

Organic and Biological Chemistry

Calculation of Bridgehead Reactivities¹

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Abstract: Carbonium ion reactivities of sixteen bridgehead systems which vary by more than eighteen powers of ten are correlated by quantitative conformational analysis. Bicyclic substrates ranging from 1-bicyclo[2.2.1]heptyl to 1-bicyclo[3.3.2]decyl and a wide variety of tricyclic and fused ring systems (Figure 1) are treated. Since correlation between the available bridgehead radical and carbonium ion reactivities is observed, the same conformational analysis program developed for carbonium ions also works well for the calculation of free radical reactivities. A number of reactivity predictions have been made on this basis. The availability of a calibrated series of similar substrates of widely varying reactivities has permitted the evaluation of two specific effects. First, we have argued that ground-state steric effects involving the leaving groups are very important in influencing observed trends in OTs/Br rate ratios. Such steric contributions to the OTs/Br ratios should be large for the tertiary systems, and may be a factor influencing the secondary ratios as well. Second, the solvolytic reactivity of 10-tricyclo[5.2.1.0^{4,10}]decyl tosylate (**12**) is found to be abnormally low. We believe this to be due to the unique torsional arrangement around the reaction center of this system. A trans-periplanar relationship between the leaving group and the β bonds (C-C or C-H) appears to be necessary to afford the maximum hyperconjugative transition state stabilization. Unlike most bridgehead systems, such arrangements are not possessed by cisoid **12**, and its solvolysis rate is much slower.

Reliable prediction of the solvolytic reactivity of any substrate under any set of conditions must be considered an ultimate goal of carbonium ion chemists. Despite the massive amount of solvolytic data available,³ this goal remains concealed by the complicated maze of effects which govern organic chemical reactivity.

In order to achieve this goal, a way must be devised to calculate the free energy differences between ground and transition states for a given set of conditions. Quantitative conformational analysis provides a practical approach for the evaluation of steric effects.⁴ If the energies of both ground and transition states could be calculated in this manner (where medium and substrate electronic effects are relatively constant) estimations of solvolytic reactivity should be possible.^{5,6}

(1) A preliminary account of this work has been published: R. C. Bingham and P. v. R. Schleyer, *Tetrahedron Lett.*, 23 (1971). This work was also presented, in part, by P. v. R. Schleyer at the International Symposium on Conformational Analysis, Brussels, Belgium, Sept 1969.

(2) (a) Taken in part from the Ph.D. Thesis of R. C. Bingham, Princeton University, 1970; (b) National Institutes of Health Predoctoral Fellow, 1968-1970.

(3) Reviews: (a) A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962; (b) C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier, New York, N. Y., 1963; (c) E. R. Thornton, "Solvolysis Mechanisms," Ronald Press, New York, N. Y., 1964; (d) D. Bethel and V. Gold, "Carbonium Ions: An Introduction," Academic, New York, N. Y., 1967; (e) E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, pp 68-142; (f) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969; (g) G. A. Olah and P. v. R. Schleyer, Ed., "Carbonium Ions," Vol. I and II, Interscience, New York, N. Y., 1968, 1970.

(4) Review: J. E. Williams, P. J. Stang, and P. v. R. Schleyer, *Annu. Rev. Phys. Chem.*, 19, 531 (1968).

(5) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 86, 1854, 1856 (1964); cf. C. S. Foote, *ibid.*, 86, 1853 (1964).

(6) Review: R. C. Fort, Jr., and P. v. R. Schleyer, *Advan. Alicycl. Chem.*, 1, 283 (1966).

The geometries and energies of many ground-state molecules are well known and may be calculated with good precision.^{4,7-9} Similar calculations of transition state energies are unfortunately frustrated by the lack of knowledge of the exact nature of such species. However, carbonium ions are known to prefer planarity strongly.^{6,10} If the transition states for their formation closely resemble the carbonium ions in both structure and energy or exhibit proportionality,¹¹ calculations of relative transition state energies should also be possible. The calculated difference in energies between ground and transition states should then be proportional to the experimental free energy of activation for solvolysis, provided entropy effects are negligible.

Bridgehead substrates are ideal for the testing of the ability of conformational analysis calculations to predict solvolytic reactivity. The conformations of these systems are generally rigid and fixed, their solvolysis reactions are mechanistically uncomplicated,¹² and the

(7) G. J. Gleicher and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 89, 582 (1967).

(8) (a) N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van-Catledge, *ibid.*, 90, 1199 (1968), and references cited therein; (b) N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *ibid.*, 93, 1637 (1971).

(9) P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *ibid.*, 92, 2377 (1970).

(10) For recent theoretical calculations see (a) J. E. Williams, R. Sustmann, L. C. Allen, and P. v. R. Schleyer, *ibid.*, 91, 1037 (1969), and references cited therein; (b) R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *ibid.*, 91, 5350 (1969); (c) J. E. Williams, V. Buss, L. C. Allen, P. v. R. Schleyer, W. A. Latham, W. J. Hehre, and J. A. Pople, *ibid.*, 92, 2141 (1970); (d) V. Buss, P. v. R. Schleyer, and L. C. Allen, *ibid.*, in press.

(11) Cf. G. S. Hammond, *ibid.*, 77, 334 (1955).

(12) (a) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *ibid.*, 92, 2538 (1970); (b) D. J. Raber, R. C. Bingham, J. M. Harris, J. L. Fry, and P. v. R. Schleyer, *ibid.*, 92, 5977 (1970); (c) D. N. Kevill, K. C. Kolwyck, and F. L. Weilt, *ibid.*, 92, 7300 (1970); (d) J. M. Harris, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *ibid.*, in press.

Table I. Calculated Strain Energies of Some Simple Hydrocarbons

Compound	Old calcd strain energies, ^a kcal	New calcd strain energies, ^b kcal	$\Delta S.E.$ (old), kcal	$\Delta S.E.$ (new), kcal	$-\Delta H^\circ$ (expt), kcal
<i>trans-n</i> -Butane	0.13	0.53			
<i>gauche-n</i> -Butane	0.83	1.49	0.70	0.96	$0.7 \pm 0.3^{c,d}$
Equatorial methyl-cyclohexane	0.22	2.26			
Axial methyl-cyclohexane	1.63	4.36	1.41	2.10	1.9 ± 0.2^c
<i>trans</i> -Decalin	0.01	3.64			
Adamantane	2.65	8.90	2.65	5.26	$4.69^{d,e}$

^a Reference 7. ^b See text. ^c See N. L. Allinger, M. A. Miller, F. A. Van Catledge, and J. A. Hirsch, *J. Amer. Chem. Soc.*, **89**, 4345 (1967), for leading references. ^d Reference 9. ^e Estimated adamantane-*trans*-decalin strain energy difference.

large variation in structure available in these systems results in a wide range of reactivities.

In earlier work from this laboratory, several bridgehead systems were examined.⁷ For each, the parent hydrocarbon was used as a model for the ground state and the corresponding carbonium ion as a model for the transition state. The calculated hydrocarbon-cation strain energy differences when plotted against $-\log$ of the relative solvolysis rates gave a satisfactory correlation. The average deviation was $10^{\pm 0.8}$ for a total rate variation of twelve powers of ten. Reactivities of other, then unknown, bridgehead systems were also predicted. In two cases, 1-bicyclo[3.3.1]nonyl¹³ and 1-homoadamantyl,¹⁴ those predictions subsequently have been substantiated experimentally.

Further tests of the quantitative conformational analysis calculations of bridgehead solvolysis rates have been equally successful. The calculated acetolysis rates of 4-nortricyclyl^{15a} and 4-tricycyl triflate^{15b} demonstrate the normal bridgehead behavior of these systems indicating the absence of significant participation by the face of the incorporated cyclopropyl rings. We have now extended and improved our calculations to include a wide variety of polycyclic substrates. Correlations of both bridgehead carbonium ion and free radical stabilities are discussed.

Results and Discussion

Correlation of Bridgehead Solvolysis Rates. The calculations involve an application by computer^{4,7-9,16} of Westheimer's¹⁷ classical treatment for the quantitative determination of steric effects operative in molecules. Only slight modifications in our previously reported⁷ parameterization of this treatment have been made. New "ideal" bond angles (112.4° for CCH_2C , 111.3° for $CCHC$, 106.1° for HCH , 110.7° for $HCHC$, and 107.8° for HCC) have been adopted to conform to those observed for simple alkanes,¹⁸ it being assumed

(13) P. v. R. Schleyer, P. R. Isele, and R. C. Bingham, *J. Org. Chem.*, **33**, 1239 (1968); W. G. Dauben and C. D. Poulter, *ibid.*, **33**, 1237 (1968).

(14) An 80% ethanolysis rate constant of $5.75 \times 10^{-8} \text{ sec}^{-1}$ at 50° is reported for 1-homoadamantyl bromide (F. N. Stepanov and S. S. Gutz, *Zh. Org. Khim.*, **4**, 1933 (1968); *Chem. Abstr.*, **70**, 28456 (1969)). The predicted value, calculated from data in the original paper,⁷ is $2.5 \times 10^{-7} \text{ sec}^{-1}$ at 25° . Assuming a typical activation enthalpy of $\sim 25 \text{ kcal/mol}$, the experimental value at 25° would be about $3 \times 10^{-6} \text{ sec}^{-1}$.

(15) (a) R. C. Bingham, W. F. Sliwinski, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 3471 (1970); (b) S. A. Sherrod, R. G. Bergman, G. J. Gleicher, and D. Morris, *ibid.*, **92**, 3469 (1970).

(16) (a) K. B. Wiberg, *ibid.*, **87**, 1070 (1965); (b) H. A. Harris, Ph.D. Thesis, Yale University, 1966.

(17) F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 12.

that the conformational mobility and relative strain-free character of these molecules allow them to assume a nearly optimal geometry.^{4,8,9} "Harder" nonbonded potentials involving carbon were also adopted. The former nonbonded potentials⁷ were made "harder"^{4,9} by translation of the $C \cdots C$ and $C \cdots H$ functions 0.14 and 0.07 Å, respectively, along the distance axis away from the origin.^{15a} These modifications in general improve the calculated energy differences between reference hydrocarbons as indicated in Table I.

It should be pointed out that the strain energies for hydrocarbons calculated by our program are generally not as accurate as those achievable by the best molecular mechanics programs available.^{8,19} In our work, attention is focused on energy differences rather than on the absolute values of the energies themselves. Errors in the absolute values tend to be diminished or eliminated when cation-hydrocarbon energy differences are taken.⁷ For this reason, our calculated geometries and energies are not reproduced in the present paper.²⁰

Table II summarizes the available solvolysis data for 16 bridgehead-substituted compounds.²¹ Relative rates, correcting for the differences in leaving groups, vary over a range of greater than eighteen powers of ten (Figure 1). Such a wide reactivity range precludes the use of a single leaving group. Tosylates are available for half of the compounds, but for the least reactive substrates the more reactive trifluoromethanesulfonates (triflates)²⁵ are much more convenient to use and permit the extension of the scale to include the very unreactive 4-nortricyclyl system.^{15a} For the

(18) D. R. Lide, Jr., *J. Chem. Phys.*, **33**, 1514, 1519 (1960), and references cited therein; K. Kuchitsu, *Bull. Chem. Soc. Jap.*, **32**, 748 (1959); R. A. Bonham and L. S. Bartell, *J. Amer. Chem. Soc.*, **81**, 3491 (1959); R. A. Bonham, L. S. Bartell, and D. A. Kohl, *ibid.*, **81**, 4765 (1959); N. Norman and H. Mathisen, *Acta Chem. Scand.*, **15**, 1747 (1961).

(19) We plan to revise our calculations to improve this situation. This has not been done here because all of the calculations carried out over the past years would have to be repeated at prohibitive cost.

(20) For details, see ref 2a.

(21) Data for alkyl-substituted adamantanes²² and bicyclo[2.2.2]octanes²³ are not included since structure and solvolysis rates differ only slightly from the parent systems. Data for bridgehead substrates containing cyclobutyl rings at the reaction site are also omitted since their solvolysis reactions are mechanistically atypical.²⁴ The birdcage system described by P. Carter, R. Howe, and S. Winstein, *J. Amer. Chem. Soc.*, **87**, 914 (1965), 1-homoadamantyl bromide,¹⁴ and 1-nortricyclyl triflate²⁵ were not included because the data are incomplete.

(22) R. C. Fort, Jr., and P. v. R. Schleyer, *ibid.*, **86**, 4194 (1964); C. A. Grob, W. Schwarz, and H. P. Fischer, *Helv. Chim. Acta*, **47**, 1385 (1964).

(23) P. v. R. Schleyer and C. W. Woodworth, *J. Amer. Chem. Soc.*, **90**, 6528 (1968).

(24) K. B. Wiberg and B. R. Lowry, *ibid.*, **85**, 3188 (1963); K. B. Wiberg and V. Z. Williams, Jr., *ibid.*, **89**, 3373 (1967); K. B. Wiberg, J. E. Hiatt, and K. Hsieh, *ibid.*, **92**, 544 (1970).

(25) T. M. Su, W. F. Sliwinski, and P. v. R. Schleyer, *ibid.*, **91**, 5386 (1969).

Table II. Solvolysis Data

Compd	X	Solvent	Temp, °C	k , sec ⁻¹ ^w	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu	ΔH (calcd) ^z	Ref
1	Cl	80% EtOH	25.0	$5.69 \pm 0.01 \times 10^{-6}$	21.3	-6.5	-2.8	a, b
			50.4	$1.04 \pm 0.01 \times 10^{-3}$				
			70.0	7.33×10^{-3}				
2	Cl	80% EtOH	51.2	$1.29 \pm 0.04 \times 10^{-4}$	20.2	-14.2	4.8	a, b
			75.5	$1.19 \pm 0.03 \times 10^{-3}$				
			70.0	7.63×10^{-4}				
3	Cl	80% EtOH	70.0	5.68×10^{-4}		4.8	c	
4	Br	80% EtOH	25.1	$1.88 \pm 0.01 \times 10^{-4}$	21.3	-4.3	6.5	a, b, d
			50.25	$3.32 \pm 0.07 \times 10^{-3}$				
			70.0	2.36×10^{-2}				
4	Cl	80% EtOH	70.0	5.18×10^{-4}	22.0	-9.7		e
5	Cl	80% EtOH	51.1	$2.59 \pm 0.09 \times 10^{-5}$	23.0	-8.8	4.7	a, b
			75.05	$3.23 \pm 0.02 \times 10^{-4}$				
			70.0	1.95×10^{-4}				
6	Br	80% EtOH	70.0	8.10×10^{-4}	23.9	-3.2	8.3	f
6	Cl	80% EtOH	50.25	$2.48 \pm 0.07 \times 10^{-6}$	25.2	-6.4		a, g
			76.3	$4.99 \pm 0.12 \times 10^{-6}$				
			70.0	2.52×10^{-6}				
7	Br	80% EtOH	50.1	$2.05 \pm 0.04 \times 10^{-6}$	23.8	-6.5	6.6	a, b
			75.3	$3.30 \pm 0.17 \times 10^{-4}$				
			70.0	1.87×10^{-4}				
7	Cl	80% EtOH	76.5	$9.02 \pm 0.02 \times 10^{-6}$	23.8	-14.0		a, g
			100.2	$8.48 \pm 0.30 \times 10^{-5}$				
			70.0	4.64×10^{-6}				
8	OTs	HOAc	70.0	1.02×10^{-1}	22.8	+3.0	12.3	h, i
8	OTs	80% EtOH	70.0	4.02×10^{-1}	20.2	-1.8		j
8	Br	80% EtOH	70.0	7.24×10^{-5}	22.5	-12.2		k
8	Cl	80% EtOH	70.0	2.45×10^{-6}	25.4	-10.4		i
9	OTs	HOAc	70.0	1.02×10^{-4}	23.4	-9.0	17.6	l
9	Br	80% EtOH	70.0	1.41×10^{-7}	24.6	-18.4		l
9	Cl	50% EtOH	70.0	1.35×10^{-7}	26.6	-12.8		l
9	Cl	80% EtOH	70.0	2.99×10^{-9}				m
10	OBs	HOAc	70.0	6.26×10^{-5}	26.2	-1.7	16.3	n
10	OTs	HOAc	70.0	2.09×10^{-5}				o
10	OTs	80% EtOH	70.0	1.00×10^{-4}	25.3	-5.4		p
10	Br	80% EtOH	70.0	3.87×10^{-8}	26.0	-16.9		p
11	OTs	HOAc	70.0	1.93×10^{-6}	28.0	-3.3	18.7	q
12	OTs	HOAc	100.1	$8.96 \pm 0.05 \times 10^{-6}$	30.1	-1.4	9.3	a, b
			124.5	$1.15 \pm 0.05 \times 10^{-4}$				
			70.0	2.33×10^{-7}				
12	OTs	80% EtOH	76.9	$1.57 \pm 0.03 \times 10^{-6}$	28.0	-5.6		a, b
			100.2	$2.05 \pm 0.04 \times 10^{-5}$				
			70.0	8.86×10^{-7}				
13	OTs	HOAc	70.0	3.13×10^{-7}	26.9	-10.1	18.8	r
13	OTs	80% EtOH	75.3	$9.39 \pm 0.07 \times 10^{-6}$	25.9	-7.4		a, g
			100.0	$1.20 \pm 0.01 \times 10^{-4}$				
			70.0	5.19×10^{-6}				
13	OTf	HOAc	70.0	2.96×10^{-2}	22.7	+0.4		s
14	OTs	HOAc	70.0	3.40×10^{-9}	32.6	-2.7	20.3	t
14	OTs	80% EtOH	124.7	$5.88 \pm 0.13 \times 10^{-6}$	30.3	-6.9		a, g
			150.0	$6.18 \pm 0.02 \times 10^{-5}$				
			70.0	1.12×10^{-8}				
14	OTf	HOAc	70.0	9.03×10^{-5}	28.7	+6.4		u
15	OBs	HOAc	70.0	3.46×10^{-11}	31.7	-14.3	23.5	v
15	OTs	HOAc	70.0	1.15×10^{-11}				o
15	OTf	HOAc	70.0	6.52×10^{-8}	28.2	-9.4		s
16	OTf	HOAc	70.0	3.0×10^{-13}			28.5	s

^a This work. ^b Rates determined conductometrically. ^c A. F. Boschung, M. Geisel, and C. A. Grob, *Tetrahedron Lett.*, 5169 (1968). ^d H. Stetter and P. Goebel [*Ber.*, 96, 550 (1963)] report k (25°, 80% EtOH) = 1.64×10^{-4} sec⁻¹. ^e Footnote d. ^f Reference 13. ^g Rates determined titrimetrically. ^h E. R. Thornton, private communication; cf. B. R. Ree and J. C. Martin, *J. Amer. Chem. Soc.*, 92, 1660 (1970); M. L. Sinnott, J. H. Storesund, and M. C. Whiting, *Chem. Commun.*, 1000 (1969). ⁱ P. v. R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, 83, 2700 (1961). ^j Reference 12c. ^k Reference 12b and references cited therein. ^l R. C. Bingham, P. v. R. Schleyer, Y. Lambert, and P. Deslongchamps, *Can. J. Chem.*, 48, 3739 (1970). ^m Calculated assuming a Grunwald-Winstein m value of 1.0 (see ref 29). ⁿ Reference 23. ^o Calculated assuming $k_{\text{brosylate}}/k_{\text{tosylate}} = 3$. ^p C. A. Grob, K. Kostka, and F. Kuhnen, *Helv. Chim. Acta*, 53, 608 (1970); cf. P. Brennisen, C. A. Grob, R. A. Jackson, and M. Ohta, *ibid.*, 48, 146 (1965). ^q K. B. Wiberg, G. N. Taylor, G. W. Klein, and V. Z. Williams, Jr., to be published. Cf. R. S. Bly and E. K. Quinn, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Paper 910. ^r J. S. Wishnok, E. Funke, P. v. R. Schleyer, A. Nickon, G. Pandit, and R. Williams, to be published. ^s Reference 15a. ^t P. v. R. Schleyer and E. Wiskott, *Tetrahedron Lett.*, 2845 (1967). ^u Reference 25. ^v C. J. Norton, Ph.D. Dissertation, Harvard University, 1955. ^w Rate constants at 70° are calculated from data at other temperatures. ^z Computer calculated hydrocarbon-carbonium ion strain energy differences (see text).

more reactive substrates, tosylates either cannot be prepared or would be too reactive for convenient rate

measurements. In these cases, chloride and bromide leaving groups have been employed. For many

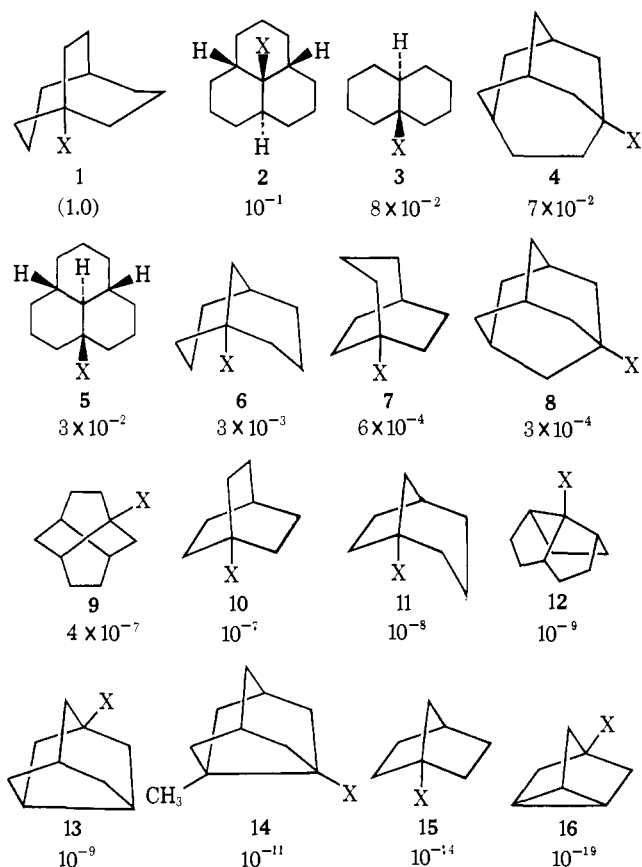


Figure 1. Approximate relative solvolysis rate constants. Corrections for differences in leaving groups and solvents are included. Actually, differences in relative rates are observed when different leaving groups are employed (see text).

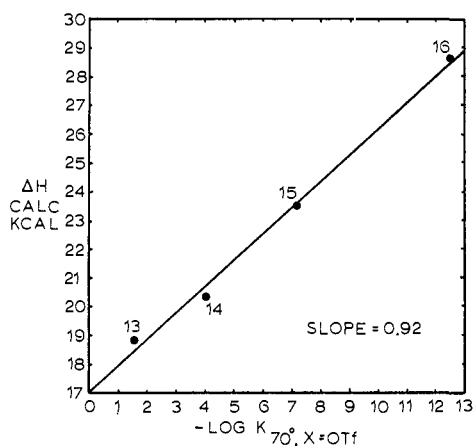


Figure 2. Calculated hydrocarbon-carbonium ion strain energy differences (ΔH) plotted against $-\log$ of the experimental triflate acetolysis rate constants at 70°.

systems, duplicate data, using different leaving groups, have been gathered.

Following expectations,⁶ the systems with the larger bridges are more reactive. This is illustrated by the bicyclic molecules where the reactivity order is: 1-bicyclo[3.3.2]decyl (**1**) \gg 1-bicyclo[3.3.1]nonyl (**6**) > 1-bicyclo[3.2.2]nonyl (**7**) \gg 1-bicyclo[2.2.2]octyl (**10**) > 1-bicyclo[3.2.1]octyl (**11**) \gg 1-bicyclo[2.2.1]heptyl (**15**). In analogous tricyclic molecules, the same trend

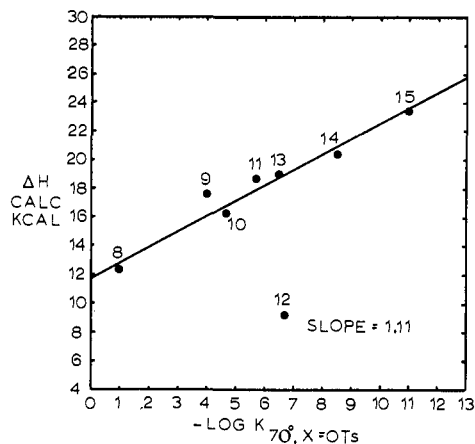


Figure 3. Calculated hydrocarbon-carbonium ion strain energy differences (ΔH) plotted against $-\log$ of the experimental tosylate acetolysis rate constants at 70°.

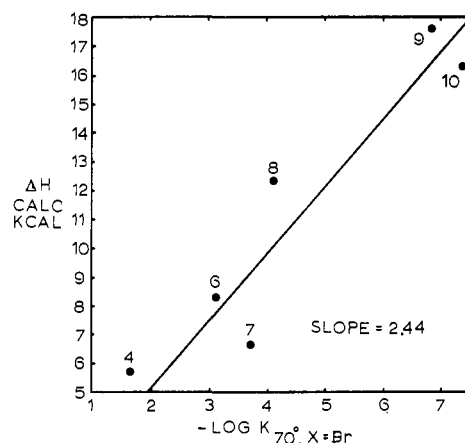


Figure 4. Calculated hydrocarbon-carbonium ion strain energy differences (ΔH) plotted against $-\log$ of the experimental bromide rate constants in 80% ethanol at 70°.

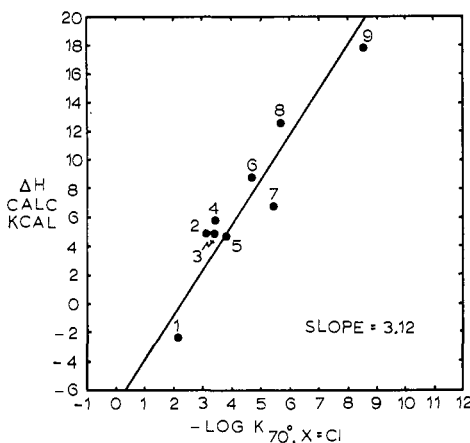


Figure 5. Calculated hydrocarbon-carbonium ion strain energy differences (ΔH) plotted against $-\log$ of the experimental chloride rate constants in 80% ethanol at 70°.

is observed, e.g., 3-homoadamantyl (**4**) > 1-adamantyl (**8**) > 7-methyl-3-noradamantyl (**14**).²⁶

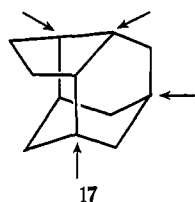
(26) It has been pointed out (V. Buss, unpublished observations) that bridgehead reactivities may be estimated by a group increment approach. Rate constant increments associated with the size of the alkyldene bridges are derived. For example, the increment for an ethylene

Table III. Statistical Data from Least-Squares Analyses

Substrates (no.)	Figure	Slope	Av dev ^a	Max dev ^a	Correlation coefficient
Triflates (4)	2	0.92	±0.28	0.448	0.997
Tosylates (7) ^b	3	1.11	±0.54	1.375	0.975
Bromides (6)	4	2.44	±0.64	1.122	0.937
Chlorides (9)	5	3.12	±0.54	1.037	0.941
Tosylates in HOAc vs. tosylates in 80% EtOH (5)	6	1.00	±0.20	0.515	0.995
Bromides vs. chlorides (5)	7	1.00	±0.08	0.124	0.999
<i>tert</i> -Butyl perester decompositions (3)	9	3.57	±0.05	0.072	0.999
Azo decompositions (5)	10	4.88	±0.09	0.223	0.987

^a Log units. ^b Point for **12** not included (see text).

Our calculations permit a general, reasonably accurate *quantitative* prediction of bridgehead reactivity. In the case of many bridgehead systems, even the qualitative reactivity order is not immediately apparent. Ethanoadamantane (**17**) illustrates this point. There are four different bridgehead positions, shown by arrows. What reactivity order is expected for these positions and what will be the absolute magnitude of the rate constants?



In the original work,⁷ composite data from different leaving groups (as presented in Figure 1) were used for quantitative analysis. We now find that it is much better to treat the data for each leaving group separately since their correlation lines have different slopes (Figures 2–5). Equations 1–4 represent the linear free

$$-\log k_{\text{triflate, HOAc, 70}^\circ} = 1.09\Delta H(\text{calcd}) - 18.52 \quad (1)$$

$$-\log k_{\text{tosylate, HOAc, 70}^\circ} = 0.90\Delta H(\text{calcd}) - 10.53 \quad (2)$$

$$-\log k_{\text{bromide, 80\% EtOH, 70}^\circ} = 0.41\Delta H(\text{calcd}) - 0.12 \quad (3)$$

$$-\log k_{\text{chloride, 80\% EtOH, 70}^\circ} = 0.32\Delta H(\text{calcd}) + 2.15 \quad (4)$$

energy relationship obtained for each leaving group. The important statistical parameters of each of the least-squares lines are summarized in Table III. In all cases, the correlations are quite satisfactory, a fact which substantially reinforces both the approach and the conclusions of the earlier work.^{7, 13–15}

Beyond showing the general success of the correlations, Figures 2–5 illustrate several other points of interest. The results are less satisfactory for the halides than for the sulfonate esters. Possibly this is due to the greater conformational flexibility of several of the halides studied (particularly **1** and **7**). True energy minima become much more difficult to locate in such flexible systems and may, in fact, have been missed.⁴ In the absence of more sophisticated energy mini-

bridge is obtained by dividing the log of the relative rate of the 1-bicyclo[2.2.2]octyl system by 3. Such increments, coupled with an additional increment for the size of the ring opposite the reaction center of the tricyclic systems, accurately reproduce the experimental relative rates of the remaining systems. This method unfortunately lacks generality. Ten of the available sixteen substrates may be treated in this manner. Half of those treated are involved in the parameterization.

mization methods, calculations of the solvolysis rates of the more mobile systems may be expected often to be much less successful.

Tosylate/Bromide Rate Ratios. The relative slopes of the different lines in Figures 1–4 emphasize a further distinct contrast in behavior between the halides and the sulfonate esters. Both $k_{\text{triflate}}/k_{\text{tosylate}}$ ratios²⁵ (Figures 2 and 3, Table III) and $k_{\text{bromide}}/k_{\text{chloride}}$ ratios (Figures 4 and 5, cf. Figure 6, Table III) remain nearly

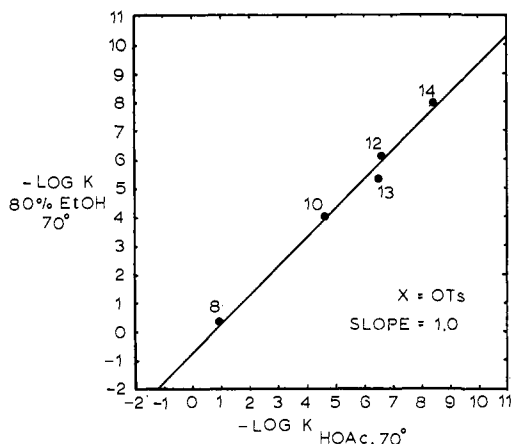


Figure 6. $-\log$ of the experimental tosylate rate constants in 80% ethanol plotted against $-\log$ of the experimental tosylate acetolysis rate constants at 70°.

constant for all systems. However, the rate differences between a given set of compounds tend to be larger for the sulfonates than for the halides. In fact, the trend of our results predicts that the tosylate/bromide rate ratios for the more unreactive substrates (e.g., **15** and **16**) should be less than unity.

The experimental data necessary to test this prediction are not available. Nevertheless, crude estimates suggest that the prediction is approached for **15**. From data for **15** (X = Br) in 40% ethanol at 216.2° ($k = 1.5 \times 10^{-6} \text{ sec}^{-1}$),²⁷ assuming the same ΔH^\ddagger for the bromide as is observed for the tosylate (cf. **8**, **9**, and **10**),²⁸ a rate of $3 \times 10^{-10} \text{ sec}^{-1}$ is calculated at 70°. This corresponds to a rate constant for **15** (X = Br) of $2 \times 10^{-12} \text{ sec}^{-1}$ in 80% ethanol at 70° assuming a Grunwald–Winstein m value of 1.0.²⁹ Thus, a

(27) M. Finkelstein, Ph.D. Thesis, Yale University, 1955.

(28) See Table II, footnote i.

(29) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, **70**, 846 (1948); S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951); A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

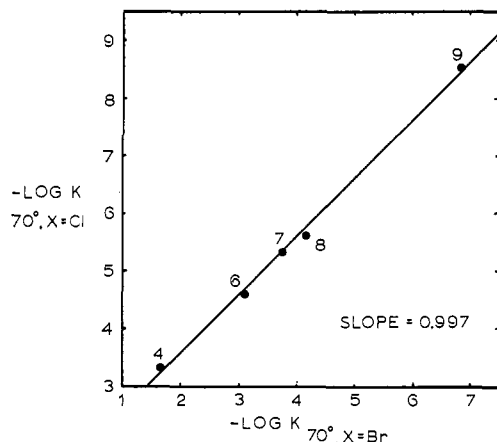


Figure 7. $-\log$ of the experimental chloride rate constants plotted against $-\log$ of the experimental bromide rate constants in 80% ethanol at 70°.

$k_{\text{tosylate, acetic acid}}/k_{\text{bromide, 80\% ethanol}}$ ratio of 6 is calculated. This value is credibly approached by the ratio of 0.06 predicted from Figures 2 and 3 and is strikingly smaller than the corresponding ratios of 1400, 720, and 540 obtained directly (Table II) for **8**, **9**, and **10**, respectively.

Solvent effects do not contribute to the observed trend in $k_{\text{tosylate}}/k_{\text{bromide}}$ ratios even though sulfonate esters in acetic acid and halides in 80% ethanol are being compared. Throughout the range of reactivity under consideration, $k_{80\% \text{ ethanol}}/k_{\text{acetic acid}}$ ratios for the tosylates are nearly constant (5 ± 3 , cf. Figure 7, Table III).

We associate the trend in $k_{\text{tosylate}}/k_{\text{bromide}}$ ratios, at least in part, with the relief of the high ground-state strain which must be present in the *tert*-sulfonate esters³⁰ but which is absent when halides are used as the leaving groups. As indicated earlier, such effects are ignored in the conformational calculations,⁷ which employ, in effect, a hydride ion as a leaving group.

The tertiary sulfonate esters suffer from 1,5-nonbonded interactions (involving the sulfonyl oxygen atoms) not possessed by the halides. This situation can be illustrated by hydrocarbon models: 2,2,4,4-tetramethylpentane (for a *tert*-butyl sulfonate) and neopentane (for a *tert*-butyl halide). For these models the strain difference is approximately 8 kcal.^{9,31} The relief of this ground-state sulfonate leaving group strain with ionization should be more pronounced for the bulky systems (e.g., 1-adamantyl) than for the more constrained compounds (e.g., 1-norbornyl) where the CH_2 groups around the reaction site are bent back.³² The result is the decrease in the $k_{\text{tosylate}}/k_{\text{bromide}}$ ratios

(30) Cf. H. C. Brown, *Chem. Soc., Spec. Publ.*, No. 16, 140 (1962).

(31) The actual ground-state steric strain in a tertiary sulfonate ester should be somewhat less than this value due, in addition to other things, to the smaller effective size of oxygen relative to methyl. Cf. E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley, New York, N. Y., 1965. Similar steric effects should also be present in secondary systems as witnessed by the difference in strain of 4 kcal/mol between 2,2,4-trimethylpentane (a model for isopropyl tosylate) and isobutane (a model for isopropyl bromide).⁹ With primary systems such steric effect differences (0.8 kcal/mol for analogous models)⁹ are negligible.

(32) The effective bulk of 1-adamantyl *vs.* 1-norbornyl systems is also manifested by the stretched central bond length of 1,1'-biadamantane *vs.* the normal central bond length of 1,1'-binorbornane (R. A. Alden, J. Kraut, and T. G. Traylor, *J. Amer. Chem. Soc.*, **90**, 74 (1968)) and by the calculated strain energies of these two systems.^{9b} The calculated strain energy of 1,1'-binorbornane is essentially the same as that for two norbornanes whereas 1,1'-biadamantane is 6 kcal more strained than two adamantanes.^{9b}

observed and the decrease in the slopes of the sulfonate ester lines relative to those of the halides (Figures 2–5 and Table III).

Other effects may also be operative here. Following a suggestion by DePuy,³³ Hoffmann³⁴ has examined in detail the use of OTs/Br leaving group rate ratios as a mechanistic probe in solvolysis reactions. He has noted that the values of such ratios are approximately 1 for SN_2 reactions and vary characteristically for solvolysis processes. For primary substrates, values on the order of 10^1 are typically observed while simple unhindered secondary substrates give $k_{\text{OTs}}/k_{\text{Br}}$ ratios commonly in the range 10^1 – 10^2 . These ratios for tertiary substrates ($\sim 10^4$) are larger by about two orders of magnitude.^{12a,34} According to Hoffmann's interpretation,³⁴ "the faster an SN_1 (and E_1) reaction, the more ionic its transition state," and "the more the charge is separated between carbon and the leaving group in the transition state, the more can toluene-*p*-sulfonate run ahead of bromide ion as a leaving group." While these arguments do, in fact, rationalize our results ($k_{\text{OTs}}/k_{\text{Br}}$ ratios are larger for the more reactive bridgehead substrates), we believe that Hoffmann's interpretation is incorrect.

Our criticisms of Hoffmann's interpretation are not based on steric effects alone. It is now realized^{12a,d,35} that the systems upon which Hoffmann³⁴ based his conclusions encompass a wide mechanistic spectrum. Limiting (SN_1) character cannot be assumed (as Hoffmann did)³⁴ for the solvolysis of simple primary and secondary substrates; even in solvents such as formic acid the degree of nucleophilic solvent participation is quite large.^{35b} In our opinion, part of the observed variation in $k_{\text{OTs}}/k_{\text{Br}}$ ratios (primary < secondary < tertiary)³⁴ is due to varying degrees of nucleophilic solvent participation (very large in simple primary, large in secondary, but negligible in tertiary substrates)^{12,35} in the solvolysis transition states rather than to varying SN_1 reactivities. Thus, while the extent of charge development in the solvolysis transition state may be reflected by the $k_{\text{OTs}}/k_{\text{Br}}$ ratios, relative reactivities may be much less important in determining charge development than the degree of nucleophilic solvent participation.

Variations in the degree of charge separation within the restricted class of limiting (k_c type) processes must be evaluated by other means, since nucleophilic solvent participation is absent. Examination of substrate response to solvent ionizing power²⁹ over a fairly large range of reactivity (Table IV) fails to indicate any

Table IV. m Values for Bridgehead Bromides, Aqueous Ethanol, 25°

Substrate (X = Br)	$k_{\text{rel.}}^a$ 25°	m
4	1.0	1.08 ^b
8	3×10^{-3}	1.20 ^c
10	6×10^{-7}	1.03 ^d

^a Cf. Table II. ^b Reference 2a. ^c Reference 12b. ^d Cf. ref 12a and b and references cited therein.

(33) C. H. DePuy and C. A. Bishop, *ibid.*, **82**, 2532 (1960).

(34) H. M. R. Hoffmann, *J. Chem. Soc.*, 6748, 6753, 6762 (1965).

(35) (a) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2540 (1970); (b) P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, **92**, 2542 (1970).

discernible trends in transition-state charge development relative to reactivity. Nevertheless, k_{OTs}/k_{Br} ratios vary greatly for k_c -type substrates. For example, the 2-adamantyl system, one of the few examples of a limiting secondary substrate,^{12a,d,35} has a k_{OTs}/k_{Br} ratio (in 80% EtOH) of 231 whereas the corresponding value for the 1-bicyclo[2.2.2]octyl system, a substrate of comparable reactivity, is 3.3×10^3 .³⁶ Steric effects provide a satisfactory rationalization for these differences.^{37,38}

We believe that k_{OTs}/k_{Br} ratios, in their present state of understanding, should be employed with caution as mechanistic criteria. While differences in nucleophilic participation (by solvent or other nucleophile) undoubtedly contribute to these ratios (and may predominate for primary systems),³⁴ we believe that steric rather than electronic effects may dominate such ratios in tertiary systems, and, perhaps, in secondary systems as well.⁴¹

Torsional and Hyperconjugative Effects on Reactivity.

We wish to draw attention to the spectacular deviation observed for 10-tricyclo[5.2.1.0^{4,10}]decyl tosylate (**12**). The acetolysis of **12** is nearly 10^9 times slower than that expected on the basis of the conformational analysis calculations.⁴² This deviation is far outside expected error limits and must indicate that a special effect is operative.

This behavior is quite unexpected. Structurally, **12** is very similar to the other bridgehead substrates. The rigid cup shape of the molecule^{45,48} prevents a

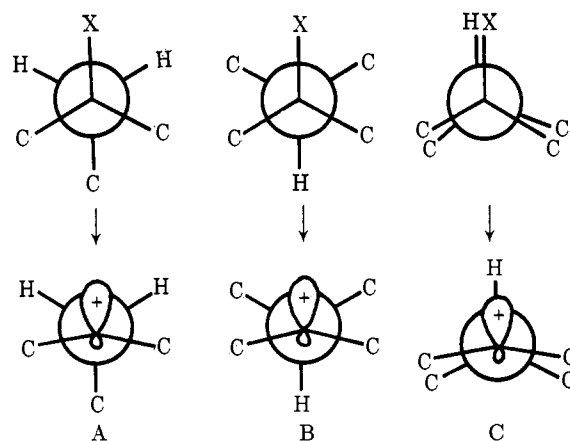


Figure 8. Torsional arrangements around the reaction centers of bridgehead substrates: (A) 1-adamantyl (**8**), (B) *trans*-9-decyl (**3**), (C) 10-tricyclo[5.2.1.0^{4,10}]decyl (**12**).

carbonium ion developing at the C₁₀ position from becoming completely planar just as in the case of most of the other bridgehead systems. Two significant structural differences do exist, nevertheless. The backside of the molecule is not shielded from the solvent as is the case for cage-like polycyclic systems. The nearly eclipsed torsional arrangements around the reaction center contrast with the staggered conformations involving the leaving groups in the other bridgehead substrates (Figure 8).

Solvation effects cannot account for the failure of **12** to conform to the model established by the conformational analysis calculations. Not only have both specific and electrostatic solvation been found not to play a significant role in the rate-determining step of tertiary substrate solvolyses,^{12b,c} but the deviation in the present case is in the *wrong direction*. Furthermore, other fused ring systems (*e.g.*, **2**, **3**, and **5**) exhibit normal bridgehead behavior, as judged by the success of our calculations. The environment at the backside of the reaction centers in these systems is similar to that in **12**.

We believe that the nearly eclipsed torsional arrangement around the reaction center of **12** must give rise to its abnormal solvolytic behavior. Among all the bridgehead systems studied, this arrangement is peculiar to **12**. Two explanations based on differences in torsional arrangements may be advanced. Either the energy surface for rotation around cationic centers has a much different shape and magnitude than previously expected (see below), or the normal stabilizing effect of alkyl substitution at a solvolytically generated cationic center requires, to a significant extent, the availability of either a C-H or C-C bond trans to the leaving group.⁴⁹

The model adopted in the conformational analysis calculations⁷ for the evaluation of torsional effects employed the traditional "bond opposition" concepts^{5,50,51} for both the ground-state hydrocarbons and the transition-state carbonium ions. That is, the empirically developed treatment of torsional effects in molecules was extended directly to the cationic species.⁷

dihedral angle of 13°. Cf. ref 43. The conformation with C_s symmetry is predicted to be 6.5 kcal less stable.

(49) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964), and private communication.

(50) H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

(51) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 699, 701 (1967).

(36) See Table II, footnote *p*.

(37) As indicated earlier, steric effects cannot be completely ruled out even for secondary substrates. In the absence of a better model, however, the k_{OTs}/k_{Br} ratio of 231 obtained for the 2-adamantyl system in 80% ethanol^{12a} may be taken as a typical value for a limiting (k_c type) solvolysis under these conditions. Larger values may be attributed to ground-state effects involving the tosylate leaving group whereas smaller values indicate nucleophilic solvent participation in the solvolysis transition state.

(38) Variations in internal return³⁹ with reactivity may also affect the k_{OTs}/k_{Br} ratios. If internal return is occurring, the ionization rate would exceed the experimentally measured solvolysis rate. The observed trend in OTs/Br rate ratios requires (if internal return is responsible) that either the less reactive tosylates or the more reactive bromides be slowed by this effect. The direct determination of the magnitude of internal return in the bridgehead substrates would be difficult.^{39b} Indirect evidence indicates that internal return is not an important contributing factor in the sulfonate solvolyses, however. It is known that internal return is generally less important in 80% ethanol than in acetic acid.^{39,40} The relative rates for bridgehead tosylates in these two solvents are observed to be constant (Figure 7, Table III). This suggests that internal return does not vary in magnitude with bridgehead reactivity.

(39) (a) S. Winstein, A. H. Fainberg, and E. Grunwald, *J. Amer. Chem. Soc.*, **79**, 4146 (1957); S. Winstein, B. Appel, R. Baker, and A. Diaz, *Chem. Soc., Spec. Publ.*, No. 19, 109 (1965); A. F. Diaz, I. Lazdins, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 1904 (1968); (b) A. F. Diaz and S. Winstein, *ibid.*, **91**, 4300 (1969).

(40) D. J. Raber, J. M. Harris, and P. v. R. Schleyer, to be published.

(41) For example, the similarity in k_{OTs}/k_{Br} ratios observed for the 1-bicyclo[2.2.2]octyl and 4-quinuclidyl systems³⁶ may be due merely to the steric similarity around the reaction sites in both systems.

(42) This result is qualitatively consistent with the reported⁴³ chromic acid oxidation of tricyclo[5.2.1.0^{4,10}]decane (**12**, X = H) which gives only the 1- and not the 10-alcohol.⁴⁴

(43) L. A. Paquette, G. A. Meehan, and S. J. Marshall, *J. Amer. Chem. Soc.*, **91**, 6779 (1969).

(44) Cf. R. C. Bingham and P. v. R. Schleyer, *J. Org. Chem.*, **36**, 1198 (1971).

(45) To confirm the original⁴⁶ structural assignment of **12** (X = OH) which was based on spectral evidence alone, we have converted this alcohol to the known hydrocarbon⁴⁷ via reduction of the corresponding bromide with triphenyltin hydride.

(46) J. W. Baum and C. D. Gutsche, *J. Org. Chem.*, **33**, 4312 (1968).

(47) I. T. Jacobsen, *Acta Chem. Scand.*, **21**, 2235 (1967).

(48) Our conformational analysis calculations predict the lowest energy conformation of **12** (X = H) to have C_s symmetry with an XCCH

Table V. β -Alkyl Effects in Limiting or Near-Limiting Solvolysis Reactions

Secondary substrates ^a		Tertiary substrates ^b	
Compd	$k_{rel. 25^\circ, TFA}$	Compd	$k_{rel. 25^\circ, 80\% EtOH}$
(CH ₃) ₂ CHOTs	1.0	(CH ₃) ₃ CCl	1.0
C ₂ H ₅ (CH ₃)CHOTs	5.9	C ₂ H ₅ (CH ₃) ₂ CCl	1.65
(C ₂ H ₅) ₂ CHOTs	30.9	(C ₂ H ₅) ₂ CH ₂ CCl	2.58

^a Reference 60. ^b References 61 and 63.

Since torsional barriers are not expected to vary significantly with substitution,⁵² it was argued that all planar carbonium ions should have rotational barriers near zero and a torsional strain of 1 kcal/mol for each C–C bond to the reaction center.⁷ Nonplanar carbonium ions were treated as having rotational barriers consistent with the extent of the bond oppositions in the system.⁷

Whereas recent molecular orbital calculations of the rotational barriers in the planar and tetrahedral ethyl cations support these expectations,^{10c} a pronounced preference for C–C *vs.* C–H bond overlap with the vacant orbital is predicted for both the *n*-propyl and isobutyl cations.⁵³ This predicted preference for C–C *vs.* C–H hyperconjugation⁵⁴ could account for the abnormal behavior of **12**. In **12**, C–H bonds are eclipsed with the developing vacant orbital whereas C–C bonds fulfill this role in most other bridgehead substrates.

Available experimental evidence suggests, however, that this torsional model derived from primary cations may not be quantitatively applicable to tertiary systems.⁵⁷ Free radical ionization potentials appear to afford the best direct quantitative measure of energy differences between cations.⁵⁸ Recent data indicate that the differences in ionization potentials due to β -methyl substitution decrease sharply in going from primary to secondary systems: $\Delta I.P.$ (ethyl–*n*-propyl) = 6.6 kcal/mol while $\Delta I.P.$ (*sec*-propyl–*sec*-butyl) = 3.2 kcal/mol.⁵⁹

Solvolysis data indicate a similar trend in β -methyl effects. In trifluoroacetic acid, the most nearly limiting solvent available, Peterson⁶⁰ has shown that the average β -methyl substitution rate enhancement effect in a series of *n*-alkyl substrates is a factor of about 6. In contrast, the β -methyl effect in tertiary systems is quite small, averaging only 1.6 per methyl⁶¹ (Table

(52) Cf. J. P. Lowe, "Progress in Physical Organic Chemistry," Vol. 6, A. Streitwieser, Jr., and R. W. Taft, Ed., Interscience, New York, N. Y., 1968, p 1.

(53) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 6380, 6987 (1970).

(54) The actual mechanism whereby alkyl groups stabilize carbonium ions appears to be quite complicated and perhaps different from traditional interpretations.^{55,56} It is convenient to continue to describe overlap effects involving bonds β to a vacant orbital as "hyperconjugation." Electron population analyses provide evidence for such specific interactions even though the actual mechanisms may be somewhat different from that traditionally assumed.⁵⁶

(55) J. E. Williams, V. Buss, and L. C. Allen, *J. Amer. Chem. Soc.*, in press.

(56) N. C. Baird, *Theor. Chim. Acta*, **16**, 239 (1970); H. Kollmar and H. O. Smith, *Angew. Chem.*, **82**, 444 (1970).

(57) It is difficult, because of the cost involved, to carry out high quality molecular orbital calculations with a geometry search on tertiary cations.

(58) Heats of formation, although also useful for this purpose, must be corrected for differences in the numbers and kinds of atoms involved, and the exact value of this correction is uncertain.

(59) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970).

(60) P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. A. Sipp, *J. Amer. Chem. Soc.*, **87**, 5169 (1965).

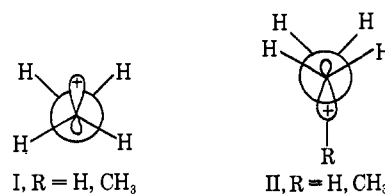
(61) H. C. Brown and R. S. Fletcher, *ibid.*, **71**, 1845 (1949); H. C. Brown and H. L. Berneis, *ibid.*, **75**, 10 (1953).

V). The ρ^* values (–7.6 for the secondary and –2.1 for the tertiary substrates listed in Table V) also illustrate this difference.⁶² Similar data for primary systems are inapplicable, because primary solvolyses do not involve carbonium ions.

Thus, whereas β -methyl substitution significantly increases the stability of primary cations, such effects are minimized for tertiary systems. No large preference for a C–C hyperconjugative interaction is indicated in these latter systems. This conclusion is also reached for a comparison of **8** (as well as most other cage-like systems) with **3** and **5**. Normal bridgehead behavior is observed in all three cases (Figure 5) even though C–C bonds are *trans* to the leaving group in **8** whereas C–H bonds are *trans* to the leaving group in **3** and **5** (Figure 8). The abnormal behavior of **12** does not, therefore, appear to arise from a failure of the adopted model for the evaluation of torsional effects generally operative in tertiary cations.

The explanation for the abnormal behavior of **12** which is most consistent with both the available experimental data and theory is a specific *trans* effect operative in the stabilization of developing cationic centers by α -alkyl groups.⁴⁹ That is, a hyperconjugative stabilization⁵⁴ which is greatest in the *trans* periplanar arrangement (relative to the leaving group) is indicated.^{64,65}

This stereoelectronic requirement for hyperconjugation in carbonium ion forming transition states is manifested by a number of other experimental observations.^{64,66} The conformational dependence of deuterium isotope effects in solvolysis reactions provides a well-known example.⁶⁷ The effect is also predicted by Hoffmann's extended Hückel calculations⁴⁹ which have been confirmed by recent *ab initio* molecular orbital calculations.^{10c,53} Both the tetrahedral ethyl and *n*-propyl cations are calculated to have a pronounced preference for conformation I with a *trans* β bond. Conformation II, which approximates



(62) Using a larger number of compounds, $\rho^*_{secondary, TFA} = -7.160$ and $\rho^*_{tertiary, 80\% EtOH} = -3.4988$ have been estimated.

(63) A. Streitwieser, Jr., *J. Amer. Chem. Soc.*, **78**, 4935 (1956).

(64) F. R. Jensen and B. E. Smart, *ibid.*, **91**, 5688 (1969).

(65) W. Hanstein, H. J. Berwin, and T. G. Traylor, *ibid.*, **92**, 829 (1970); N. A. Clinton, R. S. Brown, and T. G. Traylor, *ibid.*, **92**, 5228 (1970).

(66) M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962.

(67) V. J. Shiner, Jr., H. R. Mahler, R. H. Baker, Jr., and R. R. Hiatt, *Ann. N. Y. Acad. Sci.*, **84**, 583 (1960); V. J. Shiner, Jr., and J. S. Humphrey, Jr., *J. Amer. Chem. Soc.*, **85**, 2416 (1963); V. J. Shiner, Jr., and J. G. Jewett, *ibid.*, **87**, 1382 (1965); B. L. Murr and J. A. Conkling, *ibid.*, **92**, 3464 (1970).

the situation expected from the solvolysis of **12**, is found to be much less stable.^{10c,53}

The view, then, is that hyperconjugation provides a major contribution⁶⁸ to the well-known^{35a} stabilizing effect of alkyl groups on carbonium ion centers and that this effect is most pronounced when a trans relationship between a β bond and the leaving group may be achieved. No large preference for a C–C *vs.* a C–H bond trans to the leaving group in tertiary systems seems to be indicated.

Earlier, substituent effects had been used as evidence against C–C hyperconjugation in the 1-adamantyl system.²² This approach, however, assumes physical reality for the valence bond picture of hyperconjugation. More recent evidence indicates that this is not the case even in the 2-norbornyl cation.⁶⁴ Both methyl⁶⁹ and methoxy⁷⁰ substituents at the 6 position of the 2-norbornyl system retard the solvolysis reactions. By analogy, substituent effects may also not be expected to provide a reliable test for C–C hyperconjugation in the 1-adamantyl system. On the other hand, the abnormal bridgehead nmr chemical shifts observed in the stable 1-adamantyl cation provide evidence consistent with hyperconjugation in bridgehead systems.⁷¹

The magnitude of this trans effect on solvolysis reactions based on the 10-tricyclo[5.2.1.0^{4,10}]decyl tosylate (**12**) results is surprisingly large. At 70°, there is a 14-kcal difference in activation free energies ($\Delta\Delta F^\ddagger$) between the predicted and experimental acetolysis rates of **12**. That is, the better trans overlap relative to the cis (Figure 8) apparently is lowering the transition-state energies of solvolysis reactions by nearly 5 kcal/mol per bond.

To provide the basis for further tests of the postulated trans effect operative in the hyperconjugative⁵⁴ stabilization of cationic centers, we have extended our calculations to additional substrates. In **14** (X = OTs), a system in which the torsional arrangement around one of the bonds to the reaction center is eclipsed, the decrease in reactivity relative to the other bridgehead tosylates studied as indicated by the conformational analysis calculations ($10^{0.8\pm 0.5}$) is significantly smaller than the 10^3 deceleration predicted by the trans effect. The inductive and ground-state steric effects of the methyl substituent at C₇, although presumably small, are unknown, however. The conformational analysis calculations predict a rate of $1.5 \times 10^{-8} \text{ sec}^{-1}$ at 70° for the acetolysis of the parent 3-noradamantyl tosylate in the absence of the trans effect. Similarly, a rate of $1.7 \times 10^{-4} \text{ sec}^{-1}$ is predicted for 1-chlorotricyclo[5.2.1.0^{4,10}]decane⁷² at 70° in 80% ethanol. In all cases, the actual experimental rates should be nearly three orders of magnitude slower than predicted if the postulated trans effect is operative.⁷³

(68) Cf. K. L. Servis, S. Borčić, and D. E. Sunko, *Tetrahedron*, **24**, 1247 (1968). For recent theoretical calculations supporting this view, see ref 55 and 56 and references cited therein.

(69) P. v. R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Amer. Chem. Soc.*, **87**, 375 (1965).

(70) P. v. R. Schleyer, P. J. Stang, and D. J. Raber, *ibid.*, **92**, 4725 (1970).

(71) P. v. R. Schleyer, R. C. Fort, Jr., W. E. Watts, M. B. Comisarow, and G. A. Olah, *ibid.*, **86**, 4195 (1964).

(72) The corresponding alcohol has been reported. See ref 43.

(73) Additional test cases might be provided by the 1-bisnoradamantyl⁷⁴ and the cubyl systems.⁷⁵ Our calculations indicate, however, that even the triflates of both systems would be too unreactive to study under normal solvolytic conditions. An acetolysis rate at 70° of

Correlation of Bridgehead Free Radical Reactivities. Bridgehead free radical reactivities (Table VI) parallel

Table VI. Relative Rates of Azo and *tert*-Butyl Perester Decompositions

Substrate	X = -N=N- $k_{\text{rel. } 300^\circ, \text{ benzene}}^a$	X = -CO ₂ - <i>tert</i> -C ₄ H ₉ $k_{\text{rel. } 65^\circ, \text{ cumene}}^b$
8	1.0	1.0
10	1.3×10^{-1}	1.0×10^{-1}
9	8.7×10^{-2}	
11	9.2×10^{-2}	
15	5.0×10^{-3}	7.8×10^{-4}

^a Reference 76d,e. ^b Reference 76b,c.

those for the corresponding carbonium ions (Table II).^{6,76} A preference for planar or near-planar transition states for free radical formation at the bridgehead positions of polycyclic hydrocarbons is indicated.^{6,76} The force constants for distortion of free radicals are less than those for carbonium ions, however:^{6,76,77} $k_{1\text{-adamantyl}}/k_{1\text{-norbornyl}}$ (perester decompositions, 65°) = 7.8×10^{-4} while $k_{1\text{-adamantyl}}/k_{1\text{-norbornyl}}$ (tosylate acetolysis, 70°) = 10^{-10} (Tables II and VI).

Thus, carbonium ions and free radicals (at least in bridgehead systems)⁷⁸ both prefer planarity although to different degrees. The calculated hydrocarbon-carbonium ion strain energy differences determined for bridgehead systems by our conformational analysis calculations might, therefore, be equally applicable to the correlation of bridgehead free radical reactivities. Figures 9 and 10 and Table III establish this point. The free energy relationships obtained for the correlations are given in eq 5 and 6.

$$-\log k_{\text{rel. azo, } 300^\circ} = 0.20\Delta H(\text{calcd}) - 2.47 \quad (5)$$

$$-\log k_{\text{rel. perester, } 65^\circ} = 0.28\Delta H(\text{calcd}) - 3.48 \quad (6)$$

The slopes of the correlations of bridgehead free radical reactivities (Table III) are, as expected, larger than those observed for the solvolysis reactions. Of the two types of free radical reactions considered, the *tert*-butyl perester decompositions resemble the solvolysis reactions more closely. Several explanations for this behavior are plausible. Some polar character may be developed in the transition states for the *tert*-butyl perester decompositions.⁷⁹ Alternatively, a steric

6.6×10^{-17} ($1.4 \times 10^{-11} \text{ sec}^{-1}$ at 200° assuming a ΔH^\ddagger of 30 kcal/mol) is predicted for 1-bisnoradamantyl triflate while 1-cubyl triflate is predicted to be completely inert ($k < 10^{-12} \text{ sec}^{-1}$) even at 250°!

(74) Cf. B. R. Vogt, S. R. Suter, and J. R. E. Hoover, *Tetrahedron Lett.*, 1609 (1968); P. K. Freeman, R. B. Kinnel, and T. D. Ziebarth, *ibid.*, 1059 (1970); R. R. Sauers and B. R. Sickle, *ibid.*, 1067 (1970).

(75) P. E. Eaton and T. W. Cole, Jr., *J. Amer. Chem. Soc.*, **86**, 3157 (1964).

(76) (a) J. P. Lorand, S. D. Chodroff, and R. W. Wallace, *ibid.*, **90**, 5266 (1968); (b) R. C. Fort, Jr., and R. E. Franklin, *ibid.*, **90**, 5267 (1968); (c) L. B. Humphrey, B. Hodgson, and R. E. Pincock, *Can. J. Chem.*, **46**, 3099 (1968); (d) A. Oberlinner and C. Rüchardt, *Tetrahedron Lett.*, 4685 (1969); (e) C. Rüchardt, *Angew. Chem.*, **82**, 845 (1970), and references therein.

(77) For a recent theoretical comparison of carbonium ions and free radicals by *ab initio* methods, see ref 10d which also contains a literature summary.

(78) Both the cyclopropyl and 7-norbornyl radicals are thought to be nonplanar: P. J. Krusic, J. P. Jesson, and J. K. Kochi, *J. Amer. Chem. Soc.*, **91**, 4568 (1969), and references cited therein; P. Bakuzis, J. K. Kochi, and P. J. Krusic, *ibid.*, **92**, 1434 (1970). See ref 10d for an analysis of the behavior of such in-plane strained radicals.

(79) P. D. Bartlett and C. Rüchardt, *ibid.*, **82**, 1756 (1960); C. Rüchardt and H. Schwarzer, *Ber.*, **99**, 1861, 1878 (1966); C. Rüchardt and H. Böck, *ibid.*, **104**, 577 (1971); C. Rüchardt and I. Mayer-Rüthardt, *ibid.*, **104**, 593 (1971).

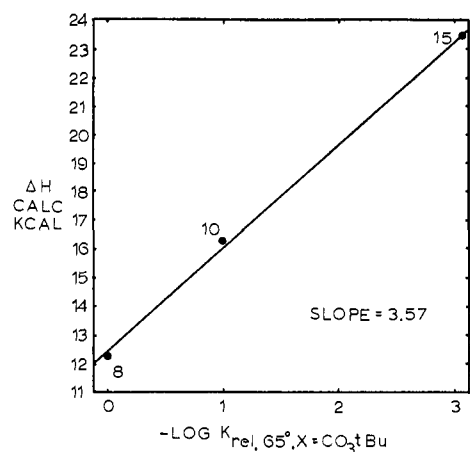


Figure 9. Calculated hydrocarbon-carbonium ion strain energy differences (ΔH) plotted against $-\log$ of the relative rates of *tert*-butyl perester decompositions at 65° in cumene.

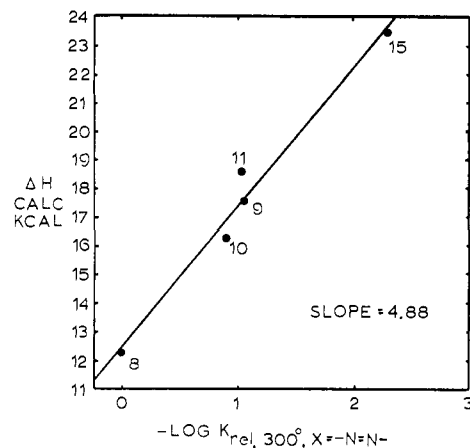


Figure 10. Calculated hydrocarbon-carbonium ion strain energy differences (ΔH) plotted against $-\log$ of the relative rates of azo decompositions at 300° in benzene.

effect similar to that discussed above for the tertiary sulfonates may increase the ground-state steric strain of the more bulky *tert*-butyl peresters (e.g., adamantyl).

Applying eq 5 and 6 to the other bridgehead systems for which calculations have been made, the bridgehead free radical reactivities of a large number of systems may be predicted. Table VII summarizes some of these

Table VII. Predicted Relative Rates of Azo and *tert*-Butyl Perester Decompositions

Substrate	X = -N=N- $k_{rel, 300^\circ, benzene}$ (pred) ^a	X = -CO ₃ - <i>tert</i> -C ₄ H ₉ $k_{rel, 65^\circ, cumene}$ (pred) ^b
1	1.1×10^3	1.8×10^4
3	3.3×10^1	1.4×10^2
4	1.5×10^1	4.6×10^1
6	6.5	1.4×10^1
7	1.4×10^1	4.3×10^1
9	Known ^c	3.5×10^{-2}
11	Known ^c	1.7×10^{-2}
12	4.1	7.6
13	5.1×10^{-2}	1.7×10^{-2}
14	2.6×10^{-2}	6.3×10^{-3}

^a Relative to **8** for which $k_{300^\circ, benzene} = 6.32 \times 10^{-4} \text{ sec}^{-1, 76c}$

^b Relative to **8** for which $k_{65^\circ, cumene} = 7.40 \times 10^{-5} \text{ sec}^{-1, 76b, c}$

^c See Table VI.

predictions.^{79a} On the basis of the present work, the most noteworthy prediction involves the free radical reactivity of the 10-tricyclo[5.2.1.0^{4,10}]decyl system **12**. As discussed above, the solvolytic reactivity of **12** (X = OTs) is abnormally low relative to other bridgehead systems. This behavior was attributed to the cisoid torsional arrangement around the reaction center of this system. Hyperconjugative stabilization of developing cationic centers is disfavored by this arrangement relative to the preferred trans-periplanar situation.

The decreased magnitudes of secondary β -deuterium isotope effects in free radical reactions relative to analogous carbonium ion reactions suggest that hyperconjugative stabilization of free radicals is much less important.⁸⁰ Since this electronic effect is not

(79a) NOTE ADDED IN PROOF. The rates of the *tert*-butyl perester decomposition of **4**, **9**, and **11** (X = CO₃-*tert*-C₄H₉) are now available. The experimental relative rates (relative to **8** at 80°) are 0.5×10^1 , 6.5×10^{-2} , and $3.5 \times 10^{-2} \text{ sec}^{-1}$, respectively.^{78e} These results may be compared with our predicted values of 4.6×10^1 , 3.5×10^{-2} , and $1.7 \times 10^{-2} \text{ sec}^{-1}$ (Table VII).

included in the conformational analysis calculations, the free radical reactivity of **12** should be much more reliably predicted. We plan to test this prediction experimentally.

Conclusions

1. Quantitative conformational analysis appears now to be established as a highly reliable approach for the calculation of carbonium ion reactivities. Bridgehead systems, differing in reactivity over 10^{18} in solvolysis rates, give excellent results. We will now turn to the analysis of other types of tertiary systems, e.g., those with attached methyl groups, with secondary substrates an eventual goal.

2. Free radical reactions are also inhibited at carbocyclic bridgehead positions, but to a lesser degree than carbonium ion processes. Correlations between the available bridgehead and carbonium ion reactivities are observed; hence, the same conformational analysis program developed for carbonium ions works well for the calculation of free radical reactivities. A number of reactivity predictions have been made on this basis.

3. Bridgehead compounds now provide a calibrated series of similar substrates of widely varying reactivities which permit the evaluation of specific effects. In particular, we have argued that trends in OTs/Br rate ratios are due largely to differing ground-state steric effects involving these leaving groups. Such steric contributions to the OTs/Br ratios should be large for tertiary systems, and may be a factor influencing the secondary ratios as well.

4. The conformational analysis calculations fail badly in estimating the reactivity of 10-tricyclo[5.2.1.0^{4,10}]decyl tosylate (**12**). We believe this to be due to the unique torsional arrangement around the reaction center of this system. In effect, the conformational analysis program assumes the transoid arrangement possessed by nearly all bridgehead systems. Trans-periplanar arrangements between the leaving group and the β bonds (C-C or C-H) appear to be necessary to afford the maximum hyperconjugative transition-state stabilization. Such arrange-

(80) S. Seltzer and E. J. Hamilton, Jr., *J. Amer. Chem. Soc.*, **88**, 3775 (1966); T. Koenig and R. Wolf, *ibid.*, **89**, 2948 (1967); T. Koenig, J. Huntington, and R. C. Cruthoff, *ibid.*, **92**, 5413 (1970).

ments are not possessed by cisoid **12**, and the solvolysis rate is much slower. In effect, cisoid **12** requires an electronic correction factor which has not been included in the conformational analysis calculations. Presumably, a family of such cisoid compounds (were it possible to construct such representatives) should also be correlated by the present conformational program.

Experimental Section

General Comments. The following compounds were prepared by established procedures: 1-chlorobicyclo[3.3.2]decane (**1**),⁴⁴ 3-bromohomoadamantane (**4**),⁸¹ 1-chlorobicyclo[3.3.1]nonane (**6**),^{13b} 1-bromobicyclo[3.2.2]nonane (**7**),⁴⁴ 1-chlorobicyclo[3.2.2]nonane (**7**),⁸² 1-noradamantyl tosylate (**13**),⁸³ and 7-methyl-3-noradamantyl tosylate (**14**).⁸⁴

Chlorides **2** and **5** were kindly supplied by W. C. Dickason and H. C. Brown.⁸⁵

10-Tricyclo[5.2.1.0^{4,10}]decyl Tosylate (12**, X = OTs).** To a solution of 10-tricyclo[5.2.1.0^{4,10}]decano¹⁸⁶ (0.465 g, 3.06 mmol) in anhydrous ether (10 ml) under nitrogen was added a 1.65 M solution of methyllithium (2.75 ml, 4.5 mmol) *via* a syringe, taking care to keep the syringe needle in the ether solution throughout the addition.⁸⁷ After gently refluxing the lithium alcoholate solution for 30 min, freshly recrystallized *p*-toluenesulfonyl chloride (1.15 g, 6 mmol) in anhydrous ether (15 ml) was added rapidly. The reaction mixture was then gently refluxed for an additional 30 min. The precipitated lithium salts were then removed by filtration and the solution was concentrated *in vacuo*. After treating the residue with pyridine (5 ml) for 10 min, the solution was poured in ice water. The precipitated tosylate was collected by filtration, dried *in vacuo*, and recrystallized from pentane (0.116 g, 13%): mp 84.5–86°; nmr (CCl₄) δ 1.37 (6 H, m), 1.87 (6 H, m), 2.39 (3 H, s), 2.83 (3 H, m), and 7.45 (4 H, AB q); ir (CCl₄) 3015, 2915, 2855, 1601, 1345, 1185, 1170, and 925 cm⁻¹.

Anal. Calcd for C₁₇H₂₅SO₃: C, 66.67; H, 7.19. Found: C, 66.52; H, 7.17.

10-Tricyclo[5.2.1.0^{4,10}]decyl Bromide (12**, X = Br).** (a) To freshly distilled thionyl bromide (0.31 ml, 4 mmol) dissolved in dichloromethane (5 ml) and cooled in an ice bath was added a solution of 10-tricyclo[5.2.1.0^{4,10}]decano¹⁸⁶ (200 mg, 1.3 mmol) in dichloromethane (5 ml). The reaction mixture was left at room temperature for 1 hr and then refluxed for 2 hr. Pentane (20 ml) was then added and the organic solution was washed with saturated Na₂CO₃ and with water and dried (MgSO₄). Solvent was then removed *in vacuo* and the residue sublimed, 80° (20 mm), to give 174 mg (62%): mp 96–97°; nmr (CCl₄) δ 1.45 (6 H, m), 1.92 (6 H, m), and 2.78 (3 H, m); ir (CCl₄) 2945, 2850, and 1450 cm⁻¹.

(b) Identical results in somewhat better yield were obtained by heating a suspension of 10-tricyclo[5.2.1.0^{4,10}]decano¹⁸⁶ (200 mg, 1.3 mmol) and zinc bromide (1.6 g) in 48% hydrogen bromide (2 ml) in a sealed glass tube at 100° for 6 hr.⁸⁸ The reaction mixture is then diluted with water and extracted three times with pentane. After washing the combined pentane extracts with concentrated

H₂SO₄, 5% NaHCO₃, and water and drying (MgSO₄), the solvent is removed *in vacuo* and the residue sublimed to give 220 mg (78%) of the desired product.

Reduction of 10-Tricyclo[5.2.1.0^{4,10}]decyl Bromide. Tricyclo[5.2.1.0^{4,10}]decane. To a solution of 10-tricyclo[5.2.1.0^{4,10}]decyl bromide (140 mg, 0.65 mmol), lithium aluminum hydride (7.4 mg, 0.195 mmol), and 2,2'-azobisisobutyronitrile (catalytic amount) in anhydrous ether (7 ml) was added triphenyltin chloride (300 mg, 0.78 mmol) in ether (20 ml) at room temperature. Care was taken to exclude moisture. A fine, light colored precipitate developed during the course of the addition (30 min). The reaction mixture was then refluxed for 3 hr, filtered, washed twice with water and brine, and dried (MgSO₄). Removal of solvent by distillation and sublimation gave a hydrocarbon product (42 mg, 47%), mp 66–67°, whose spectroscopic properties were identical in every respect with those reported for tricyclo[5.2.1.0^{4,10}]decane (lit.⁴⁷ mp 66°).

Kinetic Procedures. Titrimetric rates were determined in the usual manner⁸⁹ using approximately 0.015 M solutions. Conductometric rates were determined with a Wayne-Kerr Model B331 impedance bridge, capable of 0.1% accuracy. The conductivity cells used had bright platinum electrodes, cell constants in the range 0.2–0.4, and volumes of approximately 25 ml. Typically, 10⁻³ M solutions were used. At least twelve conductance measurements were taken during the first three half-lives of each reaction. Each reaction was run at least in duplicate. Linear conductivity-concentration plots are obtained for the aqueous ethanol solvents within the limits of experimental error.⁹⁰ Although acetic acid should not be expected to behave in this manner,⁹¹ control experiments indicate that the conductance method accurately reproduces literature data. The raw conductance data from both methods were fitted to the first-order rate equation by means of a least-squares computer program.

Strain Energy Calculations. All calculations were carried out at the Princeton University Computation Center utilizing either an IBM 7094 or an IBM 360/91 computer. The modified⁷ Wiberg-Harris¹⁶ "Strain" program is available from ref 2a.

Where comparisons are possible, calculated structures agree well with experimental results. The average deviation between calculated and experimental bond angles is about 1° while the average deviation in bond lengths is less than 0.01 Å. Strain energies are generally overestimated by the calculations. This problem becomes most severe for the more highly strained compounds. This is due to our use of a constant Hooke's law function for the evaluation of strain due to angle deformations.⁹ Although this situation is far from ideal, the problem is less serious when energy differences between hydrocarbon and cation are being calculated (see text). All calculated structures and strain energies are summarized in ref 2a.

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(89) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **77**, 3619 (1955), and references cited therein.

(90) Cf. B. L. Murr, Jr., Ph.D. Thesis, Indiana University, 1961.

(91) M. A. Sinnott, *J. Org. Chem.*, **34**, 3638 (1969).

(81) Table II, footnote *d*.

(82) C. A. Grob, M. Ohta, E. Renk, and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958).

(83) Table II, footnote *r*.

(84) Table II, footnote *t*.

(85) Cf. W. C. Dickason, Ph.D. Thesis, Purdue University, 1970.

(86) We are grateful to Dr. J. W. Baum and Professor C. D. Gutsche for kindly supplying a reference sample of this alcohol; cf. ref 46.

(87) Cf. H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Sheppele, *J. Amer. Chem. Soc.*, **89**, 370 (1967).

(88) Cf. ref 24a.