

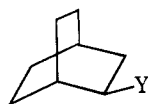
# Solvation Factors Affecting the Course of Solvolysis of Bicyclo[2.2.2]octyl Derivatives

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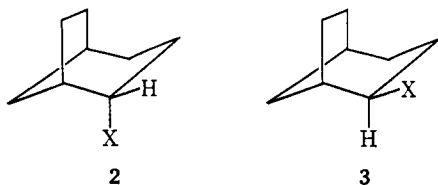
**Abstract:** In all familiar reactions having a bicyclooctyl cation intermediate, the product compositions distributed between the [2.2.2], *exo*-[3.2.1], and *endo*-[3.2.1] isomers are nearly invariant. Here, the acetolysis of the bicyclo[2.2.2]sulfoxonium ion also results in the same isomer distribution among the products. However, the change to the cationic sulfoxonium leaving group has altered several other aspects of the reaction course. The ratio of chloride to acetate product now appears to be very sensitive to the presence of LiClO<sub>4</sub>, small amounts of this additive increasing steeply the proportion of bicyclic acetate products. Moreover, added LiCl shows a pronounced induced common ion effect depressing the influence of LiClO<sub>4</sub> on the ROAc/RCl ratio. Studies of the relocation of a deuterium label in brosylate and sulfoxonium substrates have established that part of the product is formed *via* a pathway involving 7,2-hydride migration. This path is operative to the extent of 6% in the brosylate solvolysis and increases by more than a factor of 4 (26%) in the sulfoxonium case. The presence of added LiClO<sub>4</sub> can induce an additional *ca.* 40% increase in 7,2 hydride shifting in the sulfoxonium ions. These results can be reconciled with the occurrence of a multiplicity of ion pairs in the low ionizing power medium. The solvation characteristic of the various ion pair species can regulate the behavior of the cationic reaction intermediate *only* insofar as it can control its longevity, and therefore the available time for competing rate processes to occur. On this basis the data can be interpreted to support the following order of the absolute rates of the competing process: bicyclic C-C bond shifting > methide  $\cong$  hydride > phenide.

The bicyclooctyl cation produced through ionization of the carbon-oxygen bond in various derivatives of **1** has been shown to undergo ready Wagner-Meerwein



- la, Y = OSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub> (tosylate)  
 b, Y = OSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-Br (brosylate)  
 c, Y = OSAr (sulfonate)  
 d, Y = OCOCH<sub>3</sub> (acetate)  
 e, Y = NH<sub>2</sub> (amine)

rearrangement leading to products of the bicyclo[2.2.2]octyl and bicyclo[3.2.1]octyl systems. Walborsky and coworkers<sup>1</sup> found that acetolysis of **1b** resulted in about one-third of the *exo*-[3.2.1] acetate, **2**, and two-thirds of the [2.2.2] acetate, **1d**. Goering and Sloan<sup>2</sup> found that nearly the same ratio of **1** to **2** alcohols (Y or X = OH) results on deamination of **1e**, while acetolysis of the cor-

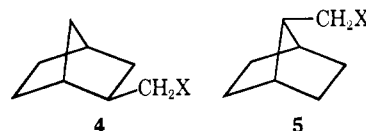


- a, X = OCOCH<sub>3</sub>  
 b, X = Cl  
 c, X = OH

responding tosylate (**1a**) yields almost a 1:1 ratio of the isomeric acetates (**2a/1d**). None of the *endo* isomer **3** was found in either of these reactions.

(1) (a) H. M. Walborsky, M. E. Baum, and A. A. Youseef, *J. Am. Chem. Soc.*, **81**, 4709 (1959); (b) *ibid.*, **83**, 988 (1961).  
 (2) H. L. Goering and M. F. Sloan, *ibid.*, **83**, 1397 (1961).

Berson and Wilner<sup>3</sup> have reported that *exo*-2-amino-methylnorbornane, **4**, produces nearly equal amounts of **1** and **2** alcohols on deamination. Later these authors<sup>4</sup> found that the same substrate gave as well a small amount of the *endo*-alcohol **3c**. More recently Berson and Poonian<sup>5</sup> studying the ring expansion of the brosylate and amino derivatives of the 7-norbornylmethyl system, **5**, obtained product composition results entirely



similar to those found<sup>4</sup> for the substrate **4**. In all cases previously investigated,<sup>1-6</sup> the intermediate cation (derived from **1**, **2**, **3**, **4**, or **5** substrates) in aqueous or acetic acid solvent resulted in nearly equal proportions of the [2.2.2] and *exo*-[3.2.1] products with only minor, if any, formation of the thermodynamically most stable *endo*-[3.2.1] isomer.

These data are all summarized in Table I. They suggest a common carbonium ion results from substrates of structures **1**  $\rightarrow$  **5**. Furthermore, in all cases the product-forming step is apparently independent of both the solvent medium (water or acetic acid) in which the intermediate is generated and the nature of the leaving group, as far as structure ([3.2.1] or [2.2.2]) is concerned.

In all instances, with the possible exception of deamination, the carbonium ion intermediate has evolved from an uncharged ground state. If a diazonium ion is the ground-state species in the deamination reaction, it apparently does not possess sufficient lifetime to surround itself with a solvent atmosphere that could in-

(3) J. A. Berson and D. Wilner, *ibid.*, **84**, 675 (1962).  
 (4) J. A. Berson and D. Wilner, *ibid.*, **86**, 609 (1964).  
 (5) J. A. Berson and M. J. Poonian, *ibid.*, **88**, 170 (1966).  
 (6) H. M. Walborsky, J. Webb, and C. G. Pitt, *J. Org. Chem.*, **28**, 3214 (1963).

**Table I.** Proportions of Isomers from Bicyclooctyl Cation (Formed in Various Rearrangements)

| Substrate                          | Ref            | Hydroxylic solvent | % [2.2.2] | % <i>exo</i> -[3.2.1] | % <i>endo</i> -[3.2.1] |
|------------------------------------|----------------|--------------------|-----------|-----------------------|------------------------|
| <b>1b</b> (brosylate) <sup>c</sup> | 6 <sup>b</sup> | HOAc               | 54        | 43                    | 2                      |
| <b>1e</b> (amine)                  | 2              | HOAc               | 64        | 36                    |                        |
| <b>1a</b> (tosylate) <sup>c</sup>  | 2              | H <sub>2</sub> O   | 55        | 45                    |                        |
| <b>4</b> (amine)                   | 3              | H <sub>2</sub> O   | 50        | 50                    |                        |
| <b>4</b> (amine)                   | 4              | HOAc               | 51        | 46                    | 4                      |
| <b>5</b> (amine)                   | 5              | <i>a</i>           | 58        | 40                    | 2                      |
| <b>5</b> (brosylate) <sup>c</sup>  | 5              | <i>a</i>           | 58        | 40                    | 2                      |

<sup>a</sup> No conditions given; presumably HOAc-H<sub>2</sub>O. <sup>b</sup> See also ref 1 by this school in which a slightly higher ratio (**2a/1d**) is reported. <sup>c</sup> Brosylate and tosylate are terms commonly employed to designate, respectively, the *p*-bromobenzene and *p*-toluenesulfonate ester derivatives.

fluence the subsequent solvolytic steps.<sup>7</sup> On the other hand, it has been established that a carbonium ion generated from a stable sulfoxonium ion ground state has inherited a solvent structure it could not have organized for itself if it had arisen from a neutral, poorly solvated ground state.<sup>7-9</sup> A striking consequence of these prior observations is to be realized in the ability to create increased stability and lifetime for the carbonium ion through solvation, properties beyond what could be expected solely on the basis of its inherent structural features.

In view of these considerations we proposed to study the solvolytic behavior of a sulfoxonium derivative of the bicyclooctyl system and compare the results obtained in the various categories of data compiled in Table I. Moreover, in the effort to gain insight into the stereochemical course of the Wagner-Meerwein rearrangements characteristic of this bicyclic system we have undertaken to trace the scrambling of a deuterium label during solvolysis of both the (neutral) brosylate and the sulfoxonium cation substrates.

**Product Composition Results and Discussion.** In earlier work<sup>7,8</sup> it has been demonstrated that the multiplicity of ground-state sulfoxonium ion pairs in acetic acid solution produce a corresponding multiplicity of ion paired reaction intermediates through transfer of their solvent structures to the carbonium ion centers developing in the transition state of solvolysis. One good way of testing for this occurrence is through study of the response of product composition to the addition of small amounts of LiClO<sub>4</sub> (and/or LiCl) to the low dielectric solvent medium. The uncharged sulfonate ester derivative shows little or no evidence<sup>1a</sup> of internal return;<sup>10</sup> no unusual influence on product composition can be traced to the presence of these additives. In terms utilized by Bartlett in his discussion of the bicyclooctyl system<sup>11</sup> it is convenient to invoke an "equilibrium" of various carbonium ion species as intermediates

(7) H. Kwart, R. W. Body, and D. M. Hoffman, *Chem. Commun.*, 765 (1967).

(8) H. Kwart and P. S. Strilko, *ibid.*, 767 (1967).

(9) H. Kwart, E. N. Givens, and C. J. Collins, *J. Am. Chem. Soc.*, **90**, 7162 (1968); **91**, 5532 (1969).

(10) As defined and illustrated by S. Winstein, *et al.*, *ibid.*, **73**, 1958 (1951); **74**, 2165, 2171 (1952).

(11) (a) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965. (b) It is not an objective of this article to establish the nature (classical or nonclassical) of the ions involved in the "equilibrium" of cationic species intervening in this reaction. To the extent that ref 11a sets the background, it is convenient to discuss our results from the same point of view.

in this sulfonate solvolysis. These apparently possess only a relatively short lifetime and then in only a single ion pairing relationship with the brosylate counterion prior to formation of covalent product.

The effect of added LiClO<sub>4</sub> (alone) and LiClO<sub>4</sub>-LiCl on the product composition obtained in acetolysis of the sulfoxonium substrate can be perceived in Table II.

**Table II.** Products<sup>a</sup> of Acetolysis of Bicyclo[2.2.2]octylsulfoxonium Ion<sup>b</sup> at *Ca.* 15°

| LiClO <sub>4</sub> , moles/l. | LiCl, moles/l. | % RCl <sup>c</sup> | % ROAc <sup>c</sup> | RCl/ROAc |
|-------------------------------|----------------|--------------------|---------------------|----------|
| 0.00                          | 0.00           | 43.1               | 56.9                | 0.76     |
| 0.06                          | 0.00           | 1.9                | 98.1                | 0.02     |
| 0.12                          | 0.00           | 0.0                | 100                 | 0.01     |
| 0.06                          | 0.12           | 34.4               | 65.4                | 0.53     |

<sup>a</sup> Products determined by glpc methods discussed in the Experimental Section. <sup>b</sup> See Experimental Section for procedures. The actual sulfoxonium ion is generated on chlorination of bicyclo[2.2.2]octan-2-ol 2,4-dinitrobenzenesulfonate in HOAc. <sup>c</sup> Considering the total number of moles of the respective chloride and acetate products of both the [2.2.2] and [3.2.1] systems regardless of the configuration of the chloride and acetate groups.

These results emphasize the increased stability and longevity of carbonium ions born in an inherited solvent environment. Their occurrence as solvolysis intermediates in a multiplicity of ion pair relationships is detected by the special salt effect criterion<sup>12</sup> and verified by the dramatic influence these additives have wrought<sup>7-9</sup> on product composition. Thus, as little as 0.06 *M* LiClO<sub>4</sub> induces a 35-fold decrease in the RCl component of the product by preventing return to the internal ion pair in which chloride is the counterion. While doubling this concentration to 0.12 *M* almost wipes out the RCl, adding 0.12 *M* LiCl to 0.06 *M* LiClO<sub>4</sub> effectively negates the influence of the latter. This is readily understood in terms of the perchlorate displacing the ion pair populations to external ion pairs and dissociated cations. Added LiCl, which by itself causes no significant common ion effect on product composition, is thus exercising an induced depression of the enhancement of ROAc formation attributed<sup>7-9</sup> to the "special salt effect" of the LiClO<sub>4</sub>. This parallels the induced common ion rate depression identified for highly stabilized carbonium ion systems such as the 3-*p*-anisyl-2-butyl.<sup>13</sup>

It is apparent that ion pairing relationships determine product proportions; *i.e.*, ion pairing controls the product-forming step as regards which product (RCl or ROAc) will be formed. But can the solvent structures which characterize the several types of ion pairs exercise control over the nature or composition of the carbonium ion? For example, can the several types of ion pairs identified be correlated with the features (or components) of the carbonium ion conceivably resulting from C-C bond shifting and/or hydride transfer? That is to ask, can solvation of the ion pair regulate the essential structural features of the carbonium ion which determine the structure of the product, [2.2.2] or [3.2.1]?

**Ion Pairing and Carbonium Ion Structures.** The experiments of previous investigators determining the proportions of [2.2.2] and [3.2.1] (Table I) products

(12) S. Winstein, *et al.*, *J. Am. Chem. Soc.*, **76**, 2597 (1954); *Chem. Ind. (London)*, 664 (1954).

(13) S. Winstein, P. E. Klindinst, Jr., and G. C. Robinson, *J. Am. Chem. Soc.*, **83**, 885 (1961).

resulting from solvolysis of sulfonate ester have been repeated to check consistency and reproducibility. These checks are listed in Table III alongside of product composition data realized from studies of sulfoxonium ion solvolysis under conditions which induce variation in the carbonium ion pairing relationships. In these runs it was possible to determine respectively how the acetate (ROAc) and chloride (RCl) product is distributed among the [2.2.2] and [3.2.1] isomers which can be isolated.

**Table III.** Proportions of Isomers Obtained on Acetolysis of Bicyclo[2.2.2]octylsulfoxonium Ion<sup>a</sup> at *Ca.* 15° Compared to Brosylate

| Reaction of   | Acetate   |                        |                         | Chloride  |                        |
|---|-----------|------------------------|-------------------------|-----------|------------------------|
|   | % [2.2.2] | % <i>exo</i> - [3.2.1] | % <i>endo</i> - [3.2.1] | % [2.2.2] | % <i>exo</i> - [3.2.1] |
| Brosylate <sup>b</sup>  | 50        | 47                     | 3                       |           |                        |
| Sulfoxonium, <sup>c</sup> no additives                                  | 52.3      | 46.2                   | 1.5                     | 58.5      | 41.5                   |
| Sulfoxonium <sup>c</sup> with 0.06 M LiClO <sub>4</sub>                 | 55.6      | 42.3                   | 2.4                     | 61.5      | 38.4                   |
| Sulfoxonium <sup>c</sup> with 0.06 M LiClO <sub>4</sub> and 0.12 M LiCl | 56.0      | 43.8                   |                         | 60        | 40                     |

<sup>a</sup> See footnote *b* in Table II. <sup>b</sup> Brosylate (6 g in 500 ml of dry HOAc + 0.031 M NaOAc) reacted at 50° for 600 min before work-up. Glpc analysis was performed on the alcohol mixture obtained on saponification. <sup>c</sup> Determined by capillary glpc analysis of reaction product; see Experimental Section.

Evidently the ratio of [2.2.2] to [3.2.1] is approximately *unity* and is almost the same for both the ROAc and RCl product. While 2 → 3% of *endo*-[3.2.1] product is formed as acetate and none is found as chloride, we do not attach any particular significance to this difference. It proved to be experimentally infeasible to detect a small amount of the *endo*-chloride in the presence of a much larger amount of the *exo*-chloride.

The origin of ROAc and RCl may be inferred from the influence of LiClO<sub>4</sub> and LiCl on the proportions of these products. The fact that LiClO<sub>4</sub> prevents return from external ion pair suggests the acetate is formed predominantly from the more stabilized carbonium ions. Moreover, LiCl effects the return of fully dissociated cations to internal ion pairs and by so doing restores the proportion of chloride product. Consequently, the predominant part of RCl must originate from internal ion pairs. In view of the near identity of isomer ([3.2.1] and [2.2.2]) distribution comprising the RCl and ROAc, as well as the fact that all substrates (Table I) solvolyze to this same isomer distribution, it may be deduced that the bicyclic carbonium ion (or equilibrium composition) in all the ion pairs in acetic acid solution consists of the same cationic species. While all these ion pairs differ in the extent and nature of their solvation, they differ very little in the manner in which they proceed to product by reaction with the nucleophiles available to them. Evidently stability as determined by solvation is not a factor in the interconversion of carbonium ion structures by C-C bond shifts. Interconversions of this nature occur much more readily and in less time than is required for their reaction (to form product) in the solvent atmosphere characteristic of the ion pair.

**Ion Pairing and Hydride Migration.** The conclusion deduced above regarding establishment of equilibrium

among the carbonium ion species applies only to those features which are determined by C-C bond shifting and resulting in interconversion of [2.2.2] and [3.2.1] structures. However, there are other events which require more time to occur and will therefore take place more extensively where the solvent shell affords greater lifetime to the reaction intermediate. One of these is clearly the 7,2-hydride shift.

Berson and Poonian<sup>5</sup> studying ring expansion of brosylate and amino derivatives of the 7-norbornyl-methyl (isomer of the bicyclooctyl system) found no hydride shift occurring. However, Bartlett<sup>11a</sup> has speculated that at least some of the racemization attending the acetolysis of optically active bicyclo[2.2.2]octyl brosylate<sup>1</sup> may have originated from 7,2-hydride shift, in view of the report by Roberts, Lee, and Saunders<sup>14</sup> that the 6,2-hydride shift occurs one-third as rapidly as the reaction of norbornyl cation with solvent HOAc. Furthermore, in solvents where the norbornyl cation can be regarded as having an infinite lifetime, Saunders, Schleyer, and Olah<sup>15</sup> have computed from nmr measurements at -120° that the process of 6,2-hydride shifting must have a rate constant at least as great as  $3 \times 10^5$  sec<sup>-1</sup> (with a limiting activation energy of 4.8 kcal/mole based on an assumed preexponential factor of  $10^{12.3}$ , the same as that for 3,2-hydride shift).<sup>11a</sup>

The acetolysis of deuterium-labeled **1b** was chosen for study since **1b** was known to undergo partial racemization and potentially, therefore, could experience hydride migration. The brosylate (prepared according to the procedures described in the Experimental Section) was deuterated at the  $\alpha$  (functionally substituted) carbon and solvolyzed under conditions which Walborsky and coworkers<sup>6</sup> found to result in 53% racemic bicyclo[2.2.2] product. The distribution of the deuterium label on the [2.2.2] skeleton was determined by mass spectral techniques.<sup>16</sup> It was found that 6% of the original deuterium content of **1b** had been scrambled, *i.e.*, had diffused from the  $\alpha$ -carbon position. Since 50% 7,2-shifted deuterium would correspond to 100% racemization, 6% 7,2 shifting accounts for only 12% racemization (about one-fourth of the amount observed). On this basis (as suspected by Bartlett<sup>11a</sup>), it must be assumed there are other routes for racemization of the bicyclooctylcarbonium ion intermediate.

The rate of 7,2-hydride transfer is not influenced directly by solvation. The lifetime of the carbonium ion is controlled by ion pair solvation and to that extent solvation regulates the observable amount of hydride transfer. Consequently, we can compute that 7,2 H migration occurs only ~0.06 as rapidly as product formation from the carbonium ion intervening in the acetolysis of **1b**; *i.e.*, the average rate at which ion pairs collapse to covalent product under these circumstances is nearly 33 times greater than the rate of D migration.<sup>17</sup> This is to be compared to the norbornonium ion generated under acetolysis conditions from sulfonate es-

(14) J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **76**, 4501 (1954).

(15) M. Saunders, P. von R. Schleyer, and G. A. Olah, *ibid.*, **86**, 5679 (1964).

(16) This is the work of Thomas A. Blazer to be reported in a future article.

(17) It is unlikely that a kinetic deuterium isotope effect has to be taken into account here since it is hydrogen which is actually migrating to the carbonium ion center developing at position 2 (see structure 6) resulting in the analogous cation with a relocated deuterium.

ter,<sup>14</sup> where product formation is only 3.3 times faster than the comparable 6,2-hydride transfer process. The conclusion suggested is that ion pair collapse in the bicyclooctylcarbonium ion intermediate is less than five times faster than the bicycloheptylcarbonium ion generated under very similar circumstances of ground-state and transition-state solvation. That is to say, the [2.2.1]carbonium ion of reference is more than ten times more stable than the corresponding [2.2.2].

Examined in yet another way, if we choose to regard the racemization of the **1** as an equilibration of classical and nonclassical ions,<sup>1,6,11a</sup> we may say that this interconversion occurs *at least* four times faster than 7,2-hydride transfer (using Walborsky's figure of 53% total racemization of the bicyclo[2.2.2]octyl product of acetyloxy of **1b**).<sup>6</sup> However, this is certainly close to the maximum value for the rate relationship of the two competing processes. In a poorer solvent and under circumstances where the life of the carbonium ion were shorter, we could expect the equilibration of classical and nonclassical ions to be almost immeasurably faster than the 7,2- (or 6,2-) hydride shift.

One available means of proving the (above) contention that longer lifetime alone increases the extent of H migration is through solvolysis of the deuterium-labeled sulfoxonium ion of **1**. Here, even though the ion pairing and solvation factors have extended the lifetime of the reaction intermediate, they have not altered the composition of the product (Table III) and therefore have not significantly disturbed the essential nature of this carbonium ion. Thus, the sulfoxonium ion (labeled with D in the same position as the brosylate **1b**, above) was solvolyzed in the presence and absence of added LiClO<sub>4</sub>. The bicyclo[2.2.2]octyl products were analyzed in the same way to obtain a measure of the degree of isotope migration in these reactions. The amount of D scrambling was 26%, corresponding to 52% racemization *via* the H-shifting route. This represents more than a fourfold increase over what is experienced in brosylate (**1b**) solvolysis where the carbonium ion pair intermediates are less stabilized by solvation. In the presence of 0.12 M LiClO<sub>4</sub> the amount of D scrambling increases to 36% (and therefore 72% racemization *via* 7,2 H transfer). This corresponds to *ca.* 40% increase in the average lifetime of the solvated intermediates.

By way of summarizing, we note that C-C bond shifting can determine the character of the cationic intermediate in the solvolysis reaction, such rearrangement processes being almost immeasurably fast and uninfluenced by solvation in the bicyclic system with which we are dealing here. Hydride shifting, on the other hand, takes place somewhat less readily and is noticeable only when the lifetime of the reaction intermediate is sufficiently protracted by solvation. This conclusion, at first glance, would appear to be completely opposite and contradictory to what we have stated previously<sup>9</sup> regarding the (entirely different) acyclic system of 3-phenyl-2-butyl cations. Therein, we observed that extending the lifetime of the carbonium ion did induce a change in its character; the internal (less stabilized) ion pairs possessed a different composition of carbonium ions than the more solvated ion pairs. The apparent discrepancy is resolved by the fact that only in the shorter lived ions (for example, those arising in deamination)<sup>9</sup> were the

competing processes of methide and hydride migration noticeable. As the life expectancy of the carbonium ion intermediate(s) in the 3-phenyl-2-butyl system is decreased the proportion of phenyl migration product decreases because this event requires more time. This suggests that equilibrium between the several species comprising the carbonium ion intermediates in some solvolytic reactions may never be attained for lack of time.

Once again it is clear that solvation (in addition to determining the rate of ionization) can influence the nature of the cationic intermediate *only* insofar as it can control the time available in which competing rate processes can take place. The data we now have at hand would confirm an order in the facility with which bond shifting and group migrations compete on the absolute time scale of rate processes (as follows): bicyclic C-C bonding shifting > methide  $\cong$  hydride > phenide.

The idea of a direct solvent effect on the absolute rate of an "interconversion and equilibration process" of this nature has attained some currency.<sup>18</sup> In view of the conclusions drawn above, this concept is at best incomplete and insufficient.

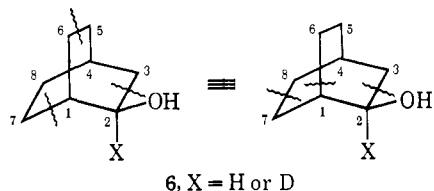
**Interpretation.** In a similar vein the observation<sup>5</sup> of "memory effects" in which an ion appears to preserve a recollection of its origin can be again attributed to ion pairing phenomena. Here a variety of isomeric (solvated) substrates are undergoing reaction to form the same products but in different proportions. The often overlooked<sup>19</sup> factor responsible for such differences may be ground-state solvation. We have shown that ground-state solvent structure organized in discreet ion pairs (as in sulfoxonium ions) can be transferred to the developing carbonium ion center completely when the group departing in the transition state is losing its charge. Conceivably, a neutral substrate may also have a degree of solvent organization<sup>19</sup> partly associated with the polar character of the leaving group and certainly influenced by the substituent structure at the carbon seat of reaction. As the leaving group departs, the developing carbonium ion arranges a solvent structure comprised of (all or part of) the material originally structured in the ground state. Clearly these circumstances will exert a measurable influence on how and with what material the solvation atmosphere will be constructed, will determine the nature of the ion pairing relationships to be experienced by the carbonium ion, and therefore the longevity of this ion. As inferred from the results reported here, the lifetime of the carbonium ion can be the most significant consideration in regulation of product proportions.

## Experimental Section

**Mass Spectral Analysis and Computation.** The procedures and calculations are based on the work of Blazer,<sup>16</sup> who, using the deuterated and nondeuterated alcohols, has shown that the peaks of *m/e* 57 and 58 were the most useful for determining the amount of isotope migration between C<sub>7</sub> and C<sub>2</sub>. These masses are believed to be (C<sub>7</sub>H<sub>9</sub>O)<sup>+</sup> and (C<sub>7</sub>H<sub>8</sub>DO)<sup>+</sup> fragments formed through breakage of the bonds indicated in **6**. The ratio of 57:58 in the deuterated alcohol would correspond to no loss of D at C<sub>2</sub>, while the 57:58 ratio in the nondeuterated alcohol would represent complete

(18) See, for example, the discussion in E. M. Kosower, "An Introduction to Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1968, p 139 ff.

(19) See, for a full discussion, E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. McC. Duggleby, *J. Am. Chem. Soc.*, **87**, 1541 (1965).



loss of D at C<sub>2</sub>. The linear relationship between the 57:58 peak ratio and the amount of D migration has been established. Since in structure 6 the 7 and 6 positions are equivalent, measurements of the extent of deuterium relocation from the 2 position require correction by a statistical factor of 2 to account for the equal probability of fragmentation (1  $\frac{1}{2}$  6 and 1  $\frac{1}{2}$  7) occurring in these two equivalent modes. The actual values of the 57:58 ratio corresponding to 100% D loss and 0% D shift are a function of the characteristics of the mass spectrometer being used. While quite reproducible, the instrumental characteristics with respect to these base values must be checked and calibrated from time to time. For example, in the CEC Model 21-103-C spectrometer used, 100% D loss corresponded to a 57:58 ratio of 7.7 and 0% D loss gives a ratio of 0.22. In a typical experiment the saponified acetolysis product [2.2.2] alcohol showed a ratio of 0.28 which calculates to be  $2\{[0.28/(7.7 - 0.22)]100\} = 6\%$  D migration. In another experiment with a deuterated sample of different isotope distribution and using a Bendix Time-of-Flight Model 12-107 spectrometer the 100% D shift value of the 57:58 ratio was 4.4 and the 0% D shift ratio was 0.37. The solvolysis reaction product showed a ratio value of 0.52 and the computed extent of D migration was therefore  $= 2\{[0.52/(4.4 - 0.37)]100\} = 26\%$ .

**Preparation of Bicyclo[2.2.2]oct-5-en-2-yl Methyl Ketone.** Cyclohexadiene, methyl vinyl ketone, and a few crystals of hydroquinone were refluxed at atmospheric pressure. The reaction was followed by glpc analysis until there was no further decrease in methyl vinyl ketone (which was in excess). Reaction time varied from 4 days to more than 2 weeks and did not seem to be dependent on size of batch.

Low-boiling material was removed by distillation at atmospheric pressure and product then distilled under 0.5–0.3 mm through a short, total take-off column. The glpc analysis indicated the product consisted mostly of two components, presumably corresponding to the *endo* and *exo* epimers; the semicarbazone prepared from the mixed product (mp 183–185°) corresponded well with the literature characteristics (lit. mp 183–184°, 20 181–183° 21).

**Hydrogenation of Bicyclo[2.2.2]oct-5-en-2-yl Methyl Ketone.** Crude olefin (100 g) was dissolved in 100 ml of absolute methanol and hydrogenated at room temperature under 30–60 lb of hydrogen. The catalyst was Pd (5%) on carbon. The theoretical amount of hydrogen was usually taken up in about 3 hr. The catalyst was filtered over Celite and the methanol stripped on the flash evaporator. Product was distilled under 0.5–0.3 mm through a short, total take-off column. The glpc analysis showed one major peak and complete absence of starting olefin. There was a strong band in the ir at 1730 cm<sup>-1</sup> and no vinylic hydrogens in the nmr spectrum. Semicarbazone had mp 196–198° (lit. 22 mp 196–197°).

**Preparation of Bicyclo[2.2.2]oct-2-yl Acetate.** This was prepared from the ketone using permaleic acid in a Baeyer–Villiger oxidation.<sup>23</sup> A typical procedure for the reaction was to mix 11.6 g of 50% H<sub>2</sub>O<sub>2</sub> (0.17 mole) in 150 ml of cold CH<sub>2</sub>Cl<sub>2</sub>. To the cold solution, in an ice bath, 49 g (0.5 mole) of maleic anhydride was added in one batch. This represents an excess of anhydride to react with both the peroxide and the water. The mixture was stirred until all of the anhydride had reacted and then heated to reflux. The ketone (15.2 g, 0.1 mole) in an equal volume of CH<sub>2</sub>Cl<sub>2</sub> was added to the refluxing solution. Titration of 1-ml aliquots indicated the reaction was complete in 1.5 hr. After cooling the maleic acid was filtered and the reaction mixture was extracted with two 100-ml portions of each of the following reagents in succession—10% Na<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>O, 10% NaHSO<sub>3</sub>, saturated NaCl. The organic layer was dried over MgSO<sub>4</sub> and stripped on the flash evaporator. The liquid product had strong odor similar to that of norbornyl acetates. The glpc analysis showed no ketone remaining and the ir had strong acetate peaks at 1760 and 1250 cm<sup>-1</sup> and no ketone at 1730 cm<sup>-1</sup>.

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(21) Y. A. Arbiznov and B. L. Dyatkin, *Dokl. Akad. Nauk SSSR*, **111**, 1249 (1956).

(22) B. A. Kazanskii and P. I. Zaberzenskaya, *ibid.*, **73**, 57 (1950).

(23) R. W. White and W. D. Emmons, *Tetrahedron*, **17**, 31 (1962).

**Saponification of Bicyclo[2.2.2]oct-2-yl Acetate.** The product from the Baeyer–Villiger reaction was dissolved in a large volume of ethanol in which a small piece of sodium had been dissolved. The solution was distilled until no ethyl acetate was coming over with the ethanol. The cooled residual alcohol solution was poured into 1 l. of water and the solid which appeared was extracted into ether. The ether was dried over MgSO<sub>4</sub> and removed on the flash evaporator. The alcohol was then either recrystallized from pentane or sublimed under aspirator vacuum at 100°. The ir spectrum (10% in CS<sub>2</sub>) matched that given in the literature<sup>1b</sup> and did not show peaks for either of the isomeric [3.2.1] alcohols. The glpc analysis showed that there was none of the [3.2.1] isomers present.<sup>1b</sup>

**Preparation of 2,4-Dinitrobenzenesulfonyl Chloride.**<sup>24</sup> A weighed amount (40 g) of bis(2,4-dinitrophenyl) disulfide was slurried in 200 ml of CCl<sub>4</sub> and treated with 2.0 ml of pyridine and 20 ml of sulfonyl chloride, followed by refluxing for 2.5 hr. After reflux, charcoal was added and the reaction mixture filtered. Solvent was evaporated from the deep red solution on a steam bath. The resulting brown mass was recrystallized from CHCl<sub>3</sub> yielding yellow crystals melting at 96–97°.

**Preparation of Sulfenyl Esters.** The same procedure was used in labeled and unlabeled alcohols. Equal weights of 2,4-dinitrobenzenesulfonyl chloride and alcohol were dissolved in dichloroethylene and 4 or 5 ml of pyridine was added. A slight exotherm and deepening of color was noted followed by formation of a small amount of yellow, high-melting solid. After sitting several hours the solvent was evaporated and the yellow solid recrystallized from 50% ethanol–benzene. After three recrystallizations, the melting point was 157°.

*Anal.* Calcd for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>6</sub>S: C, 51.84; H, 4.97; N, 8.64; S, 9.89. Found: C, 52.08; H, 5.12; N, 8.47; S, 9.75.

**Generation and Acetolysis of the Sulfoxonium Substrate.** The same general procedure was used for each reaction. The sulfenyl ester as an approximately 1% solution in dry acetic acid was rapidly mixed with a solution (0.5 M) of Cl<sub>2</sub> in the same volume of acetic acid. In those runs using added salts, the salts were dissolved in the same solution as the sulfenyl ester in a concentration to give the correct molarity when the two solutions (chlorine and sulfenyl ester) were mixed. After stirring a few minutes, the solution was poured into 1 l. of cold water and solid NaHSO<sub>3</sub> added to the point of a negative test to starch-iodide paper. The solution was then extracted with five 200-ml portions of pentane and the extracts were stirred rapidly with 300 ml of 28% NH<sub>4</sub>OH for 30 min to remove the 2,4-dinitrobenzenesulfonyl chloride side product. The pentane solution was washed with water until neutral to litmus, then dried over MgSO<sub>4</sub>. The pentane was removed on a rotary solvent evaporator while maintaining the temperature below 40°. The pentane was not completely removed to minimize possible loss of the sublimable chloride products. The product mixture was then analyzed by capillary glpc.

**Preparation of Bicyclo[2.2.2]octan-2-one.** The procedure used for this preparation was the same as that used by Walborsky for the preparation of the [3.2.1] ketone.<sup>6</sup> A weighed amount (20 g, 0.16 mole) of alcohol was dissolved in 67 ml of glacial acetic acid. The solution was cooled just above the freezing point of the mixture and a solution of 12.5 g (0.125 mole) of CrO<sub>3</sub> in 8 ml of water and 64 ml of glacial acetic acid was added slowly to keep the temperature between 13 and 15°. The dark solution was then stirred for 5 hr at room temperature. After dilution to 1 l. with water, the mixture was extracted with a total volume of 750 ml of petroleum ether (bp 30–60°). The organic layer was dried over solid NaHCO<sub>3</sub>. The major part of the solvent was removed on the flash evaporator and the remainder on the steam bath. The ir showed a strong carbonyl absorption at 1750 cm<sup>-1</sup> and a very small absorption at 3400 cm<sup>-1</sup> for the unreacted alcohol.

**Reduction of Bicyclo[2.2.2]octan-2-one with LiAlD<sub>4</sub>.** A small quantity (about 0.5 g) of LiAlD<sub>4</sub> was slurried in about 25 ml of anhydrous ether while 6.2 g (1:0.25 mole ratio) of ketone in 25 ml of anhydrous ether was added at a rate sufficient to keep the ether gently refluxing. The reaction was refluxed overnight. Petroleum ether (bp 30–60°) was added, followed by 5% sulfuric acid. The aqueous layer was extracted with additional ether and the ether combined with that from the reaction and dried over MgSO<sub>4</sub>. Solvent was removed on steam bath. It showed a free OH at 3600 cm<sup>-1</sup> and a broad bonded –OH absorption at 3300 cm<sup>-1</sup> (10% CS<sub>2</sub>). No ketone was evident and there was a C–D stretching frequency at 2100 cm<sup>-1</sup>. The glpc analysis (20 ft, 25% diglycerol)

(24) N. Kharasch, D. P. McQuarried, and C. M. Buess, *J. Am. Chem. Soc.*, **75**, 2659 (1953).

showed two small peaks corresponding to *exo*- and *endo*-[3.2.1] alcohols but these comprised less than 1% each.

**Preparation of Bicyclo[2.2.2]octan-2-yl Acetate-2-*d*.** The deuterated alcohol (0.5 g) was dissolved in 65 ml of pyridine and 6 ml of acetic anhydride. The solution was heated on a steam bath for 24 hr but was not refluxed. The cooled solution was poured into 100 ml of water and extracted with three 25-ml portions of ether. The organic layer was dried over MgSO<sub>4</sub> and evaporated slowly on the steam bath. The residue was distilled in a very short path column. The glpc analysis showed there was no remaining alcohol. A sample of this product was collected by glpc for mass spectral comparison with a sample of pure nondeuterated acetate prepared in the same way.

**Preparation of Bicyclo[2.2.2]octan-2-yl Brosylate-2-*d*.** Deuterated alcohol (3.1 g) was dissolved in 25 ml of pyridine. This was cooled in an ice bath and 8.0 g (0.03 mole) of brosyl chloride was added and stirred until most had gone into solution. The reaction mixture was then placed in the freezer for 24 hr. The solution and the crystals which had formed in it were poured over ice and allowed to melt. It was then filtered and washed with small portions of cool water. The pure product (mp 82°) compared closely to the literature<sup>1a</sup> (mp 80–81°) for the nondeuterated compound.

**Acetolysis of Bicyclo[2.2.2]octan-2-yl Brosylate 2-*d*.** The deuterated alcohol (6.0 g) was dissolved in 500 ml of glacial acetic acid containing 0.031 M NaOAc and allowed to react for 10 hr at 50°. The mixture was then diluted to 2 l. with water and extracted immediately into petroleum ether (bp 30–60°). The solution was dried over MgSO<sub>4</sub> and stripped on a steam bath yielding 2–3 g of liquid. A portion (2.0 g) of the product mixture was added to a solution of 1 g of KOH in about 30 ml of methanol. This was stirred at room temperature overnight, poured into 500 ml of H<sub>2</sub>O, and extracted with ether. The ether was dried over MgSO<sub>4</sub> and removed on the steam bath.

There were minor impurities in the glpc and three peaks with retention times corresponding to the literature.<sup>6</sup> These peaks were correlated with *exo*-[3.2.1] alcohol, [2.2.2] alcohol and *endo*-[3.2.1] alcohol. The peak areas were 47.2, 49.5, and 3.3%, respectively. The literature<sup>6</sup> gives ratios of 43.0, 54.1, and 1.7%, respectively.

**Preparation of Bicyclooctyl Chlorides with HCl.** A sample of the alcohol was placed in a flask, covered with concentrated HCl, and heated on a steam bath until there was an obvious change in the solid phase (about 15 min). The organic material was extracted into ether and dried over MgSO<sub>4</sub>, and the solvent was removed on a steam bath. Neither ir nor glpc analysis showed any alcohol remaining. There was a C–Cl absorption at 782 cm<sup>-1</sup> and no vinylic protons. The only technique found for separating these isomers was through use of a 300-ft capillary glpc column,

giving two peaks of almost identical concentration (see glpc section for conditions).

**Preparation of Bicyclooctyl Chlorides with Thionyl Chloride.** Alcohol (1.5 g) was dissolved in 25 cc of benzene and refluxed while 10 ml of SOCl<sub>2</sub> was added dropwise. The reaction mixture was refluxed overnight. Solvent was removed on a steam bath and the residue poured into water. The white solid was filtered and washed with water. Ir and glpc analysis showed that this product was identical with that prepared by reacting the alcohol with concentrated HCl.

**Vapor Phase Chromatography (Glpc).** To follow the preparative reactions a 10 ft × 0.25 in. copper column was packed with 20% diethylene glycol adipate on Chromosorb W (60–80). Temperatures varied from 120 to 165° as necessary to get good separation. Helium flow rate was 60 cc/min. This was an effective column for separations in this system. It would not separate the isomers of the alcohols, acetates, or chlorides, but would separate the various functionally substituted bicyclooctane derivatives from each other readily.

The alcohols were easily separated on a 20 ft × 0.25 in. copper column packed with 25% diglycerol on Chromosorb W (60–80). The operating temperature was 140° and He flow was 120 cc/min. According to the literature,<sup>2b</sup> this column would separate the [2.2.2] alcohol from each of the isomeric [3.2.1] alcohols. The *exo*-[3.2.1] came out first, followed by [2.2.2], then *endo*-[3.2.1]. An alcohol mixture obtained by KOH saponification of the acetates arising from solvolysis of the [2.2.2] brosylate gave three peaks, the first coming off after 25 min. These were in the ratio of 47.2, 49.5, and 3.3%. This checks with Walborsky's results of 43.0% *exo*-[3.2.1], 54.1% [2.2.2], and 1.7% *endo*-[3.2.1].<sup>6</sup>

The products from the sulfoxonium ion reactions were analyzed on a capillary column, 300 ft × 0.01 in., with a Ucon coating. Initial temperature was 100°, and after the chlorides came off the temperature was raised to 140° for elution of the acetates. The chlorides took about 55 min to come off and the acetates approximately 90 min. N<sub>2</sub> carrier gas was used at a pressure of 28 psig.

The packed column analysis was done on either a F & M Model 300 or a F & M Model 710, both using thermal conductivity detectors and helium flow. The capillary work was on a Perkin-Elmer Model 880 with H<sub>2</sub> flame detectors, N<sub>2</sub> carrier gas, and a Perkin-Elmer capillary conversion apparatus.

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(25) W. Kraus, *Ber.*, 97, 2726 (1964).