Perpendicularly Twisted Cyclopropylcarbinyl and Allyl Cations. Acetolysis of Some 2-Substituted Derivatives of 1-Adamantyl Tosylate

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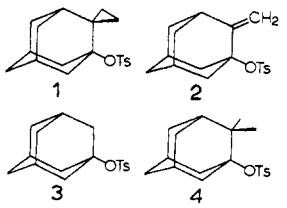
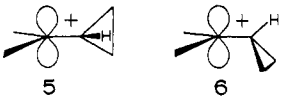
Abstract: To probe the effect of cyclopropyl and vinyl groups twisted by 90° from the most favored geometry for conjugation on the stability of an adjacent cationic center, the acetolysis rates of spiro[cyclopropane-1,2′-adamantyl] tosylate (**1**, $k_{rel}^{45°} = 6.5 \times 10^{-3}$) and 2-methyleneadamantyl tosylate (**2**, $k_{rel}^{45°} = 8.8 \times 10^{-5}$) were compared with those of model compounds adamantyl tosylate (**3**, $k_{rel}^{45°} = 1.0$) and 2,2-dimethyladamantyl tosylate (**4**, $k_{rel}^{45°} = 2.3$). In contrast to the large rate accelerations usually associated with ionizations leading to cyclopropylcarbinyl and allylic cations, compounds **1** and **2**, in which these groups are restricted to a conformation in which conjugation would be minimal, solvolyze about 10^{-2} (cyclopropylcarbinyl) and 10^{-4} (allyl) as fast as the model compounds. All acetolyses follow the first-order rate law and give unrearranged acetate as the only detected product. The observed rate depressions for the 2-spirocyclopropyl and 2-methylene compounds are not due to steric factors since the 2,2-dimethyl compound has a large relative rate. A linear correlation of log k_{rel} with the inductive substituent constant, σ_I, suggests that the major factor in determining the rates of acetolysis of these compounds is the inductive effect of the substituent adjacent to the cationic center, and that all cyclopropylcarbinyl and allylic resonance stabilization has been suppressed. Tosylate **2** was prepared by the treatment of the lithium salt of the corresponding alcohol with *p*-toluenesulfonyl chloride. Tosylates **1**, **3**, and **4** were prepared by the conversion of the alcohols to sulfinate esters and oxidation to the sulfonates by *m*-chloroperbenzoic acid or ruthenium tetroxide. The latter oxidation method, which can be applied at low temperature in nonpolar aprotic media, appears to be a generally useful procedure for the preparation of sterically hindered or very reactive tosylates.

The structural rigidity of the adamantyl ring system makes *p*-toluenesulfonates **1–4** unusually favorable models for use in probing the geometrical requirements for conjugative stabilization of allyl[2] and cyclopropylcarbinyl[2,3] cations. This paper reports the syntheses of **1–4** and kinetic studies of their acetolysis reactions.



1 2 3 4

The very large conjugative interaction between a cyclopropyl group and an adjacent electron-deficient sp^2 hybridized carbon has been the object of continuing wide interest.[4] The conformational preference for the "bisected" geometry (**5**) over the "perpendicular" geometry (**6**) has been well documented. Evidence from ultraviolet spectroscopy[5] has provided the basis for conflicting interpretations, although tending to suggest that **5** is the preferred conformation. Evidence from electron diffraction[6] and nmr[7] studies has clearly pointed to a preference for **5**, in accord with several theoretical calculations.[8]



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Although much of the nmr evidence for **5** can equally well be accommodated by a model involving a set of rapidly equilibrating bicyclobutonium ions,[9] evidence related to certain other systems has been interpreted[10] as favoring the more symmetrical formulation **5**. The detailed description may well depend on the substitu-

(1) Abstracted from the Ph.D. Thesis of B. R. Ree, University of Illinois, 1969. Rohm and Haas Co., Fellow, 1965–1966; Phillips Petroleum Co., Fellow, 1967–1968; and Hoffmann-LaRoche, Inc., Fellow, 1969.

(2) A preliminary report of this work is found in J. C. Martin and B. R. Ree, *J. Amer. Chem. Soc.*, **91**, 5882 (1969).

(3) A preliminary report of a study of chlorides related to **1** and **3** is found in P. Schleyer and V. Buss, *ibid.*, **91**, 5880 (1969).

(4) Recent reviews on cyclopropylcarbinyl systems include (a) H. G. Richey, Jr. in "Carbonium Ions," Vol. 3, G. Olah and P. V. R. Schleyer, Ed., Interscience Publishers, New York, N. Y., 1969; (b) B. Wiberg, B. A. Andes, Jr., and A. J. Ashe, in "Carbonium Ions," Vol. 3, G. Olah and P. v. R. Schleyer, Ed., Interscience Publishers, New York, N. Y., 1969; (c) M. Hanack and H. J. Schneider, *Angew. Chem. Intern. Ed. Engl.*, **6**, 666 (1967); *Fortschr. Chem. Forsch.*, **8**, 554 (1967).

(5) (a) G. W. Perold, *J. S. African Chem. Inst.*, **10**, 11 (1957); *Chem. Abstr.*, **52**, 1074*i* (1958); (b) A. L. Goodman and R. H. Eastman, *J. Amer. Chem. Soc.*, **86**, 908 (1964); (c) C. H. Heathcock and S. R. Poulter, *ibid.*, **90**, 3766 (1968); (d) M. J. Jorgenson and T. Leung, *ibid.*, **90**, 3769 (1968); (e) E. M. Kosower and M. Ito, *Proc. Chem. Soc.*, 25 (1962); (f) H. G. Richey, Jr., and N. C. Buckley, reported in ref 5a; (g) W. G. Dauben and G. H. Berezin, *J. Amer. Chem. Soc.*, **89**, 3449 (1967).

(6) (a) L. S. Bartell, B. L. Carroll, and J. P. Guillory, *Tetrahedron Lett.*, 705 (1964); (b) L. S. Bartell and J. P. Guillory, *J. Chem. Phys.*, **43**, 647 (1965); (c) L. S. Bartell, J. P. Guillory, and A. T. Parker, *J. Phys. Chem.*, **69**, 3043 (1965).

(7) (a) G. J. Karabatsos and N. Hsi, *J. Amer. Chem. Soc.*, **87**, 2864 (1965); (b) H. Gunther and N. Wendisch, *Angew. Chem. Intern. Ed. Engl.*, **4**, 251 (1966); (c) G. L. Closs and H. B. Klinger, *J. Amer. Chem. Soc.*, **87**, 3265 (1965); (d) C. U. Pittman and G. A. Olah, *ibid.*, **87**, 2998, 5123 (1965); (e) G. R. DeMare and J. S. Martin, *ibid.*, **88**, 5033 (1966); (f) S. Sarel, J. Yovell, and M. Sarell-Imber, *Angew. Chem. Intern. Ed. Engl.*, **7**, 577 (1968); (g) N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *J. Amer. Chem. Soc.*, **87**, 4533 (1965).

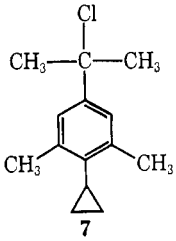
(8) (a) J. E. Baldwin and W. D. Foglesong, *ibid.*, **90**, 4311 (1968); (b) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964); (c) T. Yonezawa, H. Nakatsuji, and H. Kato, *Bull. Chem. Soc. Jap.*, **39**, 2788 (1966); (d) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

(9) W. B. Kover and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 3687 (1969).

(10) (a) G. W. Van Dine and P. v. R. Schleyer, *ibid.*, **88**, 2321 (1966); (b) H. G. Richey, Jr., and J. M. Richey, *ibid.*, **88**, 4971 (1966); (c) M. Vogel and J. D. Roberts, *ibid.*, **88**, 2262 (1966); (d) H. L. Goering and K. E. Rubenstein, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

tion pattern. We will couch our discussion in terms of structures **5** and **6**, the conformational extremes.

The diminished reactivity demonstrated for **7** (hydrolysis rate)[11] and **8** (ionization in acid solution, pK_{R^+}),[12] accompanying the introduction of *o*-methyl groups which prevent the attainment of the bisected geometry for the cyclopropyl substituent, is consistent with a reduction of the electron releasing capability of this substituent by the steric inhibition of resonance.[11-13]



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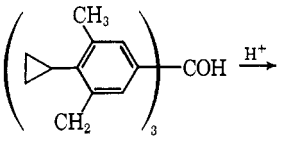

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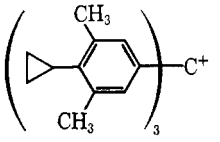

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Chemical shift arguments based on nmr studies of **8** and **9** did, however, suggest[12] that charge delocalization into the cyclopropyl ring of **9** was still important, though diminished by the flanking methyl groups. This left open the possibility that conformation **6**, though less favored than **5**, might still be capable of important conjugative electron release. The alternative explanation would suggest that the flanking *o*-methyl groups do not provide enough restraint to force the substituent into the extreme perpendicular conformation, making inhibition of resonance incomplete. It was therefore desirable to study a system in which the cyclopropyl substituent is held rigidly in the perpendicular geometry as in **1**.

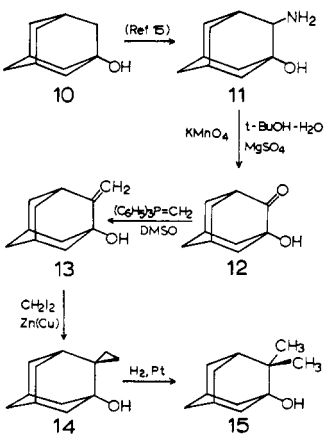
A few examples of probable steric inhibition of allylic conjugation, reflected in the reactivities of bridgehead-substituted norbornenes, have been reported.[14] Compound **2** provides a more interesting example, however, since saturated model compounds, such as **3** or **4**, solvolyze in a straightforward manner at rates rapid enough to allow measurement.

Results

Synthesis. During the course of this research Curran and Angier[15] reported an unequivocal synthetic route converting 1-adamantanol (**10**) to 2-amino-1-adamantanol (**11**). Our work on a related synthetic approach was abandoned and **11** was used as a starting point for the indicated (Chart I) syntheses of carbinols **12–15**.

The oxidation of amine **11** to ketone **12** by a method (chromic anhydride in acetic acid) reported[16] to be successful for 2-aminoadamantane proceeded in very poor yield. The best of several oxidation procedures which we tried involved potassium permanganate in *t*-butyl alcohol–water solution buffered with magnesium sulfate.[17] This procedure gave synthetically useful, but variable (25–75%) yields of **12**.

Chart I



Allylic carbinol **13** was prepared from **12** by treatment with triphenylphosphine methylide in dimethyl sulfoxide,[18] and **13** was converted to **14** by treatment with Simmons–Smith reagent.[19] Hydrogenolysis of the cyclopropyl ring over platinum in acetic acid[20] gave 95% of **15**.

Of the four tosylates **1–4**, only the least reactive, **2**, was prepared by a conventional route involving the reaction of *p*-toluenesulfonyl chloride (with the lithium salt of **13**). The reported[21] difficulty in applying a related method to the preparation of the more reactive **3** led us to use the method of Coates and Chen[22] for the preparation of **1** and **3**. This method, which involves the oxidation of the *p*-toluenesulfinate ester with *m*-chloroperbenzoic acid, failed when applied in an attempted preparation of **4**, the most reactive member of the series. Tosylate **4**, if formed, was hydrolyzed in the aqueous workup after peracid oxidation of the sulfinate ester. A successful method was devised using ruthenium tetroxide to oxidize the sulfinate ester to **4** in chloroform at −27°.

Preliminary investigations[23] suggest that this new method of preparing highly hindered or reactive sulfonate esters by ruthenium tetroxide oxidation of the corresponding sulfinates at low temperatures in aprotic solvents, such as chloroform, carbon tetrachloride, or difluorodichloromethane, can be the synthetic method of choice, even for such reactive compounds as *t*-butyl tosylate.[24] The product ruthenium dioxide can be removed from the reaction mixture by filtration or centrifugation at low temperatures, avoiding any con-

(11) H. C. Brown and J. D. Cleveland, *J. Amer. Chem. Soc.*, **88**, 2015 (1966).
(12) T. Sharpe and J. C. Martin, *ibid.*, **88**, 1815 (1966).
(13) See also J. A. Berson, G. M. Clarke, D. Wege, and R. G. Bergmann, *ibid.*, **91**, 3240 (1969).
(14) (a) E. A. Prill, *J. Amer. Chem. Soc.*, **69**, 62 (1947); (b) E. K. Fields, *ibid.*, **76**, 2709 (1954); (c) J. W. Wilt, C. T. Parsons, C. A. Schneider, D. G. Schultenover, S. J. Wagner, and W. J. Wagner, *J. Org. Chem.*, **33**, 694 (1968); (d) C. J. Norton, Ph.D. Thesis, Harvard University, 1955; (e) for a review see R. C. Fort and P. v. R. Schleyer, *Advan. Alicycl. Chem.*, **1**, 284 (1966).
(15) W. V. Curran and R. B. Angier, *Chem. Commun.*, 563 (1967).
(16) H. Stetter, H. Held, and J. Mayer, *Ann.*, **658**, 151 (1962).
(17) Similar to the conditions of S. S. Rawalay and H. Shechter, *J. Org. Chem.*, **32**, 3129 (1967).
(18) R. Greenwald, M. Chaykovsky, and E. J. Corey, *ibid.*, **28**, 1128 (1963).
(19) (a) H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **81**, 4256 (1959); (b) E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).
(20) (a) C. W. Woodworth, V. Buss, and P. v. R. Schleyer, *Chem. Commun.*, 569 (1968); (b) J. Vais, J. Barkhardt, and S. Landa, *Z. Chem.*, **8**, 303 (1968).
(21) P. v. R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, **83**, 2700 (1961).
(22) R. M. Coates and J. P. Chen, *Tetrahedron Lett.*, 2705 (1969).
(23) Unpublished results of R. Radue.
(24) H. M. R. Hoffman, *J. Chem. Soc.*, 6748 (1965).

Table I. Acetolysis of Adamantyl Tosylates (0.02 *M* Sodium Perchlorate Added)

Compd	Temp, °C ±0.05°	k, sec^{-1}	ΔH^*, kcal/mole	ΔS^*, eu	$k_{rel}^{45°}$
1	45	$(5.03 \pm 0.06) \times 10^{-5}$			
	55	$(1.84 \pm 0.09) \times 10^{-4}$			
	75	$(1.35 \pm 0.04) \times 10^{-3}$	23.3 ± 1.1	−5.0 ± 5.4	6.5×10^{-3}
2	75	$(2.81 \pm 0.07) \times 10^{-5}$			
	95	$(2.63 \pm 0.01) \times 10^{-4}$			
	105	$(6.38 \pm 0.08) \times 10^{-4}$			
	45	6.86×10^{-7} [a]	26.7 ± 0.8	−3.0 ± 2.3	8.8×10^{-5}
3	20	$(4.58 \pm 0.01) \times 10^{-4}$			
	25[b]	$(5.15 \pm 0.02) \times 10^{-4}$			
	25[c]	$(6.77 \pm 0.05) \times 10^{-4}$			
	25	$(8.89 \pm 0.01) \times 10^{-4}$			
	25[d]	$(14.4 \pm 0.10) \times 10^{-4}$			
	30	$(1.40 \pm 0.01) \times 10^{-3}$			
	30	$(1.42 \pm 0.01) \times 10^{-3}$			
	35	$(2.72 \pm 0.01) \times 10^{-3}$			
	45	$(8.09 \pm 0.05) \times 10^{-3}$			
	45	$(7.43 \pm 0.03) \times 10^{-3}$	20.3 ± 0.5	−4.5 ± 1.7	1.0
4	20	$(1.29 \pm 0.01) \times 10^{-3}$			
	30	$(4.02 \pm 0.01) \times 10^{-3}$			
	45	$(1.85 \pm 0.02) \times 10^{-2}$			
	45	$(1.68 \pm 0.02) \times 10^{-2}$			
	45	$(1.91 \pm 0.03) \times 10^{-2}$	19.0 ± 0.2	−7.0 ± 0.6	2.3

[a] Calculated from data at higher temperatures. [b] No added $NaClO_4$. [c] 0.01 *M* $NaClO_4$. [d] 0.05 *M* $NaClO_4$.

tact with protic solvents or reagents or elevated temperatures which would destroy the reactive product. The change in chemical shift difference[22] between *ortho* and *meta* protons which accompanies the conversion of a *p*-toluenesulfinate ($\Delta\delta$ = 0.22–0.33 ppm) to the tosylate ($\Delta\delta$ = 0.39–0.48 ppm) provides a method for monitoring the completeness of the oxidation step.

$$\underset{\text{or } RO^-M^+}{ROH} \xrightarrow{CH_3C_6H_4SOCl} ROSOC_6H_4CH_3 \xrightarrow[\substack{CHCl_3 \\ \text{or} \\ CF_2Cl_2 \\ -30°}]{RuO_4} ROSO_2C_6H_4CH_3$$

The acetate esters of carbinols **10**, **13**, **14**, and **15** were prepared by the acid-catalyzed[25] action of ketene on chloroform solutions of the alcohols. Analytical samples of the acetates were obtained by column chromatography on alumina and recrystallization from ether–pentane or preparative glpc.

The cyclopropyl protons of the alcohol, acetate, and tosylate derivatives of **14** appear in the nmr spectra as a pair of quartets at *ca.* δ 0.1 and 0.7 ppm, symmetrical about the midpoint. In the compound with the chiral sulfinate ester substituent, however, the two absorptions no longer have a center of symmetry and appear as two complex multiplets. A similar feature is noted in the nmr spectra of the derivatives of the *gem*-dimethyl compound, **15**. The absorption due to the methyl groups appears as a singlet at *ca.* δ 1.1 ppm in the alcohol, acetate, and tosylate but as two singlets, at δ 1.05 and 1.08, in the sulfinate.

Rate Studies. The acetolysis rates for tosylates **1**–**4** were followed by the continuous titration of the liberated *p*-toluenesulfonic acid with 0.02 *M* sodium acetate in acetic acid. All solvolyses, with the exception of those used in the determination of the salt effect on the acetolysis of adamantyl tosylate, were conducted at constant ionic strength, using 0.02 *M* sodium perchlorate in anhydrous acetic acid containing 0.5% acetic anhydride. All compounds gave normal first-order rate plots using the experimental infinity titers. These were about 10% lower than the theoretical value for **2**, about 20% low for **1** and **3**, and about 45% low for **4**. The disparity results from the presence of unreactive sulfinate and small amounts of alcohol impurities. In the case of 2,2-dimethyladamantyl tosylate (**15**), larger amounts of alcohol and appreciable quantities of carbon tetrachloride solvent were present in the samples used for solvolysis.

The rates of acetolysis of adamantyl tosylate at 25° with varying concentrations of added sodium perchlorate are shown in Table I. The variation of rate with ionic strength corresponds to a Winstein[26] *b* value of 36.4. Activation parameters, acetolysis rates at various temperatures and relative rates at 45° (0.02 *M* $NaClO_4$) are shown in Table I for the series of compounds studied.

Product Studies. The solvolysis products were determined quantitatively by gas chromatography using benzophenone as an internal standard. The yield of unrearranged acetate was consistently greater than 90% of the calculated amount based on the infinity titer. The retention times of the products were found to be identical with those of the corresponding acetates on three different glpc columns.

To establish the identity of the products, they were isolated from completed solvolysis runs and compared to authentic acetates on a glpc–mass spectrometer apparatus. The mass spectra of the products were identical with those of the corresponding acetates. The infrared and nmr spectra of the product from the acetolysis of **4** corresponded to those of authentic acetate prepared by treatment of **15** with ketene.

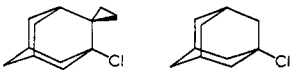
Discussion

In contrast to the accelerated ionization reactions usually seen for processes leading to cyclopropyl-

(25) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, Inc., New York, N. Y., 1967, p 529.

(26) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, 78, 2763, 2780 (1956).

carbinyl and allyl cations, the acetolyses of tosylates **1** and **2** are, respectively, about two and four powers of ten *slower* than that of saturated model compound **3** (or of **4**). The rate depression of two powers of ten observed for **1**, relative to **3**, is comparable to the rate depression seen by Schleyer and Buss[3] for the analogous chloride **16**, relative to **17**.



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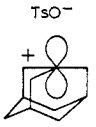
It is easily seen that the rigid framework of the adamantane ring system requires a p orbital at the 1 position of a carbonium ion, such as **18**, which is produced by tosylate ionization, to be in a perpendicularly twisted conformation relative to the cyclopropyl substituent in **1** or the vinyl group in **2**. Conjugative stabilization from these groups is therefore minimized. The geometry of **1** is unfavorable for cyclopropylcarbinyl–cyclobutyl ring expansion and precludes ring opening to an allylcarbinyl system. Similarly, allylic rearrangement in **2** is prevented. Products which would arise from these processes are not observed.



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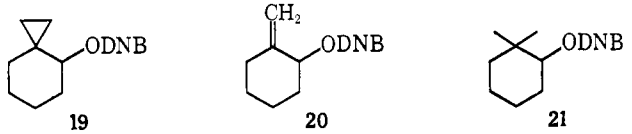
Rate accelerations typical of cyclopropylcarbinyl and allylic systems are illustrated by the observations that **19** and **20** (ODNB = 3,5-dinitrobenzoate) solvolyze 190,000 and 600 times faster, respectively, than the dimethyl compound **21**.[27] The similarly substituted but geometrically restricted compounds **1** and **2** solvolyze 360 and 26,000 times more slowly than dimethyl



19 20 21

analog **4**. Thus rate decelerations of *ca.* 10^7 are obtained by constraining these groups to the nonpreferred geometry. This corresponds roughly to an energy difference of 10 kcal/mole between the bisected and perpendicular conformations. A barrier of at least 10 kcal/mole in the 2-cyclopropyl-2-propyl cation for rotation of the cyclopropyl group in SbF_5–SO_2–SOClF[7d] has been estimated from nmr observations. The energy difference between the bisected and perpendicular geometries of the cyclopropylcarbinyl cation calculated by various quantum mechanical treatments[8] ranges from 9 to 26 kcal/mole. A value of 6 kcal/mole has been calculated[8b] for the energy difference between the planar and perpendicular conformations of the allylic cation and a barrier to rotation of 4–6 kcal/mole has been measured[28,28a] for methyl-substituted allylic cations by nmr.

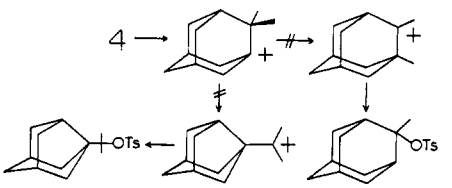
(27) T. Tsuji, I. Moritani, and S. Nashida, *Bull. Chem. Soc. Jap.*, **40**, 2338 (1967).

(28) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **90**, 6082 (1968).

(28a) NOTE ADDED IN PROOF. P. V. R. Schleyer, T. M. Su, M. Saunders, and J. C. Rosenfield, *ibid.*, **91**, (1969), suggest that the E_a value quoted[28] is too low and support a value nearer 20 kcal/mol for rotation barriers in allylic cations.

Three possible explanations for the rate depressions observed for **1** and **2** were considered; (a) steric inhibition of solvation, (b) increased transition state angle strain due to sp^2 hybridization at C-2, and (c) inductive destabilization of the transition state by the more electronegative cyclopropyl or vinyl group.

The high relative reactivity of **4** eliminates the possibility of steric inhibition of solvation as an important determining factor in the observed rate effects. However, the possibility must be considered that this rapid rate is due to rearrangement prior to or concerted with solvolysis to give a more reactive tosylate or more stable cation as shown. In either case, one would expect



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products from the rearranged cations. These possibilities are eliminated by the following observations. The nmr spectrum of **4** shows a single absorption for the *gem*-dimethyl group at δ 1.11 ppm, close to the singlet at δ 1.05 ppm observed for carbinol **15**. Two nonequivalent methyl groups would be expected for **22**. A lower field absorption would be expected for the methyl groups in **23**. The acetolysis product from **4** is identical (infrared, nmr, glpc, mass spectrum) with acetate prepared from **15**. The acetate shows a single nmr absorption for the *gem*-dimethyl group at δ 1.08 ppm. Again, one would expect two nonequivalent methyls for the acetate related to **22** and a singlet at lower field for that related to **23**. Olefinic products which might be expected from cations derived from **22** to **23** are not observed. Alkaline hydrolysis of the acetolysis product from **4** gives **15**, identical with the alcohol obtained by hydrogenolysis of **14**.

As the carbon atom at the bridgehead position rehybridizes from sp^3 toward sp^2 on going to the transition state, the angles at the adjacent carbon atoms are compressed toward 90°. The approximately sp^2 hybridization at C-2 in **1** and **2** would result in increased transition state angle strain relative to the model compounds **3** and **4** which have sp^3 hybridization at C-2. The approximate magnitude of this effect is seen by comparing the cyclobutane ring strain in compounds incorporating an sp^2 carbon atom into the ring, as in **24** and **25**, to the ring strain in cyclobutane. Wiberg

24 25

has determined the increase in cyclobutane ring strain to be *ca.* 1 kcal/mole per trigonal center.[29] A similar estimate has been made by Turner and coworkers.[30] Thus only a small part of the approximately 10^7 rate depression obtained by constraining the cyclopropyl and vinyl groups to a perpendicular geometry in **1** and **2** can be attributed to increased angle strain in these models.

(29) K. B. Wiberg and R. A. Fenoglio, *ibid.*, **90**, 3395 (1968).

(30) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *ibid.*, **90**, 4315 (1968).

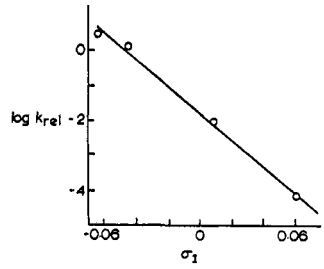

Figure 1. Hammett–Taft plot for the acetolyses of tosylates **1–4** at 45°.

Probably the most important factor slowing the solvolysis rates of **1** and **2** is the electron-withdrawing inductive effect of the cyclopropyl and vinyl groups. The sp^2 carbon atom at C-2 in these compounds is more electronegative than the sp^3 carbon atom at C-2 in **3** and **4**. The effect of the substituents at C-2 can be evaluated on a more quantitative basis by correlating the relative rates with the inductive substituent constants (σ_I) in a Hammett–Taft treatment. The appropriate σ values for the series of compounds studied are shown in Table II, taking the methyl group as the appropriate model for the substituent at C-2 in **3**.

Table II. Inductive Substituent Constants

Compd	Substituent	σ_I aliphatic	σ_I nmr
1	Cyclopropyl	+0.01[b]	−0.08[a]
2	Vinyl	+0.06[b]	+0.01[a]
3	Methyl	−0.046[c]	−0.08[a]
4	Isopropyl	−0.064[c]	+0.02[a,d]

[a] Determined by ^{19}F nmr spectroscopy [R. W. Taft, Jr., E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 709 (1963), and R. G. Pews, *ibid.*, **89**, 5605 (1967)]. [b] Calculated from σ^* values as described in the text. [c] R. W. Taft, Jr., and I. C. Lewis, *Tetrahedron*, **5**, 210 (1959). [d] Estimated from the values for methyl −(0.08) and ethyl (−0.03).

The σ_I aliphatic values in Table II for the cyclopropyl and vinyl substituents are derived from σ^* values using the following relationships.[31,32] Three experimental

$$\sigma^*_{(XCH_2)} = 0.357\sigma^*_{(X)}$$

$$\sigma_{I(X)} = 0.45\sigma^*_{(XCH_2)}$$

bases have been used to calculate σ_I for the cyclopropyl substituent. The first (+0.017) is based on a σ^* value derived from data on infrared OH stretching intensities of cyclopropanol.[33] A second value (+0.005) is calculated from dipole moment data of cyclopropyl chloride and other alkyl chlorides.[34] The third value (0.0) is calculated directly, using the Taft relationship,[35] from the acidity constants for the *meta* and *para* isomers of cyclopropylbenzoic acid. The first two of these values are derived from data which would be relatively free of contributions from resonance effects, and the third value is derived by a method[36] which is designed to factor out resonance effects to give a measure of the inductive effect. The methods agree that the cyclopropyl substituent (average σ_I = 0.01) is very similar to hydrogen in its inductive electron releasing capability and much less effective than other alkyl groups.[37]

An estimate of the value of σ^* for the vinyl substituent was made by interpolation from the values of +0.36 reported[38] for the 2-methylvinyl substituent and +0.41 for the 2-phenylvinyl substituents, noting the values of +0.08, −0.10, and −0.12 for the saturated (ethyl) analogs of the vinyl group with phenyl, hydrogen, and methyl β-substituents. This σ^* value for the vinyl substituent (+0.38) corresponds to a σ_I value of +0.06.

A Hammett–Taft plot (Figure 1) shows a good linear correlation with σ_I for the acetolyses of tosylates **1–4**. The values for σ_I determined from ^{19}F chemical shifts do not agree well with the values of σ_I aliphatic for this series of substituents and give a much poorer rate correlation. The correlation with σ^* values for the same set of substituents is also substantially poorer than that with σ_I aliphatic. This is not too surprising since σ^* values probably contain some contribution from resonance interaction. The σ_I aliphatic value for substituent X is related not to the σ^* value for X but to that for $-CH_2X$ in which X is insulated from the reaction center by a methylene group, eliminating the possibility of resonance interactions. The better correlation with σ_I aliphatic, therefore, underscores the conclusion that the principal effect of a cyclopropyl group in the perpendicular conformation is inductive in nature. The observed value of ρ_I (−36.6 ± 1.5) for this reaction indicates a sensitivity to inductive effects substantially greater than is seen for the ionization of triarylcarbinols in sulfuric acid (−12)[39] or the ethanolysis of simple tertiary alkyl chlorides (−20)[40] and approaching the value, from mass spectrometry, for the gas phase ionization of substituted methanes (−45).[41] Although the range of substituents studied here is small the correlation does give us some confidence that this reaction is unusually sensitive to polar substituent effects. This may reflect the fact that solvation of the developing charge in the 1-adamantyl system is sterically prohibited from one face of the carbonium ion. The principal mechanism for this interaction between a carbonium ion center and a perpendicularly twisted cyclopropyl substituent is clearly inductive.

The question[12] of how perfectly the two flanking *o*-methyl groups of **7** and **8** constrain the cyclopropyl substituent to the perpendicular geometry can now be examined in the light of our success in correlating the solvolysis rates for **1** with σ_I for the cyclopropyl substituent. From the rate constants of Brown and Cleveland[11] for the hydrolysis of 4-cyclopropyl-*t*-cumyl

(31) See Table II, footnote *c*.
(32) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 195 (1964).
(33) T. L. Brown, J. M. Sandri, and H. J. Hart, *J. Phys. Chem.*, **61**, 698 (1957).
(34) J. A. Landgrebe, Ph.D. Thesis, University of Illinois, 1962.
(35) R. W. Taft, Jr. and I. C. Lewis, *J. Amer. Chem. Soc.*, **80**, 2346 (1958).
(36) J. Smejkal, J. Jonas, and J. Farkas, *Collect. Czech. Chem. Commun.*, **29**, 2950 (1964).
(37) A very similar value of σ^* for the cyclopropyl substituent (+0.01) has been determined, using acidity measurements on cyclopropylacetic acid, by Y. E. Rhodes and L. Vargas (discussed by Professor Rhodes at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969).
(38) R. W. Taft, Jr. in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, Chapter 13.
(39) R. W. Taft, Jr., and I. C. Lewis, *J. Amer. Chem. Soc.*, **81**, 5343 (1959).
(40) Calculated from ρ^* quoted in A. Streitwieser, Jr., *Chem. Rev.*, **56**, 696 (1956).
(41) R. W. Taft, Jr., R. H. Martin, and F. W. Lampe, *J. Amer. Chem. Soc.*, **87**, 2490 (1965).

chloride and of **7**, a σ^+ value can be calculated[42] for the freely rotating cyclopropyl group ($\sigma^+ = 0.46$),[43] and for the cyclopropyl group twisted as in **7**, **8**, or **9** ($\sigma^+ = 0.21$). Comparison of these values with the σ_I value (+0.01) appropriate for the perpendicularly twisted conformation suggests that the cyclopropyl groups in **7** and **8** are still able to attain a geometry allowing about one-half the maximum resonance stabilization. Assuming a $\cos^2\theta$ dependence of cyclopropyl conjugation on the angle of twist away from the bisected geometry, one calculates that the cyclopropyl substituents in **7** and **8** are twisted about 47° away from the favored geometry, (rather than 90° as in **18**). This may offer an explanation for the substantial downfield shifts seen in the nmr for the cyclopropyl methylene groups upon conversion of **8** to **9**. An examination of molecular models makes it seem unlikely that a 47° angle of twist is actually possible for these carbonium ions, however.

Experimental Section

Melting points were determined on an Arthur H. Thomas hot stage apparatus, except those for carbinols **12–15** which were determined in a sealed melting point capillary in a circulating melting point bath. Infrared spectra were obtained with Perkin-Elmer Models 137 and 521 recording spectrophotometers. Proton magnetic resonance spectra were recorded on Varian Associates A-60A, A-56/60A, and HA-100 spectrometers. Chemical shifts are reported on the δ scale, parts per million downfield from tetramethylsilane internal standard. Coupling constants, J, were determined from a first-order analysis of the observed spectra. Elemental analyses were by J. Nemeth and associates. Mass spectra were run on an Atlas CH4 mass spectrometer by J. Wrona.

Oxidation of 2-Aminoadamantan-1-ol (11) with Chromium Trioxide in Acetic Acid. Amine **11**, prepared by the method of Curran and Angier[15] (54 mg, 0.32 mmol), in 6 ml of acetic acid was heated with 0.5 g of chromic anhydride at 90° for 1 hr, cooled, and diluted with 30 ml of water. The solution was neutralized (NaOH) and extracted with ether to give 50 mg of an oily solid: ir ($CHCl_3$) 1710 cm^{-1}, weak. The crude product was treated with 2,4-dinitrophenylhydrazine in ethanol–phosphoric acid to give a precipitate. One recrystallization from ethanol–water gave 18 mg (0.052 mmol, 16%) of the 2,4-DNP of **12**, mp 256–259°. *Anal.* Calcd for $C_{16}H_{18}N_4O_5$: C, 55.47; H, 5.24; N, 16.17. Found: C, 55.64; H, 5.34; N, 15.95.

A sample of the 2,4-DNP derivative (90 mg, 0.26 mmol) in 0.5 ml of ethanol was heated for 6 hr with 50 mg of acetylacetone, 1 drop of glacial acetic acid, and 1 drop of concentrated HCl. Removal of solvent left a residue which was chromatographed on alumina (5% methanol–95% ether) to give 13 mg (0.078 mmol, 30%) of **12**: ir ($CHCl_3$) 3500, 1710, 1140, 1060, 970, 940, 890 cm^{-1}.

2-Ketoadamantan-1-ol (12). To 10.7 g (52.5 mmol) of 2-aminoadamantan-1-ol hydrochloride in 120 ml of water was added 40 ml of 3 *M* NaOH, 100 ml of *t*-butyl alcohol, and 19.2 g of $MgSO_4$ in 50 ml of water. Over 90 min, at 20–25°, 22.3 g of $KMnO_4$ in 350 ml of water was added with stirring. After 3.5 hr sufficient $NaHSO_3$ was added to dissolve the precipitated MnO_2. The solution was extracted with CH_2Cl_2, the extract was washed with 1 *N* HCl, 5% sodium bicarbonate, water, and then dried over anhydrous magnesium sulfate. Evaporation of the solvent and chromatography of the residue on silica gel gave 3.3 g (19.8 mmol, 38%) of **12**: mp 278–281° (sealed tube) (lit.[3] mp 277–279°); 2,4-dinitrophenylhydrazone, mp 256–259°; ir identical with that obtained from the CrO_3 oxidation product; nmr ($CDCl_3$) δ 4.10 (broad s, 1.0, O*H*), 2.76 (broad s, 1.1), and 2.5–1.4 (m, 11.9); mass spectrum, *m/e* 166. Other runs gave yields ranging from 25 to 75%.

2-Methyleneadamantan-1-ol (13). To 2.88 g (120 mmol) of sodium hydride in a nitrogen atmosphere was added 80 ml of dimethyl sulfoxide (DMSO),[18] freshly distilled from calcium hydride. This mixture was heated to 75° for 1 hr and then cooled to room temperature. Triphenylmethylphosphonium bromide (42.9 g, 120 mmol) in 125 ml of DMSO was added to the solution. After 15 min 4.2 g (25 mmol) of **12** in 50 ml of DMSO was added. After 6 hr at 50°, the reaction was poured into 1500 ml of ice–water. The mixture was extracted with ether, the extracts were washed with water, dried ($MgSO_4$), and concentrated. Chromatography of the residue on alumina and recrystallization from ether–pentane gave 1.36 g (8.3 mmol, 33%) of **13**: mp 181–183° (sealed tube) (lit.[3] mp 180–182°); ir ($CHCl_3$) 3550, 3400, 1650, 1120, 1085, 975, 935, 895 cm^{-1}; nmr ($CDCl_3$) δ 4.84 and 4.74 (2 d, 1.9, $=CH_2$, J = 1.7 Hz), 2.74 (broad s, 1.0), 2.23 (broad s, 2.0), 2.11 (s, 1.0, O*H*), and 2.0–1.5 (m, 10.1); mass spectrum, *m/e* 164. *Anal.* Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.22; H, 9.66.

Spiro[cyclopropane-1,2′-adamantan-1-ol] (14). Zinc–copper couple[19b] (1.55 g) in 7 ml of ether reacted exothermically as 0.4 g of methylene iodide was added. Methylene iodide (3.5 g) and **13** (1.2 g, 7.3 mmol) in 10 ml of ether was added to the boiling solution over 10 min. After heating for 4 hr, the mixture was filtered into 50 ml of 1 *N* HCl and ice. The ether layer was separated, combined with ether extracts of the aqueous phase, washed with aqueous sodium thiosulfate, $NaHCO_3$, and saturated aqueous NaCl, and dried ($MgSO_4$). Evaporation under a stream of nitrogen and chromatography of the residue on alumina gave 0.25 g of recovered **13** and 0.85 g (4.8 mmol, 83%) of **14**: mp 193–195° (sealed tube) (lit.[3] mp 192–194°); ir ($CHCl_3$) 3560, 3400, 1110, 1080, 1010, 970, 935 cm^{-1}; nmr (CCl_4) δ 2.15 (broad s, 2.1), 1.72 (m, 9.5), 1.40 (broad s, 1.4, O*H*), 1.12 (broad s, 1.0), 0.66 and 0.10 (2 q, 2.0 and 2.0, C_3H_4 ring, J = 3.9 and 5.7 Hz); mass spectrum, *m/e* 178. *Anal.* Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.90; H, 10.09.

2,2-Dimethyladamantan-1-ol (15). Hydrogenolysis[20] (45 psi) of 400 mg (2.25 mmol) of **14** in 1 ml of acetic acid at 50° for 5 hr using 32 mg of PtO_2 catalyst gave 385 mg (2.14 mmol, 95%) of **15**: mp 220–222° (sealed tube); ir ($CHCl_3$) 3650, 3500, 1110, 1080, 960, 930 cm^{-1}; nmr ($CDCl_3$) δ 2.05 (m, 6.1), 1.7–1.2 (m, 8.2, O*H* spike at 1.40), and 1.05 (s, 5.7, *gem*-dimethyl). *Anal.* Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.83; H, 11.12.

1-Adamantyl *p*-Toluenesulfonate (3). Treatment of 1-adamantanol with *p*-toluenesulfinyl chloride according to the method of Wilt[44] gave 1-adamantyl *p*-toluenesulfinate: ir ($CHCl_3$) 1600, 1120, 1045, 900 cm^{-1}; nmr ($CDCl_3$) δ 7.54 and 7.24 (2d, 4.1, aromatic, J = 8 Hz), 2.35 (s, 3.2, CH_3), 2.3–1.9 (m, 8.4), 1.8–1.5 (m, 6.3). Oxidation of the crude sulfinate with *m*-chloroperbenzoic acid by the method of Coates and Chen[22] and crystallization of the product from ether–pentane at low temperature gave **3**: mp 72–75° (lit.[21] mp 65–85°); ir ($CHCl_3$) 1600, 1340, 1180, 1100, 1040, 905 cm^{-1}; nmr ($CDCl_3$) δ 7.75 and 7.27 (2 d, 4.1, aromatic, A_2B_2, J = 8 Hz), 2.42 (s, 3.1, CH_3), 2.17 (broad s, 8.8) and 1.62 (broad s, 6.0). *Anal.* Calcd for $C_{17}H_{22}O_3S$: C, 66.63; H, 7.24; S, 10.46. Found: C, 66.56; H, 7.36; S, 10.27.

Spiro[cyclopropane-1,2′-adamant-1-yl] *p*-Toluenesulfonate (1). Treatment of **14** with *p*-toluenesulfinyl chloride[45] gave spiro[cyclopropane-1,2′-adamant-1-yl] *p*-toluenesulfinate: ir ($CHCl_3$) 1600, 1120, 1045, 1015, 960, 920 cm^{-1}; nmr (CCl_4) δ 7.40 and 7.18 (2 d, 4.0, aromatic, A_2B_2, J = 8 Hz), 2.32 (s, 3.2, CH_3), 2.17 (broad s, 5.5), 1.70 (broad s, 6.5), 1.10 (broad s, 1.1), 0.63 and 0.07 (2 m, 1.9 and 1.8, C_3H_4 ring). Oxidation[22] and crystallization of the product from ether–pentane at low temperature gave **1**: mp 96–99°; ir ($CHCl_3$) 1600, 1340, 1175, 1100, 1035, 910, 875 cm^{-1}; nmr (CH_2Cl_2) δ 7.61 and 7.22 (2 d, 3.9, aromatic, A_2B_2, J = 8 Hz), 2.6–1.5 (m, 15.1, CH_3 spike at 2.33), 1.08 (broad s, 1.1), 0.66 and 0.07 (2 q, 2.0 and 1.9, C_3H_4 ring, J = 4.0 and 6.1 Hz). *Anal.* Calcd for $C_{19}H_{24}O_3S$: C, 68.64; H, 7.28; S, 9.64. Found: C, 68.84; H, 7.31; S, 9.58.

2,2-Dimethyladamant-1-yl *p*-Toluenesulfonate (4). Carbinol **15** was converted[45] to its *p*-toluenesulfinate: ir ($CHCl_3$) 1600, 1115, 1040, 905, 845 cm^{-1}; nmr (CCl_4) δ 7.48 and 7.20 (2 d, 4.2, aromatic, J = 8 Hz), 2.6–1.2 (m, 16.1, *p*-CH_3 spike at 2.40), 1.08 and 1.05 (2 s, 5.7, *gem*-dimethyl). To 0.47 mmol of the above sulfinate in 1.5 ml of purified $CHCl_3$ at −27° was added 3.5 ml of 0.07 *M* RuO_4 (1.04 equiv) in chloroform.[45] The reaction mixture immediately turned black as RuO_2 was formed. All purification steps were carried out in a cold room at −27°. Five ml of pentane was added and the mixture was centrifuged for 20 hr. The supernatant liquid, which was still fairly black, was evaporated in the cold under a stream of nitrogen. The residue was taken up in a mixture of ether and pentane and centrifuged for a further 12 hr. The supernatant

(42) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **79**, 1913 (1957).

(43) A value of −0.45 is quoted by R. C. Hahn, Ph.D. Thesis, Ohio State University, 1960.

(44) J. W. Wilt, R. G. Stein, and W. J. Wagner, *J. Org. Chem.*, **32**, 2097 (1967).

(45) Reference 25, pp 986–989; H. Nakata, *Tetrahedron*, **19**, 1959 (1963).

liquid, which was quite clear at this point, was evaporated under a stream of nitrogen. The residue was taken up in CCl_4 and transferred to another flask. Most of the RuO_2 which was left adhered to the walls of the tube and was not transferred with the CCl_4 solution. Evaporation of the CCl_4 under a stream of nitrogen gave **4**: ir ($CHCl_3$) 1600, 1335, 1175, 1100, 1080, 895, 870 cm^{-1}; nmr (CCl_4) δ 7.74 and 7.28 (2 d, 4.0, aromatic, J = 8 Hz), 2.6–1.2 (m, 16.0, *p*-CH_3 spike at 2.48), and 1.12 (s, 6.0, *gem*-dimethyl). Samples of this material were used for acetolysis studies without further purification.

2-Methyleneadamant-1-yl *p*-Toluenesulfonate (2). To an ether (6 ml) solution of **13** (89 mg, 0.54 mmol) was added 0.34 ml of 1.62 *M* *n*-butyllithium in hexane (0.55 mmol). After 5 min 103 mg (0.54 mmol) of *p*-toluenesulfonyl chloride in 2 ml of ether was added to the stirred mixture. After 24 hr the mixture was washed with 1 *N* HCl, saturated sodium bicarbonate, water, and dried over magnesium sulfate. Evaporation of the ether solution followed by chromatography on silica gel and crystallization from ether–pentane at 0° gave 127 mg (0.40 mmol, 74%) of **2**: mp 58–61°; ir ($CHCl_3$) 1650, 1600, 1340, 1180, 1100, 1035, 925, 905 cm^{-1}; nmr (CH_2Cl_2) δ 7.70 and 7.22 (2 d, 4.3, aromatic, J = 8 Hz), 4.78 and 4.63 (2 d, 1.7, $=CH_2$, J = 1.5 Hz), 2.9–1.6 (m, 16.0, *p*-CH_3 spike at 2.33). *Anal.* Calcd for $C_{18}H_{22}O_3S$: C, 67.89; H, 6.96. Found: C, 67.66; H, 6.91.

Adamant-1-yl Acetate. Ketene was bubbled into a solution of 0.30 g (2 mmol) of **10** in 5 ml of $CHCl_3$ to which had been added 2 drops of $CHCl_3$ which had been shaken with sulfuric acid. After 15 min the reaction mixture was washed with aqueous $NaHCO_3$, water, and dried over $MgSO_4$. Evaporation of the solvent and chromatography of the residue on alumina with ether gave 0.23 g (1.2 mmol, 60%) of adamant-1-yl acetate: mp 32.5–33.5°; ir ($CHCl_3$) 1725, 1360, 1240, 1060, 1015, 865 cm^{-1}; nmr ($CDCl_3$) δ 2.12 (broad s, 9.0), 1.94 (s, 3.0, CH_3), and 1.67 (broad s, 6.0); mass spectrum, *m/e* 194. *Anal.* Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.31; H, 9.36.

Spiro[cyclopropane-1,2′-adamant-1-yl] Acetate. Treatment of **14** with ketene as described above afforded a 67% yield of acetate: mp 53–55°; ir (neat) 1730, 1360, 1240, 1060, 1015, 965 cm^{-1}; nmr ($CDCl_3$) δ 2.92 (broad s, 0.9), 2.74 (broad s, 1.1), 2.3–0.9 (m, 14.1, CH_3 spike at 1.83), 0.72 and 0.09 (2 q, 2.0 and 2.0, C_3H_4 ring, J = 3.8 and 5.8 Hz); mass spectrum, *m/e* 220. *Anal.* Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.52; H, 8.95.

2-Methyleneadamant-1-yl Acetate. Treatment of **13** with ketene as described above afforded a 77% yield of acetate as a colorless liquid: ir (neat) 1730, 1650, 1365, 1250, 1230, 1065, 900 cm^{-1}; nmr (CCl_4) δ 4.65 (unresolved AB mult, 2.0, $=CH_2$) and 2.8–1.6 (m, 16.0, CH_3 spike at 2.00); mass spectrum, *m/e* 206. *Anal.* Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.64; H, 9.01.

2,2-Dimethyladamant-1-yl Acetate. Treatment of **15** with ketene as described above afforded a 70% yield of acetate: mp 51–52°; ir (neat) 1730, 1355, 1250, 1225, 1050, 960 cm^{-1}; nmr (CCl_4) δ 2.80 (broad s, 0.9), 2.62 (broad s, 1.1), 2.35–1.85 (m, 9.0, acetate CH_3 spike at 1.92), 1.75–1.20 (m, 5.1), and 1.08 (s, 5.9, *gem*-dimethyl); mass spectrum, *m/e* 222. *Anal.* Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.93; H, 9.93.

Kinetic Experiments. Commercial glacial acetic acid was purified by refluxing over potassium permanganate for 5 hr followed by distillation, collecting the constant boiling fraction. It was titrated with Karl Fischer reagent and enough acetic anhydride was added to destroy the water and make the acetic acid 0.5% in acetic anhydride. Standard 0.02 *M* sodium acetate titrant was prepared by dissolving anhydrous sodium acetate in this purified acetic acid followed by titration with standard perchloric acid (standardized *vs.* potassium acid phthalate). A 0.10 *M* solution of anhydrous sodium perchlorate in this acetic acid was diluted to give the 0.02 *M* solutions used as the reaction medium.

Acetolyses, with the exception of those used in the determination of salt effects, were conducted in 0.02 *M* sodium perchlorate and were followed by continuous titration of the liberated *p*-toluenesulfonic acid with 0.02 *M* sodium acetate (*i.e.*, at constant ionic strength). A recording pH-stat equipped with a combination glass-silver/silver chloride electrode with the aqueous KCl salt bridge replaced by a saturated solution of LiCl in acetic acid was used for solvolyses below 55°. For higher temperature runs, the acetolyses were followed by continuous manual titration to a bromophenol blue end point. The bromophenol blue end point was shown to coincide with the potentiometric end point.

In a typical solvolysis experiment, 10.00 ml of 0.02 *M* sodium perchlorate in dry acetic acid was pipetted into the solvolysis tube containing a magnetic stirring bar. A stopper holding the electrode and the delivery tip was inserted and the tube equilibrated at bath temperature. The solution was stirred by external coupling to a variable speed magnetic stirrer. Approximately 0.04 mmole of the desired tosylate was weighed out and admitted as a solid. The reactions were followed until no base was added over one half-life. A strip chart recorder recorded titer as a function of time. Zero time was taken as about 1 min after admitting the sample. This was more than twice the time required for solution at the lowest temperature.

All rate constants were calculated by a weighted least square treatment which made small adjustments in the infinity titer to minimize the standard deviation in k.

Product Studies. A completed acetolysis run of each tosylate was evaporated in a warm water bath under a stream of nitrogen. The residue was taken up in ether, filtered to remove inorganic materials, washed with aqueous sodium carbonate, and dried over anhydrous sodium carbonate. The ether was removed in a stream of nitrogen and the residue was dissolved in a small volume of methanol. These solutions were analyzed on three glpc columns: 3.5 ft × 0.25 in., 20% SE-30 on Chromosorb W, 3.5 ft × 0.25 in., 17% QF-1 6500 on Anakrom ABS, and 6 ft × 1/8 in., 3% OV-17 on Chromosorb Q. The retention times of the solvolysis products were identical with those of the corresponding authentic acetates.

The solvolysis products were compared with the authentic acetates by glpc–mass spectrometry. An Aerograph 202B gas chromatograph fitted with a 6 ft × 1/8 in., 3% OV-17 on Chromosorb Q column at 130° was interfaced to an Atlas CH4 mass spectrometer through a modified Biemann helium separator maintained at 180°. Mass spectra were run at appropriate points on the chromatogram. Spectra obtained from the solvolysis products were identical with those of the corresponding acetates.

The yields of the solvolysis products were determined quantitatively by the addition of an internal standard (benzophenone) to the completed solvolysis runs. The analyses were performed on an Aerograph 202B fitted with a 5 ft × 1/8 in., 5% SE-30 on AW-DMCS Chromosorb W column at 130° and equipped with a flame ionization detector. The solvolysis runs were compared to standard solutions of authentic acetates containing the same internal standard.

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