

The Chemistry of Protoadamantane. V. Solvolysis of 4-Methyl-4-protoadamantyl and Related 1-Methyl-2-adamantyl Derivatives¹

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Abstract: The solvolyses of the following systems were studied in detail: 4-methyl-4-*endo*-protoadamantyl (I); 4-methyl-4-*exo*-protoadamantyl (II); 1-methyl-2-adamantyl (III); and 1,2-dimethyl-2-adamantyl (IV). The 4-methyl-4-*exo*-protoadamantyl (II) and 1-methyl-2-adamantyl (III) solvolyses are *both* anchimerically assisted to the extent of about 10^1 – $10^{1.5}$ and give a common bridged intermediate, IX. Unlike the 2-norbornyl system, the addition of a 1-methyl group to adamantane *increases* bridging in the intermediate, because of balanced steric strain and electronic stabilizing factors. The solvolysis of 4-methyl-4-*endo*-protoadamantyl dinitrobenzoate (I-ODNB) does not appear to be assisted, but leads to the same intermediate, IX, by "leakage." Essentially the same product mixtures, 60–70% III-OH, 24–33% II-OH, and 2–7% olefins, are obtained in buffered 60% acetone from I-ODNB, II-ODNB, and III-OTs. Assistance in the solvolysis of 1-methyl-2-adamantyl system (III) is shown by the observed β -methyl acceleration, 24–38, and by the low α -CH₃/H ratio (IV-Br/III-Br = 10^6 vs. $10^{7.5}$ for 2-methyl-2-adamantyl bromide/2-adamantyl bromide). The β -methyl effect in the tertiary case, IV-Br, is negligibly small, 1.2. The α -methyl/H ratio is normal ($10^{7.7}$) for the 4-*endo*-protoadamantyl system, but is low ($10^{3.8}$) for the 4-*exo*-protoadamantyl series. This ratio, and the high absolute rate constants, allow an estimate of 10^4 – 10^5 for the anchimeric assistance in 4-*exo*-protoadamantyl solvolyses. Free energy diagrams utilizing rate and product data allow the estimation of the strain in protoadamantane, which exceeds that in adamantane by 11.3 kcal/mol. This value is in good agreement with the results of molecular mechanics calculations.

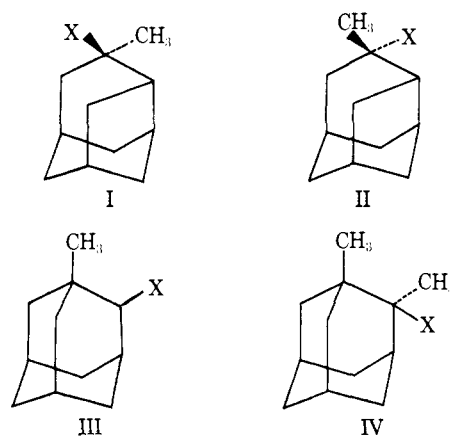
The apparent total lack of nucleophilic solvent participation in the ionization of 2-adamantyl derivatives makes them ideal model substrates against which the behavior of other secondary substrates is to be compared.³ Although such solvent participation was excluded on the basis of extensive experimental evidence,³ the extent of anchimeric assistance to 2-adamantyl solvolysis is more difficult to evaluate. A direct relationship between the 2-adamantyl and 4-*exo*-protoadamantyl cations was demonstrated, but it was concluded that the 2-adamantyl cation, if bridged, must be a highly unsymmetrical species resembling the classical 2-adamantyl cation closely.^{1b}

(1) (a) Preliminary accounts of this work were presented at the 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, Abstract PETR-040, and were published as the first paper of this series: D. Lenoir and P. v. R. Schleyer, *Chem. Commun.*, 941 (1970). (b) Paper IV: D. Lenoir, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **96**, 2138 (1974). (c) Paper VI: D. Lenoir, P. Mison, E. Hyson, P. v. R. Schleyer, M. Saunders, P. Vogel, and L. A. Telkowski, *ibid.*, **96**, 2157 (1974).

(2) (a) National Institutes of Health International Postdoctoral Fellow, 1969–1970; (b) National Institutes of Health Postdoctoral Fellow, 1968–1970.

(3) (a) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2538 (1970); (b) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **92**, 2540 (1970); (c) P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, **92**, 2542 (1970); (d) S. H. Liggero, J. J. Harper, P. v. R. Schleyer, A. P. Krapcho, and D. E. Horn, *ibid.*, **92**, 3789 (1970); (e) J. A. Bone and M. C. Whiting, *Chem. Commun.*, 115 (1970); (f) J. M. Harris, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 5729 (1970); (g) J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **93**, 2551 (1971); V. J. Shiner, Jr., and R. D. Fisher, *ibid.*, **93**, 2553 (1971); (h) D. J. Raber, J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **93**, 4821 (1971); (i) T. W. Bentley, F. L. Schadt, and P. v. R. Schleyer, *ibid.*, **94**, 992 (1972); (j) J. E. Nordlander, R. E. Gruetzmacher, and F. Miller, *Tetrahedron Lett.*, 927 (1973); (k) review, D. J. Raber and M. Harris, *J. Chem. Educ.*, **49**, 60 (1972); (l) review, P. v. R. Schleyer in "Reaction Transition States," J. E. Dubois, Ed., Gordon and Breach, New York, N. Y., 1973, p 197; (m) D. Lenoir, *Chem. Ber.*, **106**, 78 (1973); (n) *ibid.*, **106**, 2366 (1973); (o) J. L. Fry, E. M. Engler, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 4628 (1972); (p) L. M. Sinnot, H. J. Storesund, and M. C. Whiting, *Chem. Commun.*, 1000 (1969); (q) J. M. Harris, J. F. Fagan, F. A. Walder, and D. C. Clark, *Tetrahedron Lett.*, 3023 (1972).

In this paper, we examine the effects of β -methyl substitution designed to *enhance* the bridged nature of the 2-adamantyl cation. For completeness, both 4-*endo*- and 4-*exo*-4-methylprotoadamantyl (I and II) as well as 1-methyl-2-adamantyl (III) substrates were studied. The behavior of the analogous tertiary 1,2-dimethyl-2-adamantyl bromide (IV-Br) provided comparison.

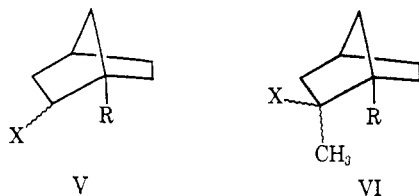


In classical carbocation systems, the observed inductive-hyperconjugative effect of β -methyl substitution on solvolysis rates is relatively minor.⁴ For example, the 2-butyl tosylate/isopropyl tosylate ratio is 5.9 for solvolysis in trifluoroacetic acid;⁵ smaller values are observed in other solvents and for β -methyl substitution in tertiary substrates.⁴ β -Methyl groups typically produce much larger rate enhancements in nonclassical systems due to the possibility of more efficient electron donation.^{4b} Thus, 1-methyl-2-*exo*-nor-

(4) (a) R. C. Bingham and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3189 (1971), and references therein cited. (b) For a summary, see W. F. Sliwinski, T. M. Su, and P. v. R. Schleyer, *ibid.*, **94**, 133 (1972).

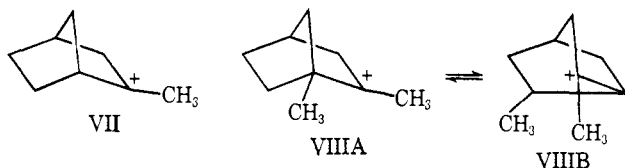
(5) P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. A. Sipp, *J. Amer. Chem. Soc.*, **87**, 5169 (1965).

bornyl derivatives (V, R = CH₃) solvolyze 52–68 times faster than the corresponding 2-*exo*-norbornyl analogs (V, R = H).⁶ The 1-methyl rate enhancement in the



2-*endo*-norbornyl series is only 1.1, indicating the classical nature of the solvolysis transition states of these compounds.⁶

In tertiary systems the electronic influence of a β -methyl group should be smaller. Because tertiary ions are inherently more stable than secondary ions, bridging ordinarily does not play as important a role.⁷ For solvolysis of the 1-R-2-methyl-2-norbornyl systems (VI), the β -CH₃/H ratios are 4.3 in the *exo* and 4.8 in the *endo* series.⁸ It is clear that 2-methyl-2-norbornyl (VII)^{8,9} and 1,2-dimethyl-2-norbornyl¹⁰ cations (VIII A and VIII B) are classical or nearly classical, unlike the parent 2-norbornyl cation.⁹



These variously substituted 2-norbornyl systems form an interesting set for comparison and contrast with corresponding 2-adamantyl derivatives. Carbocation stabilizing substituents at the 1 position of 2-adamantyl systems are already known to have a large influence on the degree of rearrangement found under conditions of kinetic control. Thus, while deamination of 2-adamantylamine in acetic acid gave only 7% of rearranged 4-*exo*-protoadamantyl acetate,^{9p} the same reaction applied to 1-hydroxy-2-adamantylamine gave 4-protoadamantanone exclusively.¹ A methyl group at the 1 position would be expected to influence the solvolysis of a secondary 2-adamantyl derivative significantly and, in contrast to the norbornyl system,^{8–10} to enhance the bridged nature of the ensuing intermediate.

Results

Syntheses. The 1:2 epimeric mixture of the 4-methyl-4-protoadamantanol obtained by methyl Grignard addition to 4-protoadamantanone¹¹ was separated by silica gel chromatography. The major isomer, eluting first, was 4-methyl-4-*exo*-protoadamantanol (II-OH).¹² The configurational assignment of the ter-

tiary compounds I and II was based initially on solvolytic behavior. The more reactive 4-methyl-4-protoadamantyl dinitrobenzoate was assigned the 4-*exo* structure (II-ODNB) by analogy with the behavior of the secondary 4-protoadamantyl derivatives.¹ Analysis of the solvolysis products provided confirmation. Reaction of either tertiary protoadamantyl ester, I-ODNB or II-ODNB, or of 1-methyl-2-adamantyl tosylate (III-OTs) in buffered 60% acetone gave (see below) only 4-methyl-4-*exo*-protoadamantanol (II-OH) and none of its epimer in the product mixture. The relationship between the 2-adamantyl and 4-*exo*-protoadamantyl cationic systems, established in the previous paper,^{1b} can reasonably be expected to hold for the tertiary cases.

Since the assignment of configuration of compounds I and II is critical, an independent confirmation was desired. The Eu(dpm)₃ shift technique,^{13a} which has been applied to secondary 4-*exo*- and 4-*endo*-protoadamantanol,^{13b} was used to examine I-OH and II-OH.^{13c} Ten of the 18 protons could be assigned with the aid of double resonance. The Eu(dpm)₃ shifts and the coupling constants of the protons at C-2, C-3, and C-5 of I-OH and II-OH correspond to those observed with the related secondary 4-protoadamantanol and are quite characteristic for *endo* and *exo* alcohols. On this basis, the assignment of I and II was established unequivocally.

1,2-Dimethyl-2-adamantyl bromide (IV-Br) was prepared by reaction of PBr₃ with the tertiary alcohol (IV-OH) produced by methyl Grignard addition to 1-methyl-2-adamantanone.¹¹ 1-Methyl-2-adamantyl bromide (III-Br) was already available.¹¹

Solvolytic Rates and Products. Solvolysis rate and relative rate data are summarized in Tables I and III, respectively. The product studies posed a dilemma. Because of the great difference in reactivities of systems I, II, and III, the same conditions and leaving groups could not be used. For example, if the same leaving groups were to be employed, the temperatures would have to be vastly different. We chose to use the same solvent and temperature, but to vary the leaving groups.¹⁴

Table II shows that the product compositions from I-ODNB, II-ODNB, and III-OTs are essentially the same, indicating that a common cationic intermediate is involved. The small variation in product compositions (if real) is to be expected because of differences in the counterions and their locations.¹⁵

Under thermodynamically controlled conditions, III-OH is the only product found.¹¹ Likewise, III-OPNB would be expected by internal return from I-OPNB or II-OPNB. III-OPNB, which would be stable to the solvolytic conditions, was not detected in the products.

Discussion

The solvolysis of 2-methyl-2-adamantyl tosylate

(12) The stereochemistry of Grignard addition contrasts with that of LiAlH₄ reduction of 4-protoadamantanone which gave predominately 4-*endo*-protoadamantanol.¹

(13) (a) J. K. M. Sanders and D. H. Williams, *J. Amer. Chem. Soc.*, **93**, 641 (1971), and references cited therein; (b) J. Boyd and K. H. Overton, *J. Chem. Soc., Perkin Trans. 1*, 2533 (1972); (c) K. H. Overton and G. P. Moss, private communication.

(14) P. v. R. Schleyer, P. Le Perchec, and D. Raber, *Tetrahedron Lett.*, 4389 (1969).

(15) *Cf.*, e.g., B. M. Benjamin and C. J. Collins, *J. Amer. Chem. Soc.*, **92**, 3183 (1970).

(6) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 3901 (1967).

(7) A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962.

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

(9) (a) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *J. Amer. Chem. Soc.*, **92**, 4627 (1970); (b) G. D. Mateescu, J. L. Riemenschneider, and G. A. Olah, *ibid.*, **94**, 2529 (1972).

(10) (a) G. A. Olah, J. R. DeMember, C. Y. Lui, and R. D. Porter, *J. Amer. Chem. Soc.*, **93**, 1442 (1971); (b) H. Goering and K. Humski, *ibid.*, **90**, 6213 (1968); H. L. Goering, C. Brown, and C. B. Schewene, *ibid.*, **90**, 6214 (1968); (c) H. C. Brown and M. H. Rei, *ibid.*, **90**, 6216 (1968); H. C. Brown and K.-T. Liu, *ibid.*, **89**, 466 (1967), and related references; (d) G. A. Olah and G. Liang, *ibid.*, **96**, 189 (1974).

(11) D. Lenoir, R. Glaser, P. Mison, and P. v. R. Schleyer, *J. Org. Chem.*, **36**, 1821 (1971).

Table I. Summary of Solvolysis Rates

Compound	Solvent	Temp., °C	k_1 , sec ⁻¹ ^a	ΔH^\ddagger	ΔS^\ddagger	β -CH ₃ /H 25°	
1-Methyl-2-adamantyl tosylate (III-OTs)	80% ethanol	74.9	$(4.02 \pm 0.02) \times 10^{-4}$	24.9	-2.9	34.6	
		50.4	$(2.45 \pm 0.04) \times 10^{-5}$				
		25.0	$8.35 \times 10^{-7}{}^b$				
	60% ethanol	75.0	$(2.40 \pm 0.01) \times 10^{-3}$	23.6	-3.1		
		50.5	$(1.68 \pm 0.01) \times 10^{-3}$				
		25.0	$6.73 \times 10^{-6}{}^b$				
	60% acetone	75.2	$(8.59 \pm 0.10) \times 10^{-4}$	23.1	-6.6		
		51.1	$(6.74 \pm 0.08) \times 10^{-5}$				
	Acetic acid	100.0	25.0	$2.69 \times 10^{-6}{}^b$	26.7		0.3
			74.8	$(2.18 \pm 0.04) \times 10^{-3}$			
25.0			$(1.51 \pm 0.02) \times 10^{-4}$				
1-Methyl-2-adamantyl bromide (III-Br)	80% ethanol	100.1	$(2.45 \pm 0.08) \times 10^{-5}$	25.0	-3.1		
		75.0	$(2.00 \pm 0.08) \times 10^{-6}$				
		25.0	$4.01 \times 10^{-9}{}^b$				
2-Adamantyl tosylate	80% ethanol	25.0	$2.41 \times 10^{-8}{}^{b,c}$	26.9	-3.0		
	60% ethanol	25.0	$2.49 \times 10^{-7}{}^{b,c}$	25.7	-2.4		
	60% acetone	25.0	$1.11 \times 10^{-7}{}^{b,d}$	25.3	-5.5		
	Acetic acid	25.0	$5.94 \times 10^{-9}{}^{b,c}$	28.1	-2.1		
2-Adamantyl bromide	80% ethanol	25.0	$1.04 \times 10^{-10}{}^{b,c}$	27.5	-11.9		
	80% ethanol	25.8	$(4.62 \pm 0.03) \times 10^{-3}$	21.5	2.6		
1,2-Dimethyl-2- adamantyl bromide (IV-Br)	0.0	$(1.39 \pm 0.01) \times 10^{-4}$					
	25.0	$4.12 \times 10^{-3}{}^b$	21.5	2.3			
2-Methyl-2-adamantyl bromide	80% ethanol	25.0			$3.46 \times 10^{-3}{}^{b,e}$		
	4-Methyl-4- <i>endo</i> - protoadamantyl 3,5-dinitrobenzoate (I-ODNB)	60% acetone	100.0	$7.45 \times 10^{-3}{}^b$	25.1	-1.4	
75.1			$(6.16 \pm 0.10) \times 10^{-4}$				
51.0			$(3.84 \pm 0.05) \times 10^{-5}$				
4-Methyl-4- <i>exo</i> - protoadamantyl 3,5-dinitrobenzoate (II-ODNB)	60% acetone	100.0	$4.37 \times 10^{-2}{}^b$	22.6	-4.6		
		51.0	$(3.76 \pm 0.12) \times 10^{-4}$				
4- <i>exo</i> -Protoadamantyl 3,5-dinitrobenzoate	60% acetone	100.2	$4.4 \times 10^{-6}{}^d$	21.0	-2.7		
		25.0	$2.8 \times 10^{-9}{}^{b,d}$				
2-Methyl-2-adamantyl 3,5-dinitrobenzoate	60% acetone	100.1	$(5.10 \pm 0.10) \times 10^{-4}$	26.0	-4.3		
		75.2	$(3.84 \pm 0.08) \times 10^{-5}$				
		25.0	$5.86 \times 10^{-8}{}^b$				
<i>tert</i> -Butyl 3,5-dinitro- benzoate	80% acetone	100.0	$1.55 \times 10^{-6}{}^f$	28.3	-5		
		25.0	$8.34 \times 10^{-10}{}^{b,f}$				
	60% acetone	100.0	$3.9 \times 10^{-4}{}^g$				
		25.0	$3.1 \times 10^{-6}{}^g$				

^a Rate constants determined conductimetrically. ^b Calculated values from data at other temperatures. ^c Reference 3c. ^d Reference 1b. ^e Reference 3b. ^f K. B. Wiberg, J. E. Hiatt, and K. Hsieh, *J. Amer. Chem. Soc.*, **92**, 544 (1970). ^g Calculated from data in 80% acetone by the equation, $\log(k/k') = m\Delta Y$, using $m = 1$ and $\Delta Y = 1.47$: A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

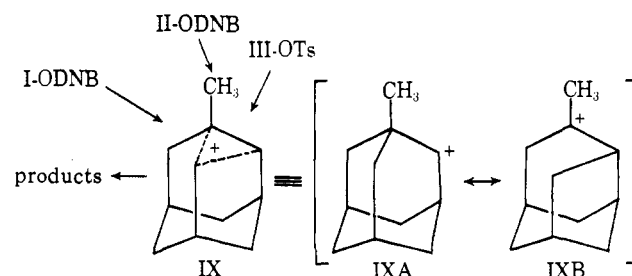
Table II. Solvolysis Products in 60% Acetone, 75°^a

Starting material	1-Methyl-2- adaman- tanol (III-OH), %	4-Methyl- 4- <i>exo</i> - protoada- mantanol (II-OH), ^c %	Olefins, ^b %
	1-Methyl-2-adamantyl tosylate (III-OTs)	70	28
4-Methyl-4- <i>exo</i> - protoadamantyl dinitrobenzoate (II-ODNB)	69	24	7
4-Methyl-4- <i>endo</i> - protoadamantyl dinitrobenzoate (I-ODNB)	60	33	7

^a Buffered with 0.01 M lutidine. Percentages given are the normalized results from glc analysis and are probably accurate to 3-4%. ^b Unidentified, but probably 4-methyl-4-protoadamantene or 4-methyleneprotoadamantane. ^c 4-Methyl-4-*endo*-protoadamantanol was not detected in the solvolysis products (*i.e.*, less than 1%).

(III-OTs) and of 4-methyl-4-*exo*-protoadamantyl 3,5-dinitrobenzoate (II-ODNB) leads directly to a common

bridged ion, IX, from which the products, chiefly II-OH and III-OH, arise. The same bridged ion, IX, is formed indirectly ("leakage") from 4-methyl-4-*endo*-protoadamantyl 3,5-dinitrobenzoate (I-ODNB). Thus, unlike the secondary 4-protoadamantyl and 2-adamantyl series,¹ the bridged ion IX dominates the chemistry of I, II, and III.



Brown has inveighed against the need to invoke σ -bridged intermediates with emphasis on the norbornyl series.¹⁶ It is clear that care must be employed be-

(16) (a) H. C. Brown, *Chem. Soc., Spec. Publ.*, No. 16, 140, 174 (1962); (b) *Chem. Brit.*, 199 (1966); (c) *Chem. Eng. News*, **45**, 86

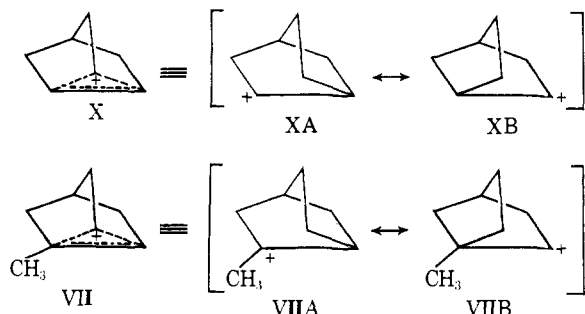
fore postulating such σ -delocalized species. Nevertheless, we feel that the evidence we have assembled is overwhelming in favor of IX. In fact, the 2-adamantyl-4-protoadamantyl system behaves according to "textbook" expectations, and is free from many of the apparent anomalies of the 2-norbornyl system, to which Brown has called attention.¹⁶

Before considering the evidence for IX in detail, we wish to contrast the differences in behavior expected because of methyl substitution in the 2-adamantyl and 2-norbornyl cations.

The bridged norbornyl cation usually represented by X can be regarded as a hybrid of structures XA and XB. Of course, these structures do *not* represent the classical norbornyl cations, since their geometries, charge distributions, etc., must be different. Since XA and XB are equivalent, the bridged norbornyl cation *may* (but is not required to) possess C_2 symmetry.

A methyl substituent at C-2 (VII) destroys this symmetry, since VIIA now contributes more than VIIIB. This means that if the 2-norbornyl cation is nonclassical, it must be unsymmetrically bridged, as has been suggested recently.⁹ The methyl group decreases bridging in the intermediate cation,⁹ but *increases* bridging at the transition state for solvolysis of 1-methyl-2-*exo*-norbornyl tosylate.⁶

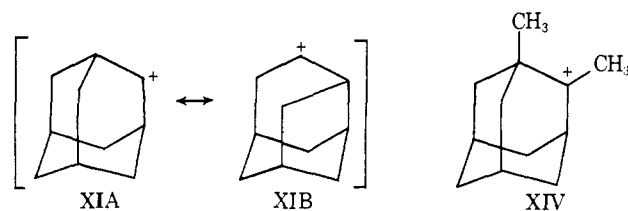
The addition of a second methyl substituent, while potentially restoring the C_2 symmetry, does not, in fact, do so, and the resulting cation is a rapidly equilibrating pair of classical or partially bridged species (e.g., VIIIA and VIIIB).¹⁰ This is due to the greater ability of



methyl groups to stabilize classical over bridged cations.¹⁷

The situation pertaining in the adamantane series is different. The bridged 2-adamantyl cation must be inherently unsymmetrical, that is, structures XIA and XIB cannot contribute equally. As has been discussed in the preceding paper, the 2-adamantyl cation, if bridged at all, must be very weakly bridged, with XIA contributing much more than XIB. The actual structure should resemble rather closely the classical 2-adamantyl cation rather than the more highly strained 4-protoadamantyl cation.^{1b}

Addition of a 1-methyl group should *increase* bridging in *both* in the intermediate (IX) and in the 1-methyl-2-adamantyl tosylate solvolysis transition state, in con-



trast to the situation pertaining in the 2-norbornyl cation. Because of the presence of the cation stabilizing methyl group, IXB should contribute significantly, and the structure of the resulting hybrid should be intermediate between the more strained but tertiary 4-methyl-4-protoadamantyl cation (XII) and the less strained but secondary 1-methyl-2-adamantyl cation (XIII).

The addition of a second methyl group should restore the very largely classical nature to the system, *i.e.*, XIV should be an adequate representation.

The chemical facts are in complete agreement with these analyses.

Products. The presence of the methyl group in IX has a major effect in product composition, increasing the percentage of protoadamantyl material obtained under kinetic conditions nearly 100-fold from 0.4% in the secondary case^{1b} to ~30% (Table II). (The 4-methyl-4-protoadamantanol is much less stable than 1-methyl-2-adamantanol and are completely converted to the latter under thermodynamic conditions.)¹¹ The product compositions from I-ODNB, II-ODNB, and III-OTs (Table II) are sufficiently similar that one can conclude that all three substrates are reacting through a common cationic intermediate. That this intermediate is bridged ion IX is suggested by the formation of only a single tertiary alcohol, II-OH, and none (<1%) of its epimer, I-OH. This result contrasts with the majority of reactions in the protoadamantyl series, where significant amounts of *endo* attack are found even though *exo* attack usually predominates.^{1,11} Examples include the reaction of 4-protoadamantone with LiAlH_4 or methyl Grignard, and the bromination,^{1,11,18} epoxidation,^{1,11} and hydroboration^{13b,19} of 4-protoadamantene. The oxymercuration of 4-protoadamantene is the only other reaction in this series which appears to give exclusive *exo* attack.^{1,11,18}

The solvolytic behavior of I-ODNB also contrasts with its secondary counterpart, 4-*endo*-protoadamantyl tosylate, which gives in buffered 60% acetone 20% of 4-*endo*-protoadamantanol (along with 2-adamantanol).^{1b} This behavior was ascribed to a not very stable degenerate 4-*endo*-protoadamantyl bridged ion which permitted extensive leakage;^{1b} as would be expected, leakage appears to be complete in the tertiary 4-methyl-4-*endo*-protoadamantyl series.

Rates. The β -Methyl Effect. The presence of the 1-methyl substituent in III-OTs produces a 24–38-fold solvolysis rate enhancement (Table I, last column). That this appreciable effect is due to bridging and not to steric or inductive effects is shown by the very low $\beta\text{-CH}_3/\text{H}$ ratio of 1.2 in the tertiary series (1,2-dimethyl-2-adamantyl bromide (IV-Br) *vs.* 2-methyl-2-adamantyl bromide, Table I).

It is possible to argue that the rate enhancement

(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); (f) for the latest comprehensive review of the 2-norbornyl cation, see G. D. Sargent in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1972, Chapter 24, pp 1099–1200.

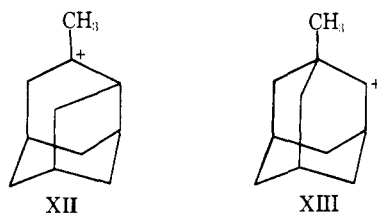
(17) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 311 (1972), and unpublished work; C. F. Wilcox, L. M. Loew, and R. Hoffmann, *ibid.*, **95**, 8192 (1973).

(18) B. D. Cuddy, D. Grant, and M. A. McKerver, *Chem. Commun.*, 27 (1971).

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produced by the 1-methyl group in the 1-methyl-2-*exo*-norbornyl system is due to the possibility of direct conversion to the more stable tertiary 2-methyl-2-norbornyl ion (VII).^{6,16} Only the transition state and not necessarily the intermediate need be bridged. Only tertiary norbornyl substitution products are formed under kinetic conditions.^{6,20}

The same argument cannot be applied to the 1-methyl-2-adamantyl case, since the rearranged 4-methyl-4-protoadamantyl ion (XII), while tertiary, is not necessarily expected to be more stable because of its much higher ring strain than the 1-methyl-2-adamantyl cation (XIII). Thus, in comparing XII and XIII, carbonium ion stability and ring strain factors tend to cancel. Direct evidence is provided by the obtention of 1-methyl-2-adamantanol (III-OH), and not the tertiary alcohol II-OH, as the major product under kinetic conditions (Table II).



Thus, the appreciable β -CH₃ rate enhancement observed with III-OTs (Table I) must mean that the intermediate is bridged. If the intermediate were the classical 1-methyl-2-adamantyl cation (XIII), no appreciable rate enhancement would be expected.²¹ If the intermediate were the classical 4-methyl-4-protoadamantyl cation (XII), it would have to be much more stable than the classical 1-methyl-2-adamantyl cation (XIII) in order to explain the observed 1-methyl rate enhancement. In that case, the product would be expected to be completely tertiary (and probably a mixture of epimers I-OH and II-OH), contrary to observation.

If the classical 1-methyl-2-adamantyl (XIII) and 4-methyl-4-protoadamantyl (XII) cations were comparably stable, and rapidly equilibrating, then one could not account for the large 1-methyl rate enhancement observed in the solvolysis of III-OTs.

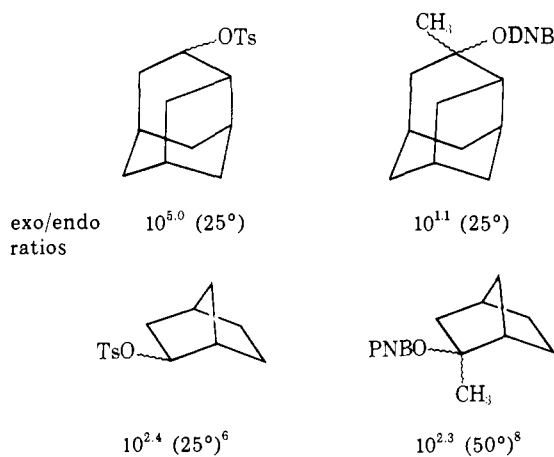
The most reasonable conclusion, then, is that bridged ion IX is the intermediate involved. IX benefits from some methyl stabilization without incurring very much destabilization due to strain increase.

Exo/Endo Ratios. The exo/endo ratios for systems in which participation is occurring with one epimer and not the other is expected to be much greater in the secondary than in the tertiary series, because of the greater stability of classical tertiary cations. Some representative exo/endo ratios are summarized below.

Although, as Brown has emphasized, there is little variation of the exo/endo ratio in going from the secondary to the tertiary 2-norbornyl series,^{8,16} the same is not true in the 4-protoadamantyl systems. The high secondary 4-protoadamantyl exo/endo ratio is reduced by nearly 10³ when 4-methyl groups are added. This large reduction occurs despite evidence for some an-

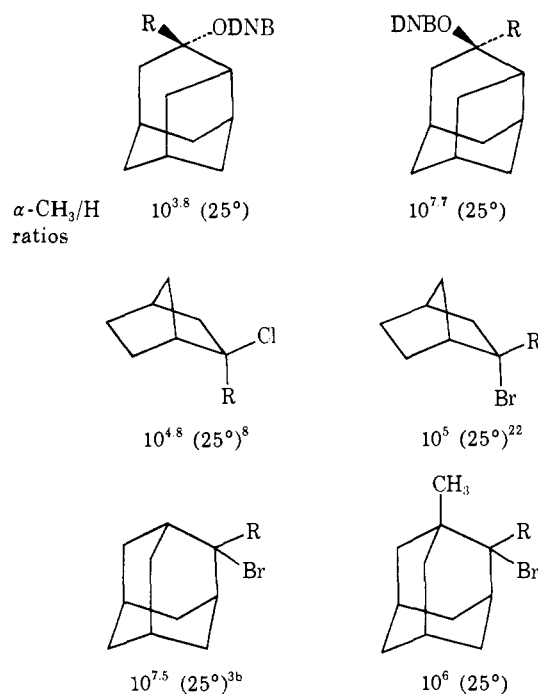
(20) Cf. the 1-methyl-2-bicyclo[2.2.2]octyl system studied by W. Kraus, C. Chassin, P. Chassin, and P. Schmutte, *Justus Liebigs Ann. Chem.*, **738**, 97 (1970). The β -CH₃/H rate ratio is 94 at 25° in 80% ethanol (D. Lenoir, unpublished observation).

(21) This conclusion is supported by the additive rather than multiplicative effect of β, β' -dimethyl substitution. See paper VI (ref 1c).



chimeric assistance in the solvolyses of 4-*endo*-protoadamantyl tosylate^{1b} and of 4-methyl-4-*exo*-protoadamantyl 3,5-dinitrobenzoate (II-ODNB) (see below); the assistance in the case of 4-*exo*-protoadamantyl 3,5-dinitrobenzoate must be much larger. This is confirmed by an analysis of the α -methyl effects.

α -Methyl/H Ratios. The magnitude of the rate increase produced by an α -methyl substituent is a measure of the amount of assistance—anchimeric or solvent—present in a system.^{3b, 4b} It has been proposed that such α -CH₃/H ratios should be $\approx 10^8$ in the total absence of solvent and anchimeric assistance.^{3b} Representative α -CH₃/H ratios are presented below.



The α -CH₃/H ratio for the 4-*endo*-protoadamantyl system is as high as that found for the 2-adamantyl standard.^{3b} Although the high value for the former may be partly due to leaving group steric effects,^{3b} it is clear that the magnitude of participation must be small in both secondary and tertiary (I) 4-*endo*-4-protoadamantyl systems.

The same is not true for the 4-*exo*-protoadamantyl series, where the low α -CH₃/H ratio of 10⁴ provides

(22) Estimated from literature and unpublished data by J. M. Harris, private communication.

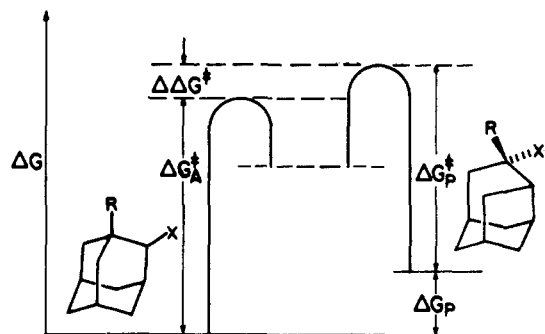


Figure 1. Free energy diagram relating protoadamantyl and adamantyl systems.

further evidence for extensive participation in the secondary derivative. The depression of the α -CH₃/H ratio from $\sim 10^8$ to 10^4 gives a direct measure of the difference in extent of anchimeric assistance in the secondary *vs.* the tertiary series, and thus provides a minimum value (10^4) for participation in 4-*exo*-protoadamantyl solvolysis.

The depression of the α -CH₃/H ratio from $10^{7.5}$ in the 2-adamantyl to 10^6 in the 1-methyl-2-adamantyl system (IV/III) is another indication of anchimeric assistance in III. The magnitude of this α -CH₃/H ratio depression— $10^{1.5}$ or a factor of 30—agrees quantitatively with the magnitude of the β -CH₃ effect on the solvolysis of 1-methyl-2-adamantyl tosylate (III-OTs) or bromide (III-Br) (Table 1). This value, although also a minimum, is probably a reasonable estimate for the magnitude of anchimeric assistance during solvolysis of III, since little or no assistance is expected in the 2-adamantyl, 2-methyl-2-adamantyl, or 1,2-dimethyl-2-adamantyl systems.^{1,3}

Thus, the α -CH₃/H ratios respond as expected in the 2-adamantyl-4-protoadamantyl series. This is in contrast to the 2-norbornyl system, where low values are found in both *exo* and *endo* series.¹⁶ These $\approx 10^5$ values can be rationalized by the postulation of anchimeric assistance in the *exo* and solvent assistance in the *endo* secondary cases,^{3b} but adverse steric effects (tertiary > secondary) may provide an alternative explanation in the latter instance.¹⁶

The relative rates of protoadamantyl derivatives (Table III and ref 1b) afford another method of estimating the magnitude of anchimeric assistance, although steric effects involving the methyl substituents and the

Table III. Relative Rates of 3,5-Dinitrobenzoates in 60% Acetone^a

Compound	Rel rates	
	25°	100°
<i>tert</i> -Butyl	1.0	1.0
2-Methyl-2-adamantyl	1.9	1.3
4-Methyl-4- <i>endo</i> -protoadamantyl (I-ODNB)	38	19
4-Methyl-4- <i>exo</i> -protoadamantyl (II-ODNB)	520	110
4- <i>endo</i> -Protoadamantyl	8×10^{-7} ^b	2×10^{-6} ^b
4- <i>exo</i> -Protoadamantyl	0.09	0.011

^a Data from Table I unless otherwise indicated. ^b Values estimated from those of 4-*endo*-protoadamantyl tosylates by the conversion procedure discussed in the preceding paper, ref 1b.

leaving groups may be influencing the reactivities somewhat.

Judging from the behavior of 4-methyl-4-*endo*-protoadamantyl dinitrobenzoate (I-ODNB) (Table III), expected to solvolyze without significant anchimeric assistance, the 4-protoadamantyl system is "inherently" more reactive than the 2-adamantyl. On the basis of all the evidence considered the following rough estimates of the degrees of anchimeric assistance can be made: 2-adamantyl, $<10^1$; 4-*endo*-protoadamantyl, 10^9 – 10^1 ; 1-methyl-2-adamantyl (III), $\sim 10^{1.5}$; 4-methyl-4-*exo*-protoadamantyl (II), $\sim 10^1$; 4-*exo*-protoadamantyl, 10^4 – 10^5 .

Other Mechanistic Criteria. A variety of criteria have established that solvent assistance is absent in 2-adamantyl solvolysis.³ It is of interest to compare some of these criteria with those of 1-methyl-2-adamantyl (III), in which participation is enhanced. Data in Table I allow the calculation of the following for III: k_{OTs}/k_{Br} (80% ethanol, 25°) = 210 (the 2-adamantyl value is 231);^{3a} $(k_{ROH}/k_{AcOH})_Y(25^\circ) = 0.3$ (the 2-adamantyl value is 0.1);^{3a} and m (60 and 80% ethanol) = 0.80 (the 2-adamantyl value is 0.91).^{3a} These parameters appear to respond to changes in the degree of anchimeric assistance as do the α -CH₃/H ratios.

Ring Strain in Protoadamantane. Free energy diagrams, first specifically applied to solvolytic systems by Goering and Schewene,²³ are very useful analytically. This approach can be used to derive the relative ground-state energies of systems interconnected by common intermediates.^{22,10b,c} The 2-adamantyl-4-protoadamantyl system affords an excellent application, since no experimental estimate of the strain energy is available and direct equilibration techniques are not feasible, protoadamantane being too highly strained to exist in amounts measurable by ordinary techniques.^{1,24}

Figure 1 illustrates the free energy diagram to be applied. ΔG^\ddagger_P and ΔG^\ddagger_A are the activation free energies available from the solvolysis rate constants (estimated for the same leaving groups); $\Delta\Delta G^\ddagger_{\text{products}} = -RT \ln (A/P)$, where A/P is the kinetically controlled product ratio in the solvent where the solvolysis rates were carried out. With these data available, the ground state of the protoadamantane system, relative to the adamantane, ΔG_P , can be evaluated from

$$\Delta G_P = \Delta G^\ddagger_A + \Delta\Delta G^\ddagger_{\text{product}} - \Delta G^\ddagger_P \quad (1)$$

The required data and calculated ΔG_P values are summarized in Table IV. The ΔG_P value derived from the secondary systems, 11.0 kcal/mol, is probably the best estimate for the protoadamantyl system itself, since the oxygen-based substituents should introduce little perturbation into the systems. This value is quite close to that (11.3 kcal/mol) derived from molecular mechanics calculations for the parent hydrocarbons (see below).²⁵

The ΔG_P values derived from the tertiary systems (13.3 kcal/mol at 25°; 14.3 kcal/mol at 100°) are somewhat larger, but not as simple to interpret since steric effects obviously are present and the II and III systems differ in substitution type.

(23) H. L. Goering and C. B. Schewene, *J. Amer. Chem. Soc.*, **87**, 3516 (1965).

(24) For example, no protoadamantane is detectable by glc (<0.01%) in AlBr₃ equilibration with adamantane.^{1a,b}

(25) E. Engler, J. Andose, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 8005 (1973).

Table IV. Estimates of Protoadamantane Strain Energies

Conditions	Rate constants, sec ⁻¹		Product ratio, A/P	$\Delta G_{\text{product}}^a$, kcal/mol
	1-R-2-adamantyl tosylate	4-R-4- <i>exo</i> -protoadamantyl tosylate		
Acetic acid, 25° (R = H)	5.9×10^{-9} ^b	2.2×10^{-3} ^c	250 ^b	11
60% acetone, 25° (R = CH ₃)	2.7×10^{-6}	4.9×10^{-3} ^d	2.3 ^e	13.3
60% acetone, 100° (R = CH ₃)	8.5×10^{-3}	8.8×10^{-5} ^f	2.3 ^e	14.3

^a Calculated by eq 1. ^b Reference 1b. ^c Calculated using the factor of 490 for converting data for dinitrobenzoate in 60% acetone at 100° to rate constants for tosylates in acetic acid at 25°: J. E. Baldwin and W. D. Foglesong, *J. Amer. Chem. Soc.*, **90**, 4303 (1968).²⁶ ^d Calculated using a OTs/ODNB leaving group ratio of 3×10^8 for 60% acetone at 25°:^{1b} K. B. Wiberg, R. A. Fenoglio, V. Z. Williams, and R. W. Ubersax, *ibid.*, **92**, 568 (1970); data for the tosylate in aqueous ethanol were converted by *mY* to 60% acetone, data for the dinitrobenzoate in 60% acetone were extrapolated to 25°. ^e Product ratio at 75°, Table II. ^f Calculated using a OTs/ODNB leaving group ratio of 2×10^7 for 60% acetone at 100°.

Table V. Molecular Mechanics Calculations²⁶ of Heats of Formation and Enthalpy Differences between Isomers, kcal/mol

Protoadamantanes	$-\Delta H_f^\circ$ (25°C)		Adamantanes	$-\Delta H_f^\circ$ (25°C)		$-\Delta \Delta H_f^\circ$ (25°C)	
	A ^a	E ^b		A ^a	E ^b	A ^a	E ^b
Protoadamantane	22.63	21.13	Adamantane	33.82	32.50	11.19	11.37
4- <i>endo</i> -Methyl-protoadamantane	29.13	27.81	1-Methyl-adamantane	42.89	41.92	13.76	14.11
4,4-Dimethyl-protoadamantane	33.42	31.73	1,2-Dimethyl-adamantane	47.21	46.05	13.79	14.32

^a Allinger force field. ^b Engler force field.²⁵

In order to probe these substituent effects, molecular mechanics calculations were carried out with methyl and dimethyl substituted model systems, the latter approximating the oxygen functions present in II and III.²⁵ The results are summarized in Table V.

All the calculated (ΔH) differences are in good agreement with the ΔG_P experimental estimates. Protoadamantane can be considered to have about 11 kcal/mol greater strain energy than that in adamantane.²⁶ At 25° this free energy difference is equivalent to an equilibrium constant of 10⁶. Little wonder, then, that protoadamantane and its derivatives cannot be detected in equilibrium with adamantane isomers.^{1,24} Since other tricyclodecanes²⁷ are expected to be at least as strained as protoadamantane,^{25,27} they are not expected to be seen in detectable amounts in equilibrium with adamantane either.

Experimental Section

For details of general procedures see preceding paper.

Separation of 4-Methyl-4-*exo*-protoadamantanol (II) and 4-Methyl-4-*endo*-protoadamantanol (I). The crude mixture of epimeric 4-methylprotoadamantanol (I and II) (150 mg) obtained from methyl Grignard addition to 4-protoadamantanone¹² was chromatographed on 200 g of silica gel using the following eluents: 250 ml of benzene, 500 ml of benzene with 1% ether, and 500 ml of benzene with 2% ether. The fractions of ca. 50 ml each were analyzed by glc. The less polar compound (74 mg, 49%) proved to be 4-methyl-4-*exo*-protoadamantanol (II): mp 79–81° after sublimation *in vacuo* and recrystallization from pentane; nmr showed a complex pattern of signals centered at τ 8.68, 8.50, 8.25, 8.10, 7.93, 7.80 (15, protoadamantyl H's and OH), and 8.75 (s,

3, CH₃); mass spectrum *m/e* (rel intensity) 166 (12, M⁺), 166.1359 (calcd for C₁₁H₁₈O, 166.1357), 151 (42), 148 (100), 133 (12), 123 (3), 119 (4), 108 (25), 106 (15), 95 (7), 93 (18), 92 (22), 91 (8), 81 (14), 79 (16), 77 (5), 71 (11), 67 (8).

Anal. Calcd for C₁₁H₁₈O: C, 79.10; H, 10.60. Found: C, 79.02; H, 10.71.

After collection of 12 mg of fractions containing both epimers, 45 mg (30%) of 4-methyl-4-*endo*-protoadamantanol (I) was obtained: mp 85–87°, after sublimation and recrystallization from pentane; nmr spectrum showed a complex pattern of signals centered at τ 8.50, 8.40, 8.20, 8.12, 7.90, 7.80 (15, protoadamantyl H's and OH), and 8.61 (s, 3, CH₃); mass spectrum *m/e* (rel intensity) 166 (23, M⁺), 166.1359 (calcd for C₁₁H₁₈O, 166.1357), 151 (12), 148 (100), 133 (12), 123 (5), 119 (5), 108 (56), 106 (20), 95 (13), 93 (26), 92 (21), 91 (17), 81 (29), 79 (27), 77 (9), 71 (27), 67 (18).

Anal. Calcd for C₁₁H₁₈O: C, 79.10; H, 10.60. Found: C, 79.46; H, 10.91.

4-Methyl-4-*exo*-protoadamantyl 3,5-Dinitrobenzoate (II-ODNB). 4-Methyl-4-*exo*-protoadamantanol (I-OH), 57 mg (0.343 mmol), was converted to the 3,5-dinitrobenzoate by the 3,5-dinitrobenzoyl chloride-pyridine method²⁸ to give 93 mg (75%) of white thin plates: mp 113.2–114.2°, after recrystallization from aqueous acetone; nmr spectrum showed broad bands centered at τ 8.72, 8.66, 8.25, 8.05, 7.70 (15, protoadamantyl H's), and 8.65 (s, 3, CH₃); mass spectrum (rel intensity) *m/e* 360 (0.2, M⁺), 345 (0.5), 212 (15), 195 (19), 182 (0.5), 166 (6), 149 (18), 148 (100), 133 (13), 120 (6), 119 (10), 107 (18), 106 (67), 105 (16), 93 (36), 92 (45), 91 (21), 79 (21), 77 (10), 75 (25), 67 (10).

Anal. Calcd for C₁₈H₂₀O₆N₂: C, 59.99; H, 5.59; N, 7.78. Found: C, 60.15; H, 5.61; N, 7.52.

4-Methyl-4-*endo*-protoadamantyl 3,5-Dinitrobenzoate (I-ODNB). The same procedure was used to convert 52 mg (0.313 mmol) of 4-methyl-4-*endo*-protoadamantanol (II-OH) to its 3,5-dinitrobenzoate; 94 mg (84%) was obtained: mp 119.5–121°, after recrystallization from aqueous acetone; nmr spectrum showed broad bands centered at τ 8.26, 8.08, 7.78, 7.75 (14 protoadamantyl H), and 8.16 (3, s, CH₃); mass spectrum (rel intensity) *m/e* 360 (0.2, M⁺), 345 (1.5), 212 (4.5), 195 (21), 182 (1.5), 166 (2.5), 149 (27), 148 (100), 133 (16), 120 (5), 119 (8), 107 (16), 106 (28), 105 (17), 93 (19), 92 (17), 91 (20), 79 (22), 77 (10), 75 (19), 67 (7).

Anal. Calcd for C₁₈H₂₀O₆N₂: C, 59.99; H, 5.59; N, 7.78. Found: C, 60.27; H, 5.41; N, 7.59.

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(28) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, Wiley, New York, N. Y., 1956.

2-Methyl-2-adamantyl 3,5-Dinitrobenzoate. 2-Methyl-2-adamantanol (32 mg, 0.002 mol) was converted with 510 mg of 3,5-dinitrobenzoyl chloride in 5 ml of pyridine into 573 mg (79%) of its 3,5-dinitrobenzoate: mp 142.5–144.0°; nmr broad signals centered at τ 8.5, 7.8, 7.4 (15 adamantyl H's), 8.20 (3, s, CH₃), and 0.80 (3, b, aromatic protons).

Anal. Calcd for C₁₈H₂₀O₆N₂: C, 59.99; H, 5.59; N, 7.78. Found: C, 60.25; H, 5.67; N, 7.67.

1-Methyl-2-adamantyl Tosylate (III-OTs). 1-Methyl-2-adamantanol (III-OH) (180 mg, 108 mmol) was converted to its tosylate by the pyridine method.²⁹ Recrystallization from pentane gave 218 mg (63%) of a white solid. A second recrystallization gave an analytically pure sample: mp 112–113.5°; nmr broad signals centered at τ 8.25, 8.25, 7.9 (15 adamantyl H), 9.32 (3, s, CH₃ at C-1), 7.55 (3, s, CH₃ at benzene ring), and 2.63 and 2.10 (AB pattern of 4 aromatic protons); mass spectrum (rel intensity) *m/e* 320 (0.7, M⁺), 320.1446 (calcd for C₁₈H₂₄O₃S, 320.1442), 149 (30), 148 (100), 135 (6), 133 (19), 120 (4), 119 (10), 107 (17), 106 (41), 105 (34), 94 (10), 93 (41), 92 (61), 91 (62), 81 (15), 80 (24), 79 (45), 77 (25), 70 (6), 67 (13), 65 (15).

1,2-Dimethyl-2-adamantanol (IV-OH). Methylmagnesium iodide was prepared by reaction of 243 mg of magnesium and 0.7 ml of methyl iodide in 15 ml of absolute ether. To this stirred solution, 500 mg (0.0035 mol) of 1-methyl-2-adamantanol¹² dissolved in 20 ml of absolute ether was added dropwise. After refluxing for 2 hr, the usual work-up gave, after vacuum sublimation, 462 mg (91%) of camphor-like 1,2-dimethyl-2-adamantanol (IV-OH): mp 185.5–187°, after recrystallization from pentane; nmr broad signals at τ 8.50, 8.35, and 8.16 (14 adamantyl-H), 9.21 (s, 3, CH₃ at C-1), and 8.75 (s, 3, CH₃ at C-2); mass spectrum (rel intensity) *m/e* 180 (5.5, M⁺), 165 (100), 162 (18), 147 (8), 135 (3), 119 (5), 107 (9), 106 (12), 105 (10), 95 (10), 93 (36), 92 (13), 91 (14), 81 (11), 79 (11).

Anal. Calcd for C₁₂H₂₀O: C, 79.94; H, 11.18. Found: C, 79.86; H, 11.16.

1,2-Dimethyl-2-adamantyl Bromide (IV-Br). 1,2-Dimethyl-2-adamantanol (IV-OH), 110 mg (0.612 mmol), was treated with 0.15 ml of phosphorus tribromide for 20 hr at room temperature. The mixture was then heated to 70° for 1 hr. After cooling, the product was dissolved in 10 ml of *n*-pentane. The pentane solution was washed twice with ice-water, with 10% potassium bicarbonate solution, and again with ice-water. After drying over sodium sulfate and evaporation of the solvent, the product was sublimed to give 112 mg of crude 1,2-dimethyl-2-adamantyl bromide (IV-Br). Since this product contained ~10% IV-OH (nmr) an acceptable elemental analysis could not be obtained. Since this impurity would not affect the solvolysis rate of the bromide, the crude sample was used without further purification. Nmr: singlets of τ 9.0 (CH₃ at C-1) and 8.0 (CH₃ at C-2), and broad signals between τ 7.8–8.9 (remaining protons).

Solvolysis. The solvents used were purified by standard procedures: ethanol,^{30a} acetic acid,^{30b} and acetone.^{30b} The kinetic

solvolyses were followed conductometrically by the method described.^{1b}

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 excellent separations of the compounds studied. For example, at 160° the following retention times were found: 4-methyl-4-*exo*-protoadamantanol (II-OH), 14 min; 4-methyl-4-*endo*-protoadamantanol (I-OH), 16 min; 1-methyl-2-adamantanol (III-OH), 18 min; with a half-width of *ca.* 0.5 min for every peak. For quantitative glc analysis of the product mixture the triangulation method was used.

Solvolysis of 4-*exo*-4-Methylprotoadamantyl 3,5-Dinitrobenzoate (II, X = ODNB) in 60% Acetone. 4-*exo*-Methylprotoadamantyl 3,5-dinitrobenzoate (2 mg) was dissolved in 0.5 ml of 60% acetone, containing 0.01 *M* 2,6-lutidine, and heated for 30 min to 75°. After cooling, the solution was injected directly into the gas chromatograph. The following analysis was found: 1-methyl-2-adamantanol (III-OH), 59%; 4-*exo*-4-methylprotoadamantanol (II-OH), 33%; olefin (unidentified), 7%.

Solvolysis of 4-*endo*-4-Methylprotoadamantyl 3,5-Dinitrobenzoate in 60% Acetone. 4-*endo*-4-Methylprotoadamantyl 3,5-dinitrobenzoate (I-ODNB) (2 mg) was dissolved in 0.5 ml of 60% acetone and heated at 75° for 3.5 hr. Direct glc analysis gave: 1-methyl-2-adamantanol (III-OH), 69%; 4-*exo*-4-methylprotoadamantanol (II-OH), 24%; and olefin (unidentified), 7%.

Solvolysis of 1-Methyl-2-adamantyl Tosylate in 60% Acetone. 1-Methyl-2-adamantyl tosylate (III-OTs) (2 mg) was dissolved in 0.5 ml of buffered 60% acetone and heated at 75° for 1 hr. Products (glc): 1-methyl-2-adamantanol (III-OH), 70%; 4-*exo*-protoadamantanol (II-OH), 28%; and olefin (unidentified), 2%.

This result was checked by nmr tube experiments using 60% acetone-*d*₆-D₂O and the distinctive methyl signals of II-OH (81 Hz downfield from acetone) and III-OH (51 Hz upfield from acetone) analytically. After heating III-OTs for 100 min in the presence of 0.1 *M* 2,6-lutidine, a ~2:1 ratio of III-OH to II-OH was found. The spectrum was not altered after additional heating at 80° for 30 min. An independent control experiment with III-OH alone verified its stability toward similar conditions (75°, 120 min).

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