrum of the other compound agreed (neglecting proton integration) with the nmr spectrum of 2-cyclopropylallyl acetate.[10] The nmr spectrum (CCl_4) contained absorptions at τ 5.09 and 5.20 (broad singlets with some fine structure, $C{=}CH_2$), 5.48 (singlet, CH_2OCOCH_3), 7.97 (singlet, $OCOCH_3$), 8.4–9.0 (multiplet, methine proton), and 9.2–9.7 (multiplet; other cyclopropyl protons). The integration of the combined areas of the peaks represented by vinyl plus allylic protons compared to the acetate methyl as 2:3.

Addition of tris-1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctan-4,6-dionatoeuropium (Pierce Chemical Co., 15 mg) to the other product produced a simplified spectrum which was essentially identical with that of authentic **13** measured under similar conditions. The cis and trans C-4 protons appeared as two separated AX doublets which corresponded to 95–100% deuterium retention in the acetoxy-substituted ring. These assignments were confined by the addition of the shift reagent (50 mg) to bicyclopropyl acetate (**9**) (40.6 mg) in carbon tetrachloride (0.5 ml) which gave a spectrum that contains two almost identical five-peak multiplets (4 H) and an upfield multiplet (4 H) in addition to the acetoxy methyl.

Acetolysis of 2,2-Dideuteriobicyclopropyl Tosylate (**14**) **at 120°.**—A mixture of tosylate **14** (383 mg, 1.50 mmol), anhydrous sodium acetate (175 mg, 2.13 mmol), and glacial acetic acid (70 ml) was stirred at 120° for 24 hr. The mixture was cooled, diluted with water (70 ml), and extracted with pentane (5 × 60 ml). The combined pentane solution was washed with saturated sodium bicarbonate solution, dried (Na_2SO_4), and concentrated to give 205 mg (96%) of crude products. Four products representing 90% of the product mixture were identified by vpc and nmr data as 2,2-dideuteriobicyclopropyl acetate (**13**) (26.3%), 2-cyclopropylallyl acetate (**16**) (11.8%), *trans*-2-cyclopropylpropenyl acetate (**17**) (31.4%), and *cis*-2-cyclopropylpropenyl acetate (**18**) (30.5%). Allylic acetate **16** readily isomerized to a mixture of **17** and **18** on vpc columns unless buildup of decomposition products on the column was minimized by use of very small samples. Columns were treated frequently with Silyl-8 conditioner (Pierce Chemical Co.).

Registry No.—**13**, 34839-53-7; **14**, 34839-54-8; **15**, 6180-99-0.

(16) Solvolysis of **14** at 120° did produce three very minor unidentified products which represented 3–5% of the total product mixture.

(17) (a) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure," McGraw-Hill, New York, N. Y., 1968, pp 786–789, 795–797; (b) Y. Pocker in "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 13; (c) J. A. Berson, *ibid.*, pp 140–145.

(18) Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were obtained with a Beckman IR-8 double grating spectrophotometer and nmr spectra were obtained with a Varian A-60 spectrometer. Chemical analyses were performed with an F & M Model 180 Carbon, Hydrogen, Nitrogen Analyzer, Department of Medicinal Chemistry, University of Kansas, Lawrence, Kans.

(19) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. I, Wiley, New York, N. Y., 1967, p 1180.