π-allyl–palladium complex coordination is possible with either the binuclear or the mononuclear species. This coordination of quadricyclene (I) may well be due to the π character of the cyclopropane bonds common to the three- and four-membered rings.[3]

The valence isomerization I $\rightarrow$ II described is, by the Woodward–Hoffmann rule for cycloadditions,[4] thermally forbidden. The catalysis observed might well be caused by the presence in the complex of occupied molecular orbitals with symmetries that make the isomerization an allowed process.[5]

[3] A. D. Walsh, *Nature*, **159**, 165, 712 (1947); C. A. Coulson and W. E., Moffitt, *J. Chem. Phys.*, **15**, 151 (1947).

[4] R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, 87, 2046 (1965).

[5] F. D. Mango and J. H. Schachtschneider, *ibid.*, 89, 2484 (1967).

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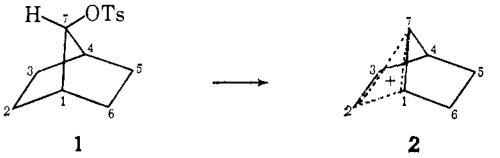
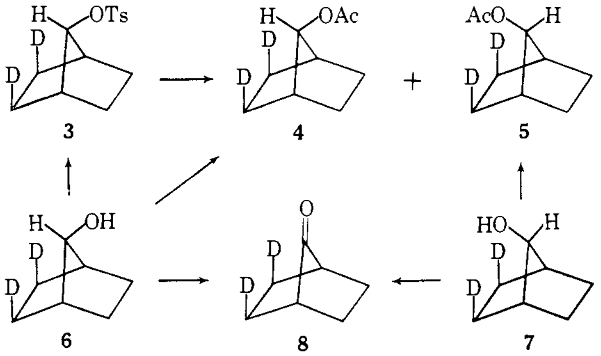
The 7-Norbornyl Cation

Sir:

The nature of the cation formed in the solvolysis of 7-tosyloxybicyclo[2.2.1]heptane (**1**) has not been clearly established. Winstein and co-workers have described the ionization of **1** as an "example of carbon participation in solvolysis" in which the delocalized ion, **2**, is formed.[1] In contrast, Foote[2] and Schleyer[3] have used the solvolysis of **1** as an example of a system which solvolyzes without anchimeric assistance.[4]

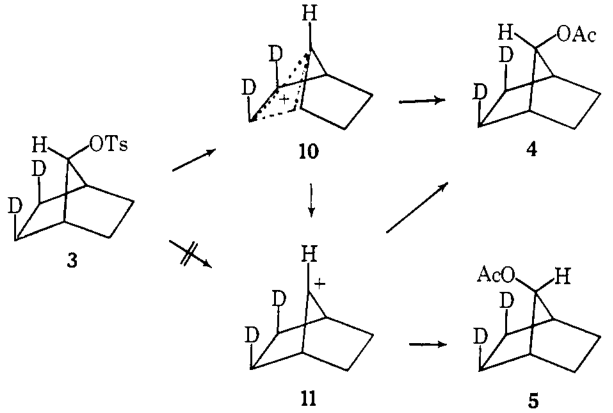


We have found that solvolysis of *exo,exo*-2,3-dideuterio-*anti*-tosyloxybicyclo[2.2.1]heptane (**3**), in acetic acid buffered with sodium acetate, gave the mixture of products previously reported in the literature.[1] Isolation of the 7-acetoxybicyclo[2.2.1]heptane, which constituted greater than 90% of the reaction product, provided a mixture of deuterium labeled compounds. Infrared analysis *vs.* standard mixtures showed that the solvolysis product consisted of 90 ± 3% of **4** and 10 ± 3% of **5**.



Both the tosylate, **3**, and the acetate, **4**, were prepared from **6**. The synthesis of **6** involved dideuteriodiimide[5,6] reduction of *anti*-7-hydroxybicyclo[2.2.1]heptene.[7] The acetate, **5**, was synthesized from **7**, which had been prepared *via* diimide reduction of the known[8] *exo,exo*-2,3-dideuterio-*syn*-7-hydroxybicyclo[2.2.1]hept-5-ene.[9] In order to ascertain that the dideuteriodiimide reduction occurred from the *exo* side, both **6** and **7** were oxidized to the same ketone, **8**. Whereas the ketones obtained from **6** and **7** were identical in all respects, the infrared and nmr spectra of each member of the epimeric pairs, **6** and **7**, **4** and **5**, and **3** and **9**, were different.

We propose that the large degree of retention of configuration observed in the solvolysis of **3** is most consistent with concerted participation of the 1,2 σ electrons to form the delocalized ion, **10**. Unlike certain explanations of the formation of the 2-norbornyl cation,[10] the formation of **10** may not be postulated to proceed *via* an intially formed classical ion such as **11** since, if **11** were an intermediate, approximately equal amounts of **4** and **5** should be formed.[11] Thus, it appears likely[12] that concerted ionization and carbon participation occur in the acetolysis of **3**.



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[1] S. Winstein, F. Gadient, E. T. Stafford, and P. E. Klinedinst, Jr., *J. Am. Chem. Soc.*, **80**, 5895 (1958).

[2] C. S. Foote, *ibid.*, **86**, 1853 (1964).

[3] P. Schleyer, *ibid.*, **86**, 1854, 1856 (1964).

[4] It is assumed in this paper that anchimeric assistance and participation of neighboring groups are interrelated phenomena. For discussion of this relationship see P. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965, and J. Berson, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.

[5] We wish to thank Professor J. Berson for providing us with experimental details for dideuteriodiimide reductions.

[6] The acetate prepared from **6** was shown to contain 90% of the theoretical amount of deuterium. All deuterium analyses were performed by J. Nemeth, Urbana, Ill.

[7] S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, 77, 4183 (1955); S. Winstein and M. Shatavsky, *ibid.*, 78, 592 (1956).

[8] B. Franzus and E. I. Snyder, *ibid.*, 87, 3423 (1965).

[9] A tosylate, **9**, prepared from **7**, was shown to contain 95% of the theoretical amount of deuterium.

[10] It has been suggested that the initial step in the solvolysis of 2-tosyloxybicyclo[2.2.1]heptane is formation of a classical carbonium ion at C-2 of the bicyclo[2.2.1]heptyl system. For a discussion of this point of view see H. C. Brown, "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962.

[11] It is assumed that the steric requirements of deuterium *vs.* hydrogen would not be sufficiently different to cause the observed product distribution.

[12] An alternate rationalization of the observed results would invoke a front-side displacement on the ion pair by solvent. Indeed, Brown has suggested[13] the possibility "that even static classical ions, where the structure inhibits approach from the back side, may well undergo substitution with retention." Obviously, special classes of molecules, such as bridgehead tosylates where back-side approach is impossible, can only solvolyze with retention.[14] However, we doubt whether the tosylate, **3**, can be justifiably classified as one in which solvent approach from the back side is hindered to the extent that the mechanism of acetolysis becomes one of "front-side displacement." In the absence of such steric hindrance to back-side approach of solvent we see no obvious reason for suggesting front-side displacement of solvent on any ion pair derived from **3**.

The occurrence of *ca.* 10% of the inverted product **5** merits comment. Two reasonable possibilities exist for the formation of **5**. A direct displacement of tosylate ion by acetic acid with inversion of configuration at C-7 could account for the presence of **5**. Alternately, **10** could be "leaking" to the classical ion **11** which would then be partitioned between **4** and **5**. Precedent for this latter type of interconversion has been noted in the bicyclo[2.2.2]octyl system.[15] Experiments aimed at distinguishing between these two possibilities are in progress.

Acknowledgment. This investigation was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society.

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(13) H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *J. Am. Chem. Soc.*, **89**, 370 (1967).

(14) It should be noted that an unusual case of partial retention has recently been found in the solvolysis of a tertiary *p*-nitrobenzoate [H. L. Goering and S. Chang, *Tetrahedron Letters*, **No. 40**, 3607 (1965)].

(15) J. A. Berson and D. Willner, *J. Am. Chem. Soc.*, **86**, 609 (1964).

(16) National Science Foundation Trainee, 1965–1967.

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Retention of Configuration in the Solvolysis of 2,3-Dideuterio-7-norbornyl *p*-Bromobenzenesulfonate

Sir:

Acetolysis and formolysis of *anti*-2,3-dideuterio-7-norbornyl *p*-bromobenzenesulfonate (Ia)[1] proceed with predominant retention of configuration. Therefore, solvolysis cannot proceed through the free classical 7-norbornyl cation.

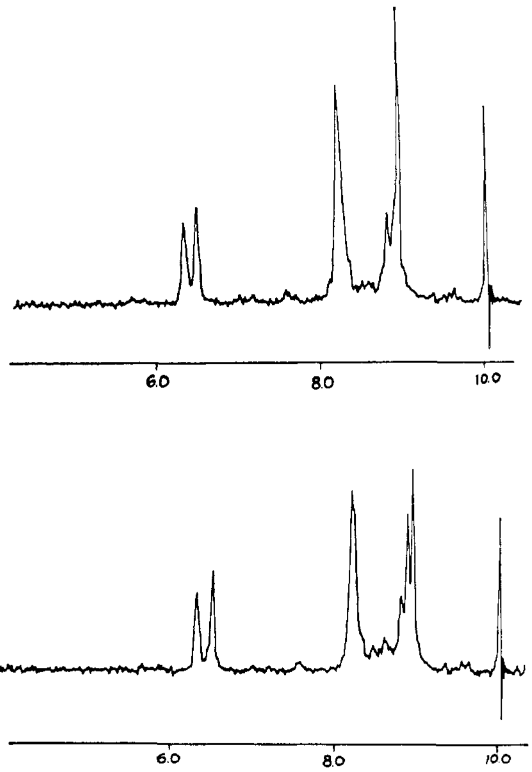


Figure 1. Nmr spectra of *anti*-2,3-dideuterionorbornan-7-ol (Ib) (top) and an equimolar mixture of *syn* and *anti* deuterated alcohols (bottom) in carbon tetrachloride containing tetramethylsilane.

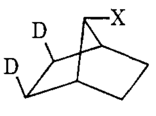
Deuterated *p*-bromobenzenesulfonate (Ia) was prepared from the corresponding alcohol (Ib) by treatment with *p*-bromobenzenesulfonyl chloride in pyridine. The alcohol was prepared by addition of deuterium gas to *anti*-7-norbornenol.[2] The *syn* isomer of alcohol Ib was prepared as an equimolar mixture with the *anti* alcohol by oxidation of *anti* alcohol with chromium trioxide in pyridine followed by lithium aluminum hydride reduction of the resulting ketone. Nuclear magnetic resonance (nmr) spectra are given in Figure 1 for *anti*-2,3-dideuterionorbornan-7-ol (Ib) and for an equimolar mixture of *syn* and *anti* deuterated alcohols.

Deuterated *p*-bromobenzenesulfonate Ia was solvolyzed for 90 min (*ca.* two half-lives) in acetic acid at 205°. The product, 7-norbornyl acetate, was isolated and purified by gas chromatography. Examination of the nmr spectrum of this acetate revealed that it consisted of 90 ± 5% *anti* acetate (Ic) (retention of configuration) and 10 ± 5% *syn* acetate (inversion of configuration).[3] The relative amounts of inversion and retention were unaffected by the presence of added sodium acetate.

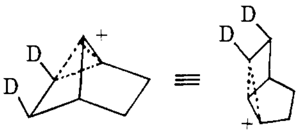
Solvolysis of deuterated *p*-bromobenzenesulfonate Ia for 16 hr (*ca.* one half-life) in refluxing formic acid containing sodium formate gave (after saponification of the product formates) deuterated 7-norbornanol with 85 ± 5% retention of configuration.[3]

The predominant retention of configuration in the solvolysis of deuterated *p*-bromobenzenesulfonate Ia may be explained in terms of nonclassical ion II or in terms of classical ion III.

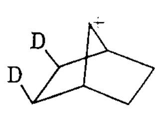
For the case of classical ion III, one assumes that



Ia, X=OBs
b, X=OH
c, X=OAc



II



III

solvolysis proceeds through front-side collapse of an ion pair. Brown and co-workers have mentioned the possibility of front-side ion-pair collapse.[4,5] Examples of this have been provided by Goering and Chang in the case of 2-phenyl-2-butyl *p*-nitrobenzoate[6] and Shoppee and Johnston in the case of 4,4-dimethylcholestan-3-yl systems.[7]

The classical ion hypothesis is further supported by the fact that on the basis of the acetolysis rate correlations of Foote[8] and Schleyer[9] (a correction has been applied to Foote's correlation[10]) there is no evidence

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[1] The terms *syn* and *anti* will be used to refer to the position of the deuterium atoms with respect to the oxygen function.

(2) Alcohol Ib and *p*-bromobenzenesulfonate Ia both contained 88% of the theoretical amount of deuterium. Deuterium analysis was by J. Nemeth, Urbana, Ill.

(3) The analysis was carried out by comparison with the nmr spectra of mixtures of *syn* and *anti* alcohols or acetates of known proportion. Acetates were prepared by acetylation of the alcohols with acetic anhydride in pyridine.

(4) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Am. Chem. Soc.*, **87**, 2137 (1965).

(5) H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *ibid.*, **89**, 370 (1967).

(6) H. L. Goering and S. Chang, *Tetrahedron Letters*, 3607 (1965).

(7) C. W. Shoppee and G. A. R. Johnston, *J. Chem. Soc.*, 3261 (1961).

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

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