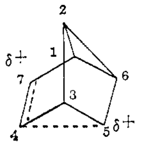
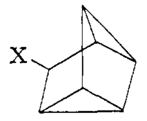
Structure of the Quadricyclic Carbonium Ion

Sir:

We wish to report new evidence in support of the structure **1** as best representing the carbonium ion intermediate derived from solvolysis of quadricyclic derivatives **2**. We also wish to report evidence concerning the isomerization of this ion to the 7-norbornadienyl cation.



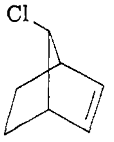
1



2

X = (a) Cl, (b) $OSO_2C_6H_4CH_3$, (c) $OSO_2C_6H_4Br$

The charge-delocalized structure **1** was first proposed[1] to account for the remarkable reactivity of the quadricyclic derivatives investigated by Richey and Buckley[2] and by ourselves.[1] It was found, for example, that 7-quadricyclic chloride (**2a**) was less reactive than *anti*-7-norbornenyl chloride (**3**)[3] by a factor of only 100 and more reactive than 7-norbornyl chloride (**4**) by approximately 10^9. Richey[2] pointed out that quadricyclic derivatives were only about 30–40 times more reactive than the corresponding tricyclic compounds (**5**) which contain a single cyclopropyl ring, *i.e.*, the net effect of the second cyclopropyl ring was negligible, in contrast to its additive effect in other systems.[2,4] As we have noted,[1] however, this phenomenon appears to be the rule rather than the exception in the case of homoallylic ions. The 7-norbornadienyl carbonium ion[5] and others[6,7] constitute examples in which a second double bond has little effect on the stability of the carbonium ion. Strong interaction of the cationic center with more than one unsaturated center is probably prevented by distortion of the ion into a delocalized structure incorporating only one of the unsaturated centers.[8]



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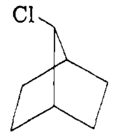

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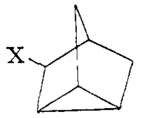
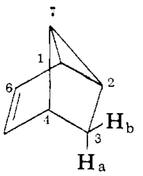


5

The structure **1** was based, then, on Winstein's formulation of charge delocalization for the tricyclic carbonium ion (the ion derived from **5**).[9] It should be noted, however, that we consider the delocalized representation, **1**, to be only an operational one at this time, and it should not be considered to provide a brief against, for example, a π-complex formulation of the general type proposed by Dewar.[10]

We previously reported[1] the reduction of quadricyclic brosylate (**2c**) with sodium borohydride in aqueous ethanol and in anhydrous diglyme using Brown's general procedure[11] in an attempt to determine the mode of charge delocalization in the ion, but were successful in isolating only quadricyclene and none of the tricyclic olefin (**6**) which should result from trapping **1** at carbon 5.

We now find, however, that treatment of quadricyclic brosylate (**2c**) with sodium borohydride in 80% aqueous diglyme gives a hydrocarbon product (15% yield, isolated) which consisted of approximately 10% tricyclene (**6**) along with $\sim$89% quadricyclene and $\sim$1% norbornadiene. The tricyclene (**6**), of course, could have arisen from reduction of the 7-norbornadienyl carbonium ion rather than from reduction of **1**, an especially likely possibility since some norbornadiene was obtained. The source of **6** was determined by the following experiment.



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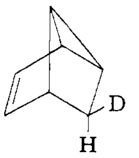
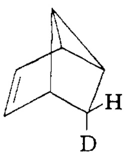


6a



6b

We have previously shown that lithium aluminum deuteride reduction of 7-norbornadienyl chloride yields tricyclic olefin containing deuterium exclusively at *endo*-C-3 (**6b**) through examination of the olefin's nuclear magnetic resonance spectrum.[12] The *endo*-C-3 hydrogen of **6** was found to generate a quartet at τ 9.5 (J_{ab} = 7.7 cps, J = 2.1 cps), and this multiplet was found to be completely absent in the nmr spectrum of the deuterated compound (**6b**). During the present investigation we have also treated 7-norbornadienyl chloride with sodium borodeuteride under the same conditions used for reduction of **2c** and found the tricyclic product to consist solely of **6b**[13] (within the limits of detection by the nmr method).[14]

On the other hand, sodium borodeuteride reduction of **2c** in aqueous diglyme yielded tricyclic olefin whose nmr spectrum contained a multiplet centered at τ 9.5, representing approximately 10% of the product. Spin decoupling of the deuterium simplified this multiplet to a doublet (J = 2.1 cps), also centered at τ 9.5. Consequently, this doublet was assigned to the *endo*-C-3 hydrogen in **6a**. The tricyclic product from sodium borodeuteride reduction of **2c** therefore consisted

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(1) P. R. Story and S. R. Fahrenholtz, *J. Am. Chem. Soc.*, **86**, 527 (1964).

(2) H. G. Richey, Jr., and N. C. Buckley, *ibid.*, **85**, 3057 (1963).

(3) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, **77**, 4183 (1955).

(4) It is noteworthy that the spatial relationship of the cation to the cyclopropyl rings in the quadricyclic carbonium ion appears, from models, to be very nearly the same as it is in the preferred conformation of the dimethylcyclopropylcarbonium ion as recently determined by Olah. See C. U. Pittman, Jr., and G. A. Olah, *ibid.*, **87**, 2998 (1965).

(5) P. R. Story, L. C. Snyder, D. C. Douglass, E. W. Anderson, and R. L. Kornegay, *ibid.*, **85**, 3630 (1963).

(6) O. L. Chapman and P. Fitton, *ibid.*, **85**, 41 (1963).

(7) C. H. DePuy, I. A. Ogawa, and J. C. McDaniels, *ibid.*, **82**, 2398 (1960).

(8) There is considerable evidence in favor of an unsymmetrical 7-norbornadienylcarbonium ion structure, thereby promoting interaction of the positive center with one of the double bonds. See ref 5 and R. Hoffman, *ibid.*, **86**, 1259 (1964).

(9) S. Winstein and E. M. Kosower, *ibid.*, **81**, 4399 (1959); S. Winstein, H. M. Walborsky, and K. Schreiber, *ibid.*, **72**, 5795 (1950).

(10) M. J. S. Dewar and A. P. Marchand, *Ann. Rev. Phys. Chem.*, **16**, 321 (1965).

(11) (a) H. C. Brown and H. M. Bell, *J. Org. Chem.*, **27**, 1928 (1962); (b) H. C. Brown and H. M. Bell, *J. Am. Chem. Soc.*, **85**, 2324 (1963).

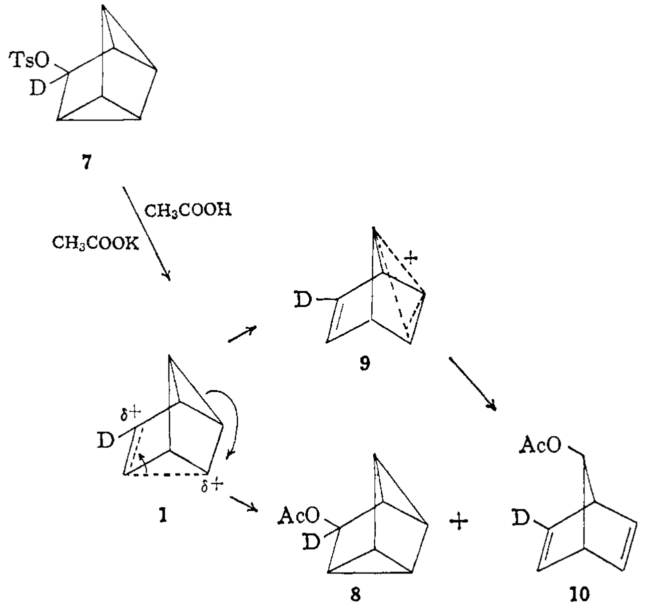
(12) P. R. Story, *ibid.*, **83**, 3347 (1961).

(13) Brown has also reduced 7-norbornadienyl chloride with sodium borohydride to generate **6**. See ref. 11b.

(14) The hydrocarbon products were isolated by preparative scale gas chromatography and further rigorously checked for purity by analytical gpc. In most cases nmr spectra were obtained from neat samples using either a Varian Associates A-60 or HA-60-DA-60 spectrometer.

of a mixture of **6a** (10%) and **6b** (90%). Since the ratio of tricyclic olefin (**6b**) to norbornadiene was within experimental error of that usually found[11b,12] upon reduction of the 7-norbornadienyl cation, we believe it to be the source of **6b** and the norbornadiene. *We further propose that* **6a** *results from reduction of the ion,* **1**, *at C-5.* We are prompted by the comments of a referee to add, however, that this conclusion is based on the assumption that all of the hydrocarbon product arises from a carbonium ion intermediate. Since the actual yield of **6a** is very low, our position is somewhat compromised. On the other hand, a direct displacement by deuteride on **2c**, which seems to be the best alternative to ionization, would be predicted to be more important in anhydrous diglyme. In fact, no **6** was obtained in this solvent.[1]

Quite remarkably, a significant amount of the quadricyclic cation **1** isomerizes to the more stable 7-norbornadienyl cation (**9**) before it is trapped by hydride. We have found, by solvolysis of 7-deuterioquadricyclic *p*-toluenesulfonate (**7**), that this isomerization undoubtedly follows the general rearrangement path suggested by both Richey[2] and ourselves.[1] Our version of this sequence is indicated by the following equation. Solvolysis of **7** (2–3 days) at 25° in acetic acid containing an excess of potassium acetate gave a 75% yield (isolated) of a product consisting of an approximately 50:50 mixture of **8** and **10**. The kinetic isotope effect, k_H/k_D, was found to be a standard 1.18. Both the quadricyclic acetate **8** and the 7-norbornadienyl acetate (**10**) contained one deuterium by mass spectral analysis and by analysis of their nmr spectra. The nmr spectra also served to establish, unequivocally, the location of the deuterium. It should be kept in mind that this method, of course, is not capable of great accuracy. For example, about 5% or less of 7-norbornadienyl acetate containing deuterium *anti* to the acetoxy would have escaped detection.



Nonetheless, this experiment has revealed some rather interesting features of the ions involved. For one, the hydrogens of the quadricyclic cation are not scrambled by rearrangement, thus ruling out a structure in which the positive center is delocalized over two or more equivalent carbons. Furthermore, the isomerization of the quadricyclic ion to the 7-norbornadienyl ion is highly (perhaps completely) stereospecific and, in addition, the 7-norbornadienyl ion, once it is formed, retains its configuration.

Acknowledgment. We thank Mr. E. W. Anderson for the determination of some of the nmr spectra.

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(15) Address correspondence to the University of Georgia, Athens, Georgia.

Paul R. Story,[15] **Susan R. Fahrenholtz**
Department of Chemistry, The University of Georgia
Athens, Georgia 30601
Bell Telephone Laboratories, Inc.
Murray Hill, New Jersey
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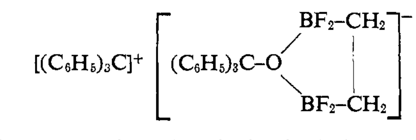
Chelate Adducts Containing a Bidentate Electron-Pair Acceptor. 1,2-Bis(difluoroboryl)ethane

Sir:

Chelate formation is a common phenomenon in coordination chemistry where many complexes are known in which a polyfunctional donor ligand is attached to a central metal acceptor. We wish to report an analogous situation in which a polyfunctional acceptor, $F_2B–CH_2–CH_2–BF_2$, is apparently coordinated to a central donor atom.

The difunctional acid 1,2-bis(difluoroboryl)ethane was synthesized according to a reported method (vapor pressure at 0° 154.6 mm obsd, lit[1] 156 mm; mp −31.2° obsd, lit[1] −31°; mol wt 128 obsd, 126 calcd).[1] Addition of this acid to dimethyl ether or to tetrahydrofuran led to 2:1 compounds as the only stable adducts, *e.g.*, $C_2H_4B_2F_4 \cdot 2OC_4H_8$.

Much more interesting behavior was observed for bis(triphenylmethyl) ether where a 1:1 compound was indicated by tensimetric titration and also by weight gain. The resulting air-sensitive golden yellow crystals melted at 113–114°. *Anal.* Calcd: C, 76.46; H, 5.45; B, 3.44; F, 12.10. Found: C, 76.26; H, 5.65; B, 3.24; F, 11.84. The infrared spectrum showed a complete absence of B–F stretching frequencies for trigonally bonded boron (1350–1380 cm^{-1}), while new peaks (*ca.* 1050 cm^{-1}) attributable to B–F vibrations of tetrahedrally bonded boron were present. Clearly, both ends of the bidentate acid are coordinated. Twin absorption maxima at 430 and 410 mμ in methylene chloride solutions of the compound showed the presence of the triphenylmethyl cation.[2] Thus, a Lewis acid cleavage of bis(triphenylmethyl) ether has occurred which is analogous to the known protolytic cleavage.[3] The simplest reaction consistent with these data is



$$F_2B–CH_2–CH_2–BF_2 + (C_6H_5)_3C–O–C(C_6H_5)_3 = [(C_6H_5)_3C]^+ \left[(C_6H_5)_3C–O \begin{matrix} \diagup BF_2–CH_2 \\ \qquad | \\ \diagdown BF_2–CH_2 \end{matrix} \right]^- \qquad (1)$$

where the product contains the desired chelate structure.

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(1) P. Ceron, A. Finch, J. Frey, J. Kerrigan, T. Parsons, G. Urry, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **81**, 6368 (1959).
(2) G. Branch and H. Walba, *ibid.*, **76**, 1564 (1954).
(3) M. Gomberg, *ibid.*, **35**, 200 (1913).