Table IX. Preparation of 2-Aryl-2-bicyclo[2.2.2]octanols[a]

Aryl group	% yield	Mp or bp, deg	Molecular formula	C, % Calcd	C, % Found	H, % Calcd	H, % Found	X,[o] % Calcd	X,[o] % Found	Mass spec (parent peak) m/e (calcd)	Mass spec (parent peak) m/e (found)
p-$CH_3OC_6H_4$[b–d]	18.5	56.5–58.0[b]	$C_{15}H_{18}O$							214	214
3,4-$(CH_3)_2C_6H_3$[e]	70.4	60–100 (0.3 mm)[f]	$C_{16}H_{22}O$							230	230
p-$CH_3C_6H_4$[b,d,g]	76	100 (0.33 mm)[b]	$C_{15}H_{18}$	90.85	89.45	9.15	9.07			198	198
p-IC_6H_4[h–j]	60	100 (0.2–0.4 mm)[f]	$C_{14}H_{17}IO$							328	328
p-BrC_6H_4[i]		120 (5–10 mm)[k]	$C_{14}H_{17}BrO$							282, 280	
p-ClC_6H_4[i,j]	40–60	125–145 (3 mm)[k]	$C_{14}H_{17}ClO$							238, 236	238, 236
p-FC_6H_4	8.6[l]	55–56	$C_{14}H_{17}FO$	76.29	76.10	7.84	7.78	8.62	8.62	220	220
C_6H_5[m]	45.4	135–152 (15 mm)	$C_{14}H_{18}O$								
m-BrC_6H_4	55	60 (0.25 mm)[f]	$C_{14}H_{17}BrO$	59.78	59.75	6.10	6.06	28.43	28.43	282, 280	282, 280
m-ClC_6H_4[i]	24	60 (0.3 mm)[f]	$C_{14}H_{17}ClO$							238, 236	238, 236
p-$CF_3C_6H_4$[b,n]	25.5	90 (10 mm)[b,f]	$C_{15}H_{15}F_3$	71.38	70.98	6.04	6.04	22.58		252	252
3,5-$(CF_3)_2C_6H_3$[b,n]	19.8	98–99[b]	$C_{16}H_{14}F_6$	60.00	59.55	4.41	4.24	35.59	36.17	320	320

[a] Alcohol unless otherwise indicated. Alcohols were prepared by the halogen–metal interconversion reaction unless otherwise indicated. [b] Olefin. [c] Dehydrated with $KHSO_4$ during distillation (see ref 45). [d] The organometallic reagent was prepared by the Grignard reaction. [e] The lithium reagent was prepared at 0°. It was then stirred at room temperature for 2 hr prior to the addition of bicyclo[2.2.2]octan-2-one (at room temperature). [f] Molecular distillation. [g] Dehydrated by overheating the alcohol. [h] Butyllithium in hexane was added to p-diiodobenzene at $-20°$. The temperature was then raised to $+10°$. After all the p-diiodobenzene dissolved the temperature was lowered to $-20°$. Bicyclo[2.2.2]octan-2-one was then added. [i] Not analyzed. [j] Partial dehydration during distillation. [k] Short-path distillation. [l] The yield of crude product was actually much greater than this value. Molecular distillation of the crude product produced a mixture of alcohol and olefin from which the alcohol was obtained pure after three recrystallizations from hexane. The yield of pure product was reduced in the fractional crystallizations. [m] See ref 8. [n] The alcohol was dehydrated in the presence of H_2SO_4 by heating to the boiling point under reduced pressure. [o] X refers to the appropriate halogen atom.

The nmr and ir spectra of the alcohols and olefins in the norbornyl and bicyclooctyl series of compounds were consistent with the assigned structures. The following are typical nmr spectra for an alcohol and olefin in each series of compounds.

Norbornyl System. 2-p-Iodophenyl-2-*endo*-norbornanol: nmr (CCl_4) τ 2.51 (AA′BB′, $\Delta\nu = 26$ Hz, $J_{AB} = 9$ Hz, 4 H), 7.70 (m, 4 H), 8.43 (m, 7 H). 2-p-Methoxyphenyl-2-norbornene: nmr (CCl_4) τ 3.04 (AA′BB′, $\Delta\nu = 31$ Hz, $J_{AB} = 9$ Hz, 4 H), 3.96 (d, $J = 3.5$ Hz, 1 H), 6.28 (s, 3 H), 6.76 (br s, 1 H), 7.06 (br s, 1 H), 8.12–9.0 (m, 6 H).

Bicyclooctyl System. 2-p-Fluorophenylbicyclo[2.2.2]octan-2-ol: nmr (CCl_4) τ 2.58 (m, 2 H), 3.09 (m, 2 H), 7.5–8.8 (m, 13 H). 2-p-Methoxylphenylbicyclo[2.2.2]oct-2-ene: nmr (CCl_4) τ 2.98 (AA′-BB′, $\Delta\nu = 31$ Hz, $J_{AB} = 9$ Hz, 4 H), 3.62 (dd, $J = 7$ Hz, 2 Hz, 1 H), 6.22 (s, 3 H), 6.98 (br s, 1 H), 7.38 (br d, $J = 7$ Hz, 1 H), 8.52 (AB q, $\Delta\nu = 17$ Hz, $J = 9$ Hz, 8 H).[48]

Acknowledgments. We are indebted to Mr. Steven Fettinger, Mr. Robert Bruggenmeier, and Miss E. Irene Pupko for technical assistance with some of the preparations and to Mr. Wayne Burkhardt and Mr. Eric Roach for assistance in the determination of some of the spectra.

(48) Decoupling experiments showed that the 2-Hz coupling at 3.62 is between the olefinic proton and the broad singlet at 6.98. Comparison of a 100-MHz spectrum with a 60-MHz spectrum of this compound indicates that the absorption centered at 8.52 is indeed an AB quartet (or two overlapping AB quartets with similar chemical shifts).

Fluorine-19 and Hydrogen-1 Nuclear Magnetic Resonance Study of an Equilibrium among Arylbicyclooctyl Cations[1]

A. D. Wolf and D. G. Farnum*

Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48824. *Received February 2, 1973*

Abstract: The following cations were characterized at $-90°$ by a ^1H nmr study: 2-p-trifluoromethylphenyl-2-bicyclo[2.2.2]octyl cation (**2a**), 2-p-trifluoromethylphenyl-2-bicyclo[3.2.1]octyl cation (**9a**), and 6-p-trifluoromethylphenyl-6-bicyclo[3.2.1]octyl cation (**11a**). Warming any of these cations to $-60°$ produced the same equilibrium mixture. By ^{19}F nmr the order of stability was found to be **11a** > **2a** ≫ **9a**. The equilibrium constant between **2a** and **11a** at $-80°$ is 3.2. Other thermodynamic parameters are presented and a mechanism for the equilibrium is discussed.

Recently we have found it desirable to examine certain chemical shifts in a series of 2-aryl-2-norbornyl cations **1** and 2-aryl-2-bicyclo[2.2.2]octyl cations **2**.[1b] During the course of this study we observed that upon ionization of their respective precursors at $-78°$, cations of type **2** in which X was a strongly withdrawing substituent (*e.g.*, **2a**, X = p-CF_3) gave proton nmr spectra substantially different from cations in which X was electron donating (*e.g.*, **2b**, X = p-F).[1b] Since

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(1) (a) This work was supported by the National Science Foundation under Grants GP 10734 and GP 27994; (b) for a related paper, see D. G. Farnum and A. D. Wolf, *J. Amer. Chem. Soc.*, **96**, 5166 (1974).

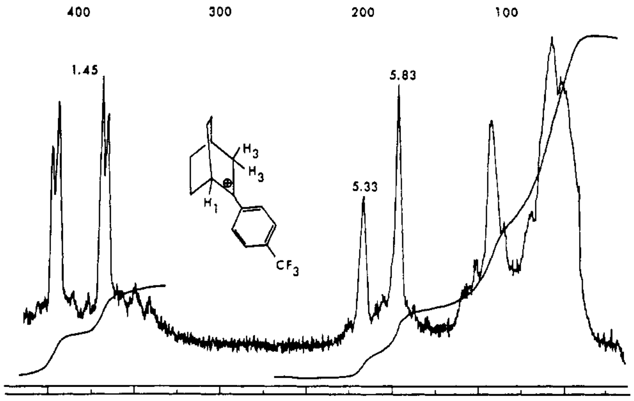
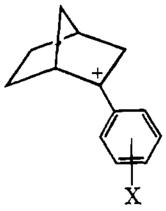
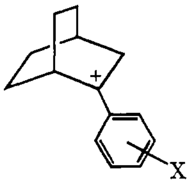


Figure 1. Spectrum (100 MHz) of **2a** at −90°.



1

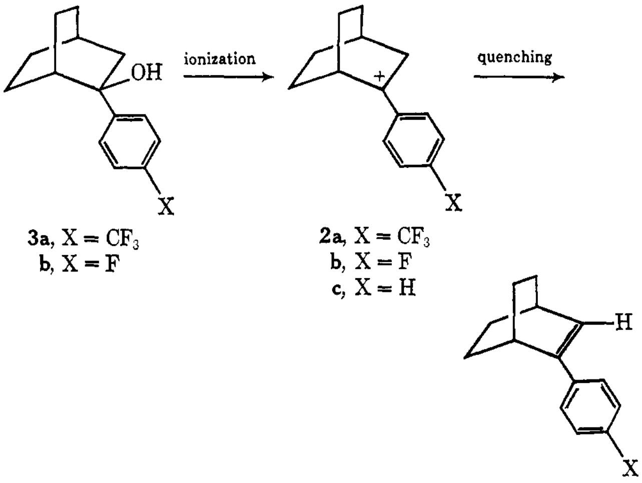


2a, X = p-CF_3
b, X = p-F

chemical shifts in the former case indicated that the aryl group was still at a carbonium ion center, it seemed likely that **2a** might have rearranged to one or more new arylcarbonium ions under the ionizing conditions. Since these circumstances would permit the determination of equilibrium constants among the cations present, we explored the hypothesis further. Thus, isomeric arylbicyclooctyl alcohols were prepared and examined under similar conditions of ionization. The results of these studies are described below.

Proton Nmr Studies

Careful ionization of p-trifluoromethylphenylbicyclo[2.2.2]-octan-2-ol (**3a**) in fluorosulfonic acid–sulfuryl chlorofluoride at temperatures lower than −100° gave rise to the 2-p-trifluoromethylphenyl-2-bicyclo[2.2.2]octyl cation **2a**. The nmr spectrum of **2a** is shown in Figure 1. The four proton AA′BB′ system centered at τ 1.45 is assigned to the trifluoromethylphenyl group. That this group is at a carbonium ion center[2] is evident when one compares the large chemical shift difference ($\Delta\nu$ = 0.67 ppm) between the ortho and meta protons in cation **2a** with their coincidence in the starting material **3a**. Furthermore, the chemical shifts of the aryl protons in **2a** are more than 1 ppm to lower field than in the alcohol **3a** (τ 2.50). The broad singlet (1 H) at τ 5.33 is assigned to the bridgehead proton H(1) α to the carbonium ion center, while the broad singlet (2 H) at τ 5.83 is assigned to the methylene group α to the carbonium ion center H(3). Deuterium labeling at C(3) in **2a** gives rise to a spectrum in which the absorption at 5.83 is essentially wiped out. There are nine other hydrogens at higher field which were not assigned. This spectrum is quite similar (as expected) to that of the previously reported and more stable cation **2c**.[3]



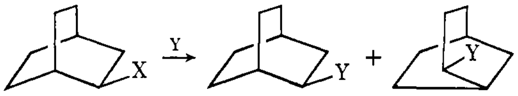
3a, X = CF_3
b, X = F

2a, X = CF_3
b, X = F
c, X = H

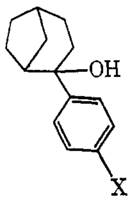
4a, X = CF_3
b, X = F

That cations **2** do indeed have the 2-bicyclo[2.2.2]-octyl skeleton was confirmed by recovery experiments. Quenching of cation **2a** in pentane/aqueous sodium carbonate at 0° gave bicyclo[2.2.2]octene (**4a**) in 55% yield and bicyclo[3.2.1]oct-6-ene (**17a**) in 45% yield.[4] The origin of **17a** will be discussed later. Quenching of **2b**[5] gave essentially pure olefin **4b**, which can be produced by simply overheating alcohol **3b** on distillation. The nmr spectra of olefins **4** are quite characteristic of their structure (see Experimental Section).

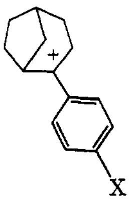
Warming **2a** to −60° in the nmr probe produces material with an nmr spectrum identical with that of the material obtained by ionization of **3a** at −78°. The chemical shift of the aryl group in this material indicated that one or more new aryl carbonium ions were present. It is well known from solvolytic studies of bicyclooctyl derivatives **5** that they generally yield approximately equal molar mixtures of compounds **6**, in which the initial skeleton is retained, and **7**, in which the initial skeleton has rearranged to the [3.2.1] system.[6] With the consideration that **2a** might have rearranged to **9a** we attempted to prepare that cation. While ionization of **8a**[7] at −78° did indeed give material having a spectrum identical with that of rearranged **2a**, ionization of **8a** at <−100° produced material having a different spectrum. That spectrum, assigned to struc-



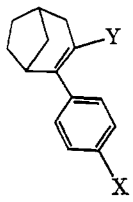
5 **6** **7**



8a, X = CF_3
b, X = F



9a, X = CF_3
b, X = F



10a, X = F; Y = H
b, X = F; Y = D

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(2) D. G. Farnum, *J. Amer. Chem. Soc.*, **89**, 2970 (1967).

(3) D. G. Farnum and G. Mehta, *J. Amer. Chem. Soc.*, **91**, 3256 (1969).

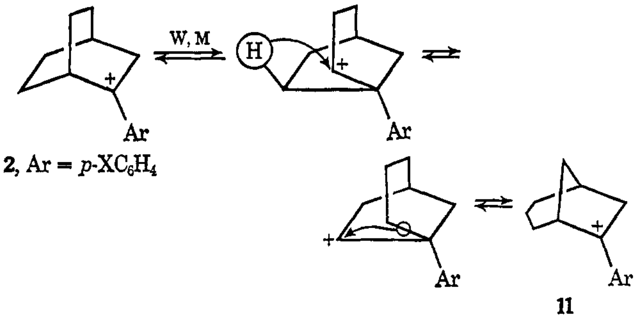
(4) See Experimental Section.

(5) The fluorophenyl derivative **2b** gives the same basic spectrum as **2a**. It is more stable to rearrangement than **2a** but it also will rearrange when warmed to 0°.

(6) H. Kwart and J. L. Irvine, *J. Amer. Chem. Soc.*, **91**, 5541 (1969).

(7) Probably a mixture of exo and endo isomers.

Scheme I



2, Ar = *p*-XC_6H_4

11

ture **9a**,[8] is shown in Figure 2.[9] There is a *p*-$CF_3C_6H_4$ group (τ 1.45) at a carbonium ion center. The broad singlet at τ 5.10 (1 H) is assigned to the bridgehead proton H(1).[11] The methylene protons α to the carbonium ion center are not magnetically equivalent as they were in structure **2a** and they give rise to a highly coupled AB pattern with one component at τ 5.86 (1 H) and the other at τ 6.36 (1 H).

Since **9a** is rather unstable toward rearrangement, labeling and quenching studies were carried out on the more stable cation **9b**. This cation gives the same basic spectrum as cation **9a**. Labeling at C(3) in **9b** gives rise to a spectrum in which the highly coupled AB pattern is nearly wiped out. In an attempt to make nmr assignments for each of the α-methylene protons and to obtain information on the conformation of **9**, deuterated olefin **10b** was prepared. Treatment of **10b** with fluorosulfonic acid–sulfuryl chlorofluoride at −105° gave deuterated **9b** having a spectrum in which the α-methylene signals were about equally reduced in intensity and in which there was a sharpening of that portion of the AB system at lowest field. Apparently **10b** is protonated equally well from both top and bottom. Thus we were not able to assign the methylene protons on the basis of these labeling experiments.

In order to completely convince ourselves that cations **9** do have the 2-substituted [3.2.1] skeleton we quenched **9b** in pentane/aqueous sodium carbonate at −78° and obtained the two olefins **10a** and **4b** in 55 and 17% yield, respectively.[12] There was also 32% of unidentified material which was composed of at least two compounds having gc retention times longer than those of the olefins. Olefin **10a** could also be produced by treatment of **8b** with *p*-toluenesulfonyl chloride/pyridine at 110° in a sealed tube for 10 hr.[13]

We have reported elsewhere[1] that 2-aryl-2-norbornyl cations **1** in which X is a strongly electron withdrawing group undergo the well known "Wagner–Meerwein–6,2-hydride shift" rearrangement very rapidly on an nmr time scale. In cations **1** this rearrangement is degenerate. It is interesting to examine the outcome of this same rearrangement in cation **2**. In this case, as is shown in Scheme I, a new cation **11** having the 6-substituted bicyclo[3.2.1]octyl skeleton is produced.

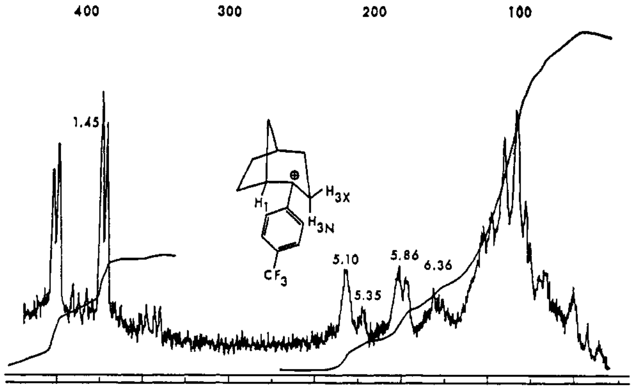
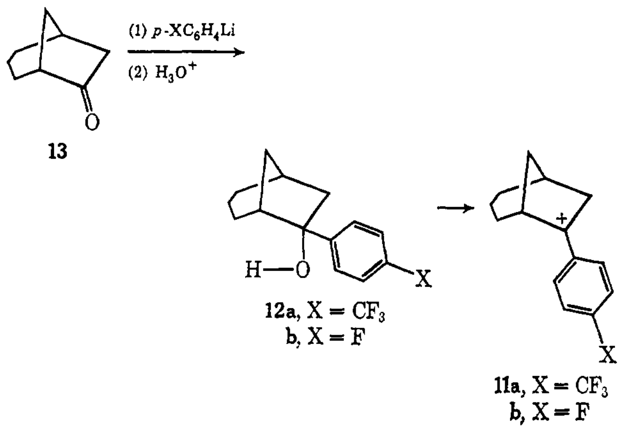


Figure 2. Spectrum (100 MHz) of **9a** at −100°.

In order to examine the possibility that **2a** (and **9a**) rearranged to cation **11a** we prepared alcohol **12a** as shown below.



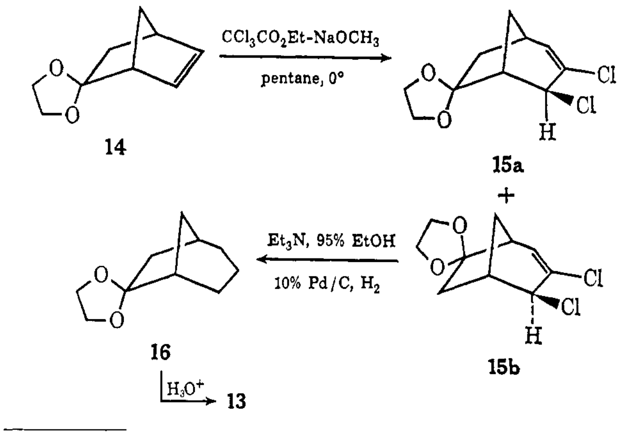
13

12a, X = CF_3
b, X = F

11a, X = CF_3
b, X = F

Although there are literature procedures available for the synthesis of **13**,[15–18] we have independently prepared it in good yield (48% based on 2-norbornenone ethylene ketal **14**) according to Scheme II. By inte-

Scheme II



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[8] There are other materials present besides **9a**. This will be discussed in the section on ^{19}F nmr.

[9] We are not assigning a conformation to cations **9** as our data do not permit distinction between the chair or boat conformation. It has been reported recently that the 2-methyl-2-bicyclo[3.2.1]octyl cation exists in the boat conformation.[10]

[10] G. A. Olah, G. Liang, J. R. Wiseman, and J. A. Chong, *J. Amer. Chem. Soc.*, **94**, 4927 (1972).

[11] The broad singlet of low intensity at τ 5.33 is due to **2a**. It has a counterpart of double intensity at τ 5.83 under the low-field portion of the "AB quartet" of **9a**. It has not been possible to produce this cation completely free from **2a**. Even in the case of the more stable cation **9b**, there is some **2b** which is always present on ionization of **8b** even at temperatures as low as −110 to −120°.

[12] See Experimental Section.

[13] Based on a procedure for dehydration of isomeric methylbicyclooctanols.[14]

[14] W. Kraus and R. DeWald, *Justus Liebigs Ann. Chem.*, **689**, 21 (1965).

[15] V. N. Ipatieff, J. E. German, W. W. Thompson, and H. Pines, *J. Org. Chem.*, 17, 252 (1952).

[16] K. B. Wiberg and B. A. Hess, Jr., *J. Org. Chem.*, 31, 2250 (1966).

[17] W. Szarkowska-Szpaczek, *Rocz. Chem.*, **36**, 235 (1962).

[18] D. Komppa, T. Hirn, W. Rohrmann, and S. Beckmann, *Justus Liebigs Ann. Chem.*, **521**, 242 (1936).

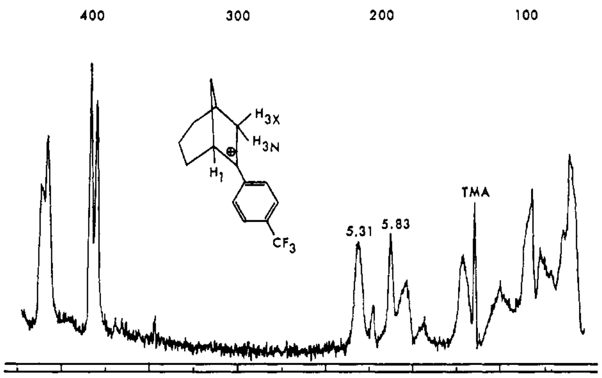
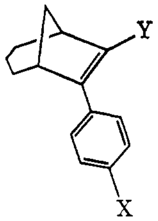


Figure 3. Spectrum (100 MHz) of **11a** at −90°.

gration of the two olefinic protons (having J = 7.6, 7.2 Hz) or the two endo C_4 protons (having J = 2.7, 2.8 Hz), it was possible to determine that dichlorocarbene addition[19] to **14** produced **15a** and **15b** in about a 1:1 ratio. The stereochemical assignment at C(4) was based on a comparison of the observed coupling constants to those for the adduct between norbornene and dichlorocarbene[21] (J_{H_1,H_2} = 7.0 Hz, J_{H_3,H_4} = 2.8 Hz). Because of the similarity between **15a** and **15b** the chemical shifts were not assigned. The mixture was not separated since each of the components yield the desired product **16** on reduction. Hydrolysis of **16** yielded ketone **13**, which on treatment with p-$CF_3C_6H_4Li$ followed by hydrolysis gave alcohol **12a**.[22]

Ionization of **12a** in fluorosulfonic acid–sulfuryl chlorofluoride below −100° produced cation **11a**. The nmr spectrum of **11a** at −90° is reproduced in Figure 3. There is an AA′BB′ system centered at τ 1.45 attributable to the p-$CF_3C_6H_4$ group at the carbonium ion center. The broad singlet at τ 5.13 (1 H) is assigned to the bridgehead proton H(1) α to the carbonium ion center. The methylene protons on C(3) give rise to the AB quartet centered at τ 5.83 (J = 24 Hz) in which the higher field component is further coupled. Deuterium labeling at C(3) in **11a** essentially wipes out the AB pattern. Preparation of olefin **17b** (partially deuterated) and ionization of this compound below −100° gave a spectrum in which the lowest field component of the AB quartet was greatly reduced in intensity while the highest field component collapsed to a broad singlet. Assuming predominantly exo protonation by fluorosulfonic acid in **17b**,[23] the endo proton is then the lowest field proton while the exo proton is at highest field.



17a, X = CF_3; Y = H
b, X = CF_3; Y = D
c, X = F; Y = H

While we have not quenched cation **11a** directly, it was mentioned earlier that olefin **17a** is produced on quenching cation **2a**. We believe that cation **11a** is actually the source of olefin **17a**. **17a** was identified by comparison with identical material produced by dehydration of **12a** with p-toluenesulfonyl chloride in pyridine.[14] Furthermore, quenching cation **11b** yields olefin **17c** (80% of recovered material) as the major product.

When cation **11a** was warmed to −60° in the nmr instrument, the spectrum obtained indicated that **11a** had produced the same material as cations **2a** and **9a** on warming to −60°. It was now evident by a comparison of the nmr spectra of the mixture and **11a** that cation **11a** was a major component in the mixture.

Fluorine Nmr Studies

From the proton nmr studies of the mixture produced by either cations **2a**, **9a**, or **11a** it was not possible to tell exactly how much of each of the cations was present or if any other materials were present. Monitoring the ^{19}F resonance (a sharp singlet) of the p-$CF_3C_6H_4$ group in the cations proved to be a convenient method for following the formation of the mixture from each of the cations and for obtaining quantitative information on both the total number of cations (and other materials having a $CF_3C_6H_4$ group) and the relative amounts of each present.[24] Using this method we were able to determine that the mixture produced from **2a** or **11a** is virtually identical and consists almost exclusively of these two cations. The equilibrium constant measured at −80° by integration of the ^{19}F resonances is 3.2 favoring cation **11a**.

Ionization of **8a** below −100° produces cation **9a** along with several other materials (up to 40%) which have not been identified and which have ^{19}F resonances at lower field than **2a**, **9a**, or **11a**. We believe these latter compounds probably arise from irreversible reactions of the starting material during the ionization process since the amounts of these materials produced were variable in different experiments while their total percentage remained relatively constant on warming **9a**.[25]

When **9a** is warmed to −80°, it disappears and produces an equilibrium mixture of **2a** and **11a** containing less than 2% **9a**. A summary of the quantitative data obtained from the ^{19}F studies in the equilibrium between these cations is shown in Table I.

From both the ^{19}F and ^1H nmr studies we have obtained data which support the mechanism shown in Scheme III.

First we reemphasize that we are dealing with a true equilibrium. Thus, cations **2a**, **9a**, and **11a** can each be observed prior to any significant rearrangement, and, on

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(19) Same conditions that were used for dichlorocarbene addition to norbornene.[20]

(20) C. W. Jefford, J. Gunsher, D. T. Hill, P. Brun, J. LeGras, and B. Waegell, *Org. Syn.*, **51**, 60 (1971).

(21) C. W. Jefford, S. Mahajan, J. Waslyn, and B. Waegell, *J. Amer. Chem. Soc.*, **87**, 2184 (1965).

(22) Although we have no evidence on the stereochemistry of **12**, it seems likely that it is the endo alcohol. The reactions of p-XC_6H_4Li (X = F and CF_3) with ketone **13** yield predominantly one product with a sharp melting point. 2-Norbornanone, a ketone of similar structure, is attacked preferentially from the exo side of the molecule by nucleophiles.

(23) Similar behavior is observed for 2-p-fluorophenyl-2-norbornene of similar structure.[1]

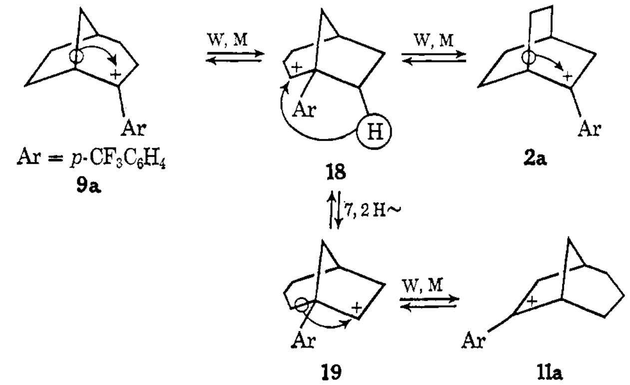
(24) While the p-FC_6H_4 derivatives of the cations were also examined, this group proved to be a less convenient probe at 56 MHz, the conditions of exploratory runs, since the ^{19}F resonance was broad due to coupling with the aromatic protons.

(25) The equilibrium mixture produced from **2a** or **11a** was essentially free from these materials.

Table I. Thermodynamic Data from ^{19}F Nmr Experiments at 94.1 MHz

$K(-80°)$	$K(50°)$	T_{inv}	ΔG, cal	ΔH, cal	ΔS, eu
3.2	1.6	200°	−450	−700	−1.5

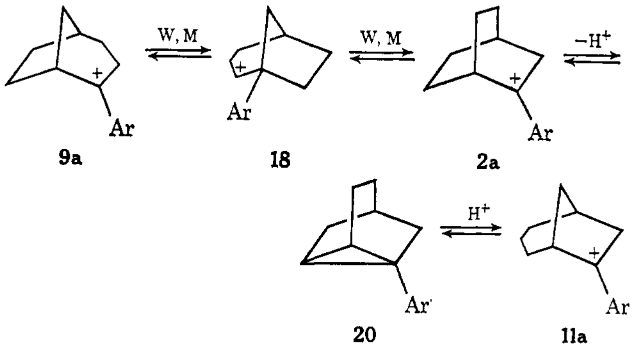
Scheme III



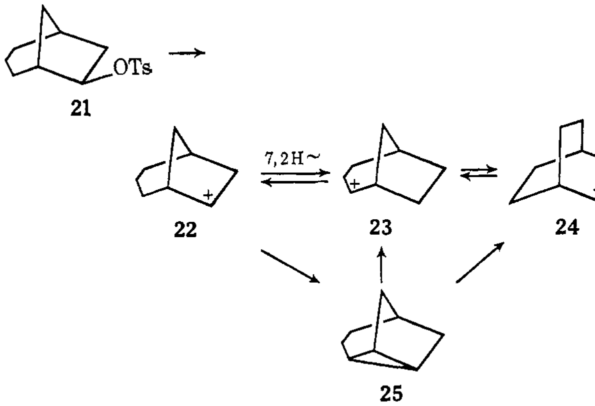
warming **2a**, **9a**, or **11a**, the same mixture[26] of cations in the same ratio is produced. A second important fact related to the mechanism was obtained by observing the approach to equilibrium starting from cation **9a** (^{19}F method). We were able to detect that an initial build-up of cation **2a** occurred while **11a** became predominant as the equilibrium was approached. This indicated that cation **2a** was formed at a faster rate than **11a**, but **11a** was more stable. The secondary cation **18** seems to be a reasonable intermediate in the transformation of **9a** into **2a** and **11a**. One would expect that the rate of partitioning of **18** between **2a** and **19** (which rearranges to **11a**) would favor **2a** as observed. The partitioning of **19** to **2a** involves a Wagner–Meerwein rearrangement which yields an arylcarbonium ion, *i.e.*, **2a**. The partitioning of **18** to **19**, a secondary carbonium ion, involves a 7,2-hydride shift (7,2 H~). Some of the stability of the arylcarbonium ion **2a** ought to show up in the transition state to its formation. Even if cation **19** is more stable than **18**, one would expect a larger activation energy for this 7,2-hydride shift than for the W,M transformation[27] of **18** → **2a**. A third observation is that in the transformation of **2a** into **11a**, the methylene group α to the carbonium ion center remains bonded to the carbon containing the aryl group. Equilibration of **2a** labeled with deuterium at C(3) produces **11a** with the C(7) methylene α to the carbonium ion center also labeled with deuterium.

An alternative mechanism which accounts for the observed results and avoids a direct 7,2-hydride shift is of the type **9a** ⇄ **2a** ⇄ **11a** as shown in Scheme IV. The required 7,2-hydride shift is accomplished indirectly *via* the cyclopropane intermediate **20**. Evidence against intermediates of type **20** was obtained by Parker and coworkers[28] in their studies of the buffered acetolysis of the unsubstituted bicyclo[3.2.1]-6-toluene-*p*-sulfonates **21** (Scheme V). They observed products resulting from trapping of **22**, **23**, and **24**. They considered that leakage of **22** into **23** and **24** might be occurring indirectly *via* the cyclopropane **25** rather than by direct 7,2-hydride shift. However, a comparison of the products obtained when **25** was submitted to the acetolysis conditions with those obtained from **21** indicated that the mechanism involving **25** could be operative to no more than 20%.[28] Assuming that the aryl group does not significantly enhance proton loss from **11a**, then the arylcyclopropane **20** should not be an important intermediate in the conversion of **2a** to **11a**. Furthermore, one would expect that proton loss to form a cyclopropane would compete even less effectively with 7,2-hydride shift in fluorosulfonic acid than in buffered acetic acid. Hydride shifts of this type are well documented in the structurally related norbornyl systems.[1,29,30]

Scheme IV



Scheme V



Experimental Section

General Procedure. Melting points (uncorrected) were measured on a Thomas-Hoover capillary melting point apparatus. Infrared spectra were measured on a Perkin-Elmer Model 137 instrument. Mass spectra were measured on a Hitachi Perkin-Elmer RMU-6 instrument. Proton and fluorine nmr spectra were taken at 60 MHz on a Varian T-60 or A 56/60 D or at 100 MHz on a HA 100 instrument. Proton chemical shifts are reported in τ values *vs.* tetramethylammonium tetrafluoroborate (τ 6.87)[2] as an internal standard.

Carbonium Ion Preparation. The fluorophenylbicyclooctyl cations were generally formed by ionization of the respective starting materials at −78° in FSO_3H. The *p*-trifluoromethylphenylcarbonium ions were ionized at temperatures below −100°. In the latter case the alcohol or olefin to be ionized was dissolved in sulfuryl chlorofluoride (1 ml) and cooled to −78°. This solution was slowly added dropwise to a rapidly stirred mixture of FSO_3H (1 ml) in SO_2ClF (1–2 ml) (N_2 atmosphere) below −100°. About a 5 wt % final solution concentration of the carbonium ion was

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(26) Though **9a** is not detectable in this mixture, it very likely is an accessible intermediate.

(27) It has been suggested elsewhere that the absolute rate of bond shifting in bicyclic systems is greater than the rate of hydride shifting.[4]

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Table II. Proton Chemical Shifts (τ Values) in Arylbicyclooctyl Cations

System	Cation	p-XC$_6$H$_4$	Bridgehead proton	α-Methylene protons
2-[2.2.2]	**2a**, X = CF$_3$	1.45 (AA'BB', $\Delta\nu$ = 67 Hz, J = 9 Hz, 4 H)	5.33 (br s, 1 H)	5.83 (br s, 1 H)
	2b, X = F	1.13 (m, 2 H), 2.39 (m, 2 H)	5.68 (br s, 1 H)	6.09 (br s, 2 H)
2-[3.2.1]	**9a**, X = CF$_3$	1.45 (AA'BB', $\Delta\nu$ = 65 Hz, J = 9 Hz, 4 H)	5.10 (br s, 1 H)	5.86 (m, 1 H), 6.36 (m, 1 H)
	9b, X = F	1.07 (m, 2 H), 2.37 (m, 2 H)	5.39 (br s, 1 H)	6.04 (m, 1 H), 6.63 (m, 1 H)
6-[3.2.1]	**11a**, X = F	1.44 (AA'BB', $\Delta\nu$ = 65 Hz, J = 9 Hz, 4 H)	5.31 (br s, 1 H)	5.83 (ABq, J = 24 Hz, 2 H)
	11b, X = CF$_3$	1.17 (m, 2 H), 2.36 (m, 2 H)	5.62 (br s, 1 H)	6.12 (ABq, J = 24 Hz, 2 H)

Table III. Preparation of n-Arylbicyclo[$k.l.m$]octan-n-ols[a]

System n-[$k.l.m$]	Aryl group	Yield	Mp or bp, deg	C, %		H, %		F, %		Mass spectra	
				Calcd	Found	Calcd	Found	Calcd	Found	m/e (calcd)	m/e (found)
2-[2.2.2]	p-FC$_6$H$_4$	8.6[b]	55–56	76.29	76.10	7.84	7.78	8.62	8.62	220	220
	p-CF$_3$C$_6$H$_4$[c]	52.2	60 (0.3 mm)[d]							270	270
	p-CF$_3$C$_6$H$_4$[e]	43.2	60 (0.3 mm)[d]							272	272 (60.3%), 271 (34.5%), 270 (5.2%)
2-[3.2.1]	p-FC$_6$H$_4$[c]		80 (0.3 mm)[d]							220	220
	p-FC$_6$H$_4$		80 (0.3 mm)[d]							222	222 (80.2%), 221 (17.4%), 220 (2.4%)
	p-CF$_3$C$_6$H$_4$	77.8	71–74[f]	66.66	66.64	6.31	6.36	21.11	21.10	270	270
	p-CF$_3$C$_6$H$_4$[e]	60.2	60 (0.2–0.4 mm)[d]							272	272 (78.5%), 271 (19.4%), 270 (3.1%)
6-[3.2.1]	p-FC$_6$H$_4$[c]	78	73–74							220	220
	p-CF$_3$C$_6$H$_4$	32	75–75.5	66.66	66.67	6.31	6.21	21.11	21.30	270	270
	p-CF$_3$C$_6$H$_4$[g]	55.3	74–77.5							272	272 (51.4%), 271 (43.1%), 270 (5.2%)

[a] All solids were crystallized from heptane. [b] The yield of crude product was actually much greater than this value. Molecular distillation of the crude product yielded a mixture of alcohol and olefin from which the alcohol was obtained pure after three recrystallizations from hexane. The yield of pure product was reduced in the fractional crystallization process. [c] Not analyzed. [d] Short-path distillation. [e] Deuterated at C(3). [f] Possibly a mixture of exo and endo alcohols. [g] Deuterated at C(7).

prepared. The sample was then transferred to nmr tubes which were maintained below −100° by a liquid N$_2$-pentane mixture.

The pertinent chemical shifts of carbonium ions prepared in this study are listed in Table II.

Preparation of Ketones. Bicyclo[3.2.1]octan-2-one was commercially available. Bicyclo[2.2.2]octan-2-one[31,32] and bicyclo[3.3.0]-octan-2-one[33] were prepared according to literature procedures.

Bicyclo[3.2.1]octan-6-one. Although there were literature procedures available for the synthesis of the title compound,[15–18] it was prepared independently and in good yield by the following method.

Addition of Dichlorocarbene to 2-Norbornenone Ethylene Ketal 14. Dichlorocarbene was generated from ethyl trichloroacetate according to Jefford's[1] procedure[20] for the addition of :CCl$_2$ to norbornene. The crude product was poured into H$_2$O and extracted three times with pentane. The pentane extracts were dried with MgSO$_4$ and pentane was stripped off on a rotary evaporator. The unreacted starting materials were distilled from the product at 90° (0.3 mm) leaving a reddish-black oil which was carried on to the next step. Ketal (64 g) yielded 100 g of the crude oil. The nmr spectra of the oil indicated that the major products were **15a** and **15b**, one of which was slightly predominant: nmr (mixture, CCl$_4$) τ 3.80, 3.95 (two doublets, J = 7.5 Hz, 1 H), 5.50, 5.80 (two doublets, J = 3 Hz, 1 H), 6.15 (m, 4 H), 7.50 (m, 2 H), 8.10 (m, J = 2.8 Hz).

Formation of 16 by Catalytic Hydrogenation of 15a and 15b. The 100 g of crude material from the preceding step was split into two 50-g samples which were each hydrogenated in the following way: 50 g of a mixture of crude **15a** and **15b** was dissolved in 100 ml of Et$_3$N and 150 ml of 95% EtOH. To this mixture was added 4 g of 10% Pd/C. The mixture was hydrogenated on a Paar apparatus. The crude product was poured into water and extracted three times with pentane. The crude products from each run were combined and the crude ketal was distilled from polymeric material and then redistilled. There was some hydrolysis of the ketal in this process, but this was not critical since the entire mixture was carried on to the next step for hydrolysis: nmr (purified sample of ketal, CCl$_4$) τ 6.16, (m, 4 H), 7.6–9.0 (m, 12 H).

Hydrolysis of Ketal 16. Preparation of Bicyclo[3.2.1]octan-6-one. The entire product from the preceding step was treated with 300 ml of pentane, 200 ml of H$_2$O, and 2 ml of concentrated H$_2$SO$_4$. The mixture was stirred for 6 hr at room temperature. The crude product was poured into saturated aqueous NaHCO$_3$. The solution was extracted three times with pentane and the pentane solution was then dried over MgSO$_4$ and the pentane solvent evaporated. The crude product was sublimed at 82° at water aspirator pressure. The yield of colorless, crystalline solid, mp 149–153° (lit.[16] 155–157°), was 25 g from 64 g of norbornenone ethylene ketal (48% overall yield): nmr (CCl$_4$) 7.5 (br s, 1 H), 7.65–9.0 (m, 9 H); ir $\nu_{\max}$ (neat) 2990, 1750 (lit.[28] $\nu_{\max}$ 1743 cm^{-1}).

Synthesis of Alcohols. The alcohols used in this study were all synthesized by reaction of the desired organometallic reagent with the appropriate ketone. The organometallic reagents were all formed by the halogen-metal interconversion reaction. In a typical experiment ether was distilled into a dried 50-ml three-neck flask containing a weighed amount of the aryl bromide. The flask was equipped with a low-temperature thermometer, a magnetic stirring bar, N$_2$ inlet, and a 15 ml constant pressure addition funnel. About a 10–30% solution of the aryl halide in ether was used. The solution was cooled to about −40° using a Dry Ice–acetone bath. To this solution was added dropwise a 10% molar excess (over the halide) of commercially available butyllithium in hexane. The reaction was kept between −30 and −40° during the addition. The mixture was then warmed to −10° for about 5 min. After

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

Table IV. Nmr and Ir Data of Isomeric *n*-Arylbicyclo[*k.l.m*]octan-*n*-ols

System *n*-[*k.l.m*]	Aryl group	Ir, cm$^{-1\,a}$	Nmr, $\tau^{b,c}$
2-[2.2.2]	p-FC$_6$H$_4$^{d}	3356 (s), 2880 (s), 860 (m), 831 (s), 815 (s)	2.58 (m, 2 H), 3.09 (m, 2 H), 7.5–8.8 (m, 13 H)
	p-CF$_3$C$_6$H$_4$	3450 (s), 2950 (s), 1630 (m), 835 (s)	2.50 (s, 4 H), 7.4–9.0 (m, 13 H)
2-[3.2.1]	p-FC$_6$H$_4$	3450 (s), 2950 (s), 1620 (s), 835 (s), 815 (s)	2.50 (m, 2 H), 3.04 (m, 2 H), 7.4–9.0 (m, 13 H)
	p-CF$_3$C$_6$H$_4$^{d,e}	3330 (s), 2850 (s), 1620 (s), 840 (s)	2.35 (s, 4 H), 7.3–9.0 (m, 13 H)
6-[3.2.1]	p-FC$_6$H$_4$^{d,e}	3350 (m), 2890 (s), 1620 (m), 858 (m), 845 (m), 828 (m), 815 (m)	2.50 (m, 2 H), 2.92 (m, 2 H), 7.3–9.0 (m, 13 H)
	p-CF$_3$C$_6$H$_4$^{d,f}	3450 (w), 2950 (s), 1640 (w), 858 (m), 830 (w)	2.4 (s, 4 H), 7.2–8.8 (m, 13 H)

[a] Neat ir sample unless otherwise indicated. [b] CCl$_4$ was the nmr solvent unless otherwise indicated. [c] TMS was used as internal nmr standard for all spectra. [d] Nujol mull. [e] CDCl$_3$ was used as the nmr solvent. [f] Freon 114-B2 was used as the nmr solvent.

Table V. Quenching Products from Several Isomeric *n*-Arylbicyclo[*k.l.m*]oct-*n*-yl Cations

System *n*-[*k.l.m*]	Aryl group	Quenching conditions	Products
2-[2.2.2]	p-FC$_6$H$_4$	Pentane/Na$_2$CO$_3$/−78°	2-*p*-Fluorophenylbicyclo[2.2.2]oct-2-ene[a]
	p-CF$_3$C$_6$H$_4$	Pentane/aq Na$_2$CO$_3$/0°	2-*p*-Trifluoromethylphenylbicyclo[2.2.2]oct-2-ene (55%) 6-*p*-Trifluoromethylphenylbicyclo[3.2.1]oct-6-ene (45%)
2-[3.2.1]	p-FC$_6$H$_4$	Pentane/Na$_2$CO$_3$/−78°	2-*p*-Fluorophenylbicyclo[3.2.1]oct-2-ene (51%) 2-*p*-Fluorophenylbicyclo[2.2.2]oct-2-ene (17%) and 32% unidentified products[b,c]
6-[3.2.1]	p-FC$_6$H$_4$	MeOH/Na$_2$CO$_3$/−78°	6-*p*-Fluorophenylbicyclo[3.2.1]oct-6-ene (77%)[d] and 23% unidentified products

[a] No other detectable products. This is based on integration of the characteristic olefinic proton in this system. [b] 60% recovery of material. [c] The unidentified material is comprised of at least two compounds. There were two peaks having a longer retention time than the olefins (20% SE-30). [d] Based on integration of the olefinic proton.

the addition of the butyllithium was completed, the temperature of the reaction mixture did not rise above −30°. Following addition of the ketone the Dry Ice–acetone bath was removed and the temperature of the reaction mixture was allowed to warm slowly to room temperature. The reaction mixture was then hydrolyzed with saturated NH$_4$Cl solution and extracted with ether. Drying the ether solution with MgSO$_4$ followed by evaporation of the ether led to a crude oil which was then purified.

Tables III and IV present a summary of the pertinent synthetic and spectral data on compounds prepared by the method mentioned above.

Labeling Experiments. 3,3-Dideuteriobicyclo[2.2.2]octan-2-one. Bicyclo[2.2.2]octan-2-one[31,32] (2.0 g), 6 ml of dioxane, 3 ml of 99.77% D$_2$O, and a catalytic amount of NaOH were refluxed for 45 hr. The reaction product was diluted with water and then extracted with pentane. The pentane extract was evaporated and the residue was sublimed (150° (3 mm)).

3,3′-Dideuteriobicyclo[3.2.1]octan-2-one. Commercially available ketone (1.5 g) was treated with 10 ml of 99.77% D$_2$O and 1 ml of trifluoroacetic anhydride. The sample was heated at 60° for 12 hr and then poured into aqueous NaHCO$_3$. Extraction with pentane followed by sublimation of the crude product obtained by evaporation of the pentane yielded 1.3 g of deuterated material.

7,7′-Dideuteriobicyclo[3.2.1]octan-6-one. This material was deuterated using a procedure similar to that of Farnum and Mehta[3] for the preparation of 3,3′-dideuterionorbornan-2-one. Bicyclo[3.2.1]octan-6-one (3.0 g), 20 ml of 99.77% D$_2$O, and 2 ml of trifluoroacetic anhydride were heated for 60 hr at 100°. The product was neutralized with Na$_2$CO$_3$ and then taken up in pentane solution. The pentane solution was washed with two 10-ml portions of D$_2$O. It was then dried with MgSO$_4$ and the pentane was evaporated on a rotary evaporator. The crude product was sublimed (80°/water aspirator pressure) yielding 2.1 g of labeled material.

Recovery Experiments. In a typical experiment the nmr sample itself was quenched. This was done by quickly pouring the sample into a quenching solution which was maintained at the desired temperature. The quenching solution was agitated vigorously with a vibro-mixer. The quenched material was then extracted with a suitable solvent. Table V summarizes the extractable products which were identified in a series of experiments.

Elimination Experiments. In a typical experiment 250 mg of 2-*p*-fluorophenylbicyclo[3.2.1]octan-2-ol was treated with 250 mg of anhydrous pyridine and 500 mg of *p*-toluenesulfonyl chloride.[14] This mixture was heated in a sealed tube for 10 hr at 110°. The crude reaction mixture was poured into NaHCO$_3$ solution. Extraction of the bicarbonate solution with pentane, drying with MgSO$_4$, and removal of the solvent with a rotary evaporator yielded a crude oil. This material was pumped at 0.3 mm of pressure in order to remove the last traces of pyridine. Nmr analysis of the product indicated a mixture of 80% of the desired 2-*p*-fluorophenylbicyclo[3.2.1]oct-2-ene and 2% of 2-*p*-fluorophenylbicyclo[2.2.2]octan-2-one. The desired olefin could be obtained essentially pure by preparative gas chromatography on 1,2,3-tris(cyanoethoxy)propane at 135°: nmr (CFCl$_3$) τ 2.65 (m, 2 H), 3.05 (m, 2 H), 4.35 (m, 1 H), 6.9–9.0 (m, 10 H).

Table VI gives the nmr spectra for a representative olefin from each bicyclooctyl system studied.

Table VI. Nmr Data (τ Values) for Representative Olefins Prepared by Dehydration[a]

System	Olefin	Chemical shifts
2-[2.2.2]	**2b**	CCl$_4$, 2.85 (m, 4 H), 3.55 (dd, J = 7, 2 Hz, 1 H), 6.97 (br s, 1 H), 7.35 (br d, J = 7 Hz, 1 H), 8.50 (AB q, 8 H)
2-[3.2.1]	**10b**	CFCl$_3$, 2.85 (m, 4 H), 4.35 (m, 1 H), 7.0–9.0 (m, 10 H)
6-[3.2.1]	**17a**	CCl$_4$, 2.45 (s, 4 H), 3.65 (d, J = 6 Hz, 1 H), 7.0 (br s, 1 H), 7.30 (br s, 1 H), 7.5–8.1 (m, 2 H), 8.3–8.7 (m, 6 H)

[a] TMS was used as internal standard.

Acknowledgments. We are grateful to Dr. David Patton who prepared several of the compounds used in this study.