

chromatography. The identification of the product as methyl reserpate iodide was originally based on undepressed mixture melting point and identical infrared spectra. The situation was resolved when it was noted that the infrared spectra of the pure iodide and bromide are identical

throughout the whole curve, while the spectrum of the new bromide differs only in very minor respects. It is apparent that the original mistaken identification was caused by the unreliability of mixture melting points in this series, as well as the unusual correspondence of the infrared spectra.

[CONTRIBUTION FROM FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, N. J.]

## The Reactivity of Bridgehead Compounds of Adamantane<sup>1,2</sup>

By PAUL VON R. SCHLEYER AND ROBERT D. NICHOLAS<sup>3</sup>

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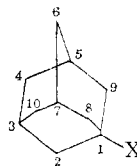
Unexpectedly, bridgehead adamantane compounds are quite reactive. Solvolysis of 1-adamantyl derivatives proceeded at rates only 1000 times slower than the corresponding *t*-butyl compounds, but almost 5000 times faster than 1-bicyclo[2.2.2]octyl and 10<sup>11</sup> faster than 1-bicyclo[2.2.1]heptyl derivatives. The difference between the reactivity of 1-adamantyl and *t*-butyl compounds appears to be largely due to angle strain in the somewhat flattened but not planar transition states of the former compounds. The impossibility of rearside solvation may play a minor role also, but there is no experimental evidence to support the theory that inhibition of bridgehead hyperconjugation can alter the reaction rate significantly. The difference between the reactivity of 1-adamantyl and 1-bicyclo[2.2.2]octyl compounds, despite their apparently identical arrangements of atoms and bonds in the vicinity of the reaction site, is due to conformational strain in the latter system.

Bartlett<sup>4</sup> first realized that reactions at a bridgehead had important mechanistic implications.<sup>5</sup> Exploitation of this idea has lead to a greater understanding of the stereochemical restrictions of many different reactions.<sup>4,5</sup> Bridgehead compounds are generally difficult to obtain despite the development of ingenious methods for their preparation.<sup>4,5</sup> However, 1-substituted adamantane derivatives have recently become readily available.

Reaction of adamantane (I)<sup>6</sup> with bromine at steam-bath temperature gave excellent yields of 1-bromoadamantane (II).<sup>7-9</sup> Excellent yields of products also resulted from carbonium ion reactions of II. Preparative solvolysis of II in refluxing aqueous solvents readily gave 1-adamantanol (III)<sup>7-9</sup>; II also reacted very satisfactorily in the Friedel-Crafts alkylation<sup>8</sup> and in the Koch carboxylation.<sup>8</sup> Adamantane (I) can be carboxylated directly by a modified Koch procedure involving an intermolecular hydride ion exchange with *t*-butyl carbonium ion.<sup>9c</sup> Treatment of III with thionyl chloride yielded 1-chloroadamantane

(IV).<sup>8,10</sup> Both II and III underwent the Ritter amidation smoothly.<sup>8,9</sup> All of these reactions were carried out under mild conditions. These results were especially surprising in view of the well known inertness of bridgehead compounds of other ring systems.<sup>4,5,10</sup>

Very recently, Stetter and co-workers<sup>9</sup> have reported a quantitative study of the reactivity of 1-bromoadamantane (II) in two solvents at one temperature. They noted an unexpected rapidity of reaction, for which they offered no explanation. The results described in the present paper, obtained prior<sup>2</sup> to the publication of the German report, serve to confirm and extend these observations and to offer an interpretation of this behavior.



- I, X = H  
 II, X = Br  
 III, X = OH  
 IV, X = Cl  
 V, X = I  
 VI, X = OTs

## Experimental Results

**Preparation of Compounds.**—1-Bromoadamantane (II), 1-adamantanol (III) and 1-chloroadamantane (IV) were prepared according to the literature procedures.<sup>7,8</sup> 1-Adamantanol (III) was also prepared by the free radical hydroxylation of adamantane.<sup>1</sup> The literature synthesis of 1-iodoadamantane<sup>7</sup> (V) could not be repeated. Instead, the compound was made by the reaction of III with HI. The m.p. of V so produced, 75.3–76.4°, was at considerable variance with that reported by Landa, Kriebel and Knobloch,<sup>7</sup> 151–152.5°. The

(10) Contrast the behavior of 1-hydroxybicyclo[2.2.1]heptane (ref. 4) and compare the behavior of 1-hydroxybicyclo[3.2.2]nonane (C. A. Grob, M. Ohta, E. Reuh and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1952)) toward this reagent.

(1) Paper V of a series on Bridged Ring Systems; paper IV, *J. Am. Chem. Soc.*, **83**, 182 (1960). This paper is taken, in part, from the Ph.D. Thesis of R. D. N., Princeton University, 1960.

(2) A preliminary account of this work was presented at the Third Delaware Valley Regional Meeting, Am. Chem. Soc., Feb., 1960, Abstracts, p. 49.

(3) Gulf Research and Development Fellow, 1959–1960. National Science Foundation Summer Fellow, 1960.

(4) P. D. Bartlett and L. H. Knox, *J. Am. Chem. Soc.*, **61**, 3184 (1939); P. D. Bartlett and S. G. Cohen, *ibid.*, **62**, 1183 (1940); P. D. Bartlett and E. S. Lewis, *ibid.*, **72**, 1005 (1950); P. D. Bartlett, *Bull. soc. chim. France*, C100 (1951); P. D. Bartlett in H. Gilman, Ed., "Organic Chemistry," Vol. III, J. Wiley and Sons, Inc., New York, N. Y., 1953, p. 58; also see ref. 5.

(5) For reviews: (a) D. B. Applequist and J. D. Roberts, *Chem. Revs.*, **54**, 1065 (1954); (b) U. Schöllkopf, *Angew. Chem.*, **72**, 147 (1960).

(6) P. von R. Schleyer, *J. Am. Chem. Soc.*, **79**, 3292 (1957); P. von R. Schleyer and M. M. Donaldson, *ibid.*, **82**, 4645 (1960).

(7) S. Landa, S. Kriebel and E. Knobloch, *Chem. Listy*, **48**, 61 (1954); S. Landa and S. Hala, *Coll. Czech. Chem. Comm.*, **24**, 93 (1959).

(8) H. Stetter, M. Schwarz and A. Hirschhorn, *Ber.*, **92**, 1629 (1959); H. Stetter and C. Wulff, *ibid.*, **93**, 1366 (1960).

(9) (a) H. Stetter, J. Mayer, M. Schwarz and K. Wulff, *ibid.*, **93**, 2263 (1960); (b) H. Stetter and C. Wulff, *ibid.*, **93**, 1366 (1960); (c) H. Koch and W. Haaf, *Angew. Chem.*, **72**, 628 (1960); (d) W. Haaf, *ibid.*, **73**, 144 (1961).

structure of our material was verified by infrared and n.m.r. spectroscopy<sup>11</sup> and elemental analysis.

The only tertiary tosylates which have been reported are those unreactive ones at a bridgehead of a norbornyl ring system.<sup>4,12</sup> The tosylation procedure which succeeded in the case of 1-hydroxybicyclo[2.2.1]heptane<sup>12</sup> gave only partial conversion with 1-adamantanol (III). Attempts at purification resulted in decomposition of material. Hence, for kinetic studies the mixture of tosylate VI with unreacted alcohol III was employed. Titration showed the tosylate to have a purity of 40.5%.

**Kinetic Procedure and Results.**—The solvolyses of the halides II, IV and V were carried out in 80% ethanol; acetic acid was used for the tosylate VI. Standard titrimetric procedures were employed.<sup>13</sup> The halide solvolyses were followed to 60–90% completion; good first-order behavior was observed. However, erratic results were obtained for the experimentally determined infinity titers, due to the reaction of the hydrogen halide with the solvolysis product or the solvent. Calculated infinity titers gave good kinetic results and were employed instead. The impure tosylate VI gave good first-order behavior. Of course, the experimental infinity titer was used in this instance. The data obtained are summarized in Table I.

TABLE I  
SOLVOLYSIS OF BRIDGEHEAD ADAMANTANE DERIVATIVES

1-Adamantyl compd.	Temp., °C.	$k_1$ , sec. <sup>-1</sup>	$\Delta H^\ddagger$ , kcal.	$\Delta S^\ddagger$ , e.u.
80% Ethanol				
1-Chloroadaman- tane (IV)	100.00	$5.35 \pm 0.37 \times 10^{-4}$	25.5	-10.2
	75.28	$4.38 \pm 0.24 \times 10^{-4}$		
	25.00	$(7.59 \times 10^{-7})^a$		
1-Bromoadaman- tane (II)	99.70	$1.13 \pm 0.06 \times 10^{-3}$	22.6	-12.0
	75.00	$1.10 \pm 0.06 \times 10^{-4}$		
	50.10	$9.25 \pm 0.36 \times 10^{-4}$		
	25.00	$(4.38 \times 10^{-7})^a$		
1-Iodoadamantane (V)	75.18	$2.68 \pm 0.14 \times 10^{-4}$	23.2	- 8.6
	50.10	$1.89 \pm 0.08 \times 10^{-4}$		
	25.00	$(8.45 \times 10^{-7})^a$		
Acetic acid				
1-Adamantyl tosyl- ate (VI)	25.00	$5.86 \times 10^{-4}$	..	....

<sup>a</sup> Calculated values.

<sup>a</sup> Calculated values.

The solvolysis product from the halides was 1-adamantanol. This was expected from the preparative solvolysis experiments described in the literature.<sup>7–9</sup>

### Discussion

In their classical studies, Bartlett and co-workers<sup>4</sup> found that bridgehead halides in the apocamphyl and the triptycyl series could not be made to undergo substitution reactions even under severe conditions. This amazing inertness—now familiar—was attributed to a number of possible factors. Backside displacement by an S<sub>N</sub>2 process, unlikely even for acyclic tertiary halides,<sup>14,15</sup>

(11) The n.m.r. spectra of all these compounds, very kindly determined by Dr. George Van Dyke Tiers, will be reported separately along with other physical measurements on adamantane derivatives.

(12) C. J. Norton, Ph.D. Thesis, Harvard University, 1955.

(13) S. Winstein, E. Grunwald and L. I. Ingraham, *J. Am. Chem. Soc.*, **70**, 821 (1948); H. C. Brown and R. S. Fletcher, *ibid.*, **71**, 1845 (1949).

(14) A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).

is excluded both by the impossibility of Walden inversion and by the inaccessibility of the rear of the reaction site to nucleophilic reagents.

Tertiary bridgehead compounds would be expected to react by an ionization (S<sub>N</sub>1) process.<sup>14,15</sup> Inductive effects in bicyclic molecules should be similar in the ground states and in the solvolysis transition states to those in equivalently substituted acyclic analogs. The inertness of bridgehead derivatives has been attributed<sup>4</sup> to three possible causes: 1. The impossibility of rear-side solvation.<sup>16</sup> 2. The higher potential energy of a non-planar carbonium ion. 3. Stereochemical inhibition or restriction of C–H and C–C hyperconjugation and, where applicable, of  $\pi$ -p conjugation.

Differentiation between these explanations on the basis of negative evidence was impossible. Consequently, Doering and co-workers<sup>17</sup> have studied thoroughly bridgehead reactivities in the bicyclo[2.2.1]heptane and the bicyclo[2.2.2]octane series.<sup>18</sup> The preparations of the compounds involved a number of extremely interesting and ingenious reactions; the results established the following points conclusively. Carbonium ion type substitution reactions were possible at a bridgehead, but these proceeded much less readily in the more strained norbornane system than in the bicyclo[2.2.2]octane series, which could more readily flatten at the bridgehead. Some of the rate data<sup>17,18</sup> have been included in Table II. Since solvation factors and hyperconjugation effects must be very similar in the two series, the large differences between them must have been due principally to strain effects associated with non-planar carbonium ions. These substitutions did not occur by a frontside bimolecular process since the rate of ethanolysis of 1-bromo-3,3-dimethylbicyclo[2.2.2]octane was independent of added ethoxide ion. Doering and co-workers interpreted these results to support "the hypothesis that a tetrahedral (sp<sup>3</sup>) carbonium ion is of higher energy than some other configuration, most probably the planar."

The sensitivity of the rates of bicyclo[2.2.2]octyl bromides to changes in the "ionizing power" of various solvolysis media was assessed by means of the Grunwald–Winstein<sup>14,19</sup> "mY" correlation.<sup>17c</sup>

(15) S. Winstein, E. Grunwald and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951); S. Winstein, S. Smith and D. Darwish, *Tetrahedron Letters*, No. 16, 24 (1959).

(16) (a) First pointed out by S. Winstein and R. E. Buckles, *J. Am. Chem. Soc.*, **64**, 2780 (1942). (b) That hindrance of solvation need not be a factor of major importance in S<sub>N</sub>1 reactions was demonstrated by P. D. Bartlett and M. S. Swain, *ibid.*, **77**, 2801 (1955).

(17) (a) W. von E. Doering and E. F. Schoenewaldt, *ibid.*, **73**, 2333 (1951); (b) W. von E. Doering, Abstracts, 123rd Mtg., Am. Chem. Soc., Los Angeles, Cal., March, 1953, p. 35M; W. von E. Doering, M. Levitz, A. Sayigh, M. Sprecher and W. P. Whelan, Jr., *J. Am. Chem. Soc.*, **75**, 1008 (1953); M. Levitz, Ph.D. Thesis, Columbia University, 1951 (*Diss. Abstr.*, **14**, 19 (1954)); A. A. Sayigh, Ph.D. Thesis, Columbia University, 1952 (*Diss. Abstr.*, **14**, 1552 (1954)); W. P. Whelan, Jr., Ph.D. Thesis, Columbia University, 1952 (*Diss. Abstr.*, **14**, 1556 (1954)); M. Sprecher, Ph.D. Thesis, Columbia University, 1953 (*Diss. Abstr.*, **15**, 2021 (1955)); A. B. Sayigh, Ph.D. Thesis, Columbia University, 1954 (*Diss. Abstr.*, **16**, 1346 (1956)); (c) M. Finkelstein, Ph.D. Thesis, Yale University, 1955. This work has been discussed in ref. 14.

(18) The acetolysis of 1-norbornyl brosylate has been investigated by R. B. Woodward and C. J. Norton (ref. 12).

(19) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).

TABLE II  
 SUMMARY OF BRIDGEHEAD SOLVOLYSIS RATES, 25°

Compound	$k_1$ , sec. <sup>-1</sup> (calcd.)	Rel. rate	$\Delta H^\ddagger$ , kcal.	$\Delta S^\ddagger$ , e.u.	Ref.
80% aqueous ethanol solvent					
1-Chloroadamantane	$7.59 \times 10^{-9}$	$2.12 \times 10^{-5}$	25.5	-10.2	<sup>a</sup>
<i>t</i> -Butyl chloride	$9.24 \times 10^{-8}$	0.0258	22.3	-6.6	19
1-Bromoadamantane	$4.38 \times 10^{-7}$	0.00122	22.6	-12.0	<sup>a</sup>
<i>t</i> -Butyl bromide	$3.58 \times 10^{-4}$	1.0	21.5	-2.3	21
1-Bromobicyclo[2.2.2]octane	$8.68 \times 10^{-11}$	$2.42 \times 10^{-7}$	26.4	-16.0	17c
3,3-Dimethyl-1-bromobicyclo[2.2.2]octane	$1.12 \times 10^{-10}$	$3.13 \times 10^{-7}$	26.2	-15.2	17c
1-Bromonorbornane	<sup>b</sup>	( $10^{-14}$ ) <sup>b</sup>	(32 est.) <sup>b</sup>		17c
1-Iodoadamantane	$8.45 \times 10^{-7}$	0.00236	23.2	-8.6	<sup>a</sup>
<i>t</i> -Butyl iodide	$9.26 \times 10^{-4}$	2.58	21.6	-0.1	22
Acetic acid solvent					
1-Norbornyl brosylate	$2.78 \times 10^{-14}$		31.7	-14.3	12
1-Norbornyl tosylate	( $9.3 \times 10^{-15}$ ) <sup>c</sup>	$1.6 \times 10^{-11c}$			
1-Adamantyl tosylate	$5.86 \times 10^{-4}$	1.0	..	....	<sup>a</sup>

<sup>a</sup> This work. <sup>b</sup> In 40% ethanol at 216°, this compound reacted  $10^8$  more slowly than 1-bromobicyclo[2.2.2]octane. Using an estimated  $\Delta H^\ddagger$  of 32 kcal./mole, the rate at 25° would be  $6.8 \times 10^{-16}$  sec.<sup>-1</sup>. The rate of *t*-butyl bromide under the same conditions and temperature is  $4.17 \times 10^{-2}$  (ref. 21). <sup>c</sup> Estimated assuming brosylates are about three times more reactive than tosylates (ref. 14). The data of refs. 17c and 12 were obtained in solvent containing added base. The effect of this salt upon the rate was ignored in this summary.

The average value of "*m*," a measure of the sensitivity of the compound to change in the ionizing power of the solvent (*Y*),<sup>20</sup> for 1-bromobicyclo[2.2.2]octane (*m* = 0.93 at 100°) was indistinguishable from that of *t*-butyl bromide (*m* = 0.94 at 25°).<sup>14,15,20</sup> This result emphasizes the mechanistic similarity of the bridgehead and acyclic solvolyses and indicates that covalent solvation is not present in the transition state of either case.<sup>14,20</sup>

While the general features of the foregoing interpretations of bridgehead carbonium ion reactions appear to be sound, the results of the present research with 1-adamantyl derivatives (Table I) permit an extension of these ideas and require some modifications. Table II summarizes comparable data for bridgehead and *t*-butyl compounds. Two features arrest attention. First, while the rates of solvolysis of *t*-butyl derivatives are about 1000 times faster than the corresponding 1-adamantyl halides, the adamantane compounds react much more rapidly than the other bridgehead systems (Fig. 1).<sup>23</sup> Second, while the energy of activation term is chiefly responsible for the large differences in rates, the activation entropies of all the bridgehead compounds are large, negative numbers.<sup>24</sup> Table III compares these parameters with those for *t*-

butyl, for similar conditions. In addition, the effect of changing the leaving group from chloride to bromide to iodide is about the same for 1-adamantyl derivatives as it is for *t*-butyl or *t*-amyl halides<sup>25</sup> (Table IV).

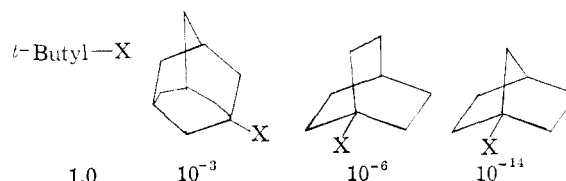


Fig. 1.—Relative rates of solvolysis of bridgehead derivatives, 25°

There seems to be no evidence which suggests that solvolyses of bridgehead derivatives differ mechanistically in any major way from those of common tertiary compounds. The chief difference in behavior is the enormous variations in rates. We should like to examine critically the three proposals, cited earlier, which have been offered to account for this behavior.

**1. The Impossibility of Rear-side Solvation.**—Doering, *et al.*,<sup>17</sup> have shown that solvation cannot be a major factor in inhibiting the ionization of the nearly inert 1-substituted norbornanes and probably also the more reactive bicyclooctyl compounds.<sup>16b</sup> Only three powers of ten in rate separate bridgehead adamantane solvolyses from those of *t*-butyl, the ionization of which, at least in principle, can be assisted by solvation from the rear. Examination of Table III reveals that about two of the three orders of magnitude of difference in reaction are due to a less favorable entropy of activation for the adamantane compounds and the remainder—about a single power of ten—to a higher energy of activation. In view of the complexities of behavior of activation entropies and energies in solvolysis reactions,<sup>26,27</sup> it would be naive to interpret these dif-

(20) More recently, it has been recognized that "*m*" is a function not only of the compound, but also of the solvent pair. Nevertheless, unlike aromatic compounds which can give considerable dispersion in an *mY* plot, aliphatic compounds undergoing a *lim.* solvolysis generally correlate satisfactorily; S. Winstein, A. H. Fainberg and E. Grunwald, *J. Am. Chem. Soc.*, **79**, 4146 (1957) and earlier papers in the same series; S. D. Ross and M. M. Labes, *ibid.*, **79**, 4155 (1957); C. Mechelynek-David and P. J. C. Fierens, *Tetrahedron*, **6**, 232 (1959); P. Bivort and P. J. C. Fierens, *Bull. soc. chim. Belg.*, **65**, 975 (1956), and earlier papers in the same series.

(21) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **79**, 1802 (1957).

(22) J. Shorter and C. Hinshelwood, *J. Chem. Soc.*, 2412 (1949).

(23) Very recently Stetter, *et al.*,<sup>9</sup> have also reported the solvolysis rate of 1-adamantyl bromide in 60 and 80% ethanol at a single temperature (25°). The value obtained for the latter solvent,  $k_1 = 1.16 \times 10^{-7}$ , does not agree well with that reported here ( $k_1 = 4.38 \times 10^{-7}$ ). This discrepancy may be due to the difficulty in measuring very slow rates accurately; our value was obtained by extrapolation from data at higher temperatures while Stetter's rate constant was based on a run carried to only 3% completion.

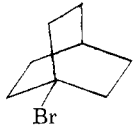
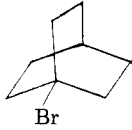
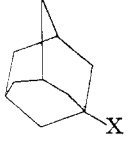
(24) This observation has been made before (refs. 12, 17c).

(25) H. C. Brown and A. Stern, *J. Am. Chem. Soc.*, **72**, 5068 (1950).

(26) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

(27) S. Winstein and A. H. Fainberg, *J. Am. Chem. Soc.*, **79**, 5937, 1597, 1602, 1608 (1957), and ref. 20.

TABLE III  
 COMPARISON OF BRIDGEHEAD AND *t*-BUTYL SYSTEMS

			
	6 solvents <sup>a</sup>	5 solvents <sup>a</sup>	X = Cl, Br, I <sup>b</sup> 80% ethanol
$\Delta\Delta S^\ddagger$ , <sup>c</sup> e.u.	$-11.9 \pm 3.5^d$	$-10.3 \pm 4.4$	$-7.3 \pm 2.4$
$\Delta\Delta H^\ddagger$ , <sup>c</sup> kcal.	$5.8 \pm 0.8^d$	$4.9 \pm 1.6^d$	$1.8 \pm 0.4$
$\Delta\Delta F^\ddagger$ , <sup>c</sup> kcal.	$8.4 \pm 1.9$	$8.0 \pm 2.9$	$4.0 \pm 1.1$
$k_1/k_1^0$ <sup>ce</sup>	$8.9 \pm 5.6 \times 10^{-7}$	$2.6 \pm 1.6 \times 10^{-6}$	$9.8 \pm 1.5 \times 10^{-4}$
$m(25^\circ)$	$1.13 \pm 0.14^{e,f}$	$1.13 \pm 0.02^{e,g}$	<sup>h</sup>

<sup>a</sup> Calculated from data of Doering, *et al.* (ref. 17). <sup>b</sup> This work. <sup>c</sup>  $\Delta S^\ddagger$  (bridgehead compound) -  $\Delta S^\ddagger$  (*t*-butyl halide in the same solvent). For the five solvents for which data were available,  $\Delta S^\ddagger = -2.3 \pm 1.1$  e.u. (average) for *t*-butyl bromide,  $\Delta\Delta H^\ddagger$  and  $\Delta\Delta F^\ddagger$  were determined similarly. The average value for  $\Delta H^\ddagger$  (*t*-butyl bromide) was  $21.7 \pm 1.8$  kcal./mole.  $k_1/k_1^0$  is the ratio of the solvolysis rate of the bridgehead compound to that of the same *t*-butyl halide in the same solvent at  $25^\circ$ . <sup>d</sup> For the comparison, the data for *t*-butyl chloride in formic acid were substituted for the unavailable bromide values. The *t*-butyl chloride data were that of ref. 19; *t*-butyl bromide, ref. 21; and *t*-butyl iodide, ref. 22. <sup>e</sup> Recalcd. from data of ref. 17c. No compensation was introduced for the effect of added salts. The methanol values were extremely inconsistent and were omitted from the averages. <sup>f</sup> Average of 3 solvent pairs. <sup>g</sup> Average of 2 solvent pairs. <sup>h</sup> Using the data of ref. 9, 60 and 80% ethanol,  $m = 1.40$  (X = Br). Using the rate value from Table I for the latter solvent,  $m = 0.89$  (see ref. 23).

TABLE IV

RELATIVE RATE DATA, 80% ETHANOL, $25^\circ$			
Compound	X = Cl	X = Br	X = I
<i>t</i> -Butyl X <sup>25</sup>	1.0	38.9	100
<i>t</i> -Amyl X <sup>25</sup>	1.0	41.6	123
1-Adamantyl X	1.0	57.7	113
<i>t</i> -BuX/1-AdX	1210	817	1080

ferences in any simple way. Nevertheless, the following argument is very tempting.

A negative entropy of activation can mean that the transition state is more ordered than the ground state.<sup>28</sup> Since the highly rigid bridgehead molecules already lack orientational freedom in the ground state, they can hardly become even more ordered in the transition state. The large, negative entropies observed<sup>29</sup> must be due to restricted motion in the solvent. Although covalent solvation is not present in the transition state of *t*-butyl solvolyses,<sup>14,15</sup> there is evidently some electrostatic (long range) solvation from the back side. This is not possible with the bridgehead compounds; hence, frontside solvation is more critical and the total ordering of the solvent during ionization is greater.<sup>30</sup> This is one extreme of interpretation. At most, the solvation factor can account for  $10^2$ – $10^3$  in rate; it can, therefore, be of only minor importance for bicycloheptane, but it can be a major factor for adamantane compounds.

An alternative interpretation<sup>27</sup> suggests that  $\Delta S^\ddagger$  is expected to be large and negative because of the increased solvation during reactions in-

volving an increase in charge. While this is true for the solvation of ordinary salts,<sup>31</sup> it is not usually the case for solvolysis reactions because here  $\Delta S^\ddagger$  depends on the structure of the substrate molecule and not solely on solvent and solvation.<sup>26,27</sup> For example, in the transition state for *t*-butyl solvolysis, because of the more flattened geometry, the methyl groups may be more free to rotate than in the ground state. No such increase of freedom is possible with the bridgehead systems. This other extreme viewpoint suggests that the magnitudes of  $\Delta S^\ddagger$  in bridged systems are "normal" and that the  $\Delta S^\ddagger$  of other compounds, with structures that can contribute to the transition state entropy, are "abnormal." Even long range rear-side solvation would be of no significance with tertiary acyclic or with bridgehead compounds.

It is not yet possible to differentiate between these interpretations. The reactive and readily available bridgehead adamantane compounds make further study of this problem attractive.

**2. The Higher Potential Energy of a Non-planar Carbonium Ion.**—It is generally assumed that carbonium ions are planar, but the evidence for this postulate is more inferential than direct.<sup>4</sup> The relative reactivities of bridgehead norbornyl and bicyclo[2.2.2]octyl derivatives and acyclic tertiary compounds are often cited in support of the planarity hypothesis,<sup>4,5,17</sup> since the strain which would be possessed by planar carbonium ions in these systems varies inversely in a qualitative manner with their reactivity. The appearance potential data for the same series of compounds in the gas phase furnishes a different kind of experimental corroboration, especially so because solvation effects are absent.<sup>32</sup>

The relative reactivities of bridgehead compounds can equally well be rationalized on the basis of non-planar structures for their respective carbonium ions. The more such a carbonium ion is

(28) E. S. Gould, "Mechanism and Structure in Organic Chemistry," H. Holt and Co., Inc., New York, N. Y., 1959, p. 181.

(29) Tertiary acyclic and cyclic compounds generally have solvolytic entropies of activation similar to those of *t*-butyl, in similar solvent systems. Numerous examples may be found in the literature cited in ref. 14; cf. H. C. Brown and M. Borkowski, *J. Am. Chem. Soc.*, **74**, 1894 (1952).

(30) The Grunwald-Winstein<sup>13</sup> "m" constant is sensitive to temperature.<sup>30,37</sup> When the bicyclo[2.2.2]octyl data of Doering, *et al.*,<sup>17</sup> is recalculated to  $25^\circ$  (Table III) for direct comparison with *t*-butyl at that temperature, it is seen that the bridgehead compounds appear to be significantly more sensitive to the ionizing power of the solvent than their acyclic counterparts.

(31) R. G. Pearson, *J. Chem. Phys.*, **20**, 1478 (1952), and ref. 27.

(32) J. L. Franklin and F. H. Field, *J. Chem. Phys.*, **21**, 550 (1953).

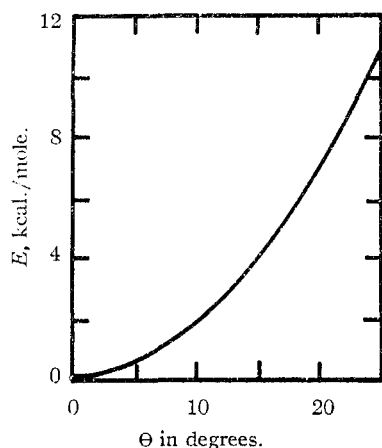


Fig. 2.—Plot of equation  $E = 0.0175 \theta^2$  kcal./mole.

forced to deviate from planarity, the higher would be its potential energy. The exact nature of the planarity-potential energy function is not known.

Calculations of the angle strain introduced in the bicyclo[2.2.2]octane molecule by the formation of a planar carbonium ion at the bridgehead have varied from 22.5 kcal./mole<sup>4</sup> to 6 kcal./mole.<sup>17b</sup> The calculations have been summarized and refined in the Experimental section of the present paper. Use of the best available data leads to an estimate of about 12 kcal. for the strain energy for the planar adamantane bridge-head carbonium ion. This value is quite incompatible with the high reactivity of 1-adamantyl halides which differ from *t*-butyl halides by only 1.8 kcal. in  $\Delta H^\ddagger$  and 4.0 kcal. in  $\Delta F^\ddagger$  for solvolysis (Table III). This suggests strongly that the transition state for solvolysis is not planar, but that a certain amount of flattening has occurred. A similar conclusion is reached by a consideration of comparable strain data for the norbornyl and bicyclooctyl systems.

Schöllkopf<sup>5b</sup> has presented a more sophisticated interpretation which comes to the same conclusion. The transition state for a  $S_N1$  solvolysis, by application of the Hammond postulate,<sup>33</sup> resembles the structure of the intermediate carbonium ion more closely than that of the starting material. The less stable the intermediate the more closely the transition state resembles it. During the ionization of a bridgehead derivative there are two opposing tendencies. The energy gain due to the flattening at the bridge-head is opposed by increasing ring strain as the angles are distorted more and more from their normal values. A balance results and the transition state is not planar, but is rather pyramidal, and hence has a higher potential energy than that of a planar structure.

The force constant for bending the C-C-C angle is generally taken to be  $0.8 \times 10^{-11}$  erg/radian<sup>2</sup> or  $E = 0.0175 \theta^2$  kcal./mole, where  $\theta$  is the angular deviation, in degrees, from the tetrahedral value.<sup>34-37</sup> Figure 2, a plot of  $E$  vs.  $\theta$  based upon

this formula, emphasizes certain features of structural behavior. Small deviations from normal angles do not introduce very much strain. For  $\theta = 2^\circ$ ,  $E$  is 0.07 kcal./mole and for  $\theta = 5^\circ$ ,  $E$  is only 0.44 kcal./mole. However, further deviations become increasingly more unfavorable energetically. If an angle is already strained, the energy required to distort it further is considerably greater. Thus, the difference in  $E$  for  $\theta$ 's of  $0^\circ$  and  $2^\circ$  is 0.07 kcal.; for  $5^\circ$  and  $7^\circ$  it is 0.42 kcal. and for  $15^\circ$  and  $17^\circ$  the difference is 1.12 kcal.

If one assumes that this potential function can be applied to estimate the strain possessed by a carbonium ion distorted from the most energetically favorable planar conformation, a number of interesting calculations can be made.<sup>38</sup> If the 1-adamantyl carbonium ion is tetrahedral, *i.e.*, it has the same geometry as adamantane itself, the strain based on distortion of angles alone is calculated to be 5.8 kcal./mole. This figure is less than the value 12 kcal./mole estimated for the total strain of the 1-adamantyl ion in the planar bridgehead conformation. As Schöllkopf<sup>5b</sup> suggested, this strain can be minimized by the cation adopting a conformation intermediate between these extremes. Calculations outlined in the Experimental section demonstrate that this energy minimum is reached when the  $C_\alpha-C^+-C_\alpha$  ( $C_2-C_1-C_8$ ) angle of adamantane is  $113.5^\circ$  instead of  $120^\circ$ . The total strain calculated for the whole molecule in this conformation is about 3.5 kcal., a figure in strikingly good agreement with the observed free energy of activation difference of 4.0 kcal. between *t*-butyl and 1-adamantyl solvolyses. The 0.5 kcal. difference between the two values could easily be accounted for by transition state solvation differences (*vide supra*). Quantum mechanical instability of a non-planar carbonium ion<sup>38</sup> does not appear to be a significant factor.

All of the C-C-C angles of the highly strained molecule, norbornane, are significantly less than  $109.5^\circ$ .<sup>39</sup> As the bridgehead flattens during ionization of a 1-norbornyl derivative, there is an initial small relief of strain of the angles at the 1-position, but this relief is overwhelmed by large increases in strain of the angles adjacent to the 1-position. In fact these angles would be constrained to values much less than  $90^\circ$  with the bridgehead carbonium ion in a planar conformation. It is easy to see why norbornane, much more difficult to distort than adamantane, gives a bridgehead ion of much higher potential energy than adamantane or bicyclo[2.2.2]octane.

Initially, the large difference in behavior between adamantane and bicyclo[2.2.2]octyl bridgehead derivatives appeared to be quite surprising. Examination of molecular models demonstrates that the geometry of the atoms adjacent to the

(37) K. S. Pitzer and W. E. Donath, *J. Am. Chem. Soc.*, **81**, 3213 (1959).

(38) G. E. Kimball (quoted by Doering, Levitz, Sayigh, Sprecher and Whelan, ref. 17b) has suggested that for quantum mechanical reasons a tetrahedral carbonium ion should be 24 kcal. higher in energy than a planar one.

(39) H. Krieger, *Suomen Kemi*, **B31**, 348 (1958); C. F. Wilcox, *J. Am. Chem. Soc.*, **82**, 414 (1960); J. C. Martin and P. D. Bartlett, *ibid.*, **79**, 2533 (1957); E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958).

(33) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(34) F. H. Westheimer in M. S. Newman, Ed., "Steric Effects in Organic Chemistry," J. Wiley and Sons, Inc., New York, N. Y., 1956, p. 523.

(35) S. Kaarsemaker and J. Coops, *Rec. trav. chim.*, **71**, 261 (1952).

(36) J. D. Dunitz and V. Schomaker, *J. Chem. Phys.*, **20**, 1703 (1952).

bridgehead of both systems *can be* precisely the same. On this basis, the solvolysis rates should be about the same.<sup>40</sup> Instead, adamantane compounds react more than  $10^3$  times faster. It is unlikely that this difference is due to the larger number of atoms in adamantane,<sup>41</sup> since this is offset by the presence of an additional ring. It is true that the strain in the 1-adamantyl ion can be lessened somewhat by distribution to a larger number of angles than is possible for the 1-bicyclo[2.2.2]octyl ion, but calculations show that the maximum possible difference between the two systems in this respect amounts to only 0.5 kcal. This is far from enough to account for the solvolysis behavior. Angle strain alone cannot explain the rate differences, but conformational considerations provide a simple rationalization.

Adamantane is uniquely free from angle (Baeyer) and conformational (Pitzer) strain, since all the angles are tetrahedral and all adjacent carbon atoms are in skew conformations. Bicyclo[2.2.2]octane is not strain free, however. The angles may all be tetrahedral, but in the most symmetrical conformation of the molecule there are three pairs of eclipsed groups ( $C_2-C_3$ ,  $C_5-C_6$  and  $C_7-C_8$ ). The total strain in the compound is therefore about  $3 \times 3.0$  kcal. = 9 kcal./mole.<sup>42</sup> Molecular models and calculations show that angle strain will not be increased appreciably by small twists about the  $C_1-C_4$  axis. Turner, Meador and Winkler<sup>43</sup> have claimed that such a twisted conformation of bicyclo[2.2.2]octane would have lower energy, because of the relief of some conformational strain. This is not the case. While twisting tends to relieve the torsional strain around *three* bonds ( $C_2-C_3$ ,  $C_5-C_6$  and  $C_7-C_8$ ), it tends to eclipse *six* bonds ( $C_1-C_2$ ,  $C_1-C_6$ ,  $C_1-C_7$ ,  $C_4-C_3$ ,  $C_4-C_5$  and  $C_4-C_8$ ). Twisting increases rather than decreases the energy content of the molecule.<sup>44</sup> Molecular structure determinations support a non-twisted structure for this molecule.<sup>45</sup>

The large amount of strain in bicyclo[2.2.2]octyl bridgehead derivatives must be responsible for their decreased reactivity relative to strain-free 1-adamantyl compounds. However, the mechanism

(40) Possible differences in "solvation energy" would have only a minor effect on rate; R. A. Clement and J. N. Naghizadeh, *J. Am. Chem. Soc.*, **81**, 3154 (1959); R. A. Clement and M. R. Rice, *ibid.*, **81**, 326 (1959).

(41) In *bicyclic* systems, an increase in the size of the rings should result in increased bridgehead reactivity, for obvious reasons. A quantitative study of this expectation is not yet available; the available literature has been reviewed (ref. 5).

(42) Mr. C. D. Woody (A.B. Thesis, Princeton University, 1957) has found that aluminum chloride converts bicyclo[2.2.2]octane into a mixture consisting chiefly of bicyclo[3.2.1]octane and of bicyclo[3.3.0]octane. Since both of the latter compounds contain five-membered rings, they must be strained to the extent of more than 6 kcal./mole. Bicyclo[2.2.2]octane must be strained to a larger extent. Cf. J. E. Germain and M. Blanchard, *Bull. soc. chim. France*, 473 (1960), and A. F. Bickel, J. Kuotnerius, E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **9**, 230 (1960).

(43) R. B. Turner, W. R. Meador and R. E. Winkler, *J. Am. Chem. Soc.*, **79**, 4116 (1957).

(44) We are indebted to Mr. Frank Fong for this observation and for further calculations on this problem.

(45) A. H. Nethercot, Jr., and A. Javan, *J. Chem. Phys.*, **21**, 363 (1953); J. J. Macfarlane and I. G. Ross, *J. Chem. Soc.*, 4169 (1960). The rather high heat of hydrogenation of bicyclo[2.2.2]octene, which lead Turner, Meador and Winkler<sup>43</sup> to postulate a twisted ground state structure for bicyclo[2.2.2]octane, can be explained satisfactorily with a non-twisted conformation.

for the transmission of a large portion of the ground state strain to the transition state is obscure. Were bicyclo[2.2.2]octane elongated along the  $C_1-C_4$  axis due to twisting or to another deforming influence, ionization at the bridgehead would be more difficult since such a process must result in a decrease of the  $C_1-C_4$  distance. Such elongation does not appear to be the case.<sup>45</sup> We are compelled to postulate a new effect, that the bending force constant of a bond angle composed of bonds already subjected to torsional strain is greater than the bending force constant of a bond angle composed of bonds whose attached atoms are perfectly staggered and therefore strain free. Compression of the  $C_1-C_2-C_3$  angle, as would take place during the ionization of a bridgehead substituent, is more favorable in adamantane than in bicyclo[2.2.2]octane because the latter has an eclipsed arrangement at  $C_2-C_3$ .

**3. Stereochemical Inhibition of Hyperconjugation.**—The behavior of bridgehead derivatives can be explained satisfactorily on the basis of strain considerations, with possibly a minor contribution from solvation effects. The experimental evidence does not appear to support the suggestion that hyperconjugation is inhibited at a bridgehead. More specifically, the evidence suggests that hyperconjugative contributions to the solvolysis transition states are either the same for the bridgehead and for the *t*-butyl systems or are completely or nearly completely absent in all these systems.

A similar conclusion concerning hyperconjugation at a bridgehead was reached during a study of the reactivity of 2-adamantyl derivatives.<sup>1</sup> In contrast is the recent observation of Shriner<sup>46</sup> that the normal  $\beta$ -deuterium secondary isotope effect is inhibited if the deuterium is situated upon a bridgehead.

**Comparison of Strain Effects.**<sup>47</sup>—In a preceding paper,<sup>1</sup> it was demonstrated that angular strain was the prime cause of the low reactivity of 7-norbornyl derivatives. The  $C_1-C_7-C_4$  angle of the 7-norbornyl cation is restricted to a value considerably smaller than  $120^\circ$ , but the carbonium ion can assume a planar structure. This "in-plane" strain caused by the inequality of the three bond angles around the ionized carbon atom seems to have at least as adverse an effect on carbonium ion stability as does a non-planar but symmetrical distortion. The differences in acetolysis activation enthalpies for the tosylates of cyclohexanol, 2-adamantanol and 7-norbornanol<sup>1</sup> can be estimated with surprising accuracy using the potential function  $E = 0.0175\theta^2$  kcal./mole. For the 7-norbornyl cation, the  $C_1-C_7-C_4$  angle is about  $100^\circ$  and the  $C_1-C_7-H$  and  $C_4-C_7-H$  angles are about  $130^\circ$ ; the total strain is therefore  $7.0 + 2 \times 1.75 = 10.5$  kcal./mole. The strain in the cyclohexyl cation, calculated similarly, is negligible (0.3 kcal./mole). The enthalpy of activation difference between the 7-norbornyl and cyclohexyl systems is 10.5 kcal.<sup>1</sup> More data are needed to test this correlation. The in-plane strain factor would, by it-

(46) V. J. Shriner, Jr., *J. Am. Chem. Soc.*, **82**, 2655 (1960).

(47) We are indebted to Professor Paul D. Bartlett for many of the ideas included in this section.

self, reduce seriously the reactivity of 1-norborn-derivatives.

Perhaps for  $sp^2$  orbitals the force constant for deformation in the plane is greater than that for deformation of the plane. Nevertheless, double bonds are permitted in cyclobutene and in cyclopropene but not in adamantene. It is unfortunate that no more is known about force constants and their behavior, especially over a large range of angular distortion where considerable rehybridization must be taking place.

At 25° acetolysis of 1-adamantyl tosylate (Table I) proceeds  $10^5$  faster than acetolysis of 2-adamantyl tosylate.<sup>1</sup> These results reflect the much greater stability of the 1-adamantyl carbonium ion over the 2-adamantyl cation and explain why ionic substitution reactions of adamantane yield bridgehead products exclusively.<sup>1,7-9</sup>

**Acknowledgments.**—A conversation with Professor S. Winstein concerning the interpretation of these results was very rewarding. We wish to thank Professor P. D. Bartlett for valuable suggestions.

### Experimental<sup>48</sup>

**1-Bromoadamantane (II).**—Adamantane,<sup>6</sup> 13 g., was treated with 96 g. of bromine by the method of Landa.<sup>7</sup> The crude product obtained, 17.8 g., was recrystallized from methanol at  $-70^\circ$ ; m.p.  $119.0$ – $120.0^\circ$  (lit.  $119.5$ – $120^\circ$ ,<sup>7</sup>  $118^\circ$ ).<sup>8</sup>

**1-Adamantanol (III).**—1-Bromoadamantane (II) was converted to 1-adamantanol by the solvolytic methods of Landa<sup>7</sup> and of Stetter.<sup>8</sup> Free radical hydroxylation of adamantane<sup>1</sup> also gave the same compound; m.p., when pure,  $287.2$ – $288.5^\circ$  (lit.  $288.5$ – $290^\circ$ ,<sup>7</sup>  $282^\circ$ ).<sup>8</sup>

**1-Chloroadamantane (IV).**—1-Adamantanol (III), 12 g., was treated with 60 ml. of thionyl chloride, using the procedure of Stetter.<sup>8</sup> Recrystallization from methanol at  $-70^\circ$  gave 10.3 g. of white solid, m.p.  $164.3$ – $165.6^\circ$  (lit.<sup>8</sup>  $165^\circ$ ).

**1-Iodoadamantane (V).**—A mixture of 5.0 g. of 1-adamantanol (III) and 75 ml. of 47% hydroiodic acid was sealed into a glass tube and heated on a steam-bath for 1 hour. After cooling, the contents were poured into water, and extracted with ether. The combined solvent was washed successively with aqueous  $\text{NaHSO}_3$ , aqueous  $\text{K}_2\text{CO}_3$  and water. After drying with solid  $\text{Na}_2\text{SO}_4$  and evaporating the solvent, a yellow solid remained. Recrystallization from methanol at  $-70^\circ$  gave 3.56 g. of white crystals, m.p.  $75.3$ – $76.4^\circ$  (lit.<sup>7</sup>  $151$ – $152.5^\circ$ ; see text).

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{15}\text{I}$ : C, 45.81; H, 5.77; I, 48.42. Found: C, 45.55; H, 5.77; I, 48.21.

**1-Adamantyl Tosylate (VI).**—Reaction of 1-adamantanol (III) with tosyl chloride by the usual procedure in pyridine either in the cold for 4 weeks or at steam-bath temperature failed to give satisfactory material. As a consequence the method used successfully by Norton<sup>12</sup> for the tosylation of 1-hydroxybicyclo[2.2.1]heptane was employed.

A solution of 0.6 g. of III in 25 ml. of dry benzene was added to a magnetically stirred mixture of 0.5 g. of 50% sodium dispersion (mineral oil) in 25 ml. of dry benzene. After refluxing 1 hour to complete formation of the alcoholate, the mixture was cooled and a solution of 1.75 g. of tosyl chloride in 25 ml. of dry benzene was added. After refluxing for 2.5 hours, the reaction was allowed to stand at room temperature overnight. The salts were filtered off and washed with petroleum ether. The combined filtrates were concentrated, treated with 10 ml. of pyridine for 5 minutes, and poured into water. Extraction with ether, followed by washing, drying and evaporating the solvent gave the product. After three recrystallizations from petroleum ether at  $-70^\circ$ , 0.7 g. of material was left. Since

the m.p.,  $65$ – $85^\circ$ , had not improved appreciably, further purification was abandoned and the sample was used for solvolysis directly. The infrared spectrum showed it to contain starting alcohol and tosylate ester. Solvolysis gave a purity of 40.5% by titration.

**Kinetic Procedures.<sup>1,13</sup>**—Solutions of the tosylate were made up in 50-ml. volumetric flasks. These were immersed in a bath maintained at  $25.00 \pm 0.01^\circ$ . At appropriate times 5-ml. samples were withdrawn by volumetric pipet and discharged rapidly into 5 ml. of petroleum ether. This quenched the reaction, and the samples were titrated promptly. The time of the sample was taken when half had been delivered into the petroleum ether. The remainder of the procedure was standard.<sup>1,13</sup>

Although the sample of VI was impure; the contaminant (III) was inert and good kinetic behavior was observed. However, in view of the heterogeneous sample used, no study was made of the solvolysis product.

Four volumes of anhydrous ethanol was mixed with one volume of distilled water to give "80% ethanol." The same batch of solvent was used for all runs. At least two runs were made for each compound at each temperature; the results, which agreed with each other satisfactorily, were averaged. The ampoule technique was used; 50 ml. of an approximately 0.02 *M* solution of the halide was divided and sealed into glass tubes. The temperatures of the baths used were constant to  $\pm 0.02^\circ$  or better, and were checked with a National Bureau of Standards calibrated thermometer. The ampoules, in a specially constructed rack, were lowered into the bath. One sample was removed and the reaction stopped by quick chilling after the bath temperature had been reached (2 to 4 minutes); the time of this sample was taken as zero. The ampoule was opened when the contents were at room temperature, 5 ml. pipetted out, and titrated with standard 0.02 *M* base to the phenolphthalein end-point. An indicator blank was used. Other samples were taken at evenly spaced intervals in the kinetic runs. Calculated infinity titers were used for the calculation of the rate constants.

The combined solutions from kinetic runs of one halide were heated to complete reaction, and poured into water. By ether extraction procedures, the solvolysis product was isolated. In each case, infrared spectroscopy showed the product to be identical with authentic 1-adamantanol. The spectra did not reveal the presence of detectable amounts of 1-adamantyl ethyl ether.

**Calculations of Strain.** 1. **Planarity at the Bridgehead.**—Bartlett and Knox<sup>4</sup> estimated that a steric strain of 22.5 kcal./mole would be present in a planar 1-bicyclo[2.2.2]octyl carbonium ion. During the flattening process, the three C–C–C angles adjacent to the bridgehead position would be distorted from  $109.5^\circ$  to (about)  $90^\circ$ . The distortion, for each methylene group, should be the same as that for each methylene group in cyclobutane, or 7.5 kcal./ $\text{CH}_2$ , as estimated from heat of combustion data. A more recent value for the strain in cyclobutane is 6.5 kcal./ $\text{CH}_2$ ,<sup>33</sup> giving a total strain of 19.5 kcal./mole for the planar bicyclo[2.2.2]octane bridgehead cation.<sup>34</sup>

Doering, Levitz, Sayigh, Sprecher and Whelan<sup>17</sup> have calculated a much lower value for the total bridgehead strain, 6 kcal./mole. They argued that part of the strain energy in cyclobutane is due to the energy of eclipsed or nearly eclipsed conformations; a correction for this was applied in obtaining the cited figure, a minimum value. Repeating their calculation with recent data<sup>35</sup> yields a minimum value of 10.5 kcal./mole for the bridgehead strain in bicyclo[2.2.2]octyl cation. This assumes, as now appears likely,<sup>49</sup> that properties of the bonds themselves and not non-bonded hydrogen repulsions are responsible for the major portion of the higher potential energy of an eclipsed conformation. The torsional energy in cyclobutane due to this source is estimated to be about 3 kcal./ $\text{CH}_2$ .<sup>50</sup> The angle deformation energy/ $\text{CH}_2$  is thus  $6.5$ – $3.0 = 3.5$  kcal./ $\text{CH}_2$ , and there are three such strained positions in the molecule. In using cyclobutane as a model, the consequences of the non-planarity of the four-membered ring and of possible 1,3-repulsions<sup>34</sup> are neglected.

(48) M.p.'s were determined in soft glass capillaries by means of a Hershberg apparatus equipped with calibrated Anschütz thermometers. Microanalyses were determined by Mr. George Robertson, Florham Park, N. J.

(49) G. H. Stewart and H. Eyring, *J. Chem. Ed.*, **35**, 550 (1958); E. B. Wilson, Jr., *Proc. Natl. Acad. Sci.*, **43**, 916 (1957); *Adv. in Chem. Phys.*, **2**, 367 (1959).

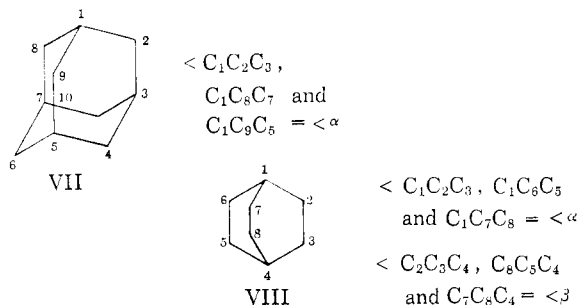
(50) The rotational barrier in ethane. This barrier is not very sensitive to the nature of the substituents; see ref. 49.



These effects tend to cancel each other, in their net influence.<sup>34</sup>

The bending force constant for the C-C-C bond angle,  $0.8 \times 10^{11}$  erg/radian<sup>2</sup> or  $E = 0.0175\theta^2$  kcal./mole<sup>34-37</sup> (*vide supra*), can be used to calculate a strain energy of 20 kcal./mole ( $\theta = 19.5^\circ$ ,  $E = -6.65$  kcal./angle,  $3 \times 6.65 = 20$  kcal./mole) for the planar 1-bicyclo[2.2.2]octyl ion. However, the unreliability of using this value for the bending force constant for large C-C-C angle deviations has been emphasized,<sup>34</sup> and this strain estimate is probably about a third too large. For smaller values of  $\theta$ , the bending force constant presumably gives more accurate results.<sup>37</sup> We shall continue to use this equation in the calculations below; however, these reservations should be borne in mind.

A number of rather obvious simplifying assumptions are included in the above estimations of strain-energy. It should be emphasized that the calculations based upon the above methods apply equally well to adamantane as to bicyclo[2.2.2]octane since the geometry about the bridgehead is the same. Certain refinements in the calculations will now be considered in an attempt to explain the differences in behavior between the two systems.



When the bridgeheads are flattened, the  $C_2$ ,  $C_8$  and  $C_9$  atoms of adamantane and the  $C_2$ ,  $C_8$  and  $C_7$  atoms of bicyclo[2.2.2]octane are thrust outward with the result that the angles  $\alpha$  (defined in VII and VIII) necessarily have a value less than  $90^\circ$ . If the lengths of the C-C bonds involving the carbonium ion all remain at 1.54 Å. and the geometry of the remainder of the molecule not involved in the bridgehead flattening remains the same, it is easy to calculate that the value of angle  $\alpha$  is  $86.7^\circ$ . This difference from  $90^\circ$  is small numerically, but the added strain is costly energetically because of the nature of the force constant (*vide supra*). The strain/CH<sub>2</sub> increases from  $E = 6.65$  kcal./CH<sub>2</sub> for  $\alpha = 90^\circ$  to  $E = 9.1$  kcal./CH<sub>2</sub> for  $\alpha = 86.7^\circ$ . The distortion in the rest of the molecule is negligibly small energetically. Bridgehead flattening also causes an increase of  $3.4^\circ$  in angle  $\beta$  (defined in VIII). In adamantane this distortion is distributed between two angles at each position for example, angles  $C_2-C_8-C_4$  and  $C_2-C_8-C_{10}$ . The total strain in adamantane due to this cause is only 0.3 kcal./mole, but in bicyclo[2.2.2]octane it is 0.6 kcal./mole since the  $3.4^\circ$  increase must be borne by a single angle.

A  $C_1$  carbonium ion should result in a decrease in the  $C_1-C_2$  bond length (and the length of other bonds involving the carbonium ion) to about 1.50 Å.,<sup>50</sup> because the bond is now of the  $sp^2-sp^3$  type.<sup>51,52</sup> This shortening alone will relieve some of the strain in angle  $\alpha$  (making  $\alpha = 88.1^\circ$ ,  $E = 8.0$  kcal./CH<sub>2</sub>) and in angle  $\beta$  (making  $\beta = 1.9^\circ$ ,  $E = 0.07$  kcal./CH<sub>2</sub>). Thus the total strain in bicyclo[2.2.2]octane would be 24.2 kcal./mole and 24.1 kcal./mole in adamantane. A partial flattening of the remaining six-membered ring in adamantane ( $C_3-C_7$ ,  $C_{10}$ ) or of the other bridgehead ( $C_4$ ) in bicyclo[2.2.2]octane will up to a certain point further

reduce the total strain. Calculations indicate that a minimization of strain is achieved in bicyclo[2.2.2]octane when the angle  $C_3-C_4-C_6$  (and the other similar angles) is about  $112.5^\circ$  and in adamantane, too, after a similar change in geometry. Angle  $\alpha$  now has the value  $89.2^\circ$  ( $E = 7.1$  kcal./CH<sub>2</sub>) and the strain in other parts of the molecule totals 0.8 kcal. for bicyclo[2.2.2]octane. The total strain calculated for the planar bicyclo[2.2.2]octyl bridgehead carbonium ion is therefore about 22 kcal./mole. Because of the larger number of angles available for strain distribution, the total strain in the planar 1-adamantyl cation is about 0.5 kcal./mole less than this. The small difference between the two systems reflects the fact that most of the strain in both planar cations comes from distortion of the angles  $\alpha$ , and the molecules can do comparatively little to widen this angle.

It should be pointed out again that the above values are probably too large by a factor of about 1.5,<sup>34</sup> but that the qualitative conclusions are still valid. The Bartlett-Doering approach, based on the known strain in cyclobutane, refined by the method above, yields an estimate of 12 kcal./mole for the minimum strain of a planar 1-adamantyl cation. The strain estimated for the planar 1-bicyclo[2.2.2]octyl cation would be slightly larger than this.

**2. Non-planar Bridgehead Carbonium Ion.**—If a carbonium ion is assumed to be planar because the three  $sp^2$  hybrid bonds are at  $120^\circ$  to each other and if angle distortions would result in strain (with no quantum mechanical effect), then the bending force constant can be used to calculate strain due to deviations from planarity. For example, if the 1-adamantyl cation has the same geometry as adamantane, then the three tetrahedral angles at the bridgehead would be distorted by  $10.5^\circ$  from their optimum value of  $120^\circ$ ;  $E = 1.93$  kcal./CH<sub>2</sub>, and the total strain would be 5.8 kcal./mole.

Between the extremes of a planar and a tetrahedral carbonium ion there is a conformation of minimum strain energy. In order to calculate this, an intermediate value of 1.52 Å. for the  $C^+-C$  distances was taken. In adamantane, a minimum total strain of 3.5 kcal./mole is achieved for the 1-ion when the value of angle  $C_2-C_1-C_8$  (and similar angles) is  $113.5^\circ$ . Angle  $\alpha$  has the value  $104.5^\circ$  and strain in other parts of the molecule is negligible. This latter fact means that the strain calculations apply equally well to the bicyclo[2.2.2]octyl bridgehead ion and that there is no significant strain difference between the two systems. If the  $C^+-C$  distances are 1.50 Å., the total strain in the molecules is 3.15 kcal./mole; if the distances are 1.54 Å., the total strain is 3.9 kcal./mole.

Since only small deviations from normal angles were involved, the bending force constant equation probably gave moderately good estimates for the strain calculations. Since the angle strain so calculated is in good agreement with that expected from the experimental reactivity of adamantyl halides, there seems to be no need to invoke quantum mechanical strain effects.<sup>35</sup>

Although the above arguments, based on estimate of angle strain, account satisfactorily for the behavior of the adamantane system, it is clear that they cannot explain the large solvolytic differences between adamantane and bicyclo[2.2.2]octane bridgehead derivatives.

The higher potential energy of eclipsed over staggered conformations is believed to be caused mainly by repelling effects between electrons of bonds to the substituents.<sup>49</sup> Thus, the  $C_1-C_2$  and  $C_3-C_4$  bonds of a chain of atoms  $C_1-C_2-C_3-C_4$  suffer greater repulsion when opposed than when skewed; hence, compression of the  $C_1-C_2-C_3$  angle is probably considerably more difficult in the eclipsed than in the staggered conformation. (As a consequence of this carbon angle contraction, the hydrogen atoms of the hydrocarbon chain move apart slightly, but this small separation increase would only partially compensate energetically for the increased difficulty of carbon angle bending in the eclipsed conformation.) This postulate would explain why an adamantane bridgehead (skewed bonds) apparently can flatten more easily than a bicyclo[2.2.2]octane bridgehead (opposed bonds).

If the C-C-C bending force constant varies with the torsional angle, as we are suggesting, calculations of strain energies must take this factor into account. It is hoped that data will be obtained to test and to evaluate this idea.

(51) The CH<sub>3</sub>-C distance is 1.488 Å. in propene (D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **27**, 868 (1957); 1.505 Å. in isobutene (L. S. Bartell and R. A. Bonham, *ibid.*, **32**, 824 (1960)); 1.515 Å. in acetone (J. D. Swalen and C. C. Costain, *ibid.*, **31**, 1562 (1959)) and 1.498 Å. as the average in four acetyl compounds (L. C. Krisher and E. B. Wilson, Jr., *ibid.*, **31**, 882 (1959)).

(52) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959); **11**, 96 (1960); G. R. Somayajulu, *J. Chem. Phys.*, **31**, 919 (1959); L. S. Bartell, *ibid.*, **32**, 827 (1960).