138.5 (ipso), 140.9 (ortho), 156.0 (para), −80 °C. Spectra were obtained at 20 °C intervals from −20 to −100 °C. The β-carbons (C3 and C5) have a -130×10^4 ppm/°C temperature shift.

1-Phenyl-1-cyclohexyl Cation (15). This cation has been previously reported,[7] but no temperature data were measured. In our work, this cation was prepared by either procedure A or C. The β-carbons (C3 and C5) have a temperature dependence for the ^{13}C shifts of about -170×10^4 ppm/°C, over the range −40 to −100 °C.

Preparation of Deuteriated Cations 2, 4, 6, 8, 18, and 19. For the α-d_4-substituted cations **2**, **4**, **6**, **8**, and **18**, the corresponding ketone was deuteriated in the α-position by a standard procedure[21] (two treatments). The corresponding alcohol was then prepared. The deuterium content of the ketones was analyzed by mass spectrometry and ^{2}D and ^{13}C NMR spectroscopy and corresponded to >95% D content in the α-position. The corresponding tertiary alcohols were also analyzed in a similar way (MS and ^{13}C NMR). The cyclohexanone-γ-d_2 needed for cation **18** was prepared by a modification of one of the several described routes.

Our synthesis started with 4-hydroxycyclohexanone, prepared from the diol by a modification of the literature procedure[22] (protecting one end as the tetrahydropyranyl ether rather than as an acetate). The synthesis proceeded

$$\text{4-hydroxycyclohexanone} \rightarrow \text{tetrahydropyranyl ether} \xrightarrow{\text{LiAlD}_4\text{ (99\% D)}}$$
$$\text{alcohol-}\gamma\text{-}d_1\text{–ether} \rightarrow \text{tosylate-}\gamma\text{-}d_1\text{–ether} \xrightarrow{\text{Superdeuteride}}$$
$$\text{cyclohexanol-}\gamma\text{-}d_2\text{–THP} \xrightarrow{[\text{H}^+]} \text{cyclohexanol-}\gamma\text{-}d_2 \xrightarrow[\text{oxidation}]{\text{Jones}} \text{cyclohexanone-}\gamma\text{-d}_2$$

The reactions were standard procedures except for the Superdeuteride reduction, which followed a published procedure.[23] The overall yield on a 0.03-mol scale was ca. 15%. The ketone was analyzed by both ^{1}H (200-MHz) and ^{2}D (30.7-MHz) NMR spectroscopy, the former showing a γ-proton area at most 10% that of the α- and β-proton area and indicating a minimum of 60% γ-d_2 compound, the latter confirming no deuterium in the α-ring position. The corresponding methyl alcohol and chloride were prepared as described for the undeuteriated case. The alcohol showed C–D stretches at 2100, 2160, and 2190 cm^{-1} and the ^{13}C NMR of both alcohol and chloride showed only a weak multiplet for the γ-carbon.

The preparation of the deuteriated cations calls for some specific comment: Cations **2** and **4** have to be prepared at very low temperatures (ca. −135 °C) in order to prevent scrambling of the α-deuteriums into β- and γ-positions, which becomes rapid at about −100 °C. This scrambling was observed with both ^{2}D and ^{13}C NMR spectroscopy. No deuterium appears in the solvent peak, so all rearrangements are internal.

The β-carbon position in **2** or **4** is so sensitive that one can pick out peaks for α-d_3 and α-d_2 ions during this scrambling (see Figure 2). For quantitative measurement of the equilibrium isotope shifts, etc., solutions containing both **1** and **2** (1:1) or **1** and **4** (1:1) were prepared and the combined spectra measured. This eliminates solvent and temperature differentials, which inevitably occur in comparing separate runs. Spectra were run at six temperatures between −89 and −129 °C, above which the ^{13}C peak corresponding to **2** or **4** is lost. Cations **6** and **8** must also be prepared at very low temperatures, and the ^{13}C spectra were run (up to about −100 °C) singly, and as mixtures with their undeuteriated analogues, at a number of low temperatures. Cation **8**, although showing almost no change in the β-carbon position, does show a C$^+$ peak that is 2.9 ppm to lower field than in the undeuteriated 7, an unusually large effect.[25] Cation **19** was prepared and handled as described for **2**. In this case, in the ^{13}C spectrum, the C4 peak is "missing", as expected. In the α-deuteriated ions, the C2,C6 peak is of low intensity and broad (C–D coupling). The 1-phenyl cation **18** is considerably more resistant to deuterium scrambling, and one can obtain spectra up to about −40 °C.

Molecular Mechanics Calculations. The program BIGSTRN, employing the Schleyer force field for cations,[10] was used. Equilibrium geometries for cations **1**, **5**, **9**, **11**, and **14** were calculated for all possible chair, boat, twist-boat, and five-carbon planar geometries. Some similar data have been published by Harris et al.[25] As expected, we found the C_s twist-boat isomer to be the best alternative to a chair, although the latter, in the best configuration, was the ground state in every case.

Molecular Orbital Calculations. The optimized geometries for cations **1**, **5**, and **10** were obtained by the MNDO semiempirical method.[26]

Acknowledgment. We thank Dr. B. P. Singh, Dr. P. Kirkbride, Dr. L. Schmitz, Susan Ranson, and John Gunn for their assistance and Drs. A. Rauk and P. v. R. Schleyer for stimulating discussions. The Natural Sciences and Engineering Research Council of Canada is thanked for generous financial support.

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Evidence for Equilibrating "Structures" in Unsymmetrical Tertiary 2-Adamantyl Cations. Possible Pyramidal Distortion of Observable Solution Carbocations

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Abstract: The observable tertiary carbocations 2,5-dimethyl-2-adamantyl and 2,4,4-trimethyl-2-adamantyl were prepared and the ^{13}C NMR spectra recorded over a wide range of temperatures and in several different solvent systems. Both the ^{13}C peak positions and the temperature dependence of these are consistent with both cations existing as a pair of rapidly equilibrating "structures". These structures involve enhanced C–C hyperconjugation on one face or the other of the 2-adamantyl framework and virtually require some nonplanarity at the C$^+$ center. We also believe that the cation structure must include the solvent and/or counterion in the description, but tight ion pairs, etc., are not thought to be involved; i.e., the effect is simply due to having a condensed phase. The 1-methyl-1-cyclohexyl cation also exists as a pair of rapidly equilibrating structures, which can now be seen to bear a close resemblance to the 2-adamantyl cation structures and are therefore also likely to be nonplanar at the C$^+$ center and to require the solvent and/or counterion in the overall description. Finally, we discuss some puzzling solvolysis results and rationalize the observations on the basis of our superacid structures.

2-Adamantane compounds (**1**) and various substituted analogues have been favored substrates for solvolysis studies,[1] partly because the molecules are rigid. Stable 2-R-2-adamantyl cations **2** have also been studied,[2] where R = methyl, ethyl, phenyl, or

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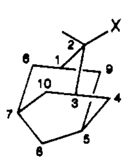
Table I. ^{13}C NMR Peak Positions and Their Relative Temperature Dependence[a]

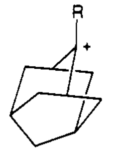
	carbon											
	1	2	3	4	5	6	7	8	9	10	C2 Me	other Me
						Cations						
3[b]	66.1	325.0	76.1	45.9	35.9	32.6	31.5	65.3	38.7	59.3	43.4	30.0, 25.5
	(15)	(205)	(65)	(335)	(55)	(15)	(−40)	(−145)	(225)	(−140)	(−20)	(−5) (25)
13[c]	65.9	322.0	65.9	52.0	28.7	36.3	28.7	52.0	52.0	52.0	41.1	
	(65)	(215)		(85)	(55)	(10)					(0)	
4[d]	66.1	321.3	66.1	47.0	30.0	43.1	31.0	62.1	47.0	62.1	40.9	26.7
	(30)	(205)		(345)	(45)	(20)	(−15)	(−260)				
14[e]	51.6	271.2	51.6	49.5	29.5	36.4	29.5	49.5	49.5	49.5		*f*
	(85)	(10)		(50)	(20)	(20)						
15[g]	50.5	271.1	50.0	53.3	31.8	43.2	30.6	50.5	53.5	50.0		26.3[h]
	(75)	(40)		(130)	(0)	(20)	(15)	(−30)				(−60)
						Ketones[i]						
5	46.1	212.0	57.4	39.4	37.1	32.5	27.1	40.6	34.7	34.7		25.7, 28.0
2-adamantanone	47.1	217.9	47.1	39.4	27.6	36.4	27.6	39.4	39.4	39.4		
7	46.6	218.6	46.6	45.4	30.0	43.2	28.0	38.4	45.4	38.4		29.1

[a] Relative to internal $CFCl_3$ (δ 117.9). The temperature shifts ($\Delta\delta$ in units of $10^4 \times$ ppm/°C) are given in parentheses and are shifts relative to the $CFCl_3$ shift; a positive number implies an upfield shift as the temperature decreases. [b] −113.5 °C. [c] −107.5 °C. [d] −119 °C. [e] −40 °C. [f] Phenyl peaks at 154.2 (−65) (para), 138.1 (−55) (ortho), 137.1 (15) (ipso), 133.2 (15) (meta). [g] −20 °C. [h] Phenyl peaks at 154.4 (−65) (para), 138.2 (−50) (ortho), 137.0 (25) (ipso), 133.2 (10) (meta). [i] In $CDCl_3$ solution relative to TMS. Data for **5**, 7, and 2-adamantanone have been previously published.[8-10] A single temperature spectrum for cation **14** has also been reported.[2]

substituted phenyl. Attempts to prepare the secondary ion **2**, R = H, have invariably led to the tertiary 1-adamantyl cation.[3]

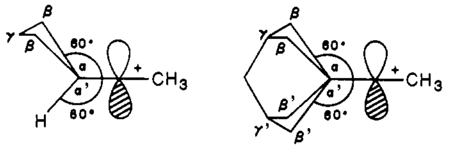


1, X = leaving group



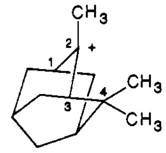
2, R = alkyl, aryl

In the accompanying paper,[4] we have shown that tertiary 1-alkyl-1-cyclohexyl cations, given a choice between simultaneous hyperconjugation with the α-H's and the C_α–C_β bonds, apparently prefer an *either/or* situation, which then leads to two distinct "structures". Because the cyclohexane ring is potentially rather flexible, we have had to be circumspect in interpreting these structures in terms of a defined geometry. We were attracted to the tertiary 2-adamantyl cation system for several reasons: (1) this cation has a conformation that is rigid; (2) the structure is composed of six-membered chair rings. Assuming, for the moment planar, classical cations, the 1-cyclo-hexyl and 2-adamantyl systems can be compared. If the cyclohexyl cation exists as two structures involving either C–C or C–H hyperconjugation, then one might reasonably wonder whether the 2-adamantyl cation might opt for a similar situation. The choices here are between a single structure, where there is simultaneous delocalization into both cyclohexane rings, or the two-structure option, one structure involving $C_{\alpha(\alpha')}$–C_β hyperconjugation and the other $C_{\alpha(\alpha')}$–$C_{\beta'}$ hyperconjugation. Obviously, for the latter situation to occur, the single ring hyperconjugative interaction would somehow have to be enhanced. However, these two structures, if they existed, would be degenerate ($K = 1$) in the 2-adamantyl case, and under conditions of rapid structural equilibration, as exists with the cyclohexyl cations, one would see only averaged and relatively normal position NMR peaks. Indeed, the previously prepared 2-alkyl-2-adamantyl cations look like straightforward, single-structure, tertiary carbocations and were interpreted as such.[2]



Both cations being viewed through the C_α–C^+–$C_{\alpha'}$ plane

We therefore sought to prepare examples of observable 2-methyl-2-adamantyl cations where the inherent C^+ symmetry of the parent system was broken. The two cases chosen were the 2,4,4-trimethyl cation **3** and the 2,5-dimethyl species **4**. The two choices are somewhat complementary in that **4** still preserves one symmetry plane, while potentially differentiating the crucial $\alpha(\alpha')$–β and $\alpha(\alpha')$–β' C^+ hyperconjugative interactions, whereas **3** has no symmetry at all. These two cations were also chosen because it appeared that they might be fairly resistant to further rearrangement, i.e., structural features such as $>C(H)CH_3$ would be susceptible to hydride shifts. In choosing these two cations, we had no preconceived ideas about what effect the extra methyl groups would have on either a single structure or on two equilibrating structures, although it seemed probable that the 5-methyl group in **4** would not seriously distort the C^+ center if indeed the molecule existed in the single-structure option.



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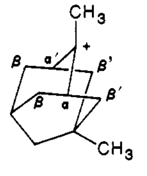

4

Results

Synthesis of Starting Materials. 4,4-Dimethyl-2-adamantanone (**5**) and the corresponding tertiary methyl alcohol **6** were prepared by literature procedures.[5,6] 5-Methyl-2-adamantanone (**7**) has been prepared in poor yield by isomerizing 2-methyl-2-adamantanol in concentrated sulfuric acid.[7] However, we used

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(1) Fort, R. C., Jr. *Adamantane—The Chemistry of Diamond Molecules*; Marcel Dekker: New York, 1976. Chapter 4 contains a discussion of the early solvolysis work in this area.

(2) (a) Whitlock, H. W., Jr.; Siefken, M. W. *J. Am. Chem. Soc.* **1968**, *90*, 4929. (b) Olah, G. A.; Liang, G.; Mateescu, G. D. *J. Org. Chem.* **1974**, *39*, 3750. (c) Kelly, D. P.; Jenkins, M. J.; Mantello, R. A. *J. Org. Chem.* **1981**, *46*, 1650.

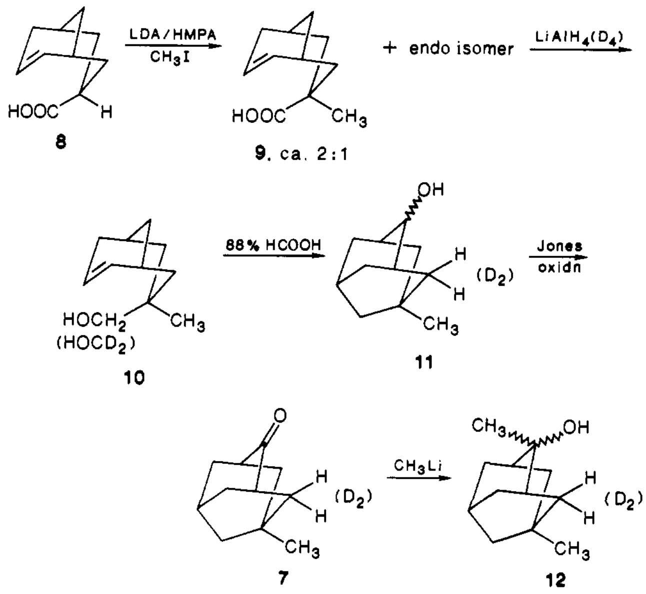
(3) We have tried to prepare the secondary 2-adamantyl cation using very dilute solutions, very low temperatures, and very rapid NMR measurements. One gets ^1H NMR spectra initially containing 1-adamantyl cation peaks *and others* that disappear rapidly with time. However, we cannot be certain that these are from the 2-adamantyl cation since they would, for instance, require a rapidly equilibrating structure. Others have also been unable to prepare this cation, see footnote 2 of ref 2b.

(4) Kirchen, R. P.; Ranganayakulu, K.; Sorensen, T. S. *J. Am. Chem. Soc.*, preceeding paper in this issue.

(5) Blaney, F.; Faulkner, D.; McKervey, M. A.; Step, G. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2697.

(6) Faulkner, D.; McKervey, M. A.; Lenoir, D.; Senkler, C. A.; Schleyer, P. v. R. *Tetrahedron Lett.* **1973**, 705.

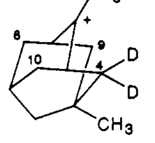
Scheme I



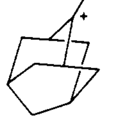
a new procedure that also allows for the preparation of the 4,4-dideuterio analogue, which was needed to confirm ^{13}C NMR peak assignments. This synthesis proceeded as shown in Scheme I.

Carbocation Results. The 2,4,4-trimethyl **3** and 2,5-dimethyl **4** cations were prepared from either the tertiary alcohol or chloride in several different acid–solvent systems: ROH in 1:1 FSO_3H–SbF_5 and SO_2ClF, ROH in 4:1 FSO_3H–SbF_5, ROH in pure FSO_3H, RCl in SbF_5–SO_2ClF, or RCl in SbF_5–SO_2ClF–SO_2F_2. The ^{13}C NMR spectrum of each cation was virtually identical in the various acid–solvent systems when the spectra were recorded at identical temperatures. In addition, it was found that a fourfold concentration change also had virtually no effect on ^{13}C chemical shifts, again comparing these at the same temperature.

2,5-Dimethyl-2-adamantyl Cation (4). Cation **4** solutions exhibit nine ^{13}C peaks (Table I), and the assignment of these is straightforward except for the double-intensity C8–C10 and C4–C9 methylene signals. On the basis of the corresponding ketone ^{13}C peak positions (see Table I), one might expect the C4–C9 peak to be about 7 ppm to lower field than the C8–C10 peak and to be assignable on this basis (deshielding by the 5-methyl substituent). However, these two carbon peaks are experimentally separated by nearly 17 ppm at the lowest temperatures used in this study (133 K). These two peak positions are also quite temperature dependent, and this is shown graphically in Figure 1. The low-field methylene peak shifts upfield with a temperature increase, while the high-field peak does the opposite. As a result, these peaks are separated by only about 7 ppm at 293 K. This temperature dependence suggested that the two peaks would eventually "cross over" if it were possible to obtain spectra at high temperatures. Unfortunately, the cation decomposes rapidly at temperatures above 298 K, and this prediction is not experimentally verifiable. Because this ^{13}C assignment is crucial to the interpretation of our results, an unambiguous assignment was made by preparing the 4,4-dideuterio cation **4**-d_2, whereupon the C4–C9 peak size is essentially halved. Otherwise the chemical shifts observed for **4**-d_2 are very similar to those found in the undeuteriated ion. This procedure proves that the high-field peak in Figure 1 is indeed the C4–C9 carbons and the low-field peak the C8–C10 carbons. In other words, the 17-ppm peak separation observed at 133 K not only is too large but is also reversed when compared with the corresponding ketone ^{13}C chemical shifts.



4-d_2



13

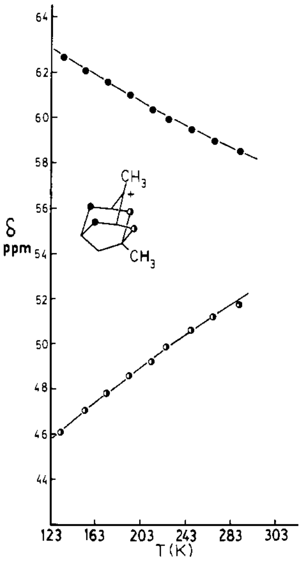


Figure 1. Chemical shift vs temperature dependence for the β-carbons in cation **4**. In order to cover this large temperature range, the data shown are a composite of two different solvent systems.

2,4,4-Trimethyl-2-adamantyl Cation (3). Cation **3**, with no symmetry, shows 13 ^{13}C peaks (Table I). The assignments are relatively straightforward if one uses the shielding and deshielding effects of the 4,4-dimethyl group obtained from comparisons of 4,4-dimethyl-2-adamantanone (**5**) and 2-adamantanone (see Table I). Thus, C3 in **3** is deshielded by about 10 ppm from the expected δ 65–66 [cf. data for the 2-methyl-2-adamantyl cation (**13**), in addition to **4**]; C5 is deshielded by ca. 6 ppm vs the expected 9.5 ppm. The γ-shielding effect of this group also shows up, wherein C6 is shielded by ca. 4 ppm. This γ-shielding can also be used to distinguish a pair of low-field CH_2 carbons found at δ 59.3 and 65.3 (−113.5 °C). This separation of 6 ppm is nearly identical with the 5.9-ppm separation found for C8 and C10 in the ketone, and we therefore assign δ 59.3 to C10 and δ 65.3 to C8.

Temperature Dependence of the Chemical Shifts in Cations 3 and 4. The chemical shifts reported in Table I for both **3** and **4** have been measured at ca. 20 °C intervals over a wide temperature range, and this temperature dependence is given in Table I. The reported Δδ vs T slope roughly covers a temperature region from about −20 to −100 °C and is given in units of 10^4 ppm shift/°C. These plots are not usually strictly linear, but these data are meant to only illustrate the approximate magnitude and direction of the shifts. It should also be noted that these shifts are relative to internal $CFCl_3$, which however appears to have only a small temperature dependence for the ^{13}C doublet.

The dominant feature of the Δδ vs T data for cation **4**, as already noted, is the fairly large *and opposite* shifts observed for the C4–C9 and C8–C10 carbons (Figure 1). There is also a moderate shift for the C^+ carbon (+205) and the C5 methyl group (−120). The remaining carbons have smaller shifts. With cation **3**, four of the five largest temperature shifts again belong to the β-carbons C4, C8, C9, and C10. As with **4**, two of these (C4 and C9) have a positive shift (+335 and +225), while the other two are negative (−144 and −137). These data are shown in graphic form in Figure 2. Like **4**, the C^+ peak is also quite temperature dependent (+205). The remaining carbons have considerably smaller Δδ shifts.

2-Methyl-2-adamantyl Cation (13). Although both ^{1}H and ^{13}C NMR data have been reported[2] for **13**, there are no data on the temperature dependence of the ^{13}C chemical shifts. By using the tertiary chloride in SbF_5–SO_2ClF–SO_2F_2, these data were obtained and are reported in Table I. The only large temperature shift

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(7) McKervey, M. A.; Alford, J. R.; McGarrity, J. F.; Rea, E. F. J. *Tetrahedron Lett.* **1968**, 5165.

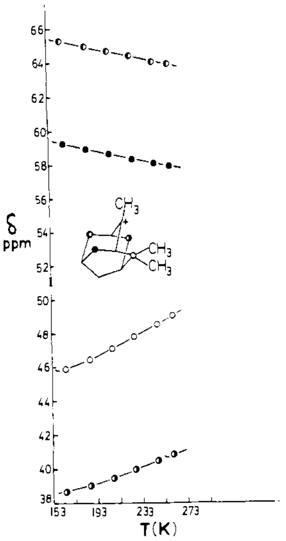
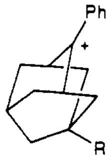


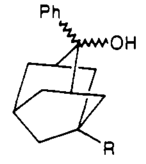
Figure 2. Chemical shift vs temperature dependence for the β-carbons in cation 3. Above 263 K, this cation rapidly and irreversibly rearranges.

(+215) occurs with the C^+ peak.

2-Phenyl-2-adamantyl (14) and 2-Phenyl-5-methyl-2-adamantyl (15) Cations. 1-Phenylcyclohexyl cations, in contrast to the 1-methyl analogues, exhibit much more "normal" ^{13}C NMR spectra.[4] To see whether this was also true of the 2-adamantyl system, we prepared the title cations **14** and **15** from the corresponding tertiary alcohols **16** and **17**. The ^{13}C NMR shifts and



14, R = H
15, R = CH_3



16, R = H
17, R = CH_3

the temperature dependence of these are listed in Table I. The chemical shift agreement between **14** and **15** is quite good, if one takes into account the effect of the 5-methyl substituent in **15** using ketone-derived correction factors. In addition, cation **14** had no Δδ values larger than +85 (C1–C3), with the β-carbons (C4, C8, C9, C10) showing a +50 value. For cation **15**, the C4–C9 carbons show a +130 value vs −30 for the other β-carbons (C8–C10). One concludes that **14** and **15** are indeed quite similar and the chemical shift difference between the C4–C9 and C8–C10 carbons is nearly normal. As with the cyclohexyl systems, the properties of these cations are not entirely a black and white situation, and one can see in **15** some small deviations[8] in the same direction as the much larger effects in the methyl cations. In any case, these results show that the anomalous NMR spectra observed for **3** and **4** are not somehow inherent to all unsymmetrical 2-adamantyl cations.

Discussion

It is pertinent at this point to review the ^{13}C NMR spectrum of the 2-methyl-2-adamantyl cation (**13**) (Table I). When one compares the line positions with those of 2-adamantanone, one notes the large downfield shift of the C2 carbon to a position typical of tertiary alkyl carbocations. Similarly, the neighboring C1–C3 carbons are deshielded by nearly 20 ppm, again an expected result. The β-carbons (C4, C8, C9, C10) are likewise deshielded by ca. 12 ppm, and one would have no problem in attributing this deshielding to "double" C–C hyperconjugation in a single-structure option (see the introduction). The remaining carbons in **13** are comparable in the ketone and the cation and obviously reflect a position that is now remote from the C^+ influence.

Let us now review the chemical shifts observed for carbocations **3** and **4**, making our comparison both internally within the cation and with external reference to the shifts observed for the 2-methyl-2-adamantyl cation (**13**). In cation **4**, the C^+, C2 Me, and C1–C3 carbons agree very well with those in **13**. Likewise, the remote carbons at C5, C6, and C7 also agree well with those in **13** if one applies the usual NMR correction factors. The carbon peak shifts in **4** not agreeing at all well with those in **13** are the β-carbons. One might have expected C4–C9 to have a shift of ca. δ 58, and for C8–C10, ca. δ 51. The observed values (133 K) are δ 46.1 and 62.7; i.e., both are ca. 12–13 ppm out of line in opposite directions.

In cation **3** one can rationalize fairly well all carbon positions, once again with the exception of C4, C8, C9, and C10. Carbons 9 and 10, for example, might have been expected to have similar chemical shifts (they are identical in the ketone because of their similar geometric location relative to the *gem*-dimethyl group). However, in **3**, these carbons differ by 20 ppm at the lowest temperatures used in this study. Carbon 8 has an environment apparently similar to the corresponding carbon in **13** but is over 13 ppm downfield of this.

What these anomalous data show is that one has a significant chemical shift dichotomy between β-carbons situated on opposite faces of the 2-adamantyl frame. In both **3** and **4**, two carbons are deshielded and two are shielded, compared with the 2-methyl-2-adamantyl cation (**13**). The two effects are essentially equal so that the average of these, corrected for substituent effects, does in fact agree well with that found in **13**.

One possible explanation for these observations would be that the 5-methyl (or 4,4-dimethyl) substitution has perturbed the C–C hyperconjugative delocalization, such that one face of the cation is preferentially involved. We believe however that the temperature dependences observed for these chemical shifts are better accommodated by postulating the existence of two equilibrium structures for each cation. In a recent paper, Lambert et al.[11] discussed the difficulties in distinguishing between ^{13}C temperature-dependent chemical shifts caused by "intrinsic" factors and those due to a very rapid equilibrium where the averaged peak positions are temperature dependent because the equilibrium constant is temperature dependent. In our case however, there are several factors pointing toward an equilibrium explanation:

1. The Δδ vs *T* shifts observed for the β-carbons in **4** (250–350 range) are quite large compared with most intrinsic shifts.
2. The two β-carbon temperature shifts in **4** are of opposite sign. Normally one would expect carbons of the same multiplicity and apparent environment to have intrinsic shifts of the same sign. In fact, the values observed, +345 and −260, are consistent with an intrinsic shift of ca. 45 overlaid on the equilibrium-induced shifts, i.e., making the latter ca. ±300. Most of the intrinsic shifts reported in Table I are indeed positive, including a +85 value for the related β-carbons in the 2-methyl-2-adamantyl cation (**13**).
3. Temperature shifts of ±300 are in good quantitative agreement with an equilibrating structures model (a van't Hoff plot).
4. The structures deduced for the two isomers of **4** (see later text) bear a striking similarity to one of the structures involved in the 1-methyl-1-cyclohexyl cation equilibrium,[4] an equilibrium whose existence is on even firmer grounds. The similarity in the two equilibria also extends to the rate constants involved; i.e., both are too fast to measure by NMR line-broadening methods.

Detailed Discussion of the Proposed Equilibrium Involving Cation 4. The anomalous β-carbon ^{13}C chemical shifts observed for cation **4**, and their temperature dependence, are consistent with a rapid equilibrium between two structures, which we will show as **4C** and **4D**, where the heavy lines in these structures imply enhanced C–C hyperconjugative delocalization on only one side, which then

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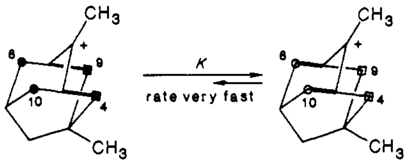
[8] Beierbeck, H.; Martino, R.; Saunders, J. K.; *Can. J. Chem.* **1980**, *58*, 102.

[9] Hirsl-Starcevic, S.; Majerski, Z. *J. Org. Chem.* **1982**, *47*, 2520.

[10] Hawkes, G. E.; Herwig, K.; Roberts, J. D. *J. Org. Chem.* **1974**, *39*, 1017.

[11] Lambert, J. B.; Vagenas, A. R.; Somani, S. *J. Am. Chem. Soc.* **1981**, *103*, 6398.

results in a quite deshielded chemical shift for the β-carbons involved. Under conditions of rapid equilibration, carbons designated ● and o will average, as will ◆ and ◇. Since we are completely unable to "freeze out" this equilibrium, the chemical shifts denoted $\delta_{\bullet}$, δ_o, $\delta_{\blacklozenge}$, and $\delta_{\lozenge}$ are not known. In order to calculate an equilibrium constant, K = [**4D**]/[**4C**], one needs estimates for these chemical shifts, e.g.



4C **4D**

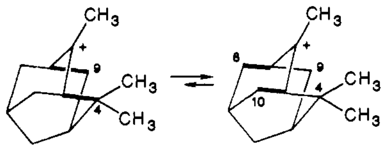
$$K = \frac{\delta_{\blacklozenge} - \delta_{av'}}{\delta_{av'} - \delta_{\lozenge}} \text{ or } K = \frac{\delta_{av} - \delta_{\bullet}}{\delta_o - \delta_{av}}$$

where δ_{av} and $\delta_{av'}$ are the experimental averaged chemical shifts for carbons ●–o (C8–C10) and ◆–◇ (C4–C9). One can see from this analysis that either chemical shift set can be used to calculate K. Conversely, K must obviously be the same number with either set.

A plot of ln K vs $1/T$ (van't Hoff plot) should be linear, and $\delta_{\bullet}$ and δ_o or $\delta_{\blacklozenge}$ and $\delta_{\lozenge}$ can in theory be adjusted to ensure a "best fit" linearity. In practice, one finds that the low-temperature chemical shift data (δ_{av} and $\delta_{av'}$) shown in Figure 1 are approaching the limiting values for carbons o and ◇; i.e., isomer **4D** is the more stable structure, and lowering the temperature drives the equilibrium toward pure **4D**. In fact, the linearity of the van't Hoff plots is quite dependent on the terms $\delta_{av'} - \delta_{\lozenge}$ or $\delta_o - \delta_{av}$, and one calculates in this way that the chemical shifts δ_o and $\delta_{\lozenge}$ are only about 3 ppm lower and higher field than the 133 K average values shown in Figure 1, e.g., δ_o 65.5 and δ 43.5. Evaluating chemical shift values for the minor isomer **4C** is not feasible using the linearity criterion of a van't Hoff plot, since the terms $\delta_{\blacklozenge} - \delta_{av'}$ or $\delta_{av} - \delta_{\bullet}$ are in any case relatively large numbers and the values assumed for $\delta_{\blacklozenge}$ and $\delta_{\bullet}$ can be varied over a wide range without much effect on this linearity criterion. In order to derive values for $\delta_{\bullet}$ and $\delta_{\blacklozenge}$, we have simply applied the 7 ppm correction due to the 5-methyl substituent, yielding $\delta_{\blacklozenge}$ 72.5 and $\delta_{\bullet}$ 36.5. Note that $\delta_{\bullet}$ and δ_o in **4C** $\rightleftarrows$ **4D** average to δ 51.0, a value virtually identical with that found in the 2-methyl-2-adamantyl cation (**13**) (where indeed $K = 1$ because the corresponding **C** and **D** structures of **13** would be degenerate). Use of the experimental data shown in Figure 1 (corrected for an estimated intrinsic shift of +45) yields an excellent van't Hoff plot, giving $\Delta H = -600 \pm 50$ cal/mol, $\Delta S = 0$. The equilibrium constant at 133 K is [**4D**]/[**4C**] = 10.

The magnitude of the chemical shift vs temperature changes ($\Delta\delta$ vs T) observed in the case of averaged ^{13}C NMR peaks is dependent on two factors: (1) the actual magnitude of the accessible K values (for a discussion see ref 4) and (2) the chemical shift separation of the peaks in the frozen-out structures. In the case of cation **4**, $\delta_o - \delta_{\bullet}$ or $\delta_{\blacklozenge} - \delta_{\lozenge}$ = 29 ppm separation, which accounts for the fact that it is uniquely these carbon peaks in **4** that are so temperature sensitive. For example, C1, C3, and C6, which have similar environments in either **4C** or **4D**, and thus a presumed similar chemical shift, have only small temperature-dependent chemical shifts, which one could not in fact have distinguished from intrinsic shifts. The moderate temperature shifts observed for the C$^+$ carbon appear unrelated to the equilibrium-derived shifts being discussed here, since one finds the same size of temperature shift for the C$^+$ carbon in cation **13**.

Equilibrating Structures Involving Cation 3. Structures for cation **3** can be represented as shown in **3C** and **3D**, where the heavy lines again denote selective and enhanced C–C hyperconjugation. In this case, we have not carried out a detailed van't Hoff analysis. However, the following points can be made:



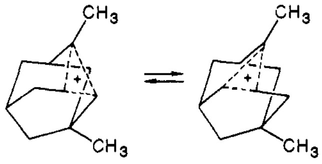
3C **3D**

1. Isomer **D** is favored over **C**. This follows from a straightforward examination of the data shown in Figure 2. Thus, the equilibrium again favors that structure where the C–C hyperconjugation involves the 2-adamantane side with no methyl substituents.

2. The equilibrium constant [**3D**]/[**3C**] is even larger (at a given T) than for cation **4**. This shows up in a smaller $\Delta\delta$ vs T dependence (corrected shifts of ca. +185 for C8 and C10 and −185 for C9). This increased K is also consistent with the actual δ_{av} values observed for **3**. For example, C8 in **3D** should have a chemical shift similar to C8 in **4D** (δ_o) (the methyl substituents in both cases are remote to this carbon). In fact δ_{av} for C8 in **3** is δ 65.3 (165 K) vs δ_{av} for C8 in **4** of δ 61.8 (165 K) and a deduced frozen-out value of δ_o 65.5 in **4D**.

3. The $\Delta\delta$ vs T shifts for C4 and C9 in **3** (Figure 2) are considerably different. A similar result is found in cyclohexyl cations, e.g., the 1,3,3-trimethyl-1-cyclohexyl cation.[4] This implies that the quaternary C4 chemical shift separation between the structures **3C** and **3D** is considerably larger than that of the methylene carbons. This same trend is also found in 1-adamantyl cations, as discussed later.

Other Possible Equilibria. In drawing **4C** and **4D** or **3C** and **3D**, we have rather arbitrarily assumed that if there are equilibrating structures involving cations **4** and **3**, then these structures involve the specific C–C hyperconjugation features described for isomers **C** and **D** in the preceding discussion. This choice was made, however, after considering two other possible options: 1. A σ-delocalization similar to that postulated in secondary 2-adamantyl cation intermediates[12] (and which is usually proposed as the reason for the retention of configuration in many solvolysis reactions), i.e., possible structures **4E** and **4F** in the case of cation **4**. However, these structures imply charge delocalization from C2 to the α-carbons C1–C3. The β-carbons occupy a pentacoordinate environment and might actually be expected to be shielded compared with those in a normal tertiary carbocation structure.[13] 2. An equilibrium between a carbocation and a covalent species formed by capture of the counterion or other nucleophile or between a free carbocation and an ion-paired species etc., where in both cases the carbocation would have to be the major species. However, the observed data fairly obviously do not fit such a proposal.[14]



4E **4F**

Theoretical Calculations on 2-Methyl-2-adamantyl Cations. It seemed worthwhile to carry out MO calculations to see whether the additional 5-methyl substituent in **4** might in some way account for the observed NMR anomalies. Completely optimized structures were computed for both **4** and **13** by using the MNDO semiempirical treatment[15] and with no imposed symmetry restraints. In each case, the single minimum structure was essentially planar about the C$^+$ center and there were only miniscule dif-

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[12] (a) Lenoir, D.; Hall, R. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 2138. (b) Storesund, H. J.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1452. (c) Nordlander, J. E.; Haky, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 1518. (d) Schleyer, P. v. R.; Lenoir, D.; Mison, P.; Liang, G.; Surya Prakash, G. K.; Olah, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 683.

[13] The partially delocalized 2-methyl-2-norbornyl cation is a good model. The C6 signal is found at the relatively high field value of δ 35.5: Kelly, D. P.; Underwood, G. R.; Barron, P. F. *J. Am. Chem. Soc.* **1976**, *98*, 3106.

[14] To rationalize the C$^+$ δ value, the major structure would have to be the free carbocation and the minor one the "ion pair". At lower temperatures, the C$^+$ signal should then shift downfield, not upfield as observed.

[15] Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

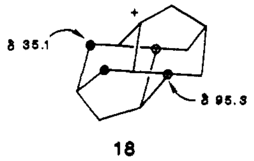
ferences in both the C_α–C_β bond lengths and in the C_β charge densities (both phenomena reflecting the magnitude of C–C hyperconjugation). In the 2,5-dimethyl analogue **4**, the bond lengths (1.57 Å) were identical to three decimal places and the charge densities differed by 0.06 unit, with the C4–C9 carbons the more positive (0.020 vs 0.014). Experimentally, if one were to regard **4** as a single structure, it is the C8–C10 carbons that are deshielded in the ^{13}C NMR spectrum.

Possible Structures for Equilibrating 2-Methyl-2-adamantyl Cations. This discussion covers both cations **3** and **4** and the 2-methyl-2-adamantyl cation (**13**), since we see no reason why the latter would not also be an equilibrating system (although completely "hidden"). Numerous authors, beginning with Schleyer,[16] have pointed out the rigidity of the adamantane ring, and only the carbocation environment has much flexibility in the sense that both an sp^2 or sp^3 center can obviously be accommodated at C2 (or any geometric variation in between these extremes). Since there is no theoretical evidence for equilibrating structures in a gas-phase and counterion-less 2-methyl-2-adamantyl cation, we begin with the premise that the *solvent and/or counterion must be part of any description.*

The pioneering work of both Olah and the Shell group in the 1960s established that "superacids" could generate observable tertiary alkyl carbocations.[17] These cations are generally regarded as "free" because their properties are relatively insensitive to solvent or concentration changes; there is no residual C–F NMR coupling and many NMR properties (chemical shift comparisons, coupling constant comparisons, etc.) are in agreement with this. However, in the case of some methylene chloride based solvent systems studied by Arnett,[18] one does see unusual chemical shift behavior, possibly indicating tight ion-pair formation. In our case, we get virtually identical NMR spectra in FSO$_3$H (R$^+$, FSO$_3^-$, FSO$_3$H solvent) as in SbF$_5$–SO$_2$ClF–SO$_2$F$_2$ (R$^+$, Sb$_2$F$_{11}^-$, excess SbF$_5$, SO$_2$ClF, and SO$_2$F$_2$ solvents). The differences in counterion size, strength of the acid system (H$_0$), and solvent polarity are considerable in this comparison and lead us to conclude that the phenomena we are observing, although typical of a condensed-phase and counterion-containing system, are not due to tight ion-pair isomers.

Given the above, one is virtually forced into the notion that the alkyl carbocations studied in this work, in a condensed phase, are able to delocalize the C2 charge *better* by having the solvation occur preferentially on one face, which probably also includes the counterion. This condensed-phase solvation "interaction" must be strong enough to overcome the slight internal energy loss that would occur in making the C$^+$ center partially pyramidal. However, since the latter distortion allows the C$^+$ orbital to be better aligned, i.e., enhanced C–C hyperconjugation on the same side of the 2-adamantane ring as the pyramidal distortion, this distortion itself is not as endothermic as one might think. More to the point, however, is that this distortion can occur on either side, thereby generating isomeric structures, degenerate or nondegenerate depending on the symmetry.

In looking for model cations that might support the above hypothesis, we were lead to the 3-biadamantyl cation (**18**). Structure **18** has been drawn to emphasize the analogy with our 2-alkyl-2-adamantyl systems and also to show the inherant C$^+$ center pyramidal distortion. The ^{13}C NMR data for **18** have been reported recently,[19] and the pertinent chemical shifts are shown with the structure. One notes that those β-carbons (o) on the same side as the pyramidal distortion are enormously deshielded relative to those (●) on the opposite side. In fact, the ● carbons in **18** have a remarkably similar chemical shift to that deduced for similar carbons in our isomer **4C** (δ 36.5). The ● carbons in **18** are considerably downfield of those deduced for similar carbons in **4C** (δ 72.5), but this may only mean that the trigonal distortion in **18** is larger than in our cases. However, cation **18** certainly establishes the principle that the chemical shifts of carbons β to a C$^+$ center could be very sensitive to a distortion of the C$^+$ center.



18

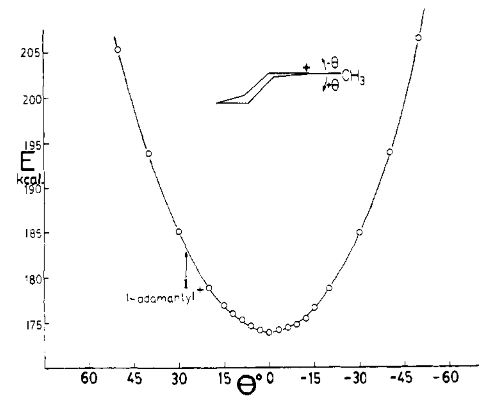
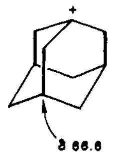
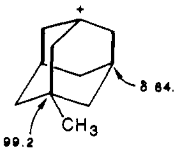


Figure 3. Calculated energy (MNDO level) of the 1-methyl-1-cyclohexyl cation as a function of the fixed distortion angle θ. All other geometric parameters were allowed to optimize at each point shown. The equivalent θ distortion angle for the optimized 1-adamantyl cation structure is also shown but the absolute energy value, of course, is different.

A comparison of the 1-adamantyl cations **19** and **20**[19,20] provides a model for the abnormally large deshielding that accompanies substitution at β-carbons involved in hyperconjugative delocalization; i.e., an abnormally large deshielding was previously inferred (from the large temperature dependence) for the C4 quaternary carbon in cation **3C**.



19



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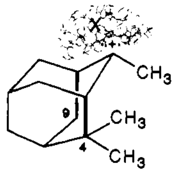

3C

Energy Considerations. Arnett and co-workers[21] have shown that solution carbocation enthalpies correlate quite well with gas-phase stabilities. Our calculated gas-phase 2-methyl-2-adamantyl cation structures do not correlate structurally with our condensed-phase cations. However, we are unable to freeze out the equilibrium rate processes in our 2-adamantyl systems, even at 133 K, and because of this, one can put a limit of $\leq$5 kcal/mol on the activation barrier involved. In other words, the assumed planar transition state is really not very different in energy and certainly would not be relevent to the rather large numbers involved in the Arnett correlation.

One might also wonder, in a quantitative way, about the energy needed to distort a gas-phase planar carbocation. To test this in an approximate way, we have computed the chair 1-methyl-1-cyclohexyl cation at the MNDO level, using a series of fixed distortion angles[22] and letting all other parameters optimize. The

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(16) Schleyer, P. v. R.; Nicholas, R. O. *J. Am. Chem. Soc.* **1961**, *83*, 182.

(17) A good review of early work in this area is provided by: Brouwer, D. M.; Hogeveen, H. *Prog. Phys. Org. Chem.* **1972**, *9*, 188.

(18) (a) Arnett, E. M.; Petro, C. *J. Am. Chem. Soc.* **1978**, *100*, 5402. (b) Arnett, E. M.; Petro, C. *J. Am. Chem. Soc.* **1978**, *100*, 5408. Other recent discussions of ionic solvation in stable carbocations can be found in: (c) Mirda, D.; Rapp, D.; Kramer, G. M. *J. Org. Chem.* **1979**, *44*, 2619. (d) Farcasiu, D. *Acc. Chem. Res.* **1982**, *15*, 46.

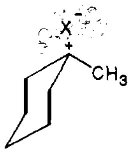
(19) Olah, G. A.; Surya Prakash, G. K.; Shih, J. G.; Krishnamurthy, V. V.; Mateescu, G. D.; Liang, G.; Sipos, G.; Buss, V.; Gund, T. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1985**, *107*, 2764.

(20) In the neutral hydrocarbon corresponding to **20**, the corresponding quaternary carbon is deshielded by only 1.4 ppm: Krishnamurthy, V. V.; Iyer, P. S.; Olah, G. A. *J. Org. Chem.* **1983**, *48*, 3373.

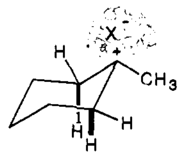
(21) (a) Arnett, E. M.; Petro, C.; Pienta, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 398. (b) Arnett, E. M.; Pienta, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 3329. (c) Arnett, E. M.; Hofelich, T. C. *J. Am. Chem. Soc.* **1982**, *104*, 3522.

results of this calculation are shown in Figure 3. The potential energy curve is fairly flat for distortions up to 15° but rises more steeply after this. In the calculated structure[23] of the 1-adamantyl cation, the planar distortion (26.5°), if applied to the 1-methylcyclohexyl cation, would yield a distortion energy of ca. 9 kcal/mol.[24] However, a 20° distortion would involve only 5 kcal/mol energy loss. We of course have no quantitative information on the size of any condensed-phase trigonal distortion in either the 2-adamantyl or 1-cyclohexyl cations, but distortions of up to ±20° do not seem unreasonable to us.

1-Alkyl-1-cyclohexyl Cation Structures. Since there are very clear-cut analogies between the properties of the C–C hyperconjugation isomer (**A**) in the cyclohexyl cation series[4] and both isomers in the 2-adamantyl series, we suggest that the cyclohexyl cations have a similar structure, i.e., one involving the solvent-counterion and the probability of some pyramidal distortion at the C$^+$ center, e.g., structures **21A** and **21B**.[25]



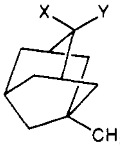
21A



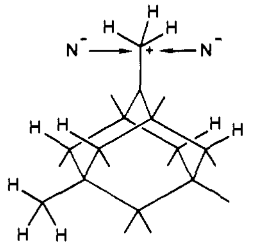
21B

The cyclohexyl and adamantyl cation studies are complementary. The former provide more definitive evidence for a rapid equilibrium of two structures, while the latter give one fewer options in actually rationalizing the nature of these structures. It would obviously be better if one had definitive NMR line-broadening evidence for these equilibria, and it is possible that very low temperature solid-state NMR spectra might be useful in this regard.

Relevance to Solvolysis Chemistry. It may be coincidental, but the results of this study do in fact correlate with some previously reported[26] (and puzzling) solvolysis data obtained on the 2,5-dimethyl-2-adamantyl compounds **23** and **24**.[27] Isomer **23**, with the methyl groups syn, solvolyzes slower than **24** and gives a product mixture with a slight net inversion of configuration at C2. Isomer **24**, however, gives a product mixture with a predominance of retention of configuration.[28] Whiting and Bone rationalize this result by assuming a planar carbocation intermediate **4** is preferentially attacked by a nucleophile on the same side as the 5-methyl group, because this group partially pushes aside the axial hydrogens on C4 and C9.[29] Our results suggest an alternative explanation based on rapidly equilibrating nonplanar cations **4C** and **4D**, in which we have found **4D** to be the more stable. Assuming these cations capture a nucleophile from the open face, then one can rationalize the results of Whiting and Bone if the **4C** ⇄ **4D** equilibration rate is only slightly faster than the nucleophile capture.



23: X = 2,4-dinitrophenolate, Y = CH$_3$
24: X = CH$_3$, Y = 2,4-dinitrophenolate



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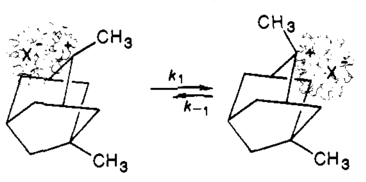

4C **4D**

Very recently, le Noble et al.[30] reported an extensive study of 2,5-disubstituted adamantanes and found several instances where a 5-substituent causes either retention or inversion at the 2-position. These authors concluded their paper with "the thought that perhaps the effects observed should be attributed to hyperconjugation, i.e. the ability of antiperiplanar bonds to delocalize charge *without* bridging. The main argument against it is that there is not precedent for the proposition that differential hyperconjugation might have *stereochemical* consequences. In other words, while in a planar 2-methyl-5-fluoro-2-adamantyl cation the distal antiperiplanar bonds may be better able to interact with the p-orbital than the proximate ones, this would not constitute an obvious reason for preferred nucleophilic approach on the fluoro side." Since superacid media are inherently very different from solvolysis media, one has to be very circumspect in making comparisons but, as with the results of Whiting and Bone, there may also be some connection between our results and those of le Nobel et al. Grob et al.[31] recently studied 2,4-disubstituted adamantanes, but these systems were secondary at the 2-position and the retention products observed seem most reasonably explained by using a σ-delocalization argument, although we find it inherently disturbing that one now proposes fundamentally different descriptions for the secondary and tertiary 2-adamantyl cations.

Conclusions

Both the 2,5-dimethyl and 2,4,4-trimethyl-2-adamantyl cations appear to exist as equilibrating structures. We assign these structures to partially pyramidalized carbocations preferentially solvated on the open face. The pyramidalization also involves enhanced C–C hyperconjugation of a type seen previously in 1-adamantyl cations. There also appear to be correlations between the stability of the above equilibrating structures and some solvolysis data, although more work remains to be done in this area.

Experimental Section

Mass spectra were obtained on a Kratos MS-80, ^{1}H NMR (in CDCl$_3$) on a Varian XL-200, and ^{13}C NMR (CDCl$_3$) on a Bruker WH-90 or

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[22] These nonplanarity distortions are expressed in terms of the angle made by the C$^+$–CH$_3$ group and the CH$_2$–C$^+$–CH$_2$ plane. Hence, a tetrahedral distortion would be $\theta = 54.7°$.

[23] The MNDO-optimized geometry corresponds closely to that reported by Sunko et al. using a STO-3G basis set: Sunko, D. E.; Hirsl-Starcevic, S.; Pollack, S. K.; Hehre, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 6163. For example, we find the identical 117.5° for the angles at the C$^+$ center.

[24] Sunko et al.[23] calculated (STO-3G) the energy of both the tetrahedral 1-adamantyl cation and the "flattened" optimized geometry, obtaining a difference of 28.6 kcal/mol. This agrees well with our 1-methyl-1-cyclohexyl cation calculations, where the difference between planar and tetrahedral structures is about 40 kcal/mol, the difference (40 − 28 = 12) corresponding approximately to the 9 kcal/mol energy still remaining in the nonplanar 1-adamantyl cation.

[25] Interestingly, the α-H/α-D kinetic isotope effect is nearly zero for the 1-adamantyl solvolysis reaction.[23] This tallies well with our finding that the differential α-C–H(D) hyperconjugation between structures A and B in cyclohexyl cations is very large, i.e., we would postulate essentially no α-C–H hyperconjugative interaction in the 1-adamantyl cation-like structure A, leaving ca. 400–600 cal/mol for the interaction difference between α-C–H and α-C–D hyperconjugation in structure B. Saunders reports an equilibrium isotope shift of 137 ± 4 cal/mol per D atom in a tertiary cyclopentyl cation case (548 cal/mol for four deuterium atoms). The hyperconjugation in the cyclopentyl ring is known to be quite efficient. Saunders, M.; Telkowski, L.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8070.

[26] Bone, J. A.; Pritt, J. R.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1447.

[27] The solvolyses of the geometric isomers of the 1,4,4-trimethyl-2-adamantyl system have been reported.[6] However, no product information was provided in the paper, probably because the primary focus of this work concerned "steric acceleration of the leaving group" as an explanation for the rapid solvolysis rates observed.

[28] About 60% of the product is the alkene and 40% is the geometric mixture of acetates. However, the proportion of alkene to acetate is very similar in both cases, and so one can make reasonably meaningful comparisons between the two different acetate ratios.

[29] The structure of 4 shown here is a plot of the actual coordinates of the MO-optimized structure. We find almost no evidence in this structure for the proposed buttressing effect of the C5 methyl; e.g., the axial H4–axial H9 distance is 2.624 vs 2.612 Å for the axial H8–axial H10 distance.

[30] Cheung, C. K.; Tseng, L. T.; Lin, M.-H.; Srivastava, S.; le Noble, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 1598.

[31] Grob, C. A.; Wittwer, G.; Rao, K. R. *Helv. Chim. Acta* **1985**, *68*, 651.

Varian XL-200 spectrometer, unless otherwise stated. Gas chromatographic analyses were made on a 530-μm (i.d.) bonded OV-1 column, ca. 20 mL/min He flow, unless otherwise noted. Melting points are uncorrected.

2,4,4-Trimethyl-2-adamantan-2-ol was prepared as described[6] from the corresponding ketone[5] and methyllithium. 2-Phenyl-2-adamantan-2-ol (**16**)[32] and 2-methyl-2-adamantan-2-ol[16] have also been described.

3-Methyl-*endo*-bicyclo[3.3.1]non-6-ene-3-carboxylic Acid (9). By use of syringe addition techniques and the general procedure of Pfeffer, lithium diisopropylamide[33] was prepared from the amine (11.7 mL, 84.6 mmol) in THF (50 mL) under argon at −20 °C by adding *n*-butyllithium in hexane (34.5 mL of 2.47 M). The acid *endo*-bicyclo[3.3.1]non-6-ene-3-carboxylic acid (**8**;[34] 4.20 g, 25.3 mmol) in a small volume of THF was then added, followed by HMPA (5.2 mL). The dark green solution was kept at 50 °C for 2 h and then cooled to 0 °C. Iodomethane (2.4 mL, 38 mmol) was then added. The color disappeared, and a solid was formed. The mixture was left overnight at room temperature and then worked up by adding 130 mL of 10% HCl, separating the organic phase, and then extracting the aqueous phase three times with pentane (3 × 100 mL). The combined organic extracts were washed consecutively with 100 mL of 10% HCl and 100 mL of saturated NaCl solution and dried over $MgSO_4$. Evaporation of the solvent gave a yellow oil. GLC analysis of this showed three peaks; the first (ca. 25%) corresponded to **8**, the second to the title acid **9** (ca. 50%), and the third (ca. 25%) to the exo isomer of **9**. These latter compounds were distinguished because **9** forms a lactone in concentrated H_2SO_4 (δ 4.5 for the ^1H H–C–O signal). Flash chromatography of the crude oil using silica gel and 9:1 pentane–ethyl acetate gave 1.49 g (32%) of pure (by GLC) acid **9** as the first eluant, followed by the other two acids. There is some **9** present in mixed fractions. An analytical sample of **9** was obtained by recrystallization from pentane: mp 114–116 °C; ^1H NMR δ 5.5–5.7 (2 H, complex), 1.25–2.5 (10 H, a number of well-resolved peaks), 1.17 (3 H, sharp s for CH_3), the COOH proton is very broad, ^{13}C NMR δ 185.32 (q), 131.13 (d), 128.99 (d), 40.43 (q), 40.20 (t), 38.84 (t), 31.85 (t), 31.79 (t), 31.15 (d), 29.34 (d or CH_3), 27.86 (CH_3 or d). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.3; H, 8.95. Found: C, 72.73; H, 8.66.

3-Methyl-*endo*-bicyclo[3.3.1]non-6-ene-3-methanol (10). The acid **9** (0.502 g, 2.8 mmol) in ether (30 mL) was added via a pressure-equalizing dropping funnel to a slurry of $LiAlH_4$ (0.9 g, 24 mmol) in ether (10 mL) under argon at room temperature. The mixture was refluxed for 12 h and left at room temperature for another 8 h. Methanol (3 mL) in ether (15 mL) was added slowly to decompose the excess hydride, and the mixture was then treated with 5% H_2SO_4 until two clear layers formed (ca. 50 mL). The two layers were separated, and the aqueous layer was extracted with four portions of ether (4 × 25 mL). The combined organic phase was washed with 5% $NaHCO_3$ and dried over $MgSO_4$. Evaporation of the solvent gave 0.437 g (94%) of a white solid, pure by GLC analysis. An analytical sample, mp 60–62 °C, was collected by preparative GLC with an OV-1 column: high-resolution mass spectrum calcd for $C_{11}H_{18}O$ 166.13577, found 166.1353; ^1H NMR δ 5.4–6.1 (2 H, alkene protons), 3.8–4.0 (2 H, CH_2O), 1.0–2.5 (10 H, complex), 0.88 (3 H, methyl); ^{13}C NMR 133.13 (d), 128.81 (d), 69.94 (t), 41.27 (t), 35.86 (t), 34.15 (q), 33.21 (t), 31.78 (t), 31.58 (d), 28.93 (CH_3), 26.87 (d). The corresponding CD_2OH compound was prepared in an analogous manner with $LiAlD_4$ as the reducing agent.

5-Methyl-2-adamantanone (7). The alcohol **10** (0.388 g, 2.33 mmol) was dissolved in 88% formic acid (22 mL) and the resultant mixture heated at reflux for 12 h. The mixture was then diluted with water and made basic with 50% NaOH. Four ether extractions (4 × 25 mL) were carried out and the combined extracts washed with water and dried over $MgSO_4$. Evaporation gave a yellow oil (partially the formates), which was saponified by passing it through a column of basic alumina, eluting with 1:9 methanol–ether. Two major compounds were collected, and these were combined and subjected to Jones oxidation, resulting after workup in 0.323 g of partially crystalline material. The GLC trace consists of two peaks in a ratio of about 3:7. The first compound is the symmetrical ether 6-methyl-2-oxatricyclo[4.3.1.1^{3,8}]undecane: ^1H NMR δ 4.14 (1 H unresolved quintet, H at C3), 368 (2 H, CH_2O), 1.4–2.1 (12 H, complex), 0.83 (3 H, CH_3), corresponding to OH addition to the double bond. This compound is not affected by the Jones oxidation conditions. The second peak is the ketone **7**. These two compounds were completely separated by flash chromatography on silica gel with 5% ether–pentane for the elution, giving 0.18 g (47%) of ketone **7** as a pure (by GLC) solid whose ^1H and ^{13}C NMR spectra were identical with those reported.[9,35] The corresponding 4,4-dideuterio ketone was prepared in an identical manner by using the corresponding deuteriated alcohol. Deuterium NMR gave a single peak at δ 1.72, and the ^{13}C NMR spectrum showed the expected splitting of the C1–C3 peak (δ 46.58 and 46.39) caused by the neighboring deuterium atoms at C4.

2,5-Dimethyl-2-adamantan-2-ol (12) and the 4,4-dideuterio analogue were obtained as a solid mixture of geometric isomers by using methyllithium in ether; cf. preparation via the Grignard addition.[35] This material was sufficiently pure to use directly for the cation preparations.

2-Phenyl-5-methyl-2-adamantanol (17) was similarly prepared as a solid ca. 1:1 geometric mixture (by GLC), which was used directly for the cation preparation.

Carbocation Preparations and NMR Spectra. These preparations involved either procedure A, B, or C, as described previously and depending on the superacid solvent system used. NMR spectra were also obtained as previously described.[4] The temperature dependence of the $CFCl_3$ peak (a doublet) was approximately measured in SO_2ClF solvent by running unlocked (XL-200) over a 60 °C temperature range and assuming that the field did not change during this procedure. The total change from −20 to −80 °C was 0.12 ppm ($+20 \times 10^4$ ppm/°C). Most of the intrinsic shifts, let alone the equilibrium-derived ones, are much larger than this.

Molecular Orbital Calculations. The MOPAC package of Dewar (QCPE No. 455) was used. On a Cyber 205 computer using the MNDO semiempirical method,[15] this program runs fully optimized structures very rapidly. We have only reported those results that were relevent to this study, but any other data are available on request.

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