The Chemistry of Protoadamantane. VI.[1] Bridged and Classical Polymethyl 2-Adamantyl Cations

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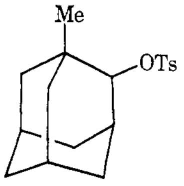
Abstract: The nature of secondary and tertiary polymethyl substituted 2-adamantyl cations was probed both solvolytically and by direct examination of the nmr spectra of stable ions in superacid media. The solvolysis rate enhancement produced by successive methyl substitution along the tosylate series, 2-adamantyl, 1-methyl-2-adamantyl, and 1,3-dimethyl-2-adamantyl, is approximately additive rather than multiplicative. Steric, inductive, and hyperconjugative effects are excluded as significant contributors to the rate enhancements, as these influences are expected to be multiplicative; participation (σ bridging) accounts for the observed behavior. This conclusion is supported by the lack of any significant rate enhancement due to methyl substitution at the adjacent bridgeheads in the tertiary 2-methyl-2-adamantyl series. Tertiary 2-adamantyl cations are classical. The proton nmr spectrum of the tertiary 1,2,3,5,7-pentamethyl-2-adamantyl cation (**28**) is unexceptional at low temperatures, but that of the secondary 1,3,5,7-tetramethyl-2-adamantyl cation (**24**) displays an anomalous >CH resonance shifted 8 ppm to higher field than that expected for a static, classical species. This behavior is attributed to a set of rapidly equilibrating partially bridged cations (**25**) which delocalize the charge away from the secondary center. The stable cations **24** or **25** and **28** undergo further rearrangements at higher temperatures involving skeletal isomerizations *via* protoadamantyl intermediates. Secondary **24** is converted to the tertiary 1,2,5,7-tetramethyl-2-adamantyl cation (**27**) by this process; the half-life is about 1 hr at −47°. The equivalent rearrangement with tertiary cation **28** is degenerate, and is much faster since steps which convert tertiary to secondary cations are avoided. The methyl groups at C_1, C_2, and C_3 of **28** interconvert with E_a = 12.1 ± 0.4 kcal/mol, log A = 13.4 ± 0.4. Molecular mechanics calculations are consistent, indicating an enthalpy difference of 9.0 kcal/mol between **28** and the postulated protoadamantyl cation intermediate, **29**. The synthesis of the compounds reported here gave difficulty. 1,3,5,7-Tetramethyladamantane did not photooximate or photochlorinate cleanly, but chromic acid oxidation produced the desired 2-functionalization. A small amount of 1,3-dimethyl-2-adamantanone (**12**) was obtained by photooximation of 1,3-dimethyladamantane; sulfuric acid oxidation of the latter did not give **12**.

As some still consider the question of σ participation by single C–C bonds, *e.g.*, in the 2-norbornyl system, to be controversial,[3,4] we decided to examine the basis for the 24–39-fold rate enhancement produced by the methyl group in 1-methyl-2-adamantyl tosylate (**1**)[1a] further. Although the magnitude of the rate enhancement observed with **1** relative to 2-adamantyl tosylates appears to be too large to be attributed to inductive or hyperconjugative[4] effects,[1a] it might be argued that this enhancement is steric in origin. Although the body of evidence we have already collected argues strongly against such an interpretation,[1] we decided to apply a symmetry test which, by now, is a well-calibrated method. The reasoning involved is illustrated by 1,3-dimethyl-2-adamantyl tosylate (**2**). If the **1**/2-adamantyl rate ratio is steric, inductive, or hyperconjugative in origin, then the presence of the second methyl group in **2** should produce a *multiplicative* effect,[5] roughly (**1**/2-adamantyl)^2. If, on the other hand, σ participation is responsible for the rate enhancement in **1** and steric, inductive, and hyperconjugative influences are negligible, then the effect of the second methyl in **2** should be *additive*[6] (strictly $2X - 1$, where X = (**1**/2-adamantyl)). Such a roughly twofold rate enhancement of **2** over **1** would be expected statistically: two σ bonds attached to methyl bearing carbons are



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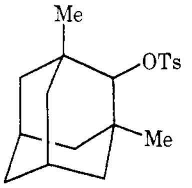

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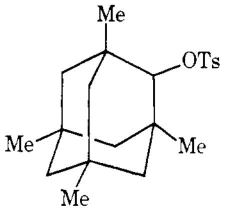

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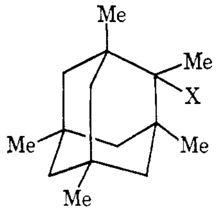

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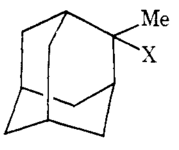

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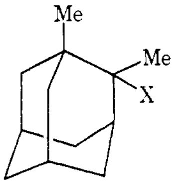

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(1) (a) Part V: D. Lenoir, D. J. Raber, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **96**, 2149 (1974). (b) Part IV: D. Lenoir, R. Hall, and P. v. R. Schleyer, *ibid.*, **96**, 2138 (1974), and preceding papers.

(2) (a) NIH Postdoctoral Fellow, 1969–1970. (b) CNRS and NATO Postdoctoral Fellow, 1970–1971. (c) A. B. Thesis, Princeton University, 1971. (d) Postdoctoral Fellow of the Stiftung für Stipendien auf dem Gebiet der Chemie, Basel, Switzerland, 1969–1971. (e) Princeton University. (f) Yale University.

(3) (a) H. C. Brown, *Chem. Soc., Spec. Publ.*, **No. 16**, 140, 174 (1962); (b) *Chem. Brit.*, 199 (1966); (c) *Chem. Eng. News*, **45**, 86 (1967); (d) "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1972, Chapters IX–XI, pp 131–205; (e) *Accounts Chem. Res.*, **6**, 377 (1973).

(4) (a) E. Kosower, "Physical Organic Chemistry," Wiley, New York, N. Y., 1968, pp 136–172; (b) F. R. Jensen and B. Smart, *J. Amer. Chem. Soc.*, **91**, 5686, 5688 (1969); (c) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *ibid.*, **93**, 5715 (1971).

(5) For multiplicative substituent effects, see *e.g.* (a) P. D. Bartlett and G. D. Sargent, *J. Amer. Chem. Soc.*, **87**, 1297 (1965); (b) P. v. R. Schleyer and G. W. van Dine, *ibid.*, **88**, 2327 (1966); (c) H. Tanida, H. Ishitobi, T. Irie, and T. Tsushima, *ibid.*, **91**, 4512 (1969).

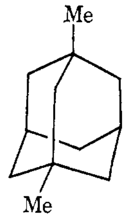
(6) For examples of additive effects, see (a) O. L. Chapman and P. Fitton, *J. Amer. Chem. Soc.*, **85**, 41 (1963); (b) C. J. Lancelot and P. v. R. Schleyer, *ibid.*, **91**, 4296 (1969).

available for backside participation during ionization of of **2**, but only one such bond in **1**.

Since **2** proved difficult to prepare in large quantities, we studied the more readily available tetramethyl analog, **3**, in greater detail. In addition, we examined tertiary compounds **4** for comparison with **5** and **6**. Direct observation of stable carbocations generated from **3**-OH and **4** provided further insight into the nature of these species and their rearrangements.

Syntheses

Methods were developed to prepare the desired 1,3-dimethyl-2-adamantyl and 1,3,5,7-tetramethyl-2-adamantyl derivatives from the readily available parent hydrocarbons, 1,3-dimethyladamantane (**7**)[7] and 1,3,5,7-tetramethyladamantane (**8**).[8] Unfortunately, this did not prove to be an easy task.



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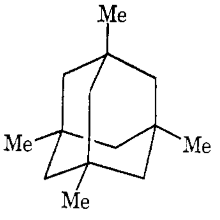

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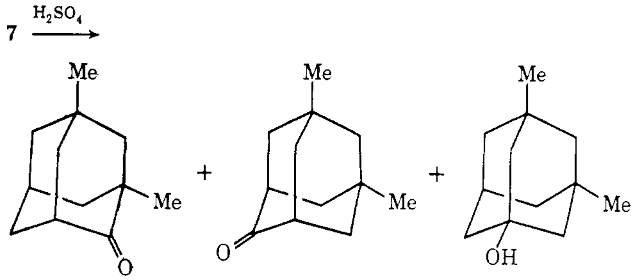
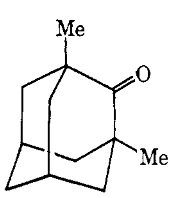
Sulfuric acid oxidation of diamondoid hydrocarbons provides routes to adamantanone[9] and to diamantanone.[10] When this reaction was applied to 1,3-dimethyladamantane (**7**), a 40% overall yield of oxidized products **9**, **10**, and **11** were obtained in a ratio of 1:2:1, but none of the desired 1,3-dimethyl-2-adamantanone (**12**) could be detected. When 1,3,5,7-tetramethyladamantane (**8**) was subjected to the sulfuric acid conditions, no simple oxidation product was found, only unreacted starting material and a small amount of tar. The lack of a tertiary hydrogen in **8** might have been responsible for this result. Since adamantanes are known to undergo intermolecular hydride exchange between secondary and tertiary positions readily,[11] we examined the oxidation of an equal molar mixture of adamantane and **8**. This approach was not successful for the production of 1,3,5,7-tetramethyl-2-adamantanone (**13**). Although some **8** was consumed (evidently being converted to tar), only adamantanone formed. Literature results on 1-methyladamantane already indicate that little ketone is formed at positions adjacent to the methyl group.[12] In addition, the overall yield using this reaction is only in the range of 10%.[13] Perhaps the reason is that 1-methyl-2-adamantyl cations have appreciable 4-methyl-4-protoadamantyl character;[1a] elimination and polymerization occur easily. The similar result with **7** should be noted. Despite the 4 : 1 statistical advantage, only half as much **9** is formed as **10**.



9 **10** **11**



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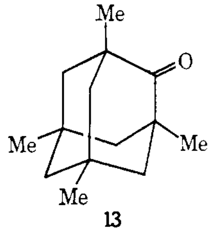

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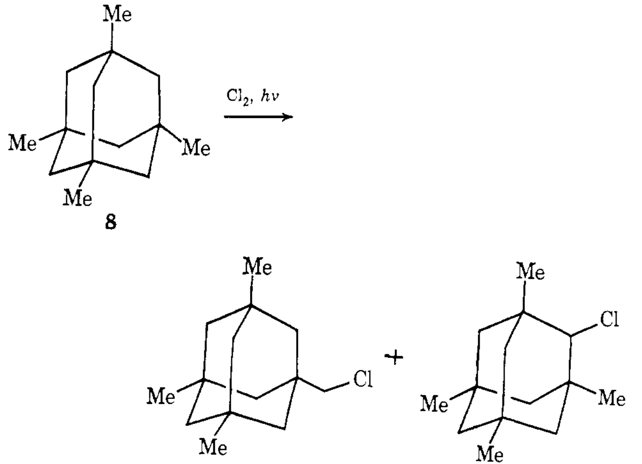
Photooximation and Photochlorination. Photooximation is another literature route to adamantanone.[14] When this reaction was applied to **7**, only a 4% overall yield of a mixture of ketones **9**, **10**, and **12** was obtained. Ketone **10** predominated and the desired **12** comprised only 5% of the product mixture. As 16% would have been expected on statistical grounds, steric hindrance may be responsible. This ketone mixture could be separated by repetitive column and gas chromatography, and a small sample of reasonably pure **12** was obtained. Further conversion by standard methods gave a limited amount of secondary tosylate **2**.

Photooximation of **8** was even less successful. At least 20 products were detected by glc and hydrolysis of this mixture gave **13** in only 0.5% yield. The photochlorination of **8** also gave rise to a complex mixture of products (see Experimental Section). The expected products, **14** and **15**, were positively identified, but formed only in low yields.



14 **15**

Chromic Acid Oxidation. Chromic acid attacks the bridgehead positions of adamantane preferentially, but

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[7] P. v. R. Schleyer and R. D. Nicholas, *Tetrahedron Lett.*, 305 (1961). The supply of 1,3-dimethyladamantane as a gift from Sun Oil Co. is gratefully acknowledged.

[8] (a) A. Schneider, R. W. Warren, and E. S. Janoski, *J. Amer. Chem. Soc.*, **86**, 5365 (1964); (b) *J. Org. Chem.*, **31**, 1617 (1966); (c) A. A. Arz, B. A. Thesis, Princeton University, 1967.

[9] H. W. Geluk and J. L. M. A. Schlatmann, *Tetrahedron*, **24**, 5367 (1968).

[10] T. M. Gund, M. Nomura, V. Z. Williams, and P. v. R. Schleyer, *Tetrahedron Lett.*, 4875 (1970).

[11] (a) P. v. R. Schleyer, L. K. M. Lam, D. J. Raber, J. L. Fry, M. A. McKervey, J. R. Alford, B. D. Cuddy, V. G. Keizer, H. W. Geluk, and J. L. M. A. Schlatmann, *J. Amer. Chem. Soc.*, **92**, 5246 (1970); (b) P. Vogel, M. Saunders, W. Thielecke, and P. v. R. Schleyer, *Tetrahedron Lett.*, 1429 (1971).

[12] H. W. Geluk and J. L. M. A. Schlatmann, *Recl. Trav. Chim. Pays-Bas*, **88**, 13 (1969).

[13] D. Lenoir and S. Pauls, unpublished results.

[14] (a) E. Müller and G. Fiedler, *Chem. Ber.*, **98**, 3493 (1965); (b) T. N. Larrimer, B. A. Thesis, Princeton University, 1968.

Table I. Summary of Solvolysis Rates

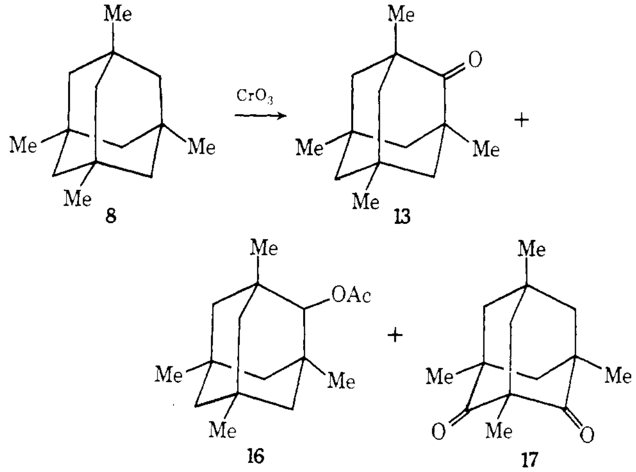
Compound	Solvent	Temp, °C	k_1, sec$^{-1\,a}$	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
1,3-Dimethyl-2-adamantyl tosylate (**2**)	80% ethanol	75.3	$(1.58 \pm 0.05) \times 10^{-3}$		
		49.7	$(9.49 \pm 0.1) \times 10^{-5}$	23.9	−3.7
		75.0	$1.53 \times 10^{-3\,b}$		
		25.0	$4.00 \times 10^{-6\,b}$		
	60% ethanol	75.3	$(7.22 \pm 0.1) \times 10^{-3}$		
		49.7	$(5.86 \pm 0.1) \times 10^{-4}$	21.3	−7.6
		75.0	$7.03 \times 10^{-3\,b}$		
		25.0	$3.47 \times 10^{-5\,b}$		
	60% acetone	75.15	$(2.28 \pm 0.06) \times 10^{-3}$		
1,3,5,7-Tetramethyl-2-adamantyl tosylate (**3**)	80% ethanol	100.0	$(3.61 \pm 0.1) \times 10^{-3}$		
		75.3	$(3.09 \pm 0.02) \times 10^{-4}$	24.1	−5.9
		75.0	$3.00 \times 10^{-4\,b}$		
		25.0	$7.52 \times 10^{-7\,b}$		
	60% acetone	75.3	$(8.74 \pm 0.75) \times 10^{-4}$		
		49.8	$(4.99 \pm 0.08) \times 10^{-5}$	24.4	−2.7
		75.0	$8.47 \times 10^{-4\,b}$		
		25.0	$1.94 \times 10^{-6\,b}$		
	Acetic acid	101.0	$(1.50 \pm 0.08) \times 10^{-3}$		
		75.3	$(5.50 \pm 0.01) \times 10^{-5}$	32.6	−7.5
		75.0	$5.28 \times 10^{-5\,b}$		
		25.0	$1.67 \times 10^{-8\,b}$		
1,2,3,5,7-Tetramethyl-2-adamantyl bromide (**4**-Br)	80% ethanol	24.95	$(1.44 \pm 0.01) \times 10^{-3}$		
		0.00	$(4.26 \pm 0.07) \times 10^{-5}$	22.3	3.1
		25.0	$1.45 \times 10^{-3\,b}$		

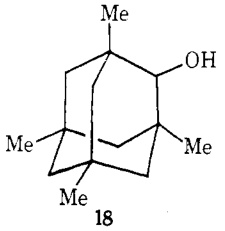
[a] Rate constants determined conductometrically. [b] Calculated values from data at other temperatures.

some ketone is also obtained.[15] Hydrocarbon **8**, lacking bridgehead hydrogens, is attacked by chromic acid to give a mixture of the desired compounds, ketone **13** and acetate **16**, as well as the dione **17**. The mixture of **13** and **16**, eluting together on column chromatography, was reduced to 1,3,5,7-tetramethyl-2-adamantanol (**18**). It was interesting that **17**, rather than the isomeric dione, **19**, was produced as a by-product. Differentiation between **17** and **19** could easily be made by nmr. In addition, reduction of **17** gave a 3:1 diol mixture of **20** and **21**; the latter displayed intramolecular hydrogen bonding in the infrared. Starting from ketone **13**, the tertiary compounds **4a–c** were prepared.

Solvolysis. Solvolysis data for **2**, **3**, and **4**-Br are summarized in Table I. Appropriate relative rate comparisons are found in Table II (secondary compounds) and Table III (tertiary derivatives).

Preparative solvolysis of **3** in 60% acetone gave a mixture of two products. The smaller component (30%) was identified as unrearranged secondary alcohol **18**. By analogy with the solvolysis product of 1-methyl-2-adamantyl tosylate,[1a] the major component (70%) was assigned tentatively the protoadamantyl structure **22**. Solvolysis of bromide **4b** gave, besides elimination, only unrearranged tertiary alcohol **4a**.





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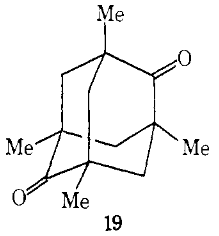

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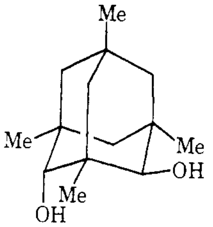

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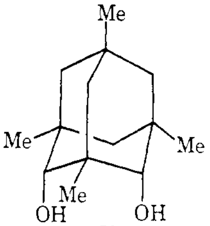

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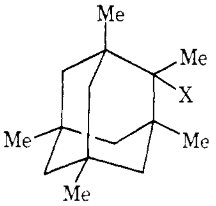

4a, X = OH
b, X = Br
c, X = Cl

Results and Discussion

Pertinent rate data of methyl- and polymethyl-substituted 2-adamantyl tosylates are summarized in Table II relative to those of the parent compound, 2-adamantyl tosylate, under the same conditions. The presence of a single methyl group adjacent to the reaction site produces a 14–21-fold rate enhancement, depending on solvent. The presence of the second flanking methyl group in 1,3-dimethyl-2-adamantyl tosylate, on the other hand, causes but a rather modest additional rate enhancement averaging 2.9 in the three solvents studied. This value is only slightly larger than

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(15) R. C. Bingham and P. v. R. Schleyer, *J. Org. Chem.*, **36**, 1198 (1971).

Table II. Rates of Methyl-Substituted 2-Adamantyl Tosylates in Various Solvents Relative to 2-Adamantyl Tosylate at 75°

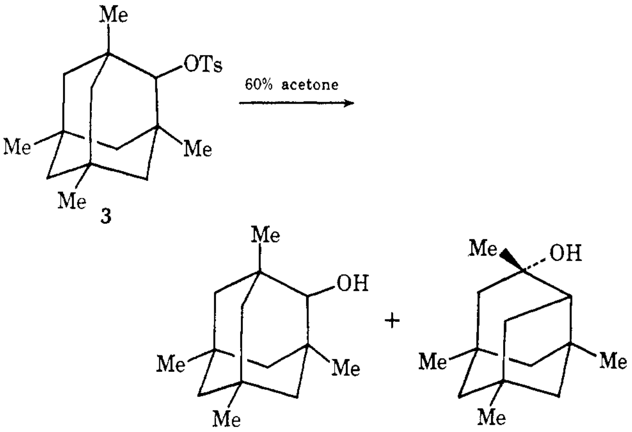
Compound	Solvent	k_{rel}[a]	$2X - 1$[b]	X^2[c]
1-Methyl-2-adamantyl tosylate (**1**)	80% ethanol	21.0[d]		
	60% ethanol	16.0[d]		
	60% acetone	14.3[d]		
1,3-Dimethyl-2-adamantyl tosylate (**2**)	80% ethanol	70 [3.3][e]	41	441
	60% ethanol	42 [2.6][e]	31	256
	60% acetone	38 [2.7][e]	27	204
1,3,5,7-Tetramethyl-2-adamantyl tosylate (**3**)	80% ethanol	15.5 (60)[f]	41	441
	60% acetone	14.2 (55)[f]	31	256
	Acetic acid	8.6 (50)[f]	27	204
1-Methyl-4-*syn*-adamantyl tosylate	Acetic acid	0.38[g]		
	TFA	0.62[g]		
1-Methyl-4-*anti*-adamantyl tosylate	Acetic acid	0.55[g]		
	TFA	0.50[g]		

[a] Calculated from rates of 2-adamantyl tosylate: P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *J. Amer. Chem. Soc.*, **92**, 2542 (1970). [b] Use of the additive model; see ref 6. [c] Use of the multiplicative model; see ref 5. [d] Reference 1a. [e] Rate relative to **1**. [f] Relative rates after correction for the effects of remote methyl groups (see text). [g] Reference 6c.

Table III. Relative Rates of Tertiary 2-Methyl-2-adamantyl Bromides in 80% Ethanol at 25°

Compound	k_{rel}[a]
2-Methyl-2-adamantyl bromide (**5-Br**)	1.0
1,2-Dimethyl-2-adamantyl bromide (**6-Br**)	1.2
1,2,3,5,7-Pentamethyl-2-adamantyl bromide (**4b**)	1.44

[a] Calculated from the rate of **5-Br**: J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2540 (1970).



that expected on an additive basis and very much smaller than the multiplicative prediction. Comparison of the third column in Table II with the last two columns emphasizes this point.

The relative rates of 1,3,5,7-tetramethyl-2-adamantyl tosylate are somewhat more complicated to interpret because of the presence of the 5- and 7-methyl groups. One might expect such distant methyl groups to have no influence on the relative rates, but the contrary is already known to be true. Rather surprisingly, methyl groups tend to decrease solvolysis rates in cage systems by significant factors.[16] The syn and anti isomers of the 1-methyl-4-adamantyl tosylates studied by Whiting afford the most pertinent examples (see Table II); decelerations range from factors of 0.38 to 0.62 depending on solvent and stereochemistry.[16c] Assuming additivity (precedent in the adamantane series already exists),[16] the average effect of *two* methyl groups at the 5 and 7 positions should be a factor of 0.26. When the experimental relative rates for 1,3,5,7-tetramethyl-2-adamantyl tosylates are corrected by dividing by this factor, the resulting corrected relative rates (shown in parentheses next to the third column in Table II) approximate the experimental relative rates for the 1,3-dimethyl-2-adamantyl tosylate solvolyses rather closely.

Thus, our conclusion that the effect of a second methyl group adjacent to the reaction site is additive rather than multiplicative is confirmed. This means that the rate acceleration observed in going from 2-adamantyl tosylate (**23**) to 1-methyl-2-adamantyl tosylate[1] is due to participation of the σ electrons and that the structures of the intermediates in the methyl-substituted cases are bridged in nature. This conclusion does not necessarily mean that the unsubstituted 2-adamantyl cation is bridged, but the difference in energy between classical and bridged structures cannot be very great. We have concluded earlier that the parent 2-adamantyl cation at most is probably only very weakly bridged, but the exact extent of this bridge or the energy difference between bridged and classical cations cannot be ascertained with accuracy.[1b]

Relative rates in the tertiary series are summarized in Table III. The rate enhancement produced by a 1-methyl group in 1,2-dimethyl-2-adamantyl bromide (**6-Br**) is only 1.2 relative to the parent 2-methyl-2-adamantyl bromide (**5**), and the substitution of all of the bridgehead position by methyl groups produces a total rate enhancement of only 1.44. (Some correction of this value due to the 5- and 7-methyl groups would be expected, but the value to be used is not available in the tertiary series.) These small rate enhancements indicate the absence of participation and a lack of any tendency toward bridging. Furthermore, there does not appear to be any significant steric effect unless a fortuitous cancellation is taking place. As pointed out earlier, the behavior of the 2-substituted 1,2-dimethyl adamantanes is not unlike that found with the 2-substituted 1,2-dimethylnorbornyl derivatives.[17] However, in contrast with the latter, the adamantane system is not capable of giving degenerate rearrangement by a simple 1,2 shift. There is a steric bias against rearrangement to the less stable protoadamantane system

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[16] (a) P. v. R. Schleyer and C. W. Woodworth, *J. Amer. Chem. Soc.*, **90**, 6528 (1968); (b) V. Buss, R. Gleiter, and P. v. R. Schleyer, *ibid.*, **93**, 3927 (1971); (c) J. A. Bone and M. C. Whiting, *Chem. Commun.*, 115 (1970).

[17] H. C. Brown and M. H. Rei, *J. Amer. Chem. Soc.*, **86**, 5004, 5008 (1964).

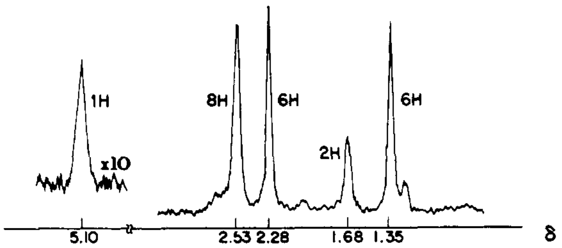
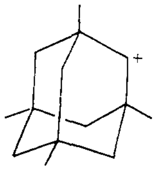


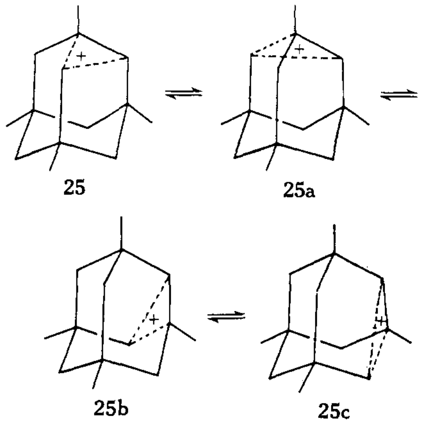
Figure 1. ^{1}H nmr spectrum of cation **24** taken rapidly at -47°.

provided the degree of carbonium ion substitution is the same. The tendency for bridging in the 2-adamantyl system, therefore, is considerably less than in the 2-norbornyl.

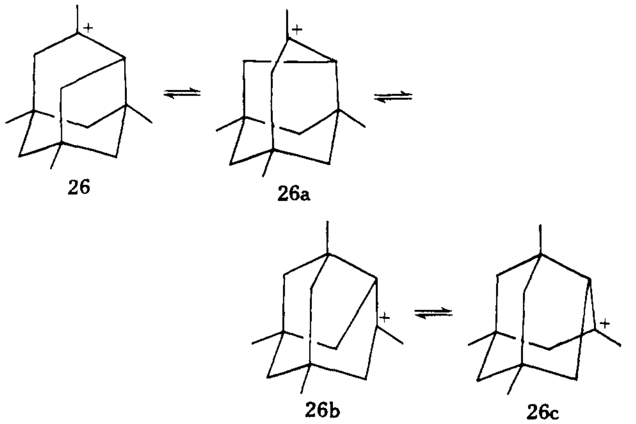
Stable Ions in Superacid. The behavior of the 1,3,5,7-tetramethyl-2-adamantyl cation in superacid media provides further illustration. The spectrum taken shortly after sample preparation at -47° (Figure 1) exhibits a simple pattern appearing superficially to resemble that expected of the classical 1,3,5,7-tetramethyl-2-adamantyl cation (**24**). As required by the symmetry of **24**, there are but two sets of methyl signals and the eight methylene hydrogens two carbons removed from the cation center exhibit but a single signal. The remote methylene shows minimal deshielding, as expected from its distant location. The remaining hydrogen is farther downfield at δ 5.1 ppm. The chemical shift of this proton provides the most direct evidence against structure **24** for the species in solution. The C–H resonance in the 2-propyl cation provides a good model of the chemical shift to be expected for hydrogen bound to the formally charged carbon in secondary cations. It is quite deshielded, at δ 13.5 ppm.[18] The fact that the methine hydrogen in the 1,3,5,7-tetramethyl-2-adamantyl cation exhibits a chemical shift 8 ppm to higher field demonstrates that there has been considerable charge delocalization away from the 2 position.



24



25 **25a** **25b** **25c**



26 **26a** **26b** **26c**

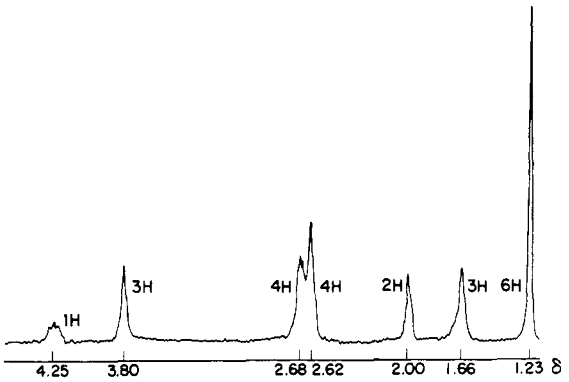
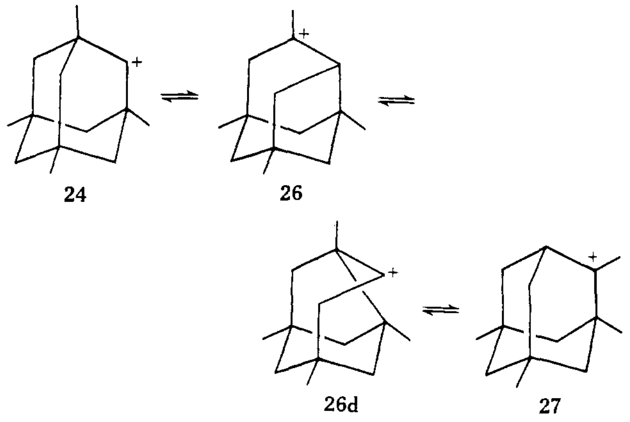


Figure 2. ^{1}H nmr spectrum of cation **27** at -47°.

The symmetry exhibited by the nmr spectrum (Figure 1) argues against a static bridged (**25**) or a static tertiary (**26**) structure for the ion in solution. However, a rapid equilibration between four equivalent bridged structures (**25**, **25a**, **25b**, **25c**) or between four classical structures (**26**, **26a**, **26b**, **26c**) provides ways to rationalize the observed behavior. For reasons already discussed in detail, we prefer the former explanation. It seems difficult to us to decide between these alternatives on the basis of a detailed analysis of the chemical shifts of the observed spectrum.

At -47°, the 1,3,5,7-tetramethyl-2-adamantyl cation rearranges to a new species with a half-life of about 1 hr. The spectrum of this new species, shown in Figure 2, is consistent with that expected for the tertiary 1,2,5,7-tetramethyl-2-adamantyl cation, **27**. Since 1,2 hydride and methyl shifts on the adamantane framework are known to have prohibitively high activation energies,[11] the mechanism of the transformation of **24** to **27** is probably that shown below.[19]



24 **26** **26d** **27**

If this mechanism is followed, the 1- and 2-methyl groups in **27** should become equivalent in the nmr at

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(18) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969).

(19) (a) Z. Majerski, P. v. R. Schleyer, and A. P. Wolf, *J. Amer. Chem. Soc.*, **92**, 5731 (1970); (b) Z. Majerski, S. H. Liggero, P. v. R. Schleyer, and A. P. Wolf, *Chem. Commun.*, 1596 (1970); (c) J. R. Alford, D. Grant, and M. A. McKervey, *J. Chem. Soc. C*, 880 (1971); (d) J. H. Wieringa, J. Strating, and H. Wynberg, *Tetrahedron Lett.*, 4579 (1970); (e) see ref 1b.

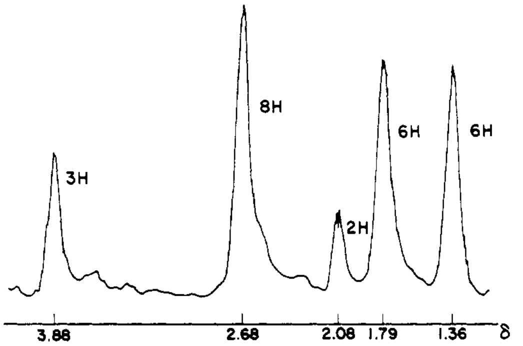


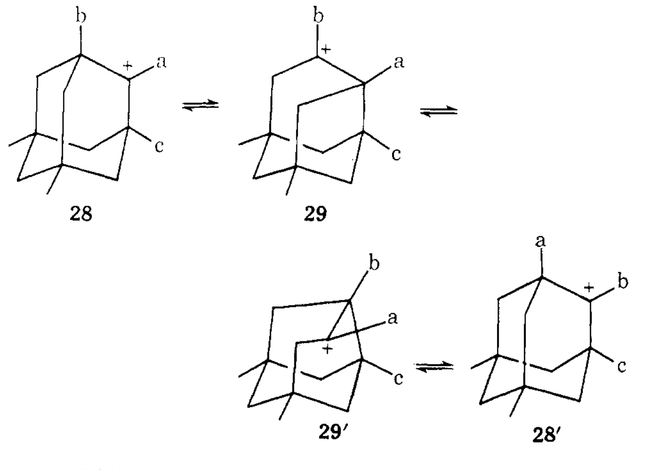
Figure 3. ^{1}H nmr spectrum of cation **28** at −72°.

higher temperatures. We studied this problem by examining the temperature dependence of the nmr spectrum of the 1,2,3,5,7-pentamethyl-2-adamantyl cation, **28**. The protoadamantyl mechanism[19] should render the methyl groups at C_1, C_2, and C_3 equivalent on time average at higher temperatures.

This is exactly what was found. At −72° the observed spectrum (Figure 3) from **4**-Cl is in accordance with that of a static cation **28**. (The broadness of the peaks is due to the viscosity of the solution.) At higher temperature, the signals for the methyl groups at 3.0 ppm (C_1–CH_3 and C_3–CH_3) and at 6.5 ppm (C_2–CH_3) broadened and eventually coalesced (Figure 4).

The line-shape analysis[20] for the two site exchange case yielded the following rate constants given as temperature (°C), k (sec^{-1}): −60.3, 17.2; −54.6, 46.5; −26.1, 1060; −10.5, 4187; −4.3, 6900; 2.0, 12650; 8.2, 19750; 14.5, 37790; 20.7, 50590. A least-squares fit gave E_a = 12.1 ± 0.4 kcal/mol; log A depends on the mechanism assumed. If **28** → **29** has the highest E_a log A = 13.5 ± 0.3, but if the the E_a for **28** → **29′** is highest, log A = 13.3 ± 0.3.

These results are consistent with the expected mechanism,[19] **28** ⇄ **29** ⇄ **29′** ⇄ **28′** (and the equivalent pro-



cess which exchanges methyls c and a). The activation energy is much lower than that for the conversion of **24** to **27** because only tertiary cations are involved and unfavorable tertiary–secondary steps such as **26** → **26d** are avoided.

Molecular mechanics was employed to estimate the energy difference between **28** and **29**.[21] The value ob-

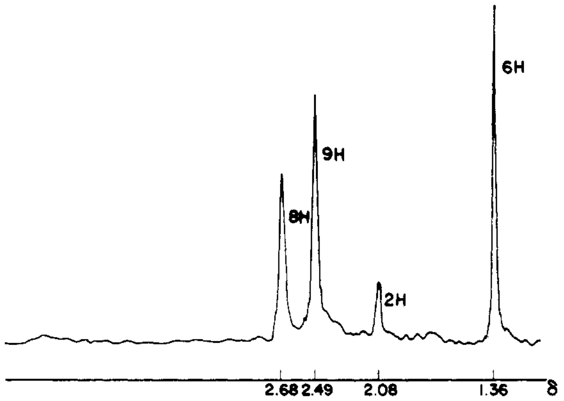


Figure 4. ^{1}H nmr spectrum of cation **28** at +27°.

tained, 9.0 kcal/mol, was 3.1 kcal/mol less the observed activation energy for the rearrangement, **28** ⇄ **28′**. This difference is reasonable if the **28** → **29** or protoadamantyl-protoadamantyl (**29** ⇄ **29**) isomerizations have a small additional activation energy; 1,2 shifts in degenerate carbocation systems are known generally to have E_a < 5 kcal/mol.[22]

Experimental Section

General. Melting points were determined on a Mettler FPI apparatus in sealed capillaries, and are uncorrected. Elemental analyses were performed by Hoffmann-La Roche, Inc., Nutley, N. J. Unless otherwise stated, pmr spectra were determined in $CDCl_3$ solution (TMS internal standard), on Varian A-60 A spectrometers. Ir spectra were recorded on a Perkin-Elmer 237 B spectrometer, the $\bar{\nu}$ (CO) and $\bar{\nu}$ (OH) were determined on a Perkin-Elmer 421 grating spectrometer in CCl_4 solution.

A Perkin-Elmer 810 gas chromatograph with flame ionization detector was used for glc analysis; 10% Carbowax 20M (10 ft × $^1/_8$ in.) columns were used unless otherwise specified. Product ratios were determined using the triangulation method. General work-up procedure means that the product was extracted with ether (unless another solvent is specified) three times; the combined ether phases were washed with 10% $NaHCO_3$ solution and with water and then dried over sodium sulfate, filtered, and evaporated *in vacuo*.

Sulfuric Acid Oxidation of 1,3-Dimethyladamantane (7). 1,3-Dimethyladamantane (10 g) and 150 ml of 96% sulfuric acid were heated at 77° for 11 hr with vigorous stirring. The solution was poured onto ice and after the general work-up procedure with ether, 4 g of crude product was obtained. Glc analysis (Carbowax 20M, 10% on Chromosorb W) showed 19% starting material and two other peaks (14 and 67%). The crude mixture (1 g) was chromatographed on a 100-g silica gel column eluting with *n*-pentane and *n*-pentane–ether mixtures. The structure of the compound eluting first as an oil (14% peak) was elucidated as 3,5-dimethyl-2-adamantanone (**9**): ir ν 1716 cm^{-1} (C=O); nmr two singlets at τ 9.12 (CH_3) and 9.09 (CH_3), and broad signals centered at 8.45, 8.28, 8.10, 7.9, and 7.55. The 2,4-dinitrophenylhydrazone was prepared from **9**, mp 160.6–162.0°.

Anal. Calcd for $C_{18}H_{22}N_4O_4$: C, 60.32; H, 6.18. Found: C, 60.70; H, 6.08.

The 67% peak consisted of material comprised of nearly equal amounts of 4,7-dimethyl-2-adamantanone (**10**) and 1,3-dimethyl-5-adamantanol (**11**);[23] these were separated by repetitive column chromatography. Ketone (**10**) was an oil: ir $\bar{\nu}$ 1723 cm^{-1} (C=O); nmr (CCl_4) singlet at τ 9.08 (2 CH_3), broad signals centered at τ 8.48, 8.30, and 7.6 (10 CH_2).

Sulfuric Acid Oxidation of 1,3,5,7-Tetramethyladamantane (8). (a) 1,3,5,7-Tetramethyladamantane (**8**) (1 g) was heated with 50 ml of 96% sulfuric acid at 77° for 8 hr with vigorous stirring. The mixture was poured onto ice; the general workup procedure with

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[20] M. Saunders, P. v. R. Schleyer, and G. A. Olah, *J. Amer. Chem. Soc.*, **86**, 5680 (1964).

[21] For the method, see J. L. Fry, E. M. Engler, and P. v. R. Schleyer, *ibid.*, **94**, 4628 (1972).

[22] (a) M. Saunders and E. L. Hagen, *J. Amer. Chem. Soc.*, **90**, 2436 (1968); (b) M. Saunders, P. Vogel, E. L. Hagen, and J. Rosenfeld, *Accounts Chem. Res.*, **6**, 53 (1973); (c) D. M. Brouwer and H. Hogeveen in "Progress in Physical Organic Chemistry," Vol. 9, A. Streitwieser and R. W. Taft, Ed., Wiley-Interscience, New York, N. Y., 1972, p 179.

[23] S. Landa, G. Vais, and J. Burkhard, *Z. Chem.*, **7**, 233 (1967).

ether gave 0.9 g of recovered starting material (glc). (b) 1,3,5,7-Tetramethyladamantane (**8**), 2.05 g, and adamantane, 2.08 g, were treated similarly with 75 ml of 96% sulfuric acid at 77° for 8 hr. The product was poured onto ice and after the general work-up 1.6 g of a crude mixture was obtained. Adamantanone was the main component of this mixture (by glc and nmr); no trace of 1,3,5,7-tetramethyl-2-adamantanone (**13**) could be detected by glc. Only 0.4 g of **8** (40%) could be recovered by sublimation, showing that some **8** was converted to tar under these reaction conditions.

Photooximation of 1,3-Dimethyladamantane (7). A photooximation apparatus described in the literature[14] was employed. 1,3-Dimethyladamantane (40 g) was dissolved in 300 ml of CCl_4 and the solution was saturated with HCl gas for 1 hr. The mixture was then photolyzed with a 100-W Hanovia lamp for 2.5 hr; during this time, HCl and NOCl gases were continually bubbled through the solution. Then HCl was allowed to bubble through the solution for 2 more hr. The oxime hydrochloride was isolated as a layer in a separating funnel. The combined fractions of oxime were refluxed in 18% sulfuric acid solution for 1 hr. After the general work-up procedure, 1.60 g of a ketone mixture, consisting of 1,3-dimethyl-2-adamantanone (**12**) (19%), 3,5-dimethyl-2-adamantanone (**9**) (73%), and 5,7-dimethyl-2-adamantanone (**10**) (18%) was obtained. Besides these ketones, 23.8 g of a mixture of mostly starting material and at least 3 chloro compounds (glc) also was obtained. One of these compounds could be isolated and identified as 3,5-dimethyl-1-chloroadamantane[24] (identified by its nmr spectrum).

The ketone mixture was chromatographed twice on a 100-g silica column, using hexane and increasing amounts of ether as eluent; 0.50 g of 1,3-dimethyl-2-adamantanone (**12**), 80% pure, was eluted first. Two distillations gave 300 mg of reasonably pure ketone (**12**). A small amount was recrystallized from *n*-pentane to give a sample: mp 40–42°; ir $\tilde{\nu}$ 1708 cm^{-1} (C=O), but an acceptable elemental analysis was not obtained; nmr singlet at τ 9.10 (2 CH_3), and broad signals at τ 8.25, 8.20, and 7.9 (10 CH_2).

1,3-Dimethyl-2-adamantyl Tosylate (2). 1,3-Dimethyl-2-adamantanone (**12**) (150 mg) was reduced with 16 mg of $LiAlH_4$ in 5 ml of ether by the standard procedure leading to 120 mg of reasonably pure 1,3-dimethyl-2-adamantanol: nmr singlet at τ 9.17 (2 CH_3), 7.0 (C*H*OH), and broad signal between 8.1 and 9.1. The alcohol was converted to the tosylate[25] with 255 mg of tosyl chloride in 2 ml of pyridine (2 weeks in the refrigerator). The resulting tosylate contained nearly 40% of starting material, shown by its nmr and ir spectra. This crude product (**8**) was used for solvolysis studies.

Photooximation of 1,3,5,7-Tetramethyladamantane (8). Tetramethyladamantane (22.6 g) dissolved in 300 ml of CCl_4 was photooximated in the same way as described for 1,3-dimethyladamantane. The resulting crude oxime mixture was hydrolyzed by refluxing with 18% sulfuric acid. After the usual work-up and chromatography on silica gel 0.1 g of ≈90% pure 1,3,5,7-tetramethyladamantanone (**13**) was obtained. In several experiments, the yield of **13** could not be raised above 0.5%. The CCl_4 layer of the photooximation reaction contained *ca.* 50% starting material, *ca.* 15% chloro compounds, and more than 20 by-products, detectable by glc. The fraction of monochloro compounds consisted of a 3:2 mixture of 1,3,5,7-tetramethyl-2-chloroadamantane (**15**) and 1-chloromethyl-3,5,7-trimethyladamantane (**14**) (see following experiment).

Photochlorination of 1,3,5,7-Tetramethyladamantane (8). Tetramethyladamantane, 3.55 g, was dissolved in 30 ml of CCl_4. Chlorine was bubbled through the solution for 20 min during irradiation with a 150-W lamp. About 3 g of chlorine was absorbed during this time. The solvent was evaporated *in vacuo*, giving 4.8 g of a mixture of at least ten compounds (glc). The three less polar compounds were separated by chromatography on silica gel using *n*-pentane as eluent to give a 2.9-g fraction. This mixture was separated by preparation glc (15% FFAP 20 ft × $^3/_8$ in.). The least polar compound was **8**. The second compound was identified as 1,3,5,7-tetramethyl-2-chloroadamantane (**15**). The structure of the third compound could be shown to be 1-chloromethyl-3,5,7-trimethyladamantane (**14**): ir (film) $\tilde{\nu}$ 2940–2820 and 765 cm^{-1}; nmr singlet at τ 9.17 (3 CH_3), two signals at 8.97 and 8.90 (12 CH_2), and singlet at 6.35 (CH_2Cl).

Chromic Acid Oxidation of 1,3,5,7-Tetramethyladamantane (8). 1,3,5,7-Tetramethyladamantane (2.9 g) (0.0145 mol) was dissolved in 40 ml of acetic acid and 40 ml of acetic anhydride; 5 g of chromium trioxide was added over a 10-min period and the mixture was stirred for an additional 40 hr at 35°. The solution was poured onto ice and the product was isolated by 5 × 50 ml extraction with ether. The combined ether extracts were washed with saturated Na_2CO_3 solution until neutral. The ether phase was washed with H_2O and the general work-up procedure followed to give 3 g of crude reaction product. Separation on 85 g of silica gel using *n*-pentane as solvent yielded 0.95 g (33%) of starting material, **8**. When a mixture of *n*-pentane–1% ether was used as solvent, 1.20 g of a mixture of 1,3,5,7-tetramethyl-2-adamantanone (**13**) and 1,3,5,7-tetramethyl-2-adamantyl acetate (**16**) was isolated, followed by a third fraction consisting of 0.55 g (18%) of pure 1,3,5,7-tetramethyl-2,4-adamantanedione (**17**): mp 138–139.5° (*n*-pentane); ir 1733 and 1704 cm^{-1} (CO); nmr singlets at τ 9.03 (1 CH_3), 8.90 (2 CH_3), 8.90 (2 CH_3), 8.88 (1 CH_3), and broad peaks centered at 8.50, 8.22, and 8.10 (8 adamantyl H).

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.25; H, 9.08.

1,3,5,7-Tetramethyl-2-adamantanol (18). The second fraction above (ketone **13** and acetate **16**) (1.2 g) was reduced with an excess of $LiAlH_4$ in anhydrous ether by the standard procedure to give 1.1 g of 1,3,5,7-tetramethyl-2-adamantanol (**18**): mp 86.5–88.5° (*n*-hexane); ir 3620 cm^{-1}; nmr singlet at τ 9.15 (CH_3 at C-1 and C-3), double peak at 9.22 (CH_3's at C-5 and C-7), broad signals centered between 8.4 and 9.4 (11 adamantyl H and OH), and broad singlet at 6.09 (C*H*OH).

Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C 80.54; H, 11.60.

1,3,5,7-Tetramethyl-2-adamantyl Tosylate (3). The alcohol (**18**) was converted into its tosylate, mp 107.0–108.5° (*n*-pentane), by the tosyl chloride–pyridine method[25] (15 days at room temperature): nmr singlets τ 9.72 (CH_3 at C-1 and C-3), 7.70 (tolyl CH_3), and 5.68 (b, CH-OTs), double peak at 9.22 (CH_3's at C-5 and C-7), 2.8, and 3.2 (AB of 4 aromatic H), and broad peaks between 8.5 and 9.1 (10 adamantyl H).

Anal. Calcd for $C_{21}H_{30}SO_3$: C, 69.57; H, 8.38. Found: C, 69.37; H, 8.35.

1,3,5,7-Tetramethyl-2-chloroadamantane (15). 1,3,5,7-Tetramethyl-2-adamantanol (0.5 g) was treated with 3 ml of PCl_3 for 24 hr at room temperature and then heated to 70° for 30 min. The mixture was poured onto ice; the usual ether extraction and washing gave 0.55 g of 1,3,5,7-tetramethyl-2-chloroadamantane: ir (film) 2940–2820 and 765 cm^{-1}; nmr singlet at τ 9.07 (CH_3's at C-1 and C-3) and 6.35 (C*H*Cl), double peak at 9.16 (CH_3's at C-5 and C-7), and broad signals between 8.15 and 9.35 (10 H, CH_2's).

Anal, Calcd for $C_{14}H_{23}Cl$: C, 74.14; H, 10.22; Cl, 15.24. Found: C, 74.05; H, 10.00; Cl, 15.71.

1,3,5,7-Tetramethyl-2-adamantanone (13). To 0.58 g of 1,3,5,7-tetramethyl-2-adamantanol dissolved in 5 ml of acetone was added 2 ml of Jones CrO_3 reagent,[26] and the mixture was stirred for 3 hr. After the excess CrO_3 was destroyed by addition of methanol, the mixture was poured into 30 ml of water. After the usual extractive work-up, the crude product was chromatographed on 80 g of silica gel using a mixture of hexane–1% ether as eluent. Pure 1,3,5,7-tetramethyl-2-adamantanone (**13**) was obtained (0.53 g, 90% yield): mp 109–110° (*n*-pentane); ir $\tilde{\nu}$ 1707 cm^{-1} (CO) (sharp); nmr singlet at τ 9.07 (4 CH_3's) and 7.52 with shoulder at 7.53 (5 CH_2's).

Anal. Calcd for $C_{14}H_{22}O$: C, 81.49; H, 10.75. Found: C, 81.50; H, 10.69.

Reduction of 1,3,5,7-Tetramethyl-2,4-adamantanedione (17). 1,3,5,7-Tetramethyl-2,4-adamantanedione (60 mg) was reduced with 30 mg of $LiAlH_4$ by refluxing overnight in 10 ml of absolute ether. After the usual work-up procedure, 51 mg of a crude mixture was obtained which was separated by preparative tlc (20 g of silica gel G on 20 × 20 cm plate); a 15-mg portion of the mixture was eluted with *n*-pentane–5% ethyl acetate. The less polar compound (29.3 mg, 48%) was shown to be 1,3,5,7-tetramethyl-2a,2e-adamantanediol (**20**): mp 153.5–155°; ir 3640 cm^{-1}; nmr singlets at τ 9.19, 9.15, 9.11 (4 CH_3's), 6.88, and 6.70 (CHOH), and broad signals between 8.35 and 8.95 (10 H for CH_2 and OH).

Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78; O, 14.26. Found: C, 74.73; H, 10.80; O, 14.47.

The more polar compound (10.2 mg, 16%) was shown to be 1,3,5,7-tetramethyl-2a,4a-adamantanediol (**21**): mp 170.5–172.0°; ir 3640 and 3530 cm^{-1}; nmr singlet at τ 9.24 (CH_3), 9.10 (2 CH_3),

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[24] R. L. Fort, Jr., and P. v. R. Schleyer, *J. Org. Chem.*, **30**, 789 (1965).

[25] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1968, p 1180.

[26] C. Djerassi, P. R. Engle, and A. Bowers, *J. Org. Chem.*, **21**, 1547 (1956).

8.90 (CH_3), and 6.95 (2 C*H*OH), and broad signals centered at 8.8 (10 H for CH_2 and OH).

Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.29; H, 10.54.

1,2,3,5,7-Pentamethyl-2-adamantanol (4-OH). Methylmagnesium iodide (5 m*M*) was prepared by reaction of 0.12 g of magnesium and 0.35 ml of methyl iodide in 5 ml of absolute ether. To this solution, 0.41 g (2.0 m*M*) of 1,3,5,7-tetramethyl-2-adamantanone dissolved in 20 ml of absolute ether was added dropwise with stirring. After the mixture was refluxed for 2 hr, the usual work-up procedure gave 0.4 g (90%) of crude 1,2,3,5,7-pentamethyl-2-adamantanol (4-OH): mp 39.0–40.5° (*n*-pentane); ir 3610 cm^{-1} (film); nmr singlets at τ 9.27 (2 CH_3), 9.20 (2 CH_3), and 8.84 (CH_3 at C-2), and broad signals centered at 9.32, 9.15, 8.94, 8.65, 8.38, and 8.18 (11 H for CH_2 and OH).

Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.76. Found: C, 80.95; H, 11.83.

1,2,3,5,7-Pentamethyl-2-chloroadamantane (4-Cl). 1,2,3,5,7-Pentamethyl-2-adamantanol (4-OH) (0.27 g, 0.8 m*M*) was dissolved in 1 ml of phosphorus trichloride and the mixture stirred for 24 hr. After heating to 75° for an additional 2 hr, the mixture was poured onto ice.

The standard isolation procedure gave 0.25 g (87%) of crude 1,2,3,5,7-pentamethyl-2-chloroadamantane (14-Cl) as a semisolid: nmr singlets at τ 9.18 (2 CH_3), 9.01 (2 CH_3), 9.01 (2 CH_3), and 8.42 (CH_3 at C-2), and broad signals centered at 8.9, 8.8, 8.15, and 7.85 (5 CH_2's).

Anal. Calcd for $C_{15}H_{25}Cl$: C, 74.81; H, 10.46; Cl, 14.72. Found: C, 74.98; H, 10.37; Cl, 14.59.

1,2,3,5,7-Pentamethyl-2-bromoadamantane (4-Br). 1,2,3,5,7-Pentamethyl-2-adamantanol (0.4 g, 1.8 m*M*) was dissolved in 1 ml of phosphorus tribromide and the mixture was stirred for 3 hr at room temperature. An additional 4 ml of PBr_3 was added and the stirring continued for 20 hr; the mixture was then heated to 70° for 2 hr. After the mixture was cooled, ice was added to hydrolize excess PBr_3. The bromide was extracted with ether; the general work-up procedure gave 0.5 g (90%) of crude 1,2,3,5,7-pentamethyl-2-bromoadamantane (4-Br): mp 133.0–136.0°; nmr singlets at τ 9.19 (CH_3), 9.15 (CH_3), 8.93 (2 CH_3), and 8.76 (CH_3 at C-2), and complex signals centered at 8.85, 8.47, 8.22, 8.00, and 7.8 (5 CH_2's).

Anal. Calcd for $C_{15}H_{25}Br$: C, 63.15; H, 8.83; Br, 28.01. Found: C, 62.98; H, 8.86; Br, 28.29.

Solvolysis. Ethanol, acetone, and acetic acid were purified by standard procedures.[27] The kinetic solvolyses were followed conductometrically with a Wayne-Kerr Model B 337 impendence bridge, capable of 0.1% accuracy. The conductivity cells used had bright platinum electrodes, cell constants of 0.2–0.4, and a volume of approximately 25 ml. In a typical experiment a 10^{-3} *M* solution was placed in the cell, which was sealed and equilibrated with shaking for 5 min in a constant-temperature bath. In general 10–15 points were taken. The raw conductance data were then fitted to the first-order rate equation by means of a LSKIN least-squares computer program.[28]

Product Analysis. A Perkin-Elmer 810 gas chromatograph with flame ionization detector was used for glc analyses. Carbowax 20M (5% M Chromosorb W) $^1/_8$-in. columns were found to give good separations at 145°. Peaks ratios were determined by triangulation.

Solvolysis of 1,3,5,7-Tetramethyl-2-adamantyl Tosylate in 60% Acetone. 1,3,5,7-Tetramethyl-2-adamantyl tosylate (2 mg) was dissolved in 0.2 ml of 60% acetone buffered with 0.02 *M* 2.6-lutidine. The solution was heated for 30 min at 75° (6 half-lives).

After cooling, the solution was injected directly into the gas chromatograph. Besides a peak corresponding to 1,3,5,7-tetramethyl-2-adamantanol (**18**) (30%) (retention time 8.5 min), a second peak, believed to be due to 1,4,6,8-tetramethyl-4-*exo*-protoadamantanol (**22**) (70%) (retention time 11 min) was observed. The same solution was heated for a period of 60 and 90 min. The same result was obtained in either case. When the tosylate was solvolyzed in unbuffered 60% acetone for 60 min at 75°, only one peak corresponding to 1,3,5,7-tetramethyl-2-adamantanol was observed.

Attempts to isolate (**22**) by preparative column chromatography using silica gel gave only **18** in 40% yield, due, evidently, to rearrangement to the thermodynamically more stable **18**. The low yield may also indicate that most of the product polymerized or was otherwise lost during chromatography.

Solvolysis of 1,2,3,5,7-Pentamethyl-2-adamantyl Bromide in 60% Acetone. 1,2,3,5,7-Pentamethyl-2-adamantyl bromide (2 mg) was dissolved in 0.2 ml of 60% acetone buffered with 0.05 *M* 2,6-lutidine. The solution was heated to 50° for 3 min (6 half-lives). The solution was directly injected into the gas chromatograph. Besides a peak (62%) with retention time indicating a hydrocarbon (apparently elimination product) a second peak (38%) could be detected. The second peak was identified as unrearranged alcohol (4-OH) by coinjection with authentic material.

Preparation of Solutions of Stable Cations. Ionization of 1,3,5,7-Tetramethyl-2-chloroadamantane (15). 1,3,5,7-Tetramethyl-1-chloroadamantane (0.12 g) was distilled into mixture of 3 g of SbF_5 and 4.2 ml of SO_2ClF *in vacuo*. At −100° a colorless mixture was obtained, containing crystallized SbF_5. At −60°, SbF_5 dissolved and the spectrum was recorded. TMS was the external standard.

Ionization of 1,2,3,5,7-Pentamethyl-2-chloroadamantane (4-Cl). 1,2,3,5,7-Pentamethyl-2-chloroadamantane (0.1 g) was introduced into a reaction flask as a solution in 0.5 ml of CCl_4. Evacuation removed the solvent and 1.0 ml of SO_2ClF was distilled on a vacuum line into the reaction vessel and allowed to dissolve the chloride. Upon addition of 6.5 g of SbF_5 at low temperature, a colorless ion solution resulted, which was transferred at −90° to an nmr tube and sealed *in vacuo*, and the spectra (Figures 3 and 4) were recorded. At +27° appreciable decomposition occurred.

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[27] (a) H. Lund and J. Bjerrum, *Justus Liebigs Ann. Chem.*, **64**, 210 (1937); (b) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1961, p 171.

[28] D. F. Detar, "Computer Programs for Chemistry," Vol. 1, W. A. Benjamin, New York, N. Y., 1968.