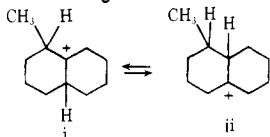


be seeing either a counterion effect (moving slowly from one side of the molecule to the other) or some more selective and large relaxation effect. However, we have studied the related 2-methyl-2-adamantyl cation **7** at temperatures down to  $-144\text{ }^\circ\text{C}$  and have noted no line broadening analogous to that observed for **10**. We therefore feel that we are seeing a genuine conformational change. This implies that  $\Delta H^\ddagger$  is small, and for this to occur,  $\Delta S^\ddagger$  must be reasonably negative. In considering the conformational process involved, i.e., symmetrical intermediate, this seems reasonable. The Arrhenius plot, although subject to large errors, is consistent with this.

- (24) The "averaged"  $\beta$  peak in **10b** is found at 48.9 ppm. A 10-ppm separation for the "frozen-out" peaks was used in the simulated spectra since this gives the higher field peak a value very close to that in **7**.
- (25) Peaks ( $^{13}\text{C}$ ) appear in the region characteristic of equilibrating cations.



- The most probable structures are based on the [4.4.0] skeleton, e.g., i and ii. From solvolysis results on the secondary [3.3.1] system, the [4.4.0] skeleton is readily formed: C. S. Foote and R. B. Woodward, *Tetrahedron*, **20**, 687 (1964). It is, in fact, strange that the [4.4.0] skeleton does not seem to be the first-formed rearrangement ion from **10**.
- (26) It should be possible to determine the effect of substituents on the chair-TB equilibrium in **3**, as long as these substituents are not attacked or protonated by the acid solvent, i.e., alkyl groups. However, the presence of the substituents will change the reference  $\beta$  carbon chemical shifts and require some analysis. It should also be possible to study cyclohexyl cations with other substituents on the cationic center, i.e., phenyl, halogen, OR, etc., but these will probably also require different reference chemical shifts.
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- (28) M. Godchot and P. Bedos, *C. R. Acad. Sci.*, **184**, 208 (1927).
- (29) H. C. Brown and M. Borkowski, *J. Am. Chem. Soc.*, **74**, 1894 (1952).
- (30) H. B. Williams and W. R. Edwards, *J. Am. Chem. Soc.*, **69**, 336 (1947).
- (31) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **97**, 2892 (1975).
- (32) P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 182 (1961).
- (33) We thank Mr. Kim Wagstaff for the synthesis of this compound.
- (34) M. Saunders, private communication.

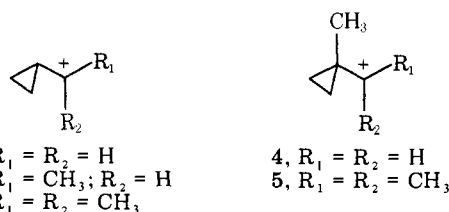
## On the Structure of Cyclopropylcarbinyl and Cyclobutyl Cations. 8,9-Dehydro-2-adamantyl and 2,5-Dehydro-4-protoadamantyl Cations<sup>1,2</sup>

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**Abstract:** The parent 8,9-dehydro-2-adamantyl cation (**12**) has been prepared under stable ion conditions from a variety of precursors. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **12** indicate that it is a carbenium ion that is undergoing a threefold degenerate cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement which is fast on the NMR time scale at  $-120\text{ }^\circ\text{C}$ . Warming **12** to  $-78\text{ }^\circ\text{C}$  leads irreversibly to the 2-tricyclo[4.4.0.0<sup>5,9</sup>]dec-3-enyl cation. A series of 2-substituted 8,9-dehydro-2-adamantyl cations has been prepared under stable ion conditions at  $-78\text{ }^\circ\text{C}$ . All of these ions have been shown by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy to be static carbocations with varying degrees of charge delocalization into the cyclopropane ring. In striking contrast, three precursors which potentially could have afforded the 1-methyl-8,9-dehydro-2-adamantyl cation were shown by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy to give the 4-methyl-2,5-dehydro-4-protoadamantyl cation (**32**) under stable ion conditions. Carbocation **32** also undergoes a threefold degenerate rearrangement which is fast on the NMR time scale at  $-120\text{ }^\circ\text{C}$ . By  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy it was determined that under stable ion conditions the 1,2-dimethyl-8,9-dehydro-2-adamantyl cation is a static carbenium ion from  $-95$  to  $-10\text{ }^\circ\text{C}$ . Mechanisms are proposed to account for the degenerate rearrangements of ions **12** and **32** and for the formation of the other observed ions.

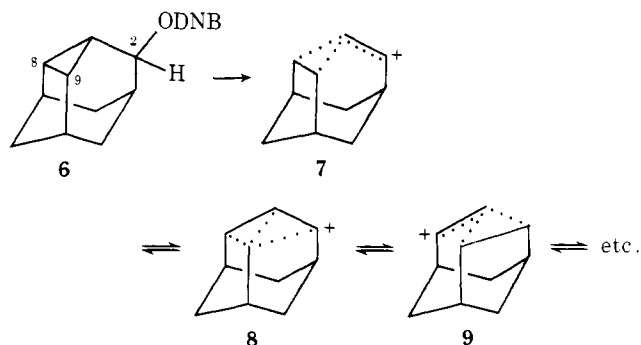
The rapid interconversion of cyclopropylcarbinyl, cyclobutyl, and homoallyl derivatives in solvolytic systems has attracted considerable attention.<sup>7</sup> Recently, we have studied by NMR spectroscopy a series of cyclopropylcarbinyl cations under stable ion conditions.<sup>2,8-12</sup> We have concluded from these observations that whereas the primary cyclopropylcarbinyl cation **1** involves degenerate equilibration of rapidly



equilibrating  $\sigma$ -delocalized nonclassical ions in which there is little or no contribution to the NMR parameters by the cyclobutyl cation, the corresponding secondary (**2**) and tertiary (**3**) ions are static classical carbocations with varying degrees of charge delocalization into the cyclopropane ring.<sup>8</sup> Intro-

duction of a methyl substituent at C-1 of the cyclopropyl moiety (ion **4**) does not substantially alter the nature of these ions<sup>12,13</sup>. In contrast, tertiary ion **5** is a static classical carbocation which adopts the bisected geometry characteristic of cyclopropylcarbinyl cations.<sup>12</sup> These studies have now been extended to cyclopropylcarbinyl cations with rigid carbon skeletons.<sup>9-11</sup>

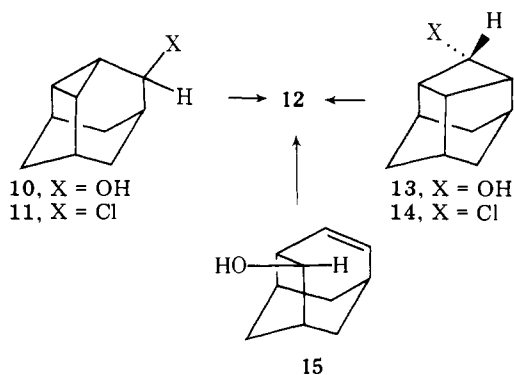
In 1967 Baldwin and Foglesong first reported on the "stability and symmetry" of the 8,9-dehydro-2-adamantyl cation.<sup>14</sup> They observed that solvolysis of 8,9-dehydro-2-adamantyl 3,5-dinitrobenzoate (**6**) occurs with the marked rate acceleration characteristic of cyclopropylcarbinyl systems<sup>7</sup> and that the original C-2, C-8, and C-9 skeletal positions of **6** achieve nearly complete equivalence during solvolysis.<sup>14</sup> In view of these results, Baldwin and Foglesong suggested the bridged nonclassical representation **7** for the charge-delocalized 8,9-dehydro-2-adamantyl cation and proposed that scrambling of the skeletal positions occurred via migration of the C-8 to C-9 bond to give **9**, etc. The ion linking degenerate cyclopropylcarbinyl cations **7** and **9** was represented as bicyclobutonium ion **8**.<sup>14</sup> We now wish to report the direct observation by NMR



spectroscopy of the 8,9-dehydro-2-adamantyl cation under stable ion conditions and the effect of the introduction of methyl substituents at C-1 and/or C-2 upon the structure of this cation.

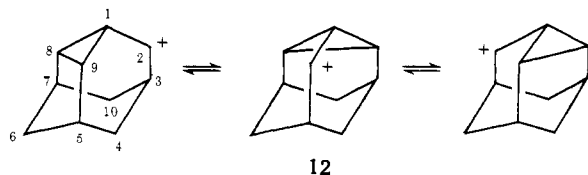
## Results and Discussion

**The 8,9-Dehydro-2-adamantyl Cation.** Addition of 2-hydroxy-8,9-dehydroadamantane<sup>15</sup> (**10**) or 2-chloro-8,9-dehydroadamantane<sup>17,18</sup> (**11**) to a solution of fluorosulfonic acid (FSO<sub>3</sub>H) in sulfonyl chloride fluoride (SO<sub>2</sub>ClF) at -120 °C gives the parent 8,9-dehydro-2-adamantyl cation (**12**). Cation **12** also can be cleanly generated from 4-*endo*-hydroxy-2,5-



dehydroprotoadamantane<sup>19</sup> (**13**) or 4-*endo*-chloro-2,5-dehydroprotoadamantane<sup>18</sup> (**14**) in SbF<sub>5</sub>-SO<sub>2</sub>ClF solution at -120 °C. In contrast, 2-*exo*-hydroxyprotoadamantane<sup>20</sup> (**15**) in SbF<sub>5</sub>-SO<sub>2</sub>ClF solution at -120 °C leads to extensive polymer formation and only a ca. 25% yield of ion **12**.

The <sup>1</sup>H NMR spectrum of ion **12** (Figure 1) consists of a deshielded doublet of doublets at δ 7.96 (three protons), a quartet at δ 4.92 (one proton), and two broad peaks at δ 3.20 and 2.60 (three and six protons, respectively). These data are consistent with ion **12** being the 8,9-dehydro-2-adamantyl



cation which is undergoing a facile threefold degenerate cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement which is fast on the NMR time scale even at -120 °C. Accordingly, the three-proton doublet of doublets at δ 7.96 is assigned to the homotopic protons at C-2, C-8, and C-9 which couple with both the apical proton at C-1 and the homotopic protons at C-3, C-5, and C-7. The proton at C-1 thus gives rise to the quartet at δ 4.92. In view of the relative intensities of the signals at δ 3.20 and 2.60, the former is assigned to the bridgehead protons at C-3, C-5, and C-7 and the latter to the methylene protons at C-4, C-6, and C-10. Consistent with the proposed structure of ion **12**, the proton noise decoupled natural abundance Fourier transform (FT) <sup>13</sup>C NMR spectrum of **12** (Figure 1) shows

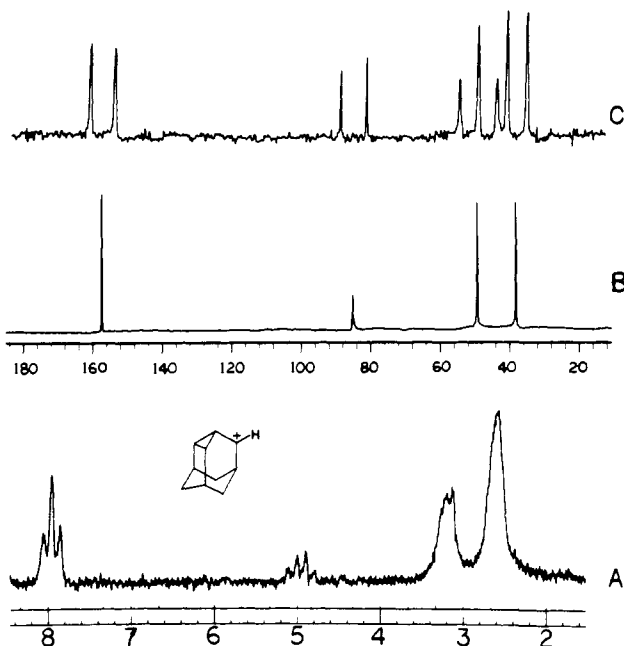
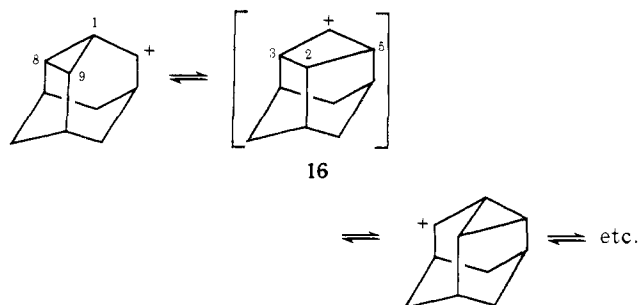


Figure 1. (A) <sup>1</sup>H NMR (60 MHz) spectrum of ion **12** in FSO<sub>3</sub>H-SO<sub>2</sub>ClF at -120 °C. (B) <sup>13</sup>C proton noise decoupled NMR spectrum of ion **12**. (C) <sup>13</sup>C proton-coupled NMR spectrum of ion **12**.

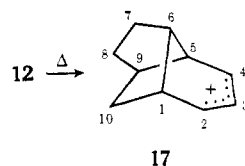
only four carbon resonances. The complete <sup>13</sup>C NMR parameters with resonance assignments for ion **12** are summarized in Table I.

An examination of molecular models of the 8,9-dehydro-2-adamantyl cation suggests that the C-8 to C-9 bond in this ion is situated in an unfavorable alignment for a direct Wagner-Meerwein type migration (as suggested by Baldwin and Foglesong<sup>14</sup>). Alternatively, the degenerate equilibration of the parent 8,9-dehydro-2-adamantyl cation may be accounted for by an initial shift of the C-1 to C-9 bond to give as an intermediate the 2,5-dehydro-4-protoadamantyl cation (**16**). Subsequent migration of the C-2 to C-3 bond in **16** would re-



generate **12**. This sequence is reminiscent of the adamantyl to protoadamantyl rearrangement<sup>21</sup> and is consistent with the observation that 2,5-dehydro-4-protoadamantyl derivatives **13** and **14** lead directly to the 8,9-dehydro-2-adamantyl cation.

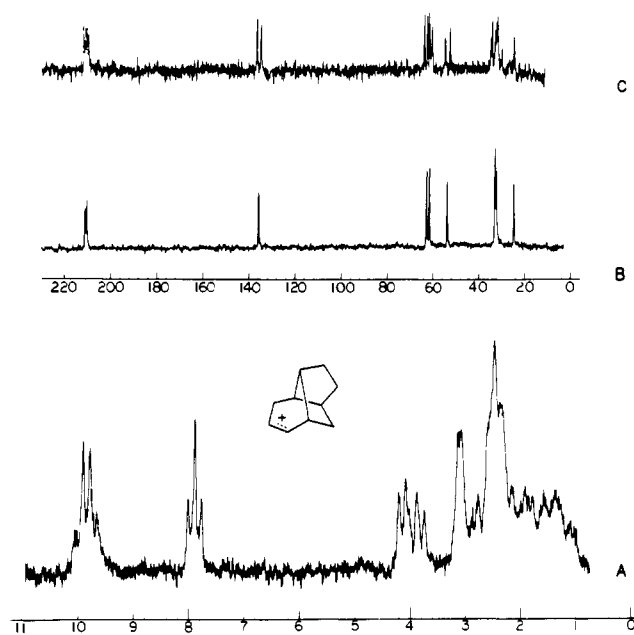
**Thermal Rearrangement of the 8,9-Dehydro-2-adamantyl Cation.** When a solution of cation **12** in FSO<sub>3</sub>H-SO<sub>2</sub>ClF is slowly warmed to -78 °C, a facile irreversible rearrangement occurs to give the 2-tricyclo[4.4.0.0<sup>5,9</sup>]dec-3-enyl cation (**17**).



**Table I.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Parameters of Observed Cations<sup>a</sup>

Ion	1	2	3	4	5	6	7	8	9	10	Other	
<b>12</b>	$\delta_{1\text{H}}$ 4.92	7.96	3.20	2.60	3.20	2.60	3.20	7.96	7.96	2.60		
	$\delta_{13\text{C}}$ 85.1	157.0	38.2	49.3	38.2	49.3	38.2	157.0	157.0	49.3		
	(d, 186.2)	(d, 177.7)	(d, 143.2)	(t, 134.2)	(d, 143.2)	(t, 134.2)	(d, 143.2)	(d, 177.7)	(d, 177.7)	(t, 134.2)		
<b>17</b>	$\delta_{1\text{H}}$ 4.14	9.82	7.86	9.82	3.83	1.90	2.42	2.42	1.20	3.08		
										Endo: 1.45		
	$\delta_{13\text{C}}^b$ 64.3	211.0	157.2	210.3	63.1	55.3	33.9	34.4	34.6	26.3		
	(63.1)	(210.3)		(211.0)	(64.3)		(34.4)	(33.9)				
<b>24</b>	$\delta_{1\text{H}}$ 4.25		3.43	2.58	2.94	2.60 <sup>c</sup>	2.94	5.69	5.69	2.58	CH <sub>3</sub> : 3.35	
	$\delta_{13\text{C}}$ 71.8	274.4	47.3	47.3	34.5	47.3	34.5	100.7	100.7	47.3	CH <sub>3</sub> : 33.5	
	(d, 186.9)	(s)	(d, 142.4)	(t, 134.3)	(d, 144.1)	(t, 134.3)	(d, 144.1)	(d, 181.5)	(d, 181.5)	(t, 134.3)	(q, 127.7)	
<b>25</b>	$\delta_{1\text{H}}$ 4.45		4.22	2.60	2.95	Exo: 2.60	2.95	5.20	5.20	2.60	C <sub>6</sub> H <sub>5</sub> : 7.8–8.6	
						Endo: 2.10						
<b>26</b>	$\delta_{1\text{H}}$ 3.72		2.42	2.42	2.42	Exo: 1.92	2.42	4.60	4.60	2.42	CH: 3.42; CH <sub>2</sub> : 2.75	
<b>32</b>	$\delta_{1\text{H}}$ 3.56	4.52	4.52		4.52	3.56	2.15	3.56	2.15	2.15	CH <sub>3</sub> : 2.62	
	$\delta_{13\text{C}}$ 50.5	83.3	83.3	187.0	83.3	50.5	42.1	50.5	42.1	42.1	CH <sub>3</sub> : 26.2	
	(d, 142.3)	(d, 174.5)	(d, 174.5)	(s)	(d, 174.5)	(d, 142.3)	(t, 134.2)	(d, 142.3)	(t, 134.2)	(t, 134.2)	(q, 131.5)	
<b>35</b>	$\delta_{1\text{H}}$		3.32	2.36	2.86	Exo: 2.90	2.86	5.40	5.40	2.36	CH <sub>3</sub> -C <sub>1</sub> : 1.70	
	$\delta_{13\text{C}}$ 82.0	266.3	47.5	47.1	36.2	Exo: 1.94	47.1	36.2	108.6	108.6	47.1	CH <sub>3</sub> -C <sub>2</sub> : 3.05
	(s)	(s)	(d, 138.0)	(t, 135.0)	(d, 143.0)	(t, 135.0)	(d, 143.0)	(d, 143.0)	(d, 184.5)	(d, 184.5)	(t, 135.0)	CH <sub>3</sub> -C <sub>1</sub> : 19.5 (q, 128.5)
												CH <sub>3</sub> -C <sub>2</sub> : 31.7 (q, 129.5)

<sup>a</sup> Proton and carbon-13 chemical shifts are in parts per million from external Me<sub>4</sub>Si (capillary). Multiplicities and coupling constants ( $J_{\text{CH}}$  in hertz) are in parentheses. Multiplicities: d = doublet, s = singlet, q = quartet, t = triplet. <sup>b</sup> Alternative assignments are indicated by the chemical shifts in parentheses. <sup>c</sup> AB quartet,  $J = 11.2$  Hz.

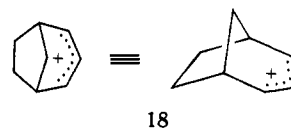


**Figure 2.** (A)  $^1\text{H}$  NMR (60 MHz) spectrum of ion **17** in  $\text{SbF}_5\text{-SO}_2\text{ClF}$  at  $-78^\circ\text{C}$ . (B)  $^{13}\text{C}$  proton noise decoupled NMR spectrum of ion **17**. (C)  $^{13}\text{C}$  proton-coupled NMR spectrum of ion **17**.

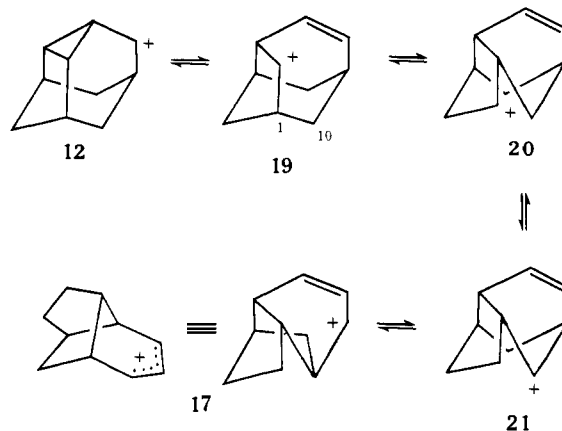
This ion is also cleanly obtained when **10**, **11**, **13**, or **14** is ionized in  $\text{SbF}_5\text{-SO}_2\text{ClF}$  solution at  $-78^\circ\text{C}$ . The complete  $^1\text{H}$  and  $^{13}\text{C}$  NMR parameters with resonance assignments for ion **17** are summarized in Table I and the spectra are presented in Figure 2.

The  $^1\text{H}$  NMR spectrum of **17** contains the characteristic resonances for a typical allylic cation with a broadened two-proton doublet of doublets centered at  $\delta$  9.82 and a one-proton apparent triplet at  $\delta$  7.86 ( $J = 7.6$  Hz).<sup>22</sup> More informative is the  $^{13}\text{C}$  NMR spectrum of **17**, which shows resonances for ten different carbons. In addition to the resonances for the allylic cation moiety, the proton-coupled FT  $^{13}\text{C}$  NMR spectrum of

**17** indicates that three secondary and four tertiary carbons are present. Of course, these data do not uniquely define the structure of ion **17**. The structure assignment for **17** follows from the observation that the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **17** are strikingly similar to the corresponding spectra of the 2-bicyclo[3.2.1]oct-3-enyl cation (**18**).<sup>11</sup>



The unexpected rearrangement of **12** to **17** can be rationalized as proceeding by the initial formation of the 2-protoadamantanyl cation (**19**) which undergoes migration of the C-1 to C-10  $\sigma$  bond in **19** to give the 2-isotwistanyl cation (**20**). Acid-catalyzed solvolysis reactions of 8,9-dehydro-2-adamantyl<sup>17</sup> and 2-exo-substituted protoadamantyl<sup>23</sup> derivatives which parallel **12**  $\rightarrow$  **19** and **19**  $\rightarrow$  **20**, respectively, have been reported. A subsequent 1,3-hydride shift in **20** would provide ion **21** which could give allylic cation **1** by a Wagner–Meerwein shift.



**2-Substituted 8,9-Dehydro-2-adamantyl Cations.** Addition of 2-hydroxy-2-methyl-8,9-dehydroadamantane<sup>16</sup> (**22**) or

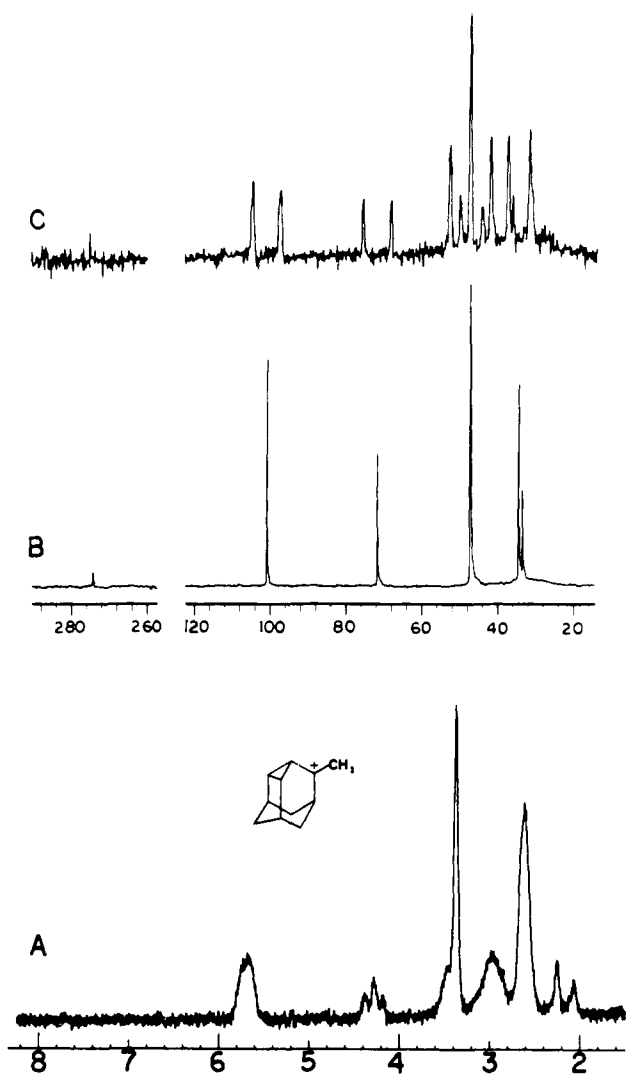
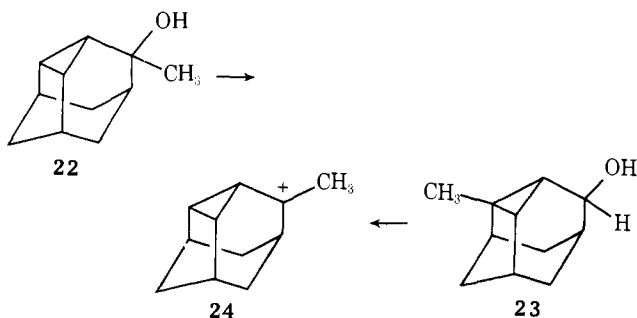


Figure 3. (A)  $^1\text{H}$  NMR (60 MHz) spectrum of ion **24** in  $\text{FSO}_3\text{H}-\text{SO}_2\text{ClF}$  at  $-78^\circ\text{C}$ . (B)  $^{13}\text{C}$  proton noise decoupled NMR spectrum of ion **24**. (C)  $^{13}\text{C}$  proton-coupled NMR spectrum of ion **24**.

2-hydroxy-8-methyl-8,9-dehydroadamantane (**23**) to a  $\text{FSO}_3\text{H}-\text{SO}_2\text{ClF}$  or  $\text{SbF}_5-\text{SO}_2\text{ClF}$  solution at  $-78^\circ\text{C}$  provides the 2-methyl-8,9-dehydro-2-adamantyl cation (**24**).



Although this ion is stable in  $\text{FSO}_3\text{H}-\text{SO}_2\text{ClF}$  solution up to  $10^\circ\text{C}$ , it does undergo rapid decomposition at room temperature.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (Figure 3) of the static tertiary carbenium ion **24** are substantially different from those of the parent 8,9-dehydro-2-adamantyl cation. In the  $^1\text{H}$  NMR spectrum of ion **24** the bridgehead proton at C-1 appears as a triplet ( $J = 5.8$  Hz) at  $\delta$  4.25, since it is coupled with the enantiotopic protons at C-8 and C-9. The latter occur as a broad multiplet at  $\delta$  5.89. The complete  $^{13}\text{C}$  NMR parameters

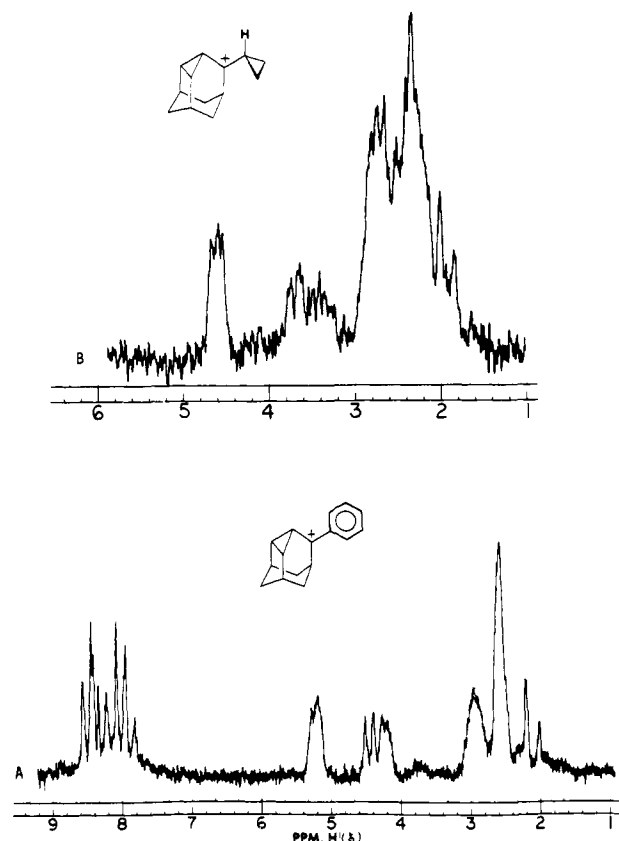
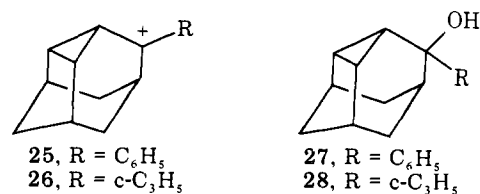


Figure 4. The  $^1\text{H}$  NMR (60 MHz) spectra of (A) ion **25** and (B) ion **26** in  $\text{FSO}_3\text{H}-\text{SO}_2\text{ClF}$  at  $-78^\circ\text{C}$ .

with resonance assignments for ion **24** are summarized in Table I. These data are indicative of the presence of a plane of symmetry in **24**.

The 2-phenyl-8,9-dehydro-2-adamantyl (**25**) and 2-cyclopropyl-8,9-dehydro-2-adamantyl (**26**) cations were also prepared from their corresponding tertiary alcohols **27** and **28**,



respectively, in  $\text{FSO}_3\text{H}-\text{SO}_2\text{ClF}$  solution at  $-78^\circ\text{C}$ . The  $^1\text{H}$  NMR spectra of ions **25** and **26** (Figure 4) indicate that these tertiary cations are also static carbenium ions in which some charge is being delocalized into the cyclopropane ring. The relative chemical shifts of the protons at C-8 and C-9 in ions **24-26** suggest that the extent of positive charge being delocalized into the dehydroadamantyl framework decreases in the order **24** > **25** > **26**.

It is apparent that substitution of a methyl, phenyl, or cyclopropyl group for the hydrogen at C-2 in ion **12** stops the rapid equilibration of the 8,9-dehydro-2-adamantyl cation.<sup>24</sup> Similar observations have been made for the 2,4-dehydro-5-homoadamantyl cation<sup>10</sup> and the 3-homonortricyclyl cation.<sup>11</sup> It is not surprising that these substituents significantly increase the energy barrier for the cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement, since in the presence of a substituent at C-2 or C-8 the rearrangement can no longer be degenerate.

**The 4-Methyl-2,5-dehydro-4-protoadamantyl Cation.** In order to further determine the influence of substituents on the behavior of the 8,9-dehydro-2-adamantyl cation, 2-hydroxy-

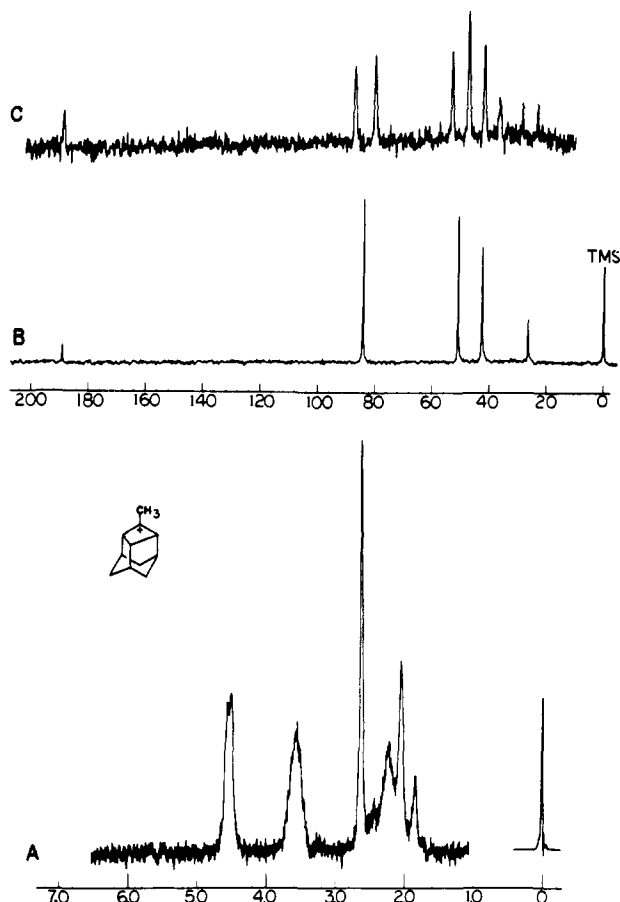
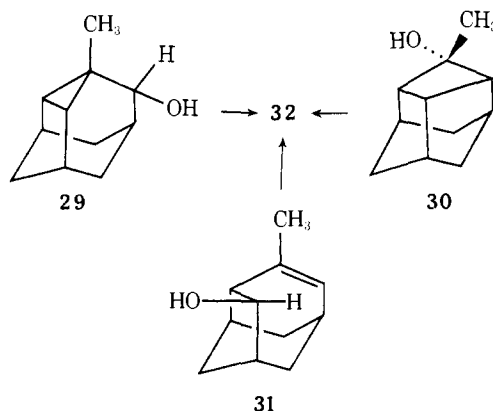


Figure 5. (A)  $^1\text{H}$  NMR (60 MHz) spectrum of ion **32** in  $\text{SbF}_5\text{-SO}_2\text{ClF}$  at  $-120^\circ\text{C}$ . (B)  $^{13}\text{C}$  proton noise decoupled NMR spectrum of ion **32**. (C)  $^{13}\text{C}$  proton-coupled NMR spectrum of ion **32**.

1-methyl-8,9-dehydroadamantane<sup>19</sup> (**29**), 4-*endo*-hydroxy-4-*exo*-methyl-2,5-dehydroprotoadamantane<sup>19</sup> (**30**), and 2-*exo*-hydroxy-4-methylprotoadamantane<sup>19</sup> (**31**) were ionized



under stable ion conditions. A common cation (**32**) is produced from each of these precursors in  $\text{SbF}_5\text{-SO}_2\text{ClF}$  solution even at  $-120^\circ\text{C}$ . Ion **32** is stable in  $\text{SbF}_5\text{-SO}_2\text{ClF}$  solution up to  $-45^\circ\text{C}$  and then undergoes slow decomposition.<sup>25</sup>

The  $^1\text{H}$  NMR spectrum of ion **32** (Figure 5) consists of two three-proton multiplets at  $\delta$  4.52 and 3.56, a sharp methyl singlet at  $\delta$  2.62, and a six-proton AB quartet ( $J = 12.8$  Hz) centered at  $\delta$  2.15. The proton-decoupled FT  $^{13}\text{C}$  NMR spectrum of **32** (Figure 5) contains only five carbon resonances. The proton-coupled FT  $^{13}\text{C}$  NMR spectrum of **32** (Figure 5) shows that as one progresses from the resonance that is most deshielded to increasingly more shielded ones that the signals correspond to a single carbon bearing most of the positive

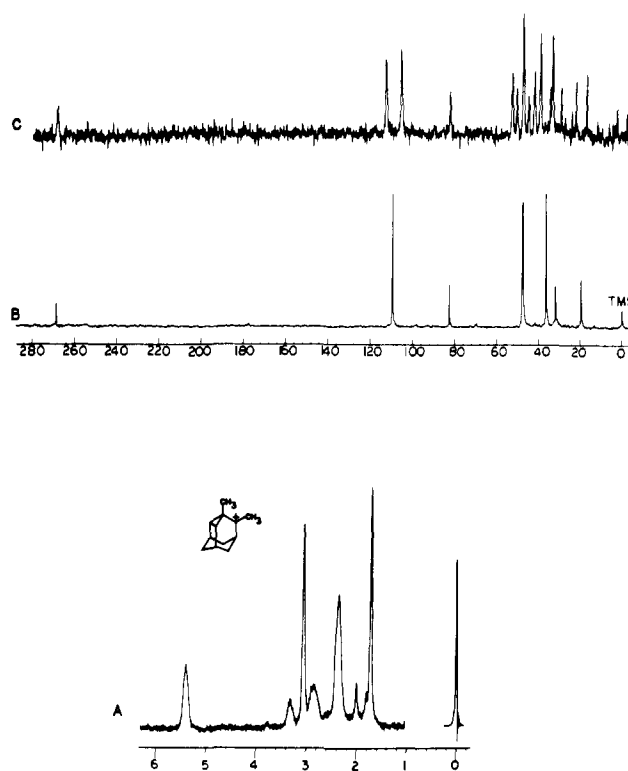
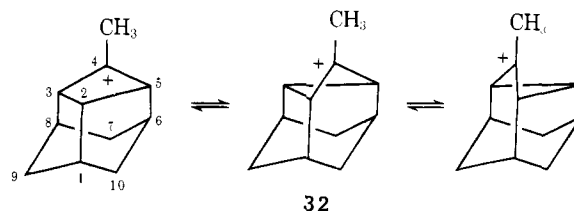


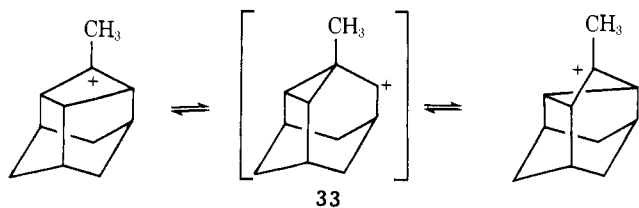
Figure 6. (A)  $^1\text{H}$  NMR (60 MHz) spectrum of ion **35** in  $\text{FSO}_3\text{H-SO}_2\text{ClF}$  at  $-78^\circ\text{C}$ . (B)  $^{13}\text{C}$  proton noise decoupled NMR spectrum of ion **35**. (C)  $^{13}\text{C}$  proton-coupled NMR spectrum of ion **35**.

charge, three equivalent tertiary carbons, three other tertiary carbons which are also mutually equivalent, three equivalent secondary carbons, and the methyl carbon. These data clearly suggest that on the NMR time scale at  $-120^\circ\text{C}$  ion **32** possesses a threefold axis of symmetry. However, it is to be emphasized that whereas in the parent 8,9-dehydro-2-adamantyl cation (**12**) the most shielded resonance integrates for three carbons, in ion **32** this signal integrates for only one carbon. Thus, it is apparent that ion **32** is not the 1-methyl-8,9-dehydro-2-adamantyl cation. We assign to cation **32** the structure of the 4-methyl-2,5-dehydro-4-protoadamantyl cation. It is apparent that this ion is undergoing a facile threefold degenerate rearrangement which is fast on the NMR time scale even at  $-120^\circ\text{C}$ . In accord with this structure, the multiplet at  $\delta$  4.52 in the  $^1\text{H}$  NMR spectrum of **32** is assigned to the homo-



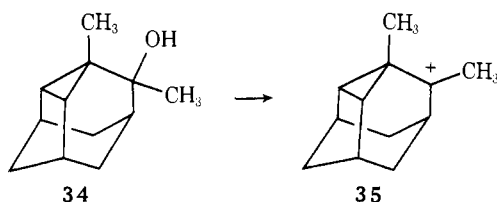
topic protons at C-2, C-3, and C-5, whereas the multiplet at  $\delta$  3.56 is assigned to the bridgehead protons at C-1, C-6, and C-8. It follows that the six-proton AB quartet centered at  $\delta$  2.15 is assigned to the diastereomeric pair of homotopic protons at C-7, C-9, and C-10. The complete  $^{13}\text{C}$  NMR parameters with resonance assignments for ion **32** are summarized in Table I.

The degenerate equilibration of the 4-methyl-2,5-dehydro-4-protoadamantyl cation (**32**) may be rationalized as proceeding via the 1-methyl-8,9-dehydro-2-adamantyl cation (**33**) as an intermediate. However the  $^{13}\text{C}$  NMR data suggest that ion **32** is not a simple  $\text{sp}^2$  hybridized classical 4-methyl-

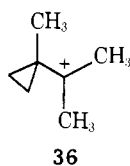


2,5-dehydroprotoadamantyl cation, but the charge is significantly  $\sigma$ -delocalized into the adjacent C–C bonds.

**The 1,2-Dimethyl-8,9-dehydro-2-adamantyl Cation.** The substantially different data observed with methyl substitution of C-1 (ion **32**) or C-2 (ion **24**) in the parent dehydroadamantyl skeleton led us to examine the ionization of 1,2-dimethyl-2-hydroxy-8,9-dehydroadamantane (**34**) in  $\text{FSO}_3\text{H}-\text{SO}_2\text{ClF}$  solution at  $-78^\circ\text{C}$ . The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the resulting ion (Figure 6) clearly show that the 1,2-dimethyl-8,9-dehydro-2-adamantyl cation (**35**) is obtained exclusively.



As is the case with other 2-substituted 8,9-dehydro-2-adamantyl cations (**24**–**26**), ion **35** is a static carbenium ion. Cation **35** proved to be stable in  $\text{FSO}_3\text{H}-\text{SO}_2\text{ClF}$  solution up to  $-10^\circ\text{C}$  and only minor broadening of the  $^1\text{H}$  NMR signals of **35** were detected when it was recooled to  $-95^\circ\text{C}$ . Consistent with this observation, the  $1,\alpha,\alpha$ -trimethylcyclopropylcarbinyl cation (**36**) also has been shown to be a static tertiary carbocation.<sup>12</sup>



## Experimental Section

Melting points were obtained in sealed capillary tubes using a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were obtained on Perkin-Elmer 180 or 337 spectrophotometers. Proton magnetic resonance spectra of the alcohols were recorded with Varian A-60A or Perkin-Elmer R-12B 60-MHz spectrometers and are referenced to an internal standard of tetramethylsilane. Apparent splittings are reported in all cases. Elemental analyses were performed by Micro-Analysis, Inc., Wilmington, Del.

**2-Hydroxy-8-methyl-8,9-dehydroadamantane (23).** A solution of 8-methyl-8,9-dehydro-2-adamantanone<sup>16</sup> (130 mg, 0.80 mmol) in methanol (5 mL) was added dropwise to a stirred solution of sodium borohydride (60 mg, 1.6 mmol) in methanol (5 mL) at  $0^\circ\text{C}$ . The reaction mixture was stirred at  $0^\circ\text{C}$  for 1 h and at room temperature for 1 h and then diluted with water (10 mL). The resulting solution was saturated with sodium chloride and extracted with ether ( $3 \times 50$  mL). The combined ether extracts were dried over anhydrous magnesium sulfate. Evaporation of the solvent under reduced pressure gave a white solid (118 mg, 95% yield) which was sublimed ( $25^\circ\text{C}$ , 0.1 mm) to afford **23** as a waxy, white solid: mp  $74\text{--}76^\circ\text{C}$ ;  $\delta$  ( $\text{CDCl}_3$ ) 4.01 [br s, 1 H,  $\text{CH}(\text{OH})$ ] and 2.5–0.8 (br m, 15 H, which contains a methyl singlet at  $\delta$  1.21);  $\nu$  ( $\text{CCl}_4$ ) 3620, 3400 (br), 2925, 2855, 1440, 1050, 1035, 1005, and  $910\text{ cm}^{-1}$ .

Anal. Calcd for  $\text{C}_{11}\text{H}_{16}\text{O}$ : C, 80.44; H, 9.80. Found: C, 80.63; H, 9.59.

**2-Cyclopropyl-2-hydroxy-8,9-dehydroadamantane (28).** A solution of cyclopropyllithium<sup>26</sup> (25 mL of a ca. 1.0 M solution) in ether was added at  $0^\circ\text{C}$  to a stirred solution of 8,9-dehydro-2-adamantanone<sup>16</sup> (501 mg, 3.38 mmol) in anhydrous ether (50 mL). The reaction mixture was stirred at  $0^\circ\text{C}$  for 1 h and at room temperature for 12

h at which point water (20 mL) was added. The resulting mixture was saturated with sodium chloride and extracted with ether ( $3 \times 50$  mL). The combined ether extracts were dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave a colorless liquid which was distilled ( $70^\circ\text{C}$ , 0.02 mm) using a molecular distillation apparatus to provide pure **28** (516 mg, 80% yield):  $\delta$  ( $\text{CCl}_4$ ) 2.65 to  $-0.35$  (br m);  $\nu$  ( $\text{CCl}_4$ ) 3615, 3460 (br), 3085, 2930, 2865, 1460, 1400, 1330, 1150, 1040, 1030, and  $990\text{ cm}^{-1}$ .

Anal. Calcd for  $\text{C}_{13}\text{H}_{18}\text{O}$ : C, 82.06; H, 9.54. Found: C, 82.10; H, 9.72.

**2-Hydroxy-2-phenyl-8,9-dehydroadamantane (27).** A solution of 8,9-dehydro-2-adamantanone<sup>16</sup> (156 mg, 1.0 mmol) in anhydrous ether was added over 15 min at  $0^\circ\text{C}$  to a freshly prepared solution of phenylmagnesium bromide in ether. The reaction mixture was stirred at  $0^\circ\text{C}$  for 1 h and at room temperature for 1 h. The reaction was then quenched by the addition of a saturated aqueous ammonium chloride solution and the resulting organic layer was washed successively with 5% aqueous sodium hydroxide, water, 5% hydrochloric acid, water, and brine. The organic layer was then dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave a solid which was recrystallized from petroleum ether to afford 105 mg (45% yield) of **27** as a white solid: mp  $84\text{--}88^\circ\text{C}$  dec;  $\delta$  ( $\text{CDCl}_3$ ) 7.6–7.2 (br m, 5 H, aromatic protons) and 2.65–0.85 (br m, 13 H).

Anal. Calcd for  $\text{C}_{16}\text{H}_{18}\text{O}$ : C, 84.91; H, 8.01. Found: C, 85.01; H, 8.14.

**1,2-Dimethyl-2-hydroxy-8,9-dehydroadamantane (34).** A solution of methylolithium (4.8 mL of a 1.84 M solution, ca. 8.9 mmol) in ether was added at  $0^\circ\text{C}$  to a stirred solution of 1-methyl-8,9-dehydro-2-adamantanone<sup>19</sup> (350 mg, 2.16 mmol) in anhydrous ether (10 mL). The reaction mixture was stirred at  $0^\circ\text{C}$  for 1 h and at room temperature for 1 h, and then water (25 mL) was added. The resulting mixture was saturated with sodium chloride and extracted with ether ( $3 \times 50$  mL). The combined ether extracts were dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave a quantitative yield (410 mg) of alcohol **34**. Molecular distillation ( $90^\circ\text{C}$ , 0.1 mm) provided pure **34** as a colorless oil:  $\delta$  ( $\text{CDCl}_3$ ) 2.34–0.62 (br m which contains methyl singlets at  $\delta$  1.31 and 0.93);  $\nu$  ( $\text{CHCl}_3$ ) 3600, 3380 (br), 2930, 2865, 1445, 1260, and  $920\text{ cm}^{-1}$ . The molecular weight determined by high-resolution mass spectroscopy was 178.139 (calcd, 178.136).

**Preparation of Carbocations.** The cation precursor (alcohol or chloride) was dissolved in  $\text{SO}_2\text{ClF}$  which had been cooled to  $-120^\circ\text{C}$  (dry ice–ethanol bath temperature) or  $-78^\circ\text{C}$  (dry ice–acetone bath temperature). An aliquot of the resulting solution was slowly added with vigorous stirring to a freshly prepared solution of a fourfold excess of  $\text{FSO}_3\text{H}$  in  $\text{SO}_2\text{ClF}$  or  $\text{SbF}_5$  in  $\text{SO}_2\text{ClF}$  which was maintained at the same temperature. This procedure afforded an approximately 10–15% solution of the ion. After the addition had been completed, the sample was immediately transferred to a precooled NMR tube.

$^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance spectroscopic studies were carried out as previously described.<sup>27</sup>

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- (24) The observation that **23** → **24** suggests that substitution of any of these groups for the hydrogen at C-8 (or C-9) in **12** would also lead to a static ion.
- (25) Ion **32** can also be formed from the same precursors in FSO<sub>3</sub>H-SO<sub>2</sub>ClF solution at -120 °C. However, in this medium the ion is only stable below -78 °C. Upon further warming, **32** is slowly transformed into a mixture of two ions. Since the <sup>1</sup>H NMR spectrum of the minor product is very similar to that of **17**, it is tentatively identified as the 4-methyl-2-tricyclo[4.4.0.0<sup>5,9</sup>]dec-3-enyl cation. The structure of the major product has not been determined.
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## The Effect of Carbonyl Substituents on the Barriers to Rotation in *N,N*-Dimethylamides

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**Abstract:** The barriers to rotation about the carbonyl-nitrogen bond were determined for 14  $\alpha$ -alkyl- and  $\alpha$ -halo-substituted *N,N*-dimethylacetamides by NMR total line-shape analysis. Free energies of activation were found to be insensitive to relatively nonpolar aprotic solvents and concentrations. Regression analyses were performed with a variety of inductive and steric parameters. The best correlations with  $\Delta G^\ddagger$  were obtained using  $\sigma_1$  and  $\nu$  values. When amides containing substituents capable of direct resonance interaction were included in the regression analysis, the addition of  $\sigma_{R^-}$  as a third independent variable produced a reasonably good correlation. The relative importance of these effects is discussed.

While it is generally believed that the rotational barriers in amides are governed by steric and electronic effects, the relative magnitudes of these effects and the quantitative structural relationships used to describe them have remained virtually unexplored.<sup>1,2</sup> The present study has as its primary objective the identification and quantification of the factors related to the effect of carbonyl substituents on the barriers in *N,N*-dimethylamides. In order to trace these effects systematically in a set of relatively simple substituents, the activation parameters for 14 alkyl- and halo-substituted *N,N*-dimethylacetamides were determined by total line-shape analysis and then correlated with various structural and electronic quantities.

### Experimental Section

The amides studied were commercially available or were prepared by the reaction of the appropriate acid halide with dimethylamine. All except *N,N*-dimethyl-2-fluoroacetamide (bp 94 °C (30 mm); yield 81%. Anal. Calcd for C<sub>4</sub>H<sub>8</sub>NOF: C, 45.71; H, 7.67. Found: C, 45.72; H, 7.69) have been reported previously. The purity of the amides as monitored by NMR spectroscopy exceeded 95%.

NMR spectra were obtained on a Varian A-60D spectrometer equipped with variable temperature accessory V-4341/V-6057. Spectra were calibrated by the side-banding method using a Hewlett-Packard 200CD audio oscillator and Model 522B electronic counter. For the total line-shape analysis at least three traces were run at low rf field on a 50-Hz sweep width at each temperature. Temperatures were measured with standard methanol and ethylene glycol samples and the equations of Van Geet.<sup>3</sup>

The limiting chemical shift difference,  $\Delta\nu$ , at each temperature used in the total line-shape analyses was extrapolated from a least-squares

plot of  $\Delta\nu$  vs.  $T$  obtained from spectra taken at four temperatures 25–50 °C below coalescence. Transverse relaxation values,  $T_2$ , were similarly extrapolated from a least-squares plot of  $T_2$  vs.  $T$ . The  $T_2$  values were calculated from the half-height width of the sharpest peak of the N-CH<sub>3</sub> doublet. The extrapolated  $\Delta\nu$  and  $T_2$  values were then used as constants in the Gutowsky-Holm equation<sup>4</sup> (programmed in FORTRAN IV) and  $\tau$  was varied until the computer-generated curve displayed on a Honeywell Model 530 x-y plotter matched the NMR spectrum as closely as possible. For most amides the peaks of the N-CH<sub>3</sub> doublet were equally intense. When the intensities were slightly dissimilar the more intense peak was used for the fit. For several compounds  $\tau$  values obtained by visual comparison were checked with the computer minimization of errors method described previously.<sup>5</sup>

Activation energies were calculated from least-squares Arrhenius plots constructed from five to nine points. The correlation coefficients for the Arrhenius plots were in all cases greater than 0.97. Free energies of activation were obtained at 25 °C from the Eyring equation (transmission coefficient = 1) and at the coalescence temperature from the approximate method<sup>6</sup> using  $\Delta\nu$  extrapolated from four low-temperature values.

Solvents were dried over molecular sieves (Linde type 4A).

### Results and Discussion

The results of the total line-shape analyses are presented in Table I, along with previously reported free energies of activation. The free energies of activation calculated from the total line-shape analysis have an associated error range of  $\pm 0.3$  kcal/mol at the 90% confidence level as determined by application of the  $t$  test to three separate total line-shape analyses of compound II. In general the free energies of activation determined by the approximate method agree well with those