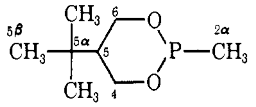
said for the chair form with *tert*-butyl axial. Additional evidences for conformation **3** are gained from the ^{13}C spectra (Table II) of the isomers of **1a**. For 14 examples of 5-*tert*-butyl-1,3-dioxanes and *tert*-butyl substituted trivalent and pentavalent six-membered ring phosphorus compounds, for which pmr analysis has established the equatorial position of the *tert*-butyl, a chemical shift of 101 ± 0.22 ppm for the *tert*-butyl methyls (5β) has been noted.[7] Several *cis*-5-*tert*-butyl-1,3-dioxanes with axial *tert*-butyl showed downfield shifts for the *tert*-butyl methyls of about 2 ppm relative to those for the equatorial analogs. These results indicate that the *tert*-butyl is equatorial in *cis*-**1a** as depicted in **3**. A *predominantly* equatorial *tert*-butyl is indicated for *trans*-**1a** (form **4**) which may be in rapid equilibrium with a lesser proportion of a conformation **5** with *tert*-butyl axial, leading to a time-averaged 0.7 ppm downfield shift in *trans*-**1a** compared to *cis*-**1a**. Comparison of chemical shifts and carbon–phosphorus couplings (Table II) shows the methyl group on phosphorus in the two stereoisomers to be in significantly different environments. Axial methyls have previously been shown to be shifted upfield compared to equatorial ones in cyclohexanes.[8] A reasonable conclusion is that the methyl is axial in *cis*-**1a** and largely equatorial in *trans*-**1a**. Using a value[1c,d] of -1.5 kcal/mol for ΔG°_{25} for the axial → equatorial interconversion of a 5-*tert*-butyl in the 1,3-dioxane series and an assumed axial preference of the methyl of -1.2 kcal/mol, a 2:1 ratio of **4** to **5** is calculated in reasonable agreement to the ratio predicted by the time-averaged ^{13}C *tert*-butyl chemical shift of *trans*-**1a**.

Table II. ^{13}C Spectral Data[a] for **1a**



Carbon	Chemical shifts (coupling constant, J_{CP}) Cis isomer	Trans isomer
2α	114.2_1 (42.8)	108.9_0 (32.2)
4,6	67.3_8 (4.0)	63.9_5 (1.2)
5	81.8_4 (4.8)	81.7_9 (7.0)
5α	97.7_2	97.4_2
5β	101.2_0	100.5_4

[a] 75% (v:v) solution in C_6D_6, 40°. Shifts in parts per million upfield from benzene as internal standard. Coupling constants in hertz.

The methyl equatorial preference in **2a** is so great that the trans isomer is the thermodynamically more stable form, and the cis chair conformation has the *tert*-butyl group axial and methyl equatorial. At least two important factors may contribute to the exceptional differences in conformational properties of systems **1a** and **2a**. First, syn-axial interactions may be greatly reduced in **1a**, since the phosphorus–oxygen bonds are considerably longer than carbon–oxygen bonds, and because of possible consequent flattening of the ring about phosphorus. Second, the conformational competition in **1a** is between methyl and an electron pair rather than between methyl and a hydrogen. An important result is that the interaction of the lone pair on phosphorus with adjacent lone pairs, nuclei, and bonding electrons may play a decisive role in determining the configuration at phosphorus.[9] The probable significance of vicinal lone-pair–lone-pair interactions in systems showing large single bond rotational barriers has been recently emphasized.[10]

Acknowledgment. This work was supported by a grant to W. G. B. from the National Cancer Institute, Public Health Service Research Grant No. CA-11045, and by a grant from the National Institutes of Health (GM-08521-10) to D. M. G.

---

(7) D. M. Grant, E. L. Eliel, W. G. Bentrude, J. H. Hargis, A. R. Jones, and R. D. Bertrand, unpublished results.

(8) D. K. Dalling and D. M. Grant, *J. Amer. Chem. Soc.*, **89**, 6612 (1967).

(9) See, *e.g.*, A. Rauk, S. Wolfe, and I. G. Csizmadia, *Can. J. Chem.*, **47**, 113 (1969); L. C. Allen, *Chem. Phys. Lett.*, **2**, 597 (1968).

(10) M. Raban, G. W. J. Kenney, Jr., and F. G. Jones, Jr., *J. Amer. Chem. Soc.*, **91**, 6677 (1969); A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *ibid.*, **92**, 5206 (1970).

Wesley G. Bentrude,* K. C. Yee
Richard D. Bertrand, David M. Grant
Department of Chemistry, University of Utah
Salt Lake City, Utah 84121

Received August 4, 1970

Synthesis and Solvolysis of 1-Cyclopropylcyclopropyl Tosylate

Sir:

Solvolytic reactions of simple cyclopropyl derivatives usually afford only allyl products.[1] Theoretical[2] and experimental[3] evidence suggests that the mechanism of these reactions involves a concerted ionization and ring opening to an allyl cation. However, in bicyclic systems in which there is an extrasymmetric[4] steric prohibition of the favored disrotatory ring opening, unrearranged products have been obtained. In these cases, mechanisms involving partially opened ions[5–7] and nonconcerted[7] ionization and ring opening have been postulated. Landgrebe and Becker reported the first example of a simple cyclopropyl derivative, 1-cyclopropylcyclopropyl chloride, that afforded solvolysis products of unrearranged structure.[8]

In an effort to determine the extent to which extrasymmetric *conjugative* interactions can alter the mechanism of such reactions, we are investigating the solvolytic behavior of a variety of 1-substituted cyclopropyl tosylates. The results of our initial study of 1-cyclopropyl-, 1-vinyl-, and 1-isopropylcyclopropyl tosylates (**1**, **2**, **3**)[9] bear on this question. In addition,

---

(1) J. D. Roberts and V. C. Chambers, *J. Amer. Chem. Soc.*, **73**, 5034 (1951).

(2) (a) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965); (b) W. Kutzelnigg, *Tetrahedron Lett.*, 4965 (1967); (c) D. T. Clark and D. R. Armstrong, *Theor. Chim. Acta*, **13**, 365 (1969).

(3) (a) C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *J. Amer. Chem. Soc.*, **87**, 4006 (1965); (b) S. J. Cristol, R. M. Sequerra, and C. H. DePuy, *ibid.*, **87**, 4007 (1965); (c) P. von R. Schleyer, G. W. Van Dine, U. Schollkopf, and J. Paust, *ibid.*, **88**, 2868 (1966); (d) P. von R. Schleyer, T. M. Su, M. Saunders, and J. C. Rossenfeld, *ibid.*, **91**, 5174 (1969), and references therein.

(4) J. A. Berson and S. S. Olin, *ibid.*, **92**, 1087 (1970).

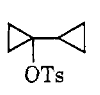
(5) U. Schollkopf, K. Fellenberger, M. Patsch, P. von R. Schleyer, T. Su, and G. W. Van Dine, *Tetrahedron Lett.*, 3639 (1967).

(6) D. M. Ledlie and E. A. Nelson, *ibid.*, 1175 (1969).

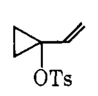
(7) D. T. Clark and G. Smale, *Chem. Commun.*, 868, 1050 (1969).

(8) J. A. Landgrebe and L. W. Becker, *J. Amer. Chem. Soc.*, **89**, 2505 (1967).

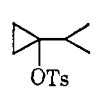
(9) (a) The alcohols used in this study were prepared by the method of Wasserman[10] and were converted to tosylates by the Tipson proce-



1



2

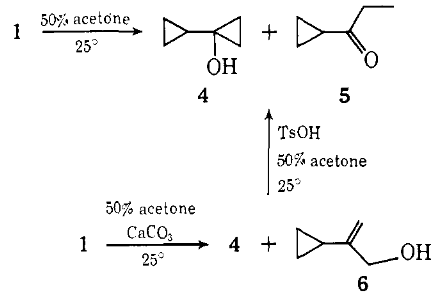


3

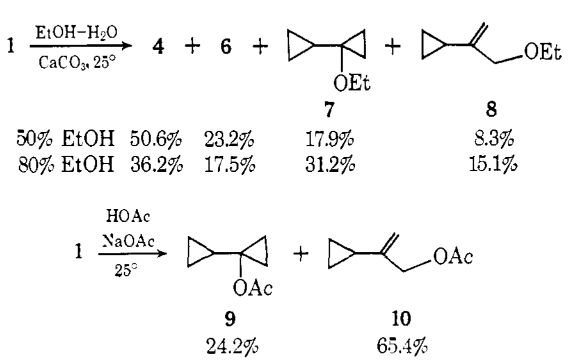
we have observed a surprisingly facile acid-catalyzed rearrangement of 2-cyclopropylallyl alcohol to ethylcyclopropyl ketone (**6** → **5**).

Hydrolysis of **1** in aqueous acetone at 25° afforded 62.9% of unrearranged alcohol **4**, 24.3% of ketone **5**, and two other minor products (3.7 and 9.1%), as yet unidentified. This result is in accord with the previous report[8] that hydrolysis of the corresponding chloride at 56° afforded only ketone **5**, which was presumed to arise exclusively from homoketonization[12] of **4**. However, we have found that the cyclopropanol **4** is essentially stable to the conditions of the present solvolysis experiments (<5% conversion to **5**). Hydrolysis of **1** at 25° in the presence of calcium carbonate afforded 59.2% of **4**, 40.8% of 2-cyclopropylallyl alcohol (**6**), and only a trace of ketone **5**. When subjected to the conditions of the unbuffered hydrolysis, the mixture of alcohols **4** and **6** was converted to the same mixture of products obtained in the unbuffered hydrolysis (Scheme I). These results demonstrate that an acid-catalyzed rearrangement of **6** constitutes the principal, if not exclusive, pathway for the formation of ketone **5** in the unbuffered hydrolysis of **1** at 25°. The scope and detailed mechanism of this rearrangement remain to be established by work in progress, but a revision of the generally accepted mechanism[12] for the acid-catalyzed homoketonization of cyclopropanols may be required to accommodate these results.

Scheme I



Solvolysis of **1** in aqueous ethanol at 25° in the presence of calcium carbonate afforded the expected 1-cyclopropylcyclopropyl and 2-cyclopropylallyl alcohols and ethers (**4**, **6**, **7** **8**,) in the indicated amounts. Similarly, acetolysis of **1** at 25° afforded the expected acetates **9** and **10**.[13] Thus, the kinetically controlled products of acetolysis, hydrolysis, and aqueous ethanolysis of **1** are *formally* derived either from partially opened ions or discrete cyclopropyl and allyl cations of similar energy. In contrast to this behavior, buffered hydrolysis of 1-vinylcyclopropyl tosylate (**2**) afforded no detectable (glpc) amount of unrearranged alcohol.[14] Buffered hydrolysis of 1-isopropylcyclopropyl tosylate (**3**) afforded only 2-isopropylallyl alcohol, the product expected from concerted ionization and ring opening.



The rate data for aqueous ethanolysis of **1**, **2**, and **3** are presented in Table I. The rate and product data for the solvolysis of **1** clearly indicate cyclopropyl cation character in the rate-determining transition state and subsequent intermediate. On the other hand, the data for solvolysis of **2** and **3** are consistent with rate-determining concerted ionization and ring opening. The solvolysis of **1** is apparently uncomplicated by competitive bimolecular and ring expansion processes (cyclopropylcarbinyl → cyclobutyl). Thus, the present results provide a particularly straightforward demon-

Table I. Solvolysis Rate Data for 1-Substituted Cyclopropyl Tosylates in Aqueous Ethanol

Compd	Solvent[a]	T, ° C	$k \times 10^4$, sec^{-1} [b]	Rel rate, 50E, 70°
1[c]	80E	15.0	0.362 ± 0.001	
	80E	25.0	1.293 ± 0.001	15,929[d]
	80E	35.0	4.228 ± 0.011	
	90E	35.0	1.134 ± 0.003	
	50E	70.0	2915[d]	
2	50E	70.0	1.883 ± 0.001	10.3
	50E	60.0	0.626 ± 0.001	
3	50E	70.0	0.183 ± 0.001	1.0

[a] 50E refers to 50% aqueous ethanol, v/v before mixing. [b] Rate constants determined spectrophotometrically (C. G. Swain and C. R. Morgan, *J. Org. Chem.*, **29**, 2097 (1964)) except those for **2** which were determined conductometrically. Data treated by doubly weighted least-squares analysis. [c] Good first-order behavior is observed through *ca.* 60% reaction, after which there is a slight downward drift in the integrated rate constants. Experimental infinity values are within 5% of calculated values. [d] Estimated from experimental data using $m = 0.77$, $\Delta H^{\ddagger} = 21.08$ kcal/mol, and $\Delta S^{\ddagger} = -5.6$ eu.

---

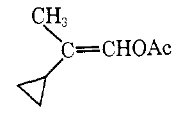
dure.[11] (b) All new compounds in this study gave satisfactory elemental analysis and exhibited spectral properties consistent with the proposed structures.

(10) H. H. Wasserman, R. E. Cochoy, and M. S. Baird, *J. Amer. Chem. Soc.*, **91**, 2375 (1969).

(11) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

(12) (a) C. H. DePuy, F. W. Breitbeil, and K. R. DeBruin, *J. Amer. Chem. Soc.*, **88**, 3347 (1966); (b) A. Nickon, J. L. Lambert, R. O. Williams, and N. H. Westruik, *ibid.*, **88**, 3354 (1966); (c) C. H. DePuy, *Accounts Chem. Res.*, **1**, 33 (1968).

(13) At elevated temperatures, the allylic acetate **10** is converted to the mixture of *cis*- and *trans*-enol acetates (**11**) obtained in the acetolysis of 1-cyclopropylcyclopropyl chloride.[8] Professor J. A. Landgrebe has informed us that the positions of the methyl and acetoxy groups were



11

inadvertently interchanged in the structures proposed for the enol acetates in ref 8 (personal communication, 1970).

(14) Three products in approximately equal amounts are formed in the hydrolysis of **2**.

stration of the superior efficiency of "vertical"[15] stabilization of electron deficiency by an adjacent cyclopropyl group relative to a double bond. A more detailed description of the charge distribution in the solvolytic transition state for **1** awaits the results of an isotope effect study in progress.

---

(15) W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, **92**, 829 (1970).

Acknowledgment. The authors wish to thank the National Science Foundation (Grants GP 8703, GP 21307) for support of this work.

B. A. Howell, J. G. Jewett*
Clippinger Research Laboratories, Department of Chemistry
Ohio University, Athens, Ohio 45701

Received October 14, 1970

Book Reviews

Advances in Electrochemistry and Electrochemical Engineering. Volume 7. Electrochemistry. Edited by Paul Delahay, Department of Chemistry, New York University, New York, N. Y. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1970. xi + 366 pp. 16 × 23.5 cm. $18.50.

The volume under review contains five articles by leading authorities in the respective fields, all of which are of considerable contemporary interest.

The first article, by Payne, deals with the electrical double-layer in nonaqueous solutions. The available data in this area are comprehensively reported and critically discussed, separately for the various solvents that have been used—particularly alcohols, amides, ammonia, DMSO, cyclic esters and lactones, formic acid, and acetonitrile; available data on other solvents are also reported, and there are useful sections in which the behavior of the several primary alcohols, and of the various amides, are compared for each class of compound. This review will be indispensable reading for anyone whose work touches on double-layer effects, not only because of the completeness with which the literature is covered but also for the critical manner in which the reported data are discussed. A clear inference from this review is that we badly need to understand what produces the various capacity humps observed in so many systems. This seems to be an area to which more workers could well devote specific attention.

The article by Butler on reference electrodes in aprotic organic solvents meets a long-felt need. It is evident from the literature cited that a great deal of work in this area has been published in the form of reports to various contracting agencies, and Butler has performed a task of considerable value by reviewing this material as well as that available in the regular journals. A particularly satisfactory aspect of this review is the fact that there are sections devoted specifically to the purification of solvents and to the analysis of solvents for impurities.

The chapter by Parsons on faradaic and nonfaradaic processes has less the character of a review than the other chapters in this volume. Parsons gives a thoughtful discussion of the problem of the interdependence of faradaic and nonfaradaic currents. This subject was, and continues to be, a mattter of some controversy, and discussions have usually been cast in the framework of the considerations published by Delahay several years ago. In the article under review, Parsons takes a more comprehensive approach and shows the conceptual similarity between the ideas put forward by Delahay, the idea of partial charge transfer originated by Lorenz, and the work by Barker on the development of a complete equivalent circuit for electrodes. In addition to a discussion of the concepts involved, this chapter includes a section dealing with experimental evidence for the necessity of invoking the general concept of interdependence of faradaic and nonfaradaic currents. Although, as Parsons says in his conclusion, this report is of an interim nature, it is nevertheless an extremely valuable contribution on a subject of considerable contemporary interest. The last two chapters in the book are written from a somewhat more personal viewpoint than the earlier chapters. Hoytink reviews the electrochemical reduction of aromatic hydrocarbons with emphasis on the work carried out in his own research group. Generalizations are given about rates and mechanisms of the relevant processes, the application of quantum mechanics is discussed (though in no great detail), and the influence of the electrical field in the double layer is considered.

The final chapter, by Krishtalik, on hydrogen overvoltage represents the third part of a discussion of which the first two parts (by Frumkin) appeared in Volumes 1 and 3 of this series. Krishtalik discusses specifically the relationship between heats of adsorption, activation energy, and hydrogen discharge, and devotes a section to the matter of barrierless discharge of hydrogen ions. The latter is an idea that was proposed by Krishtalik, and it is developed in detail here together with a discussion of possible experimental evidence in support of the concept.

It should be clear from the above remarks that each of the chapters in this volume is of considerable interest. This high quality affords ample justification for publication of volumes of this sort.

Henry H. Bauer
Department of Chemistry, University of Kentucky
Lexington, Kentucky 40506