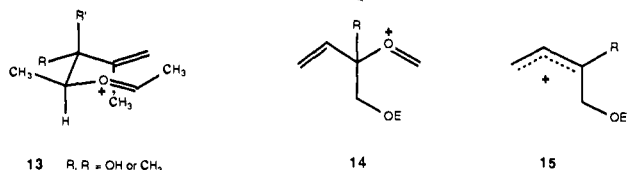


a preference for cyclization to occur in the most stable chair conformation¹² via an *E* oxonium ion^{13,14} intermediate (e.g., see **13**). The fact that both allylic diol stereoisomers rearrange to



give the same tetrahydrofuran product is rationalized also by this model. Success of this tetrahydrofuran synthesis requires that ring opening of the starting acetal to form **14** is readily reversible and that oxonium ion **10** is "trapped" by the intramolecular alkene group more rapidly than the starting acetal undergoes ionization at the tertiary allylic oxygen to afford an allyl cation (e.g., **15**).¹⁵

In summary, polyfunctional tetrahydrofurans can be prepared stereoselectively in three steps from readily available α -hydroxy ketone precursors. The key rearrangement demonstrates, moreover, that simple acetals can be employed in a rational fashion to "trigger" complex reorganizations. New opportunities in the area of stereocontrolled synthesis of oxygenated materials are opened up by these observations.

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Supplementary Material Available: Typical experimental procedures and characterization data (preparation of **7b**) (2 pages). Ordering information is given on any current masthead page.

(11) This experiment does not rule out the rather unlikely sequence in which initially formed **11** undergoes intramolecular aldol cyclization more rapidly than it relaxes (by C-C bond rotation) to an achiral conformation. This possibility arises since intermediate **11** (produced from **10** containing a substituent at C-2), although devoid of stereogenic centers, would likely be formed in a chiral chairlike conformation.

(12) A preference for chair reaction topographies has been seen in cyclization of acetals to form hydrofuran products, see: e.g., Kay, I. T.; Williams, E. G. *Tetrahedron Lett.* **1983**, *24*, 5915. Melany, M. L.; Lock, G. A.; Thompson, D. W. *J. Org. Chem.* **1985**, *50*, 3925. Overman, L. E.; Castaneda, A.; Blumenkopf, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 1303.

(13) Inversion and rotation barriers for oxonium ions are sufficiently low¹⁴ that reaction via only the more stable oxonium ion stereoisomer is expected.

(14) Cremer, D.; Gauss, J.; Childs, R. F.; Blackburn, C. *J. Am. Chem. Soc.* **1985**, *107*, 2435.

(15) (*E*)-3-Butyl-3-penten-2-one, the major product formed from attempted rearrangement of **6c**, is presumed to result from pinacolic (or semipinacolic) rearrangement of an intermediate related to **15**, followed by conjugation of the enone product.

The Molecular Structure of a Substituted 2-Norbornyl Cation, 2-Methoxy-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylum Fluoroborate

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The structure, bonding, and chemistry of the 2-norbornyl cation have been focal points of physical-organic research for almost four decades.^{1,2} In spite of unparalleled effort, a universally accepted picture of this fascinating carbocation system has not been achieved.² Rapidly equilibrating classical, symmetrical non-

classical, and rapidly equilibrating unsymmetrical nonclassical intermediates have been invoked to accommodate the results of numerous experimental and theoretical findings.² Further complicating the situation is the concern that gas-phase, stable-ion, and solvolytic experiments may involve different species.² Since a central issue in the norbornyl controversy is the precise geometry of the cation, it is astonishing that there has been so little published research devoted to acquiring its absolute structure.³ On the other hand, the dearth of information may be understandable; securing X-ray crystallographic data for all but the most stable carbocations is difficult.³⁻⁵ Our own experience confirms that the experimental problems are formidable. We have been able to isolate a stable salt³ of the 2-norbornyl cation from 2-fluoronorbornane and antimony pentafluoride, but we have not succeeded in obtaining a single-crystal X-ray structure. Although our work along these lines is continuing, we have also undertaken studies of substituted analogues. Our first successful attempt is related in this communication.

One point on which norbornyl cation researchers seem to agree is that placing electron-releasing substituents at the 2-position tips the balance toward the classical end of the spectrum.^{1,2} In fact, it has been asserted that a methyl group provides sufficient stabilization to ensure that 2-methyl derivatives are essentially classical.^{6,1f} In light of accumulating evidence, it is probably more prudent to conclude that methyl substitution produces an unsymmetrical species (classical or nonclassical).^{7,1f,2d} The carbocation reported here, 2-methoxy-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylum fluoroborate, has the more strongly electron-releasing methoxy group in the 2-position. On the basis of methoxyl exchange studies of camphor dimethyl ketal in methanol-*d*₄, Traylor and Perrin⁸ have argued cogently that 2-methoxy-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylum is a classical ion. Our X-ray results indicate that it does, indeed, have a structure with a distinct classical bias. A careful look at the molecular parameters reveals some unusual features, however.

The fluoroborate salt was prepared⁹ by the reaction of triphenylmethyl fluoroborate with the dimethyl ketal of (1*R*)-(+)-camphor (inert-atmosphere techniques). The X-ray crystallographic data were collected^{9,10} in a dry-nitrogen atmosphere at -155 °C. Selected bond lengths and angles for 2-methoxy-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylum are given in Table I (atom-numbering scheme, Figure 1). The structure of the fluoroborate anion is normal¹¹ (average B-F = 1.376 (8) Å). The

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(9) [C₁₁H₁₉O⁺][BF₄⁻]: P₂, a = 8.015 (4) Å, b = 7.246 (3) Å, c = 11.285 (6) Å, β = 104.30 (4)°, Mo K α radiation, 6 < 2 θ < 65°, MULTAN78, Fourier, non-hydrogens anisotropic, 1297 reflections (5954 total), |F_o| > 3 σ (|F_o|), R = 0.061 and R_w = 0.064.

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Table I. Selected Bond Distances (Å) and Bond Angles (deg)

parameter	X-ray	CSD ^a	parameter	X-ray	CSD ^a
C1C2	1.488 (6)	1.515 (2)	C4C5	1.541 (7)	1.533 (2)
C1C6	1.603 (8)	1.549 (2)	C4C7	1.546 (6)	1.548 (2)
C1C7	1.570 (6)	1.551 (2)	C5C6	1.531 (9)	1.540 (3)
C1C10	1.497 (7)	1.514 (2)	C7C8	1.530 (7)	1.530 (2)
C2C3	1.476 (7)	1.519 (2)	C7C9	1.542 (6)	1.530 (2)
C2-O	1.256 (5)	1.209 (2)	C11-O	1.493 (6)	
C3C4	1.544 (6)	1.532 (2)	∠C2C1C6	98.8 (4)	103.4 (1.2) ^b

^a Camphor model, Cambridge Structural Database, ref 12. ^b Mean.

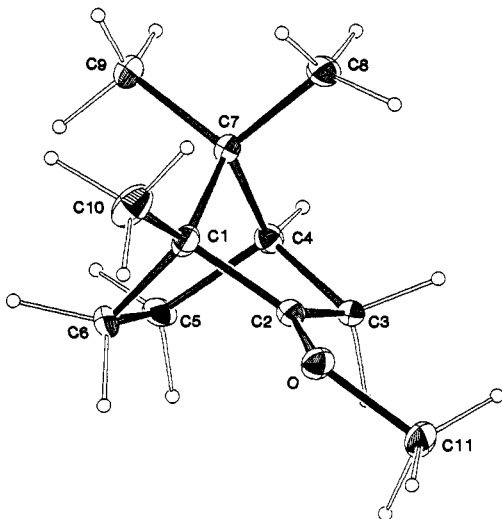


Figure 1. ORTEP drawing of 2-methoxy-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylum.

C-C distances that are several bonds removed from C2 (C7C9, C7C8, C5C6, C4C7, and C4C5) are compared with the corresponding weighted mean bond lengths of substituted camphor compounds with high quality X-ray structures¹² in Table I and are very similar.¹³ C2-O is about 0.05 Å longer than the mean camphor carbonyl distance;¹² it is, nonetheless, at least 0.1 Å shorter than the typical C-O length in ethers,¹⁴ indicating predominant oxonium ion character. For a methoxy group attached to a positive carbon 1.256 (5) Å is reasonable.⁴ The C-C bonds near the cationic center are the most interesting; C1C6 is highly abnormal. At 1.603 (8) Å it is one of the relatively few single bonds that is over 1.60 Å.¹⁵ This is 0.05 Å longer than the average value in simple bicyclo[2.2.1]heptanes¹³ or the camphor model.¹² The remaining structural units in the vicinity of C2 are altered in a less dramatic fashion. Notably, C1C2, C2C3, and C1C10 appear to be on the short side, whereas C1C7 is slightly long.¹² A plausible explanation for the considerable lengthening of C1C6 is carbon-carbon hyperconjugation, although alternative explanations are conceivable.¹⁶ The "vacant" orbital on C2 and the C1C6 bond are properly aligned for such an effect. The dihedral angle formed by C1C6, C1C2, and a line perpendicular to the C1C2C3-O plane at C2 is about 18°. The quantitative pattern of the neighboring parameters is also compatible with this interpretation. Because of the presence of the strongly electron-releasing methoxy group, it is somewhat surprising that C1C6 is in the same general range (1.62 (2) Å) as the C_αC_β bonds in the 3,5,7-trimethyladamantyl carbenium ion.¹⁷ A final point

worth noting is that the nonbonded distance between C2 and C6 is 2.35 Å (∠C2C1C6 = 98.8 (4)°), which is 0.05 Å shorter than the mean C2...C6 camphor distance¹² (∠C2C1C6 = 103.4 (1.2)°). This could reflect slight bridging by C6, although some reduction in C2...C6 is expected because of the decreased electron density at C2.

The major contribution of our study is to provide a reliable structural benchmark to be used in spectroscopic, thermodynamic, kinetic, and theoretical comparisons. It has been suggested that hyperconjugation and bridging are related rather than independent phenomena.¹⁸ Moreover, it has been stated¹⁹ that there should be a bonding continuum in 2-norbornyl cations ranging from hyperconjugation without significant motion toward bridging, to unsymmetrical bridging,^{20,21} to symmetrical bridging. Crystal structures of less drastically functionalized²⁰ norbornyl systems and the parent carbocation now appear feasible and will afford a rigorous basis for testing the above proposals.

Supplementary Material Available: Cell parameters, fractional coordinates, thermal parameters, bond distances, and bond angles of 2-methoxy-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylum (4 pages). Ordering information is given on any current masthead page.

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Biomimetic Aerobic 1,4-Oxidation of 1,3-Dienes Catalyzed by Cobalt Tetraphenylporphyrin-Hydroquinone-Palladium(II). An Example of Triple Catalysis

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The use of macrocyclic metal complexes, in particular metalloporphyrins, as biomimetic catalysts in oxidation reactions has attracted considerable attention recently.²⁻⁷ Most of the me-

(11) Cambridge Structural Database (CSD), 47 structures, mean B-F = 1.350 (23) Å.

(12) Camphor model, CSD, 10 structures, weighted mean parameters.

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