

servicing the nmr spectra of dyes III and V at low temperatures when it might be expected that the rotation would be slowed sufficiently to inhibit the averaging process. The spectra of III and V have been determined at  $-60^\circ$  in deuteriochloroform, but in neither case was any change in the AA'XX' pattern observed. This information enables the maximum possible height of the energy barrier to free rotation to be estimated at about 10 kcal.<sup>5c</sup>

An acceptable model for the dye molecules under consideration would seem to be that they exist in a planar conformation, thus accounting for the observed deshielding effect of the carbonyl group, but that the *p*-phenylenediamine ring "flips" over rapidly between the two positions in which it is coplanar with the pyrazolone ring. The preference for the planar conformation, rather than the less hindered conformation in which the *p*-phenylenediamine ring is perpendicular to the rest of the molecule, suggests that it is stabilized by resonance.

## Experimental Section

3-Methyl-1-phenylpyrazolin-5-one and 4-amino-3-methyl-N,N-diethylaniline were obtained from Eastman Kodak Co., and 4-amino-N,N-diethylaniline was purchased from May and Baker Ltd. 1-Phenylpyrazolin-5-one was prepared from 1,1,3,3-tetraethoxycarbonylpropene<sup>7</sup> and phenylhydrazine according to the procedure of Ruhemann and Morrell.<sup>8</sup>

Dyes III-VI were prepared using the method previously described<sup>9</sup> for the preparation of indoanilines and since used<sup>2</sup> for the preparation of these pyrazolone azomethine dyes. They were purified by plc on silica gel.

The 60-Mc/sec spectra were run on a Varian A-60A spectrometer and the 100-Mc/sec spectra on a Varian HA-100 spectrometer.

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(7) C. K. Ingold and E. A. Perren, *J. Chem. Soc.*, **119**, 1582 (1921).

(8) S. Ruhemann and R. S. Morrell, *ibid.*, **61**, 791 (1892).

(9) P. W. Vittum and G. H. Brown, *J. Am. Chem. Soc.*, **68**, 2235 (1946).

## Conformational Analysis of Bridgehead Carbonium Ions

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**Abstract:** Solvolysis rates of bridgehead substituted polycyclic bromides vary over 12 powers of ten. A computer conformational analysis of these systems shows that this variation can be accounted for satisfactorily in terms of the increase of strain in going from ground to transition state. For five substrates, *t*-butyl, 3-homoadamantyl, 1-adamantyl, 1-bicyclo[2.2.2]octyl, and 1-norbornyl, the average deviation of the rates calculated from the experimental values was  $10^{\pm 0.8}$ . This deviation is extremely creditable in view of the numerous simplifying assumptions which had to be made in carrying out the computations. The ground states were approximated by the parent bridged hydrocarbons, and the transition states by the corresponding carbonium ions. The energy minimization program developed by Wiberg and Harris was employed. The chief modifications were the use of "harder" nonbonded potential functions and necessary changes owing to the presence of the charged sites in the carbonium ions. Meaningful results were obtained only when the C-C<sup>+</sup>-C bending force constants were at least four times "stiffer" than the normal C-C-C values. Although the most important effect influencing bridgehead solvolysis rates, according to this analysis, is increase in angle strain during ionization, other effects cannot be dismissed. In particular, a large measure of the 5000-fold rate difference between solvolysis rates of 1-adamantyl and 1-bicyclo[2.2.2]octyl bromides is due to the development of very unfavorable nonbonded C<sub>1</sub>...C<sub>4</sub> interactions in the latter case on going to the ion. Solvolysis rates of three systems have been predicted, the 1-homoadamantyl, the 1-bicyclo[3.3.1]nonyl, and the 1-bicyclo[3.2.1]octyl.

Many effects govern organic chemical reactivity. These can be divided into two main classes depending on their electronic or steric origin. Electronic effects, such as inductive and resonance interactions, are now commonly treated quantitatively, by empirical or by quantum mechanical approaches.<sup>2</sup> Steric effects, by contrast, are seldom evaluated precisely, despite the availability of a body of attractive theory.<sup>3</sup> There exist, however, simple and often highly empirical correlations of steric effects with chemical reactivity.

An especially pertinent example is the relationship observed by Foote<sup>4</sup> between the rate of unassisted solvolyses of certain secondary tosylates and the carbonyl frequency of the corresponding ketones. The rationale behind this correlation is that both carbonyl stretching frequencies and tosylate solvolysis rates should be some (not necessarily the same) function of bond angle, and they should therefore be related to one another. In other words, solvolysis rates should depend on angle strain,<sup>3</sup> and ketone carbonyl frequencies are a convenient method of evaluating this strain.

The Foote relationship applies to a limited number of cases where only angle strain factors affect reaction rates significantly. In order to generalize this ap-

(1) Alfred P. Sloan Foundation Fellow, 1962-1966.

(2) A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961.

(3) H. C. Brown, *J. Chem. Soc.*, 1248 (1956). Cf., however, R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13.

(4) C. S. Foote, *J. Am. Chem. Soc.*, **86**, 1853 (1964).

proach, Schleyer<sup>5</sup> included terms assessing the effect of torsional strain, nonbonded interactions, and, where necessary, inductive effects. This amounts to a conformational analysis of carbonium ion reactivity, with angle strain effects evaluated not by calculation but by recourse to carbonyl frequency comparisons. This imposes the restriction that ketone models be available, obviously impossible when tertiary solvolysis substrates are to be considered. A perfectly general approach would evaluate angle strain effects by implicit calculation, and this is the subject of the present paper.

The classical treatment for the quantitative determination of steric effects operative in molecules was developed by Westheimer.<sup>6</sup> Steric effects were considered as the sum of various independent strain-producing mechanisms, expressed in energy terms in eq 1.

$$E_{\text{total strain}} = E_{\text{bond length strain}} + E_{\text{bond angle strain}} + E_{\text{torsional strain}} + E_{\text{nonbonded interaction strain}} \quad (1)$$

There have been relatively few applications of the Westheimer approach and these have been nearly always concerned with ground-state phenomena. The problem has been one of computational complexity, for a full strain analysis required a fearful number of mathematical operations. Hendrickson<sup>7</sup> first took advantage of the capabilities of the modern digital computer and calculated energy differences between conformations of various alicyclic hydrocarbons. His results, for example, for the energy difference between the chair and boat forms of cyclohexane and for the energy barrier for interconversion between them, were generally in satisfactory agreement with experimental estimates. Hendrickson made certain simplifications within the general Westheimer framework. Geometries for systems were assumed, all bonds maintaining their expected equilibrium values. Possible bond compression on stretching was neglected, based on the reasonable argument that such distortions would be relatively inefficient as a strain relief mechanism.<sup>8</sup> More seriously, while C···C, C···H, and H···H interactions were considered, optimum results were obtained only when carbon-carbon and carbon-hydrogen interactions were neglected. This procedure cannot be justified for general use.

A significant advance was made by Wiberg<sup>8</sup> who outlined a general scheme for digital computer which not only includes all terms but also utilizes an energy minimization iterative approach. Such a technique ensures against a faulty assumption of an original geometry which may, in actuality, be far from a minimal one in terms of strain energy. This scheme has great utility, since it in effect seeks out optimal geometries. Although the Wiberg approach might be expected to be greatly superior to that of Hendrickson, it should be pointed out that the results obtained by both are often quite compatible. Wiberg's and Hendrickson's<sup>9</sup> calculations on medium-sized rings are in general agreement.

(5) P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1854, 1856 (1964); P. von R. Schleyer, W. E. Watts, and C. Cupas, *ibid.*, **86**, 2722 (1964).

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

(7) J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961).

(8) K. B. Wiberg, *ibid.*, **87**, 1070 (1965).

(9) J. B. Hendrickson, *ibid.*, **86**, 4854 (1964).

Allinger and co-workers<sup>10,11</sup> have further applied this approach in conjunction with molecular orbital calculations. The strain for the underlying  $\sigma$  framework of several conjugated  $\pi$  systems has been determined. It has been shown that the planar geometry favored by the  $\pi$  system may not in fact be encountered because of strain associated with the  $\sigma$  portion of the molecule in such an arrangement. Inclusion of these strain effects has led to results which are in agreement with ultraviolet spectral data.

Garbisch has correlated strain effects with both equilibrium<sup>12</sup> and rates<sup>13</sup> of reaction. Although not conforming completely to the Westheimer methodology, this study represents the first modern truly quantitative application of conformational analysis to a kinetics problem. The reaction considered was the diimide reduction of olefins. Over 40 compounds of varying structural type were examined. Although the relative reactivities vary over a range of 3800, extraordinarily good agreement was obtained between experimental and calculated rates. The major departure from the standard Westheimer approach was the use of a disposable parameter to define the optimal geometry of the transition state. This is, however, a reasonable assumption which the final results seem to justify.

The reaction chosen in the present paper for analysis is the solvolysis of a series of polycyclic bridgehead bromides, in which there has long been interest. In 1939, Bartlett and Knox<sup>14</sup> noted that the bridgehead positions in bicyclic systems were inert toward nucleophilic attack. It was pointed out that study of such systems could yield important information on the preferred geometries of transition states. Bridgehead reactivities have since been the subject of much investigation; comprehensive reviews are available.<sup>15-17</sup>

By means of a crude strain analysis, Schleyer and Nicholas<sup>18</sup> accounted for the alteration of rates of solvolysis along a series of bridgehead derivatives. Rate differences between *t*-butyl and polycyclic bridgehead systems were semiquantitatively attributed to increases of angle strain in passing from ground to transition state. Of course, carbonium ions cannot readily assume a planar conformation at the bridgehead positions. The large ( $10^3$ ) difference in rates between 1-bicyclo[2.2.2]octyl and 1-adamantyl bromides cannot be explained on the basis of angle strain alone, as the geometries of the two systems are virtually identical at the reaction site.<sup>18</sup> Although other explanations for this 5000-fold difference were considered,<sup>18-20</sup> the most attractive rationalization was based on nonbonded strain considerations. In 1-bicyclo[2.2.2]octyl bromide alone the bridgehead carbon atoms 1 and 4 approach

(10) N. L. Allinger, M. A. Miller, L. W. Chow, R. A. Ford, and J. C. Graham, *ibid.*, **87**, 3430 (1965).

(11) N. L. Allinger, *Tetrahedron*, **22**, 1367 (1966).

(12) E. W. Garbisch, Jr., *J. Am. Chem. Soc.*, **87**, 505 (1965).

(13) E. W. Garbisch, Jr., S. M. Schilcrout, D. B. Patterson, and C. M. Sprecher, *ibid.*, **87**, 2932 (1965).

(14) P. D. Bartlett and L. H. Knox, *ibid.*, **61**, 3184 (1939).

(15) D. E. Applequist and J. D. Roberts, *Chem. Rev.*, **54**, 1065 (1954).

(16) U. Schöllkopf, *Angew. Chem.*, **72**, 147 (1960).

(17) R. C. Fort, Jr., and P. von R. Schleyer, *Advan. Alicyclic Chem.*, **1**, 283 (1966).

(18) P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 2700 (1961).

(19) R. C. Fort, Jr., and P. von R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).

(20) R. C. Fort, Jr., and P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 4194 (1964).

one another closely even in the ground state, and flattening on going to the carbonium ion is hindered.

As both angle strain and nonbonded interactions are included implicitly in eq 1, a full machine strain calculation might verify these conclusions. It seemed desirable to us to make the attempt, and the results are reported in the present paper.

### Approach and Choice of Parameters

To use the basic Westheimer approach, it is first necessary to calculate the ground-state energies of the molecules of interest. The solvolysis transition-state energies next must be estimated, using some reasonable model for the transition state. In the present work, the energies of the carbonium ion intermediates themselves have been calculated, it being assumed that the transition-state energies are proportional thereto. For the series of related tertiary compounds here considered, this assumption does not appear to be unreasonable. In such a series of compounds of similar structural type it is further possible that differences in inductive and other electrical effects, solvation, and entropy effects should be so small as not to cause significant perturbation,<sup>17-20</sup> thus reducing the problem to strictly steric terms. Explicitly, calculated energy differences between bridgehead bromides and the corresponding cations are to be compared with experimentally determined solvolysis rates. This, at least, is a necessary first step in the solution of the problem of quantitative assessment of the relationship between structure and carbonium ion reactivity.

In theory, the parameters making up the various terms of eq 1 will be different for different combinations of atoms. In order to analyze bromide substrates conformationally it is necessary to know constants for carbon-bromine and hydrogen-bromine nonbonded interactions as well as carbon-bromine stretching and carbon-carbon-bromine bending force constants. At present, many of these are unknown, or are of poor reliability, and so an immediate impasse is reached. This ignorance may not be an insurmountable obstacle. The relative rates of solvolysis for many bridgehead compounds seem somewhat independent of the nature of the leaving group,<sup>21</sup> suggesting that a rather large assumption can be made. If the leaving group is generally unimportant, hydride may be a good model for bromide. The parent hydrocarbon will therefore be considered as the ground state, rather than the corresponding bromide.<sup>22</sup>

Although we are now limited, as were past workers, to systems containing hydrogen and carbon, it is still desirable to elaborate on the various functions making up the terms in eq 1. It is also necessary to decide which, of any, of these terms will require modification owing to the presence of a positively charged carbon atom in the carbonium ion.

(21) See ref 17-19 for tables of the rates of bromide and tosylate solvolysis.

(22) For the compounds considered in this study, this should be a very good approximation. Since both hydride and bromide are non-atomic, there will be no deformations within the leaving group. The number of stretching and bending modes concerning this atom are the same in all compounds studied here and should cancel out. The major difference will be in the nonbonded interactions. However, because of the general geometry of these molecules, in which the leaving group is nicely directed away from the remainder of a rigid system, few, if any unfavorable repulsions should be present and only slight differences, between bromine and hydrogen should arise.

**Bond Stretching or Compression.** It might be expected from the results of Hendrikson<sup>7,9</sup> that bond deformation should be relatively unimportant in both the ground state and the transition state. The energy associated with a change of bond length from its equilibrium value is given by eq 2. The values of the equilib-

$$E_{\text{bond length strain}} = (k/2)(r - r_e)^2 \quad (2)$$

rium bond length,  $r_e$ , for  $sp^3$ - $sp^3$  carbon-carbon and  $sp^3$  carbon-hydrogen bonds are taken as 1.533 and 1.108 Å, respectively.<sup>7</sup> The stretching force constants  $k$  are almost identical and the value of  $5 \times 10^5$  dynes/cm used by Wiberg<sup>8</sup> was employed. Values of  $k$  and  $r_e$  must also be obtained for the carbon-carbon bonds at the positively charged center. The positively charged carbon should be in an  $sp^2$ -hybridization state. A shortening in bond length on going from an  $sp^3$ - $sp^3$  to an  $sp^3$ - $sp^2$  carbon-carbon bond is to be expected; a value of  $1.501 \pm 0.004$  Å has been suggested as a representative length based upon several accurate measurements.<sup>23</sup> The effect of a positive charge on the trigonal carbon must also be considered. X-Ray structure determinations on stable (conjugated) carbonium ions show C-C<sup>+</sup> ( $sp^2$ - $sp^2$ ) bond lengths of 1.40-1.45 Å.<sup>24</sup> These values are shorter than those for uncharged  $sp^2$ - $sp^2$  carbon-carbon bonds. It is likely that a comparable shortening for C<sup>+</sup>-C ( $sp^3$ - $sp^2$ ) bonds also occurs; an approximate value of 1.480 Å was chosen for our calculations. The force constant for a carbon-carbon bond of this length ( $k = 7.17 \times 10^5$  dyne/cm) was found utilizing eq 3, empirically developed by Dewar and Schmeising.<sup>25</sup>

$$k = -46.978r_e^{-2} + 194.813r_e^{-4} - 136.486r_e^{-6} \quad (3)$$

Because of the relatively large values of these bond deformation force constants bond lengths should not appreciably deviate from their equilibrium values.<sup>6</sup> Molecules should rather prefer to relieve strain *via* angle deformation, an energetically more favorable process. Rough calculations show, for example, that it requires about 70 times more energy to remove the unfavorable hydrogen-hydrogen interaction in phenanthrene *via* bond deformation than *via* angle deformation.<sup>26</sup>

**Torsional Strain.** Although several hypotheses have been suggested, the exact cause of torsional strain in molecules is not understood.<sup>27</sup> Despite this, a simple relationship exists which allows for calculation of this quantity (eq 4)

$$E_{\text{torsional strain}} = (V_0/2)(1 + \cos 3\Phi) \quad (4)$$

where  $V_0$  is the height of the barrier to rotation and  $\Phi$  is the dihedral angle. For any substituted ethane,  $V_0$  will have a value of  $\sim 3.0$  kcal/mole. A symmetrical or

(23) D. H. Lide, Jr., *Tetrahedron*, **17**, 125 (1962).

(24) (a) R. F. Bryan, *J. Am. Chem. Soc.*, **86**, 733 (1964); (b) M. Sundaralingham and L. H. Jensen, *ibid.*, **85**, 3302 (1963); **88**, 198 (1966); (c) A. H. Gomes de Mesquita, C. H. MacGillavry, and K. Eriks, *Acta Cryst.*, **18**, 437 (1965).

(25) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **11**, 96 (1960).

(26) S. Senent and M. A. Herraes, *Anal. Fis. Quim.*, **53B**, 257 (1957).

(27) E. B. Wilson, Jr., *Advan. Chem. Phys.*, **2**, 367 (1959); *cf.*, however, W. H. Fink and L. C. Allen, *J. Chem. Phys.*, in press; J. P. Lowe and R. G. Parr, *J. Chem. Phys.*, **44**, 3001 (1966); J. P. Lowe, *ibid.*, **45**, 3059 (1966); R. A. Scott and H. A. Scheraga, *ibid.*, **44**, 3054 (1966); E. Clementi and D. R. Davis, *ibid.*, **45**, 2593 (1966); J. Dale, *Tetrahedron*, **22**, 3373 (1966).

even a nearly symmetrical arrangement of groups around adjacent carbon atoms will not often be found in the distorted cyclic systems considered here. It would therefore be incorrect to use a single dihedral angle to define the situation about this bond. We have adopted Wiberg's suggestion that separate bond interactions be used rather than a single simple group interaction. There will be nine such bond interactions for an  $sp^3$ - $sp^3$  carbon-carbon bond and six for an  $sp^3$ - $sp^2$  carbon-carbon bond. Modifying the potential energy barrier accordingly yields eq 5, where  $\Phi_i$  signifies a single bond interaction.

$$E_{\text{torsional strain}} = \sum_i 0.1667(1 + \cos 3\Phi_i) \quad (5)$$

The use of this relationship and the concept of "bond torsional energies" rather than "group torsional energies" also simplifies matters in describing the interactions about a positively charged center. Single bonds involving one tricoordinate and one tetra-coordinate carbon can be discussed by considering the three limiting conformations shown in Figure 1. Carbonium ions usually can be planar as in A (covalent models for this case would be toluene,  $\text{CH}_3\text{BF}_2$ ,  $\text{CH}_3\text{CO}_2^-$ , and  $\text{CH}_3\text{NO}_2$ ), but if they are constrained owing to incorporation in a rigid cyclic system, extreme conformations B and B' are possible (a covalent model is  $\text{CH}_3\text{NH}_2$ , if the lone pair is neglected). The torsional strains for these three conformations are different: for A, 1.0 kcal/mole, for B', 2.0 kcal/mole, but B is without such strain.

The barriers to rotation differ between the planar and nonplanar carbonium ion classes. If the carbonium ion center is planar (A) and the substituents are equivalent, then the barrier to rotation should be negligibly small.<sup>5</sup> This is a consequence of the sixfold nature of the barrier; when one  $\text{C}^+\text{-H}$  bond is eclipsed, the other is staggered. Experimentally, sixfold barriers are observed to be of the order of only 6-12 cal/mole.<sup>27-30</sup> This leads to the important conclusion that all planar carbonium ions of a given substitution type should have the same degree of torsional strain around the positive carbon, independent of the torsional angles involved.<sup>5</sup> Since, on the average, one bond is eclipsed per substituent, planar carbonium ions are not torsionally strain free. For example, the torsional strain in the planar *t*-butyl cation is 3.0 kcal/mole, 1.0 kcal/mole for each of the three methyl substituents.

Because of the fixed geometry encountered in cyclic systems, there may be a large decrease of torsional energy upon solvolysis.<sup>5</sup> This was first pointed out by Brown<sup>3,31</sup> as part of his "I-strain" concept. Although the concept of "bond oppositions" was used, only the bonds external to rings were considered. In other words, planar cyclopentane was said to have ten "bond oppositions," not 15 as would be the present

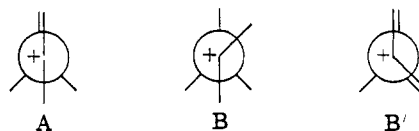


Figure 1. Rotational conformations of planar and nonplanar carbonium ions.

viewpoint.<sup>5,7,8,27-29</sup> Torsional barriers, to a first approximation, do not vary with substituents.<sup>27</sup> Torsional strain should depend, therefore, only on the dihedral angles, and not on the presence or absence of the system in a ring.

A different torsional situation should be present in systems incorporating a nonplanar carbonium ion. If, for illustration, tetrahedral angles are assumed as in Figure 1, B and B', then the rotational barrier should be 2.0 kcal/mole. B', the conformation of maximum energy, has two bonds in opposition, while in B there are none. The vacant orbital is assumed to play no role in determining the torsional energy. In methylamine, the barrier to rotation is very nearly 2.0 kcal/mole.<sup>27,29</sup> This is about the best model available, despite the presence of the extra lone-pair electrons. A good case can be made that such electrons do not affect rotational barriers, for along the series  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{NH}_2$ , and  $\text{CH}_3\text{CH}_3$  (barriers 1, 2, and 3 kcal/mole, respectively) only the number of opposed bonds seem to be important. This is a much more complicated question that such simple arguments indicate,<sup>27</sup> but nothing is known experimentally about energy barriers in simple carbonium ions, let alone distorted ones, and our arguments seem reasonable enough in light of present knowledge.

Torsional strain differences between planar and nonplanar carbonium ions lead to important consequences, which have not been appreciated before. These can be illustrated by the bridgehead 1-adamantyl cation. In the nonplanar conformation (approximated by Figure 1, B) there will be no torsional strain, but with the cation planar (A), this strain will be 3.0 kcal/mole. Of course, angle strain considerations favor the planar species, but these are opposed by torsional strain which favors nonplanar conformation B.

**Nonbonded Interactions.** The nonbonded interaction terms will be composed of both a repulsive and an attractive component. The attractive component, arising from London dispersion forces, is usually taken as a function of the inverse sixth power of the internuclear separation. The values determined by Pitzer and Catalano<sup>32</sup> are generally used. More controversial are the functions to be used for the repulsive potential. These are functions of either the inverse twelfth power of internuclear distance or an exponential function. The potentials used by most workers<sup>5,7,9,12-16</sup> have been obtained by modifying the repulsive functions for helium-helium and neon-neon interactions obtained from scattering experiments<sup>33</sup> to hydrogen-hydrogen and carbon-carbon interactions, respectively. The carbon-hydrogen function is found by interpolation. These functions are rather "soft," in that interactions between nonbonded atoms are not large at the distances normally encountered in organic molecules.

(32) K. S. Pitzer and E. Catalano, *ibid.*, **78**, 4844 (1956).

(33) I. Amdur and A. L. Harkness, *J. Chem. Phys.*, **22**, 644 (1954); I. Amdur and E. A. Mason, *ibid.*, **23**, 415 (1955).

(28) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(29) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965.

(30) Compare recent discussion of toluene by W. R. Woolfenden and D. M. Grant, *J. Am. Chem. Soc.*, **88**, 1496 (1966); for  $\text{C}_3\text{FNO}_2$ , see W. M. Tolles, E. T. Handelman, and W. D. Gwinn, *J. Chem. Phys.*, **43**, 3019 (1965).

(31) (a) H. C. Brown, R. S. Fletcher, and R. B. Johannessen, *ibid.*, **73**, 212 (1951); (b) H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952).

It is by no means certain whether inert gases provide a suitable model for the atoms in question.<sup>6</sup> Even if they be suitable models, however, there is still a valid question over whether functions derived for free atoms may accurately describe atoms when incorporated into molecules. In molecules the spherical symmetry possessed by a free atom is no longer present. Also, forces, rather than acting through empty space, may be strongly influenced by the effective dielectric constant of the molecule itself.

Other, "harder," sets of functions exist in the literature.<sup>34-36</sup> Those developed by Bartell<sup>34</sup> were selected, because they are based empirically on the behavior of atoms in molecules. The opinion that the nonbonded functions used to date are not satisfactory has been reached by another worker in the field.<sup>37</sup> The actual functions employed here are given in eq 6-8.

$$E_{C-C} = 3.0 \times 10^5/r^{12} - 325.0/r^6 \quad (6)$$

$$E_{C-C} = 38,075 \exp(-4.21r) - 125.0/r^6 \quad (7)$$

$$E_{H-H} = 6600 \exp(-4.08r) - 49.6/r^6 \quad (8)$$

A recent attempt has been made by Simmons and Williams<sup>36</sup> to calculate the repulsive portion of the hydrogen-hydrogen interaction term. The empiricism of this approach results in an excellent estimation of rotational barriers. The repulsion potential determined by these workers is even "harder" than that given in eq 8. This may well be another indication that the Amdur<sup>33</sup> potentials previously used<sup>7-11</sup> may be inadequate.

In summing up all the nonbonded interactions, those of a 1-3 type were neglected. Bartell<sup>34</sup> has pointed out that in effect these interactions have been tacitly included in the term describing angle strain. This is almost equally true for deformation to angles smaller or larger than the preferred value, since the distance between groups in a 1,3 relationship is almost always smaller than the sum of their van der Waal's radii. Harmonicity is not to be expected in angle bending. Even in the most favorable cases commonly encountered, inclusion of 1,3 interactions would lead to results widely at variance with experiment.

It is difficult to decide if new functions should be used to describe interactions with the positively charged carbon. Such an atom should be smaller in size; consequently, the repulsive interaction component might well be lessened. However, charge-dipole interactions may well mitigate against this. If the positive end of the C-H bond dipole is, as seems likely, on the carbon atom,<sup>38</sup> then the repulsion between some "normal" carbon atom bearing a small increment of positive charge and a fully charged, trigonal carbon will be much greater than between two "normal" carbons. Conversely there will be a strong attraction between the positively charged carbon and all hydrogens in the molecule. In view of our present state of ignorance regarding these matters, the same functions will be

(34) L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960).

(35) E. A. Mason and M. M. Kreevoy, *J. Am. Chem. Soc.*, **77**, 5808 (1955).

(36) H. E. Simmons and J. K. Williams, *ibid.*, **86**, 3222 (1964).

(37) N. L. Allinger, private communication; also see D. E. Williams, *J. Chem. Phys.*, **45**, 3770 (1966).

(38) See D. R. Lide, Jr., *ibid.*, **33**, 1514 (1960), for a discussion of the dipole moment of propane. Also, V. W. Laurie and J. S. Muentzer, *J. Am. Chem. Soc.*, **88**, 2883 (1966).

used for charged carbon atoms as employed for uncharged ones.

**Angle Strain.** The strain associated with bond angle bending may readily be calculated from eq 9.

$$E_{\text{angle strain}} = (k/2)(\tau - \theta)^2 \quad (9)$$

where  $k$  is the bending force constant,  $\tau$  the "normal" equilibrium value for the type of angle in question, and  $\theta$  is the actual value of the angle. For the ground state,  $\tau$  is usually assigned the tetrahedral value; however, small differences from this value for different substitution patterns may be resorted to.<sup>39</sup> Table I below lists the value of  $k/2$ <sup>40</sup> and  $\tau$ <sup>41</sup> used in this study.

Table I. Equilibrium Angles and Bending Force Constants

Angle	$\tau$ , deg	$k/2$ , kcal/mole radian <sup>2</sup>	
C-C-C	109.5 <sup>39</sup>	56.5	(70.5) <sup>a</sup>
C-C-H	108.7	39.6	(37.9) <sup>a</sup>
H-C-H	111.0 <sup>39</sup>	23.0	(22.1) <sup>a</sup>

<sup>a</sup> Average values of Shachtschneider and Snyder.<sup>42</sup>

Recently, extensive normal coordinate calculations by Shachtschneider and Snyder<sup>42</sup> on the infrared spectra of paraffins have led to new values for force constants. Their values for bending force constants (Table I) are in good agreement with those reported above. Their value for C-C-C bending is somewhat larger than that used here, but the values for C-C-H and H-C-H bending are nearly identical. The older values are used here, mostly for the sake of continuity with previous calculations.<sup>8,41</sup> For small angular deviations, not much error is introduced thereby. For large angular deviations, neither value is satisfactory, and a smaller one is preferable.

The selection of a bending force constant for the C-C<sup>+</sup>-C angle encountered at the reaction site posed the most difficult problem in this work. The force constants for C<sup>+</sup>-C-C and C<sup>+</sup>-C-H angles should be nearly identical with those of their uncharged analogs. The C-C<sup>+</sup>-C case is, however, nowhere as trivial. It is generally agreed that carbonium ions should tend strongly toward planarity with angles between substituents equal to 120°. Physical measurements on simple acyclic carbonium ions, such as *t*-butyl, have substantiated this view.<sup>43</sup> This, in itself, gives no aid in determination of the force constant. Unfortunately, unlike the case for bond stretching, there exists no simple relationship between bending force constant and atom hybridization (or some related property such as covalent radius or electronegativity).<sup>44</sup> Choice of the parameter to be used involves a good deal of intuition. The simplest approach would be to presume that the bending force constant for C-C-C angles is unaffected by changes in hybridization and charge

(39) In particular, for the C-CH<sub>2</sub>-C angle there is debate whether to use the tetrahedral value of 109.5° for the "normal" angle, or value 112.4° found experimentally for numerous hydrocarbons.<sup>39</sup> A similar problem exists for H-C-H angles.

(40) G. Herzberg, "Infra-Red and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945.

(41) H. A. Harris, Ph.D. Thesis, Yale University, 1966.

(42) J. H. Shachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963).

(43) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Am. Chem. Soc.*, **86**, 1360 (1964).

(44) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934).

distribution.<sup>45</sup> An alternate view has been advanced by Gillespie and Nyholm<sup>46</sup> and elaborated by Fort and Schleyer.<sup>17</sup> In going from an  $sp^3$  to an  $sp^2$  carbon there will be an increase in electronegativity. The electrons comprising the bonds to the attached groups will be drawn in closer to the central atom and hence to each other. Any distortion from the optimal planar arrangement will require greater energy in the carbonium ion than in the  $sp^3$  case because of the closer proximity of the bonding electron pairs in the former. A greater force constant must be present if the central carbon in a C-C-C angle is  $sp^2$ . The further effect of placing a positive charge on this atom should be to magnify the above and enhance the force constant even more. Some substantiation for the hybridization effects noted above may be found in the literature. The bending force constant for C=C-H is *ca.* 24% greater than for C-C-H,<sup>40</sup> while that for benzene is *ca.* 60% greater.<sup>47</sup> The additional presence of a positive charge might be expected to increase the force constant several fold. It is probably safe to assume that various C-C-C angles will behave in a manner similar to the C-C-H angles noted above.

A third possibility is that the bending force constant may be weaker in the carbonium ion. Davis,<sup>48</sup> utilizing Hoffmann's<sup>49</sup> extended Hückel method, has calculated that bending force constants in the planar methyl cation would be weaker than in methane itself.

Because of the uncertainty concerning the magnitude of the C-C<sup>+</sup>-C force constant, it was decided to proceed in an empirical manner. This force constant was systematically varied in our calculations and the effect of such variations assessed.

**Hybridization Effects.** Although not implicitly included in strain energy calculations, hybridization effects represent a closely related phenomenon. Some years ago, Kimble<sup>50</sup> calculated that a planar carbonium ion should be some 24 kcal/mole more stable than a tetrahedral one. This value was one-quarter of the energy needed to promote an electron from a 2s to a 2p orbital. The promotional energy of several positively charged carbon species have subsequently become available.<sup>51</sup> The difference in promotional energy between a tetrahedrally and a trigonally hybridized positively charged carbon is 3.233 eV (74.53 kcal/mole). It is possible that this entire energy can be equated with that needed to bend three bonds from 120 to 109.5°. If so, a value of  $k/2$  equal to 790.0 kcal/mole radian<sup>2</sup> must be invoked. This is nearly 14 times that of the corresponding saturated C-C-C value! This is most likely too large a value, for upon deformation some energy may be used to compress the bond lengths of attached groups. There may also be an inherent energy associated with quantum mechanical considerations which cannot be equated to any classical interactions. Despite the inadvisability of utilizing this entire difference in promotional energies to define a bending

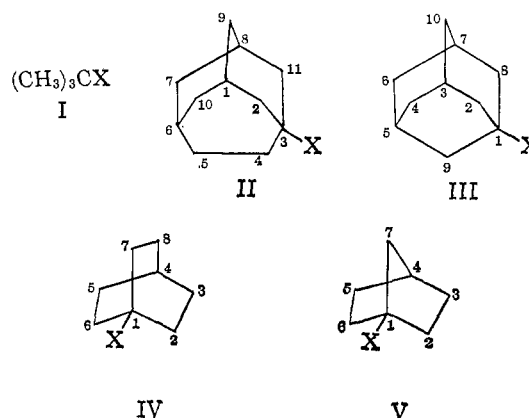
force constant, it may be considered as more or less of a hypothetical upper limit.

## Calculations

The strain energies of both the ground-state hydrocarbons and the carbonium ions considered as the transition state were calculated utilizing programs developed by Wiberg<sup>8</sup> and Harris.<sup>41</sup> An assumed initial geometry for each system served as input data. A strain energy was calculated for this geometry, and the coordinates of each atom were altered until an energy minimum was reached. Variation of coordinates was carried out in two different ways, along Cartesian coordinates or along the four bonds connected to a tetrahedral carbon. Only slight modification of the Wiberg-Harris program was needed to handle trigonal carbon atoms. All calculations were carried out at the Princeton University Computation Center utilizing an IBM 7094 computer.

## Results

The reaction chosen for study was the solvolysis of a series of bridgehead bromides (I-V, X = Br) at 25° in 80% ethanol. The corresponding hydrocarbons (I-V, X = H) were chosen as models for the ground states, following the arguments detailed above. Table II



summarizes the terms contributing to the ground-state energies of these systems.

**Table II.** Ground-State Strain<sup>a</sup>

	Iso-butane	Homo-adamantane	Adamantane	Bicyclo-[2.2.2]-octane	Norbornane
Bond strain	0.068	0.309	0.123	0.255	0.329
Angle strain	0.129	7.449	0.282	0.308	15.025
Torsional strain	0.000	6.253	0.002	9.004	8.921
Nonbonded interactions	0.549	-0.396	1.249	2.951	1.432
Total strain	0.746	13.615	1.656	12.518	25.707

<sup>a</sup> In kcal/mole.

"Strain" (*i.e.*, a net unfavorable energy) was indicated even in the ground states of isobutane and of adamantane, mostly attributable to nonbonded interactions.<sup>52</sup>

(52) As usually defined, "strain" is the difference in energy between a molecule of interest and some other "strain-free" model substance. In absolute terms, all molecules may be strained. Thus, isobutane and adamantane can be considered to be "strained" or "strainless," depending on the point of view.

(45) H. J. Dauben, Jr., cited by M. E. H. Howden and J. D. Roberts, *Tetrahedron, Suppl.*, **2**, 404 (1963).

(46) R. J. Gillespie and R. S. Nyholm, *Quart. Rev.* (London), **11**, 339 (1957).

(47) K. W. F. Kohlrausch, *Z. Phys. Chem.*, **B30**, 305 (1935).

(48) R. E. Davis, personal communication; R. E. Davis and A. Ohno, *Tetrahedron*, in press.

(49) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963), and subsequent papers.

(50) G. E. Kimble, quoted in W. Von E. Doering, M. Levitz, A. Sayigh, M. Sprecker, and W. P. Whelan, Jr., *J. Am. Chem. Soc.*, **75**, 1008 (1953).

(51) J. Hinze and H. H. Jaffé, *ibid.*, **84**, 540 (1962).

These interactions are particularly noticeable in the bicyclo[2.2.2]octane where the distance between bridgehead carbons 1 and 4 (2.592 Å) is less than the sum of the van der Waal's radii. Generally speaking, the ground-state strain energies are reasonable with the possible exception of that for norbornane. The calculated value of 25.71 kcal/mole is appreciably higher than the experimental value of 18.5 kcal/mole.<sup>53</sup> Use of the Shachtschneider and Snyder<sup>42</sup> values of the bending force constants would increase the calculated value. Undoubtedly this discrepancy with experiment lies in the fact that the simple harmonic form of the angle deformation function must break down for large displacement from the desired angle.<sup>6,45</sup> A case in point is that of cyclobutane where, even allowing for ring puckering, the calculated strain using the functions here adopted is still 8–10 kcal/mole greater than the experimental value of 26.2 kcal/mole. Use of interorbital angles in place of interatomic angles would be one approach at solution of this problem,<sup>54</sup> but these angles are not experimentally assessable.

Our calculated ground-state geometries are given in Table III. Some experimental structural data exist in the literature to allow comparison. Information on the structure of isobutane is available from microwave spectroscopy.<sup>55</sup> The average deviation between the calculated angles and the experimental values is about 1°. The average deviation in bond lengths is less than 0.01 Å. Structure determinations on adamantane by electron diffraction<sup>56</sup> and X-ray<sup>57</sup> techniques yield results which, though of poor precision, are in accord with the calculated value presented here. All carbon-carbon bonds are  $1.54 \pm 0.01$  Å and all C–C–C angles  $109.5 \pm 2^\circ$ . This is not a critical example.

The structure of norbornane has been calculated several times in the literature.<sup>58</sup> Experimental values for the parent hydrocarbon<sup>59</sup> and derivatives<sup>60</sup> are also available. The various values obtained are in reasonable agreement with our calculations (Table III). Wilcox<sup>58</sup> has pointed out that drastic changes in parameters do not make much difference in the final structures computed for norbornane.

No detailed structure determinations have been carried out for the other two molecules considered. Our calculations on bicyclo[2.2.2]octane favor the structure having  $D_{3h}$  symmetry. This is contrary to the conclusion of Turner, Meador, and Winkler<sup>61</sup> who favored

(53) A. F. Bedford, A. E. Beezer, C. T. Mortimer, and H. D. Springall, *J. Chem. Soc.*, 3823 (1963).

(54) K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965.

(55) D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **29**, 914 (1958); D. R. Lide, Jr., *ibid.*, **33**, 1519 (1960).

(56) W. Nowacki and K. W. Hedberg, *J. Am. Chem. Soc.*, **70**, 1497 (1948).

(57) G. Giacomelli and G. Illuminati, *Gazz. Chim. Ital.*, **75**, 246 (1945).

(58) (a) H. Krieger, *Suomen Kemistilehti*, **B31**, 348 (1958); **B32**, 109 (1959); (b) C. F. Wilcox, Jr., *J. Am. Chem. Soc.*, **82**, 414 (1960); (c) A. I. Kitaygorodsky, *Tetrahedron*, **9**, 183 (1960); **14**, 230 (1961).

(59) By electron diffraction: V. Schoemaker and W. C. Hamilton, unpublished data; W. C. Hamilton, Ph.D. Thesis, California Institute of Technology, 1954.

(60) By X-ray analysis: (a) G. Ferguson, C. J. Fritchie, J. M. Robertson, and G. A. Sim., *J. Chem. Soc.*, 1976 (1961); (b) D. A. Bruechner, T. A. Hamer, J. M. Robertson, and G. A. Sim, *ibid.*, 799 (1962); (c) A. F. Cesur and D. F. Grant, *Acta Cryst.*, **18**, 55 (1965); (d) A. C. MacDonald and J. Trotter, *ibid.*, **18**, 243 (1965); (e) *ibid.*, **19**, 456 (1965).

(61) R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Am. Chem. Soc.*, **79**, 4166 (1957); *cf.*, also, J. B. Hendrickson, *Chem. Eng. News*, **39**, 40 (Nov 20, 1961).

Table III. Calculated and Experimental Structures for Hydrocarbons<sup>a</sup>

	Bond lengths or angles <sup>a</sup>	
	Calcd	Exptl
(CH <sub>3</sub> ) <sub>3</sub> CH <sup>b</sup>		
C–C	1.540	1.525
C <sub>1</sub> –H	1.109	1.108
C <sub>2</sub> –H	1.107	1.100
C <sub>1</sub> –C <sub>2</sub> –H	109.5	108.0
C–C–C	109.6	111.1
C <sub>2</sub> –C <sub>1</sub> –H	109.1	109.4
H–C <sub>1</sub> –H	109.8	108.5
Adamantane (III, X = H) <sup>c</sup>		
C–C	1.537	1.54 ± 0.01
C <sub>1</sub> ··C <sub>4</sub>	2.945	
C <sub>2</sub> ··C <sub>5</sub>	2.941	
C <sub>2</sub> ··C <sub>6</sub>	3.541	
C–C–C	109.5	109.5 ± 2
Norbornane (V, X = H) <sup>d</sup>		
C <sub>1</sub> –C <sub>2</sub>	1.543	All C–C 1.555
C <sub>2</sub> –C <sub>3</sub>	1.547	
C <sub>1</sub> –C <sub>7</sub>	1.531	
C <sub>2</sub> ··C <sub>5</sub>	2.911	
C <sub>2</sub> –C <sub>1</sub> –C <sub>7</sub>	102.6	99.7
C <sub>2</sub> –C <sub>7</sub> –C <sub>6</sub>	106.1	105.2
C <sub>1</sub> –C <sub>2</sub> –C <sub>3</sub>	102.9	104.2
C <sub>1</sub> –C <sub>7</sub> –C <sub>4</sub>	93.9	96.3
Bicyclo[2.2.2]octane (IV, X = H) <sup>e</sup>		
C <sub>1</sub> –C <sub>2</sub>	1.540	
C <sub>2</sub> –C <sub>3</sub>	1.543	
C <sub>1</sub> ··C <sub>4</sub>	2.592	
C <sub>2</sub> ··C <sub>5</sub>	2.944	
C <sub>2</sub> –C <sub>1</sub> –C <sub>7</sub>	109.0	
C <sub>1</sub> –C <sub>2</sub> –C <sub>3</sub>	109.9	
	Calcd bond length <sup>a</sup>	Calcd bond angle <sup>a</sup>
Homoadamantane (II, X = H)		
C <sub>3</sub> –C <sub>4</sub>	1.541	C <sub>2</sub> –C <sub>3</sub> –C <sub>4</sub> 113.9
C <sub>4</sub> –C <sub>5</sub>	1.536	C <sub>2</sub> –C <sub>3</sub> –C <sub>11</sub> 113.2
C <sub>2</sub> –C <sub>3</sub>	1.544	C <sub>3</sub> –C <sub>4</sub> –C <sub>5</sub> 117.8
C <sub>1</sub> –C <sub>2</sub>	1.539	C <sub>1</sub> –C <sub>2</sub> –C <sub>3</sub> 113.3
C <sub>1</sub> –C <sub>9</sub>	1.535	C <sub>2</sub> –C <sub>1</sub> –C <sub>10</sub> 111.2
C <sub>8</sub> ··C <sub>6</sub>	2.973	C <sub>2</sub> –C <sub>1</sub> –C <sub>9</sub> 110.4
		C <sub>1</sub> –C <sub>9</sub> –C <sub>8</sub> 109.1
Bicyclo[3.3.1]nonane (VII, X = H) <sup>f</sup>		
C <sub>1</sub> –C <sub>2</sub>	1.532	C <sub>2</sub> –C <sub>1</sub> –C <sub>8</sub> 109.9
C <sub>2</sub> –C <sub>3</sub>	1.540	C <sub>2</sub> –C <sub>1</sub> –C <sub>9</sub> 112.0
C <sub>2</sub> –C <sub>9</sub>	1.539	C <sub>1</sub> –C <sub>2</sub> –C <sub>3</sub> 113.0
C <sub>8</sub> ··C <sub>7</sub>	2.960	C <sub>2</sub> –C <sub>3</sub> –C <sub>4</sub> 113.5
		C <sub>1</sub> –C <sub>9</sub> –C <sub>5</sub> 106.0
Bicyclo[3.2.1]octane (VIII, X = H)		
C <sub>1</sub> –C <sub>2</sub>	1.536	C <sub>2</sub> –C <sub>1</sub> –C <sub>7</sub> 110.6
C <sub>2</sub> –C <sub>3</sub>	1.550	C <sub>2</sub> –C <sub>1</sub> –C <sub>8</sub> 107.5
C <sub>1</sub> –C <sub>7</sub>	1.543	C <sub>7</sub> –C <sub>1</sub> –C <sub>8</sub> 113.8
C <sub>6</sub> –C <sub>7</sub>	1.548	C <sub>1</sub> –C <sub>2</sub> –C <sub>3</sub> 111.3
C <sub>2</sub> –C <sub>8</sub>	1.530	C <sub>2</sub> –C <sub>3</sub> –C <sub>4</sub> 113.2
C <sub>8</sub> ··C <sub>6</sub>	2.939	C <sub>1</sub> –C <sub>7</sub> –C <sub>6</sub> 105.4
		C <sub>2</sub> –C <sub>8</sub> –C <sub>5</sub> 101.4

<sup>a</sup> Bond lengths in angstrom units, angles in degrees. <sup>b</sup> Experimental values from ref 55. <sup>c</sup> See ref 56 and 57. <sup>d</sup> See ref 59; *cf.* 58 and 60. <sup>e</sup> See ref 61–63. <sup>f</sup> See ref 73 and 74.

a structure (point group C<sub>3</sub>) twisted about the threefold axis of symmetry through C-1 and C-4. They felt that such a twisted structure should relieve some of the unfavorable torsional strain in the system. It has been pointed out that<sup>11</sup> the total torsional strain in the molecule may actually be adversely affected by such a deformation. The twisted molecule must also have a shorter C<sub>1,4</sub> internuclear distance, thus increasing the already appreciable nonbonded repulsions in this

Table IV. Carbonium Ion Strain Energies

Cation	Strain in kcal/mole for values of $k/2$ C-C <sup>+</sup> -C, kcal/mole radian <sup>2</sup>					
	28.75	57.50	115.0	230.0	345.0	790.0
<i>t</i> -Butyl	3.600	3.600	3.600	3.600	3.600	3.600
3-Homoadamantyl	12.485	12.702	13.149	13.848	14.311	15.468
1-Adamantyl	6.183	7.319	9.236	11.818	13.660	17.662
1-Bicyclo[2.2.2]octyl	17.477	19.117	21.940	25.452	27.885	33.186
1-Norbornyl	31.658	36.355	43.026	50.096	54.360	61.448

Table V. Strain Energy Differences (Carbonium Ions-Hydrocarbons)

System	Rel rate, 25 <sup>o</sup> <sup>a</sup>	Strain in kcal/mole for $k/2$ C-C <sup>+</sup> -C, kcal/mole radian <sup>2</sup>					
		28.75	57.50	115.0	230.0	345.0	790.0
<i>t</i> -Butyl	1.00	2.854	2.854	2.854	2.854	2.854	2.854
1-Homoadamantyl	$4.58 \times 10^{-1}$	-1.130	-0.913	-0.466	0.233	0.716	1.853
1-Adamantyl	$1.22 \times 10^{-3}$	4.527	5.663	7.580	10.162	12.004	16.006
1-Bicyclo[2.2.2]- octyl	$2.43 \times 10^{-7}$	4.949	6.599	9.322	12.934	15.367	20.668
1-Norbornyl	$1.96 \times 10^{-12}$	5.951	10.648	17.319	24.389	28.653	35.791

<sup>a</sup> Reference 11. The rates presented above are of unequal reliability. Most have been extrapolated from data obtained at other temperatures and, in the case of the slower reacting compounds, these extrapolations are major ones.

molecule. The infrared studies of Macfarlane and Ross<sup>62</sup> support the D<sub>3h</sub> structure. Nethercote and Javan<sup>63</sup> have studied the microwave spectra of the 1-chloro and 1-bromo derivatives of this hydrocarbon. Their results also tended to argue against possible twisting. However, no truly definitive structural determination on bicyclo[2.2.2]octane is yet available.

Unfortunately, no structural data exist at all for homoadamantane. The calculations predict the system to have C<sub>2v</sub> symmetry (carbons 3, 4, 5, 6, and 9 defining a plane) rather than C<sub>2</sub> symmetry (a twisted form, with an axis of rotation passing through C<sub>3</sub> and bisecting the C<sub>4</sub>-C<sub>5</sub> bond). If this structure is correct, homoadamantane serves as an example of the limitations of most sets of molecular models examination of which would lead one to predict the C<sub>2</sub> structure to be the more stable. Such models tend to overemphasize angle strain at the expense of nonbonded repulsions and torsional strains.

Table IV presents the strain energies of the carbonium ions. These have been calculated several times using different values for the C-C<sup>+</sup>-C bending force constant. Rather than break down all of the terms into component parts, the listing of both component strains and calculated structures will be deferred until a single likely force constant is decided upon. Because the structure must be planar with equal angles, the *t*-butyl cation is invariant to changes of the C-C<sup>+</sup>-C bending force constant. The 3-homoadamantyl cation shows a comparatively slight dependence on this constant. This would indicate that the angles at the cation (C-3) must be fairly close to the planar value. The remaining three systems show an approximate twofold variation of strain over the range of bending force constants utilized.

It is necessary to examine the results of Table V from a quantitative point of view. At 25°, a power of ten in rate is equivalent to 1.36 kcal/mole in activation free energy. The use of weak C-C<sup>+</sup>-C bending force constants ( $k/2 < 115$  kcal/mole radian<sup>2</sup>) can be ruled

(62) J. J. Macfarlane and I. G. Ross, *J. Chem. Soc.*, 4169 (1960); *cf.*, however, P. Brtesch and H. H. Günthard, *Spectrochim. Acta*, 22, 877 (1966).

(63) A. H. Nethercote and A. Javan, *J. Chem. Phys.*, 21, 363 (1953).

out on the basis that the magnitudes of the strains are less than needed to explain the observed rate differences. There should further not be a direct equivalence between the strain energy differences in Table V and the experimental rates, expressed in energy terms. Strain differences are enthalpy effects, while rates are determined by both enthalpy and entropy influences. Along the series of bridgehead compounds II-V, entropy effects may be constant or they may be proportional, but they certainly are present, and are not taken into account in our calculations. Even more important, we are using the carbonium ions themselves as models for the transition state. Strains present in the ions will only partially be developed in the reaction transition states. Hence, the calculated strain differences of Table V must be substantially *larger* than the activation free energies of the various systems.

Table VI summarizes the results of fitting the data of Table V to an equation for a straight line, using a least-squares approach. As the value for  $k/2$ , the C-C<sup>+</sup>-C bending force constant, is increased, the correlation coefficient and the average deviation steadily improve until  $k/2 = 230$  kcal/mole radian<sup>2</sup>. Thereafter, further improvement is not significant. The slope of the correlation line, expressed in units of kcal/mole of strain per power of ten in rate, also reaches a reasonable value (2.12 kcal/mole) when  $k/2 = 230$  kcal/mole radian<sup>2</sup>. A plot using this value is given in Figure 2. Such a C-C<sup>+</sup>-C force constant is four times that for "normal" C-C-C angles, agreeing with expectations based on the Gillespie and Nyholm postulates<sup>46</sup> and on the effect of promotional energy, discussed earlier. While such a magnitude at first sight may seem large, we have adopted it here, since it represents an optimum balance between experimental and theoretical considerations.

Having chosen  $k/2$  C-C<sup>+</sup>-C equal to 230 kcal/mole radian<sup>2</sup>, the component strains for the various carbonium ions can be presented. This is done in Table VII; data for structures calculated on this basis are given in Table VIII.

Although *t*-butyl bromide seems like an obvious reference compound for this study, the analogy with bridgehead structures II-V is highly imperfect. Solva-



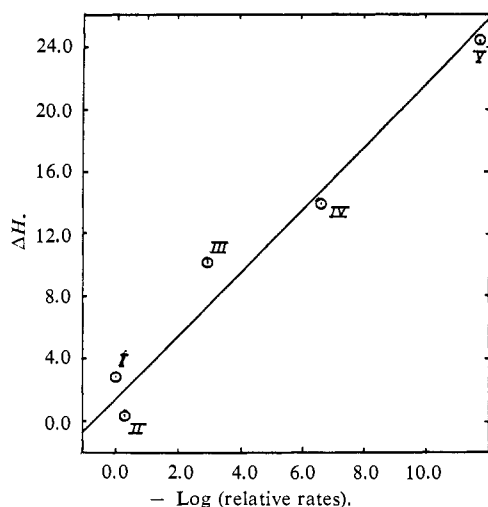


Figure 2. Plot of the calculated hydrocarbon-carbonium ion strain differences ( $\Delta H$ ) plotted against  $-\log$  of the experimental relative rate constants. The data used are compiled in Table IX.

tion effects can be quite dissimilar. A difference in the behavior of the activation parameters between *t*-butyl and the bridgehead substances has been noted in the literature.<sup>18</sup> In addition, inductive effects in the bridgehead substances should not be properly represented by

Table VI. Calculated Parameters from Strain Energy Calculations

$k/2$ C-C <sup>+</sup> -C, kcal/mole radian <sup>2</sup>	Slope, kcal/mole/ power of 10	Intercept, kcal/mole	Correlation coefficient	Av dev
28.75	-0.776	0.187	-0.754	$10^{\pm 2.56}$
57.50	-1.043	0.824	-0.912	$10^{\pm 1.70}$
115.0	-1.537	1.116	-0.963	$10^{\pm 1.11}$
230.0	-2.118	1.503	-0.978	$10^{\pm 0.80}$
345.0	-2.487	1.828	-0.981	$10^{\pm 0.74}$
790.0	-3.162	2.900	-0.982	$10^{\pm 0.70}$

Table VII. Component Strain in Carbonium Ions

	<i>t</i> -Butyl	3-Homo- adamantyl	1-Ada- mantyl	1-Bicyclo- [2.2.2]- octyl	1-Nor- bornyl
Bond strain	0.008	0.646	0.003	0.378	1.369
Angle strain	0.274	5.941	8.422	8.465	38.311
Nonbonded interactions	0.319	0.691	3.015	7.288	1.893
Torsional strain	3.000	6.570	0.378	9.321	8.523
Total	3.601	13.848	11.818	25.452	50.096

*t*-butyl; triethylcarbinyl would be a better reference in this respect. Other objections to *t*-butyl can be raised. The simplified approach presented in this paper stands a good chance of working only along a series of highly related molecules, and *t*-butyl is not well related structurally to the other substrates. Despite these considerations, exclusion of *t*-butyl does not improve the correlation observed, at least in a statistical sense.

Inspection of the data in Tables II and VII provide support for published interpretations of carbonium ion reactivity at bridgeheads of various systems. The high rate observed for 3-homoadamantyl bromide<sup>64</sup> is

Table VIII. Calculated Structures for Carbonium Ions

Bond length <sup>a</sup>		Bond angle <sup>a</sup>	
(CH <sub>3</sub> ) <sub>3</sub> C <sup>+</sup>			
C-C	1.481	C-C-C	120.0
C-H	1.109	C-C-H	107.7
		H-C-H	111.1
1-Adamantyl Cation (III, X = +)			
C <sub>1</sub> -C <sub>2</sub>	1.481	C <sub>2</sub> -C <sub>1</sub> -C <sub>8</sub>	115.5
C <sub>2</sub> -C <sub>3</sub>	1.533	C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	102.5
C <sub>3</sub> -C <sub>4</sub>	1.534	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	109.5
C <sub>1</sub> ·C <sub>4</sub>	2.771	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	109.5
C <sub>2</sub> ·C <sub>5</sub>	1.936		
1-Norbornyl Cation (V, X = +)			
C <sub>1</sub> -C <sub>2</sub>	1.470	C <sub>2</sub> -C <sub>1</sub> -C <sub>7</sub>	111.4
C <sub>1</sub> -C <sub>7</sub>	1.459	C <sub>2</sub> -C <sub>1</sub> -C <sub>6</sub>	113.8
C <sub>2</sub> -C <sub>3</sub>	1.559	C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	95.0
C <sub>3</sub> -C <sub>4</sub>	1.551	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	103.3
C <sub>4</sub> -C <sub>7</sub>	1.544	C <sub>3</sub> -C <sub>4</sub> -C <sub>7</sub>	105.4
C <sub>2</sub> ·C <sub>5</sub>	2.916	C <sub>3</sub> -C <sub>4</sub> -C <sub>7</sub>	102.5
		C <sub>1</sub> -C <sub>7</sub> -C <sub>4</sub>	85.8
1-Bicyclo[2.2.2]octyl Cation (IV, X = +)			
C <sub>1</sub> -C <sub>2</sub>	1.484	C <sub>2</sub> -C <sub>1</sub> -C <sub>6</sub>	115.1
C <sub>2</sub> -C <sub>3</sub>	1.535	C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	103.3
C <sub>3</sub> -C <sub>4</sub>	1.546	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	109.9
C <sub>1</sub> ·C <sub>4</sub>	2.401	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	108.8
C <sub>2</sub> ·C <sub>5</sub>	2.941		
1-Bicyclo[3.3.1]nonyl Cation (VII, X = +)			
C <sub>1</sub> -C <sub>2</sub>	1.478	C <sub>2</sub> -C <sub>1</sub> -C <sub>8</sub>	117.4
C <sub>1</sub> -C <sub>9</sub>	1.476	C <sub>2</sub> -C <sub>1</sub> -C <sub>9</sub>	116.5
C <sub>2</sub> -C <sub>3</sub>	1.542	C <sub>2</sub> -C <sub>2</sub> -C <sub>3</sub>	107.7
C <sub>3</sub> -C <sub>4</sub>	1.551	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	112.0
C <sub>4</sub> -C <sub>5</sub>	1.547	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	114.3
C <sub>3</sub> ·C <sub>7</sub>	3.055	C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub>	110.0
		C <sub>4</sub> -C <sub>5</sub> -C <sub>9</sub>	111.2
		C <sub>1</sub> -C <sub>9</sub> -C <sub>5</sub>	100.4
3-Homoadamantyl Cation (II, X = +)			
C <sub>3</sub> -C <sub>4</sub>	1.487	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	118.4
C <sub>3</sub> -C <sub>8</sub>	1.480	C <sub>2</sub> -C <sub>3</sub> -C <sub>11</sub>	118.3
C <sub>1</sub> -C <sub>2</sub>	1.533	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	111.1
C <sub>1</sub> -C <sub>9</sub>	1.543	C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub>	116.4
C <sub>4</sub> -C <sub>5</sub>	1.535	C <sub>5</sub> -C <sub>6</sub> -C <sub>7</sub>	113.9
C <sub>5</sub> -C <sub>6</sub>	1.545	C <sub>6</sub> -C <sub>7</sub> -C <sub>8</sub>	113.5
C <sub>6</sub> -C <sub>7</sub>	1.543	C <sub>7</sub> -C <sub>6</sub> -C <sub>10</sub>	113.3
C <sub>3</sub> ·C <sub>8</sub>	2.757	C <sub>7</sub> -C <sub>8</sub> -C <sub>9</sub>	111.1
C <sub>1</sub> ·C <sub>7</sub>	2.965	C <sub>2</sub> -C <sub>1</sub> -C <sub>9</sub>	110.7
		C <sub>2</sub> -C <sub>1</sub> -C <sub>8</sub>	107.9
1-Homoadamantyl Cation (VI, X = +)			
C <sub>9</sub> -C <sub>4</sub>	1.545	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	113.7
C <sub>2</sub> -C <sub>3</sub>	1.540	C <sub>2</sub> -C <sub>3</sub> -C <sub>11</sub>	112.3
C <sub>1</sub> -C <sub>2</sub>	1.480	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	117.9
C <sub>1</sub> -C <sub>9</sub>	1.482	C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	106.7
C <sub>4</sub> -C <sub>5</sub>	1.537	C <sub>5</sub> -C <sub>6</sub> -C <sub>7</sub>	113.2
C <sub>3</sub> -C <sub>11</sub>	1.551	C <sub>6</sub> -C <sub>7</sub> -C <sub>8</sub>	113.6
C <sub>8</sub> -C <sub>9</sub>	1.535	C <sub>2</sub> -C <sub>1</sub> -C <sub>10</sub>	117.0
C <sub>3</sub> ·C <sub>8</sub>	2.980	C <sub>7</sub> -C <sub>8</sub> -C <sub>9</sub>	111.4
C <sub>1</sub> ·C <sub>7</sub>	2.790	C <sub>2</sub> -C <sub>1</sub> -C <sub>9</sub>	116.6
		C <sub>2</sub> -C <sub>1</sub> -C <sub>8</sub>	100.8
		C <sub>7</sub> -C <sub>8</sub> -C <sub>11</sub>	110.0
1-Bicyclo[3.2.1]octyl Cation (VIII, X = +)			
C <sub>1</sub> -C <sub>2</sub>	1.478	C <sub>2</sub> -C <sub>1</sub> -C <sub>8</sub>	116.3
C <sub>1</sub> -C <sub>7</sub>	1.478	C <sub>2</sub> -C <sub>1</sub> -C <sub>7</sub>	116.9
C <sub>1</sub> -C <sub>8</sub>	1.470	C <sub>7</sub> -C <sub>1</sub> -C <sub>8</sub>	113.3
C <sub>2</sub> -C <sub>3</sub>	1.545	C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	105.1
C <sub>3</sub> -C <sub>4</sub>	1.551	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	111.0
C <sub>4</sub> -C <sub>5</sub>	1.551	C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub>	109.6
C <sub>5</sub> -C <sub>6</sub>	1.563	C <sub>4</sub> -C <sub>5</sub> -C <sub>8</sub>	111.1
C <sub>6</sub> -C <sub>7</sub>	1.551	C <sub>6</sub> -C <sub>5</sub> -C <sub>8</sub>	102.4
C <sub>5</sub> -C <sub>8</sub>	1.534	C <sub>5</sub> -C <sub>6</sub> -C <sub>7</sub>	106.6
C <sub>3</sub> ·C <sub>8</sub>	2.974	C <sub>1</sub> -C <sub>7</sub> -C <sub>6</sub>	95.6
		C <sub>1</sub> -C <sub>8</sub> -C <sub>5</sub>	90.9
		C <sub>3</sub> -C <sub>4</sub> -C <sub>6</sub>	112.4

<sup>a</sup> Bond lengths in angstrom units, angles in degrees.

due to the fortuitous similarity of the substantial strains in ground and transition states. Angle strain

(64) H. Stetter and P. Goebel, *Ber.*, **96**, 550 (1963).

actually decreases somewhat (1.5 kcal) in going from homoadamantane to the 3-cation, which assumes a nearly planar conformation (Figure 2). This loss in angle strain is compensated by increases in the other factors. The most important of these, an increase in the nonbonded interactions, is caused by flattening around the bridgehead. The bridgehead carbon is "pulled back" into the rest of the molecule and the nonbonded repulsions are increased. There will also be an increase in torsional energy as the groups attached to the trigonal center approach planarity (*i.e.*, in going from conformation B, Figure 1, to A). These two effects are also operative in the other bridgehead systems.

The severe increase of strain in going from norbornane to its 1-cation is due almost completely to angle strain. The  $C_1-C_7-C_4$  angle, already highly strained ( $93.9^\circ$ ) in the ground state, is distorted to  $85.8^\circ$  in the ion. The other two equivalent angles adjacent to the reaction site are reduced from  $102.9$  to  $95.0^\circ$ ! Some bond deformation is also present in the ion; some of the bonds lengthen slightly in an attempt to relieve strain, but the  $C_1-C_7$  bond is shortened. In spite of all this, an average angle of only  $113^\circ$  instead of  $120^\circ$  can be maintained at the bridgehead.

The increase in angle strain on ionization in both the 1-adamantyl and 1-bicyclo[2.2.2]octyl systems is almost exactly the same, and both molecules have nearly identical geometry around the bridgehead positions.<sup>18</sup> The angles there are  $115.5$  and  $115.1^\circ$ , respectively, in the 1-adamantyl and 1-bicyclo[2.2.2]octyl cations. The striking difference in reactivity is due to nonbonded repulsion terms.<sup>17,19,20</sup> The  $C_1-C_4$  distance in the bicyclo[2.2.2]octyl system decreases from 2.59 Å in the ground state to 2.40 Å in the ion, resulting in an increase of 4.29 kcal/mole repulsion energy. In adamantane, which is made up of chair, not boat, form cyclohexane rings, such 1,4 interactions are much less critical. The calculated increase in nonbonded strain in going to the ion is only 1.77 kcal/mole, but this value may well be too large. The 1,4-C,C interactions in adamantane and its cation are "through" the molecule in the sense that the interaction effect "passes by" other atoms. We have already commented that the dielectric constant of the molecule itself may influence the magnitude of the nonbonded interactions. Examination of models leaves one with the strong impression that the 1,4 interactions are of quite a different type in adamantane and in bicyclo[2.2.2]octane.

The more than 5000-fold reactivity difference between 1-adamantyl bromide and 1-bicyclo[2.2.2]octyl bromide, compounds possessing virtually identical structures around the reaction sites, is the most difficult and interesting facet of bridgehead carbonium ion reactivity requiring explanation. While the nonbonded repulsion theory supported here seems attractive, our calculations indicate that the magnitude of the energy differences is not quite sufficient to account quantitatively for the observed behavior. This is shown visually in Figure 2. The points for homoadamantane, bicyclo[2.2.2]octane, and norbornane describe an excellent straight line, but the point for adamantane deviates significantly. Either the measured rate is too fast or the calculated strain difference is too large. The trouble may partly be the latter, because of the 1,4-interaction problem mentioned

in the previous paragraph. Even assuming that there is no increase in nonbonded strain in going to the 1-adamantyl cation, and the full increment of change is still observed during the 1-bicyclo[2.2.2]octyl ionization, the resulting calculated energy difference between the two cases is too small to explain the observed solvolysis rates.

Since we are already employing "hard" nonbonded and "stiff"  $C-C^+-C$  potentials, a potential solution to this dilemma, the use of yet "harder" and "stiffer" potentials seems unreasonable. As Table V emphasizes, the use of weaker  $C-C^+-C$  potentials makes the situation much worse, and this fact might be used as evidence against such potentials.

The possibility of some special feature stabilizing the 1-adamantyl cation remains. It has been attractive to consider that the backside  $C-H$  orbitals at the remaining three bridgehead positions overlap with the vacant p orbital at C-1 extending into the interior of the molecule.<sup>17,19,20</sup> Some experimental support for this idea exists in the abnormally low chemical shift of the bridgehead hydrogens in the 1-adamantyl cation.<sup>65</sup> However, the reported esr study on the adamantyl radical anion,<sup>66</sup> which formerly<sup>17,19,65</sup> was cited in support of this idea, has been seriously questioned and appears to be in error.<sup>67</sup> Although the adamantyl cation has a uniquely favorable geometry for the manifestation of backside orbital charge delocalization, the matter is far from settled whether such an effect is actually operative and even, if operative, whether it is of sufficient magnitude to account for the observed behavior.

There is an unfortunate tendency in the interpretation of organic phenomena to invent *ad hoc* explanations for each fact not conforming to some pattern of expectation. A corollary to this tendency, no less unfortunate, is the overrating of an effect. Some influence known to be operative is often proposed as an explanation for a phenomenon, when the magnitude of the influence falls tenfold short when the energies needed are considered. Often, "point fitting" is employed. Points falling on a line are accepted without discussion, but those deviating from a relationship (as adamantyl, in the present instance) are rationalized to agreement. Were the same ingenuity to be applied to the nondeviating points, they could likely be moved as far away from the line as the recalcitrant points toward it!

We regard the present paper as merely a guidepost along a possible path toward interpretation of carbonium ion reactivity. Our knowledge of bond angle bending, torsional, nonbonded, and bond length potential functions even for saturated hydrocarbons is in a crude state, and next to nothing is known about such functions for carbonium ions. The present skeletal treatment omits more than it includes. Nevertheless, agreement of our calculations with experimental data is not at all bad, especially considering the limited number of compounds available. The average deviation (Table VI) is only slightly larger than that for

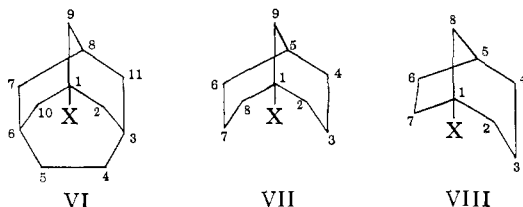
(65) P. von R. Schleyer, R. C. Fort, Jr., W. E. Watts, M. B. Comisarow, and G. A. Olah, *J. Am. Chem. Soc.*, **86**, 4195 (1964).

(66) K. W. Bowers, G. J. Nolfi, Jr., and F. D. Greene, *ibid.*, **85**, 3701 (1963).

(67) M. T. Jones, *ibid.*, **88**, 174 (1966); F. Gerson, E. Heilbronner, and J. Heinzer, *Tetrahedron Letters*, 2095 (1966); *cf.* K. W. Bowers, G. J. Nolfi, Jr., F. H. Lowry, and F. D. Greene, *Tetrahedron Letters*, 4063 (1966).

the Foote-Schleyer equation<sup>4,5</sup> ( $10^{\pm 0.25}$ , involving many more points).

We hope further that this paper will encourage gathering of additional data in a field by no means settled. The present method needs to be calibrated accurately before possible nonclassical behavior can confidently be assessed. Although the calculation scheme presented here is by no means in final form, we have used it to predict<sup>68</sup> the reactivities of other bridgehead systems.



The systems chosen were 1-homoadamantyl (VI), 1-bicyclo[3.3.1]nonyl (VII), and 1-bicyclo[3.2.1]octyl (VIII). The strain calculations for the parent hydrocarbons and their ions are summarized in Table IX, and Tables III and VIII present the structures corresponding to conformations of lowest energy. Rates predicted for compounds VI–VIII are given in Table X, which includes the calculated and observed rates of I–V for comparison purposes.

**Table IX.** Composite Strain Energies for Compounds and Ions VI–VIII<sup>a</sup>

Compound or ion	Bond length strain	Angle strain <sup>b</sup>	Torsional strain	Non-bonded interactions	Total strain
Bicyclo[3.3.1]-nonane (VII, X = H)	0.437	6.093	3.352	1.803	11.685
Bicyclo[3.3.1]-nonyl cation	0.959	8.088	3.620	2.121	14.788
Bicyclo[3.2.1]-octane (VIII, X = H)	0.877	7.166	8.862	1.359	18.262
Bicyclo[3.2.1]-octyl cation	0.920	20.585	7.522	1.678	30.705
Homo-adamantane (VI, X = H)	0.309	7.449	6.253	-0.396	13.615
1-Homo-adamantyl cation	0.857	12.103	7.844	0.575	21.379

<sup>a</sup> In kcal/mole. <sup>b</sup> Calculated using  $k/2 = 230$  kcal/mole radian<sup>2</sup> for C–C<sup>+</sup>–C.

Of the three systems VI–VIII, only the bicyclo[3.2.1]octyl (VIII) has been the subject of prior investigation.<sup>69</sup> The bridgehead bromide (VIII, X = Br), a

(68) In current scientific literature, the word "predict" is often used rather curiously as a synonym for "explain" or "rationalize" rather than for "foretell, tell beforehand, prophecy," as favored by dictionaries. It is impossible to "predict" something when the fact is known beforehand. An aphorism, original source unknown, stresses this point: "Predictions are risky, especially if they deal with the future." True quantitative predictions, in organic chemistry at least, are quite rare.

(69) A. B. Sayigh, Ph.D. Thesis, Columbia University, 1956; *Dissertation Abstr.*, **16**, 1346 (1956).

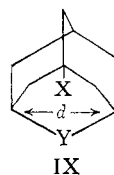
**Table X.** Calculated Relative Rate Constants

System	Calculated energy difference, kcal <sup>a,b</sup>	Calculated rel rate constants, 25 <sup>°c</sup>	Experimental rel rate constants 25 <sup>°d</sup>
<i>t</i> -Butyl	2.85	0.22	1.0
3-Homoadamantyl	0.23	4.65	0.46
1-Adamantyl	10.16	$4.6 \times 10^{-5}$	$1.2 \times 10^{-3}$
1-Bicyclo[2.2.2]-octyl	12.93	$1.8 \times 10^{-6}$	$2.4 \times 10^{-7}$
1-Norbornyl	24.39	$3.1 \times 10^{-12}$	$2.0 \times 10^{-12}$
1-Homoadamantyl	7.76	$7.0 \times 10^{-4}$	
1-Bicyclo[3.3.1]-nonyl	3.10	0.12	
1-Bicyclo[3.2.1]-octyl	12.44	$3.3 \times 10^{-6}$	(See text)

<sup>a</sup> Calculated using  $k/2 = 230$  kcal/radian<sup>2</sup> for C–C<sup>+</sup>–C. <sup>b</sup> Data from Tables V and IX. <sup>c</sup> Calculated using Figure 2. <sup>d</sup> Data from ref 17–19; Table IV.

component of a mixture, was solvolyzed in 70% aqueous dioxane at 131°. The rate obtained was some five times slower than that for 1-bromobicyclo[2.2.2]octane (IV, X = Br). According to the calculations summarized in Table X, the [2.2.2] isomer should be about two times slower at 25°. Within the error limits of the present method, agreement between these data is satisfactory, but it seems desirable to recheck the experimental work using pure material over a range of temperatures so that a comparison at 25° can be made. The activation parameters for both bicyclooctane isomers will probably be different.

One unsatisfactory result of these calculations should also be mentioned, to emphasize that further refinement is needed. Equilibration studies show that bicyclo[2.2.2]- and -[3.2.1]octanes are comparably stable; the isomerization enthalpy between them is practically zero.<sup>70</sup> According to our calculations, bicyclo[2.2.2]octane is strained to the extent of 12.5 kcal/mole (Table II), but the [3.2.1] isomer (18.3 kcal/mole strain, Table IX) is less stable by 5.8 kcal/mole! The origin of this discrepancy appears to be similar to that for norbornane, discussed earlier. Both norbornane and bicyclo[3.2.1]octane, in contrast to adamantane and bicyclo[2.2.2]octane, suffer from appreciable angle strain, which is being overestimated by the present program.<sup>71</sup> Although we hardly regard this to be a satisfactory state of affairs,<sup>71</sup> this defect is not nearly as serious when energy differences between hydrocarbon and cation are being calculated for a given system. Errors owing to inappropriate choice of parameters tend to be minimized when such internal comparisons are made.<sup>7</sup>



Y = CH<sub>2</sub>  $d = 2.52$  Å  
 Y = (CH<sub>2</sub>)<sub>2</sub>  $d = 2.97$  Å  
 Y = H, H  $d = 2.96$  Å

(70) P. von R. Schleyer, K. R. Blanchard, and C. D. Woody, *J. Am. Chem. Soc.*, **85**, 1358 (1963).

(71) Wiberg<sup>8</sup> and Harris<sup>41</sup> avoid this difficulty by using "soft" potentials for nonbonded interactions; most of these then turn out to be attractive and compensate for any overestimation in the bond angle strain term. We have employed "hard" nonbonded potentials, and it will be necessary to weaken the bond angle strain potentials in order to obtain agreement with experimental thermochemical ground-state data. We are exploring such possibilities.

The basic skeletons of homoadamantane (IX, Y = (CH<sub>2</sub>)<sub>2</sub>) and of bicyclo[3.3.1]nonane (IX, Y = H, H) are very similar (Table VIII). Distortion from the "perfect" adamantane structure is caused in the former by the ethylene bridge and in the latter by repulsions between the two *endo*-hydrogen atoms (Y = H, H in IX). The distance, *d* in IX, is calculated to be almost identical in the two molecules.<sup>72</sup> If the ground-state structures are very similar, it might be anticipated that the bridgehead bromides IX, X = Br (Y = (CH<sub>2</sub>)<sub>2</sub> and H,H), would solvolyze at similar rates. Our full analysis (Tables IX and X) predicts that this will not be the case. 1-Bicyclo[3.3.1]nonyl bromide (VII,

(72) This distance has been measured experimentally as 3.06 and 3.02 Å by X-ray studies of two related molecules.<sup>73,74</sup>

(73) W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc.*, 1844 (1965).

(74) M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, 47, 695 (1964).

X = Br) should react quite rapidly, only a little less rapidly than *t*-butyl bromide and 10<sup>2</sup> faster than 1-homoadamantyl bromide (VI, X = Br). This is a consequence of the greater flexibility of the bicyclic molecule in absorbing the angular distortion at the bridgehead position in the ion. We plan to study these cases experimentally.

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## The Electrochemical Formation of Carbonium and Iodonium Ions from Alkyl and Aryl Iodides

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**Abstract:** The electrochemical oxidation of organic iodides at a platinum electrode has been studied in acetonitrile solution containing lithium perchlorate as supporting electrolyte. It has been discovered that alkyl iodides are oxidized and converted *via* alkyl carbonium ions to N-alkylacetamides. Contrastingly, cations resulting from electrooxidation of aryl iodides do not undergo carbon-iodine bond scission but can attack aromatic molecules forming diaryliodonium ions.

Previous work on the electrooxidation of organic halides has been limited to oxidations of aryl halides. In early work,<sup>1</sup> iodobenzene was found on nonpotentiostatic anodization in aqueous sulfuric acid to form benzoquinone and iodine. In contrast, phenyl iodosoacetate and iodoxybenzene were produced in aqueous acetic acid. In nonaqueous media, anodic half-wave potentials at a rotating platinum electrode have been tabulated for bromobenzene<sup>2</sup> and iodobenzene,<sup>3</sup> and iodobenzene has been converted in a silver fluoride-acetonitrile mixture to iodobenzene difluoride.<sup>4</sup> This paper reports some observations on the products and gross mechanistic features of the electrooxidation of both aryl and alkyl halides.

### Results

The oxidations reported here were performed potentiostatically in 0.5 M lithium perchlorate-acetonitrile solution at a platinum foil anode. Preliminary studies established that under these conditions the halobenzenes as well as simple alkyl iodides could be conveni-

ently oxidized in the potential range limited by the background oxidation of solvent and/or electrolyte at 2.4 v.<sup>5</sup> Alkyl bromides and chlorides, however, could not be oxidized before background.

**Alkyl Iodides.** Analysis of the products of methyl iodide oxidation at 1.9 v established the presence of iodine (92% yield), N-methylacetamide (75%), acetamide, and traces of methanol.

The buildup of iodine, N-methylacetamide, and acetamide with time is illustrated by some typical data in Table I. Aliquots were removed at various times from the anolyte and analyzed for the above compounds as well as for methyl iodide. The analytical method for the latter, however, was highly irreproducible and gave only qualitative data. These data were sufficient, however, to demonstrate the lack of correlation of current with methyl iodide concentration since, for example, roughly two-thirds of the methyl iodide was consumed when the current had only decreased from 640 to 500 ma. It can be noted that approximately two electrons per molecule of methyl iodide were consumed when the reaction was terminated. In other runs *n* values as large as 3.5 were determined.

(5) All potentials refer to Ag|0.01 M AgNO<sub>3</sub> in acetonitrile. The rotating platinum electrode potentials were measured against sce, but were normalized to the Ag|Ag<sup>+</sup> scale by adding -0.30 v.

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