

striking contrast to the nearly complete inversion found with typical secondary systems.<sup>5,7</sup> In contrast to all other secondary systems for which data are available, 2-adamantyl exhibits more limiting character and provides a new standard against which the behavior of other secondary systems can be calibrated and reevaluated.<sup>21</sup> The following papers present further evidence and methods for estimating the magnitude of solvent participation.<sup>12,23</sup>

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dominated by steric effects involving the tosylate but not the bromide leaving group. We attribute the very high tertiary values to relief of ground-state tosylate nonbonded strain. (b) J. A. Bone and M. C. Whiting, *Chem. Commun.*, 115 (1970), work with *syn*- and *anti* 5-methyl-2-adamantyl tosylates. We thank Professor Whiting for communicating results prior to publication.

(21) It now seems necessary to reexamine the basis for the success of the Foote-Schleyer relationship.<sup>22</sup>

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

(23) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **92**, 2540 (1970).

(24) National Institutes of Health Postdoctoral Fellows: (a) 1967-1969; (b) 1969-1970; (c) 1968-1970.

(25) National Institutes of Health Predoctoral Fellows: (a) 1967-1968; (b) 1968-1970.

(26) American Can Company Fellow, 1966-1967; Ph.D. Thesis, Princeton University, 1970.

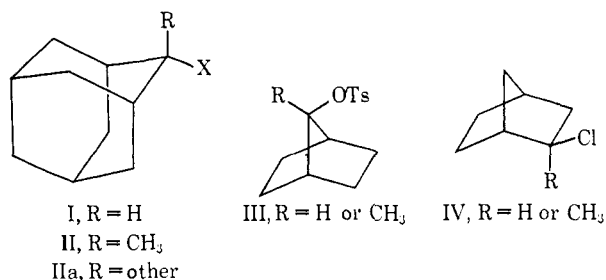
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## Solvent Assistance in the Solvolysis of Secondary Substrates. II. The $\alpha$ -Methyl/Hydrogen Rate Ratio for the 2-Adamantyl System

Sir:

According to the results of three standard tests to delineate the nature of solvolysis, secondary 2-adamantyl derivatives (I) behave like tertiary systems and quite unlike typical secondary substrates (isopropyl, cyclohexyl, etc.).<sup>1</sup> This behavior has been attributed to a basic difference with respect to the magnitude of nucleophilic solvent participation: large in ordinary, unhindered secondary (and primary) systems and small or absent in crowded substrates such as 2-adamantyl and tertiary derivatives.<sup>1</sup> We report here the results of a fourth diagnostic test, the effect of  $\alpha$ -methyl substitution.



(1) 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, *J. Amer. Chem. Soc.*, **92**, 2538 (1970), preceding paper.

The variation of behavior along the series methyl, ethyl, isopropyl, *t*-butyl has always played an important role in mechanistic studies of the solvolysis reaction: for SN<sub>2</sub> processes the rates fall along the series, whereas for SN<sub>1</sub> reactions they rise sharply.<sup>2</sup> In a similar manner, the effect on reaction rate produced by substitution of a methyl group for a hydrogen atom at the reaction site has become an important mechanistic tool to probe for charge delocalization in the transition state of a solvolysis reaction.<sup>2,3</sup> The theory is direct and reasonable. A tertiary cation is considerably more stable than a secondary ion; hence the latter should benefit more than the former from stabilization by resonance or by neighboring group participation in the solvolysis transition state. Thus, once a "normal"  $\alpha$ -CH<sub>3</sub>/H rate ratio has been established, downward deviations from this "normal" value have been taken to indicate that charge delocalization is less in the methyl-substituted compound than in the parent.<sup>2,3</sup>

This diagnostic tool is only valid, however, when *k<sub>c</sub>-type*<sup>1</sup> (carbonium ion) behavior is involved. If there is significant nucleophilic solvent assistance in the solvolysis of secondary derivatives, then  $\alpha$ -CH<sub>3</sub>/H rate ratios will not be reliable criteria for intramolecular charge delocalization. The extent of such solvent assistance will vary not only with the conditions, but also from substrate to substrate. For this reason it is important to establish what the limiting value of the  $\alpha$ -CH<sub>3</sub>/H rate ratio should be.

Following Winstein and Marshall,<sup>2b</sup> Streitwieser<sup>2c</sup> estimated 10<sup>6</sup> to be "the minimum stabilization of a tertiary carbonium ion relative to a secondary in a limiting solvolysis."<sup>4</sup> This value, widely quoted,<sup>2,3</sup> seems generally to have been accepted because (until recently) it had never been exceeded experimentally for any system.<sup>2,3</sup> For example, the highest  $\alpha$ -CH<sub>3</sub>/H rate ratio ever reported for an unstrained system is the value 10<sup>5.6</sup> for formolysis of isopropyl- vs. ethylmercuronium perchlorates.<sup>2d</sup>

Theoretically, an even higher value than 10<sup>6</sup> (8.3 kcal/mol at 25°) may be expected. From gas-phase values,<sup>2e,6a</sup> energy differences in the range 12-16 kcal/mol (equivalent to  $\alpha$ -CH<sub>3</sub>/H rate ratios of 10<sup>9</sup>-10<sup>12</sup>) are found for corresponding tertiary and secondary

(2) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, Chapter VII, p 418 ff; (b) S. Winstein and H. Marshall, *J. Amer. Chem. Soc.*, **74**, 1120 (1952); (c) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962; (d) F. R. Jensen and R. J. Ouellette, *J. Amer. Chem. Soc.*, **85**, 363 (1963); (e) D. Bethell and V. Gold, "Carbonium Ions: An Introduction," Academic, New York, N. Y., 1967; (f) E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, pp 68-142.

(3) (a) S. Winstein and E. Grunwald, *J. Amer. Chem. Soc.*, **70**, 828 (1948). For recent, leading references, see: (b) E. F. Fox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *ibid.*, **83**, 2719 (1961); (c) H. C. Brown and M. H. Rei, *ibid.*, **86**, 5008 (1964); H. C. Brown, *Chem. Brit.*, **2**, 199 (1966); (d) T. Tsuji, I. Moritani, S. Nishida, and G. Tadokoro, *Bull. Chem. Soc., Jap.*, **40**, 2344 (1967); (e) H. Tanida, Y. Hata, S. Ikegami, and H. Ishitobi, *J. Amer. Chem. Soc.*, **89**, 2928 (1967); (f) K. L. Servis, S. Borčić, and D. E. Sunko, *Tetrahedron*, **24**, 1247 (1968).

(4) This estimate, based on the formolysis rates of *t*-butyl vs. isopropyl bromide, was very crude, due to the unavailability of the necessary data at that time. Using better but still incomplete data,<sup>5</sup> a ratio of 10<sup>5.34</sup> can be estimated at 25°.

(5) (a) S. Winstein, E. Grunwald, and H. W. Jones, *J. Amer. Chem. Soc.*, **73**, 2700 (1951); (b) A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1602 (1957); (c) E. D. Hughes, C. K. Ingold, and U. G. Shapiro, *J. Chem. Soc.*, 225 (1936).

(6) G. A. Olah and P. v. R. Schleyer, Ed., "Carbonium Ions," Vol. I, Interscience, New York, N. Y., 1968: (a) J. L. Franklin, Chapter 2, p 85; (b) E. M. Arnett and J. W. Larsen, Chapter 12, p 441.

Table I. Rate Constants for Derivation of  $\alpha$ -CH<sub>3</sub>/H Ratios

Bromide	Solvent	Temp, °C	$k_1$ , sec <sup>-1</sup> <sup>a</sup>	$\Delta H^\ddagger$ , kcal/mol	$\Delta S^\ddagger$ , eu	$\alpha$ -Me/H ratios, 25° <sup>e</sup>
2-Adamantyl (I-Br)	80% ethanol	149.9	$(1.25 \pm 0.13) \times 10^{-4}$	27.5	-11.9	
		124.7	$(1.76 \pm 0.01) \times 10^{-5}$			
		100.3	$(1.44 \pm 0.01) \times 10^{-6}$			
		50.0	$4.08 \times 10^{-6b}$			
		25.0	$1.04 \times 10^{-10b}$			
		150.0	$(1.16 \pm 0.05) \times 10^{-5}$			
2-Methyl-2- adamantyl (II-Br)	80% ethanol	25.45	$(3.66 \pm 0.03) \times 10^{-3c}$	21.5	2.3	10 <sup>7.5</sup>
		0.0	$(1.14 \pm 0.01) \times 10^{-4c}$			
		25.0	$3.46 \times 10^{-3b}$			
		17.57	$(2.05 \pm 0.01) \times 10^{-5}$			
		25.05	$(5.82 \pm 0.14) \times 10^{-5}$			
		40.15	$(4.11 \pm 0.04) \times 10^{-4}$			
Isopropyl	80% ethanol	25.0	$6.60 \times 10^{-6b,d}$	22.5 <sup>d</sup>	-15.8 <sup>d</sup>	10 <sup>8.1</sup>
		100.0	$8.90 \times 10^{-7e}$			
		25.0	$3.58 \times 10^{-45b}$			
<i>t</i> -Butyl	80% ethanol	25.0	$3.58 \times 10^{-45b}$	21.5	-2.3	10 <sup>8.7</sup>
		100.0	$1.50 \times 10^{-2b,f}$			
		100.0	$1.50 \times 10^{-2b,f}$			
	CH <sub>3</sub> COOH-0.02 M NaOOCCH <sub>3</sub>	174.6	$(1.10 \pm 0.03) \times 10^{-4}$	33.6	-2.5	
	CH <sub>3</sub> COOH-0.02 M NaOOCCH <sub>3</sub>	25.0	$4.41 \times 10^{-13b}$			
	CH <sub>3</sub> COOH-0.02 M NaOOCCH <sub>3</sub>	17.57	$(2.05 \pm 0.01) \times 10^{-5}$	23.4	0.7	
	CH <sub>3</sub> COOH-0.02 M NaOOCCH <sub>3</sub>	25.05	$(5.82 \pm 0.14) \times 10^{-5}$			
	CH <sub>3</sub> COOH-0.02 M NaOOCCH <sub>3</sub>	40.15	$(4.11 \pm 0.04) \times 10^{-4}$			
	CH <sub>3</sub> COOH-0.06 M LiOOCCH <sub>3</sub>	100.0	$1.50 \times 10^{-2b,f}$	24.4	-1.9	10 <sup>4.2</sup>

<sup>a</sup> Determined titrimetrically unless otherwise noted. <sup>b</sup> Calculated. <sup>c</sup> Determined conductometrically. <sup>d</sup> From data of ref 5c. <sup>e</sup> W. C. Coburn, Jr., E. Grunwald, and M. P. Marshall, *J. Amer. Chem. Soc.*, **75**, 5735 (1953). <sup>f</sup> A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1602 (1957).

cations.<sup>6,7</sup> Remarkably, the best available estimates for the tertiary-secondary cation energy difference in solution (in strong acid solvents) fall in the same range.<sup>6b,8,9</sup>

Recently, Tanida<sup>3e</sup> has reported a  $\alpha$ -CH<sub>3</sub>/H rate ratio of 10<sup>7.7</sup> for acetolysis at 50° of the 7-norbornyl tosylates (III). This high value was considered to be exceptional and was attributed to the "enormous demand on substituents for further stabilization" made by this unusually unstable, strained cation.<sup>10a</sup>

The 2-adamantyl system (I and II) is free from this defect: the bond angles are normal. Since nucleophilic solvent assistance is minimal,<sup>1</sup> this system should be ideal for study. We deliberately chose a leaving group, bromide, prone to nucleophilic displacement.<sup>11</sup> In the relatively nucleophilic solvent, 80% ethanol, at 25°, the *t*-BuBr/*i*-PrBr rate ratio is only 10<sup>3.7</sup> (Table I). The  $\alpha$ -CH<sub>3</sub>/H rate ratio (II-Br/I-Br) for the 2-adamantyl system is 10<sup>7.5</sup>, the largest by far ever recorded under these conditions,<sup>2,3</sup> and exceeds the *t*-Bu/*i*-Pr ratio by nearly four orders of magnitude. In acetic acid the II-Br/I-Br ratio is 10<sup>8.1</sup> (25°); *t*-BuBr/*i*-PrBr = 10<sup>4.2</sup> at 100°. Values of 10<sup>7.5</sup>-10<sup>8.1</sup>, corresponding to free

energy of activation differences of ~11 kcal/mol, approach closely the range for carbonium ion stabilization based on the gas-phase differences in the stabilities of the ions themselves (see above).

We attribute the substantial increase of the II-Br/I-Br over the *t*-BuBr/*i*-PrBr rate ratio largely to the presence of considerable nucleophilic solvent participation in the solvolysis of *i*-PrBr and the sharp reduction if not complete absence of such assistance in the reaction of 2-adamantyl bromide (I-Br). Another possible contribution to the high II-Br/I-Br rate ratio—release of axial methyl strain during solvolysis of II-Br—probably plays only a minor role. At most, relief of all of the ~2.0-kcal/mol extra methyl group strain in II over I would lead to a 10<sup>1.5</sup> rate enhancement. The actual strain relief probably is much less than this.<sup>12</sup> The II-Br/*t*-BuBr ratio is only 10<sup>1</sup> (Table I); this can be accounted for entirely on the basis of inductive effects. Using Streitwieser's  $\rho^* = -3.3$  for *t*-halide solvolysis<sup>2c</sup> and approximating the degree of chain branching in the 2-methyl-2-adamantyl system by two isopropyl substituents [ $\Sigma\sigma^* = -0.38$ ], a II-Br/*t*-BuBr ratio of 10<sup>1.3</sup> is estimated.

It is in the context of the value 10<sup>8</sup>, which we now propose as a new provisional limiting value for the  $\alpha$ -CH<sub>3</sub>/H rate ratio, that other such ratios should be interpreted.<sup>2,3</sup> For example, the 10<sup>4.3</sup>–10<sup>4.8</sup> <sup>13a,13b</sup>  $\alpha$ -CH<sub>3</sub>/H rate ratios for the 2-*exo*-norbornyl system (IV) may take on an entirely new meaning. Formerly, such values appeared "normal";<sup>3c</sup> on the new basis they seem to indicate that 2-*exo*-norbornyl chloride (IV, R = H) solvolysis is accelerated by several powers of ten. Since solvent assistance is not likely in the 2-*exo*-norbornyl system—the backside is hindered and only products corresponding to retention of configuration are generally observed in secondary 2-norbornyl

(7) Franklin's estimate (20 kcal/mol)<sup>6a</sup> is too high because the contribution to the heat of formation by the additional methyl group in going from isopropyl to *t*-butyl cations (~7 kcal/mol) was not taken into account.

(8) *E.g.*, 11–15 kcal/mol (M. Saunders and E. L. Hagen, *J. Amer. Chem. Soc.*, **90**, 2436, 6881 (1968); M. Saunders, E. L. Hagen, and J. Rosenfeld, *ibid.*, **90**, 6882 (1968)).

(9) The correspondence of gas and solution values, if verified by future experiments, suggests that the degree of electrostatic solvation may not vary significantly among different carbonium ions. Already there are indications from the literature that kinetic and thermodynamic parameters for conversions of one cation to another are independent of solvent in the wide range of media which have been employed.<sup>10</sup>

(10) M. Saunders in "Magnetic Resonance in Biological Systems," A. Ehrenberg, B. G. Malmström, and T. Vänngård, Ed., Pergamon, Oxford, 1967, p 85; T. S. Sorenson, *J. Amer. Chem. Soc.*, **89**, 3782, 3794 (1967); **91**, 6398 (1969).

(10a) NOTE ADDED IN PROOF. Relief of steric ground-state strain involving 1,5-nonbonded interactions in tertiary tosylates would enhance  $\alpha$ -CH<sub>3</sub>/H rate ratios when tosylates are used as leaving groups. Halide leaving groups do not have such 1,5 interactions.

(11) C. H. DePuy and C. A. Bishop, *J. Amer. Chem. Soc.*, **82**, 2532 (1960); H. M. R. Hoffmann, *J. Chem. Soc.*, 6753, 6762 (1965).

(12) See J. L. Fry and P. v. R. Schleyer, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. ORGN 133, for evidence based on  $\beta$ -D isotope effects<sup>3d</sup> (IIa, R = CD<sub>3</sub>) and further substitution (IIa, R = C<sub>2</sub>H<sub>5</sub>, *i*-C<sub>4</sub>H<sub>7</sub>, and *t*-C<sub>4</sub>H<sub>9</sub>).

(13) (a) Chlorides, 80% ethanol, 85°;<sup>3f</sup> (b) chlorides, ethanol, 25°.<sup>3e</sup>

solvolyses<sup>14</sup>—anchimeric assistance would seem to be implicated as the accelerating factor. Similarly,  $\alpha$ -methyl/hydrogen rate ratios in cyclopropylcarbinyl systems are found to be in the range  $10^3$ – $10^5$ .<sup>3</sup> This apparently “normal” value seemed inconsistent with the known delocalization to the cyclopropane ring.<sup>3d</sup> The new limiting  $\alpha$ -CH<sub>3</sub>/H ratio of  $10^8$  removes this dilemma.<sup>15</sup>

The following paper provides an alternative method of estimating the magnitude of solvent assistance in secondary systems.<sup>16</sup>

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(14) G. D. Sargent, *Quart. Rev. Chem. Soc.*, **20**, 301 (1966); ref. 6, Vol. III, in press.

(15) Cf. P. v. R. Schleyer and V. Buss, *J. Amer. Chem. Soc.*, **91**, 5880 (1969).

(16) P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, **92**, 2542 (1970).

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

(18) National Institutes of Health Postdoctoral Fellow, 1969–1970.

(19) National Institutes of Health Predoctoral Fellow, 1968–1970.

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### Solvent Assistance in the Solvolysis of Secondary Substrates. III. A Method for Estimating the Magnitude of Solvent Assistance

Sir:

The preceding papers have emphasized the marked difference in behavior between 2-adamantyl derivatives and other simple secondary substrates.<sup>1</sup> Such substrates, e.g., isopropyl tosylate, react with considerable nucleophilic solvent participation, but this participation appears to be largely or wholly absent in the reactions of the 2-adamantyl system. In this paper, a method is suggested whereby the magnitude of solvent assistance can be put on a quantitative basis.

Definitions are in order. It is convenient to designate solvolysis processes by three rate constants,  $k_{\Delta}$  (anchimerically assisted),  $k_s$  (nucleophilically solvent assisted), and  $k_c$  (anchimerically and nucleophilically unassisted).<sup>2,3</sup> Following Winstein's usage, as the degree of assistance decreases to zero,  $k_{\Delta}$  or  $k_s$  approaches  $k_c$ . When assistance is present,  $k_c$  is a theoretical number not directly derivable from the measured rate constant,  $k_t$ . The ratio  $k_s/k_c$  thus is a measure of the degree of nucleophilic solvent participation in the absence of anchimeric assistance; when no such participation is present  $k_s/k_c = 1$ .<sup>4,5</sup> Clearly, for bridgehead systems  $k_s/k_c = 1$ , because backside nucleophilic solvent participation is impossible. Other tertiary, nonbridgehead compounds behave similarly and therefore should have  $k_s/k_c \cong 1$  as well.

Because of the inaccessibility of the theoretical  $k_c$  values, there has never been any way to determine  $k_s/k_c$  ratios for secondary systems. While it is clear from the literature that solvent assistance decreases along the series: alcoholic solvents > acetic acid > formic acid, the magnitude of this assistance has been a matter of uncertainty and debate.<sup>1</sup> The consensus has been that secondary substrates, such as isopropyl tosylate, have  $k_s/k_c$  ratios approaching 1 in formic acid,<sup>1a</sup> i.e., nucleophilic participation by formic acid is very small.

In contrast, we have pointed out that the formolysis and acetolysis of secondary  $\beta$ -aryllalkyl systems can be best understood in terms of two *strongly assisted* processes:  $k_{\Delta}$ , neighboring aryl assisted, and  $k_s$ , solvent assisted.<sup>7</sup> Thus, according to this view,  $k_s/k_c$  for such  $\beta$ -aryllalkyl as well as for simple alkyl systems should be quite large even in formic and acetic acids. A way of estimating  $k_s/k_c$  is clearly needed.

Fortunately, a model for limiting or nearly limiting behavior in secondary systems is now available.<sup>1</sup> The 2-adamantyl system responds to changes in solvent as do tertiary bridgehead and nonbridgehead systems<sup>1</sup> and should therefore also solvolyze *via* a process approaching  $k_c$  in character. In this paper, we compare the behavior of 2-adamantyl tosylate with isopropyl tosylate, a typical secondary system in which nucleophilic solvent participation is important. The requisite data are given in Table I and relative rate comparisons are presented in Table II.

The remarkable variation in relative rates—over five powers of ten—between isopropyl and 2-adamantyl tosylates in different solvents is apparent from Table II. In CF<sub>3</sub>COOH, the least nucleophilic solvent employed,<sup>8,9</sup> the adamantyl compound is actually 176 times more reactive, but as the nucleophilicity of the solvent increases, so does the relative reactivity of isopropyl tosylate, which eventually becomes >1000

(4) Similarly,  $k_{\Delta}/k_c$  is a measure of anchimeric assistance. Such ratios appeared in the early literature<sup>9</sup> until it was realized that for most systems  $k_s$  might not be identical with  $k_c$ . The more commonly employed  $k_{\Delta}/k_s$  ratios often give a distorted impression of the magnitude of anchimeric assistance, especially when  $k_s \gg k_c$ .<sup>2,7</sup>

(5) These definitions have certain important mathematical consequences. The equation,  $k_t = k_s + k_{\Delta}$ , is a proper one because  $k_s$  and  $k_{\Delta}$  processes are regarded as being discrete. However, equations such as  $k_t = k_s + k_{\Delta} + k_c$  are *not proper* and should not be used, since  $k_c$  is not regarded as a discrete process, but merely the limit to which  $k_s$  and  $k_{\Delta}$  tend as assistance vanishes. If a different view of solvolysis mechanisms is taken, e.g., that SN1 and SN2 processes are competitive and discrete, then Winstein's terminology should not be used.

(6) E.g., S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Amer. Chem. Soc.*, **70**, 821 (1948); S. Winstein and E. Grunwald, *ibid.*, **70**, 828 (1948).

(7) P. v. R. Schleyer and C. J. Lancelot, *ibid.*, **91**, 4297 (1969); also see C. J. Lancelot and P. v. R. Schleyer, *ibid.*, **91**, 4291, 4294, 4296 (1969); J. M. Harris, C. J. Lancelot, F. L. Schadt, and P. v. R. Schleyer, *ibid.*, **91**, 7508 (1969).

(8) (a) P. E. Peterson, R. E. Kelly, Jr., R. Belloli, and K. A. Sipp, *ibid.*, **87**, 5169 (1965); (b) A. Streitwieser, Jr., and G. A. Doffon, *Tetrahedron Lett.*, 1263 (1969).

(9) I. L. Reich, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 5635 (1969), and references therein cited. Also see A. Diaz, I. L. Reich, and S. Winstein, *ibid.*, **91**, 5637 (1969); P. C. Myhre and K. S. Brown, *ibid.*, **91**, 5639 (1969); P. C. Myhre and E. Evans, *ibid.*, **91**, 5641 (1969).

(1) (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, *J. Amer. Chem. Soc.*, **92**, 2538 (1970); (b) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **92**, 2540 (1970).

(2) The terminology adopted here is that first proposed by Winstein.<sup>3</sup> One of the best summaries of Winstein's work may be found in a series of lectures presented in Milan, in Oct 1965: S. Winstein, *Chimica Teorica, Conferenze, VIII Corso Estivo di Chimica, Accademia Nazionale dei Lincei, Rome, 1965*, p 239 ff.

(3) (a) S. Winstein, E. Allred, R. Heck, and R. Glick, *Tetrahedron*, **3**, 1 (1958); (b) S. Winstein, E. Grunwald, and H. W. Jones, *J. Amer. Chem. Soc.*, **73**, 2700 (1951); (c) S. Winstein, A. H. Fainberg, and E. Grunwald, *ibid.*, **79**, 4146 (1957); (d) S. Winstein, private communication.