We conclude that in considering relations between rate and acidity one must consider not only the molecularity of the reaction, but also the position of the positive charge in the transition state, especially insofar as it governs hydrogen bonding with the solvent. We are testing our generalizations that acid hydrolyses which involve transition states which are strongly hydrogen bonded to water will be favored by acids having anions of high charge density. It seems probable that an anion of low charge density, such as perchlorate, stabilizes carbonium ion like transition states.
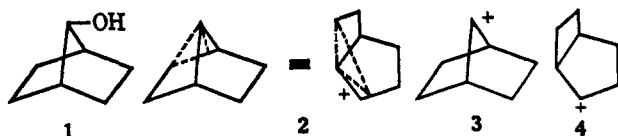
Solvolysis of 7-Norbornyl p-Bromobenzenesulfonate[1]

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Abstract: Solvolysis of deuterium-labeled 7-norbornyl p-bromobenzenesulfonate in a variety of solvents leads to 7-norbornyl product with 10-20% inversion and 90-80% retention of configuration. From this information and literature data it is concluded that, no matter what position one takes in the nonclassical ion controversy, ionization of 7-norbornyl p-bromobenzenesulfonate leads to a system in which the difference in stability between classical and nonclassical ions is small.

The acetolysis of derivatives of 7-norbornanol (1) is an example of a solvolysis which has been interpreted in terms of both classical and nonclassical carbonium ions.[2-4] On the basis of Foote's[2] and Schleyer's[3] acetolysis rate correlations there is no evidence for anchimeric acceleration in the acetolysis of 7-norbornyl p-toluenesulfonate. However, product studies indicate that nonclassical ion 2 is an intermediate in the acetolysis of 7-norbornyl p-bromobenzenesulfonate.[4] The rearranged acetate formed in this solvolysis, 2-bicyclo[3.2.0]heptyl acetate, is exclusively the *trans* isomer. None of the *cis* isomer was detected.

1   2   3   4

In order to obtain further information on this apparent anomaly we have studied the solvolysis of anti-2,3-dideuterio-7-norbornyl p-bromobenzenesulfonate (5).[5] We find in a variety of solvents (acetic acid, aqueous methanol, aqueous acetone, and formic acid) that the 7-norbornyl product is predominantly the *anti* isomer (retention of configuration), but that 10-20% of the *syn* isomer is also formed. Results are summarized in Table I.

(1) (a) A preliminary account of part of this work has appeared: F. B. Miles, *J. Amer. Chem. Soc.*, **89**, 2488 (1967). (b) P. G. Gassman and J. M. Hornback, working independently, have published a preliminary account of similar work on the corresponding p-toluenesulfonate: *ibid.*, **89**, 2487 (1967).

(2) C. S. Foote, *ibid.*, **86**, 1853 (1964). The fact that two of Foote's original 20 compounds have since been shown to have structures different from those accepted at the time the correlation was published does not affect the correlation appreciably. For further details, see footnote 10 of ref 1a.

(3) P. von R. Schleyer, *ibid.*, **86**, 1854 (1964).

(4) S. Winstein, F. Gadient, E. T. Stafford, and P. Klinedinst, Jr., *ibid.*, **80**, 5895 (1958).

(5) The terms *syn* and *anti* as used here refer to the position of the deuterium atoms with respect to the oxygen function.

Table I. Retention of Configuration as a Function of Solvent in the Solvolysis of 2,3-Dideuterio-7-norbornyl p-Bromobenzenesulfonate

Solvent[a,b]	Y^c	Temp, °C	Reaction time, hr	% retention
Acetic acid	−1.68	205	1.5	90 ± 5[d]
Methanol–water (70:30)	+0.96	150	20	80 ± 5
Acetone–water (50:50)	+1.40	150	20	85 ± 5
Formic acid	+2.05	100	16	85 ± 5

[a] In all cases, sufficient base was added to neutralize liberated p-bromobenzenesulfonic acid. Sodium acetate was used in acetic acid; sodium formate was used in formic acid; 2,6-lutidine was used in aqueous methanol and aqueous acetone. [b] Percentages given are vol % at 25°. [c] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2770 (1956). [d] No change was observed in per cent retention when sodium acetate was omitted.

Deuterated p-bromobenzenesulfonate recovered after 90 min (*ca.* two solvolysis half-lives) in acetic acid at 205° showed 0 ± 5% ion-pair return to *syn*-deuterated p-bromobenzenesulfonate in the presence and in the absence of added sodium acetate.

Explanation Assuming Nonclassical Ions Are Involved. Clearly, the experimental results cannot be explained exclusively in terms of nonclassical ion 6. Classical ion 7 is also needed. The observed predominant retention of configuration is readily explained in terms of nonclassical ion 6 (as a free ion or as an ion pair) while the 10–20% inversion observed in the 7-nor-

5   6   7
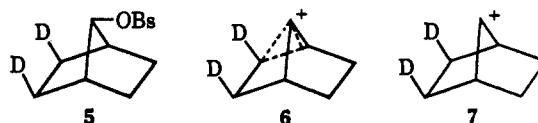
bornyl product may be explained by ionization to 7 in competition with ionization to 6, *i.e.*, by assuming

R_{320}-OAc formation
+38.8 —————*

R_{320}-OBs ionization
+37.7 —————*

R_{221}-OAc formation
+37.2 —————*

R_{221}-OBs ionization
+36.1 —————*

ion-pair interconversion
≤+35.8 —————*

≥+31.0 ————— $R_{320}{}^{+}$

$R_{221}{}^{+}$
—————

R_{320}-OBs
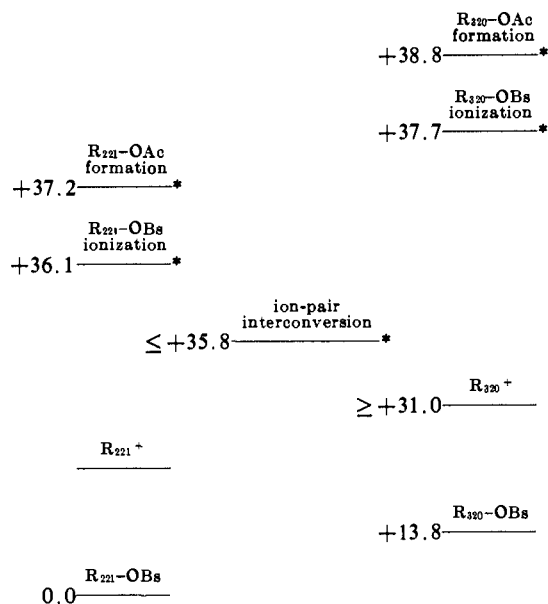+13.8 —————

R_{221}-OBs
0.0 —————

Figure 1. Ground- and transition-state free energy diagram for classical ion (or ion pair) intermediates. All energies are free energies at 25°. The zero of energy is taken to be the free energy of 7-norbornyl p-bromobenzenesulfonate in acetic acid. R_{221} denotes 7-norbornyl and R_{320} denotes *trans*-substituted 2-bicyclo[3.2.0]heptyl. An asterisk denotes a transition state.

that nonclassical ion **6** and classical ion **7** are of nearly equal stability in acetic acid solvent. The approximate constancy of the amount of retention can be explained by assuming the k_Δ and $k_s{}^6$ show the same temperature and solvent dependence, a not unreasonable assumption if nonclassical ion **6** and classical ion **7** are of nearly equal stability.

An alternative explanation would involve "leakage" from nonclassical ion **6** to classical ion **7**. One would expect the true mechanism to be a combination of these two indistinguishable mechanisms.

The fact that 7-norbornyl p-toluenesulfonate undergoes acetolysis at the rate predicted[7,8] for solvolysis *via* a classical ion by both the Foote and Schleyer correlations is easily explained as follows.

(a) The difference in stability between classical ion **3** and nonclassical ion **2** is small. One would therefore expect only a slight rate enhancement. It is to be expected that compounds showing only a small rate enhancement will appear to fit the correlations since rate enhancements of up to a factor of 10 or so are not distinguishable from the scatter in the correlations.

(b) The thermodynamic considerations in the next section indicate that an ion pair from 7-norbornyl p-bromobenzenesulfonate (whether the cation is classical or nonclassical) collapses more readily with p-bromobenzenesulfonate ion to give 7-norbornyl p-bromobenzenesulfonate than with acetic acid solvent to give 7-norbornyl acetate. Thus, the titrimetric rate constant for 7-norbornyl p-bromobenzenesulfonate is in

fact *less* than the ionization rate constant (we estimate that the former is 20–40% of the latter[9]) and therefore 7-norbornyl p-toluenesulfonate in fact ionizes somewhat faster than predicted by the Foote and Schleyer correlations.

Explanation Assuming Only Classical Ions Are Involved. It is instructive to inquire whether all available information on the 7-norbornyl system can be explained solely in terms of classical ions and ion pairs. Examination of data in the literature indicates that it is possible to do so, but that, nevertheless, classical ion **4** and nonclassical ion **2** must be of comparable free energy. The reasoning leading to this conclusion and to the free energy diagram in Figure 1 will now be given. *For simplicity of discussion, ion pairing will usually not be mentioned, although it doubtless occurs.* All energies will be free energies at 25°, with the zero of energy being taken as the free energy of 7-norbornyl p-bromobenzenesulfonate in acetic acid. R_{221} will be used to denote 7-norbornyl and R_{320} to denote *trans*-substituted 2-bicyclo[3.2.0]heptyl. The reactions which are considered are given in Scheme I.[10]

(a) The free energy of activation for acetolysis of R_{221}-OTs is 36.75 kcal/mol at 25°.[11] Assuming that the rate constant for R_{221}-OBs is three times that for R_{221}-OTs,[12] the free energy of activation for acetolysis of R_{221}-OBs is 36.1 kcal/mol at 25°.

(b) Acetolysis of R_{320}-OBs at 25° results in 85% ion-pair return to R_{221}-OBs and 14% formation of R_{221}-OAc.[13] This product ratio, 85/14 = 6.1, is equal to the ratio of rate constants $k_{\text{collapse to } R_{221}\text{-OBs}}/k_{\text{collapse to } R_{221}\text{-OAc}}$. Hence, at 25°, the transition state for collapse to R_{221}-OBs is 1.1 kcal/mol lower in energy than is the transition state for collapse to R_{221}-OAc. By microscopic reversibility, the former transition state is the same as that for ionization of R_{221}-OBs. Therefore, the free energy of the transition state for collapse to R_{221}-OAc

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(6) The rate constants for anchimerically accelerated and for unaccelerated ionization, respectively.

(7) The observed and predicted rate constants agree within 0.1 log unit in both correlations. This statement remains true even if 7-norbornyl is omitted in determining the line in the Foote correlation (see footnote 10 of ref 1a).

(8) We assume that the mechanisms of solvolysis of the p-toluenesulfonate and p-bromobenzenesulfonate are the same. The amounts of retention in acetolysis of deuterated p-toluenesulfonate[1b] and p-bromobenzenesulfonate (present work) are the same.

(9) We assume that the acetolyses of 7-norbornyl and *trans*-2-bicyclo[3.2.0]heptyl p-bromobenzenesulfonates proceed *via* the same intermediates. (Both give the same solvolysis products and in nearly the same ratio; cf. next section.) J. A. Berson (in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 189) gives the per cent ion-pair return to 7-norbornyl p-bromobenzenesulfonate in acetolysis of *trans*-2-bicyclo[3.2.0]heptyl p-bromobenzenesulfonate as a function of temperature. Using the data for 50 and 100° gives $\Delta E_a = 1.26$ kcal/mol, in agreement with the value quoted by Winstein of 1.3 kcal/mol.[4] (Here, ΔE_a is the difference in Arrhenius activation energies for solvolysis and ion-pair return. We do not use the 25° data given by Berson because they clearly contain a typographical error.) Taking $\Delta E_a = 1.26$ or 1.3 kcal/mol gives 85% ion-pair return and 15% solvolysis at 25° and 72% ion-pair return and 28% solvolysis at 205° for *trans*-2-bicyclo[3.2.0]heptyl p-bromobenzenesulfonate and presumably also for 7-norbornyl p-bromobenzenesulfonate. Thus, the titrimetric rate constant for 7-norbornyl p-bromobenzenesulfonate is *ca.* 20% of the ionization rate constant at 25° and *ca.* 40% of the ionization rate constant at 205°.
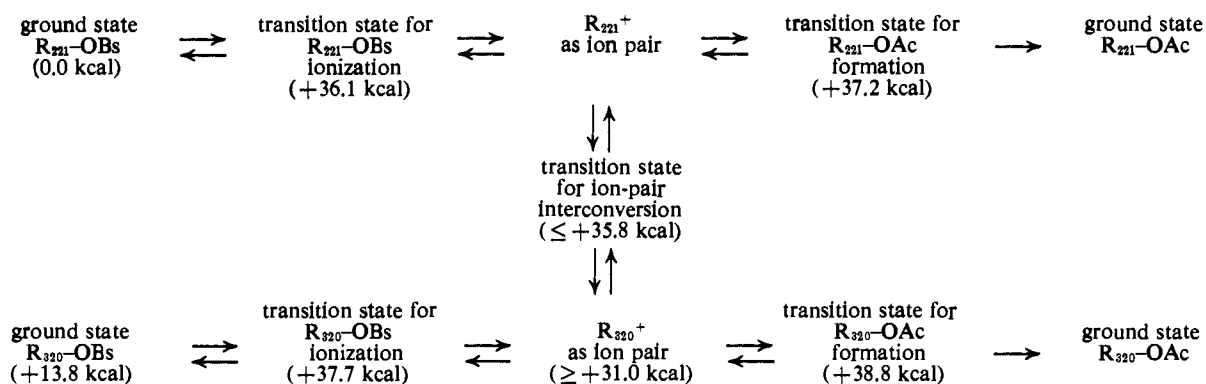
(10) Scheme I has been included at the suggestion of a referee.

(11) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, 77, 4183 (1955).

(12) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 82.

(13) These data are obtained from data at other temperatures. Reference 9 gives the estimate of 85% ion-pair return. The effect of temperature on the ratio of solvolysis products is small. R_{320}-OBs at 100° gives (excluding ion-pair return) 92% R_{221}-OAc, 5% R_{320}-OAc, and 3% olefin (F. Gadient, unpublished work). At 50°, R_{320}-OBs gives 94% R_{221}-OAc, 5% R_{320}-OAc, and 1% olefin.[4] We therefore assume that at 25° 93% of the solvolysis product is R_{221}-OAc. Hence, R_{221}-OAc is 93% × (100 − 85)% = 14% of the total product. If the experimentally observed values for 50° (83% ion-pair return and 16% R_{221}-OAc) are used instead, the effect is to change the energy difference calculated from 1.1 kcal/mol to 1.0 kcal/mol. The energies for ground-state $R_{320}{}^{+}$ and the ion-pair interconversion transition state become ≥ +30.9 and ≤ +35.7, respectively; the difference between these two quantities is not changed.

Scheme I. Ground States, Intermediates, and Transition States in Acetolysis of 7-Norbornyl p-Bromobenzenesulfonate and trans-2-Bicyclo[3.2.0]heptyl p-Bromobenzenesulfonate, Assuming Only Classical Ions Are Involved[a]

ground state
R_{221}–OBs
(0.0 kcal)
$\rightleftharpoons$
transition state for
R_{221}–OBs
ionization
(+36.1 kcal)
$\rightleftharpoons$
R_{221}^+
as ion pair
$\rightleftharpoons$
transition state for
R_{221}–OAc
formation
(+37.2 kcal)
$\longrightarrow$
ground state
R_{221}–OAc

$\downarrow\uparrow$

transition state
for ion-pair
interconversion
($\leq$ +35.8 kcal)

$\downarrow\uparrow$

ground state
R_{320}–OBs
(+13.8 kcal)
$\rightleftharpoons$
transition state for
R_{320}–OBs
ionization
(+37.7 kcal)
$\rightleftharpoons$
R_{320}^+
as ion pair
($\geq$ +31.0 kcal)
$\rightleftharpoons$
transition state for
R_{320}–OAc
formation
(+38.8 kcal)
$\longrightarrow$
ground state
R_{320}–OAc

[a] All energies are free energies at 25°. The zero of energy is taken to be the free energy of 7-norbornyl p-bromobenzenesulfonate. R_{22} denotes 7-norbornyl and R_{320} denotes trans-substituted 2-bicyclo[3.2.0]heptyl.

is 36.1 + 1.1 = 37.2 kcal/mol greater than the free energy of ground-state R_{221}–OBs.

(c) The acetate product from acetolysis of R_{221}–OBs at 205° or from R_{320}–OBs at 50° is a mixture of R_{221}–OAc and R_{320}–OAc in the ratio 16:1.[14] It is therefore clear that both acetolyses result in the same mixture of rapidly equilibrating classical ions R_{221}^+ and R_{320}^+. By the same line of reasoning as in b, $k_{\text{collapse to } R_{221}-OAc}/k_{\text{collapse to } R_{320}-OAc} = 16$ and the transition state for collapse to R_{221}–OAc is 1.6 kcal/mol lower in free energy than is the transition state for collapse to R_{320}–OAc. Therefore, the free energy of the transition state for collapse to R_{320}–OAc is 37.2 + 1.6 = 38.8 kcal/mol greater than the free energy of ground-state R_{221}–OBs.

(d) Again using the fact that acetolyses of R_{221}–OBs and R_{320}–OBs give essentially the same mixture of acetates, if classical ions are involved they must interconvert considerably faster than either cation collapses with solvent to give either acetate. Assuming that "considerably faster" means at least ten times faster, the transition state for interconversion of classical ions must be at least 1.4 kcal/mol lower in free energy than the transition state for collapse to R_{221}–OAc. Therefore, the free energy of the transition state for interconversion of cations is at most 37.2 − 1.4 = 35.8 kcal/mol greater than the free energy of ground-state R_{221}–OBs. We shall consider this transition state to be a very close approximation to nonclassical ion 2.

(e) Winstein has shown that the rate constant for reaction of solvent-separated ion pairs with acetic acid solvent is greater than 10^6 sec^{-1} in acetolysis of threo-3-anisyl-2-butyl p-bromobenzenesulfonate at 25°.[15] We may therefore safely take the rate constant for reaction of solvent-separated ion pair R_{320}^+OBs$^-$ to be at least 10^7 sec^{-1}, since R_{320}^+ should be considerably less stable

(14) The effect of temperature on the product ratio in acetolysis is small (cf. ref 13). R_{221}–OBs at 205° gives 91% R_{221}–OAc, 7% R_{320}–OAc (a ratio of 13.0:1), and 2% olefin.[4] R_{320}–OBs at 50° gives (excluding ion-pair return to R_{221}–OBs) 94% R_{221}–OAc, 5% R_{320}–OAc (a ratio of 18.8:1), and 1% olefin.[4] We assume these ratios do not differ significantly and use the average ratio 16:1 above. (If the difference in ratios is significant and R_{221}–OBs ionizes first to classical ion R_{221}^+ and R_{320}–OBs ionizes first to classical ion R_{320}^+ and then R_{221}^+ and R_{320}^+ interconvert incompletely while collapsing to R_{221}–OAc and R_{320}–OAc, respectively, it follows that R_{221}–OBs would give relatively more R_{221}–OAc than does R_{320}–OBs. This is not the case.)

(15) S. Winstein, B. Appel, R. Baker, and A. Diaz, Special Publication No. 19, The Chemical Society, London, 1965, p 119. See pp 109–130 for a general discussion of intimate and solvent-separated ion pairs with many leading references.

than the threo-3-anisyl-2-butyl cation. Hence, at 25°, the free energy of activation for collapse of R_{320}^+ with solvent is at most 7.8 kcal/mol and therefore the free energy of ground-state R_{320}^+ is at least 38.8 − 7.8 = 31.0 kcal/mol greater than the free energy of ground-state R_{221}–OBs.[16]

(f) From d and e, the free energy of activation for conversion of R_{320}^+ to R_{221}^+ is at most 35.8 − 31.0 = 4.8 kcal/mol and the rate constant for this reaction is therefore at least 2 × 10^9 sec^{-1}. The estimates of "considerably faster" in d and $k_{\text{collapse of } R_{320}^+}$ in e are the lowest that can reasonably be made (e.g., k_{collapse} could easily be 10^8 or greater instead of 10^7). It is therefore highly probable that the free energy of activation for conversion of R_{320}^+ to R_{221}^+ is somewhat less than 4.8 kcal/mol and that the rate constant for this reaction is greater than 10^{10} sec^{-1}.[16] Clearly, then, there is only a small difference in stability between classical ion 4 and nonclassical ion 2.

For the sake of completeness (although it is not relevant to the point at hand) the free energy of ground-state

(16) The intermediate from which R_{320}–OAc is formed must be a solvent-separated ion pair. (It is hard to explain the fact[4] that no cis-2-bicyclo[3.2.0]heptyl acetate is formed if the intermediate is an intimate ion pair.) Parts e and f assume, of course, that there is only one R_{320}^+OBs$^-$ ion pair and therefore that R_{320}^+ is present as a solvent-separated ion pair.
Another possibility is that R_{320}–OBs ionizes initially to an intimate ion pair and that the R_{320}^+ to R_{221}^+ interconversion occurs between intimate ion pairs but that acetate is formed from solvent-separated ion pairs.
The transition states for formation of R_{221}–OBs and R_{221}–OAc presumably differ primarily in that the former closely resembles an intimate ion pair while the latter closely resembles the corresponding solvent-separated ion pair. These two transition states have been found (see part b) to differ in free energy by 1.1 kcal/mol. We therefore estimate the free energy difference between solvent-separated and intimate ion pairs for R_{320}^+ to be 1.1 kcal/mol. Thus, R_{320}^+ as an intimate ion pair has a free energy of at least +29.9 kcal/mol relative to ground-state R_{221}–OBs. The difference in energy between nonclassical ion 2 and classical ion 4, both as intimate ion pairs, is then at most 5.9 kcal/mol and the rate constant for conversion of R_{320}^+ to R_{221}^+ is at least 3 × 10^8 sec^{-1}.
Alternatively, we may visualize two transition states for interconversion of R_{320}^+ and R_{221}^+, one for interconversion of intimate ion pairs and one for interconversion of solvent-separated ion pairs. On the same basis as in the preceding paragraph, we estimate that these two transition states differ in free energy by 1.1 kcal/mol. The free energy of nonclassical ion 2 as a solvent-separated ion pair is then at most 36.9 kcal/mol and the energy difference between ions 2 and 4, both as solvent-separated ion pairs, is at most 5.9 kcal/mol (the same energy difference as that obtained above for intimate ion pairs).
Note that again there is a high probability that the energy difference is appreciably smaller than the calculated maximum (5.9 kcal/mol) and that the rate constant for the R_{320}^+ to R_{221}^+ conversion is correspondingly higher than 3 × 10^8 sec^{-1}.

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R_{320}–OBs and of the transition state for ionization of R_{320}–OBs has been estimated and included in Figure 1 and Scheme I. Assuming that the transition states for collapse to R_{320}–OBs and R_{320}–OAc differ by 1.1 kcal/mol (the same amount that the transition states for collapse to R_{221}–OBs and R_{221}–OAc do) gives a free energy of 37.7 kcal/mol (relative to ground-state R_{221}–OBs) for the transition state for ionization of R_{320}–OBs. R_{320}–OBs solvolyzes 10^9 times as fast as R_{221}–OBs does.[4] Therefore, $\Delta F^{\pm}$ for ionization of R_{320}–OBs is 12.2 kcal/mol less than $\Delta F^{\pm}$ for ionization of R_{221}–OBs, i.e., $\Delta F^{\pm}$ for R_{320}–OBs is 23.9 kcal/mol and the free energy of ground-state R_{320}–OBs is 13.8 kcal/mol greater than the free energy of R_{221}–OBs.

In order to explain predominant retention of configuration in solvolysis of deuterium-labeled 7-norbornyl p-bromobenzenesulfonate in terms of classical ions, it is necessary to invoke front-side collapse of an ion pair with solvent. Indeed, in one respect front-side collapse should be favored over back-side collapse in solvent-separated ion pairs; back-side collapse increases the separation between anion and positive charge while front-side collapse decreases it. (This effect may or may not be appreciable.) Examples of front-side collapse of ion pairs to give solvolysis product are known in cases where there appears to be greater steric hindrance at the back side of the cation than at the front side.[17] However, it is difficult to imagine an appreciable difference in steric hindrance between the front and back sides of an ion pair derived from 3 unless the three bonds to C-7 in the ion are not coplanar.[18]

That ion-pair collapse to deuterated p-bromobenzenesulfonate occurs with predominant retention of configuration is to be expected on the basis of either the classical ion interpretation just presented or the nonclassical ion interpretation.

Summary

It is clear that the 7-norbornyl 2-bicyclo[3.2.0]heptyl system is a marginal one with respect to the formation of nonclassical ions. The difference in stability between classical and nonclassical ions is quite small; further, this conclusion does not depend on the position one takes in the nonclassical ion controversy.

(17) See, e.g., H. L. Goering and S. Chang, Tetrahedron Letters, 3607 (1965); C. W. Shoppee and G. A. R. Johnston, J. Chem. Soc., 3261 (1961).

(18) This is conceivable. Ring strain in 7-norbornanone as measured by its infrared carbonyl frequency of 1773 cm^{-1} ^{2} is appreciable. It may be that in forming three coplanar bonds to C-7 in the cation the increase in strain is great enough to outweigh electronic factors favoring the planar structure.

Experimental Section

anti-7-Norbornenol was prepared by the method of Story.[19]

anti-2,3-Dideuterionorbornan-7-ol was prepared by addition of Matheson technical grade deuterium gas to a solution of *anti*-7-norbornenol in 95% ethanol in the presence of palladium on carbon catalyst. The product, mp 154–155° [20] after two recrystallizations from pentane, contained 87% of the theoretical amount of deuterium.[21] The deuterium is presumed to be *exo*.

Anal. Calcd for $C_7H_{10}D_2O$: C, 73.63. Found: C, 73.74.

anti-2,3-Dideuterio-7-norbornyl p-bromobenzenesulfonate was prepared from the corresponding alcohol by reaction with p-bromobenzenesulfonyl chloride in pyridine.[22] The product, mp 87–89°, after recrystallization from hexane, contained 88% of the theoretical amount of deuterium.[21]

anti-2,3-Dideuterio-7-norbornyl acetate was prepared from the corresponding alcohol by reaction with acetic anhydride in pyridine.

Solvolysis products were isolated by partitioning the reaction solution between ether or ether–hexane and water. The organic extracts were washed with water, then, as appropriate, were washed with dilute hydrochloric acid (to remove lutidine) or with aqueous sodium carbonate (to remove acetic acid) or were stirred over aqueous sodium hydroxide (to remove formic acid and to saponify formates). The organic layer was washed again with water and dried. The solvent was removed by distillation. The product 7-norbornyl acetate or 7-norbornyl alcohol was purified by preparative gas chromatography. The amount of retention of configuration was determined by comparison of the nmr spectrum of the solvolysis product with the nmr spectra of mixtures of *syn* and *anti* deuterated alcohols or acetates of known proportion. We estimate the error in this method to be ±5%. The mixtures of known proportion were prepared using weighed amounts of pure *anti*-deuterated compound and of an equimolar mixture of *syn*- and *anti*-deuterated compounds. (The equimolar mixture was prepared by oxidation of the deuterated alcohol with chromium trioxide in pyridine followed by lithium aluminum hydride reduction of the resulting ketone, then, if necessary, acetylation with acetic anhydride in pyridine.) No accuracy is sacrificed by using an equimolar mixture of *syn*- and *anti*-deuterated compounds rather than pure *syn* deuterated compound in preparing the mixtures of known proportion since weighing errors are clearly negligible with respect to the errors of several per cent encountered in estimating composition by nmr.

Nmr spectra are given in ref 1a for *anti*-2,3-dideuterionorbornan-7-ol and for an equimolar mixture of *syn*- and *anti*-deuterated alcohols.

(19) P. R. Story, J. Org. Chem., 26, 287 (1961).

(20) The corresponding undeuterated alcohol, prepared in a similar manner, had mp 155–155.7° after two recrystallizations from pentane. *Anal.* Calcd for $C_7H_{12}O$: C, 74.95; H, 10.79. Found: C, 75.14; H, 10.94. S. Winstein and M. Shatavsky [J. Amer. Chem. Soc., 78, 592 (1956)] report mp 150–151° for the undeuterated alcohol.

(21) Deuterium analysis was by J. Nemeth, Urbana, Ill.

(22) The undeuterated p-bromobenzenesulfonate, prepared in the same manner from undeuterated alcohol, had mp 90–91°. *Anal.* Calcd for $C_{13}H_{15}BrO_3S$: C, 47.14; H, 4.56; Br, 24.13. Found: C, 47.25; H, 4.81; Br, 24.10.