as an internal standard. Hydrogen chloride gas was bubbled through the solution in an NMR tube. The compound rearranged quantitatively to IId: ^{1}H NMR (220 MHz, $CDCl_3$) δ 6.51 ($H_{2,3}$, t, J = 2.0 Hz, 1.91 H), 5.80 (H_6, t, J = 2.6 Hz, 0.99 H), 4.76 (H_5, s, 0.93 H), 3.10 ($H_{1,4}$, q, J = 2.1 Hz, 2.03 H), 2.10 (6-OAc, s), 2.03 (5-OAc, s, 6.14 H); IR (neat film) 3012 (w), 1730 (s), 1428 (w), 1358 (m), 1292 (w), 1235 (s), 1180 (w), 1121 (m), 1068 (m), 1030 (w), 783 (m) cm^{-1}; mass spectrum (chemical ionization), *m/e* (relative intensity) no parent ion at 196, major fragments at 138 (9), 137 (100), 118 (4), 113 (8), 109 (6), 96 (4), 95 (44), 93 (9), 90 (5), 89 (24), 79 (5), 73 (7), 67 (13), 66 (20), 61 (12).

4,6-Dibromobicyclo[3.1.0]hexene (IIIa). A crude sample of IIa (8 g, 3.14 mmol/g, 25.1 mmol) was warmed on a steam bath for 20 min. Distillation [bp 45 °C (0.5 mm)] yielded 6.20 g (103%) of IIIa which displayed 60-MHz ^{1}H NMR resonances (CCl_4) at δ 6.09, 5.74 ($H_{2,3}$, 5.6 Hz doublets, 1.96 H), 4.89 (H_4, m, 0.89 H), 2.67 ($H_{1,5}$, m, 2.10 H), 2.23 (H_6, 2.0 Hz t, 1.05 H). An analytical sample was prepared by two reduced pressure distillations. Anal. Calcd for $C_6H_6Br_2$: C, 30.28; H, 2.54; Br, 67.17. Found: C, 30.42; H, 2.65; Br, 67.55.

The structure of IIIa was proved by reduction, in 2 steps, to bicyclo[3.1.0]hexene. IIIa (2.4 g, 10 mmol) dissolved in 5 mL of dry ether was added to a stirred mixture of $LiAlH_4$ (750 mg, 20 mmol) in 50 mL of ether in a nitrogen atmosphere. The mixture was stirred at room temperature for 6 h; excess $LiAlH_4$ was then destroyed by addition of H_2O and 15% NaOH. The ethereal solution was filtered and concentrated under reduced pressure. Bulb-to-bulb distillation [bp 50 °C (10 mm)] yielded 1.15 g (72%) of 6-*anti*-bromobicyclo[3.1.0]hexene; ^{1}H NMR (CCl_4) δ 5.88, 5.58 ($H_{2,3}$, 2 d), 2.56 (H_3, m), 2.20 ($H_{1,4}$, m), 2.05 (H_6, m).

6-*anti*-Bromobicyclo[3.1.0]hexene (500 mg, 3.12 mmol) was added to a stirred mixture of Na metal (ca. 230 mg, 10 mmol) in *t*-BuOH (520 mg, 7 mmol) and 5 mL of dry THF at ambient temperature under nitrogen. The mixture was refluxed for 6 h and then cooled to room temperature. The supernatant was decanted from unreacted Na, diluted with 60 mL of isopentane, washed with 150 mL of H_2O, dried over $MgSO_4$, and filtered. The isopentane was removed by spinning-band distillation (Nester/Faust, Annular Teflon spinning-band column) at atmospheric pressure. The pot residue was distilled at room temperature (15 mm) into a liquid N_2 cooled receiver. The distillate was further concentrated by micro spinning-band distillation to 1.6 g. The NMR spectrum of the residue indicated the presence of 11 mol % bicyclo[3.1.0]hexene (by integration of the olefinic and δ -0.25 resonances against THF resonances). A 68% yield was obtained (NMR spectrum identical with authentic material, a sample of which was prepared as described by Wittig).[7]

Rearrangement of IIa-d_2 to IIIa-d_2. An NMR sample of IIa-d_2 in CCl_4 was warmed on a steam bath for 10 min. A 60-MHz ^{1}H NMR was observed as follows: δ 6.09, 5.74 ($H_{2,3}$, 2 d, 1.61 H), 4.89 (H_4, m, 0.84 H), 2.67 ($H_{1,5}$, br s, $W_{1/2}$ = 2.5 Hz, 1.55 H), 2.23 (H_6, m, 0.12 H).

4,6-Dichlorobicyclo[3.1.0]hexene (IIIb). IIIb was prepared in the same fashion as dibromide IIIa, bp 50 °C (3 mm); ^{1}H NMR (60 MHz, CCl_4) δ 6.20, 5.71 ($H_{2,3}$, 2 d, J = 5.0 Hz, 1.01 H, 1.04 H), 4.93 (H_4, m, 0.96 H), 2.45 ($H_{1,5,6}$, m, 2.99 H).

4-Cyano-6-chlorobicyclo[3.1.0]hexene (IIIc). The products from several kinetic runs were combined and chromatographed on silica gel with petroleum ether. The solvent was removed under reduced pressure and the residue was bulb-to-bulb distilled at 50 °C (0.3 mm); ^{1}H NMR (220 MHz, CCl_4) δ 6.11, 5.48 ($H_{2,3}$, 2 d, J = 5.5 Hz, 0.99 H, 0.99 H), 3.54 (H_4, m, 0.94 H), 2.43 (H_6, m, 1.12 H), 2.28 ($H_{1,5}$, m, 1.97 H).

Kinetic Measurements. The rate of conversion of IIa–d into IIIa–d at several temperatures was determined as follows. A ^{1}H NMR tube containing a weighed sample of II, nitrobenzene as internal standard, and 350 μL of solvent was kept in an ice bath until a run was started. Temperature was controlled with a YSI Thermistep Model 63 temperature controller (Yellow Springs Instrument Co., Yellow Springs, OH) to within ±0.1 °C. The sample was withdrawn at intervals and cooled in a dry ice–acetone bath, and the ratio of the integrals of all the resonances of II, III, and nitrobenzene was determined. Duplicate or triplicate runs were made at each temperature and the reaction was followed for at least 3 half-lives. Linear regression analysis of the Arrhenius plots obtained [times vs. ln (mg of II)] gave slopes and half-lives with uncertainties at the 95% confidence level.

Acknowledgment. We are grateful to Dr. Nancy Acton for helpful discussions, the George Mason University Foundation for its financial assistance, and the National Science Foundation (NSF-GP-30669X).

Degenerate Cyclopropylcarbinyl Cation Rearrangement in 2-Bicyclo[*n*.1.0]alkyl Cations[1]

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Received September 18, 1979

The ionization of bicyclo[*n*.1.0]alkan-2-ols in superacids (SbF_5, FSO_3H, FSO_3H–SbF_5) to the corresponding carbocations has been investigated by ^{13}C NMR spectroscopy over the temperature range of 0 to −140 °C. The bicyclic system, $n = 4$, gave a degenerate pair of equilibrating cyclopropylcarbinyl cations, whose interconversion can be frozen out [$\Delta G^{\ddagger}(-85\ ^{\circ}C) = 8.50 \pm 0.5$ kcal/mol]. This interconversion probably occurs through an unpopulated bicyclo[3.1.1]heptyl cation (cyclobutyl cation). On the other hand, the bicyclo[5.1.0]octyl system gave a mixture of static 2-bicyclo[5.1.0]octyl cation **27** and equilibrating 1-bicyclo[3.3.0]octyl cations **28** at −139 °C. Above −130 °C, ion **27** irreversibly rearranged to ion **28**. The $n = 3$ and 6 bicyclic systems gave rearranged ions, namely, the 3-cyclohexenyl and 1-cyclopropyl-1-cyclohexyl cations, respectively. The effect of C_1 and C_2 substitution on the cyclopropylcarbinyl cation rearrangement process in the 2-bicyclo[4.1.0]heptyl system has been explored. The ionization of the bicyclo[3.2.0]heptan-6-ol (**9**) and its 6-methyl (**10**) and 6-phenyl (**11**) derivatives was also carried out. Each of **9** and **10** yielded a degenerate equilibrating pair of cyclopropylcarbinyl cations, which were also obtained upon the ionization of the parent bicyclo[4.1.0]heptan-2-ol and its 1-methyl analogue. Alcohol **11**, however, yielded only a static tertiary carbocation.

The ease of interconversion of cyclopropylcarbinyl, cyclobutyl, and homoallyl derivatives in solvolytic studies has been investigated in considerable detail.[2] We have previously studied the nature of cyclopropylcarbinyl cation

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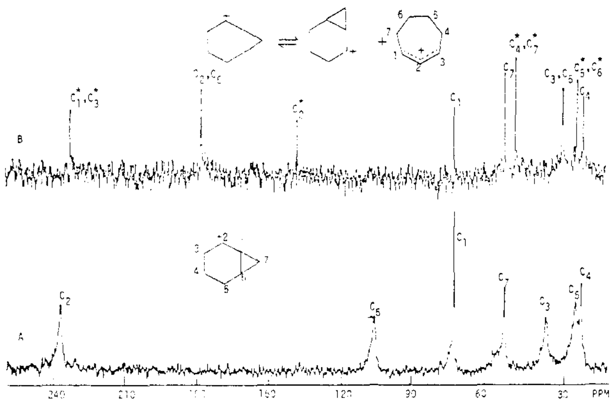

Figure 1. A: proton noise decoupled ^{13}C NMR spectrum of static 2-bicyclo[4.1.0]heptyl cation at -110 °C in SbF_5/SO_2ClF solution. B: proton noise decoupled ^{13}C NMR spectra of equilibrating 2-bicyclo[4.1.0]heptyl cation and 3-cycloheptenyl cation (*) in SbF_5/SO_2ClF solution at -52 °C.

rearrangements in several mono-, tri-, tetra-, and pentacyclic systems by dynamic NMR spectroscopy under stable-ion conditions.[3-7] In continuation of our work, we now wish to report a ^{13}C NMR study of degenerate cyclopropylcarbinyl cation equilibria of carbocations obtained by the ionization of bicyclo[*n*.1.0]alkan-2-ols **1**–**8** and bicyclo[3.2.0]heptan-6-ols **9**–**11**, respectively, under superacidic conditions. These alcohols and their esters (acetates, benzoates, tosylates, etc.) have been extensively studied under solvolytic conditions, and the corresponding cyclopropylcarbinyl cations were postulated as the involved intermediates.[8-17] No direct observation, however, of these ions or their respective rearrangements has hitherto been

Table I. ^{13}C NMR Chemical Shifts[a] of Observed Carbocations in SbF_5, FSO_3H, and SbF_5-FSO_3H in SO_2ClF Solutions

carbocation	T, °C[b]	atom							
		C_1	C_2	C_3	C_4	C_5	C_6	C_7	others
14, equilibrating	-50	76.60	179.8	32.30	23.50	32.30	179.80	55.60	
14, static	-110	76.50 (J_{CH} = 189.8 Hz)	238.90 (J_{CH} = 162.6 Hz)	38.10	23.50	25.80	109.60 (J_{CH} = 171.7 Hz)	55.40	
17	-80	80.10 (J_{CH} = 176.7 Hz)	271.80	42.60	23.30	21.20	65.50 (J_{CH} = 186.7 Hz)	53.50	37.10 (CH_3)
20	-90	89.00	178.30	32.10	25.80	32.10	178.30	59.00	23.90 (CH_3)
27, static	-139	69.50	215.30		br		74.1	60.20	
32	-80	287.50	51.00[c]	35.30	25.90	35.30	40.10[c]		54.50 (C_α), 52.30 (C_β)
26	-80	31.60	24.10	28.20	45.40	87.50	251.30	48.10	158.50 (C_p), 142.90 (C_o), 141.10 (C_i), 133.90 (C_m)

[a] Shifts are in ppm from external capillary tetramethylsilane. [b] Temperature at which chemical shifts are reported. [c] Assignment interchangeable.

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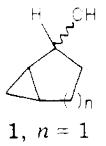
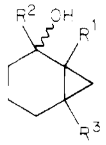
made. The results of the study of the stable carbocations obtained via ionization of alcohols **1**–**10** in superacidic media are compared with the results of the solvolytic studies on these alcohols.

Results and Discussion

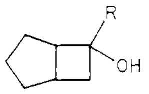
cis-Bicyclo[*n*.1.0]alkan-2-ols **1**–**8** and bicyclo[3.2.0]heptan-6-ols **9**–**11** utilized in this work were synthesized by published procedures.[18,19] These alcohols were ionized in superacidic solutions of SbF$_5$, FSO$_3$H, and SbF$_5$–FSO$_3$H in SO$_2$ClF at −140 °C, and the ^{13}C NMR spectra of the resulting solutions were recorded over the temperature range of 0 to −140 °C. The ^{13}C NMR chemical shifts of the observed carbocations are listed in Table I. In order to be able to assign the chemical shifts, we determined the off-resonance and proton-coupled spectra of the ions. Chemical shift assignments were also made by comparison with those of closely related ions. The proton-decoupled ^{13}C NMR spectra of the static and equilibrating 2-bicyclo[4.1.0]heptyl cations are shown in Figure 1 as an illustration.



1, $n = 1$
2, $n = 2$
3, $n = 3$
4, $n = 4$

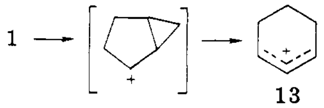


5, R^1 = H; R^2 = CH$_3$; R^3 = H
6, R^1 = CH$_3$; R^2 = H; R^3 = H
7, R^1 = Ph; R^2 = H; R^3 = H
8, R^1 = R^2 = H; R^3 = CH$_3$



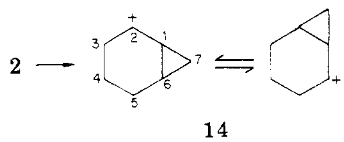
9, R = H
10, R = CH$_3$
11, R = Ph

Bicyclo[3.1.0]hexan-2-ol (1). Upon ionization in SbF$_5$/SO$_2$ClF solution at −140 °C, **1** gave the 3-cyclohexenyl cation **13** as the sole product as evidenced by its ^{13}C NMR spectrum.[20] The instantaneous rearrangement of the initially formed cyclopropylcarbinyl cation **12** to ion **13** could not be prevented. This was also the case when various other superacids were employed. This result is in agreement with the perchloric acid catalyzed acetolysis of **1**[8,11] and is also consistent with the product mixtures obtained from the hydrolysis of esters of **1** (benzoates[8] and tosylates[11]) as well as the solvolysis of 2-bicyclo[3.1.0]hexyl-*N*-methyl-4-oxopyridinium iodides[21] and 2-bicyclo[3.1.0]hexyl chloride.[22] In these solvolytic studies, the actual ratios of products vary, depending on the nature of the leaving group and the solvent used. However, in all cases, the products arise either from the trapping of the initially formed cyclopropylcarbinyl cation **12** or from reaction of solvent with the rearranged allylic ion **13**.



12 **13**

Bicyclo[4.1.0]heptan-2-ol (2) and Derivatives. The proton-decoupled ^{13}C NMR spectra of the solution obtained upon ionization of **2** in SbF$_5$/SO$_2$ClF at −100 and −52 °C are shown in Figure 1. At −110 °C, the ^{13}C NMR spectrum consists of seven signals at δ 238.9, 109.6, 76.5, 55.4, 38.1, 25.8, and 23.5. On the basis of the chemical shift and respective multiplicity data, the ion is readily assigned to the 2-bicyclo[4.1.0]heptyl cation **14**, a secondary cyclopropylcarbinyl cation. It is interesting to note that ion **14** is a secondary cyclohexyl cation with substantial charge delocalization into the cyclopropyl ring. When the temperature of the solution of ion **14** was slowly allowed to rise, the ^{13}C NMR signals at δ 238.9, 109.6, 38.1, and 25.8 broadened and eventually merged into the base line, while the signals at δ 76.5, 55.4, and 23.5 remained relatively sharp. At −52 °C, an average shift for the peaks at δ 238.9, 109.6, and 38.1, 25.8 was observed. At this temperature, additional absorption, due to the 3-cycloheptenyl cation **16**, had started to appear. The above observations are consistent with a degenerate cyclopropylcarbinyl cation equilibrium for ion **14** above −85 °C. This equilibration process most probably occurs through an unpopulated puckered cyclobutyl cation such as **15**.[12,13] The coalescence temperature for the merging of the signals at δ 38.1 and 25.8 was found to be −85 °C. The ^{13}C NMR chemical shift assignments for the static and equilibrating ions are shown in Table I. On the basis of the coalescence of the C$_3$ and C$_5$ carbons, the free energy of activation is estimated[23] to be $\Delta G^{\ddagger} = 8.5 \pm 0.5$ kcal/mol at −85 °C. Similar behavior of other cyclopropylcarbinyl cations has been previously observed.[3,6,7]



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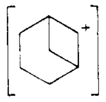

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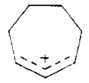

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Friedrich and Cooper,[12,13] on the basis of the results of perchloric acid catalyzed acetolysis studies, suggested that the degenerate cyclopropylcarbinyl cation rearrangement in **14** most probably involves cation **15** or related delocalized species as intermediates or transition states. The degenerate equilibrium in **14** in the fast-exchange limit (−85 °C) should lead to the averaging of the C$_2$, C$_6$ and C$_3$, C$_5$ carbons. However, at −52 °C, the signal arising from the rapidly exchanging C$_2$ and C$_6$ carbons occurs at δ 179.8, deviating by about 3.6 ppm from the expected average of C$_2$ and C$_6$ in the slow-exchange region (−110 °C). A deviation of 0.4 ppm is observed for the C$_3$ and C$_5$ carbons. These deviations are most probably temperature induced. However, the presence of a low concentration (a few percent) of a higher energy species such as **15** at the studied, relatively elevated temperatures (such as −52 °C) cannot be completely ruled out, although this is considered unlikely. Above −50 °C, the equilibrating ion **14** smoothly rearranges to the allylic ion **16**.[20]

In order to investigate the effect of substituent on the degenerate cyclopropylcarbinyl cation rearrangements, we also investigated the ionization of some methyl- and phenyl-substituted bicyclo[4.1.0]heptan-2-ols **5**–**8**.

The ionization of alcohol **5** at −140 °C in SbF$_5$/SO$_2$ClF solution yielded the expected tertiary ion **17**, whose ^{13}C NMR data are listed in Table I. Ion **17** is a regular tertiary cyclopropylcarbinyl cation[3] with significant charge delocalization into the cyclopropyl ring. It remains essentially unchanged up to 0 °C. Thus, no indication for any cyclopropylcarbinyl rearrangement was obtained between the

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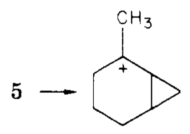
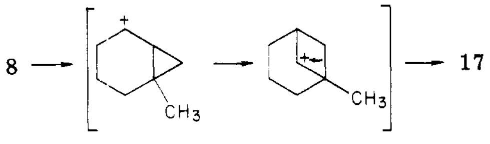


17

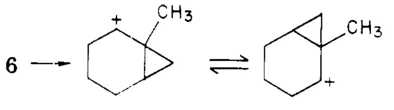
studied temperature limits, in contrast to the parent ion **14**. This difference can be attributed to enhanced stabilization of the positive charge by the methyl group[24] in ion **17** as compared to ion **14**.

The ionization of the isomeric alcohol **8** in SbF_5/SO_2ClF at -140 °C also gave the tertiary ion **17**. Rearrangement of the unstable secondary ion **18** readily takes place through the puckered cyclobutyl cation **19** to yield the stable tertiary ion **17**.



18 19

The corresponding 1-methyl-substituted alcohol **6** in SbF_5/SO_2ClF solution at -140 °C gave a ^{13}C NMR spectrum with five resonances at δ 178.3, 89.0, 59.0, 32.1, and 25.8. No significant line broadening or change in relative chemical shifts was obseved between -80 and -140 °C. This demonstrates the presence of a degenerate cyclopropylcarbinyl cation equilibrium for **20**, which is similar to the one observed in the case of the parent ion **14** (above -85 °C). The above equilibrium could not be frozen even at -140 °C.[25] Thus, the free energy of activation for such a process must be lower than 6.0 kcal/mol. The degenerate equilibrium is expected to occur through a puckered cyclobutyl cation, **21**, similar to that postulated for the equilibrium in **14**. Ion **21**, however, does not contribute to the NMR parameters in the studied temperature range. Moreover the methyl substitution at the C_1 position seems to substantially lower the barrier of the degenerate equilibration process. Similar results have been obtained in solvolytic studies, where the degree of degenerate cyclopropylcarbinyl rearrangement increases "to the theoretical maximum expected" upon the introduction of a methyl group at the C_1 position of ion **14**.[13] Ion **20**, above -80 °C, rearranges to the corresponding 3-methyl-3-cycloheptenyl cation **22**.



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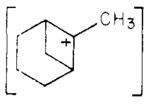

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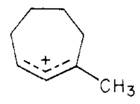

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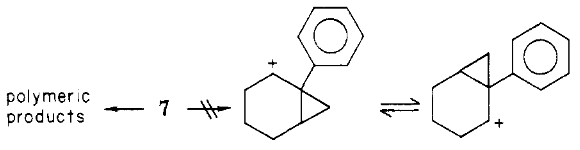
These results seem to indicate that degenerate cyclopropylcarbinyl rearrangements in **14** (and similar ions) are favored by substitution at the C_1 carbon; on the other hand, stabilization of charge by positions other than C_1 seems to decrease or altogether eliminate such rearrangements.

Since a phenyl substitutent is known to stabilize charge better than a methyl group, it was expected that the puckered cyclobutyl cation **24** should be more stabilized than **21**. When 1-phenylbicyclo[4.1.0]heptan-2-ol (**7**) was ionized in FSO_3H/SO_2ClF at -140 °C, however, only polymeric products were obtained. Attempted ionization of **7** in various other superacids was also unsuccessful.



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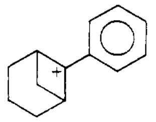
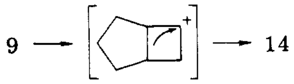


24

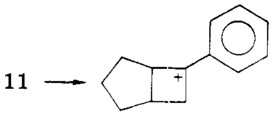
Bicyclo[3.2.0]heptan-6-ol (9) and Derivatives. Wiberg and co-workers[19] have carried out extensive solvolytic studies on 6-bicyclo[3.1.1]- and 6-bicyclo[3.2.0]heptyl derivatives. These systems behaved in an analogous manner to 5-bicyclo[4.1.0]heptyl derivatives, indicating a common intermediate or transient state under solvolytic conditions. To directly prove this suggestion, we have carried out the ionization of the corresponding 6-bicyclo[3.2.0]heptanol (**9**) and its derivatives **10** and **11**.

Bicyclo[3.2.0]heptan-6-ol (**9**), upon ionization in SbF_5/SO_2ClF solution at -140 °C, gave the same ion as that obtained upon ionization of alcohol **2**. This demonstrates that the initially formed 6-bicyclo[3.2.0]heptyl cation **25** rearranges instantaneously to a 2-bicyclo[4.1.0]heptyl cation, most probably through a Wagner–Meerwein shift.



25

The corresponding 6-methyl derivative, **10**, upon ionization in SbF_5/SO_2ClF at -140 °C, yields, as the sole product, the equilibrating 1-methylbicyclo[4.1.0]hept-2-yl cation **20**. These results are in good agreement with the solvolytic studies.[19] On the other hand, ionization of 6-phenylbicyclo[3.2.0]heptan-6-ol (**11**) in FSO_3H/SO_2ClF at -140 °C gave the static unrearranged parent ion **26**.



26

Apparently, phenyl substitution stabilizes the charge at the C_6 position of the bicyclo[3.2.0]heptyl skeleton. Under solvolytic conditions, however, products due to rearranged 1-phenylbicyclo[4.1.0]hept-2-yl cations were also observed. As mentioned earlier, it was not possible to prepare the parent 1-phenylbicyclo[4.1.0]hept-2-yl cation under similar stable-ion conditions. These results can be rationalized by the greater internal electron demand on the cationic center under nonnucleophilic stable-ion conditions.

Bicyclo[5.1.0]octyl System. The proton-decoupled ^{13}C NMR spectrum of a solution of alcohol **3** in SbF_5/SO_2ClF at -139 °C exhibited sharp lines at δ 218.6, 215.3, 74.1, 69.5, and 60.1 followed by broad peaks in the high-field region. When the solution was warmed to -100 °C, the spectrum became rather simple with sharp signals at δ 218.6, 40.3, and 31.5. Cooling the solution back to -140 °C, however, did not regenerate the original spectrum. The multiplicity

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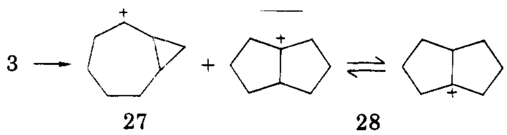
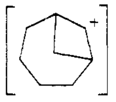
[24] G. A. Olah and D. J. Donovan, *J. Am. Chem. Soc.*, **99**, 5026–39 (1977).

[25] We were unable to freeze the rapid equilibration process even on a 200-MHz instrument at -140 °C.



27 28



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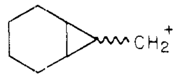

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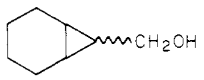


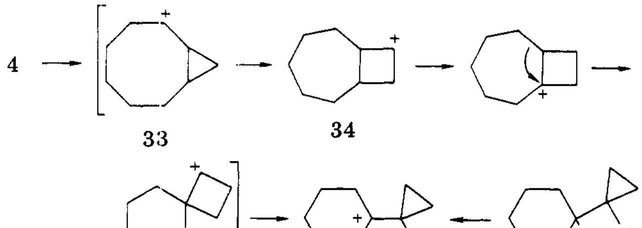
31

data obtained by an off-resonance experiment at −139 °C indicate the formation of a mixture of static 2-bicyclo[5.1.0]octyl cation **27** and equilibrating 1-bicyclo[3.3.0]octyl cation **28**.[26] The secondary cyclopropyl carbinyl cation **27** irreversibly rearranges to the thermodynamically more stable ion **28** upon warming to −100 °C.

No evidence for any process involving degenerate cyclopropylcarbinyl cation equilibrium was obtained in the present case. However, a degenerate equilibrium process has been observed for **3** under solvolytic conditions by Friedrich and Jassawalla,[13] who suggested that ion **29** is likely to be involved as either a transition state or an intermediate.

An attempt was also made to generate the ion **30** from the alcohol precursor **31** (mixture of syn and anti) in SbF_5/SO_2ClF solution at −140 °C. The ^{13}C NMR spectrum of the solution, however, showed the presence of only equilibrating 1-bicyclo[3.3.0]octyl cation **28**. Hence, both ions **27** and **30** readily rearrange to the equilibrating ion **28** under stable-ion conditions.

Bicyclo[6.1.0]nonyl System. The ionization of bicyclo[6.1.0]nonan-2-ol (**4**) in either FSO_3H/SbF_5 or SbF_5/SO_2ClF at −140 °C gave the same ion, whose proton-decoupled ^{13}C NMR spectrum showed peaks at δ 287.5 (s), 54.5 (d), 52.3 (t), 51.0 (t), 40.1 (t), 35.3 (t), and 25.9 (t). The chemical shift and the multiplicity data seem to indicate the formation of a tertiary ion. The substantial shielding of the carbocation center as compared to that in other tertiary ions seems to indicate the presence of a charge-delocalizing group as the α substituent. On the basis of these considerations, the assignment can be made to the 1-cyclopropyl-1-cyclohexyl cation **32**. The formation of ion **32** can be rationalized through the intermediacy of 2-bicyclo[6.1.0]- and 8-bicyclo[5.2.0]nonyl cations **33** and **34**, respectively, followed by hydride and Wagner–Meerwein shifts.



33 34 32 35

Solvolyses of various stereoisomeric bicyclo[6.1.0]nonyl derivatives have been shown to involve ions such as **34** as well as some ring-opened[28] intermediates. However, under nonnucleophilic stable-ion conditions, the cyclopropylcarbinyl cation rearranges to the thermodynamically more stable tertiary ion **32**. The structure of ion **32** was independently confirmed by ionizing the corresponding 1-cyclopropyl-1-cyclohexanol (**35**) in SbF_5/SO_2ClF at −78 °C.

Ion **32** is a typical cyclopropylcarbinyl cation with the cyclopropyl ring bisecting the electron-deficient sp^2 center. Because of this bisection, the C_1 and C_6 carbons of the cyclohexyl ring experience significant anisotropy, and hence, they exhibit chemical shifts differing by almost 10 ppm. A similar anisotropy effect has also been observed in the case of the 1-cyclopropyl-1-cyclopentyl cation by Sorensen and co-workers.[29]

Conclusion

Comparison of our stable-ion studies on 2-bicyclo[*n*.1.0]alkyl systems with solvolytic investigations suggests that carbocations in nonnucleophilic superacidic media provide reasonable models for the limiting intermediate ionlike transition states in solvolysis, provided one takes into account the greater internal electron demand of the carbocation center in the former. The cyclopropylcarbinyl cation equilibrium process is more favored in the bicyclo[4.1.0]heptyl system than in the bicyclo[3.1.0]hexyl, -[5.1.0]octyl, and -[6.1.0]nonyl systems under stable-ion conditions. The obtained results thus provide evidence for the nature of involved ions in the solvolysis of 2-bicyclo[*n*.1.0]alkyl derivatives[8-17] with the exception of the bicyclo[5.1.0]octyl system. The barriers for the degenerate cyclopropylcarbinyl cation equilibration processes seem to depend on the ring size and also upon the nature of the substituents at the C_1 or C_2 carbons in the bicyclic system.

Experimental Section

Precursor alcohols **1–11** and **31** were synthesized by previously published procedures.[18,19] Alcohol **35** was prepared by the addition of cyclopropylmagnesium bromide to cyclohexanone in tetrahydrofuran solution.

Preparation of Ions. A solution of the appropriate freshly distilled superacid (FSO_3H, SbF_5, or SbF_5–FSO_3H) was prepared in about a twofold amount of SO_2ClF cooled at dry ice–acetone temperature (ca. −78 °C) or at petroleum ether/liquid nitrogen slush temperature (ca. −140 °C). To this solution was slowly added with vigorous stirring a cooled slurry or solution of the appropriate alcohol precursor in SO_2ClF, resulting in an approximately 10–15% solution of the ion. Preparation of the ions can be directly carried out in 10-mm NMR tubes.

^{13}C NMR spectra were recorded by using either a Varian Model FT-80 NMR spectrometer equipped with a variable-temperature broad-band probe or a Bruker 200-MHz supercond instrument. An external capillary of Me_4Si was used as the reference.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

Registry No. **2**, 6376-96-1; **3**, 72657-57-9; **4**, 38433-06-6; **5**, 71205-70-4; **6**, 72610-45-8; **8**, 72610-46-9; **9**, 42577-33-3; **10**, 72657-58-0; **11**, 72657-59-1; **14**, 72610-47-0; **17**, 72610-48-1; **20**, 72610-49-2; **26**, 72610-50-5; **27**, 72610-51-6; **32**, 72610-52-7.

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(27) A. C. Cope, S. Moon and C. J. Park, *J. Am. Chem. Soc.*, **84**, 4850–5 (1962).

(28) K. B. Wiberg and T. Nakahira, *J. Am. Chem. Soc.*, **93**, 5193–8 (1971).

(29) T. Sorensen and R. P. Kirchen, *J. Am. Chem. Soc.*, **99**, 6687–93 (1977).