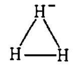
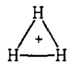
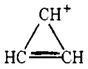
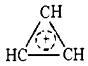
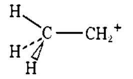
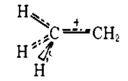
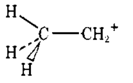
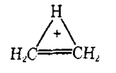
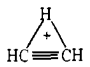
Table V

	→		27	*a*
	→		118	*a*
	→		−40	This work
	→		202	This work
$H_2C{=\!=}CH^+$	→		110	*b*

[a] Reference 8. [b] Reference 3.

schemes do in general overestimate resonance effects.[2,7,9,10,35,37] This is due to inadequate treatment of two-electron effects, especially electron–electron repulsions, rather than to neglect of correlation energies.

Conclusions

The stabilities of alkyl cations are not dominated by their ability to neutralize or disperse positive charge, but by optimum utilization of the most stable orbitals. The electron-deficient nature of these molecules is important because it lowers electron–electron repulsion, thus allowing electrons to crowd close together at places of high positive potential. As a result of the greater ability of a methyl carbon than of a hydrogen substituent to take advantage of this lowered repulsion (by forming strong bonds with the cationic carbon through involvement of the 2s orbitals), the ethyl cation is more easily formed from its neutral precursor than is the methyl cation.

Stable Carbocations. CXII. Preferential Formation of the Bicyclo[3.3.0]-1-octyl Cation from Bicyclooctyl Precursors and Its Rearrangement to the 2-Methylnorbornyl Cation[1]

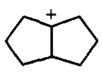
George A. Olah* and Gao Liang

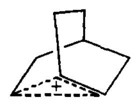
Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received May 21, 1971*

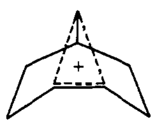
Abstract: The bicylo[3.3.0]-1-octyl cation (I) is formed from all bicyclooctyl precursors in FSO_3H-SbF_5-SO_2ClF or in SbF_5-SO_2ClF solutions at −78°. When I is heated to 0°, it irreversibly rearranges to 2-methylnorbornyl cation.

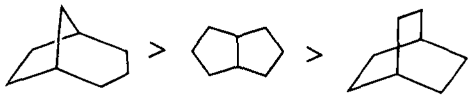
In the solvolytic studies of bicyclo-2-octyl derivatives,[2–7] it was shown that two distinct carbocation intermediates are involved, the asymmetrical nonclassical ion II formed from *exo*-bicyclo[3.2.1]-2-octyl isomers and the symmetrical nonclassical ion III formed from *endo*-bicyclo[3.2.1]-2-octyl isomers. Similar observations were made in the solvolyses of both *exo*- and *endo*-2-norbornecarbinyl[8–12] and 7-norbornanecarbinyl systems.[13,14]

The solvolytic products involve both bicyclo[2.2.2]- and [3.2.1]octyl structures. No further rearrangement products were observed. However, when initial rearrangement can produce bicyclo[3.3.0]octyl cations, bicyclo[3.3.0]octyl products are dominant.[15–20] In the aluminum bromide catalyzed isomerization of a series of bicyclooctanes, the following stability order is revealed.[21]


I


II


III



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(1) Part CXI: G. A. Olah, R. D. Porter, and D. P. Kelly, *J. Amer. Chem. Soc.*, **93**, 464 (1971).

(2) H. M. Walborsky, M. E. Baun, and A. A. Youself, *ibid.*, **81**, 4709 (1959); **83**, 988 (1961).

(3) H. M. Walborsky, J. Webb, and C. G. Pitt, *J. Org. Chem.*, **28**, 3214 (1963).

(4) H. L. Goering and M. F. Sloan, *J. Amer. Chem. Soc.*, **83**, 1397, 1992 (1961).

(5) H. L. Goering and R. W. Thies, *ibid.*, **90**, 2968 (1968).

(6) H. L. Goering and G. N. Fickes, *ibid.*, **90**, 2848 2858, 2862 (1968).

(7) H. Kwart and J. L. Irvine, *ibid.*, **91**, 5541 (1969).

(8) J. A. Berson and D. Willner, *ibid.*, **86**, 609 (1964); **84**, 675 (1962).

(9) J. A. Berson and P. R. Warnhoff, *ibid.*, **86**, 595 (1964); **84**, 682 (1962).

(10) W. Kraus, *Chem. Ber.*, **97**, 2726 (1964).

(11) R. R. Sauers and R. J. Tucker, *J. Org. Chem.*, **28**, 876 (1963).

(12) K. Alder and R. Reubke, *Chem. Ber.*, **91**, 1525 (1958).

(13) J. A. Berson, M. S. Poonian, and W. J. Libbey, *J. Amer. Chem. Soc.*, **91**, 5567 (1969).

(14) J. A. Berson and M. S. Poonian, *ibid.*, **88**, 170 (1966).

(15) S. Foot and R. B. Woodward, *Tetrahedron*, 687 (1964).

(16) A. C. Cope and P. E. Peterson, *J. Amer. Chem. Soc.*, **81**, 1643 (1959).

(17) A. C. Cope, J. M. Grisar, and P. E. Peterson, *ibid.*, **82**, 4299 (1960).

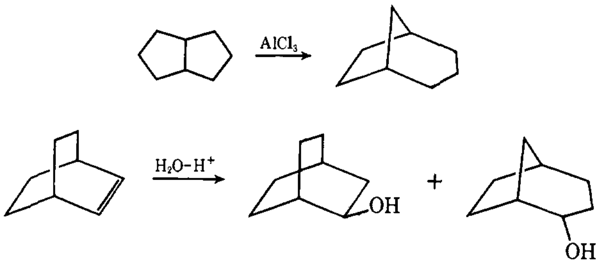
(18) A. C. Cope, S. Moon, and P. E. Peterson, *ibid.*, **84**, 1935 (1962).

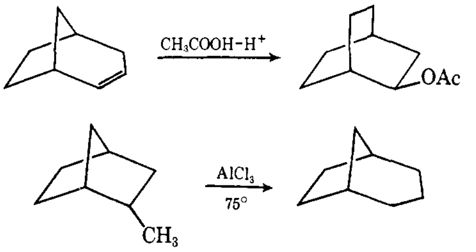
(19) W. D. Closson and G. T. Kwiatkowski, *ibid.*, **86**, 1887 (1964); *Tetrahedron, Lett.*, 6435 (1964).

(20) A. C. Cope, R. W. Gleason, S. Moon, and C. H. Park, *J. Org. Chem.*, **32**, 942 (1967).

(21) P. v. R. Schleyer, K. R. Blanchard, and C. C. Woody, *J. Amer. Chem. Soc.*, **85**, 1358 (1963).

cis-Bicyclo[3.3.0]octane has been isomerized to bicyclo[3.2.1]octane.[22] Acidic hydrolysis of bicyclo[2.2.2]octene yields both bicyclo[2.2.2]- and [3.2.1]-octanols.[23] Solvolysis of bicyclo[3.2.1]octene in acidic acid yields bicyclo[2.2.2]-2-octyl acetate.[24] 2-Bromobicyclo[2.2.2]octane is also isomerized to 2-bromobicyclo[3.2.1]octane in the presence of silver bromide.[25] However, when 2-methylnorbornane is treated with $AlCl_3$ at 75° complete conversion to bicyclo[3.2.1]octane is found.[26,27]





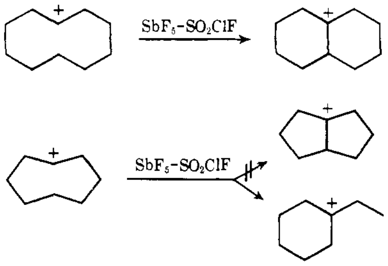
In continuation of our studies on the bicyclo[2.2.1]-heptyl (norbornyl) system it was of interest to see whether the nonclassical intermediates can be observed under stable ion conditions from bicyclooctyl derivatives. We now report all bicyclooctyl derivatives rearrange to the stable bridgehead bicyclo[3.3.0]-1-octyl cation in $FSO_3H-SbF_5-SO_2ClF$ or SbF_5-SO_2ClF solution at low temperature.[28] Ion I is also found to undergo thermal transformation to form 2-methylnorbornyl cation.[29,30]

Results and Discussion

Formation of the Bicyclo[3.3.0]-1-octyl Cation. Bicyclo[3.3.0]-1-octyl cation I was generated either in $FSO_3H-SbF_5-SO_2ClF$ or in SbF_5-SO_2ClF at −78° from a series of bicyclo[2.2.2]octyl, bicyclo[3.3.1]octyl, bicyclo[3.3.0]octyl, 2-norbornanecarbinyl, and tricyclo[3.3.3.$0^{2,6}$]octyl derivatives (Chart I).

The mechanism of the ion I formation was recently described.[28] When 1-chlorobicyclo[2.2.2]octane was ionized in SbF_5-SO_2ClF at −78°, ion I was formed immediately. Thus the bridgehead cation IV formed must undergo fast 1,2-hydride shift to give the 2-bicyclo-[2.22]octyl cation V also produced by ionization or protonation of the secondary derivatives **2**, **3**, and **4**. Bicyclo[3.2.1]-2-octyl cation VI could then be formed through Wagner–Meerwein rearrangement of ion V. The same ion could be obtained directly from 2-bicyclo-[3.2.1]octanols and 2-chlorobicyclo[3.2.1]octanes. Further rearrangement would give bicyclo[3.3.0]-2-octyl IV, also obtained directly by ionization of *endo-cis*-2-bicyclo[3.3.0]octanol **8** or protonation of 2-*cis*-[3.3.0]octene **9** and tricyclo[3.3.0.$0^{2,6}$]octane **5** in $FSO_3H-SbF_5-SO_2ClF$. The bridgehead ion I could then be expected through a final 1,2-hydride shift. Ion I was also directly formed from ionization of *cis*-bicyclo[3.3.0]-1-octanol **10** and hydride abstraction of *cis*-bicyclo[3.3.0]octane **11** and protonation of 1-bicyclo[3.3.0]octene **12**[31b] (Chart I).

As the transannular hydride transfer reaction was observed in cyclodecyl cation,[31c] we were interested to see whether the same reaction would take place in the cyclooctyl system. When cyclooctanol IV was ionized in $FSO_3H-SbF_5-SO_2ClF$ or SbF_5-SO_2ClF only 1-ethylcyclohexyl cation was observed.[31c] Ionization of cyclooctyl chloride in SbF_5-SO_2ClF (or SO_2) also failed to give ion I. In $FSO_3H-SbF_5-SO_2ClF$ cyclooctyl cation gave *tert*-butyl cation exclusively after standing at 0° for 2 hr. Obviously the transannular hydride shift did not occur in the first formed cyclooctyl cation.



Comparison of the 60-MHz pmr spectrum of ion I[28] with that of the decalyl ion[31] and the bicyclo[4.3.0]-nonyl ion[32] indicates that I 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-MHz spectrum[28,33] which shows the 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.

The bicyclo[2.2.2]-2-octyl intermediate cations involved in the acetolysis of bicyclo[2.2.2]- and -[3.2.1.]-octyl derivatives have been shown to undergo rapid Wagner–Meerwein rearrangement resulting in bicyclo-[2.2.2]octyl and bicyclo[3.2.1]octyl products. *exo*- and

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

[23] M. S. Newman and Y. T. Yu, *J. Amer. Chem. Soc.*, **74**, 507 (1952).

[24] (a) A. F. Bickel, J. Knotherus, E. C. Kooyman, and G. C. Vegter, *Tetrahedron*, **9**, 230 (1960); (b) K. Alder, H. Krieger, and H. Weiss, *Ber.*, **88**, 144 (1955).

[25] W. F. Doering and M. Farber, *J. Amer. Chem. Soc.*, **71**, 1514 (1949).

[26] M. B. Turova-Polyuk J. E. Sosnina, I. G. Gohetrina, and T. P. Yudkina, *Zh. Obshch. Khim.*, **29**, 1078 (1959); *Chem. Abstr.*, **54**, 1356 (1960).

[27] N. A. Belikoona, H. A. Bibleva, and A. F. Plate, *Zh. Org. Khim.*, **2**(11), 2031 (1966).

[28] G. A. Olah, J. M. Bollinger, and D. P. Kelly, *J. Amer. Chem. Soc.*, **92**, 1432 (1970).

[29] G. A. Olah, J. R. DeMember, C. Y. Lui, and A. M. White, *ibid.*, **91**, 3958 (1969).

[30] G. A. Olah, J. R. DeMember, C. Y. Lui, and R. D. Porter, *ibid.*, **93**, 1462 (1971).

[31] (a) We are indebted to Professor R. Fort for a sample of *cis*- and *trans*-bicyclo[3.3.0]-1-octanol. (b) R. E. Hornish, Ph.D. Thesis, Kent State University, 1970. (c) G. A. Olah, R. D. Kelly, and R. G. Johanson, *J. Amer. Chem. Soc.*, **92**, 4139 (1970).

[32] G. A. Olah and G. Liang, to be published.

[33] The 220-MHz spectrum was obtained through the courtesy of Varian Associates, Palo Alto, Calif., whose help and cooperation we acknowledge.

Chart I

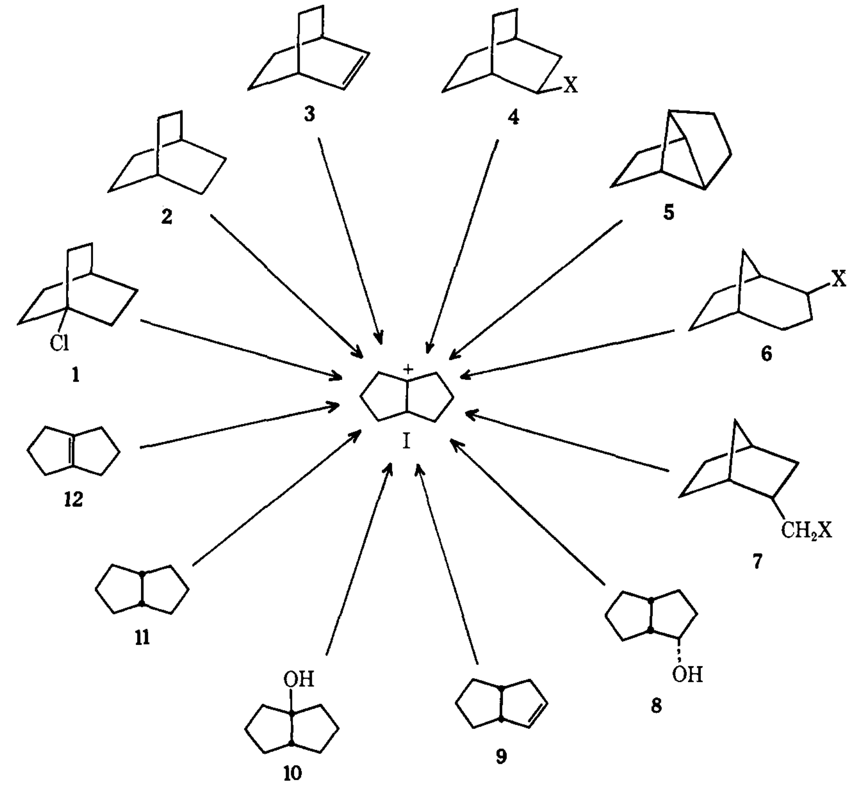
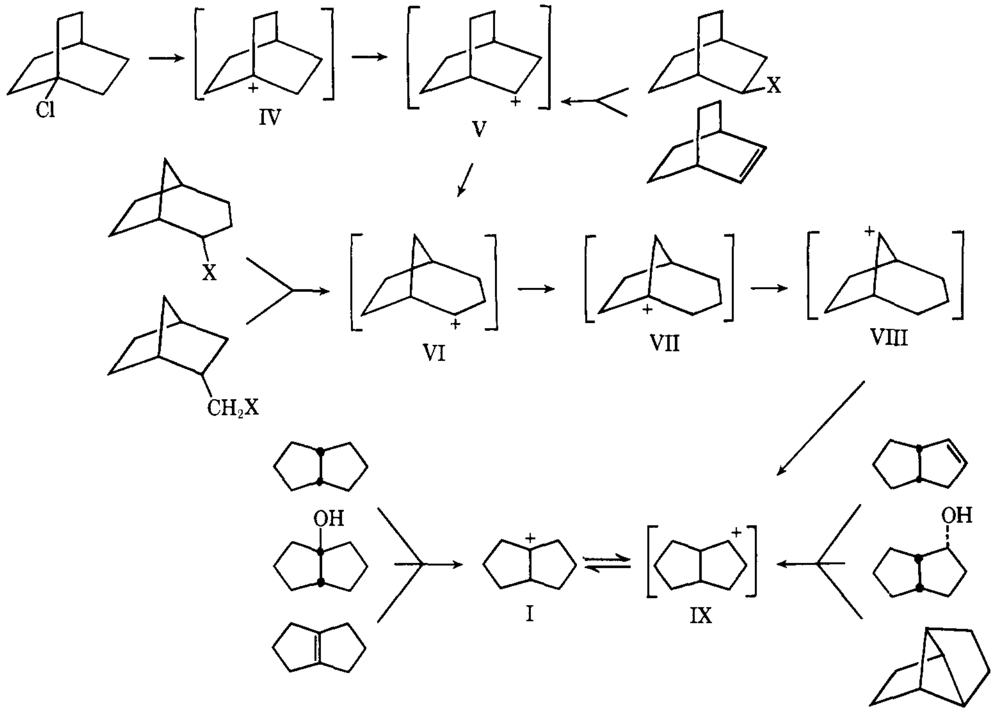


Chart II



endo-6-bicyclo[3.2.1]octyl[34] esters also gave similar product distributions.

In all cases, there is only indication of the intermediacy but no direct evidence for the formation of bicyclo[3.3.0]octyl products. In solvolysis reaction, the solvent must trap the carbocation intermediate before further rearrangement takes place. Under stable ion conditions, the initially formed carbocation would have a long enough lifetime to allow secondary intramolecular rearrangements to take place and the thermodynamically more stable carbocation is formed.

Formation of the 2-Methylnorbornyl Cation from the Bicyclo[3.3.0]-1-octyl Cation. The bicyclo[3.3.0]-1-octyl cation I was found to be unrearranged under stable ion conditions at temperatures below −30°. When ion I was heated to 0°, the 2-methylnorbornyl cation X was formed. The rearrangement is irreversible. The pmr spectrum of the rearranged cation

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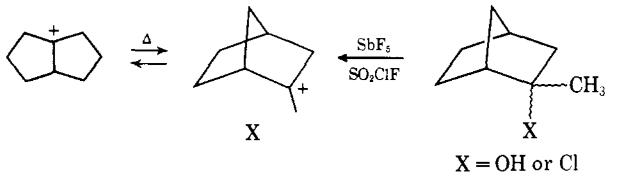
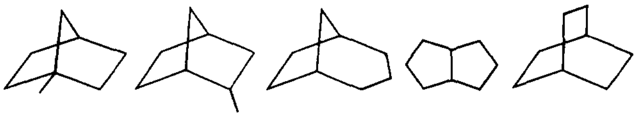
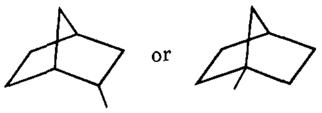
(34) R. A. Appleton, J. C. Fairlie, R. McGindle, and W. Paker, *J. Chem. Soc. C*, 1716 (1968).

was identical with that generated directly from 2-methylnorbornyl derivatives.[29,30] Quenching of the solution with KOH–ice–SO_2ClF at various temperatures yielded epimeric 2-methylnorborneols which were identical with authentic samples.[35]

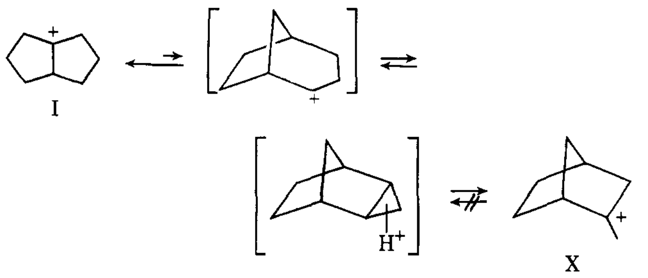


The rearrangement of ion I to the 2-methylnorbornyl cation is novel. 2-Methylnorbornanes were found to isomerize to bicyclo[3.2.1]octane in the presence of $AlCl_3$ at 75°,[26,27] *i.e.*, direction of the rearrangement is exactly reversed to that of cationic transformation under stable ion conditions. At 50°, 2-methylnorbornane and 1-methylnorbornane, respectively, gave the following common product distributions.[21,27]

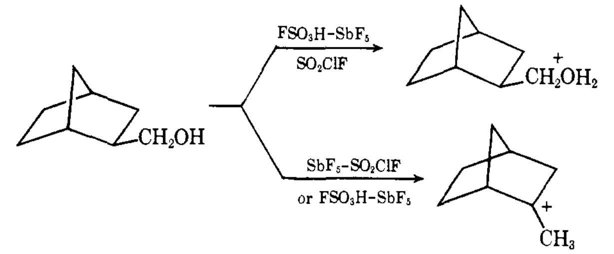


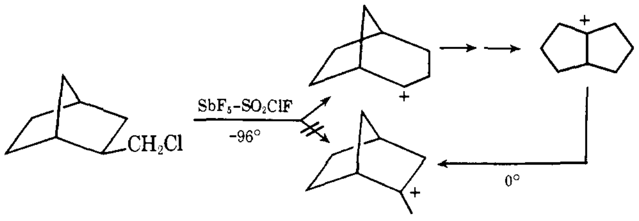
	$\xrightarrow{50°}$	trace	3%	55.8%	37.5%	3.6%
bicyclooctanes	$\xrightarrow{25°}$	—	trace	63.4%	32.7%	3.7%

Schleyer has recently established the stability order for bicyclooctanes.[21] Bicyclo[3.2.1]octane is more stable than bicyclo[3.3.0]octane which is in turn more stable than bicyclo[2.2.2]octane. This stability order was found mostly controlled by entropy factors. However, under stable ion conditions tertiary bridgehead bicyclo[3.3.0]octyl cation obviously is the most stable structure among all bicyclooctyl cations. The introduction of the sp^2 carbon into the bicyclooctyl structure must substantially increase the internal strain in bicyclo[2.2.2]octyl and -[3.2.1]octyl cations. Under thermodynamically controlled stable ion conditions, facile intramolecular hydride shift and Wagner–Meerwein rearrangement take place immediately. When ion I was heated, it was expected to undergo rearrangement back to 2-bicyclo[3.2.1]octyl cation. The latter can then undergo a cyclohexyl–methylcyclopentyl type cyclopropyl ring insertion[36,37] reaction to form the 2-methylnorbornyl cation X.



Deamination of *exo*- and *endo*-2-norbornylmethylamines[8,9] and the acetolysis of *exo*- and *endo*-2-norbornylcarbinyl esters gave both bicyclo[2.2.2]- and -[3.2.1]octyl products. No 2-methylnorbornyl products were found. Evidently, the carbon–carbon shift is more favorable then the 1,2-hydride shift in this system.[4] We expect that the same phenomenon could be observed in carbocation reactions. 2-Norbornylmethanols[38] and 2-chloromethylnorbornanes[39] were prepared and ionized. In FSO_3H–SO_2ClF or FSO_3H–SbF_5–SO_2ClF, 2-norbornylmethanols were only protonated and did not ionize even at 0°. However, slow ionization took place in neat FSO_3H–SbF_5 or SbF_5–SO_2ClF when heated to −10° giving the 2-methylnorbornyl cation X. In all cases, no bicyclo[3.3.0]octyl cation was observed. At higher temperature (> −30°) ion I was no longer stable and further rearrangement to 2-methylnorbornyl cation X took place immediately. When 2-chloromethylnorbornanes were ionized in SbF_5–SO_2ClF at −96° ion I was immediately formed. At this temperature, no 2-methylnorbornyl cation was observed. Consequently the latter was formed when the initially formed ion solution was heated to 0°. Thus, as found by Kwart and Irvine,[7] carbon–carbon shift was favorable in this case.





Conclusion

Under stable ion conditions, the bicyclo[3.3.0]-1-octyl cation can be generated from all bicyclooctyl derivatives at low temperatures. Ion I is static and does not undergo rapid equilibration of the bridgehead proton. The novel rearrangement of ion I to the 2-

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(35) C. Y. Lui, Ph.D. Thesis, Case Western Reserve University, 1970.

(36) G. J. Karabatsos and F. M. Vane, *J. Amer. Chem. Soc.*, **85**, 729 (1963). Also see C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions," Academic Press, New York, N. Y., 1968.

(37) G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **89**, 2227 (1967).

(38) Purchased from Aldrich Chem. Co., Milwaukee, Wis.

(39) Prepared by the method of J. K. Stille and F. M. Sonnenberg, *J. Amer. Chem. Soc.*, **88**, 4915 (1966).

methylnorbornyl cation was observed in the reverse direction as observed in bicyclononyl cations.[32] The driving force for this intramolecular transformation might be the result of strain involved in ion I.

Experimental Section

Proton Nuclear Magnetic Resonance Spectra. All pmr spectra were recorded at 60 MHz using a Varian Associates Model A56-60A spectrometer equipped with a variable temperature probe. TMS contained in a concentric capillary was used as a reference signal.

Preparation of Solutions of the Bicyclo[3.3.0]-1-octyl Cation. The bicyclo[3.3.0]-1-octyl cation can be generated from five bicyclo[2.2.2]octyl derivatives **1–5**, five bicyclo[3.3.0]octyl derivatives **9–13**, bicyclo[3.2.1]-2-octanol, 2-norbornanecarbinyl derivatives **8** (X = OH and Cl), and tricyclo[3.3.0.0^{2,6}]octane **6** in $FSO_3H-SbF_5-SO_2ClF$ (or SO_2) or in SbF_5SO_2ClF (or SO_2) at −78°. A solution of FSO_3H and SbF_5 (or SO_2) is prepared and cooled to −78° in a Dry Ice–acetone bath. To this solution is added with continuous vigorous stirring using a vortex-type stirrer a cold (−78°) solution of bicyclooctyl derivatives to give an approximately 10% solution. The solution is then transferred with a cold pipet to a precooled nmr tube.

The Rearrangement of the Bicyclo[3.3.0]-1-octyl Cation to the 2-Methylnorbornyl Cation. The bicyclo[3.3.0]-1-octyl cation solution prepared as described above is slowly heated to −10° in nmr probe. The 2-methylnorbornyl cation is slowly formed, and the solution is cooled back to −70° and the spectrum recorded. The nmr spectrum of the 2-methylnorbornyl cation has been reported previously.[29,30]

Quenching experiments with methanol of KOH–ice were carried out as described previously.[37]

Materials. Compounds **1**, **3**, **10**, **12**, and **8** (X = OH) are commercially available and were used without further purification.

Tricyclo[3.3.0.0^{2,6}]octane (6). Compound **6** was prepared in low yields by the method of Baldwin and Greeley.[40]

Bicyclo[3.2.1]-2-octanol.[4] 2-Bicyclo[3.2.1]octanone (Aldrich) was reduced by lithium aluminum hydride in the usual manner. Work-up of the reaction mixture gave a mixture of alcohols which was used without separation, mp 179–181°.

2-Chlorobicyclo[3.2.1]octanes (7, X = Cl). The method of Stille and Sonnenberg[39] was used to prepare the chlorides from bicyclo[3.2.1]octanols.

2-Norbornanemethyl Chloride (8, X = Cl). Compound **8** was prepared by treating the commercially available 2-norbornanemethanol with $SOCl_2$–pyridine;[39] bp 69–70°.

Acknowledgment. Support of this work by a grant of the National Science Foundation is gratefully acknowledged.

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[40] J. E. Baldwin and R. H. Greeley, *J. Amer. Chem. Soc.*, **87**, 4514 (1965).

Stable Carbocations. CXXI.[1a] Carbon-13 Magnetic Resonance Spectroscopy Study of Ethylenarenium Ions (Spiro[2.5]octadienyl Cations)[1b,c]

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Abstract: The parent ethylenebenzenium ion **8**-H has been obtained *via* phenyl participation from β-phenylethyl chloride in SbF_5-SO_2ClF solution and examined by carbon-13 (cmr) as well as proton (pmr) magnetic resonance spectroscopy. Other ethylenarenium ions were studied where aryl = *p*-anisyl, mesityl, and *p*-tolyl, and were also completely characterized by cmr spectroscopy. The unsymmetrical ethylene-2,4-dimethylbenzenium ion was also examined. The results of these studies show the stable, long-lived ions obtained to be symmetrically bridged ethylenarenium ions, *i.e.*, spiro[2.5]octadienyl cations. Delocalization of charge in secondary cyclopropylcarbinyl ions into the cyclopropane ring resembles closely the spirocyclopropane ring portion of the studied ions. The cyclohexadienyl ring portion of the ions shows charge distribution similar to that of the analogous arenium ions (protonated arenes). The bisected conformation of the ions as well as their geometry is essentially the same as originally suggested by Cram. The carbocations derived from 2,3-dimethyl-3-(*p*-X-phenyl)-2-butyl systems **11**-X were also examined by cmr and, in the cases where X = H, Br, and CF_3, are shown to be bridged in nature by comparison to suitable models for which pertinent ^{13}C parameters were measured. The model compound, tetramethylethylenebromonium ion, was reexamined because of the available new data and is now shown to be a symmetrically bridged species.

Since the pioneering studies of Cram,[2] solvolytic β-arylethyl systems have been some of the most carefully scrutinized in organic chemistry. Cram demonstrated the existence of a discrete molecular species in

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[1] (a) Part CXX: G. A. Olah and Y. Halpern, *J. Org. Chem.*, submitted for publication. (b) Preliminary communication: G. A. Olah and R. D. Porter, *J. Amer. Chem. Soc.*, **92**, 7627 (1970). Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 15, 1970, Abstract ORGN 57. (c) Concerning the definition and naming of carbocations (the generic name for all cations of carbon compounds, as carbanions are the anions) we recently suggested a clear differentiation between trivalent carbenium and penta- or tetracoordinated carbonium ions (G. A. Olah, *J. Amer. Chem. Soc.*, in press). Consequently the name ethylenarenium ions is used for ethylenarylonium ions (ethylenephenonium ions) which are carbenium and not pentacoordinated carbonium ions and should not be considered "nonclassical." Similarly $C_6H_7^+$ is the benzenium ion and not the benzenonium ion.

[2] (a) D. J. Cram, *J. Amer. Chem. Soc.*, **71**, 3863 (1949); (b) D. J. Cram and R. Davis, *ibid.*, **71**, 3871 (1949); D. J. Cram, *ibid.*, **71**, 3875 (1949); (c) the use of dotted lines as in **1′** to represent ions of the type **1** has become common, but the structure **1′** as it implies "nonclassicality" is not consistent with our experimental findings. σ-Bond delocalization