Acknowledgment. We are grateful to Dr. H. H. Freedman for a sample of 3,4-dibromotetraphenylcyclobutene. Partial support of the work by the National Science Foundation and the C. F. Mabery Fund of Case Western Reserve University is gratefully acknowledged.

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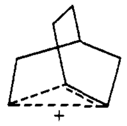
Stable Carbonium Ions. CII.[1]

The Bicyclo[3.3.0]-1-octyl Cation and Its Preferential Formation from Bicyclo[3.2.1]- and -[2.2.2]octyl Systems under Long-Lived Ion Conditions

Sir:

Solvolytic carbonium ion reactions of bicyclo[2.2.2]-2-octyl derivatives yield both bicyclo[2.2.2]- and -[3.2.1]-octyl products, the result of rearrangements of the initially formed bicyclo[2.2.2]-2-octyl cation.[2,3] Further rearrangements are necessary to produce bicyclo[3.3.0]-octyl cations, but apparently solvent capture occurs before this can proceed. However, when initial rearrangement can produce these ions, bicyclo[3.3.0]octyl products are dominant, as in the case of solvolysis of *exo-* and *endo*-bicyclo[3.2.1]octyl 8-tosylates.[4] Solvolysis of bicyclo[3.3.0]-2-octyl derivatives give mainly unrearranged products[5] or the rearranged bicyclo-[3.3.0]-1-octyl and -8-octyl derivatives. Bicyclo[3.3.0]-octyl products have also been observed upon the treatment of decalin with aluminum chloride,[7] or cyclooctene oxide with lithium diethylamide,[8] and from a variety of unsaturated precursors, *e.g.*, cyclooct-4-en-1-ly tosylate,[6] *cis,cis*-1,5-cyclooctadiene,[9,10] octamethyltricyclooctadienes,[11] benzobicyclo[2.2.2]octadienol,[12] and cyclooctadienyllithium.[13]

Barrett and Linstead reported the conversion of the [3.3.0]octane to the [3.2.1] isomer with aluminum chloride.[14] Schleyer and coworkers have equilibrated all three hydrocarbons with aluminum bromide at 23–72° and have shown the order of stability of the ring systems to be [3.2.1] > [3.3.0] > [2.2.2].[15] Although bicyclo[3.3.0]octane is more strained (1.9 kcal/mol)[16] than either of the other two isomers, its high entropy indicates it should be the most stable of the isomers above 378°K.[15]



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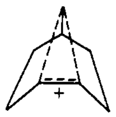

2

Although the carbonium ions in solvolysis reactions of bicyclo[2.2.2]- and -[3.2.1]octyl derivatives have been ascribed nonclassical character, as in **1** and **2**, respectively,[2] we wish to report that, under long-lived ion conditions in superacid media, all bicyclooctyl systems rearrange to the more stable tertiary bridgehead bicyclo-[3.3.0]-1-octyl cation **14**. This ion is produced by ionization, hydride abstraction, or protonation from a variety of precursors as shown in Scheme I.

When bicyclo[2.2.2]-1-octyl chloride (**3**) is ionized in $FSO_3H-SbF_5-SO_2ClF$ at −70°, the tertiary ion formed (**7**) must undergo a 1,2-hydride shift to give the secondary ion **8**, also produced by ionization of the secondary derivatives **4** and **5**, or by hydride abstraction (in SbF_5-SO_2ClF) from the hydrocarbon **6**. A Wagner–Meerwein shift would then yield ion **10**, also obtained directly by ionization of bicyclo[3.2.1]-2-octanol (**9**). Hydride shifts and a second rearrangement would give the secondary [3.3.0] ion **15**, also obtained directly by ionization of *endo-cis*-bicyclo[3.3.0]-2-octanol (**17**) or bicyclo[3.-3.0]octane (**18**) or by protonation and ring opening of the tricyclic hydrocarbon **16** in $FSO_3H-SbF_5-SO_2ClF$. A final 1,2-hydride shift would give the observed tertiary [3.3.0] ion **14** (Figure 1), which on quenching in either KOH–ice or MeOH–MeONa suspensions at low temperature gives *cis*-bicyclo[3.3.0]-1-octanol or its methyl ether, respectively, as shown by nmr and glpc comparisons with authentic materials.[17] That the [3.3.0] ion **14** is formed in preference to the other possible tertiary ions may be due simply to the fact that in the latter cases (*i.e.*, the [2.2.2]- and [3.2.1]-1-octyl cations) the carbonium ion center is at the bridgehead and cannot become planar.[18] Secondary ions require stabilization by σ delocalization (**1** and **2**) and are obviously less favorable than a classical planar tertiary ion.[19]

As we observed that cyclodecanol undergoes a transannular reaction in $FSO_3H-SbF_5-SO_2ClF$ to give the bicyclo[4.4.0]decyl cation,[20] we were interested in whether cyclooctanol would give the [3.3.0] ion **14** under the same conditions. No evidence of *cis*-1-methoxybicyclo[3.3.0]octane[21] was found in the meth-

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[1] Part CI: G. A. Olah and Gh. D. Mateescu, *J. Amer. Chem. Soc.*, **92**, 1430 (1970).

[2] J. Berson in "Molecular Rearrangements," P. deMayo, Ed., Interscience Publishers, New York, N. Y., 1963, pp 213–226; H. Kwart and J. L. Irvine, *J. Amer. Chem. Soc.*, **91**, 5541 (1969).

[3] Solvolysis of bicyclo[3.2.1]-2-octyl tosylate also gives some bicyclo[2.2.2]octyl products: H. L. Goering and G. N. Fickes, *ibid.*, **90**, 2848, 2856, 2862 (1968).

[4] C. S. Foote and R. B. Woodward, *Tetrahedron*, **20**, 687 (1964).

[5] H. C. Brown and W. J. Hammar, *J. Amer. Chem. Soc.*, **89**, 6378 (1967). Small amounts ($\sim$8%) of bicyclo[3.3.0]-1-octyl and -[3.2.1]-8-octyl acetates were observed by Closson and Kwiatkowski.[6]

[6] W. D. Closson and G. T. Kwiatkowski, *Tetrahedron Lett.*, 6345 (1966); A. C. Cope, J. M. Grisar, and P. E. Peterson, *J. Amer. Chem. Soc.*, **82**, 4299 (1960); A. C. Cope and P. E. Peterson, *ibid.*, **81**, 1643 (1959).

[7] R. L. Jones and R. P. Linstead, *J. Chem. Soc.*, 616 (1936).

[8] A. C. Cope, H. H. Lee, and H. E. Petree, *J. Amer. Chem. Soc.*, **80**, 2849 (1958).

[9] K. E. Moller, *Angew. Chem.*, **75**, 1122 (1963).

[10] D. Wittenberg and H. Mueller, German Patent 1,240,852; *cf. Chem. Abstr.*, **67**, 108331 (1967).

[11] J. M. Bollinger and G. A. Olah, *J. Amer. Chem. Soc.*, **91**, 3380 (1969).

[12] A. C. Gray, T. Kakihana, P. M. Collins, and H. Hart, *ibid.*, **89**, 4556 (1967).

[13] R. B. Bates and D. A. McCombs, *Tetrahedron Lett.*, 977 (1967).

[14] J. W. Barrett and R. P. Linstead, *J. Chem. Soc.*, 611 (1936).

[15] P. von R. Schleyer, K. R. Blanchard, and C. D. Woody, *J. Amer. Chem. Soc.*, **85**, 1358 (1963).

[16] This value is somewhat less than that calculated (5.6 kcal/mol) by N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van-Catledge, *ibid.*, **90**, 1199 (1968).

[17] We are indebted to Professor R. Fort for a sample of *cis*-bicyclo-[3.3.0]octan-1-ol (nmr δ 2.05 (m), 1.79 (m)), from which we prepared the methyl ether by a modification (refluxing THF for 2 days) of the method of C. H. Hurd and W. H. Saunders, *ibid.*, **74**, 5324 (1952); nmr δ ($CDCl_3$) 3.2 (s, 3 H, OMe), 2.1–1.0 (m, 13 H); ir ν_{C-O} 1090 cm^{-1}.

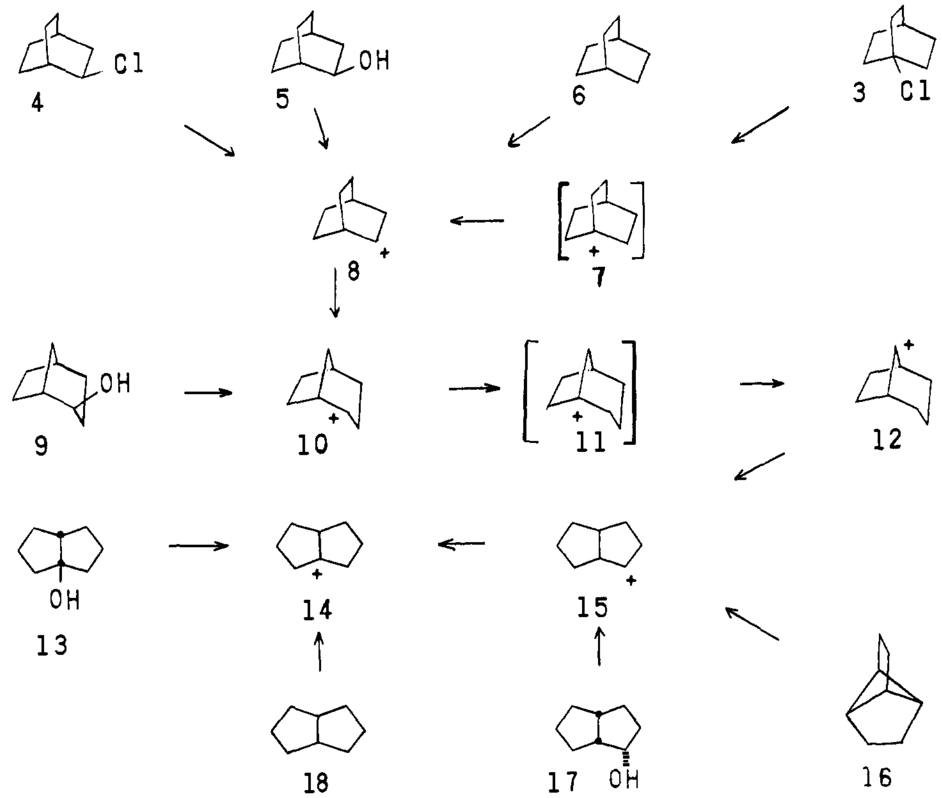
[18] R. C. Fort, Jr., and P. von R. Schleyer, *Advan. Alicyclic Chem.*, **1**, 284 (1967); G. J. Gleicher and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 582 (1967).

[19] This is not the case in the bicyclo[2.2.1]heptyl system, however, since the corresponding tertiary [3.2.0] ion could not become planar.

[20] To be published.

[21] Less than 1% of quenched material with the same retention time as an authentic sample.

Scheme I



anol quench products of cyclooctanol in FSO_3H-SbF_5-SO_2ClF.

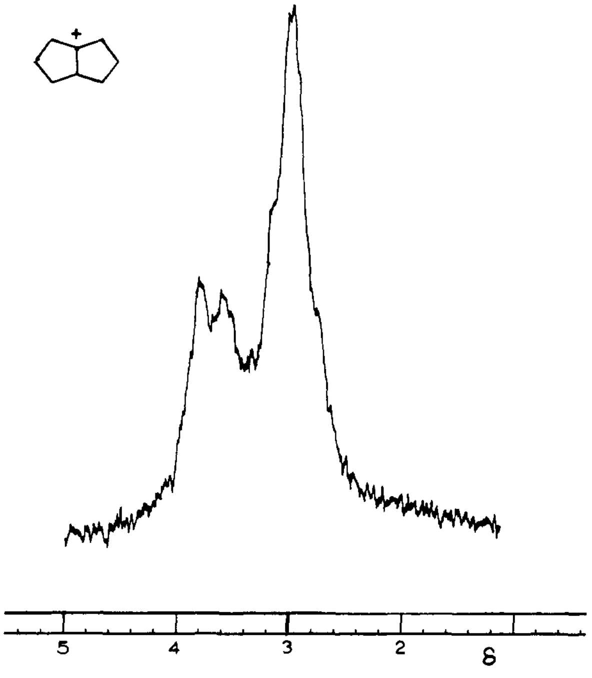


Figure 1. The 60-MHz spectrum of bicyclo[3.3.0]-1-octyl cation prepared from bicyclo[3.2.1]-2-octanol in SbF_5-SO_2ClF at −78°.

Comparison of the 60-MHz spectrum of the [3.3.0]-octyl ion **14** (Figure 1) with that of the decalyl ion[20] and the bicyclo[4.3.0]nonyl ion[22] indicates that **14** does not have a rapidly equilibrating bridgehead proton, since the lower field absorptions (α to positive charge) are only half as intense as the higher field absorptions. The intensities would be reversed (9:4) for a rapidly equilibrating bicyclo[3.3.0]octyl ion. This is confirmed by the 220-Hz spectrum[23] (Figure 2) which shows the

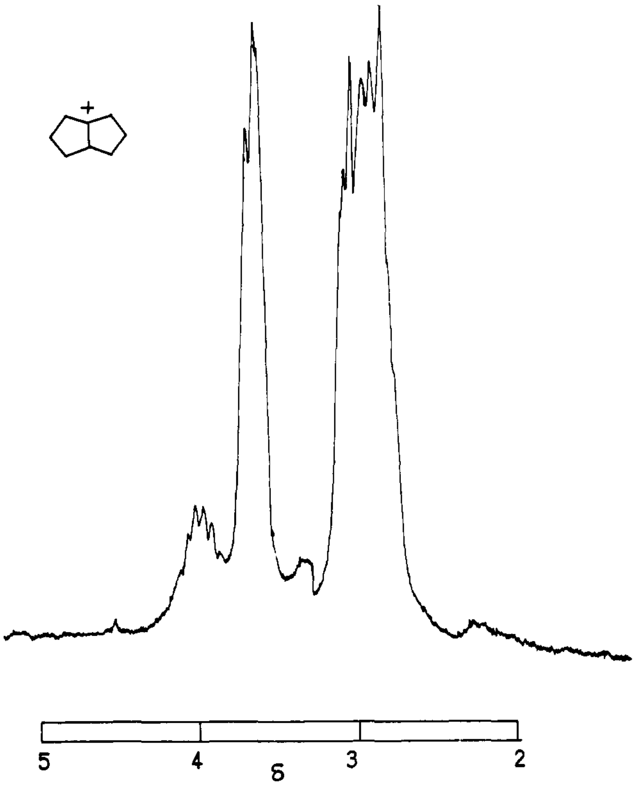


Figure 2. The 220-MHz spectrum of bicyclo[3.3.0]-1-octyl cation.

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(22) G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **90**, 933 (1968).

(23) The 220-MHz spectrum was obtained by Dr. Gh. D. Mateescu of this laboratory, at Varian Associates, Palo Alto, Calif., whose help and cooperation we acknowledge.

bridgehead proton at δ 4.01, four methylenes α to the positive charge at 3.63, and two sets of four methylene protons centered at 2.96 ppm.

We are at present investigating the synthetic utility of ionizing and quenching readily available bicyclo-[2.2.2]- and -[3.2.1]octyl precursors to prepare bridgehead [3.3.0] derivatives which are difficult to prepare by conventional routes.

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(24) Postdoctoral Research Associate, 1969

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Electron Spin Resonance Spectrum of the 7-Norbornenyl Radical

Sir:

There has been considerable controversy recently concerning the nonclassical nature of the 7-norbornenyl radical.[1-3] Chemical studies have largely formed the basis for these speculations. According to a recent SCF-MO-CNDO calculation,[4] almost all the spin density in the 7-norbornenyl radical has been transferred from carbon atom 7 to the two equivalent carbon atoms 2 and 3. Furthermore, the calculated structure has been found to be highly distorted with the carbon atom 7 strongly displaced toward the double bond and with a pronounced pyramidal structure for the trigonal carbon. This radical is thus purported to be at least as nonclassical as the corresponding cation.[5]

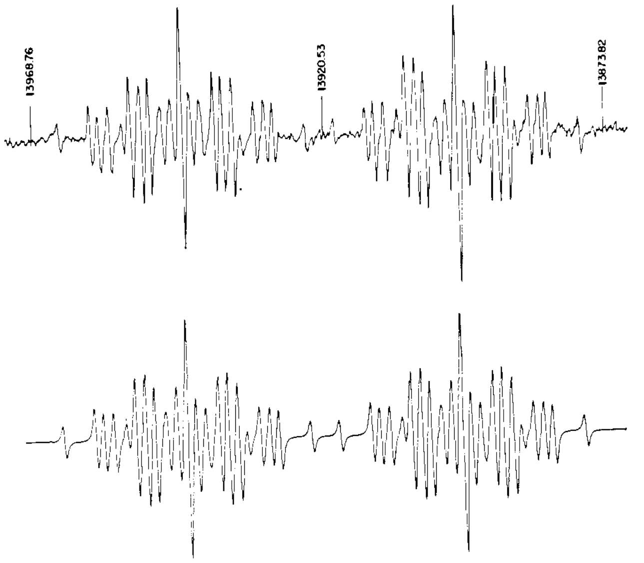
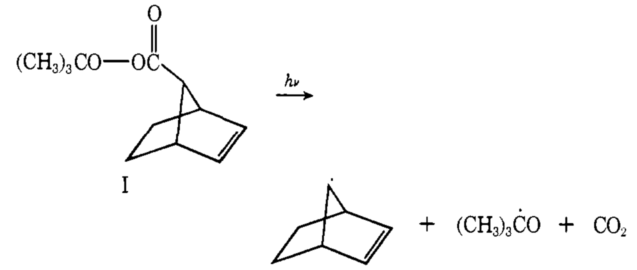
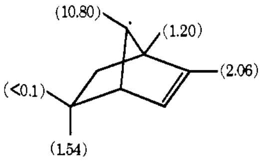


Figure 1. Experimental and calculated esr spectra of the 7-norbornenyl radical in ethane–cyclopropane solution at −134°. The proton nmr field markers are in kilohertz.

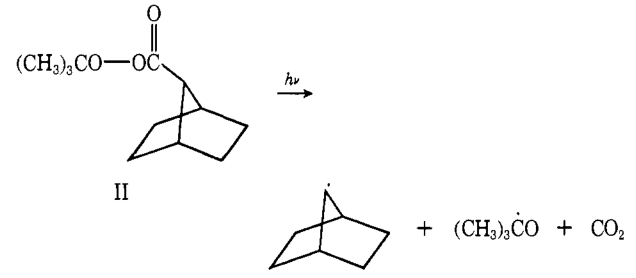
We feel that the most definitive evidence for the structure of the 7-norbornenyl radical would be obtained by examination of its electron spin resonance spectrum which we present in Figure 1. This spectrum was obtained by photolysis (2500–3000 Å) of a solution of *t*-butyl *anti*-peroxy-2-norbornene-7-carboxylate (I) in cyclopropane or mixtures of ethane and cyclopropane.[6] The spectrum was essentially unchanged when observed between −98 and −134°.[7]



The most prominent feature of this spectrum is a doublet splitting (10.80 G) which is, no doubt, due to the single H-7. Further splitting into three triplets (2.06, 1.54, and 1.20 G) is substantiated by computer simulation (Figure 1). The tentative assignments for the hyperfine coupling constants of the 7-norbornenyl radical given below are partly based on analogy with the 7-norbornyl radical (*vide infra*).[8]



The esr spectrum of the saturated analog (Figure 2), 7-norbornyl radical, was obtained similarly from *t*-butyl 7-peroxynorbornanecarboxylate (II). This spectrum consists of a doublet (16.78 G) of triplets (1.05 G) split further into a pair of quintets (3.53 and 0.72 G).



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(1) J. Warkentin and E. Sanford, *J. Amer. Chem. Soc.*, **90**, 1667 1968).

(2) G. A. Russell and G. W. Holland, *ibid.*, **91**, 3969 (1969).

(3) S. J. Cristol and A. L. Noreen, *ibid.*, **91**, 3870 (1969).

(4) (a) H. O. Ohorodnyk and D. P. Santry, *ibid.*, **91**, 4711 (1969); *Chem. Commun.*, 510 (1969). (b) It should be pointed out that CNDO theory neglects the one-center atomic exchange integrals and, therefore, the spin-polarization mechanism for isotropic hyperfine interaction in radicals. Spin densities calculated by this theory are therefore questionable.

(5) S. Winstein, *Quart. Rev.* (London), **23**, 141 (1969).

(6) (a) The general technique for production of a specific alkyl radical for esr study has been described: J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3940 (1969); (b) the photolysis of pure *t*-butyl *syn*-peroxy-2-norbornene-7-carboxylate was not examined but a mixture containing 70% *syn* and 30% *anti* isomer gave the same esr spectrum.

(7) There is a slight increase in two of the four coupling constants with increasing temperature. T(°C), a_{H7}, a_{H2}, a_{endo}, a_{bridge} (G): −98, 10.98, 2.17, 1.57, 1.17; −102, 10.80, 2.06, 1.54, 1.20; −134, 10.72, 1.98, 1.58, 1.24.

(8) The preparation of deuterated derivatives now in progress will allow us to make unambiguous assignments for the three pairs of protons involved in the fine structure of the spectrum.