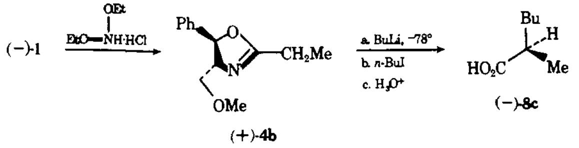
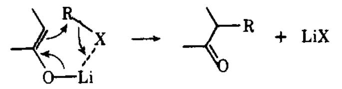
(4) Absolute configuration of the (1*R*,2*R*)-(−)-**1** was chemically related to (1*R*,2*R*)-(−)-nor-ψ-ephedrine: M. C. Rebstock, H. M. Crooks, J. Controulis, and R. R. Bartz, *J. Am. Chem. Soc.*, **71**, 2458 (1949); G. Fodor, J. Kiss, and I. Sallay, *J. Chem. Soc.*, 1858 (1951). Confirmation of the absolute configuration of (−)-**1** was reported by J. Dunitz, *J. Am. Chem. Soc.*, **74**, 995 (1952), in an x-ray determination.
(5) A. I. Meyers, D. L. Temple, R. L. Nolen, and E. D. Mihelich, *J. Org. Chem.*, **39**, 2778 (1974).
(6) (a) G. E. Coates, M. L. H. Green, and K. Wade, Ed., "Organometallic Chemistry", Vol. I, Methuen, London, 1967, pp 34–35. (b) H. O. House, "Modern Synthetic Reactions", 2nd ed, W. A. Benjamin, Inc., Menlo Park, Calif., pp 529, 589.
(7) H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969).
(8) K. Kitatani, T. Hiyama, and H. Nozaki, *J. Am. Chem. Soc.*, **97**, 949 (1975).
(9) S. Kanao, *J. Pharm. Soc. Jpn.*, **48**, 947 (1928); W. N. Nagai and S. Kanao, *Justus Liebigs Ann. Chem.*, **470**, 157 (1929). (+)-Norephedrine was obtained by resolution in 13–17% yield, $[\alpha]^{22}_{589}$ +14.15° (*c* 9.82, EtOH), 95.9%, optical purity.
(10) (a) W. S. Johnson and E. N. Schubert, *J. Am. Chem. Soc.*, **72**, 2187 (1950); (b) W. Leithe, *Ber.*, **65**, 660 (1932); K. Freudenberg, E. Schoeffel, and E. Braun, *J. Am. Chem. Soc.*, **54**, 234 (1932).
(11) When (1*R*,2*R*)-(−)-1-phenyl-2-amino-1,3-propanediol [(−)-**1**] was employed in the preparation of the enantiomeric oxazoline (+)-**4b**, it gave, after metalation with *n*-butyllithium, alkylation with *n*-butyl iodide, and hydrolysis, the enantiomeric (*R*)-(−)-2-methylhexanoic acid [(−)-**8c**] in 46% optical purity ($[\alpha]^{22}_{589}$ −8.5° (neat)). This is quite comparable to the synthesis of (+)-**8c** from (−)-**4b** (see Table IV).



(12) A. I. Meyers, E. M. Smith, and M. S. Ao, *J. Org. Chem.*, **38**, 2129 (1973); J. E. Dubois and C. Lion, *C. R. Acad. Sci.*, **274**, 203 (1972).
(13) Many examples in the literature have described great differences in the stereochemistry of alkylations of enolates using various metal cations. The fact that lithium enolates are usually more stereoselective than sodium, potassium, or magnesium is not readily understood (House, ref 6b, pp 586–589), and the reason could well lie in the strong complexation of the lithium ions with the approaching alkyl halide such that lithum halide is freed simultaneously with the carbon–carbon bond formation:



This factor may be at least as important as the steric hindrance to approach.
(14) E. L. Eliel, A. A. Hartmann, and A. G. Abatjoglou, *J. Am. Chem. Soc.*, **96**, 1807 (1974).
(15) All melting points are uncorrected. Microanalyses performed by Midwest Microlabs, Inc., Indianapolis, Ind.
(16) A. W. Dox, "Organic Synthesis", Collect. Vol. I, Wiley, New York, N.Y., 1942, p 5.
(17) E. H. Amonoo-Neizer, R. A. Shaw, D. O. Skovlin, and B. C. Smith, *J. Chem. Soc.*, 2997 (1965).
(18) M. C. Rebstock, G. W. Moersch, A. C. Moore, and J. M. Vanderbelt, *J. Am. Chem. Soc.*, **73**, 3666 (1951).
(19) The use of LDA and other alkylating conditions did not improve the optical yield of **8c**.
(20) M. Miyano, G. D. Searle & Co., Skokie, Ill., personal communication.
(21) Shorter hydrolysis time (3 *N* HCl, 1 hr) gave (+)-**8c** in 36% optical yield, but the chemical yield was only 42%. Thus, racemization of the intermediate amino ester is enhanced with longer hydrolysis times (cf. ref 3).
(22) Hydrolysis was also performed in a stepwise acid–base–acid manner[3] with no significant increase in optical purity.
(23) Some recently published studies wherein the underside attack of the electrophile are consistent with the observed steric course of the reaction are: A. I. Meyers and E. D. Mihelich, *J. Org. Chem.*, **40**, 1186 (1975); A. I. Meyers and K. Kamata, *ibid.*, **39**, 1603 (1974); A. I. Meyers, E. D. Mihelich, and K. Kamata, *Chem. Commun.*, 768 (1974).

Stable Carbocations. 184.[1a] 2,4-Dehydro-5-homoadamantyl Cations

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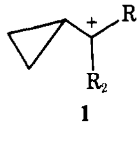
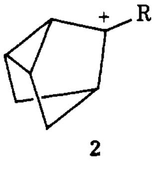
Abstract: The parent secondary 2,4-dehydro-5-homoadamantyl cation (**4**) has been prepared under stable ion conditions from both 5-*endo*-hydroxy-2,4-dehydrohomoadamantane and 2-*endo*-hydroxyhomoadamant-4-ene. Examination of cation **4** by ^{1}H and ^{13}C NMR spectroscopy shows that, although **4** is static at −120°C, upon warming to −60°C it undergoes a degenerate cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement. The static tertiary 5-methyl-2,4-dehydro-5-homoadamantyl and 5-phenyl-2,4-dehydro-5-homoadamantyl cations (**7** and **10**) have been prepared under stable ion conditions at low temperature from both the corresponding tertiary alcohols and, unexpectedly, from 2-*endo*-hydroxy-2-*exo*-methylhomoadamant-4-ene and 2-*endo*-hydroxy-2-*exo*-phenylhomoadamant-4-ene, respectively. Ions **7** and **10** have been characterized by ^{1}H and ^{13}C NMR spectroscopy. Ions **4**, **7**, and **10** are all classical carbenium ions with varying degrees of charge delocalization into the cyclopropane ring. Mechanisms are proposed to account for the degenerate rearrangement of ion **4** and for the formation of 2,4-dehydro-5-homoadamantyl cations from 2-homoadamant-4-enyl precursors.

The rapid interconversion of cyclopropylcarbinyl, cyclobutyl, and homoallyl derivatives in solvolytic systems has attracted considerable attention.[2] We have previously reported the direct observation of a series of cyclopropylcarbinyl cations **1** under stable ion conditions.[3] This work has been extended to the study of cyclopropylcarbinyl cations with rigid carbon skeletons, such as the 3-nortricyclyl cations **2**.[4] More recently, we have shown that both secondary and tertiary 8,9-dehydro-2-adamantyl cations **3** are of a carbenium ion nature with charge delocalization into the cyclopropane ring.[5] We now report the continuation of our studies with secondary and tertiary 2,4-dehydro-5-homoadamantyl cations which are homologous with **3**.



1



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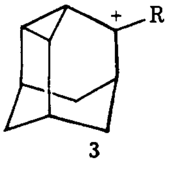


3

Results and Discussion

The parent 2,4-dehydro-5-homoadamantyl cation (**4**) was prepared from alcohol **5**[6] in FSO_3H-SO_2ClF (SO_2) so-

Table I. Proton and Carbon-13 NMR Parameters of 2,4-Dehydro-5-homoadamantyl Cations[a]

Ion	T, °C	1	2	3	4	5	6	7	8	9		10	11	CH_3
										Exo	Endo			
4	$\delta\,^{1}$H −110		6.94	5.68	4.96	10.64	3.70	2.60	~2.60	1.80	~2.60	2.60	2.10^{b}	
	$\delta\,^{1}$H −60	3.40	8.78	5.68	4.96	8.78	3.40	2.60	3.0–1.8					
	$\delta\,^{13}$C −110	29.33 (d, 132.8)	127.83 (d, 184.3)	86.51 (d, 173.6)	82.94 (d, 188.2)	239.25 (d, 174.6)	42.32 (d, 148.9)	27.89 (t, 128.9)	24.08 (d, 134.8)	23.39 (t, 133.0)		30.68 (t, 129.4)	61.07 (t, 131.8)	
	$\delta\,^{13}$C −45	35.43	(183.6)	88.36	83.49	(183.6)	35.43	26.53	24.48	26.53		31.33	61.08	
7	$\delta\,^{1}$H −60		5.60 (m)	5.30 (m)	4.20 (d-d)^{c}		3.58 (m)	2.60	2.38	1.58	~2.30	2.58	2.02^{b}	3.18 (s)
	$\delta\,^{13}$C −60	25.6 (d, 133.8)	95.3 (d, 174.0)	85.4 (d, 172.7)	71.4 (d, 187.4)	267.2 (s)	48.2 (d, 143.4)	29.7 (t, 129.9)	24.4 (d, 137.9)	23.0 (t, 132.4)		31.1 (t, 128.7)	51.8 (t, 135.8)	37.3 (q, 129.3)
10^{d}	$\delta\,^{1}$H −60	2.70	4.70	4.70	4.70		4.22	2.42	2.42	1.50	~2.40	2.42	1.94^{b}	
	$\delta\,^{13}$C −60	25.02 (d, 136.5)	80.17 (d, 172.1)	73.35 (d, 169.4)	59.90 (d, 178.0)	244.44 (s)	42.50 (d, 137.8)	30.08 (t, 133.9)	24.73 (d, 136.5)	25.50 (t, 133.8)		30.99 (t, 132.9)	45.30 (t, 133.9)	

[a] Proton and carbon-13 chemical shifts are in parts per million from external Me_4Si (capillary). Multiplicities and coupling constants (J_{CH} in Hz) are in parentheses. Multiplicities: d = doublet, m = multiplet, q = quartet, s = singlet, t = triplet. [b] AB quartet, J = 14 Hz. [c] d-d = doublet of doublets; $J_{2,4}$ = 4.0 Hz and $J_{3,4}$ = 8.0 Hz. [d] $\delta\,^{1}$H: ortho, 8.14; meta, 7.82; para, 7.98. $\delta\,^{13}$C: ortho, 132.35 (d-t, 163.9, 6.0); meta, 130.77 (d-d, 167.4, 7.0); para, 142.50 (d-t, 172.0, 7.0); ipso, 140.0 (s).

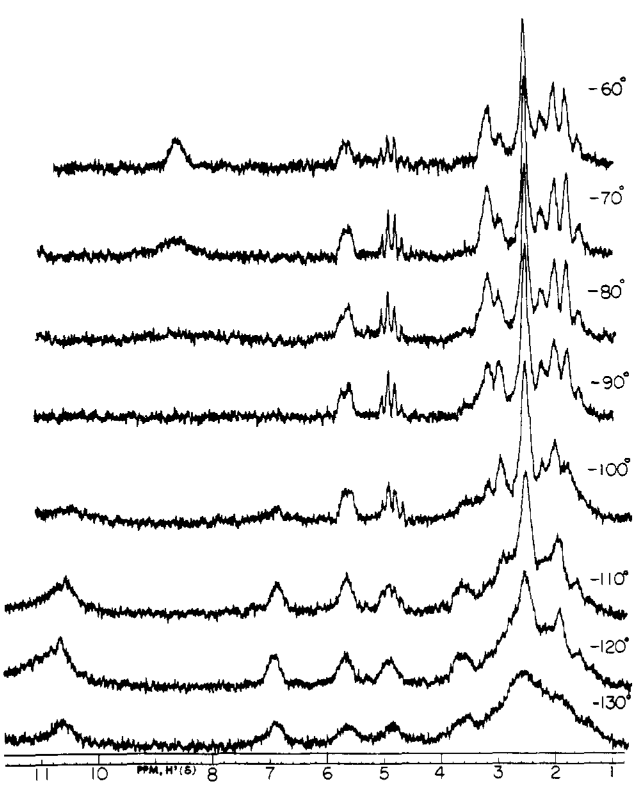
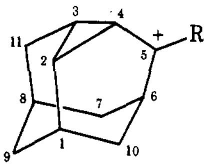
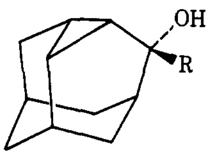


Figure 1. The temperature-dependent 60-MHz ^{1}H NMR spectra of the 2,4-dehydro-5-homoadamantyl cation in FSO_3H-SO_2ClF (SO_2) solution.

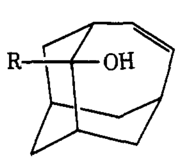
lution at −120°C. The same cation also was obtained when alcohol 6[6] was subjected to identical conditions. At temper-



4, R = H
7, R = CH_3
10, R = C_6H_5

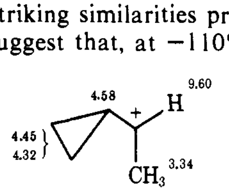


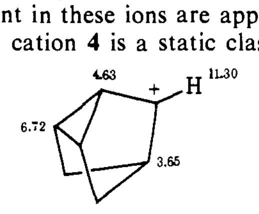
5, R = H
8, R = CH_3
11, R = C_6H_5

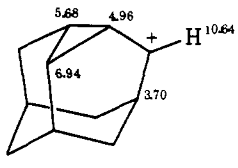


6, R = H
9, R = CH_3
12, R = C_6H_5

atures below −120°C, the ^{1}H NMR spectrum of ion 4 (Figure 1) shows deshielded broad one-proton signals at δ 10.64, 6.94, 5.68, 4.96, and 3.70 and a group of unresolved peaks from δ 3.0–1.5 (ten protons). Our assignments of the ^{1}H NMR parameters of 4 at −110°C are summarized in Table I, and the ^{1}H NMR chemical shifts of selected protons in cation 4 are compared with the corresponding protons in the methylcyclopropylcarbinyl cation (1, R_1 = H, R_2 = CH_3) and the parent 3-nortricyclyl cation (2, R = H). The striking similarities present in these ions are apparent and suggest that, at −110°C, cation 4 is a static classical







ion with the usual charge delocalization into the cyclopropane ring.

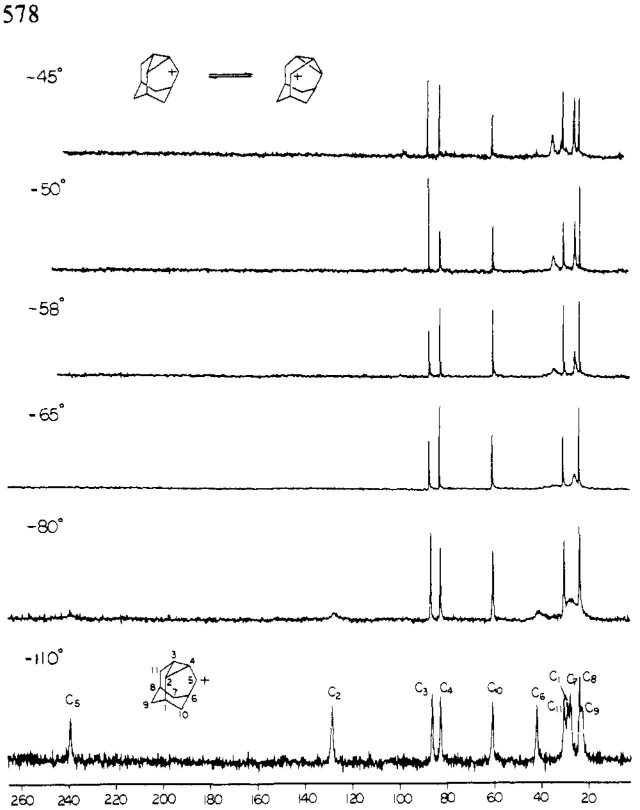


Figure 2. The temperature-dependent proton-decoupled ^{13}C NMR spectra of the 2,4-dehydro-5-homoadamantyl cation in FSO_3H-SO_2ClF (SO_2) solution.

The low-field one-proton signal centered at δ 10.64 is assigned to H_5 on the basis of comparison with the ^1H NMR spectrum of 5-deuterated 2,4-dehydro-5-homoadamantyl cation prepared from the corresponding alcohol.[6] The ^1H NMR spectrum of 5-deuterated ion in FSO_3H-SO_2ClF at $-110°$ is essentially identical with that of **4** except the absence of the low-field one-proton signal at δ 10.64. In addition, the one-proton resonance at δ 4.96 becomes a broad triplet, instead of a quartet as in ion **4**. The assignment for the two one-proton resonances centered at δ 6.94 and 5.68 was made on the basis of the ^1H NMR spectrum of 2-deuterated 2,4-dehydro-5-homoadamantyl cation similarily prepared from the corresponding alcohol.[6] The ^1H NMR spectrum of 2-deuterated ion in FSO_3H-SO_2ClF solution at $-110°$ shows the absence of one-proton resonance at δ 6.94, while resonances at δ 5.68 and 4.96 now become a broad doublet and triplet, respectively. The four deshielded one-proton resonances at δ 10.64, 6.94, 5.68, and 4.96 are assigned to H_5, H_2, H_3, and H_4, respectively.

As is evident in Figure 1, the ^1H NMR spectra of the ion generated from **5** or **6** show reversible temperature-dependent behavior between -120 and $-60°C$. No further changes in the ^1H NMR spectrum of this ion were observed above $-60°C$.[7] The temperature dependent ^1H NMR spectra of cation **4** show that, as the temperature is raised to $-60°C$: (a) the signals at δ 10.64 and 6.94 that are present in ion **4** at $-110°C$ become equilibrated to produce a two-proton signal at δ 8.78; (b) the signal at δ 3.70 in **4** at $-110°C$ becomes equilibrated with a one-proton signal which is buried under the broad ten-proton peak in **4** to give a two-proton multiplet centered at δ 3.40; and (c) the chemical shifts of the one-proton signals at δ 5.68 and 4.96 remain unchanged. Thus, as the temperature is raised, ion **4** undergoes an equilibration process which gives a more symmetrical ion at $-60°C$.

In principle, the 2,4-dehydro-5-homoadamantyl cation might undergo degenerate (process I) or nondegenerate (process II) cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement.

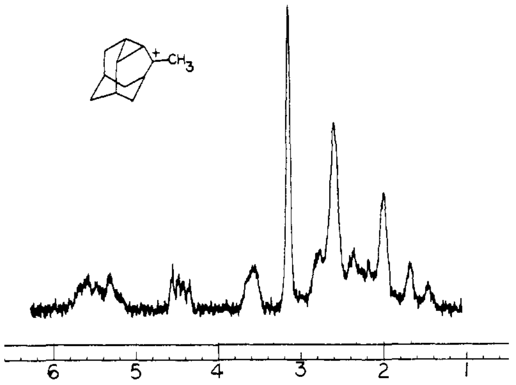
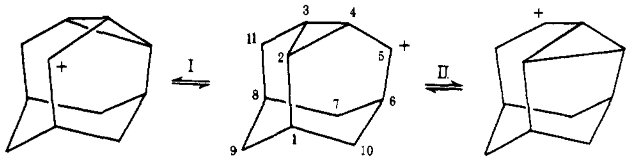
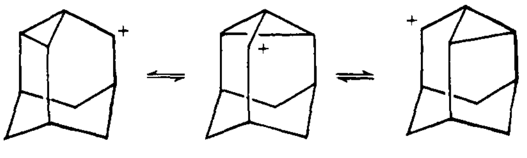


Figure 3. The 60-MHz ^1H NMR spectrum of the 5-methyl-2,4-dehydro-5-homoadamantyl cation in $FSOH_3-SO_2ClF$ (SO_2) solution at $-78°C$.



If process I becomes fast on the NMR time scale, then the hydrogens at C-2 and C-5 become enantiotopic, as do the pair of equatorial hydrogens at C-7 and C-9, the pair of axial hydrogens at C-7 and C-9, and the bridgehead hydrogens at C-1 and C-6. Of course, the hydrogens at C-2 and C-5 would be expected to be the most deshielded. By contrast, if process II becomes fast on the NMR time scale, no plane of symmetry develops. Consequently, we conclude that *the temperature-dependent behavior of ion **4** is consistent with process I, but not with process II.*[8] This conclusion is supported by the temperature-dependent Fourier transform ^{13}C NMR spectra of **4** (Figure 2) which are summarized in Table I. Thus, at $-110°C$ ^{13}C NMR resonances of the 11 different carbons in ion **4** are present, whereas at $-45°C$ the ^{13}C NMR resonances of only 7 different carbons are observed.[9] By process I, C-2 and C-5 become enantiotopic, as do the pair of bridgehead carbons C-1 and C-6 and the pair of methylene carbons C-7 and C-9. By process II, the chemical shifts of any pair of carbons can be identical only by accidental coincidence.

In contrast to these results, we have previously shown that, even at $-120°C$, the parent 8,9-dehydro-2-adamantyl cation (**3**, R = H) undergoes a facile threefold degenerate cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement.[5]



Examination of molecular models clearly shows that, in static ion **4**, the vacant p orbital at C-5 is much more favorably situated for overlap with the C-3 to C-4 bond in **4** than with the C-2 to C-4 bond. Consequently, it is proposed that the degenerate cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement in **4** proceeds by initial cleavage of the C-3 and C-4 bond and formation of either twisted cyclobutyl cation **13** or homoallylic cation **14**, followed by ring closure to give the enantiomer of ion **4** (Scheme I).

The assignment of structure **4** for the ion obtained from both **5** and **6** at $-110°C$ was further confirmed by the direct observation of the tertiary 5-methyl-2,4-dehydro-5-

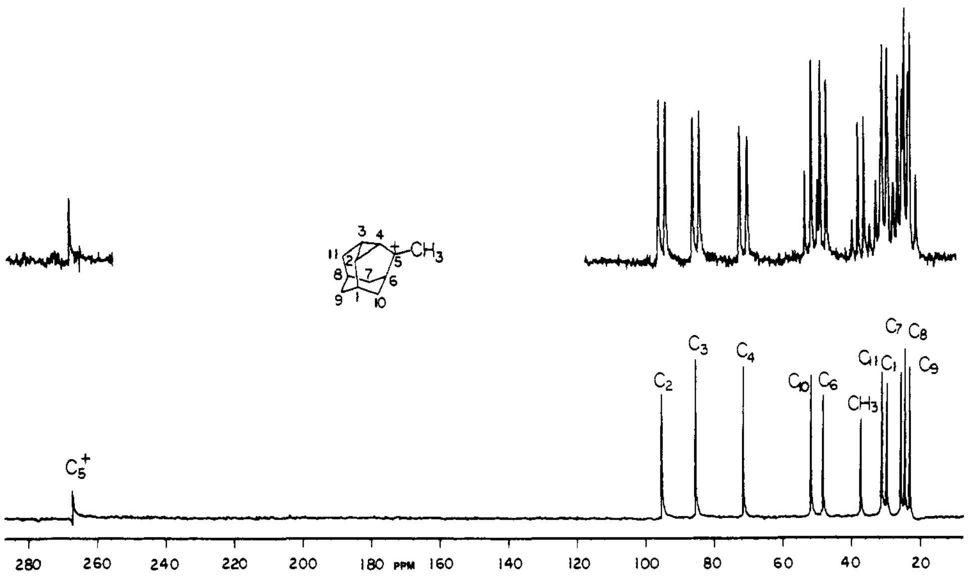
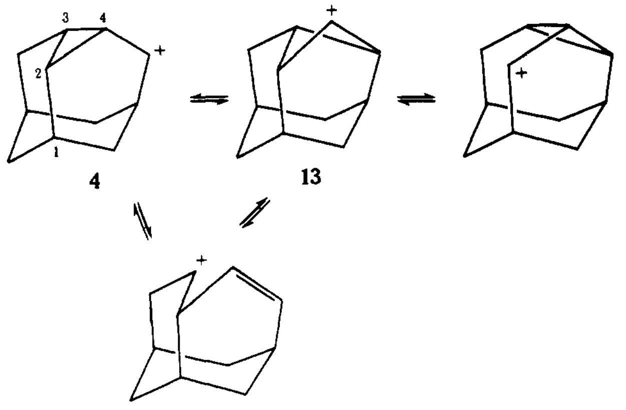


Figure 4. The ^{13}C NMR spectrum of the 5-methyl-2,4-dehydro-5-homoadamantyl cation in FSO_3H-SO_2ClF (SO_2) solution at −78°C: (top) proton coupled; (bottom) proton decoupled.

Scheme I



homoadamantyl cation **7**, which was prepared from alcohol **8**[10] in FSO_3H-SO_2ClF solution at −78°C. The relevant parameters of the ^{1}H (Figure 3) and ^{13}C (Figure 4) NMR spectra of **7** are summarized in Table I. It is apparent that tertiary ion **7** is a static ion with substantial delocalization of charge into the cyclopropane ring. The 2-methyl-8,9-dehydro-2-adamantyl cation (**3**, R = CH_3) has also been shown to be static.[5] Moreover, cation **7** can also be generated from alcohol **9**[10] in FSO_3H-SO_2ClF solution at −78°C. Thus, ions **4** and **7** can both be obtained by σ and π routes.

Even a phenyl substituent at C-2 fails to prevent the rapid isomerization of the 2-homoadamant-4-enyl cation to the 2,4-dehydro-5-homoadamantyl cation. Thus, ionization of phenyl alcohols **11**[10] and **12**[10] in FSO_3H-SO_2ClF (SO_2) at −120°C both give 5-phenyl-2,4-dehydro-5-homoadamantyl cation (**10**) as the only observable ion. The relevant parameters of the ^{1}H (Figure 5) and ^{13}C NMR spectra of **10** are summarized in Table I.

It is apparent that 2,4-dehydro-5-homoadamantyl cations **4**, **7**, and **10** are of classical carbenium ion nature, but that the degree of charge delocalization into the cyclopropane ring is dependent on the nature of the substituent at C-5. Thus, the difference in deshielding at C-2 and C-3 in the 2,4-dehydro-5-homoadamantyl cations is greatest in the parent ion **4** ($\Delta\delta_{^{13}C}$ 41.32 ppm, $\Delta\delta_{^1H}$ 1.26 ppm), less in the methyl-substituted ion **7** ($\Delta\delta_{^{13}C}$ 9.9 ppm, $\Delta\delta_{^1H}$ 0.3 ppm), and least in the phenyl-substituted ion **10** ($\Delta\delta_{^{13}C}$ 6.82 ppm, $\Delta\delta_{^1H}$ 0 ppm).

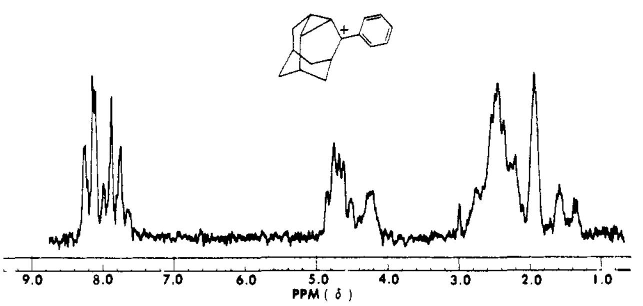
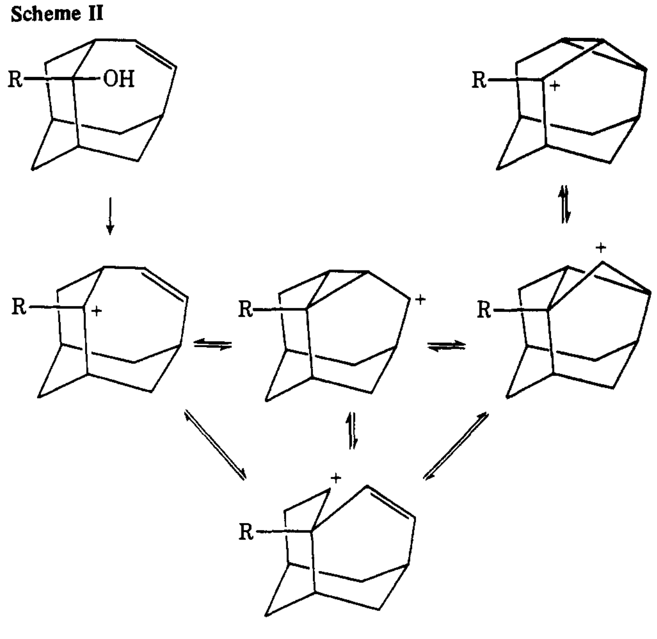


Figure 5. The 60-MHz ^{1}H NMR spectrum of the 5-phenyl-2,4-dehydro-5-homoadamantyl cation in FSO_3H-SO_2ClF (SO_2) solution at −60°C.

The formation of **7** from **9** and **10** from **12** suggests that 2,4-dehydro-5-homoadamantyl cations are not obtained from allylcarbinyl precursors (i.e., **6**, **9**, and **12**) by one-step mechanisms. In view of the arguments presented earlier, we propose that 2,4-dehydro-5-homoadamantyl cations arise from these precursors in the manner shown in Scheme II.

Scheme II



Experimental Section

For the synthesis of 5-*endo*-hydroxy-2,4-dehydrohomoadamantane (**5**) and 2-*endo*-hydroxyhomoadamant-4-ene (**6**), see ref 6.

5-*endo*-Hydroxy-5-*exo*-methyl-2,4-dehydrohomoadamantane (8). A solution of 15.9 mmol of methyllithium in 10 ml of ether was added at 0°C to a solution of 731 mg (4.51 mmol) of 2,4-dehydro-5-homoadamantanone[6] in 10 ml of anhydrous ether. Stirring was maintained for 1 hr at 0°C and for an additional hour at 25°C, at which point 40 ml of water was carefully added. The reaction mixture was saturated with sodium chloride and extracted with ether (3 × 40 ml), and the combined ether extracts were dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure provided a white solid which was sublimed (50°C (0.2 mm)) to give 726 mg (90% yield) of **8:** mp 75-95°C dec; ($CDCl_3$) δ_{Me_4Si} 2.4-0.8 (br m, containing a methyl singlet at δ 1.46); ν ($CHCl_3$) 3600, 3420 (br), 2900, 2835, 1460, 1380, 1135, 1125, 1055, 990, 930, and 890 cm^{-1}.

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.89; H, 10.03.

2-*endo*-Hydroxy-2-*exo*-methylhomoadamant-4-ene (9). Treatment of 311 mg (1.92 mmol) of homoadamant-4-en-2-one[6] with methyllithium by the procedure described above gave 283 mg (83% yield) of **9:** mp 179.5-185°C; δ_{Me_4Si} ($CDCl_3$) 6.37-5.53 (m, 2 H, CH=CH) and 2.9-1.1 (br m, 16 H, containing a methyl singlet at δ 1.33); ν ($CHCl_3$) 3590, 3450, 2910, 2855, 1375, 1295, 1140, 1060, and 1030 cm^{-1}.

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.86; H, 10.11.

5-*endo*-Hydroxy-5-*exo*-phenyl-2,4-dehydrohomoadamantane (11). A solution of 5.75 mmol of phenyllithium in 2.5 ml of 70:30 benzene:ether was added at 0°C to a solution of 400 mg (2.47 mmol) of 2,4-dehydro-5-homoadamantanone[6] in 10 ml of anhydrous ether. Stirring was maintained for 1 hr at 0°C and for an additional 8 hr at 25°C, at which point 30 ml of water was carefully added. The reaction mixture was saturated with sodium chloride and extracted with ether (3 × 40 ml), and the combined ether extracts were dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure provided a yellow oil which was sublimed (120°C (0.3 mm)) to give 544 mg of a white waxy solid which contained biphenyl. The sublimate was column chromatographed on silica gel with 25:75 benzene:heptane as eluent. Sublimation of the combined residues of the fractions containing **11** afforded 385 mg (65% yield) of **11:** mp 105-108°C; δ_{Me_4Si} (CCl_4) 7.7-7.0 (br m, 5 H, aromatic protons) and 2.5-0.6 (br m, 15 H); ν (CCl_4) 3625, 3475 (br), 3010, 2910, 2850, 1485, 1445, 1030, and 975 cm^{-1}.

Anal. Calcd for $C_{17}H_{20}O$: C, 84.96; H, 8.39. Found: C, 85.20; H, 8.52.

2-*endo*-Hydroxy-2-*exo*-phenylhomoadamant-4-ene (12). Treatment of 357 mg (2.20 mmol) of homoadamant-4-en-2-one[6] with phenyllithium by the procedure described above gave 320 mg (60% yield) of **12:** mp 72-73°C; δ_{Me_4Si} (CCl_4) 7.6-6.9 (br m, 5 H, aromatic protons), 6.37-5.63 (m, 2 H, CH=CH), and 3.2-0.8 (br m, 13 H); ν (CCl_4) 3570, 3025, 2920, 2855, 1450, 1380, 1315, 1300, 1155, 1050, and 1020 cm^{-1}.

Anal. Calcd for $C_{17}H_{20}O$: C, 84.96; H, 8.39. Found: C, 85.21; H, 8.39.

Preparation of Cations 4, 7, and 10. Slow addition with vigorous stirring of a solution of either alcohol **5** or **6** in SO_2ClF which was maintained at ca. −120°C (dry ice-ethanol bath temperature) to a freshly prepared FSO_3H-SO_2ClF solution at −120°C provided secondary ion **4**. For NMR studies, the resulting solution was immediately transferred to a precooled NMR tube. Tertiary ion **7** was similarly prepared at ca. −78°C (dry ice-acetone bath temperature) from either alcohol **8** or **9**. The ^1H NMR spectra of ion **7** generated at −78 or −120°C are identical. Tertiary ion **10** was also similarly obtained at ca. −78 or −120°C from either alcohol **11** or **12.**

^1H and ^{13}C nuclear magnetic resonance spectroscopic studies were carried out as previously described.[11]

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References and Notes

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(7) The ion slowly decomposed when maintained at −45°C.

(8) The cationic species present at −60°C cannot be the static 2,11-dehydro-4-homoadamantyl cation as the signals at δ 8.78 and 5.70 in this ion would integrate for one and two protons, respectively.

(9) The resonance for C-2 and C-5 (which is expected at ca. δ 183.5) slowly merges into the baseline, and is not observed.

(10) The stereochemistry of the substituents in **8**, **9**, **11**, and **12** follow from the stereospecific sodium borohydride reductions of 2,4-dehydro-5-homoadamantanone and homoadamant-4-en-2-one.[6]

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