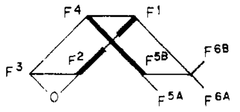
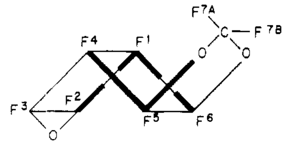
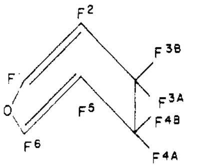
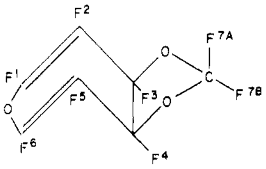
Table I. ^{19}F NMR of Some Perfluorobicyclohexene Oxides and Their Isomers

compd	formula	assign	chem shift^a (ppm from $CFCl_3$)	J, Hz ± 1
1		F(2,3) exo F(5A,6A) endo F(5B,6B) exo F(1,4)	181.6 117.5 135.0 199.5	J(5A,5B) = J(6A,6B) = 234; J(1,2) = J(1,3) = J(1,5A) = J(1,6B) = J(2,4) = J(3,4) = J(4,5B) = J(4,6A) = J(4,6B) = 9
2		F(7A) endo F(7B) exo F(2,3) exo F(5,6) endo F(1,4)	56.0 63.9 181.5 129.6 197.6	J(7A,7B) = 67.3; J(7B,6) = J(7B,5) = 5.5; J(1,2) = J(3,4) = 12; J(3,5) = J(2,6) = 8; J(1,6) = J(4,5) = 12
3		F(1,6) F(3A,4A) endo F(3B,4B) exo F(2,5)	96.3 118.3^b 118.3^b 181.3	J(1,2) = J(5,6) = 26
4		F(7A) endo F(7B) exo F(1,6) F(3,4) endo F(2,5)	56.1 61.8 93.3 111.2 176.9	J(7A,7B) = 71.0; J(7B,3) = J(7B,4) = 8.9; J(1,2) = J(5,6) = 30; J(1,3) = J(4,6) = 12; J(2,3) = J(4,5) = 23

^{a} Parts per million from $CFCl_3$. ^{b} Collapsed AA′BB′ system.

101) was used to record the IR absorptions. The detector was set at 180 °C, the IR cell was maintained at 162 °C (which was measured with a thermocouple), and the injection port was at 160 °C.

The GC/MS (LKB9000 at 13 eV) of the unisomerized molecules 1 and 2 showed m/e values of parent ions at 240 ($C_6F_8O^+$) for 1 and at m/e 284 ($C_7F_8O_3^+$) for 2. After the sample was heated at 190 °C for 45 min, the GC/MS data recorded two identical m/e values of parent ions m/e at 240 ($C_6F_8O^+$) and 284 ($C_7F_8O_3^+$) but with different elution times and mass cracking patterns indicating the presence of isomers 3 for the former and 4 for the latter.

Mass spectroscopic molecular weight (CEC21-110-B) of 3: Calculated for C_6F_8O: 239.9821. Found: 239.9814.

Mass spectroscopic molecular weight (CEC21-110-B) of 4: Calculated for $C_7F_8O_3$: 283.9720. Found: 283.9721.

Acknowledgments. We thank the Air Force Office of Scientific Research for support under Contract F44620-76-C-0027, Dr. D. Thomas for mass spectra, and Mr. L. Cary for ^{19}F NMR.

Registry No. 1, 69655-83-0; 2, 69655-85-2; 3, 69655-87-4; 4, 70428-88-5; $CF_2(OF)_2$, 16282-67-0; Dewar C_6F_6, 6733-01-3.

Communications

Evidence for the Formation of a Symmetrical Ion during Neighboring Group Participation by the Cyclopropyl Moiety. Solvolysis of Methylated Derivatives of Tricyclo[3.2.1.0^{2,4}]octan-8-ol

Summary: Solvolysis of methylated derivatives of tricyclo[3.2.1.0^{2,4}]octan-8-ol p-nitrobenzoate esters gave products which were only consistent with the intermediacy of highly delocalized nonclassical ions.

Sir: The dialogue concerning the nature of certain types of carbocations generated in solvolysis reactions has been a long and vigorous one.[1] Among those systems, for which the nature of neighboring group participation has been questioned,[2] is tricyclo[3.2.1.0^{2,4}]octan-8-ol.[3,4] The basic question which required answering was whether 1 ionized to produce the rapidly equilibrating pair of ions represented by the mirror image structures 2 and 3, or whether the trishomocyclopropenyl cation, 4, was the crucial intermediate. Some time ago we demonstrated that methyl substitution on the participating function could be used to establish the symmetrical nature of the participation

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(1) For a recent summation of one point of view see H. C. Brown, "The Nonclassical Ion Problem", Plenum Press, New York, N.Y., 1977.

(2) Reference 1, p 273.

(3) J. S. Haywood-Farmer and R. E. Pincock, *J. Am. Chem. Soc.*, **91**, 3020 (1969); M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. S. Haywood-Farmer, *ibid.*, **89**, 1954 (1967); M. Tanida, T. Tsuji, and T. Irie, *ibid.*, **89**, 1953 (1967); J. S. Haywood-Farmer, R. E. Pincock, and J. I. Wells, *Tetrahedron*, **22**, 2007 (1966). See also J. Haywood-Farmer, *Chem. Rev.*, **74**, 315 (1974).

(4) The existence of neighboring group participation by the cyclopropyl moiety of this system is supported by the 10^{14} rate difference between this system and the 7-bicyclo[2.2.1]heptyl system. Thus, the existence of neighboring group participation has not been questioned. Only the nature of the transition state and the structure of the cationic intermediate have been debated.

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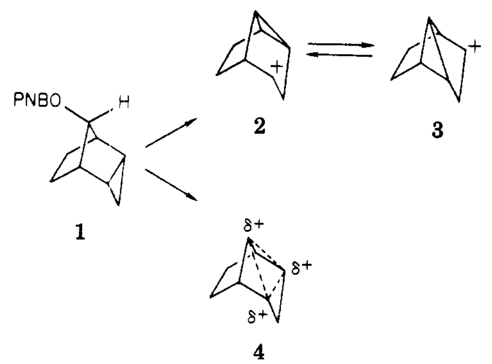


by the double bond in the 7-*anti*-bicyclo[2.2.1]heptenyl system.[5,6] We now wish to report that the application of this same test to the tricyclo[3.2.1.0^{2,4}]oct-8-yl system provides convincing evidence for the intermediacy of the highly delocalized ion **4**.

In order to utilize the test of methyl substitution for the nature of neighboring group participation in the tricyclo[3.2.1.0^{2,4}]oct-8-yl system, we needed to obtain the relative rates of solvolysis and the products derived from **1**,[3] **5**, and **6**. The critical intermediates needed for the preparation of **5** and **6** were the ketones, **7** and **8**, respectively. These were obtained by the addition of the appropriate cyclopropene to 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene, followed by dechlorination, reduction, and hydrolysis.[3,7] Lithium in liquid ammonia reduction of **7** gave a 64% yield of **9**, which was readily converted into **5**. In the same manner, **8** was reduced in 69% yield to **10**, which was converted into **6**.

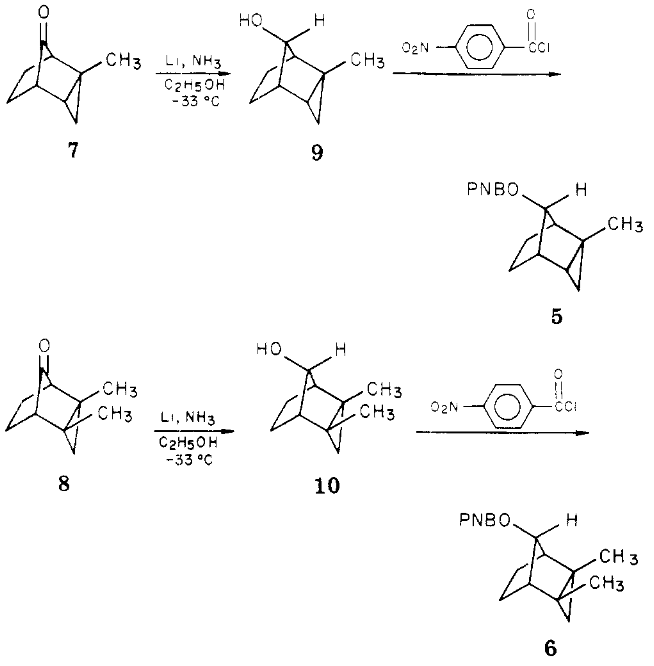
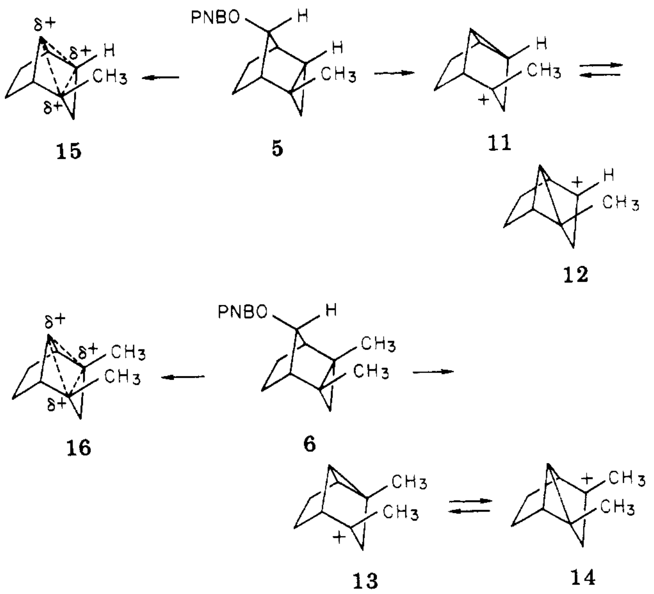


Table I. Rates of Solvolysis of Methyl-Substituted Tricyclo[3.2.1.0^{2,4}]oct-8-yl *p*-Nitrobenzoates in 70% Acetone-Water at 80.00 °C

compd	rate, s^{-1}	k_{rel} (80.00 ± 0.01 °C)	statistical	cumulative
1	(8.40 ± 0.17) × 10^{-5}	1	1	1
5	(1.85 ± 0.08) × 10^{-4}	2.2	2.2	2.2
6	(3.95 ± 0.03) × 10^{-4}	4.7	4.4	4.8



In principle, the solvolysis of **1**, **5**, and **6** should yield rate data which would permit a distinction to be made between an unsymmetrical and a symmetrical transition state. If an unsymmetrical, classical transition state were involved, the ionization of **5** should lead to the tertiary cation **11**. The formation of a tertiary, classical carbonium ion should provide sufficient driving force for a sizable rate increase relative to **1** (which could only yield a secondary cation). Any equilibration between **11** and **12** would be expected to be overwhelmingly in favor of **11**. If an unsymmetrical transition state leading to a classical tertiary cation were involved in the solvolysis of derivatives of tricyclo[3.2.1.0^{2,4}]octan-8-ol, the addition of a second methyl group, as in **6**, should have little effect. At most, a statistical (doubling) rate effect would be expected in the formation of **13** and **14** from **6**. In contrast, if **5** were to yield the delocalized ion **15**, and **6** were to give **16**, two effects might be predicted. First, the effect of a single methyl on the rate of solvolysis of **5** might be small due to charge delocalization and second, the addition of the second methyl should have the same effect as the first. Thus, for an unsymmetrical, classical transition state the rate ratios of **1**/**5**/**6** should be 1:x:2x, whereas for a symmetrical transition state the relative rates should be 1:y:y^2, where y is smaller than x. The relative rates of solvolysis of **1**, **5**, and **6** in 70% acetone–water are listed in Table I. As can be seen from the table, the rate effect of methyl substitution was very small. In fact the rate differences were so small that they did not permit a definitive distinction to be made between a statistical (localized) influence and a cumulative (delocalized) effect. However, the relatively small effect of methyl substitution was consistent with a similar small change of 4.8 in rate observed as a result of methyl substitution on the participating cyclopropyl moiety of the

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(5) P. G. Gassman and D. S. Patton, *J. Am. Chem. Soc.*, 91, 2160 (1969).

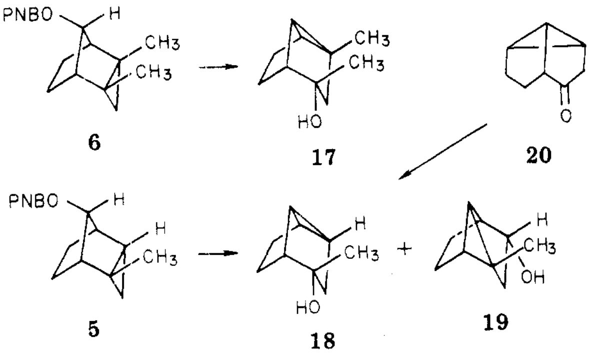
(6) This approach has been widely accepted as having established the symmetrical nature of the transition state. However, it has not been accepted as providing definitive evidence for the symmetrical nature of the cationic intermediate (ref 1, p 61; H. C. Brown, private communication).

(7) Satisfactory elemental analysis and/or exact mass molecular weights were obtained on all new compounds reported. In addition, spectral data were consistent with the assigned structures in all cases.

9-pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonyl system,[8] which is commonly acknowledged to yield a nonclassical cation.[8,9]

Fortunately, product studies provided reasonably solid evidence for the symmetrical nature of the cation generated from the tricyclo[3.2.1.0^{2,4}]octyl system. The solvolysis of **6** gave, after ten half-lives, an 85% yield of **17** as the only observable product. A detailed lanthanide shift reagent study of **17**, in combination with NMR spectral comparisons with tricyclo[3.3.0.0^{2,8}]octan-*endo*-4-ol and **18**, left no doubt as to the endo nature of the substitution. This represents a case where the attacking nucleophile, water, added from the more hindered side of the molecule.[10] It has been argued that most tertiary cations are classical.[1] If this were true in the present case, the solvolysis product should have had the hydroxyl function in the exo position, not in the endo position.

The solvolysis of **5** gave, after ten half-lives, 82% of a 97:3 mixture of **18** and **19**. Again, NMR studies[11] left little doubt that the attacking nucleophile had added to the cationic intermediate from the endo (more hindered) side. In addition, an authentic sample of **18** was prepared by the addition of methylmagnesium iodide to **20**.[12] The formation of only endo products was inconsistent with the intermediacy of classical cationic species such as **11** and **12**. More significantly, the formation of substantial amounts of **19** would require that solvent capture by **12** compete effectively with solvent capture by **11**.[13]



6 **17** **20** **5** **18** **19**

Analogy can be made with the 1-methyl- and 2-methylbicyclo[2.2.1]hept-2-yl cations, where the tertiary cation is reported to be 5.5–7.5 kcal/mol more stable than the secondary ion.[14,15] It has been postulated that these ions are not mesomerically associated.[14,16] Extrapolation of these arguments to the pair of ions represented by **11** and **12** would require that **11** be the only ion present. The classical ion **11** would be expected to undergo nucleophilic attack from the exo side. Significantly, the product which would result from nucleophilic attack on **11** has the wrong stereochemistry. In addition, 3% of the product mixture was the secondary alcohol **19**, which also has endo stereochemistry. If **11** and **12** were equilibrating ions and we accepted the minimal value of 5.5 kcal/mol as the difference between these ions, greater than 99.95% of the product mixture should result from **11**.[17,18] This is inconsistent with the experimental data. In summary, the solvolysis of 2-methyl- and 2,4-dimethyltricyclo[3.2.1.0^{2,4}]oct-8-yl *p*-nitrobenzoates provides products which are only consistent with the formation of a delocalized (trishomocyclopropenium) type ion.

Acknowledgments. We are indebted to the National Science Foundation for a grant which supported this investigation.

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[8] R. M. Coates and J. L. Kirkpatrick, *J. Am. Chem. Soc.*, **92**, 4883 (1970); R. M. Coates and E. R. Fritz, *ibid.*, **99**, 297 (1977).

[9] H. C. Brown and M. Ravindranathan, *J. Am. Chem. Soc.*, **99**, 299 (1977).

[10] It has been demonstrated that both hydride reduction[3] and the addition of organometallic reagents occur on the exo face of both tricyclo[3.3.0.0^{2,8}]octan-4-one and 2-methyltricyclo[3.3.0.0^{2,8}]octan-4-one.

[11] For instance, the structural assignment of **19** was based on a detailed comparison of its NMR spectrum with that of tricyclo[3.3.0.0^{2,8}]octan-*endo*-4-ol (**21**)[3] and by decoupling experiments at 270 MHz. In the NMR spectrum of **19**, a one-proton sextuplet at δ 4.28 corresponded to the hydrogen at C-4. This was coupled to the protons at C-3 (J = 8.9 Hz) and to the proton at C-5 (J = 6.4 Hz). These values are almost identical with those observed for the similar proton of **21**.[3]

[12] The ketone **20** was identical in all respects with that reported in the literature: R. G. Buckeridge, K. J. Fayne, and B. L. Johnson, *Aust. J. Chem.*, **28**, 1311 (1975).

[13] Control experiments established that **18** and **19** were not equilibrated under the reaction conditions.

[14] Reference 1, p 152; R. Haseltine, E. Huang, T. S. Sorensen, and N. Wong, *Can. J. Chem.*, **53**, 1876 (1975).

[15] A more typical value for secondary cation–tertiary cation energy differences would be the 14.5 ± 0.5 kcal/mol noted for the *sec*-butyl vs. *tert*-butyl cation: E. W. Bittner, E. M. Arnett, and M. Saunders, *J. Am. Chem. Soc.*, **98**, 3734 (1976).

[16] M. H. Rei and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 5335 (1966); H. C. Brown, F. J. Chloupek, and M. H. Rei, *ibid.*, **86**, 1247 (1964); see also H. C. Brown, *Chem. Br.*, 199 (1966). See also H. C. Brown, M. Ravindranathan, C. G. Rao, F. J. Chloupek, and M. H. Rei, *J. Org. Chem.*, **43**, 3667 (1978).

[17] This prediction of percentages assumes diffusion-controlled collapse of the cations with solvent, or nonselective collapse with solvent. It should be noted that the 2-methylbicyclo[2.2.1]hept-2-yl cationic system gives only tertiary products.[16] The same reasoning which has been used to support the presence of a classical structure for this cation can be used to argue against the presence of **11** in the solvolysis of **5**.

[18] A similar capture of solvent by both secondary and tertiary centers has been observed by Coates and Fritz[8] for the methylated 9-pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonyl system. This product mixture was deemed to represent what might be expected from a nonclassical carbonium ion.[8,9]

[19] Lando Undergraduate Fellow, Summer 1975.

α-Palladated Thioamides. σ or π Complexes?

Summary: α-Palladated thioamides (**3**) have been prepared by the addition reaction of soft carbonucleophiles to α,β-unsaturated thioamides in the presence of an equimolar amount of Pd(II). The structures of these yellow crystalline solids have been characterized by spectroscopic studies (^{1}H NMR, ^{13}C NMR, and IR) and chemical degradations (hydrogenation, carbonylation, base-induced cyclization to give dihydrofuran derivatives **8**, etc.).

Sir: Recently it has been shown that α,β-unsaturated thioamides serve as excellent Michael acceptors for a variety of organolithium and -magnesium compounds possessing hard anion character, such as alkyllithium, phenylmagnesium bromide, dimsyllithium,[1] and enolates of ketones, esters, and amides.[2] On the other hand, so-

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[1] Y. Tamaru, T. Harada, H. Iwamoto, and Z. Yoshida, *J. Am. Chem. Soc.*, **100**, 5221 (1978).

[2] Y. Tamaru, T. Harada, and Z. Yoshida, *J. Am. Chem. Soc.*, **101**, 1316 (1979).