Solvolytic Reactivity of 4-Tricyclyl, 1-Apocamphyl, and 1-Methyl-4-tricyclo[2.2.2.0^{2,6}]octyl Trifluoromethanesulfonates. Observations on the Interaction of the Face of the Cyclopropane Ring with Electrophiles and on the Interpretation of Activation Parameters for Solvolytic Reactions[1]

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Received November 12, 1971

Abstract: Ionization of 4-tricyclyl derivatives **13** produces a carbonium ion **14** in which the empty, charge-carrying p orbital is situated directly above the face of the cyclopropane ring on the opposite side of the molecule. The ionization of 4-tricyclyl trifluoromethanesulfonate (**25**) has been studied in buffered aqueous ethanol in the neighborhood of 230°; this compound is the least reactive *tert*-alkyl system whose solvolysis rate has ever been measured. The corresponding tosylate is estimated to undergo ionization with a half-life of 4×10^9 years at 25°, and **25** is $\sim 10^{-4}$ times as reactive as its bicyclic analog apocamphyl trifluoromethanesulfonate (**30**). These studies show that no stabilization is gained by the interaction of a positively charged center with the face of a cyclopropane ring. Strain energy calculations completely account for the slow rate of solvolysis of **25**, and indicate that the three-membered ring has a negligible inductive effect when oriented as in **14**. In addition, the activation entropy for the ionization of **25** is quite negative at 230°; it is suggested that this may be due to the effect of an appreciably negative heat capacity of activation, and a *caveat* is expressed regarding mechanistic interpretation of activation parameters which are measured at unusual temperatures.

Three-membered carbon rings have long been known to interact readily with electrophiles.[3–5] A large number of intermolecular reactions are known in which ring opening has been achieved with halogens,[3a] acylium ions,[3b] and protons.[3c–m] Protonated cyclopropanes have also been established as intermediates in a number of ionization reactions of *n*-propyl derivatives.[4] Intramolecular examples of cyclopropane–electrophile interactions are provided by the well-established stability of cyclopropylcarbinyl,[5a] 1-cyclopropylvinyl,[5b–d] and homocyclopropylcarbinyl[5e,f] cations. Although cyclopropane rings are often considered to be intermediate between single and double bonds in many types of chemical behavior, they react in some cases even more rapidly with electrophiles than do double bonds.[3k]

Intuitively, it is relatively easy to predict the most favored approach of an electrophile to a double bond. If one assumes that attack occurs at the region of highest electron density in the substrate, it seems reasonable that an electrophile will approach perpendicular to (*z* axis, Figure 1) rather than in the plane of the molecule (*x* or *y* axis, Figure 1), since the latter approach involves steric interference from the vinyl hydrogens as well as bonding to a region in which there is a node in the filled π molecular orbital.[6] The cyclopropane situation is less clear, however. Two extreme avenues of electrophilic approach are toward the "face" of the ring (*z* axis, Figure 2) or the "edge" of the ring (*y* axis, Figure 2). The Walsh model of cyclopropane (Figure 3) predicts[7] relatively high electron density in both locations, the first associated with the sp^2 orbitals directed toward the center of the ring, and the latter associated with the p orbitals on the periphery of the ring.

A number of theoretical studies have predicted that attack upon the face of a cyclopropane ring is clearly less favored than other modes of approach.[8] Testing

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[1] (a) Some of the results described in this paper have been reported in preliminary form: S. A. Sherrod, R. G. Bergman, G. J. Gleicher, and D. G. Morris, *J. Amer. Chem. Soc.*, **92**, 3469 (1970); (b) for complementary observations, see R. C. Bingham, W. F. Sliwinski, and P. v. R. Schleyer, *ibid.*, **92**, 3471 (1970).

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[3] (a) N. C. Deno and D. N. Lincoln, *J. Amer. Chem. Soc.*, **88**, 5357 (1966); (b) H. Hart and R. H. Schlosberg, *ibid.*, **88**, 5030 (1966); **90**, 5189 (1968), and earlier papers; (c) R. L. Baird and A. A. Aboderin, *Tetrahedron Lett.*, 235 (1963); *J. Amer. Chem. Soc.*, **86**, 252 (1964); (d) R. T. LaLonde and J. J. Batelka, *Tetrahedron Lett.*, 445 (1964); (e) R. T. LaLonde and L. S. Forney, *J. Amer. Chem. Soc.*, **85**, 3767 (1963); (f) R. T. LaLonde and M. A. Tobias, *ibid.*, **85**, 3771 (1963); **86**, 4068 (1964); (g) E. J. Corey and R. F. Atkinson, *J. Org. Chem.*, **29**, 3703 (1964); (h) C. H. DePuy, H. L. Jones, and D. H. Gibson, *J. Amer. Chem. Soc.*, **90**, 1830 (1968); (i) G. A. Olah and J. Lukas, *ibid.*, **90**, 933 (1968); (j) N. C. Deno, W. E. Billups, D. LaVietes, P. C. Scholl, and S. Schneider, *ibid.*, **92**, 3700 (1970), and references cited therein; (k) P. E. Peterson and G. Thompson, *J. Org. Chem.*, **33**, 968 (1968); (l) C. C. Lee, *Progr. Phys. Org. Chem.*, **7**, 129 (1970); (m) C. J. Collins, *Chem. Rev.*, **69**, 541 (1969).

[4] (a) G. J. Karabatsos, C. Zioudrou, and S. Meyerson, *J. Amer. Chem. Soc.*, **92**, 5996 (1970); (b) G. J. Karabatsos, M. Anand, D. O. Rickter, and S. Meyerson, *ibid.*, **92**, 1254 (1970), and earlier papers; (c) C. C. Lee and D. J. Woodcock, *ibid.*, **92**, 5992 (1970).

[5] (a) P. v. R. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2321 (1966); (b) R. G. Bergman and D. R. Kelsey, *ibid.*, **93**, 1953 (1971); (c) R. G. Bergman and D. R. Kelsey, *ibid.*, **93**, 1941 (1971); (d) R. G. Bergman and S. A. Sherrod, *ibid.*, **93**, 1925 (1971); (e) M. J. S. Dewar and J. M. Harris, *ibid.*, **90**, 4468 (1968), and references cited therein; (f) Y. E. Rhodes and T. Takino, *ibid.*, **90**, 4469 (1968), and references cited therein.

[6] M. J. S. Dewar, *J. Chim. Phys.*, **46**, 268 (1949), and subsequent papers.

[7] A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

[8] (a) R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 5350 (1969); (b) J. D.

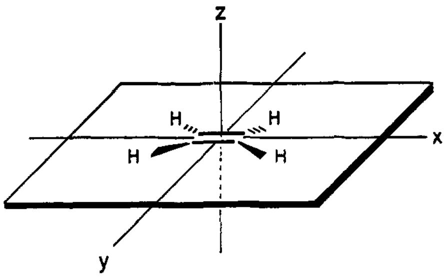


Figure 1. Possible extreme directions of approach for electrophilic attack on a double bond.

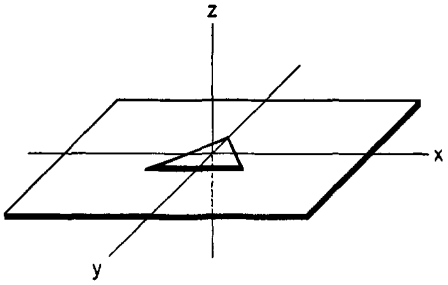
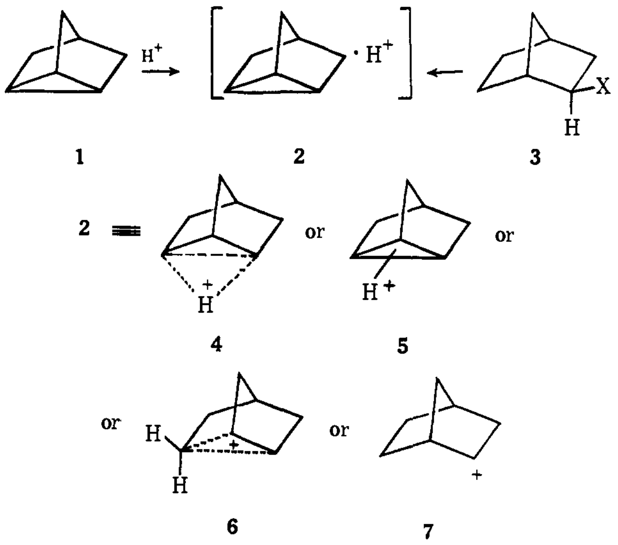


Figure 2. Possible extreme directions of approach for electrophilic attack on a cyclopropane ring.

these predictions, however, has generated significant controversy. The most vigorous of these has centered around the structure of protonated nortricyclene (2),



which in principle can be generated by bimolecular reaction of nortricyclene (1) and H+, or alternatively by solvolysis of norbornyl derivatives 3. Much discussion[9] has centered around the question of whether the most stable cationic intermediate in these reactions is the "classical" ion 7 or the bridged (recently referred to[9d] as "corner-protonated") ion 6. In addition, there is the problem of the structure of the intermediate or transition state which interconverts 6 with its mirror image by 6,1- or 6,2-hydride shift; Roberts initially raised the possibility[10] that this intermediate might be either edge or face protonated (4 or 5). Recent results seem to favor 6 as the most likely alternative for the structurally stable ion,[9d] and edge-protonated intermediate 4 as the species responsible for hydride shift.[11]

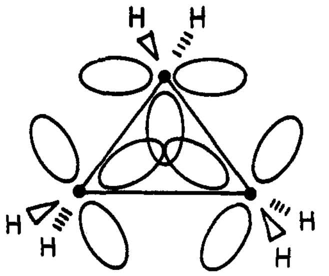
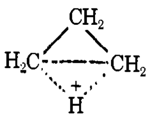


Figure 3. Basis set atomic orbitals used in construction of Walsh model ring bonding in cyclopropane.

Similar alternatives exist in the acyclic parent system, intensively investigated in recent years by the groups of Karabatsos[4a,b] and Lee.[31] Once again, edge- and face-protonated alternatives 8 and 9 are available, along with



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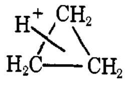

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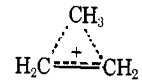

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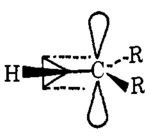
methyl-bridged ("corner-protonated") ion 10, and the available evidence[3,4] seems to favor 8 as the most stable structure.

Studies in intramolecular series (*e.g.*, 11 and 12) have



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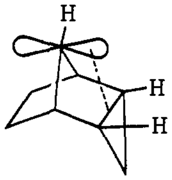

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supported the favorability of edge–electrophile interaction. In most cases the electrophile here is an empty carbon 2p orbital, and greatest stabilization is achieved in such cases by orienting this orbital so that it has appropriate symmetry for interaction with the p orbital on an adjacent edge of the ring.[5]

The studies summarized above have provided a great deal of information about edge- and corner-associated cyclopropane–electrophile complexes. At the outset of our study very little experimental information was available, however, concerning face-complexed cyclopropanes. In order to study such intermediates, therefore, and to compare their chemical behavior with those of edge-complexed analogs, we initiated the work reported here.

Results

Because of the tendency of flexible systems to select edge or corner complexation, it was clear at the beginning of our study that in order to ensure interaction of an electrophile with the face of a cyclopropane ring,

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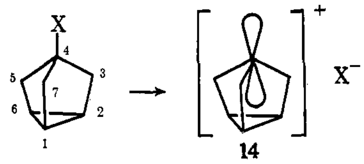
Petke and J. L. Whitten, *ibid.*, 90, 3338 (1968); (c) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *ibid.*, 93, 1813 (1971); (d) N. Bodor and M. J. S. Dewar, *ibid.*, 93, 6685 (1971).

[9] See, for example, (a) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, New York, N. Y., 1965; (b) G. D. Sargent, *Quart. Rev., Chem. Soc.*, 20, 299 (1966); (c) H. C. Brown, *Chem. Brit.*, 199 (1966); (d) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *J. Amer. Chem. Soc.*, 92, 4627 (1970); (e) G. A. Olah, J. R. DeMember, C. Y. Lui, and R. D. Porter, *ibid.*, 93, 1442 (1971).

[10] (a) J. D. Roberts and C. C. Lee, *ibid.*, 73, 5009 (1951); (b) J. D. Roberts, C. C. Lee, and W. H. Saunders, *ibid.*, 76, 4501 (1954).

[11] J. A. Berson and P. W. Grubb, *ibid.*, 87, 4016 (1965).

we would have to build both components into a structure rigid enough to allow only that interaction. One of the few carbocyclic systems which possesses the appropriate symmetry and rigidity is 4-nortricyclyl (**13**).



13 **14**

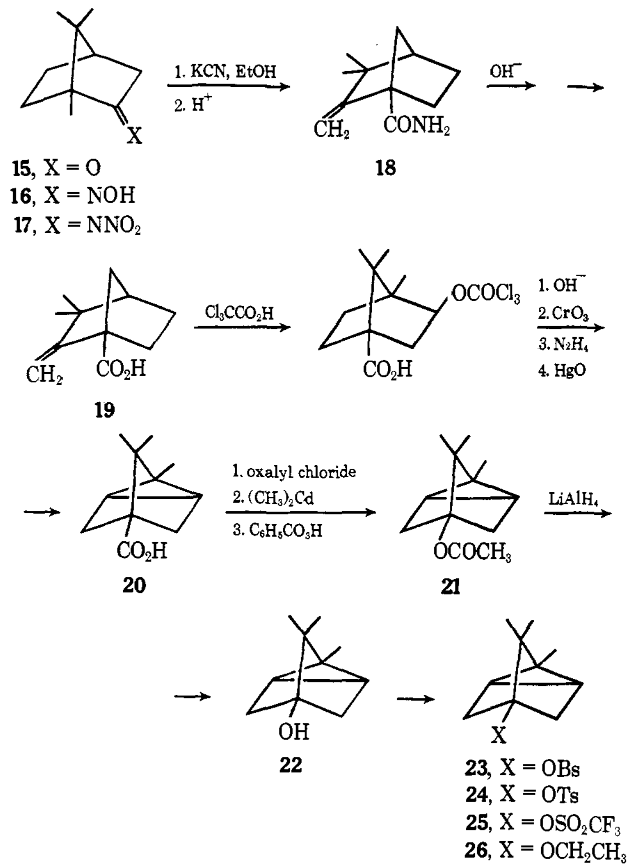
Ionization of a substrate such as **13** must necessarily generate a carbonium ion in which the empty p orbital is situated directly above the face of the ring. Furthermore, the 4-carbon atom in **13** is located only 2.08 Å from the plane of the ring,[12] assuring the possibility of overlap of the empty p orbital at C-4 in **14** with at least the threefold-symmetric combination of sp^2 orbitals in the three-membered ring. If this interaction were a stabilizing one, it would be expected that derivatives of **13** undergo solvolysis at rapid rates relative to suitable model systems. If the interaction were less favorable, the solvolysis rate of **13** would be slower, and a comparison of this rate with a model might provide a quantitative estimate of the unfavorability of the interaction.

Syntheses. Accordingly, we set out to prepare and solvolyze molecules related to **13**. We decided on 4-tricyclyl sulfonates such as **23** because 4-tricyclenecarboxylic acid (**20**) was a known compound[13] and we felt that the carboxylic acid group could easily be converted into a sulfoxy function without skeletal perturbation (*cf.* Scheme I). We were not able to convert the 2-ethynyl borneol epimeric mixture into 4-acetylisobornyl formate *via* Rupe rearrangement[14] in sufficient quantity to render a synthetic method based on this intermediate a feasible proposition.

Our first synthetic objective was camphene-1-carboxylic acid (**19**). Nitrous acid is known to convert camphoroxime (**16**) to camphornitrimine (**17**),[15] whose structure has been unequivocably established.[16a] This reaction, which appears to be applicable only to certain terpenoid and steroidal oximes,[15a] may proceed by either initial N- or O-nitrosation.[16b] The role of the intense purple coloration in the ethereal layer during this reaction is not clear; however, when the reaction is carried out using acetic acid as solvent and acid source, this color is only transient.

The conversion of camphornitrimine to camphene-1-carboxamide (**18**)[15,17] is achieved in a two-stage process involving attack of cyanide ion at C$_2$ of **17**; the salt formed is decomposed by excess mineral acid to give **18** directly. Gas evolution accompanied the second stage of this reaction and this was identified as nitrous oxide by high-resolution mass spectrometry, no other gas being present in comparable amount.

Scheme I



Conversion of camphene-1-carboxylic acid (**19**) into an isoborneol-4-carboxylic acid derivative was effected by means of trichloroacetic acid. This is achieved by initial protonation of the *exo*-methylene group in **19**, followed by 3–2 methyl shift, Wagner–Meerwein rearrangement, and solvent capture under thermodynamic control. Saponification and oxidation to the corresponding ketone were achieved by standard reactions. Conversion of the ketone to **20** was carried out in modest though reproducible yield by decomposition of its hydrazone with mercuric oxide. The structure of **20** was evident from spectral data (see Experimental Section). The AB pattern exhibited by the methylene protons of **20** is in accord with the known absence of coupling between methylene and cyclopropyl hydrogens in nortricyclene derivatives.[18] Further, the ir spectrum exhibited characteristic cyclopropyl C–H stretch at 3054 cm^{-1}, accompanied by the diagnostic first overtone of this frequency[18c,19] at 5990 cm^{-1}.

It was then possible to effect transformation of **20** to **22** *via* the acid chloride and 4-acetyltricyclene. Baeyer–Villiger oxidation of this methyl ketone led directly to acetate **21**, whose spectral properties indicated that the tricyclene skeleton had survived unperturbed (see Experimental Section). Reduction with lithium aluminum hydride produced alcohol **22**.

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(12) J. F. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, *Tetrahedron*, **25**, 369 (1969).

(13) H. L. Hoyer, *Chem. Ber.*, **87**, 1849 (1954).

(14) M. Kagawa, *Chem. Pharm. Bull.*, **7**, 306 (1959).

(15) (a) S. G. Brooks, R. M. Evans, G. F. H. Green, J. S. Hunt, A. G. Long, B. Mooney, and L. J. Wayman, *J. Chem. Soc.*, 4614 (1958); (b) J. Houben and E. Pfankuch, *Chem. Ber.*, **60**, 596 (1927).

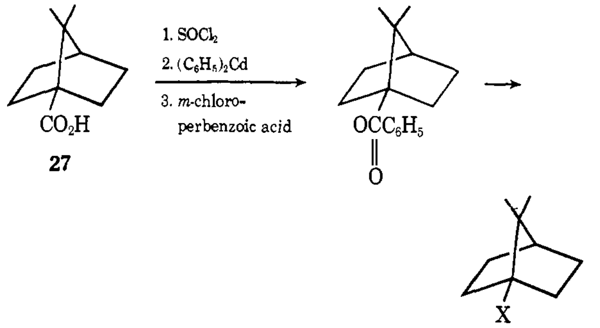
(16) (a) P. K. Freeman, *Chem. Ind. (London)*, 1624 (1960); (b) P. K. Freeman, *J. Org. Chem.*, **26**, 4192 (1961).

(17) J. Houben and E. Pfankuch, *Justus Liebigs Ann. Chem.*, **483**, 271 (1930).

(18) (a) B. H. Jennings and G. B. Herschbach, *J. Org. Chem.*, **30**, 3902 (1965); (b) R. A. Finnegan and R. S. McNees, *ibid.*, **29**, 3234 (1964); (c) A. T. Blomquist and R. J. Himics, *Tetrahedron Lett.*, 3947 (1967); (d) R. R. Sauers and R. J. Kiesel, *J. Amer. Chem. Soc.*, **89**, 4695 (1967).

(19) (a) H. Tanida, Y. Hata, Y. Matsui, and I. Tanaka, *J. Org. Chem.*, 30, 2259 (1965); (b) P. G. Gassman and F. V. Zalar, *ibid.*, 31, 166 (1966); (c) H. E. Simmons, E. P. Blanchard, and H. D. Hartzler, *ibid.*, 31, 295 (1966).

The closely related 1-apocamphyl system was chosen for model rate studies. 1-Apocamphanol (**28**) was prepared from 1-apocamphanecarboxylic acid (**27**) by a modification of the method of Hawthorne, Emmons, and McCallum,[20] and the alcohol converted to the corresponding sulfonates by standard methods (see Experimental Section).



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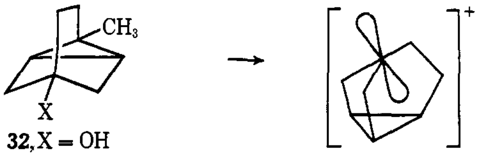
28, X = OH
29, X = OBs
30, X = OSO_2CF_3
31, X = OCH_2CH_3

In order to provide a further comparison, we also decided to examine the 1-methyl-4-tricyclo[2.2.2.0^{2,6}]octyl system **33**. The carbonium ion **35** derived from this substrate also has a cyclopropane face-complexed p orbital, but the orientation of this orbital relative to the ring is somewhat skewed, and in addition is located at a slightly longer distance (2.44 Å) from the plane of the ring.[21]



32, X = OH
33, X = OSO_2CF_3
34, X = OCH_2CH_3

35

Kinetic Studies. Initially, *p*-bromobenzenesulfonates (brosylates) **23** and **29** were prepared from the corresponding alcohols and reaction conditions were sought which would allow a comparative kinetic study of their solvolytic reactivities. Until recently 1-nortricyclyl was the least reactive *tert*-alkyl system whose rate had ever been measured.[22a] Solvolysis of 1-norbornyl bromide in 40% aqueous ethanol required[22b,c] a reaction temperature of 216°, and solvolysis of the corresponding chloride has been carried out[22d] in *m*-cresol at 322°.

We initially intended to follow the solvolyses titrimetrically. In the case of brosylate **29**, unbuffered acetolysis allowing direct titration of forming *p*-bromobenzenesulfonic acid probably would have been experimentally feasible. However, in the interest of comparability it was desirable to solvolyze brosylates **23** and **29** under as nearly identical conditions as possible, and at high temperatures we found that even buffered acetic acid attacks the cyclopropane ring in **23**. Thus it was necessary to seek a buffered medium that would be compatible with both **23** and **29**. Initially use of sodium hydroxide as a "buffer" was explored. Aliquots of a solution of brosylate **29** in 70% aqueous dioxane containing sodium hydroxide were heated in sealed Pyrex tubes for a few hours at about 200°. Titration showed that the samples had a pH less than 8, in spite of the fact that a considerable excess of sodium hydroxide had been used. Controls showed that sodium hydroxide apparently reacts rapidly with Pyrex under these conditions; recently a detailed account of similar observations in another laboratory has appeared.[23a] Attempts to use triethylamine as a buffer also failed; we could not find conditions which would allow titration of aqueous triethylamine at low concentrations to sharp end points.

The titrimetric approach was therefore abandoned and a modification of the ultraviolet (uv) spectrophotometric method of Swain and Morgan[23b] was adapted to the solvolysis of brosylate **29** in 70% aqueous dioxane buffered with triethylamine. The kinetic measurements were complicated by a side reaction of the solvent system which resulted in impurities having appreciable absorbance at 265 nm, the wavelength that was monitored, but an approximate correction for this could be made. At 200.1°, the solvolysis rate constant was calculated to be $4.44 \pm 0.25 \times 10^{-5}$ sec^{-1}.

Attempts to solvolyze brosylate **23** under the same conditions gave no reaction. The temperature was raised, but at 200° a significant fraction of the Pyrex sample tubes exploded in the kinetic bath, and it was apparent that a considerably higher reaction temperature would be needed to solvolyze brosylate **23**. We therefore resorted to stainless steel sample tubes with threaded caps and Teflon gaskets. These allowed us to explore much higher reaction temperatures. After brosylate **23** was heated in the same solvent at 250° for 12 hr, more than 95% of the starting material could be recovered. Even at 295° the reaction was very slow, allowing about 50% recovery after 14 hr. At the higher temperature the reaction mixture became dark and three products were observed, none of which was alcohol **22**, but the instability of **22** under the reaction conditions was demonstrated. The mode of reactivity exhibited by brosylate **23** at 292° is not known but obviously its first-order reactivity with respect to heterolytic cleavage of the bridgehead carbon–oxygen bond must be vastly lower than that of brosylate **29**.

In order to measure the difference in reactivity more accurately, therefore, we turned to the trifluoromethanesulfonate (triflate) leaving group. Triflates have been found[22a,24a,b,c] to be more reactive than tosylates

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[20] M. F. Hawthorne, W. D. Emmons, and K. S. McCallum, *J. Amer. Chem. Soc.*, 80, 6393 (1958). We are grateful to Professor John D. Roberts for a generous gift of 1-apocamphanecarboxylic acid.

[21] S. Julia and G. Gueremy, *Bull Soc. Chim. Fr.*, 3002 (1965). We are grateful to Professor Julia for a sample of 1-methyl-4-tricyclo[2.2.2.0^{2,6}]octanol.

[22] (a) T. M. Su, W. F. Sliwinski, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 5386 (1969); (b) R. C. Fort, Jr., and P. v. R. Schleyer, *Advan. Alicycl. Chem.*, 1, 300 (1966); (c) M. Finkelstein, Ph.D. Dissertation, Yale University, 1955; (d) K. B. Wiberg and B. R. Lowry, *J. Amer. Chem. Soc.*, **85**, 3188 (1963).

[23] (a) J. MacMillan and R. J. Pryce, *J. Chem. Soc. B*, 338 (1970); (b) C. G. Swain and R. Morgan, *J. Org. Chem.*, **29**, 2097 (1964).

[24] (a) R. L. Hansen, *ibid.*, 30, 4322 (1965); (b) A. Streitwieser, Jr., C. C. Wilkins, and E. Kiehlmann, *J. Amer. Chem. Soc.*, 90, 1598 (1968); (c) P. J. Stang and R. Summerville, *ibid.*, **91**, 4600 (1969); (d) we are indebted to Dr. R. L. Hansen of the Minnesota Mining and Manufacturing Co. for a generous gift oftrifluoromethane sulfonic acid; we are also grateful to Dr. Hansen and to Dr. A. Dafforn of Professor A. Streitwieser's group for suggestions regarding the preparation of triflates; (e) trifluoromethanesulfonic anhydride was made from the acid in accord with the procedure of Gramstad and Haszeldine (T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 4069 (1957)).

Table I. Kinetic and Product Data from Solvolyses of Some Bridgehead Triflates[a]

Substrate	T, °C[b]	10^5k, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Product ratio[c] (ROH:ROEt)
25	246.0	14.6 ± 0.3			
	232.8	7.35 ± 0.1	26.9 ± 0.9	−25.2 ± 1.7	72:28
	221.1	3.75 ± 0.05			
30	108.5	46.5 ± 0.7			
	99.0	17.8 ± 0.1	28.0 ± 0.4	−0.8 ± 1.1	63:37
	89.0	6.02 ± 0.06			
33	50.4	52.8 ± 0.4			
	41.0	14.8 ± 0.3	25.5 ± 0.4	5.0 ± 1.3	69:31
	31.3	4.16 ± 0.08			

[a] Trifluoromethanesulfonates (0.02 M) solvolyzed in 60% (by wt) aqueous ethanol containing 0.06 M triethylamine. [b] ±0.1°. [c] In all cases the products were the unrearranged alcohol and corresponding ethyl ether.

by a factor of 10^4–10^5, and with this much more reactive leaving group we hoped to be able to measure a first-order solvolysis rate for the 4-tricyclyl system. Triflates **25** and **30** were prepared by treating the corresponding alcohols in pyridine with trifluoromethanesulfonic anhydride.[22a, 24d,e] A sample of 1-methyl-4-tricyclo[2.2.2.0^{2,6}]octyl triflate (**33**) was prepared in the same way.[21] With some difficulty the triflates could be purified by gas–liquid chromatography (glc).

The triflates were solvolyzed in 60% aqueous ethanol buffered with triethylamine, and by taking certain precautions (see Experimental Section) it was possible to follow the reactions quantitatively by glc. Triflate **30** reacted at a convenient rate at 100°, and triflate **33** was even more reactive, requiring only about 40°. However, in order to obtain a comparable reaction rate with triflate **25** temperatures near 250° were required. In all cases the reactions were cleanly first order. The reaction rates for each triflate were measured at three temperatures covering in each case a range of about 20°, and good Arrhenius plots were obtained. Table I presents the measured rate constants and calculated activavation parameters. The Arrhenius plot for solvolysis of triflate **25** can be used to extrapolate the reaction rate to 25°, and correction for the average triflate–tosylate reactivity difference[22a, 24a–c] of $10^{4.8}$ leads (assuming only a negligible effect due to methyl substitution) to a calculated rate constant of 4.77×10^{-18} sec^{-1} for 4-tricyclyl tosylate in 60% aqueous ethanol at 25°. This represents the least reactive *tert*-alkyl system known[1b] and corresponds to a half-life of 4.6×10^9 years, approximately the radioactive half-life of ^{238}U.

Product Studies. The major products from the solvolyses of the triflates were in each case the unrearranged alcohol and the corresponding ethyl ether. The ratios of alcohol to ether were measured by glc and are reported in Table I. The products were isolated and identified by comparison of their infrared (ir) and in some cases nuclear magnetic resonance (nmr) and mass spectra with those of the starting alcohols and of samples of the ethyl ethers independently synthesized from the starting alcohols.

A sample of 1-apocamphyl methyl ether (**31**) was readily obtained by treating alcohol **28** with triethyloxonium tetrafluoroborate[25] in methylene chloride, but treatment of alcohol **22** under the same conditions gave camphor (**15**) as the only isolated product (its spectra were compared with those of a known sample). A speculative mechanism for the latter reaction involves catalysis by the fluoroboric acid produced in the alkylation.

Carbon–Oxygen Bond Fission. A number of studies have shown that aryl sulfonates, which have extraordinarily low SN1 reactivity, undergo reactions involving sulfur–oxygen bond cleavage. Some of these studies employed particularly strong nucleophiles and activated aryl groups,[26] but the hydrolysis of phenyl tosylate in the presence of dilute sodium hydroxide[27] and the hydrolysis of phenyl benzenesulfonate in the presence of hydrochloric acid[28] also have been shown to proceed by this route. This raised the question of whether some or all of the triflate solvolyses described above (especially the very slow ones) might involve sulfur–oxygen cleavage. Other groups have considered this problem in general and have cited the extreme unreactivity of phenyl triflates in a number of media[22a] as evidence against the likelihood of sulfur–oxygen bond cleavage in more reactive triflates;[22a, 24c] however, no one has yet reported a labeling experiment designed to rigorously rule out this pathway. In addition, the remarkable difference between the entropy of activation for solvolysis of triflate **25** and those for the solvolyses of the other triflates (Table I) suggested that a different, perhaps bimolecular, mechanism might be involved in the solvolysis of **25**.

It was therefore important to determine whether this reaction involved carbon–oxygen or sulfur–oxygen bond cleavage, and so we carried out a labeling experiment to check this point. When triflate **25** was solvolyzed in ^{18}O-enriched medium the sample of alcohol **22** produced was found by high-resolution mass spectrometric analysis to have incorporated the label quantitatively.[29] This experiment establishes that exclusive C–O bond fission occurs in **25**. Because this is the least reactive triflate in the series, exclusive C–O cleavage undoubtedly occurs in the other substrates as well.

Strain Energy Calculations. The kinetic and product studies described above establish the unusually low solvolytic reactivity of 4-tricyclyl derivatives, and hence the presumably great instability of the derived *tert*-carbonium ion. The cyclopropane ring in this molecule affords

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[25] H. Meerwein, E. Battenborg, H. Gold, E. Pfeil, and G. Willfang, *J. Prakt. Chem.*, **154**, 83 (1940).

[26] J. F. Bunnett and J. Y. Bassett, Jr., *J. Amer. Chem. Soc.*, **81**, 2104 (1959).

[27] C. A. Bunton and Y. F. Frei, *J. Chem. Soc.*, 1872 (1951).

[28] S. Oae, T. Fukumoto, and R. Kiritani, *Bull. Chem. Soc. Jap.*, **36**, 346 (1963).

[29] This technique has been used to establish carbon–oxygen cleavage in sulfonates; *cf.* ref 27 and P. G. Gassman, J. M. Hornbeck, and J. M. Pascone, *Tetrahedron Lett.*, 1425 (1971).

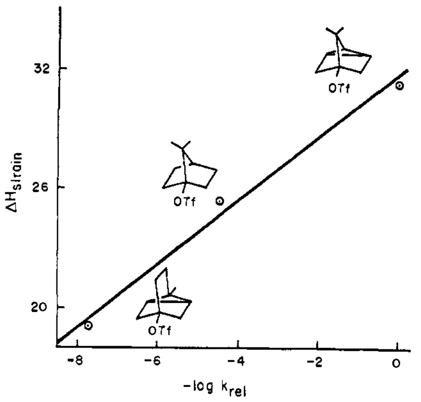

Figure 4. Plot of the calculated strain energies of ionization *vs.* negative log of the experimental relative rate constants for three bridgehead triflates.

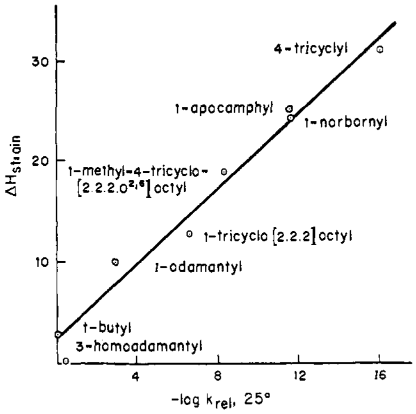

Figure 5. Plot of the calculated strain energies of ionization *vs.* negative log of the experimental relative rate constants for some tertiary systems.

no stabilization to the interacting p orbital, and its presence in fact appears to be responsible for the large decrease in rate relative to its bicyclic analog **30** and the tricyclic triflate **33**. In order to investigate the cause of this strong deceleration, we decided to carry out strain energy calculations on the ionizations studied here, using the method of Gleicher and Schleyer.[30]

Employing semiempirical potential energy functions for changes in bond lengths, bond angles, torsional effects, and nonbonded interactions, the method is used to calculate the minimum strain energies of a carbonium ion and of the corresponding hydrocarbon. The absolute values of strain energies are normally calculated to be unrealistically high, due to the inapplicability of simple harmonic potentials to regions of large deformation. For these reasons one focuses on the energy *difference* between ion and substrate. Even though the calculations refer to expulsion of hydride—rather than sulfonate—anion, the calculated energies have been shown to correlate well with experimental strain energies involved in sulfonate and halide solvolyses.[30] The existence of such a proportionality can be taken as evidence that the effect of electronic (as opposed to strain and steric) effects on the correlatable ionization reactions is negligible.

The calculated increases in strain energy involved in the ionizations of the 4-nortricyclyl, 4-tricyclyl, and 1-methyl-4-tricyclo[2.2.2.0^{2,6}]octyl systems are given in Table II. The calculated ΔH_{strain} values for the nortricyclyl and tricyclyl systems are very large, and indicate that this is almost completely due to distortion of carbon–carbon bond angles at and adjacent to the cationic center. The change in strain energy associated with the 1-apocamphyl system can be estimated to be about 1 kcal greater than that calculated previously for the 1-norbornyl system,[30] based on the observation that a similar difference is calculated between the tricyclyl and nortricyclyl systems and is primarily associated with the geminal methyl groups.

Table II. Relative Solvolysis Rates and Calculated Strain Energies of Ionization for Some Bridgehead Triflates

Substrate	k, sec^{-1}, 25° [a]	k_{rel}, 25°	ΔH_{strain},[b] kcal/mol
25	3.01×10^{-13}	1.0	31.26[c]
30	8.57×10^{-9}	2.84×10^{4}	25.39
33	1.65×10^{-5}	5.45×10^{7}	19.07

[a] Extrapolated from higher temperatures for reaction in 60% (by wt) aqueous ethanol buffered with triethylamine. [b] Calculated strain energy difference between the carbonium ion and the analogous hydrocarbon. [c] The corresponding value for the nortricyclyl system is 30.44 kcal/mol.

Having obtained activation parameter data for triflates **25**, **30**, and **33**, one can extrapolate the reaction rates to any given temperature (assuming a linear temperature dependence over the entire range—*vide infra*) in order to estimate the relative rates at that temperature. The relative rates calculated in this way for the triflates at 25° are given in Table II.

A plot of the calculated change in strain energy *vs.* the negative of the log of the relative rate constants is shown in Figure 4 and is reasonably linear. More convincing, however, would be a correlation of the rate and strain data of triflates **25**, **30**, and **33** with those of other bridgehead systems. One difficulty in this regard is the paucity of rate data for bridgehead triflates, but knowledge of a triflate–bromide rate ratio would allow estimation of the solvolysis rates of the corresponding bromides. An approximate triflate–bromide rate ratio (1.86×10^{6}) can be obtained from the solvolysis rates of 1-apocamphyl triflate (**30**) and 1-norbornyl bromide,[22b,31] and the strain energies and estimated rate data[31] for the tricyclyl, apocamphyl, and tricyclooctyl systems can then be correlated together with those for several bridgehead systems included by Gleicher and Schleyer in their original treatment.[30] The appropriate rates and strain energies appear in Table III and are plotted in Figure 5. The new values fit rather nicely with the earlier ones. The slope based on all points is 1.88 (kcal/mol)/log, and the intercept appropriately is very close to the change in strain energy calculated for the *tert*-butyl system. The relative rate constants predicted by the correlation for the tricyclyl, apocamphyl, and tricyclooctyl systems can be

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[30] (a) G. J. Gleicher and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 582 (1967); see also (b) V. R. Koch and G. J. Gleicher, *ibid.*, **93**, 1657 (1971); (c) since the completion of our calculatiosn, the method has been modified somewhat; *cf.* R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **93**, 3189 (1971).

[31] In this calculation corrections for the different ionizing powers (Y values) of the solvents were necessary. See (a) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2770 (1956); (b) S. Winstein, A. H. Fainberg, and E. Grunwald, *ibid.*, **79**, 4146 (1957). An additional level of approximation is introduced by the recent finding[30c] that there is some variation in the slope of correlation lines with leaving group.

Table III. Relative Solvolysis Rates and Calculated Strain Energies of Ionization for Some Tertiary Systems

System	ΔH_{strain},[a] kcal/mol	Exptl k_{rel}, 25°	Calcd[e] k_{rel}, 25°
tert-Butyl	2.85[b]	1.0[b,c]	
3-Homoadamantyl	0.23[b]	0.46[b,c]	
1-Adamantyl	10.16[b]	1.2×10^{-3} [b,c]	
1-Bicyclo[2.2.2]octyl	12.93[b]	2.4×10^{-7} [b,c]	
1-Methyl-4-tricyclo-[2.2.2.0^{2,6}]octyl	19.07	4.3×10^{-9} [d]	1.1×10^{-9}
1-Norbornyl	24.39[b]	2.0×10^{-12} [b,c]	
1-Apocamphyl	25.39	2.0×10^{-12} [d]	0.33×10^{-12}
4-Tricyclyl	31.26	7.8×10^{-17} [d]	35×10^{-17}

[a] Calculated difference in strain energy between the carbonium ion and the analogous hydrocarbon. [b] Given in ref 18. [c] Based on solvolyses of bromides in 80% aqueous ethanol. [d] From estimated rates for the bromides based on experimental rates for the triflates (**39**). [e] Calculated from the plot in Figure 4.

obtained from Figure 5 and are shown in Table III; these compare favorably with the experimental relative rates.

Discussion

The results reported in this paper, along with complementary observations made by Schleyer's group,[1b] demonstrate that ionization at the bridgehead (C-4) position of the bicyclo[2.2.1.0^{2,6}]heptyl system is an extremely difficult process. By implication, therefore, the derived carbonium ion **14** (and its 1,7,7-trimethyl analog) is a very unstable species, and may well be the least stable carbonium ion ever to have been generated by solvolytic ionization.

It seems incontrovertible, therefore, that the cyclopropane ring in ion **14** provides no stabilization to the electron-deficient carbon atom located very close to its face. The extreme slowness of the solvolysis of tricyclyl triflate, **25**, however, raises the possibility that the three-membered ring may actually *destabilize* the ion electronically. It was to answer this question that we carried out the strain energy calculations described in the preceding section. Because these calculations are of the "ball and spring" type and contain no quantum mechanical information, electronically caused rate effects appear as deviations from the correlation pictured in Figure 5. As one can see from this figure, however, both 4-tricyclyl and 1-tricyclo[2.2.2.0^{2,6}]octyl fit the correlation line as well as (or better than) simple tertiary systems such as 1-adamantyl. We can therefore conclude with reasonable confidence that within the limits of error of the computation method, neither tricyclic system gives evidence of electron stabilization *or destabilization* by the cyclopropyl ring in the derived carbonium ions. The slow rates of solvolysis are accounted for completely by the "stiff" potential function which describes the deviation of C-4 from planarity,[30] and the distortion of the C–C–C angles at the methylene carbons caused by the partial flattening at C-4 which does occur.

However, the distance between the ring and the ionization center is not so great as to preclude substantial overlap. From the crystal structure of 1-chloronortricyclene[12] this distance can be estimated as only 2.1 Å, and in the strain-minimized calculation for ion **14** this distance is only 1.96 Å. We must draw the conclusion, therefore, that even though the interaction exists, it results in little or no net change in the electronic energy of the interacting system.

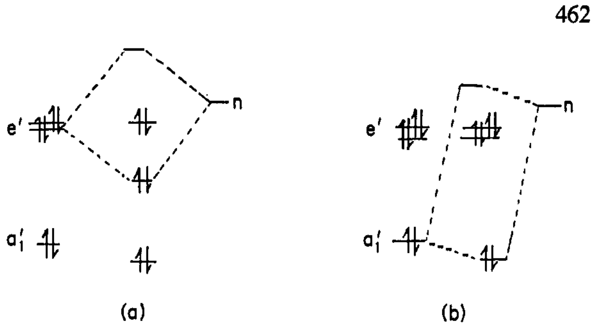

Figure 6. Interaction diagrams for approach of a nonbonding orbital toward (a) the edge and (b) the face of a cyclopropane ring.

A qualitative explanation for this phenomenon can be obtained by examining an interaction diagram of the type outlined in Figure 6. In the Walsh model[7] of cyclopropane (*cf.* Figure 3), the three sp^2 orbitals directed toward the center of the ring interact to produce (because of the symmetry of the interaction) three "cyclopropenium-like" molecular orbitals: a strongly bonding a_1' molecular orbital and two degenerate antibonding e' orbitals. The p orbitals on the periphery of the ring interact with "Möbius cyclopropenium" symmetry,[32] giving a bonding e' set of MO's and an antibonding a_2' level.

Consider now the interaction of an empty orbital n (at approximately the nonbonding level of energy) with the cyclopropane orbitals. If n approaches the edge of the ring (Figure 6a), it has appropriate symmetry to mix with the a_1' MO and with one of the levels in the degenerate bonding e' set. It mixes strongly only with the latter because n and e' are of relatively comparable energies. This produces a significant total energy lowering due to the stabilization of the symmetric e' level. If the empty orbital approaches the face of the ring (Figure 6b), it now is close to the a_1' orbital, and symmetry allows quantum mechanical interaction. However, the energies of the two orbitals are so disparate that only small splitting takes place and the a_1' level is only slightly stabilized.

Another, more qualitative, way of comparing the two approaches is to say that it is relatively easy to move electron density out of the MO's on the periphery of the ring, because they are constructed of linear combinations of p orbitals and therefore have relatively high absolute energies. Moving electron density out of the a_1' level, however, is much more difficult because of the large degree of s character in this level and its resulting high ionization potential.[33] Therefore, even though the electron density in a_1' is high and the distance between it and the empty orbital is small, little energy is gained by the transfer of electron density between these two orbitals.

An extended Hückel (EHT) calculation[34] on 4-nortricyclyl cation in the conformation predicted by the

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(32) E. Heilbronner, *Tetrahedron Lett.*, 1923 (1964).

(33) The ionization potential of a carbon sp^2 orbital can be approximated as 14.7 eV by taking one-third of the sum of the ionization potentials[34a] of a carbon 2s orbital and two carbon 2p orbitals. For comparison, the ionization potential of a carbon p orbital has been given as 11.4 eV.[34a]

(34) (a) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); (b) the Slater exponents for hydrogen and carbon were taken as 1.300 and 1.625, respectively. The Coulomb integral for hydrogen 1s orbitals was taken as −13.6 eV, and the Coulomb integrals for the carbon 2s and 2p orbitals were taken as −21.4 and 11.4 eV, respectively.

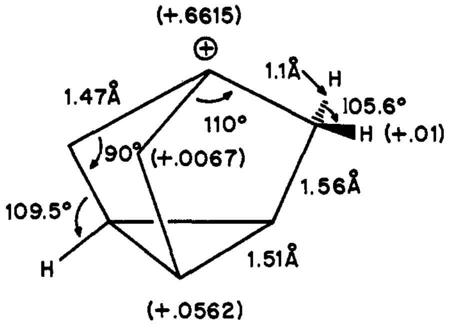
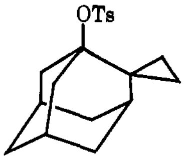


Figure 7. Strain-minimized conformation and EHT charge densities of 1-nortricyclyl cation **14**.

strain-minimizing empirical treatment confirms these qualitative ideas. Only a small fraction of the positive charge is delocalized to the cyclopropyl carbons (Figure 7). Still more revealing is the fact that the overlap population (roughly corresponding to a bond order) between carbons 1 and 4 is slightly negative (−0.03)—hardly what one would expect from strong mixing with the a_1' MO.

Inductive Effect of the Cyclopropane Ring. The agreement between observed and strain-calculated ionization rates for 4-tricyclyl triflate suggests that the inductive effect of the cyclopropane ring plays little or no role in retarding ionization in this system. Whether this result is to be expected is not clear. The inductive effect of the cyclopropyl group is not easy to assess because of its strong tendency to interact conjugatively with reactive centers. One therefore needs to examine systems in which this conjugative interaction is prohibited, and the results at first glance are confusing. It is reasonably well established that double bonds are electron withdrawing, and inductively retard solvolysis rates. It might therefore be expected that three-membered rings would be electron withdrawing also, albeit more weakly than truly unsaturated groups. However, 2-cyclopropylethyl and isoamyl brosylates undergo ionization in a number of solvents at almost exactly the same rates,[35] and the pK_a of *m*-cyclopropylbenzoic acid is almost exactly the same as that of benzoic acid itself.[36] This suggests that the inductive effects of cyclopropyl and hydrogen are almost identical. Estimation of the cylopropyl Hammett–Taft σ_I (which is presumably most appropriate for aliphatic systems) gives values ranging from +0.017 to 0.0, depending on the method of estimation used.[36] The sign of σ_I suggests that cyclopropyl is electron withdrawing, but the effect appears to be a weak one.

Interestingly, Ree and Martin have found that adamantyl derivative **36**, in which the cyclopropane ring is held rigidly out of conjugation with the developing p orbital at C-1, undergoes acetolysis some 10^3 times slower than either its dimethyl analog **37** or 1-adamantyl itself.[37a] Similar results have been reported by Buss, Gleiter, and Schleyer.[37b,c] Ree and Martin considered the possibility that the slow rate of ionization of **36** might be due to the difficulty of constricting the spirane C–C–C angle at C-2, but decided on the basis of a number of precedents and a good Hammett–Taft correlation between the solvolysis rates of **36**, **37**, and 1-adamantyl and 2-methyleneadamantyl tosylates that the inductive explanation was more satisfactory.[37a] Schleyer and coworkers also invoked an inductive effect to explain the rate depression.[37b,c] However, if cyclopropyl is truly capable of exerting such a profound inductive effect, it is strange that this effect is not felt strongly in the 4-tricyclyl system, where all three carbons of the cyclopropane ring are connected *via* methylene groups to the ionization center. It seems more reasonable to us to reopen the possibility that **36** is retarded by a strain rather than an electronic effect.[37d]



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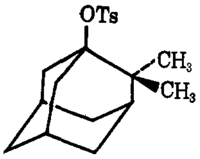

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Entropies of Activation in Solvolytic Reactions. We are somewhat concerned about the large negative entropy of activation measured for 4-tricyclyl triflate (Table I), especially considering that the $\Delta S^{\neq}$ values for the other very similar compounds listed in the table are much closer to zero. Taking into account the extreme unreactivity of the tricyclic system, we briefly considered the possibility that the mechanism had changed and we were observing a frontside S_N2 displacement. Such a mechanism, however, in order to be consistent with our observations, would be subject to a number of constraints. Most important of these is the fact that we observe first-order kinetics, which requires that any direct displacement taking place between substrate and solvent molecules must not be taking place between substrate and triethylamine buffer. In addition, other studies have led to the generalization that frontside displacements are unimportant in solvolyses of bridgehead substrates,[22b,c] and the predominance of a different mechanism in the solvolysis of triflate **25** from that involved in the solvolyses of triflates **30** and **33** could be only fortuitously consistent with closely similar alcohol–ether product ratios such as are observed (Table I). Finally, the solvolysis rate constant for triflate **30** in pure water has been measured[38] as 2.95×10^{-3} sec^{-1} at 65.04°. From this value and our kinetic data for solvolysis in 60% aqueous ethanol, a value of 1.1 can be calculated for Winstein's *m*, which is consistent with a rate-limiting ionization mechanism (the *m* value for solvolysis of 1-tricyclo[2.2.2]octyl bromide is 1.13[22b,c]). We therefore conclude that the solvolyses of all three triflates must proceed *via* carbonium ion mechanisms.

Having come to this conclusion, we have yet to explain the anomalous $\Delta S^{\neq}$ associated with **25**. After rejecting a number of mechanistic explanations, we considered the possibility that the difference in $\Delta S^{\neq}$ in Table I was due to a temperature effect, resulting from the fact that the solvolysis of **25** was carried out at a

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[35] Y. E. Rhodes and T. Takino, *J. Amer. Chem. Soc.*, 90, 4469 (1968).

[36] R. W. Taft and I. C. Lewis, *ibid.*, 80, 2346 (1958).

[37] (a) B. R. Ree and J. C. Martin, *ibid.*, **92**, 660 (1970); see also, (b) P. v. R. Schleyer and V. Buss, *ibid.*, **91**, 5880 (1969); (c) V. Buss, R. Gleiter, and P. v. R. Schleyer, *ibid.*, **93**, 3927 (1971); (d) Professor Schleyer has informed us that strain energy calculations carried out very recently in his group do in fact predict that the majority of the rate retardation in **36** is due to angle strain influences. Professor Martin has indicated that he agrees with this reinterpretation.

[38] Private communication from R. E. Robertson and Sohair Aly, University of Calgary.

reaction temperature about 130° higher than that used with **30**.

The temperature dependence of the entropy and enthalpy of activation (by analogy to ground-state thermodynamics) may be expressed[39] by the following equations

$$d\Delta S^{\ddagger}/dt = \Delta C_p^{\ddagger}/T \qquad (1)$$

$$d\Delta H^{\ddagger}/dt = \Delta C_p^{\ddagger} \qquad (2)$$

where $\Delta C_p^{\ddagger}$ is the change in heat capacity at constant pressure associated with activation. The implication of these equations is that the entropy and enthalpy of activation are not essentially temperature independent. In order to calculate the quantities $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta C_p^{\ddagger}$ one fits accurate rate data to an extended temperature-dependence equation of the form[40]

$$\log k_{\text{obsd}} = C + A/T + B \log T \qquad (3)$$

A number of studies of this sort have been carried out.[40-43] Most instructive are the activation parameters calculated for the aqueous solvolyses of allylic chlorides by Robertson and coworkers; in these studies significant changes in $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ were observed over relatively moderate temperature ranges. The largest absolute change is in $\Delta S^{\ddagger}$; for example, in the hydrolysis of α-methallyl chloride,[40] $\Delta S^{\ddagger}$ changes from +10.9 eu at 5° to +0.04 eu at 40°; $\Delta H^{\ddagger}$ changes by 3.2 kcal/mol over the same range. This requires a $\Delta C_p^{\ddagger}$ of -92 cal mol^{-1} deg^{-1}. A number of other allylic chlorides are covered in the same study;[40] all exhibit profound temperature dependence in their activation entropies, and all activation entropies become more negative as the temperature is raised.

If $\Delta C_p^{\ddagger}$ for **25** were -79 cal mol^{-1} deg^{-1}, then at 99° $\Delta S^{\ddagger}$ for solvolysis of **25** would be -0.8 eu, the same value as for **30**. We may ask whether this is a reasonable magnitude for $\Delta C_p^{\ddagger}$ under our conditions. Robertson and coworkers have generalized that for S$_N$1 hydrolyses $\Delta C_p^{\ddagger}$ is about -90 cal mol^{-1} deg^{-1},[40] but for a given reaction $\Delta C_p^{\ddagger}$ varies in a complicated way on going from pure water to mixed aqueous solvents. Robertson and Sugamori have shown that for the solvolysis of *tert*-butyl chloride $\Delta C_p^{\ddagger}$ varies from -83 cal mol^{-1} deg^{-1} in pure water to -136 cal mol^{-1} deg^{-1} in 20.8% (v/v) aqueous ethanol, and to -34 cal mol^{-1} deg^{-1} in 50% aqueous ethanol.[41] For solvolysis of *tert*-butyl chloride in aqueous isopropyl alcohol $\Delta C_p^{\ddagger}$ is -135 cal mol^{-1} deg^{-1} in 19% isopropyl alcohol, increases to only -21 cal mol^{-1} deg^{-1} in 32% isopropyl alcohol, and decreases again to -52 cal mol^{-1} deg^{-1} in 51.5% isopropyl alcohol.[41] The studies with aqueous ethanol did not employ greater than 50% ethanol, but by analogy to the results with isopropyl alcohol, use of more than 50% ethanol might cause a decrease in $\Delta C_p^{\ddagger}$. Apparently it is not unreasonable to think that a $\Delta C_p^{\ddagger}$ of -79 cal mol^{-1} deg^{-1} might be associated with solvolysis of **25** in our solvent system (65.5% (v/v) aqueous ethanol). It is therefore possible that most if not all of the difference between the entropies of activation of **25** and **30** is due to a temperature effect.[44]

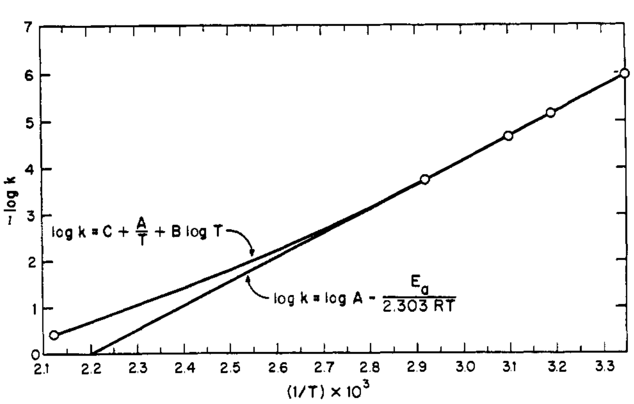

Figure 8. Arrhenius and extended temperature-dependence curves for the solvolysis of allyl chloride in water. All points are experimental except the one at 200°, which was calculated from eq 3. Data are taken from ref 40.

The strong temperature dependence in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ raises the possibility that for solvolytic reactions in general the Arrhenius plot, normally used for extrapolation over wide temperature ranges, might give rate constants which are seriously in error. In order to investigate this possibility, we extrapolated Robertson's solvolysis data for allyl chloride,[40] measured over the range 25–70°, to 200° using the simple Arrhenius law. This gives a predicted rate constant of 1.74 sec^{-1}. If, on the other hand, the rate constant for allyl chloride at 200° is calculated using eq 3 and Robertson's values[40] for the constants A, B, and C, the extrapolated k_{obsd} = 0.38 sec^{-1}. This differs from the Arrhenius-determined rate constant by nearly an order of magnitude. The activation parameters for this reaction, however, vary even more strongly. Using Robertson's data and the integrated forms of eq 1 and 2 to calculate activation parameters for the allyl chloride hydrolysis at 200°, we find (assuming $[d\Delta C_p^{\ddagger}/dt] = 0$) that $\Delta H^{\ddagger}{}_{200}$ = 14.5 kcal/mol and $\Delta S^{\ddagger}{}_{200} = -30.7$ eu. The variation in $\Delta H^{\ddagger}$ is such that it tends to increase the rate to a greater extent with increasing temperature, whereas the variation in $\Delta S^{\ddagger}$ tends to retard the rate as the temperature increases. There exists, therefore, a *compensating* variation in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ with temperature.

This compensation can be understood with reference to Figure 8, which shows a combined plot of the log of the allyl chloride rate constants, one measured and the other calculated from expanded eq 3, *vs.* the reciprocal of temperature. One can see that the curvature in the presumably "true" temperature-dependence line is pronounced when viewed over the complete (but normally unmeasurable) 200° range. The activation parameters calculated from eq 3 correspond to those which could be obtained from the slopes and intercepts of straight "Arrhenius" lines tangent to each point on the curve. One can see by inspection, then, that although the rate constant at 200° differs from that predicted by the 25–70° Arrhenius line by less than an order of magnitude, the slope of the line tangent to

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(39) For a review, see G. Kohnstam, *Advan. Phys. Org. Chem.*, **5**, 121 (1967).

(40) L. J. Brubacher, L. Treindl, and R. E. Robertson, *J. Amer. Chem. Soc.*, **90**, 4611 (1968).

(41) R. E. Robertson and S. E. Sugamori, *ibid.*, **91**, 7254 (1969).

(42) R. E. Robertson, B. Rossall, S. E. Sugamori, and L. Treindl, *Can. J. Chem.*, **47**, 4199 (1969).

(43) W. J. Albery and B. H. Robinson, *Trans. Faraday Soc.*, 980 (1969).

(44) Professor Schleyer has informed us recently that a discussion of the effect of $\Delta C_p^{\ddagger}$ on activation energy is included in the Ph.D. Dissertation of W. Sliwinski, Princeton University, 1971.

the eq 3 curve is much lower than that of the Arrhenius line (hence the low "true" $\Delta H^{\ddagger}$). The shape of the curve dictates that such lowering in the tangent slope will of necessity lower the intercept, from which log A is calculated, as well; *i.e.*, it will require that $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ will vary in a compensating manner. This is also a consequence of the fact that the first derivatives of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are simple functions of the same quasi-thermodynamic parameter, $\Delta C_p^{\ddagger}$, which have the same sign.

We draw the following conclusions from these considerations. First, rate constants calculated by extrapolation of Arrhenius data for solvolytic reactions in polar solvents over wide temperature ranges may be expected to be in error by about an order of magnitude, and possibly by more if the reaction in question is characterized by a large negative $\Delta C_p^{\ddagger}$. Second, activation parameters calculated over a certain temperature range are approximately valid *only* in the neighborhood of the temperature at which they are determined and will be essentially worthless at other temperatures deviating greatly from the range of measurement. *One should not attach mechanistic significance to a difference in enthalpies or entropies of activation measured for two compounds at different temperatures unless the temperature effect can be unequivocally shown to be unimportant.*

Experimental Section

General. Infrared (ir) spectra were determined on Perkin-Elmer IR 225 (Mrs. F. Lawrie) and 257 instruments, the samples being 10% solutions in carbon tetrachloride. Near-infrared spectra were determined with a Unicam SP-100 Mark II spectrophotometer equipped with an SP-130 sodium chloride prism grating double monochromator operated under vacuum. Nuclear magnetic resonance (nmr) spectra were obtained on Varian A60-A and HA-100 spectrometers; carbon tetrachloride and $CDCl_3$ were used as solvents and chemical shifts are reported in parts per million downfield from tetramethylsilane. Mass spectra were obtained on a CEC-21-013C instrument at 10-μA ionizing current and 70-V ionizing potential; the inlet temperature was 250°. Ultraviolet (uv) spectra were obtained on a Cary 14 spectrophotometer. Elemental analyses were performed by Spang Microanalytical Lab., Ann Arbor, Mich., and by Mr. J. M. L. Cameron and his staff at the University of Glasgow. Boiling and melting points are uncorrected. Qualitative and preparative gas-liquid chromatography (glc) was carried out on Varian Aerograph 90-P3 instruments. Quantitative analytical glc was carried out on Hewlett-Packard 5750 and Perkin-Elmer F11 instruments (flame ionization detectors). In most cases the following columns were used: column A, 5 ft × $^1/_4$ in. stainless steel, 3% SE-30 on 100–120 Varaport 30; column B, 12 ft × $^1/_4$ in. glass, 3% SE-30 on 60–80 Chromosorb W (acid washed, DMCS); column C, 10 ft × $^1/_4$ in. glass, 3% SE-30 on 60–80 Chromosorb W (acid washed, DMCS); column D, 2.5 ft × $^1/_4$ in. aluminum, 8% TCEP on 60–80 Chromosorb G; column E, 6 ft × $^1/_8$ in. stainless steel, 10% UCC-W98 on 100–120 Chromosorb W (acid washed, DMCS); column F, 6 ft × $^1/_4$ in. glass, 6% SE-30 on 60–80 Chromosorb W (acid washed, DMCS). Where other columns were used, they are described explicitly.

Camphornitrimine (17). To a solution of d-camphor oxime (50 g, 0.30 mol) in 500 ml of ether contained in a 1-l. separating funnel was added a concentrated aqueous solution of sodium nitrite (50 g, 0.72 mol). Concentrated sulfuric acid (30 g, 0.30 mol) diluted to a 20% aqueous solution was then added cautiously over 10 min with vigorous swirling. Over a further 10 min the ethereal layer assumed a deep purple color and a white precipitate of camphor immonium nitrate formed from this layer. The precipitate was filtered off and the ether layer separated; the ether was removed on a rotary evaporator with the water bath temperature not greater than 40°. After removal of the ether the purple color was discharged and the crude camphornitrimine was taken up in petroleum ether (bp 40–60°), washed with water, and dried ($MgSO_4$). Recrystallization from petroleum ether (bp 40–60°) gave camphornitrimine: 38 g; 65%; mp 42–43° (lit.[15a] 43°); ir (CCl_4) 1645 (medium), 1560 (strong), 1312 cm^{-1} (strong).

Camphene-1-carboxamide (18). To a solution of camphornitrimine (65 g, 0.35 mol) in 200 ml of ethanol was added a solution of potassium cyanide (25 g, 0.38 mol) in 100 ml of water. The solution was then refluxed for 20 min and cooled in ice and excess 3 *N* hydrochloric acid was added over 5 min with stirring. The almost immediate precipitation of camphene-1-carboxamide was accompanied by gas evolution.[45] The amide was filtered off, washed with 200 ml of water, and recrystallized from absolute ethanol giving white needles of camphene-1-carboxamide (53.5 g, 90%): mp 209–210° (lit.[17] 209–210°); ir (CCl_4) 1692, 3418, 3535 cm^{-1}; nmr (DMSO-d_6) δ 1.06 (N, 6 H), 4.64 (N, 1 H), 4.82 (N, 1 H), and 6.87 (br s, 2 H). *Anal.* Calcd for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.66; H, 9.62; N, 7.55.

Camphene-1-carboxylic Acid (19). A solution of camphene-1-carboxamide (85 g, 0.47 mol) and potassium hydroxide (220 g) in 650 ml of methanol was refluxed for 20 hr. The solution was then cooled and brought to pH 8–9 at which point a small amount (*ca.* 1 g) of unsaponified amide precipitated. An excess of 3 *N* hydrochloric acid then precipitated **4**. This was dissolved in petroleum ether (60–80°), washed with water (two 150-ml portions) and brine, and dried ($MgSO_4$). Recrystallization from petroleum ether (60–80°) gave **19**: 74 g (87%); mp 82–83° (lit.[17] 83–84°, lit.[46] 81–82.5°); ir (CCl_4) 3300–2550 (br), 1750 (weak), 1702 (strong), 895, 897 cm^{-1}; nmr ($CDCl_3$) δ 1.12 (s, 6 H), 4.75 (s, 1 H), 5.01 (s, 1 H), 11.52 (br s, 1 H). *Anal.* Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.30; H, 8.76.

Isoborneol-4-carboxylic Acid. Camphene-1-carboxylic acid (50 g, 0.28 mol) and trichloroacetic acid (180 g, 1.1 mol) were heated together, with exclusion of moisture, at 60–70°. A solution gradually formed and was stirred for 4 hr. After cooling, the solution was diluted with 500 ml of water and cooled in ice. Sodium bicarbonate (84 g, 1 mol) was cautiously added over 45 min with vigorous stirring. Ether (300 ml) was then added and the aqueous layer separated. The ether layer was washed with water (four 150-ml portions) and without drying the ether was removed on a rotary evaporator.

The crude trichloroacetate so obtained was saponified by refluxing for 1 hr with a solution of potassium hydroxide (50 g) in 300 ml of water. On cooling, the odor of chloroform was observed. The solution was made acid with 3 *N* hydrochloric acid to yield a precipitate of the highly insoluble alcohol, which was recrystallized from boiling xylene to yield 37.6 g (68%): mp 230–231° (lit.[47] 216–220°, lit.[14] 220°, lit.[13] 231–232°); ir (CCl_4) 3630, 3530, 1740 (weak), 1692 cm^{-1}. *Anal.* Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.59; H, 9.05.

Camphor-4-carboxylic Acid. To a solution of isoborneol-4-carboxylic acid (18.2 g, 0.092 mol) in 180 ml of purified acetone cooled in ice was added dropwise over 5 min with vigorous stirring 26.0 ml of Jones reagent.[48] After a further 15 min the solution was diluted with 600 ml of water and extracted with three 300-ml portions of pentane. The combined pentane extracts were reduced in volume to *ca.* 200 ml, washed with water and brine, and dried ($MgSO_4$). Removal of the remaining pentane followed by recrystallization from petroleum ether (60–80°) yielded 15.7 g (87%) of the ketone: mp 239–240° (lit.[13] 241°, lit.[49] 238–240°); ir (CCl_4) 1697 (strong), 1752 (strong), 3300–2500 (br); nmr ($CDCl_3$) δ 0.93 (s, 3 H), 0.97 (s, 3 H), 1.09 (s, 3 H), AB pattern 2.85 (1 H, 3 exo), 2.19 (1 H, 3 endo), J_{AB} = 18.4 Hz, $H_{3\,exo}$ further split by coupling with $H_{5\,exo}$, $J_{3\,exo-5\,exo}$ = 3.2 Hz. *Anal.* Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.18; H, 8.08.

Tricyclene-4-carboxylic Acid (20). A solution of camphor-4-carboxylic acid (20 g, 0.102 mol) and 60 ml of 70% hydrazine hydrate was heated at 100° (oil bath) for 12 hr. The solution was cooled and made acid with excess 3 *N* hydrochloric acid and filtered

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(45) In a small scale experiment this gas was identified by high-resolution mass spectrometry (AEI MS9) as nitrous oxide; *m/e* 44.001; calcd, 44.0010.

(46) A. Nickon, T. Nishida, J. Frank, and R. Muneyuki, *J. Org. Chem.*, **36**, 1075 (1971).

(47) J. Houben and E. Pfankuch, *Chem. Ber.*, **59**, 2292 (1926). The discordant literature values for this melting point may be due to differences in optical purity.

(48) Jones reagent was made from chromium trioxide (26.7 g) and concentrated H_2SO_4 (23 ml) diluted to 100 ml with distilled water.

(49) J. Houben and E. Pfankuch, *Justus Liebigs Ann. Chem.*, **489**, 216 (1931).

and to the acidic solution was added sodium acetate. The precipitate of camphorhydrazone-4-carboxylic acid was recrystallized from ethanol to give 15.3 g (71.5%). An indeterminate melting point was observed in the range 235–245° (lit.[13] 240–245°); ir (KBr) 1700, 3359 cm^{-1}.

This material (17.0 g, 0.085 mol) was dissolved in 250 ml of methanol and yellow mercuric oxide (32.5 g, 0.15 mol) added with vigorous stirring. The solution was refluxed overnight. After cooling and filtering, methanol was removed from the filtrate on a rotary evaporator. The resulting solid was steam distilled to give, after recrystallization from petroleum ether (60–80°), tricyclene-4-carboxylic acid: 2.24 g (14.5%); mp 168–170°; ir (CCl$_4$) 1693 (strong), 1741 (medium), 3054 (medium) cyclopropyl C–H stretch,[16] 5990 cm^{-1} first overtone;[15c,16] nmr (CDCl$_3$) δ 0.95 (s, 6 H), 0.99 (s, 2 H), 1.06 (s, 3 H), AB pattern 2.04 (2 H), 1.49 (2 H), J_{AB} = 10.5 Hz, 10.82 (s, br, 1 H). *Anal.* Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.11; H, 8.90.

4-Tricycloyl Chloride. To a stirred solution of tricyclene-4-carboxylic acid (4.5 g, 0.025 mol) in 25 ml of benzene at room temperature with protection from moisture was added oxalyl chloride (7.5 g, 0.059 mol). Stirring was continued for 4 hr at room temperature. Benzene was then distilled off and the solution kept 40 min (0.1 mm) leaving 4-tricycloyl chloride (4.98 g) as a colorless oil; ir (film) 1783, 3057 cm^{-1}.

4-Acetyltricyclene. Methyl magnesium bromide was prepared by distilling methyl bromide under a nitrogen atmosphere onto degreased, activated magnesium turnings (3.12 g, 0.126 atom) covered by 25 ml of anhydrous ether in a three-necked flask fitted with a Dry Ice condenser. After stirring for 1 hr cadmium chloride (23 g, 0.126 mol) was added portionwise over 5 min to the ice-cooled solution of methyl magnesium bromide. The flask was quickly arranged for distillation, 10 ml of benzene added, and the ether distilled off under nitrogen and replaced further with 20 ml of benzene. This solution was left to stir at 0° for 90 min and then at room temperature for 90 min. A solution of 4-tricycloyl chloride ($\sim$5 g, 0.025 mol) in 10 ml of benzene was added under nitrogen from a pressure equalizing dropping funnel and the solution stirred for 2 hr. The contents of the flask were then poured onto ice and 2 *N* HCl and the aqueous layer brought to pH 4. The benzene layer was washed with water (two 15-ml portions) and dried (MgSO$_4$). Benzene was removed by careful distillation through a Vigreux column to leave 4-acetyltricyclene as a light straw colored oil, 3.86 g (86%). After bulb-to-bulb distillation, 4-acetyltricyclene was obtained pure as determined by gas-liquid chromatography (50 ft × 0.030 in. i.d. TCEP, 120°) and had ir bands (CCl$_4$) at 1690, 3058 cm^{-1}; nmr (CDCl$_3$) δ 0.97 (s, 6 H), 1.00 (s, 2 H), 1.08 (s, 3 H), AB pattern 1.91 (2 H), 1.48 (2 H), J_{AB} = 10.8 Hz, 2.12 (s, 3 H). *Anal.* Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.74; H, 10.27.

4-Tricyclanol (22). A solution of trifluoroperacetic acid was made from the dropwise addition of trifluoroperacetic anhydride (12 ml) to a stirred heterogeneous solution of 99% hydrogen peroxide in 40 ml of methylene chloride at 0°. The solution was stirred at 0° for 4 hr before use.

To a stirred solution of 4-acetyltricyclene (4.5 g, 0.025 mol) in 25 ml of methylene chloride at 0° was added successively finely powdered disodium hydrogen phosphate (16.5 g, 0.116 mol) and the solution of trifluoroperacetic acid (above). After *ca.* 2 hr the solution had attained room temperature and was stirred for a further 20 hr. Inorganic salts were dissolved in water and the methylene chloride layer washed with 10% aqueous sodium bicarbonate solution and dried (MgSO$_4$). Removal of methylene chloride left 4-tricyclyl acetate (**21**) as a pale straw colored oil, 4.22 g (86%), ir (CCl$_4$) 3058, 1728, 1242 cm^{-1}, which in ethereal solution was directly reduced with lithium aluminium hydride to 4-tricyclanol; yield, 3.55 g (87%). Recrystallization twice from the minimum volume of petroleum ether (60–80°) gave material with mp 132–133°: ir (CCl$_4$) 3625, 3055 (medium), cyclopropyl C–H stretch,[19] 5985 cm^{-1} first overtone;[18c,19] nmr (CDCl$_3$) δ 0.84 (s, 6 H), 0.88 (s, 2 H), 1.03 (s, 3 H), AB pattern 1.73 (2 H), 1.43 (2 H), J_{AB} = 10.1 Hz, 1.63 (s, 1 H exchangeable with D$_2$O). This material was homogeneous as determined by gas-liquid chromatography (50 ft × 0.030 in. i.d. TCEP, 120°). *Anal.* Calcd for $C_{11}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.82; H, 10.58.

1-Apocamphanol (28) was prepared from 1-apocamphanecarboxylic acid in accord with the method of Hawthorne, Emmons, and McCallum[20] with the exception that *m*-chloroperbenzoic acid instead of pertrifluoroacetic acid was used in the Baeyer–Villiger step as follows: crude 1-apocamphyl phenyl ketone (3.6 g) and *m*-chloroperbenzoic acid (4.8 g) were dissolved in 50 ml of dichloroethane. The solution was refluxed for 6 hr and allowed to stand overnight. Solvent was removed on a rotary evaporator, and 80 ml of cold 20% sodium hydroxide solution was added to the residue. Vigorous agitation of the mixture was followed by extraction with ether. The ethereal solution was washed with water and brine and dried over anhydrous magnesium sulfate; removal of solvent on a rotary evaporator afforded 3.8 g of crude 1-apocamphyl benzoate as a yellow oil. The benzoate was hydrolyzed as reported[20] and 1.27 g (about 58% yield from 1-apocamphyl phenyl ketone) of alcohol **28** was obtained (mp 153–157°). Recrystallization from pentane afforded pure samples (mp 163–164.5°; lit. 160°[20]). A more efficient synthesis was reported recently.[50]

1-Apocamphyl Brosylate (29). In a 10-ml flask a mixture of 260 mg of alcohol **28**, 2.3 ml of pyridine (dried over molecular sieves), and 700 mg of *p*-bromobenzenesulfonyl chloride (recrystallized from carbon tetrachloride) was heated at 50° for 20 hr and then after addition of 5 ml of water was allowed to stand at room temperature for 24 hr. A 5-ml portion of 6 *N* hydrochloric acid was added and the mixture was extracted with ether. The ethereal extract was washed with water, saturated sodium bicarbonate solution, water, and brine, and was dried over anhydrous magnesium sulfate. Removal of the solvent on a rotary evaporator left 331 mg of an off-white solid (mp 90–110°), which was dissolved in the minimal amount of warm pentane. Cooling the solution to −78° and scratching gave a white precipitate. A second recrystallization from pentane afforded 194 mg (32% yield) of white crystals (mp 118–118.5°). The ir spectrum displayed bands at 2960, 2880, 1263, 1020, and 870 cm^{-1}. The nmr spectrum consisted of an aromatic multiplet (4 H) centered at 7.6 ppm, a multiplet from 1.0 to 2.2 ppm (9 H) due to methylene and methine protons, and a singlet (6 H) at 0.97 ppm due to the methyl protons. *Anal.* Calcd for $C_{15}H_{19}O_3SBr$: C, 50.11; H, 5.33; S, 8.92; Br, 22.24. Found: C, 50.17; H, 5.11; S, 8.99; Br, 22.26.

4-Tricyclyl Brosylate (23). A mixture of 300 mg of 4-tricyclenol (**22**), 750 mg of *p*-bromobenzenesulfonyl chloride, and 3 ml of dry pyridine was heated at 62° for 30 hr. Treatment of the reaction mixture in the manner described for the preparation of brosylate **29** gave 261 mg (36% yield) of brosylate **23** as a white solid (mp 99–100°). The ir spectrum displayed bands at 3060, 1580, 1395, 1382, 1360, 1285, 1205, 1195, 1067, and 880 cm^{-1}. The nmr spectrum consisted of an aromatic multiplet (4 H) centered at 7.68 ppm, a singlet at 1.84 ppm (4 H) due to the methylene protons, a singlet at 1.02 ppm (3 H) due to the bridgehead methyl protons, a singlet at 0.93 ppm (2 H) due to the cyclopropyl methine protons, and a singlet at 0.83 ppm (6 H) due to the protons of the geminal methyl groups. *Anal.* Calcd for $C_{16}H_{19}O_3SBr$: C, 51.75; H, 5.16; S, 8.64; Br, 21.52. Found: C, 51.86; H, 4.96; S, 8.67; Br, 21.68.

1-Apocamphyl Triflate (30). To a solution of 164 mg of alcohol **28** in 3 ml of pyridine contained in a 5-ml flask was added dropwise under nitrogen 642 mg (1.96 equiv) of trifluoromethanesulfonic anhydride.[24d–f] During the addition the solution was stirred magnetically and cooled in an ice bath. A white solid which precipitated soon dissolved and the solution became pink. The flask was stoppered and allowed to stand in a freezer overnight. The dark red reaction mixture was poured into ice water, which was then extracted with ether. The ethereal extract was washed with 6 *N* hydrochloric acid, water, saturated sodium bicarbonate, and brine, and was dried over anhydrous magnesium sulfate. Concentration on a rotary evaporator left 272 mg of a yellow oil. On standing several hours at room temperature an orange resinous material precipitated; the oil was taken up in pentane and decanted from the resin. Concentration on a rotary evaporator gave a colorless oil which remained clear on standing. Pure triflate **30** (159 mg; 50% yield) was isolated from a solution of the above oil in carbon tetrachloride by preparative glc on column A at 100° and a flow rate of 2 ml/sec. The ir spectrum of **30** displayed bands at 2975, 2900, 1415, 1247, 1215, 1150, 1000, 968, and 908 cm^{-1}. The nmr spectrum consisted of a multiplet from 1.85 to 2.40 ppm (5 H), a multiplet from 1.17 to 1.85 ppm (4 H), and a singlet at 1.1 ppm (6 H) due to the methyl protons. The mass spectrum showed the parent ion (0.74%) at *m/e* 272, the base peak at *m/e* 55, and other major peaks at *m/e* 69 and 41. Subsequent attempts to purify other samples of triflate **30** revealed that it is sensitive to the glc conditions. During preparative glc an oily substance accumulated in the glass injector insert which, unless removed at regular intervals, resulted in severe decomposition of **30**. Also, a column which worked well on one oc-

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(50) P. Beak, R. J. Trancik, and D. A. Simpson, *J. Amer. Chem. Soc.*, **91**, 5073 (1969).

casion subsequently resulted in decomposition of **30** and had to be replaced. *Anal.* Calcd for $C_{10}H_{15}O_3SF_3$: C, 44.11; H, 5.55; S, 11.78. Found: C, 44.26; H, 5.58; S, 12.01.

4-Tricyclyl Triflate (25). Under the above reaction conditions 192 mg of 4-tricyclenol (**22**) in 4 ml of pyridine was treated with 1.16 g (3.2 equiv) of trifluoromethanesulfonic anhydride. After working up the reaction mixture as described above, pure triflate **25** (188 mg; 52.6% yield) was obtained through preparative glc on column B at 155° and a flow rate of 2 ml/sec. Under these conditions the triflate had a retention time of 18 min and was followed closely by a minor product which was also a triflate according to its ir spectrum but was not identified. The ir spectrum of triflate **25** displayed bands at 3070, 2965, 1440, 1250, 1215, 1155, 1090, 1045, 960, and 910 cm^{-1}. The nmr spectrum consisted of a broad singlet at 2.04 ppm (4 H) due to the methylene protons, a broad singlet at 1.07 ppm (5 H) due to the bridgehead methyl and cyclopropyl methine protons, and a singlet at 0.94 ppm (6 H) due to the protons of the geminal methyl groups. The mass spectrum showed the parent peak (24.1%) at *m/e* 284, the base peak at 41, and major peaks at 43, 69, 119, and 269. *Anal.* Calcd for $C_{11}H_{15}O_3SF_3$: C, 46.47; H, 5.32; S, 11.28. Found: C, 46.78; H, 5.27; S, 11.44.

1-Methyl-4-tricyclo[2.2.2.0^{2,6}]octyl Triflate (33). A solution of 1.57 g (5.8 equiv) of trifluoromethanesulfonic anhydride in 5 ml of dry pyridine in an ice bath was stirred magnetically, under nitrogen. A solution of 134 mg of 1-methyl-4-tricyclo[2.2.2.0^{2,6}]octanol (**32**, **33**) in 2 ml of pyridine was added dropwise. After 40 min the reaction mixture was poured into a separatory funnel containing ice, water, and ether. Shaking was followed by addition of cold 6 *N* hydrochloric acid, shaking, and separation of the ether layer. The ethereal solution was washed with 6 *N* hydrochloric acid, saturated sodium bicarbonate, and brine, and was dried over magnesium sulfate and concentrated on a rotary evaporator. Initial attempts at glc purification showed that triflate **33** decomposes readily. Glc purification of 149 mg (60.4% yield) of **33** was achieved by using a glass injector insert, which had to be replaced after each few injections, and a glass column (column C) at 115° and a flow rate of 1 ml/sec. The ir spectrum displayed bands at 3030, 2950, 2870, 1405, 1245, 1205, 1145, 1020, 925, and 905 cm^{-1}. The nmr spectrum consisted of broad singlets at 2.23 (4 H) and 2.06 ppm (4 H) due to methylene protons, a broad singlet at 1.24 (2 H) due to cyclopropyl methine protons, and a sharp singlet at 0.92 (3 H) due to bridgehead methyl protons. The mass spectrum showed the appropriate parent peak at *m/e* 270 but also showed peaks from 281 to 285. The latter peaks may be due to a minor impurity or to decomposition of the triflate in the heated inlet system of the mass spectrometer. The base peak was at *m/e* 105 and other major peaks were at 69, 92, and 120. *Anal.* Calcd for $C_{10}H_{13}O_3SF_3$: C, 44.44; H, 4.85; S, 11.86. Found: C, 44.35; H, 4.91; S, 11.78.

1-Apocamphyl Ethyl Ether (31). A 10-ml round-bottomed flask was charged with 80 mg of alcohol **28**, 400 mg (3.7 equiv) of triethyloxonium tetrafluoroborate,[25] and 5 ml of methylene chloride, and was fitted with a reflux condenser. The reaction mixture was refluxed for 12 hr and then partitioned between water and ether. The ethereal extract was washed with saturated sodium bicarbonate and brine and dried over anhydrous magnesium sulfate. Most of the solvent was carefully removed on a rotary evaporator. Pure ether **31** (78.3 mg; 82% yield) was obtained through preparative glc on column B at 170°. Its ir spectrum displayed bands at 2960, 2880, 1480, 1468, 1453, 1385, 1365, 1210, 1140, and 1075 cm^{-1}. The nmr spectrum consisted of a quartet at 3.33 ppm (2 H, J = 6.5 Hz) due to the methylene protons of the ethyl group, a muliplet from 1.27 to 2.10 ppm (about 3 H, J = 6.5 Hz) due to the methyl protons of the ethyl group, and a singlet at 0.90 ppm (6 H) due to the protons of the geminal methyl groups. The mass spectrum showed the parent peak at *m/e* 168 (P + 1, 11.7%; P + 2, 0.88%; $C_{11}H_{20}O$ required, P + 1, 12.25%; P + 2, 0.89%). *Anal.* Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.44; H, 12.20.

4-Tricyclyl Ethyl Ether (26). A 10-ml flask containing 94 mg of alcohol **22** in 3 ml of dry ether (distilled from $LiAlH_4$) was purged with nitrogen. The solution was stirred magnetically while 0.40 ml of 1.75 *M* methyllithium (1.14 equiv) was added, producing a white precipitate. The ether was removed under pump vacuum and the white solid was dissolved in 2 ml of dimethyl sulfoxide (distilled from calcium hydride). Addition of 105 mg (1.1 equiv) of ethyl iodide was followed by stirring for 2 hr. The reaction mixture was poured into water and then extracted with pentane. The pentane extract was washed with 1 *N* hydrochloric acid and saturated sodium bicarbonate, dried over anhydrous magnesium sulfate, and concentrated on a rotary evaporator. Analytical glc revealed mainly starting material but also a minor product. Preparative glc on column D with temperature programming from 50 to 130° and a flow rate of 1 ml/sec allowed isolation of 21.7 mg (19.5%) of ether **26**. The ir spectrum of **26** displayed bands at 3050, 2950, 2870, 1465, 1295, 1197, 1145, 1125, and 840 cm^{-1}. The nmr spectrum consisted of a quartet at 3.37 ppm (2 H, J = 6.5 Hz) due to the methylene protons of the ethyl group, a triplet centered at 1.11 ppm (J = 6.5 Hz) with a singlet at 1.0 ppm superimposed on one element of the triplet (total of 6 H) due to the methyl protons of the ethyl group and the bridgehead methyl protons, and a singlet at 0.75 ppm (8 H) due to the cyclopropyl methine protons and the protons of the geminal methyl groups. The mass spectrum showed the parent peak at *m/e* 180. *Anal.* Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.78; H, 11.20.

1-Methyl-4-tricyclo[2.2.2.0^{2,6}]octyl ethyl ether (34) was prepared by the method used in preparing ether **26**. Starting with 55 mg of alcohol **32**, a 20% yield (13.4 mg) of ether **34** was obtained after glc purification on column D. The ir spectrum displayed bands at 3020, 2935, 2860, 1445, 1360, 1175, 1120, 1050, and 845 cm^{-1}. The nmr spectrum consisted of a quartet at 3.25 ppm (2 H, J = 6.5 Hz) due to the methylene protons of the ethyl group, a multiplet from 1.1 to 2.1 ppm (about 8 H) due to methylene protons, a triplet at 1.05 ppm (J = 6.5 Hz) due to the methyl protons of the ethyl group overlying a multiplet due to the cyclopropyl methine protons (total of about 5 H), and a singlet at 0.87 ppm due to the bridgehead methyl protons. The mass spectrum showed the parent peak (16.7%) at *m/e* 166 and the base peak at 151. *Anal.* Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.72; H, 11.16.

Reaction of 4-Tricyclenol (22) with Triethyloxonium Tetrafluoroborate. A mixture of 25.5 mg of alcohol **22**, 0.3 g of triethyloxonium tetrafluoroborate, and 2 ml of methylene chloride was refluxed for 2 hr and then partitioned between water and ether. The ethereal extract was washed with saturated sodium bicarbonate and brine and was dried over anhydrous magnesium sulfate. Analysis of the concentrated sample on column E showed one major product, which had the same retention time as ether **26**. However, this product was isolated by preparative glc (column B at 170°, 2 ml/sec), and its ir and nmr spectra were identical with those of an authentic sample of camphor (**15**) (Eastman).

Solvolysis of 1-Apocamphyl Brosylate (29). The rate of solvolysis of brosylate **29** in 70% (by wt) aqueous *p*-dioxane was determined using a modification of the uv spectrophotometric method described by Swain and Morgan.[21] For each run a solution 0.01 *M* in brosylate and 0.015 *M* in triethylamine in 70% aqueous dioxane (*p*-dioxane was Matheson Coleman and Bell spectroquality) was prepared. Portions (1.05 ml) of this solution in sections of $^1/_4$-in. heavy-walled Pyrex tubing (previously washed with 5% sodium hydroxide, glacial acetic acid, ammonium hydroxide, and distilled water, and dried *in vacuo* at 100° for at least 24 hr) were cooled in liquid nitrogen and sealed under aspirator vacuum. The sealed samples were placed simultaneously in a kinetic bath (Gebrüder Haake Ultrathermostat, Model NBB) previously equilibrated at 200.1°. After a 15-min equilibration period, samples were removed at intervals and quenched in water. Each sample was treated as follows: by pipet 1.00 ml of the sample was transferred to a 3-ml volumetric flask and to the flask were added 1 ml of reagent diethyl ether and 1 ml of solution A (an aqueous solution 0.05 *N* in sodium hydroxide and 10% by weight sodium chloride). After extraction, the ether layer was removed by pipet and the aqueous layer was extracted with a second 1-ml portion of ether and finally with 1 ml of cyclohexane (Matheson Coleman and Bell spectroquality). The above extraction sequence was effective in avoiding troublesome emulsions. After removal of the cyclohexane extract the aqueous solution was diluted to the line with solution A, and the uv spectrum (1-cm cell) was measured. The absorbance at 265 nm, the longest wavelength maximum of the brosylate anion, was determined as a function of reaction time. From the extinction coefficient for brosylate anion (measured at 337 and 265 nm; a Beer's law plot was linear over the required concentration range), and the absorbance data, the concentrations of brosylate anion, and, in turn, the extent of reaction of brosylate **29** could be calculated. When a 1-ml portion of the solution of brosylate **29** was worked up as above prior to solvolysis a uv sample was obtained which exhibited an absorbance of only 0.005 at 265 nm. This required only a small correction of the raw absorbance data. However, the absorbance measured after 7 half-lives exceeded the expected infinity "titer" by about 30%, and tailing beyond 300 nm was observed, whereas brosylate anion does not absorb appreciably at 300 nm. When samples of 70% aqueous dioxane, 0.015 *M* in triethylamine, were heated under the same conditions and subjected to the above work-up, uv analysis revealed a broad absorption that tailed beyond 300 nm. Since in these samples the ratio of the absorbance at 265 nm to that at 300 nm was essentially constant (about 2.3) and since brosylate anion does not absorb at 300 nm, it was possible to approximately correct the absorbance data at 265 nm obtained in the solvolysis to brosylate anion absorbance by substracting 2.3 times the absorbance at 300 nm. This correction gave approximately the correct infinity "titer." The first-order rate constant at 200.1° was determined to be $4.44 \pm 0.25 \times 10^{-5}$ sec^{-1}.

In order to determine the reaction products several samples were heated for 7 half-lives and worked up as above. The combined ethereal extracts were dried over magnesium sulfate and analyzed by glc on column E. The one product observed had the retention time of alcohol **28**, and comparison with a solution of **28** of known concentration suggested a yield of greater than 80%. A sample of the product was isolated by glc and its ir spectrum was identical with that of **28**.

Solvolysis of 4-Tricyclyl Brosylate (23). A solution of brosylate **23** in 70% aqueous dioxane buffered with triethylamine was prepared as described in the case of brosylate **29**. A sample of this solution was sealed in a stainless steel tube (these tubes have a volume of 1.5 ml and a wall thickness of 4 mm, and are sealed by threaded caps which employ Teflon gaskets) and was heated for more than 12 hr at 250° in a tube oven. The sample was diluted with solution A (*vide supra*) and extracted with ether. The extract on evaporation to dryness left a white solid, the ir spectrum of which was essentially identical with that of brosylate **23**. The recovery was about 97%. A second sample sealed in a steel tube was heated for more than 14 hr at 295°. After a work-up as above, analysis of the ethereal extract on column E at 150° revealed three products, the retention times and relative percentages of which follow: 1.9 min, 3%; 2.1 min, 13%; 2.3 min, 84%. Comparison with a solution of alcohol **22** of known concentration showed that the minor (3%) product had the retention time of **22** and that this product had formed in less than 1% absolute yield. Concentration of the ethereal extract left a yellow oil, the ir spectrum of which suggested that it was mostly brosylate **23**. The recovery was apparently about 50%. In a second run under the same conditions but allowing only an 8-hr reaction period, three products were again observed, but none had the retention time of alcohol **22**. Under the same conditions solvolysis of a mixture of brosylate **23** and alcohol **22** gave a mixture of these three products with no remaining **22**. Alcohol **22** is apparently unstable under the reaction conditions; therefore, the 3% component observed in the first run is probably not **22**, although it has the same retention time. The products were not identified.

Solvolyses of Triflates in Aqueous Ethanol. Kinetics. The solvent used in the solvolysis of triflates **25, 30,** and **33** was 60% (by wt) aqueous ethanol (ethanol was U.S.I. absolute reagent). For each kinetic run a solution 0.02 *M* in triflate, 0.06 *M* in triethylamine, and 0.01 *M* in biphenyl (internal standard) was prepared, and 0.65-ml aliquots were sealed in stainless steel tubes (described above). The tubes were placed simultaneously in a kinetic bath (Gebrüder Haake Ultra-thermostat, Model NBB) previously equilibrated at the desired temperature. After a 15-min equilibration period tubes were withdrawn at intervals and quenched in ice water. For the kinetic run with triflate **33** at 31.3°, the entire sample contained in a 10-ml volumetric flask was placed in a Sargent water bath (S-84810) controlled by a Sargent Thermonitor, Model SW (S-82055). Aliquots were taken at intervals by pipet.

In all kinetic runs each sample was transferred to a 2-ml ampoule, to which was added 100 μl of ether and about 1 ml of a solution prepared by mixing 100 g of saturated brine with 100 g of 20% aqueous sodium bisulfate. The ampoule was shaken and the ethereal layer analyzed by glc on column G at 130°. It was necessary to inject the first sample of each series several times before a reproducible ratio of triflate to biphenyl could be obtained. Then each sample was analyzed at least twice and the averages were used in calculating the ratio of the initial concentration of triflate, A_0, to the observed concentration, A, as a function of time, t. The data points were computer fitted to the first-order rate equation, $\ln A_0/A = kt$, by the method of least squares. The rate constants are presented in Table I; the error limits given are the standard deviations of the slopes.

In the case of triflate **30** it was shown that stainless steel has no effect on the rate. When samples in a stainless steel tube and in a Pyrex tube were simultaneously solvolyzed at 97°, analysis after 1 half-life showed the ratios of triflate to internal standard to be essentially identical.

Each of the triflates was solvolyzed at three temperatures covering a range of about 20°. The activation parameters given in Table I are weighted averages based on the differential error analysis given by Benson.[51b] The error limits are standard deviation.[51]

Products of Triflate Solvolyses. The product distributions shown in Table I are based on glc analysis (column F at 120°) of samples taken after 1 half-life and are not corrected for relative response. There was no apparent change in the product distributions during the course of the reactions. The sum of the glc integrals of the products was approximately equal to the decrease in the integral of the starting triflate; although these integrals were not corrected for relative response, this observation suggests a reasonable material balance. The retention times of the major products from each triflate were shown to be the same as those of the corresponding alcohols and ethyl ethers by coinjection of authentic or independently synthesized samples. In order to isolate the products, in the case of each triflate the samples from the kinetic runs were combined; the ether layer was separated and washed with saturated sodium bicarbonate and brine, dried over sodium sulfate, and concentrated on a rotary evaporator. Preparative glc on column A with temperature programming from 100 to 160° and a flow rate of 2 ml/sec allowed collection of the solvent and products together and separate collection of the unreacted triflate. Then the major products were isolated through preparative glc on column D with temperature programming from 50 to 120° and a flow rate of 1 ml/sec.

The products isolated from the solvolyses of triflates **25** and **30** were shown to be the corresponding alcohols and ethers by comparison of their ir spectra with those of known samples. However, the products isolated in this way from the solvolysis of triflate **33** gave ir and nmr spectra that were different from those of the expected alcohol **32** and ether **34**. One of the products was an alcohol. Its ir spectrum displayed bands at 3600, 3310 (broad), 3000, 2925, 2850, 1448, 1334, 1165, and 1092 cm^{-1}, and its nmr spectrum consisted of a multiplet from 5.10 to 5.25 ppm (1 H), a sharp singlet at 2.95 ppm (1 H), a multiplet from 2.0 to 2.5 ppm (3 H), and a multiplet from 1.2 to 2.1 ppm (9 H). The other product was apparently an ethyl ether. Its mass spectrum displayed the parent peak (99.7%) at *m/e* 166 and the base peak at 151, indicating that it is isomeric with ether **34**. Its ir spectrum displayed bands at 2930, 2860, 1450, 1390, 1335, 1186, 1165, 1109, and 1050 cm^{-1}. Due to the small amount of material available, its nmr spectrum could not be integrated accurately but consisted of multiplets at about 5.1, 2.3, and 1.7 ppm, a quartet centered at 3.51 ppm (J = 7 Hz), and a triplet at 1.14 ppm (J = 7 Hz). The absence of absorption at 3020 cm^{-1} in the ir spectra of these compounds suggests that neither has a cyclopropyl ring. The absence of a bridgehead methyl signal in their nmr spectra suggested that deep-seated rearrangements have occurred. When the solvolysis was repeated and worked up immediately, two major products could be isolated by the above procedure; these were identified as alcohol **32** and ether **34** by comparison of their ir and nmr spectra with those of known samples. In the former product study the kinetic samples had been allowed to stand in a refrigerator for 2 weeks before work-up; perhaps contact with aqueous sodium bisulfate over that period was sufficient to cause the observed rearrangements. The rearranged products were not identified.

Solvolysis of 4-Tricyclyl Triflate (25) in ^{18}O Enriched Medium. A sample of 60% (by wt) aqueous ethanol was prepared from absolute ethanol and ^{18}O-enriched water (Bio-Rad; reportedly 50 atom % ^{18}O and 7 atom % ^{2}H). In 0.6 ml of this solvent were dissolved 23 mg of triflate **25** and 26 mg of triethylamine. Samples of the solution were sealed in stainless steel tubes and heated at 246° for 10 hr (about 8 half-lives). The combined samples were partitioned between water and ether, and the ethereal extract was washed with 1 *N* hydrochloric acid, saturated sodium bicarbonate, and brine, dried over sodium sulfate, and concentrated. Preparative glc on column D allowed isolation of a sample of 4-tricyclenol (**22**), the identity of which was indicated by its ir spectrum. In high-resolution mass spectra[52] of this sample and of a sample of the ^{18}O-enriched water, separate peaks corresponding to each of the isotopic species in the respective parent ions could be observed. This allowed direct com-

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(51) (a) H. Margenau and G. Murphy, "The Mathematics of Physics and Chemistry," 2nd ed, Van Nostrand, Princeton, N. J., 1956, p 519; (b) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, p 91.

(52) (a) Obtained on an MS-902 by Dr. R. L. Foltz, High Resolution Mass Spectrometry Center, Battelle Memorial Institute, Columbus, Ohio; (b) error limits are standard deviation based on five mass spectra.

parison of the abundance of corresponding ^{18}O and ^{16}O components. The enriched water contained 68.68 ± 0.44 atom % ^{18}O, and the sample of alcohol **22** contained 69.94 ± 0.49 atom % ^{18}O. Thus the incorporation of ^{18}O in product **22** on solvolysis of triflate **25** was 101.8 ± 1.4%.

Acknowledgments. We are grateful for helpful discussions with Professors J. E. Leffler, R. E. Robertson, and P. von R. Schleyer, and for financial support from the National Institutes of Health.

Steric Assistance in the Solvolysis of 2-Alkyl-2-adamantyl *p*-Nitrobenzoates[1]

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Abstract: In order to estimate the relative importance of alkyl inductive and steric effects in the 2-adamantyl system, rates of solvolysis of a series of 2-alkyl-2-adamantyl *p*-nitrobenzoates were determined in 80% aqueous acetone. The relative first-order rate constants at 25° were: CH_3, 1.0; C_2H_5; 7.7; $CH_2C(CH_3)_3$, 10.0; *i*-C_3H_7, 33.5; *t*-C_4H_9, 225,000. The solvolysis products are the unrearranged alcohols and exocyclic olefins, except in the case of 2-*tert*-butyl-2-adamantyl *p*-nitrobenzoate where the methyl-shifted olefin, 2-methyl-2-(2′-isopropenyl)-adamantane, was formed in addition to the unrearranged alcohol. Conformational analysis calculations were performed and the relative strain energy differences between the hydrocarbon and the corresponding cation were calculated (kcal/mol) to be: CH_3, 0.0; C_2H_5, 0.5; $CH_2C(CH_3)_3$, 1.4; *i*-C_3H_7, 1.8; *t*-C_4H_9, 4.5. A good correlation of the hydrocarbon–cation strain energy change *vs.* the log of the rate of solvolysis is observed, the average deviation in rates being $10^{\pm 0.3}$. Steric effects are shown to play the dominant role in the 2-alkyl-2-adamantyl system. The question of steric assistance in the observed 2-adamantyl α-CH_3/H ratio, 10^8, is also considered. No significant steric acceleration is indicated; the observed α-CH_3/H rate ratio originates almost entirely from electronic considerations.

Very recently, the 2-adamantyl system has been used as a model to approximate the behavior of an idealized secondary substrate that is resistant to changes in solvent nucleophilicity in solvolytic reactions.[3,4] That this system does, to a remarkable degree, approximate such "limiting" (carbonium ion-like) behavior has been attributed to the inhibition of backside approach of nucleophilic solvent by the nonbonded repulsive interactions with the methylene hydrogens in the adamantane structure.

One of the characteristics displayed by the 2-adamantyl system is the enormous solvolytic rate enhancement observed when the methine hydrogen at C-2 is replaced by a methyl group. Rate enhancement factors for the solvolysis of bromides **1**-Br and **2**-Br were $10^{7.5}$ (25°, in 80% aqueous ethanol) and $10^{8.1}$ (25°, acetolysis).[3b] Under the same conditions, the rate ratio *tert*-butyl bromide (*t*-BuBr)/isopropyl bromide (*i*-PrBr) is only $10^{3.7}$. The rate ratio **1**-Br/*i*-PrBr of 1.6 × 10^{-3} is much less than the 9.7 rate ratio for **2**-Br/*t*-BuBr. These data suggested that isopropyl bromide alone of the four bromides was behaving exceptionally; isopropyl bromide, unlike 2-adamantyl bromide, benefits from considerable nucleophilc solvent assistance. The value 10^8 was therefore assigned as the new provisional limiting value of the α-methyl/hydrogen rate ratio in the absence of anchimeric and solvent assistance.

If the value of 10^8 for the limiting α-methyl/hydrogen rate ratio is to have any generality for the interpretation of solvolytic behavior, electronic stabilization must be the principle cause and not relief of ground-state steric strain. We wished to see whether or not this was true. It is known that 2-aryl-2-adamantyl substrates are quite sensitive to aryl substituent effects,[5] but no information was available concerning the relative importance of alkyl inductive and steric effects in 2-alkyl-2-adamantyl substrates.

In order to determine the importance of these effects, a series of 2-alkyl-2-adamantyl *p*-nitrobenzoates was prepared and the rates of solvolysis were determined. Since specific nucleophilic solvent participation should not be present in any of these compounds, observed reactivity differences should only reflect inductive and "B-strain"[6,7] effects.

Results

2-Alkyl-2-adamantanols were prepared by addition of the appropriate alkyl Grignard or lithium compound to adamantanone. Only 2-methyl- (**2**-OH) and 2-neopentyl-2-adamantanol (**4**-OH) could be prepared in good yield (~90%) by the Grignard addition; 2-ethyl-

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(1) Presented, in part, at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, Abstract No. ORGN-133, and at the Sixth Middle Atlantic Regional Meeting of the American Chemical Society, Baltimore, Md., Feb 1971, Abstract P-70.

(2) National Institutes of Health Postdoctoral Fellow, 1967–1969.

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