Bridgehead Reactivities of Ethanoadamantane. Bromination and Solvolysis of Bromides[1,2]

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The four different kinds of bridgehead positions of 2,4-ethanoadamantane (1) exhibit different reactivities. Bromination with liquid bromine gave a mixture of 1-bromo- and 6-bromoethanoadamantanes. Structural assignments were made by ^{13}C NMR, by conversion of the bromides to the corresponding alcohols and methyl derivatives, and by independent synthesis of the remaining bridgehead methylethanoadamantane isomers. 6-Bromoethanoadamantane is less stable than the 1-isomer; a 4:96 ratio can be established by equilibration with *tert*-butyl bromide–AlBr₃, but the other isomers were not detected. The solvolysis rates at 75 °C in 80% ethanol, relative to 1-bromoadamantane, were as follows: 1-bromoethanoadamantane, 2.6; 6-bromoethanoadamantane, 13. Empirical force field and MINDO/3 calculations agree that the 6-cation should be considerably more stable than the other bridgehead cations; relief of leaving group strain also contributes to the faster solvolysis rate of the 6-bromide.

2,4-Ethanoadamantane (1, tetracyclo[6.3.1.0²,⁶.0⁵,¹⁰]dodecane), the most stable $C_{12}H_{18}$ isomer,[4] can be prepared
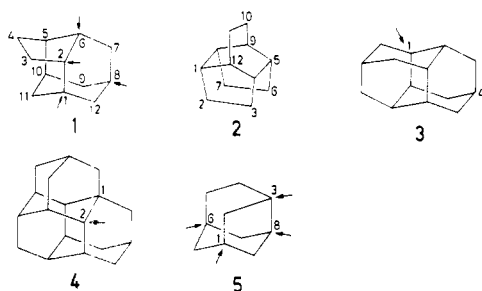
conveniently by Lewis acid catalyzed isomerization of appropriate precursor hydrocarbons like **2** (tetracyclo-[6.4.0.0⁴,¹².0⁵,⁹]dodecane).[2,5] **1** is also the simplest of several known ethano-bridged diamond hydrocarbons.[6,7] The four different bridgehead positions of **1** (shown by arrows) afford a challenging test of the ability of empirical force field[8] and semiempirical MO (MINDO/3)[9] methods to predict carbocation reactivity. A wide range of bridgehead solvolysis rates have been successfully correlated with

Table I. Product Distribution in the Bromination of Ethanoadamantane (1)

brominating agent	solvent	temp, °C	time, h	composition, %[a]	
				6-Br-1	1-Br-1
bromine[b]	bromine	3	4	45.8	52.3[c]
		58	1.5	35.4	64.6
		58	2	33.7[d]	66.3[d]
t-BuBr–AlBr₃[e]	CH₂Br₂	18	4.5	4.2	95.8
		18	52.5	4.4	95.6

[a] Composition from GLC analysis of the mixtures of corresponding alcohols obtained by direct hydrolysis of the crude bromide mixtures. [b] Reference 11a, 15. [c] A small peak corresponding to 1.9% of the total GLC area appears on the higher retention side of 1-OH-1, but it is absent in the other products. [d] On the basis of isolated weights of pure alcohols after preparative GLC. [e] Reference 12b.

calculated carbonium ion stabilities,[10–13] but only a few molecules having nonequivalent bridgehead positions have been studied.[12–14] Bromination of the regular polyamantanes is known to occur preferentially at bridgehead positions with the greatest number of β branches: C_1 of diamantane (3)[12] and C_2 of triamantane (4).[14] However, protoadamantane (5) reacts preferentially at C_6, which has the least branched environment;[13] the distortions introduced by the five-membered ring in **1** similarly complicate any simple prediction. We show here that competitive bromination of the different bridgeheads of **1** and solvolysis of two bromoethanoadamantanes can be interpreted adequately by means of the calculative approaches which were successful with **3**, **5**, and other bridgehead systems.

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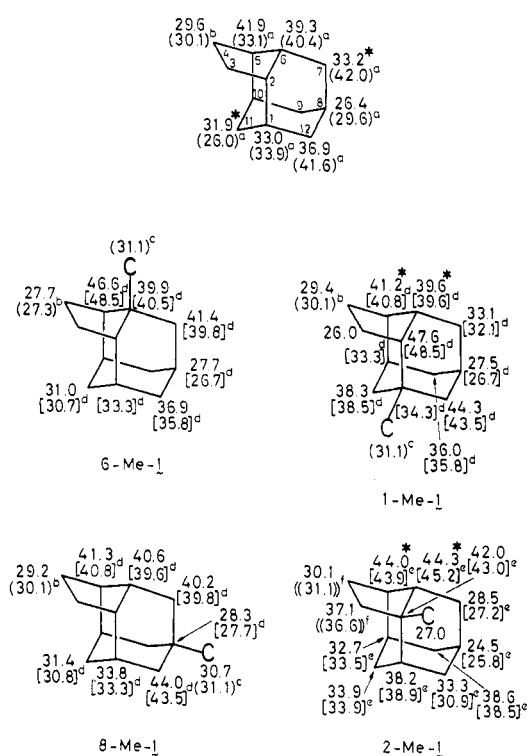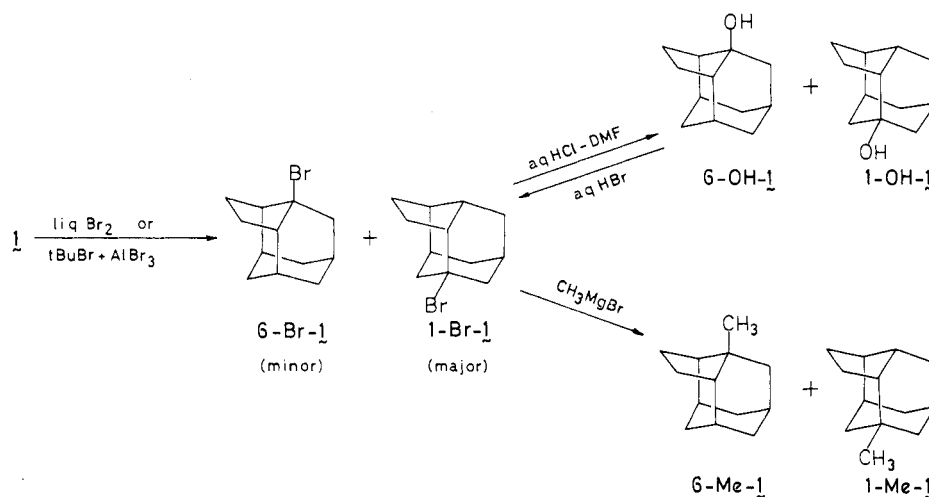
Scheme I

Figure 1. ^{13}C NMR chemical shifts of ethanoadamantane (1) and the four bridgehead methylethanoadamantanes in ppm downfield from Me₄Si. ᵃCalculated values based on the chemical shift of adamantane[19] and twice the effect of the methyl group in 2-methyladamantane.[20] See footnote 18 for discussion. ᵇBased on chemical shifts of norbornane and methylnorbornanes.[21] ᶜChemical shift of methyl carbon in 1-methyladamantane.[19] ᵈCalculated based on the bridgehead methyl effect on 1. See text. ᵉCalculated based on the methyl effects in 2-methyladamantane. See footnote 18. ᶠCalculated based on the effect of a bridgehead methyl on norbornane.[21] Asterisks indicate interchangeable assignments.

Results

Bromination of 1 and Product Analysis. Like adamantane[15] and several other diamond hydrocarbons,[11] 1 brominates rapidly even without heating. Both liquid bromine and *tert*-butyl bromide/aluminum bromide[12b] gave a mixture of *two* monobromides in high yield. The product composition varied with the reaction conditions, but reached an equilibrium value of 4:96 under thermo-

dynamic control which can be achieved readily in the presence of the Lewis acid catalyst, AlBr₃ (Table I). For facilitation of isomer separation by preparative GLC and identification, the bromide mixture was converted to the corresponding methyl derivatives by treatment with excess methylmagnesium iodide in ether at 100 °C.[16] Preparative GLC separation of the reaction mixture afforded two isomeric methylethanoadamantanes, mp 129 °C (major) and 169 °C (minor).

Proton NMR showed that the methyl groups in both were on bridgehead positions (C₁, C₂, C₆, or C₈). Both 6-methyl-1 and 8-methyl-1 have C_s symmetry and nine different types of carbon atoms; all 13 carbons in 1-methyl-1 and 2-methyl-1 are nonequivalent. Only seven resonance signals were found in the proton-decoupled ^{13}C NMR spectrum of the 169 °C minor product; hence it is likely to be either 6- or 8-methyl-1.[17] The choice between these two possibilities requires the knowledge of the carbon NMR spectrum of the parent hydrocarbon 1, which shows the expected two sets of doublets of double intensity, two doublets, one carbon each, two triplets of double intensity, and two triplets of single intensity. Assignments of chemical shifts are given in Figure 1.[18-22] The chemical

(16) Ōsawa, E.; Majerski, Z.; Schleyer, P. v. R. *J. Org. Chem.* **1971**, *36*, 205.

(17) Extreme difficulty in collecting pure minor product prevented us from repeating the spectral determination to seek more signals.

(18) We assumed that the effect of the ethano bridge on the chemical shifts of the adamantyl carbon atoms in 1 should be approximately twice that of the methyl group of 2-methyladamantane. Comparison of the methylene (38.0 ppm) and methine (28.6 ppm) ^{13}C chemical shifts of adamantane[19] with those reported for 2-methyladamantane (A)[19b,20] allows the 2-methyl group effects (B) to be assessed. The adamantane chemical shifts modified by the composite effects of 2,4-dimethyl groups (C) (assuming no interaction) are given on 1 (Figure 1) in parentheses. Agreement is good only for three of the bridgehead positions (C₁/C₁₀, C₆, C₈) but poor for α (C₂/C₅) and γ (three different methylene) positions with regard to the ethano bridge. The disagreement at C₂/C₅ is hardly surprising since our model should be the most deficient here. Among the four methylene signals observed, the double-intensity triplet at the higher field (29.6 ppm) most likely corresponds to the ethano bridge carbons;[21] therefore, the other double-intensity triplet at 36.9 ppm can be assigned to C₉/C₁₂. This leaves the two single-intensity triplets (31.9 and 33.2 ppm) for either of the two γ positions (C₇ and C₁₁). They are too high for C₇ and too low for C₁₁ on the basis of the *endo,endo*-2,4-dimethyladamantane model, and thus provide the most characteristic feature of the spectrum of 1. As a whole, our crude model adequately assigns the observed chemical shifts of 1, except for the ambiguity of C₇ and C₁₁.
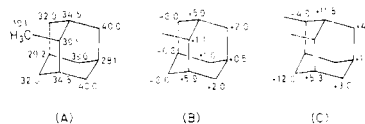

(15) Ōsawa, E. *Tetrahedron Lett.* **1974**, 115.

Scheme II
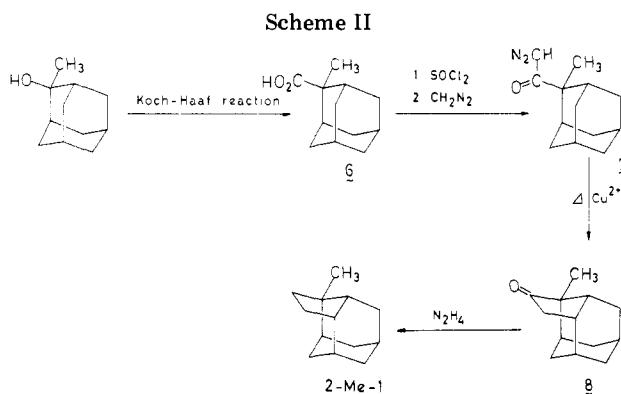
shifts for 6- and for 8-methyl-1 can be calculated by assuming that the effect of a methyl group on the chemical shifts of skeletal carbon atoms in 1-methyladamantane (α effect 1.3 ppm, β 6.6, γ 0.3, and δ −1.1)[23] is transferable to 1. The six chemical shift values and multiplicities observed for the 169 °C isomer do not fit those calculated for 8-methyl-1 but do correspond to those for 6-methyl-1 (Figure 1).

In an independent investigation, a different, liquid $C_{13}H_{20}$ isomer with one bridgehead methyl displaying nine carbon NMR signals was isolated from the reaction of 9-methyl-2 with aluminum bromide (eq 1);[24] its chemical
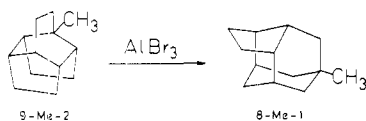
shifts and multiplicities agree well with those calculated for 8-methyl-1 (Figure 1). On this basis, the 169 °C minor product was recognized as 6-methylethanoadamantane (6-Me-1, Scheme I).

Ten signals (six triplets and four doublets, all of comparable intensity) were detected from the 129 °C major product, which could therefore be either 1- or 2-methyl-1, but not 6- or 8-methyl-1. The observed chemical shifts and multiplicities agree well with those calculated for 1-methyl-1 (Figure 1). In order to eliminate the other possibility completely, an authentic sample of 2-methyl-1, mp 155 °C (the final bridgehead isomer), was prepared by a sequence of reactions (Scheme II) involving intramolecular ketocarbene insertion as the bridge-forming step. The carbon NMR spectrum of 2-methyl-1 (13 signals) agreed well with the spectrum calculated by assuming the transferability of the methyl effect on the chemical shifts of skeletal carbon atoms in 2-methyladamantane[18] and 1-methylnorbornane[21] (Figure 1). The agreement between observed and calculated carbon NMR spectra of 2-methyl-1 provides support to our analysis of carbon NMR spectra of all the other methylethanoadamantane isomers, as well as their parent, 1.

The individual bromoethanoadamantanes, 1-Br-1 and 6-Br-1, were obtained by first hydrolyzing the bromination
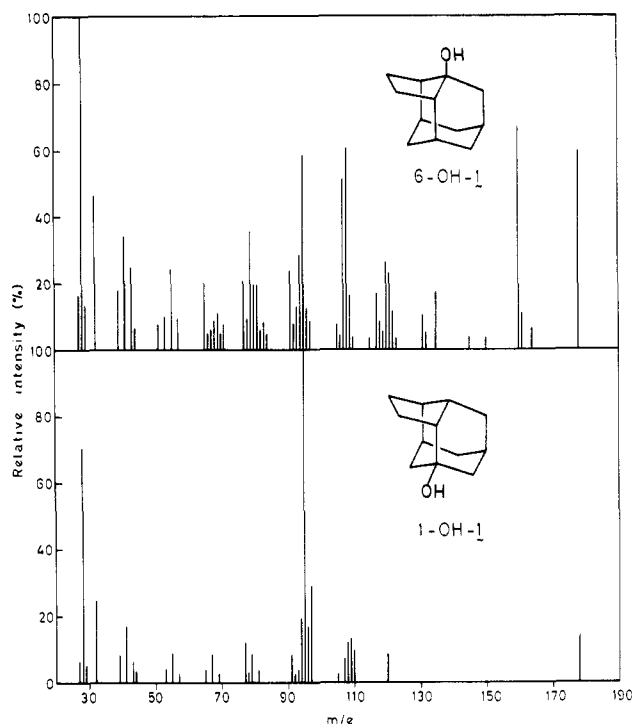

Figure 2. Mass spectra (80 eV) of 6-ethanoadamantanol (6-OH-1) and of 1-ethanoadamantanol (1-OH-1).

product to a mixture of alcohols, separating the alcohols (1-OH-1 and 6-OH-1) by preparative GLC, and converting each to the individual bromides by treatment with concentrated hydrobromic acid (Scheme I). Portions of the pure bromides thus obtained were once again converted into the respective methylethanoadamantanes, by the Grignard reactions, to confirm that no carbonium ion rearrangement or change of substituent site had taken place.

The isomeric ethanoadamantanols provided a confirmation of the positional assignments. Use of Siever's Eu(fod)$_3$ lanthanide shift reagent[25] gave partial resolution of the ^{1}H NMR spectrum of 6-OH-1: C$_7$ protons (d) were visible at the lowest field, C$_2$/C$_5$ protons (m) as well as two exo protons on the ethano bridge were also separated, and the two C$_{11}$ protons appeared as an AB quartet at the highest field. In contrast, the proton NMR spectrum of 1-OH-1 did not show any sign of resolution by addition of Eu(fod)$_3$ up to 50 mol %, consistent with a structure in which all 18 protons are magnetically nonequivalent.

The mass spectra of 1-OH-1 and of 6-OH-1 (Figure 2) are quite different. The base peak at m/e 95 dominates the spectrum of 1-OH-1, whereas in 6-OH-1 this peak has about the same intensity as those at m/e 178 (M$^+$), 160, 108, and 107. A dominant m/e 95 base peak has also been observed for 1-adamantanol and has been interpreted as being due to protonated phenol, formed by α cleavage of the ionized bridgehead alcohol followed by double C–C γ cleavages.[26] A similar mechanism can be written for 1-OH-1 (eq 2), but not for 6-OH-1.[27,31]
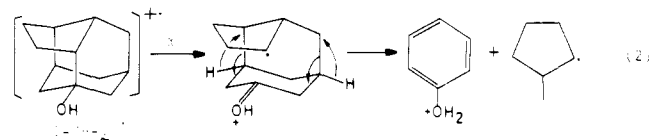
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(21) Grutzner, J. B.; Jautelat, M.; Dence, J. B.; Smith, J. A.; Roberts, J. D. *J. Am. Chem. Soc.* **1970**, *92*, 7107.

(22) Dalling, D. K.; Grant, D. M. *J. Am. Chem. Soc.* **1972**, *94*, 5318.

(23) According to ref 19a, the chemical shifts of 1-methyladamantane are 29.9 (α), 44.6 (β), 28.9 (γ), and 36.9 (δ) ppm. Also see ref 19b.

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Table II. Solvolysis Data in 80% Aqueous Ethanol

compound	temp, °C	k, s^{-1}	k_{rel}^{75} °C	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	ref
1-bromoadamantane	75.0	1.35×10^{-4}	1.0	22.4	-12.3	a
1-bromodiamantane (1-Br-3)	75.0	1.09×10^{-3}	8.1	22.8	-6.8	b
4-bromodiamantane (4-Br-3)	75.0	3.60×10^{-5}	0.27	24.1	-14.2	b
6-bromoethanoadamantane (6-Br-1)	75.5	1.80×10^{-3}				c
	75.0	$1.71 \times 10^{-3\ d}$	12.7	22.6	-6.5	
	50.1	1.28×10^{-4}				
	25.0	$6.10 \times 10^{-6\ d}$				
1-bromoethanoadamantane (1-Br-1)	75.5	3.49×10^{-4}				c
	75.0	$3.32 \times 10^{-4\ d}$	2.5	21.9	-12.0	
	50.1	2.70×10^{-5}				
	25.0	$1.42 \times 10^{-6\ d}$				

^{a} Raber, D. J.; Bingham, R. C.; Harris, J. M.; Fry, J. L; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 5977. ^{b} Reference 12b. ^{c} Present study. ^{d} Calculated.

Table III. Relative Stabilities of the Isomeric Bridgehead Ethanoadamantyl Cations Calculated by Empirical Force Field^a and MINDO/3^b Methods (kcal/mol)

	Engler–Schleyer force field			MINDO/3	
	steric energy	branching correction^c	rel ΔH	ΔH_f°	rel ΔH
6-cation	-2.25	-5.0	0.0	216.1	0.0
1-cation	0.12	-1.5	3.9	219.9	3.8
2-cation	1.67	-3.0	3.9	219.9	3.8
8-cation	-1.02	0.0	4.2	220.9	4.8
adamantyl 1-cation	-8.12	0.0	-2.9	199.7	-16.4

^{a} Reference 33. ^{b} Reference 9. ^{c} Stabilization of 1.5 kcal/mol per β-alkyl branching. See text.

Solvolysis of 6-Br-1 and 1-Br-1.

Results of solvolysis of the two bromoethanoadamantanes in 80% aqueous ethanol are summarized in Table II. 6-Br-1 solvolyzes five times faster than 1-Br-1 and 13 times faster than 1-bromoadamantane under the same conditions.

(27) Another remarkable feature in the mass spectral fragmentation of the ethanoadamantanols is the intense peak at m/e 160 (M$^+$ - 18) in 6-OH-1 and the complete absence of a similar peak in 1-OH-1. The ease of dehydration of 6-OH-1 under electron impact resembles that of 2-adamantanol[28] and several other alicyclic alcohols[29] wherein a hydroxyl group and a hydrogen atom take close syn-parallel disposition at a short distance (2.5–2.6 Å). The ground state structures of our alcohols, as predicted by MMI[30] force field calculations, indicate essentially the same distance for the closest nonbonded H/O pairs, but considerably different dihedral angles between the closest C–H/C–O bond pairs. The ranges shown below refer to the three C–O rotamers.
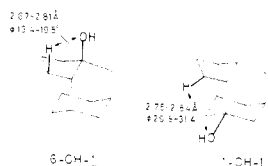
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(29) Green, M. M.; Cook, R. J.; Schwab, J. M.; Roy, R. B. *J. Am. Chem. Soc.* **1970**, *92*, 3076. Kwart, H.; Blazer, T. A. *J. Org. Chem.* **1970**, *35*, 2726.
(30) (a) Allinger, N. L.; Chung, D. Y. *J. Am. Chem. Soc.* **1976**, *98*, 6798. (b) Allinger, N. L.; Yuh, Y. H. *QCPE* **1979**, *11*, 318.
(31) The hydroxy stretching spectrum of 6-OH-1 (high dilution) consists of two peaks at 3622 and 3608 cm^{-1}, in agreement with predictions based on C–OH rotamer types termed "C" and "D" in ref 32. However, the OH peak of 1-OH-1 is symmetrical with a single maximum at 3606 cm^{-1} which has been assigned to the rotamer type C; we could not locate a peak near 3614 cm^{-1} expected for the rotamer type E.[32] These assignments will be discussed elsewhere.
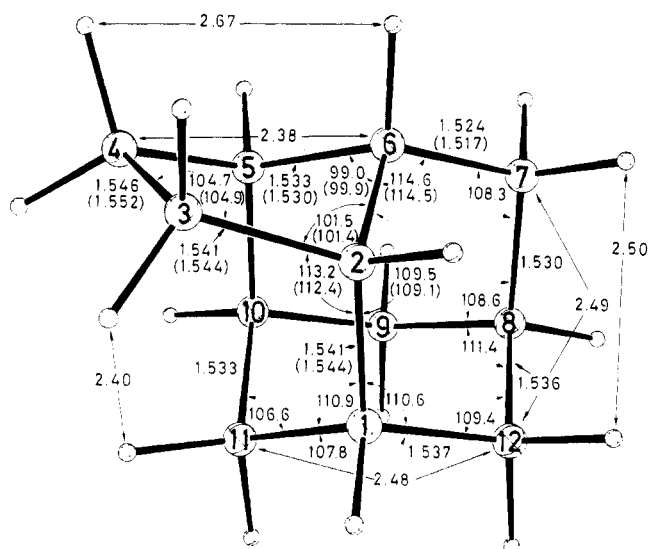(32) Joris, L.; Schleyer, P. v. R.; Ōsawa, E. *Tetrahedron* **1968**, *24*, 4579.

Figure 3. Structure of ethanoadamantane (1) as calculated by MMI force field. Corresponding values of C_s-ethanodiamantane observed by X-ray analysis are in parentheses: Rao, S. T.; Sundaralingham, M. *Acta Crystallogr., Sect. B* **1972**, *28*, 694. Bond lengths are in angstroms and angles in degrees.

Discussion

Bromination of Ethanoadamantane and the Relative Stability of the Bridgehead Ethanoadamantyl Cations.

Although no quantitative study has yet been carried out, the qualitative ease of bromination of polycyclic hydrocarbons often seems to parallel the solvolysis rates of the resulting bromides and thus to be related to the stability of the corresponding carbenium ions.[11-13] However, steric hindrance can play a definite role and it is doubtful that the bromination mechanism involves a simple hydride ion abstraction. Pentacoordinate intermediates or transition states, or even radical cation pathways, may be involved.

The four different bridgehead types in ethanoadamantane afford potential reaction sites. Only the 6- and the 1-positions are attacked, even with AlBr$_3$ catalyst. Although the 1-bromide is more stable than the 6-bromide, the latter is formed in comparable amounts initially. This is consistent with its greater solvolysis rates.

Using Engler's carbocation force field,[33] the steric energies of the four isomeric bridgehead ethanoadamantyl
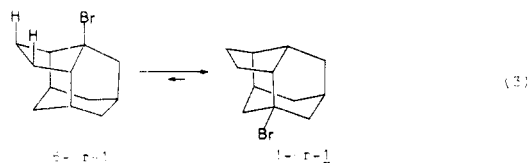
(33) (a) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005. (b) Engler, E. M.; Farcasiu, M.; Sevin, A.; Cense, J. M.; Schleyer, P. v. R. *Ibid.* **1973**, *95*, 5769. (c) Andose, J. D.; Engler, E. M.; Collins, J. B.; Hummel, J. P.; Mislow, K.; Schleyer, P. v. R. *QCPE* **1979**, *11*, 348.

cations were calculated (Table III, column 2). The results indicate the 6-cation to be preferred. However, such calculations do not take inductive and hyperconjugative effects, known to influence carbenium ion stabilities in diamond molecules, into account.[12b] Hence, a simple correlation of 1.5 kcal/mol for each β-alkyl branch[33b] was applied (Table III, column 3).[34] The resulting stability order (Table III, column 4) indicates the 6-cation is considerably more stable than the other three alternatives.

Since such empirical procedures requiring branching corrections seemed a bit dubious, MINDO/3[9] calculations were carried out on the same set of cations. Such molecular orbital methods include the effects of strain, branching, etc., and, whatever their inherent inaccuracies, should give reasonably reliable results when such closely related species are being compared. In point of fact, the MINDO/3 relative stabilities of the isomeric ethanoadamantyl cations (Table III, last column) are in remarkably good agreement with the corrected force field estimates (Table III, column 4). This helps to justify the procedures used here and earlier.[12b,33b]

However, such calculations refer to ions in the gas phase where energy differences tend to be larger in magnitude than those expected in solution. In this regard, it is puzzling that the 1- but neither the 2- nor the 8-cation was produced upon bromination or even as reaction intermediates during equilibration of the bromides. Ethanoadamantane seems to behave like protoadamantane in affording only some of the possible bridgehead products.[13]

Relative Stabilities of the Bromoethanoadamantanes. The observed equilibrium composition of 4:96 for 6-Br-1 and 1-Br-1 (eq 3) corresponds to a free-

energy difference of 1.79 kcal/mol at 18 °C. Compared to the reported equilibrium between 1- and 4-bromodiamantane (1-Br-3 and 4-Br-3, eq 4),[35,36] the equilibrium
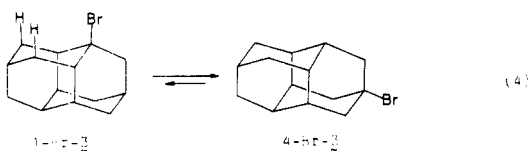
in eq 3 is shifted more to the right, despite apparently similar, unfavorable 1,3-diaxial repulsive interactions involving bromine in both 6-Br-1 and 1-Br-3.[12b,37] The structure of ethanoadamantane (Figure 3), as calculated by Allinger's MMI force field,[30b] reveals that the ethano bridge is bent toward C_6, as noted by valence angles at C_2. Thus, we anticipate higher 1,3-diaxial H/Br repulsion for 6-Br-1 than for 1-Br-3.[38]

Calculations with Allinger's halide force field (Table IV)[38,39] indicate that 8-bromoethanoadamantane (8-Br-1) should be the most stable isomer. We again express our surprise that equilibration conditions (Table I) do not yield this isomer.

Relative Solvolysis Rates of Bridgehead Bromides. The observed solvolysis rates of the ethanoadamantyl bromides (Table II) are qualitatively reasonable: 6-Br-1 reacts more rapidly than 1-Br-1 because the former gives a more stable carbocation and also benefits from greater relief of leaving group strain.

By utilizing empirical force field calculations, it is possible to predict the solvolysis rates of bridgehead systems quantitatively.[10,11,12b,13a] The equation applicable to bromide leaving groups in 80% ethanol at 70 °C, -log $k_{Br}^{70°C} = 0.41(\Delta$ strain$) - 0.12$,[10] is applicable to polycyclic systems where neither leaving group strain nor chain branching is present. The "Δ strain" term (Table IV, column 4) refers to the difference in steric energy between a carbocation and its parent hydrocarbon as calculated with the Bingham force field.[10,40]

The importance of taking into account initial-state energy effects, e.g., those involving steric effects involving the leaving group, is well established.[41] The calculated energetic differences among the bridgehead ethanoadamantyl bromides (Table IV, column 3) can be used to correct the predicted solvolysis rates if it is assumed that all the extra strain involving the leaving group is relieved in each solvolysis transition state.[42] The correction factors shown in column 5 of Table IV result.

As discussed above, chain branching adjacent to the reaction site results in electronic stabilization not taken into account in the empirical force field parameterization. A correction factor of about 2.8 for each β branch was employed earlier for analysis of the diamantyl system. Alternatively, one could scale the 1.5-kcal/mol correction of Table III by multiplying by 0.41 (see equation above[10]). This amounts to 0.62 kcal/mol, or a rate correction factor of 2.4 per β branch. We have arbitrarily employed a value of 3.0 in Table IV (column 7).

Multiplication of the three factors results in calculated relative rates which can be compared with the experimental results (last two columns of Table IV) for adamantyl, diamantyl, and ethanoadamantyl systems. The agreement is gratifying and encourages further refinements

(34) In contrast to the highly sophisticated treatment of the steric energy in the empirical force field calculations, the correction for the β-alkyl branching effect[33b] is rather crude. More elaborate methods of evaluating carbocation energies are under investigation.

(35) Hamilton, R.; Johnston, D. E.; McKervey, M. A.; Rooney, J. J. *J. Chem. Soc., Chem. Commun.* 1972, 1209.

(36) Courtney, T.; Johnston, D. E.; McKervey, M. A.; Rooney, J. J. *J. Chem. Soc., Perkin Trans. 1* 1972, 2691.

(37) Note that the strain energy of 1-Br-1 is about equal to that of 8-Br-1, which must be similar to 4-bromodiamantane regarding strain around the bromide group, and that entropy contribution favoring 1-Br-1 over 6-Br-1 should only be -0.42 kcal/mol.

(38) Calculations of bromides of 1 and 3 by Allinger's halide force field (ref 39) gave inconsistent results (Table IV). The results appear all right with bromoethanoadamantanes. For example, calculated angles at C_2 of 6-Br-1 are 103.2° for C_3-C_2-C_6, 109.8° for C_1-C_2-C_6, and 111.5° for C_1-C_2-C_3, which are not much different from those of 1 (Figure 3), while the 1,3-diaxial distance between bridge hydrogen and bromine is 3.02 Å (corresponding to a repulsion energy of 0.40 kcal/mol per pair). Indeed, the calculated enthalpy difference for 6-Br-1 and 1-Br-1 (1.15 kcal/mol) combined with the entropy of mixing for 1-Br-1 (-RT ln 2) leads to a calculated free-energy difference of 1.57 kcal/mol, in fair agreement with experimental value of 1.79 kcal/mol. However, the calculated enthalpy difference for 1-Br-3 and 4-Br-3 (2.45 kcal/mol) is too much higher than the observed value of 0.59 kcal/mol (ref 35, 36). Close examination of the calculated structure of 1-Br-3 revealed that the force field employed led to a large C_1-C_2-C_3 angle (112.7°), small C_{14}-C_1-Br angle (107.5°), large C_2-C_3-H_{axial} angle (112.2°), and rather small 1,3-diaxial H/Br distance (2.92 Å, corresponding to a strain of 0.68 kcal/mol per pair). We therefore excluded the calculated results from relative rate calculations in Table IV, but the relative stability orders among isomers are probably correct.

(39) Meyer, A. Y.; Allinger, N. L. *Tetrahedron* 1975, *31*, 1971.

(40) Fry, J. L.; Engler, E. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1972, *94*, 4628. Also see: Harris, J. M.; Shafer, S. G.; Smith, M. R.; McManus, S. P. *Tetrahedron Lett.* 1979, 2089.

(41) Slutsky, J.; Bingham, R. C.; Schleyer, P. v. R.; Dickason, W. C.; Brown, H. C. *J. Am. Chem. Soc.* 1974, *96*, 1969. Lomas, J. S.; Luong, P. K.; Dubois, J.-E. *Ibid.* 1977, *99*, 5478.

(42) Schleyer, P. v. R. *J. Am. Chem. Soc.* 1964, *86*, 1854.

Table IV. Calculated Enthalpies, Strain Energies, and Relative Solvolysis Rates in 80% Aqueous Ethanol at 75 °C of Bridgehead Adamantyl, Diamantyl, and Ethanoadamantyl Bromides

bromides	$\Delta H_f°$ (MMI),[a] kcal/mol	rel Br strain,[b] kcal/mol	Δ strain $(R^+ - RH)$,[c] kcal/mol	relative solvolysis rates				
				Br strain factor[d]	R^+ strain factor[e]	β-alkyl effect factor[f]	calcd pro-duct	obsd
1-adamantyl	-33.25	0.00	12.3	1.0	1.0	1.0	1.0	1.0
1-diamantyl (1-Br-3)	-34.97	0.34[g] (2.20)[h]	13.0	1.6	0.52	6.0	5.1	8.0
4-diamantyl (4-Br-3)	-37.42	-0.25	13.4	0.69	0.35	1.0	0.24	0.34
ethanoadamantyl								
(1-Br-1)	-25.36	0.57	13.6	2.3	0.29	3.0	2.0	2.6
(2-Br-1)	-24.76	1.17	17.4	5.4	0.0081	6.0	0.26	
(6-Br-1)	-24.21	1.96[i] (1.72)[h]	13.0	17.1	0.52	3.0	26.7	13.3
(8-Br-1)	-25.95	-0.02	12.2	0.97	1.1	1.0	1.1	

[a] Reference 30b, 39. [b] $[\Delta H_f°(RBr) - \Delta H_f°(RH)] - [\Delta H_f°(1\text{-AdBr}) - \Delta H_f°(\text{AdH})]$: the $\Delta H_f°$(MMI)'s are: adamantane (AdH), -33.34; diamantane, -37.26; 2,4-ethanoadamantane, -26.02 kcal/mol. [c] Differences in steric energies of cation (R^+) and the corresponding polycycloalkane (RH) calculated by the Bingham force field (ref 10; also see ref 12b). [d] Calculated by assuming all relative Br strain (column 3) is relieved on ionization. [e] Rate constants calculated with the equation: $-\log k_{Br}^{80\% \text{ EtOH,}70\ °C} = 0.41(\Delta \text{ strain}) - 0.12$ and then set relative to that of 1-adamantyl bromide. [f] A factor of 3.0 per β branch assumed. A slightly smaller factor was taken in ref 12b. [g] Based on the experimental enthalpy difference between 1-Br-3 and 4-Br-3 (eq 4, ref 35, 36, 0.59 kcal/mol) and then set relative to 1-bromoadamantane. [h] Based on calculated enthalpy but not used in the calculation of relative solvolysis rate. See footnote 38. [i] Based on experimental free-energy difference between 6-Br-1 and 1-Br-1 (eq 3), corrected for entropy contribution (0.40 kcal/mol), and then made relative to 1-bromoadamantane.

of such calculative approaches to problems in chemical reactivity.

Conclusions

The 6-ethanoadamantyl cation is the most stable among the bridgehead carbenium ions. This is shown both by experimental and by calculated results. The 6-cation benefits from lower strain and from electronic stabilization afforded by the two β branches. The 6-bromide, however, is sterically congested and isomerizes to the more stable 1-bromide; empirical force field calculations rationalize the experimental energy difference and the relative solvolysis rates of these two bromides. However, a negative observation is puzzling. The 8-bromide (8-Br-1) should be the thermodynamically most stable isomer. Likewise, the 8-cation should be no less stable than the 2-cation. Nevertheless, 8-bromoethanoadamantane (as well as the 2-isomer) was apparently not formed even under Lewis acid catalyzed conditions. We do not understand why the alternative bridgehead positions resist electrophilic attack.

Experimental Section

Melting points are corrected. IR spectra were obtained with a JASCO Model IR-G spectrometer. ¹H NMR spectra were measured on JEOL JNM PS-100 (100 MHz) and Hitachi R-20B (60 MHz) spectrometers. ¹³C NMR spectra were recorded at 25.14 MHz on a JEOL JNM PS-100 spectrometer equipped with JNM PFT-100 pulse transform. Mass spectra were recorded on a JEOL Model JMS-D300 mass spectrometer with an ionizing energy of 80 eV and an accelerating voltage of 1800 V. The sample and ionizing chambers were both at 200 °C and at pressures of 3 × 10⁻⁷ torr. Elemental analyses were performed at the Analysis Center, Department of Pharmacy, Hokkaido University.

Tetracyclo[6.4.0.0⁴,¹².0⁵,⁹]dodecane (2) was prepared from α-pyrone and 1,5-cyclooctadiene according to the method of Akhtar et al.[5]

Ethanoadamantane (1). (a) With Williams' Sludge Catalyst.[43] To a solution of 2.14 g of 2 (mp 120-4 °C) in 20 mL of carbon disulfide was slowly added 4 mL of freshly prepared sludge catalyst under an atmosphere of hydrogen bromide gas and vigorous stirring. The course of reaction was monitored by GLC

analysis (0.01 in. × 150 ft Carbowax Golay column at 80 °C or 3 mm × 2 m SE-30 at 145 °C) of aliquot samples. The starting material disappeared in 35 min and a single product peak appeared instead along with small amounts of several fragmentation products with shorter retention times. No reaction intermediates could be detected. The carbon disulfide solution was decanted from the catalyst layer, which was then washed with fresh carbon disulfide. The combined carbon disulfide solution was washed well with water and dried over calcium chloride, and the solvent evaporated to leave 1.47 g of an oil. GLC analysis revealed the oil to contain 22% of fragmentation products. Purification by preparative GLC (3/8 in. × 50 ft FFAP at 205 °C) and sublimation at 100 °C (4 torr) gave 0.84 g (39%) of waxy solid, mp 174-6 °C.[44] Proton NMR, IR, and mass spectra of this sample were identical with those of synthetic[2] as well as natural[45] ethanoadamantane: ¹H NMR (CCl₄) δ 1.95, 1.83, 1.72, 1.63, 1.60, 1.55, 1.52, 1.43, 1.35, 1.21 (all overlapping); IR (CCl₄ solution) 2915, 2855, 1474, 1458, 1440, 1180, 1095 cm⁻¹; mass spectrum, m/e 162 (M⁺, 100%), 133 (19%), 120 (43%), 119 (55%), 91 (46%), 80 (71%), 79 (54%). Anal. (C₁₂H₁₈) C, H.

Fragmentation products having short GLC retention times consisted of at least seven components; the two most abundant were collected by preparative GLC and identified as 1,3-dimethyl- and 1-ethyladamantanes by means of ¹H NMR spectra.[46]

In a larger scale run, a solution of 13 g of 2 in 50 mL of carbon disulfide was added slowly with stirring to 5 mL of sludge catalyst covered with 50 mL of carbon disulfide at 1 to 6 °C. The mixture was stirred at 0 to -1 °C for 80 min. The crude pasty product obtained by usual workup was distilled using a short-path apparatus under reduced pressure. Solid distillate was pressed onto a porcelain plate and sublimed at 100 °C (4 torr) to give 6.4 g (49%) of ethanoadamantane, mp 160 °C.

(b) With Aluminum Chloride. A solution of 22 g of 2 in 50 mL of methylene chloride was added dropwise in the course of 20 min to a magnetically stirred suspension of 50 g of pulverized aluminum chloride in 300 mL of methylene chloride in a 1-L flask protected from moisture with a calcium chloride tube. During the addition, the temperature was maintained below 27 °C by cooling with a water bath. After the addition was complete, the mixture was stirred at room temperature for 1 h. The catalyst was decomposed by slow addition of 200 mL of water to the

(43) (a) Williams, V. Z., Jr.; Schleyer, P. v. R.; Rodewald, L. B. *J. Am. Chem. Soc.* 1966, 88, 3862. (b) Gund, T. M.; Ōsawa, E.; Williams, V. Z., Jr.; Schleyer, P. v. R. *J. Org. Chem.* 1974, 39, 2979.

(44) Landa's 95% pure ethanoadamantane isolated from petroleum melted at 153-158 °C.[45]

(45) Hala, S.; Landa, S.; Hanus, V. *Angew. Chem., Int. Ed. Engl.* 1966, 5, 1045.

(46) (a) Fort, R. C., Jr.; Schleyer, P. v. R. *J. Org. Chem.* 1965, 30, 789. (b) Warren, R. W.; Schneider, A.; Janoski, E. J. *Appl. Spectrosc.* 1968, 22, 115.

reaction mixture with ice cooling. A clear solution resulted. The organic layer was separated, washed with water, and dried over calcium chloride. Evaporation of solvent left an oil, which was distilled in a short-path apparatus under vacuum. Solid distillate was sublimed twice under vacuum to give 12.5 g (57%) of colorless crystals of crude 1, mp 150 °C.

Bromination of 1 with Liquid Bromine. Ethanoadamantane (1, 0.84 g) was heated in liquid bromine under reflux with magnetic stirring for 1.5 h. The resulting mixture was cooled to room temperature, 10 mL of carbon tetrachloride and 20 mL of water were added, and excess bromine was reduced with solid NaHSO$_3$ while the solution was stirred and cooled in an ice-water bath. The organic layer was washed with water and dried over calcium chloride, and the solvent was evaporated under vacuum. The crude oil thus obtained was dissolved in 10 mL of hot methanol; the solution was cooled to −98 °C to give colored crystals, which were purified by sublimation under vacuum to give 1.14 g (91%) of colorless, ill-defined crystals. Most of the product, a mixture of bromides, was subjected to hydrolysis (see below). An analytical sample, mp 135–8 °C, was obtained by crystallization from ethanol: mass spectrum, m/e 242 (p + 2), 240 (p), 161 (base peak, C$_{12}$H$_{17}$$^+$); calcd for C$_{12}H_{17}$Br p + 2, 97.7%; found p + 2, 97.8%; ^{1}H NMR (60 MHz) δ 1.8, 2.4, 2.6 (all unresolved). Anal. (C$_{12}$H$_{17}$Br) C, H, Br.

In another run, 0.26 g of 1 was treated at 3 °C under an otherwise similar way as above. Conversion of 1 was complete in 4 h. Workup gave 0.4 g of an oil, which was subjected directly to hydrolysis (see below).

Bromination of 1 with *tert*-Butyl Bromide and Aluminum Bromide. 1 (0.2 g) was stirred with 0.34 g of *tert*-butyl bromide and a trace of aluminum bromide in 20 mL of methylene bromide in a flask kept at 18 to 20 °C by means of a water bath. About one-third of the reaction mixture was withdrawn after 5 h, another one-third after 20.5 h, and the remainder after 52.5 h. Each aliquot was washed separately with water and dried with Na$_2$SO$_4$, and the solvent was evaporated to dryness under vacuum. The residue was hydrolyzed by adding 3 mL of 0.67 N HCl and 2.6 mL of dimethylformamide and refluxing the mixture for 1 day with stirring. The reaction mixture as well as the material which had sublimed onto the wall of condenser were extracted with petroleum ether and analyzed by GLC. The product mixture contained two components identified as alcohols 6-OH-1 and 1-OH-1 by comparison of the retention times with authentic samples (see below). All three aliquots showed the same composition (4:96) within experimental error.

1- and 6-Methylethanoadamantanes from the Mixture of 1- and 6-Bromoethanoadamantanes. The crystalline mixture of 1- and 6-bromoethanoadamantanes (0.40 g, 1.7 mmol), obtained by bromination of 1 with liquid bromine under reflux, and 5 mL of a 2 M ether solution of methylmagnesium bromide (10 mmol) were heated in an aerosol bottle at 100 °C for 20 min with stirring. Excess Grignard reagent was decomposed by slowly adding 5% HCl to the reaction mixture (cooled with ice–water). The ether layer was separated, washed with water, and dried. GLC analysis of the solution revealed two products in a ratio 65:35. They were separated by preparative GLC on a $^3/_8$ in. × 50 ft FFAP column at 175 °C (retention time with a He flow rate of 40 mL/min: 175 and 188 min for the major and minor product, respectively) and further purified by sublimation under vacuum.

1-Methylethanoadamantane (major product): mp 127–9 °C (sealed tube); ^{1}H NMR (CCl$_4$) δ 0.68 (s, CH$_3$), 0.95–2.0 (m); mass spectrum, m/e 176 (M$^+$, 14%), 161 (M$^+$ − CH$_3$, base peak), 133 (15%), 119 (13%), 105 (20%), 93 (30%), 91 (27%); IR (CCl$_4$) 2960, 2925, 2880, 2860, 1475, 1462, 1454, 1374, 1356, 1105 cm^{-1}. Anal. (C$_{13}$H$_{20}$) C, H.

6-Methylethanoadamantane (minor product): mp 167–9 °C (sealed tube); ^{1}H NMR (CCl$_4$) δ 0.79 (s, CH$_3$), 1.1–2.0 (m); mass spectrum m/e 176 (M$^+$, 9.8%), 161 (M$^+$ − CH$_3$, base peak), 148 (M$^+$ − C$_2$H$_4$, 3%), 133 (M$^+$ − C$_3$H$_7$, 13%), 118 (12%), 105 (11%), 91 (20%), 79 (23%). Anal. (C$_{13}$H$_{20}$) C, H.

2-(2-Methyladamantyl)carboxylic Acid (6). A Koch–Haaf reaction was carried out under high dilution conditions (800:1) in the presence of carbon tetrachloride as the cosolvent.[47,48] To

1.6 L of concentrated sulfuric acid and 200 mL of carbon tetrachloride in 3-L three-necked flask were added slowly (over 2.5 h) and simultaneously with vigorous stirring 250 mL of 100% formic acid and a solution of 2.0 g (12 mmol) of 2-methyl-2-hydroxyadamantane (mp 213–214 °C)[40] in 100 mL of carbon tetrachloride. During the addition, the temperature was kept between 13 and 21 °C. After the addition was complete, stirring was continued for 15 min more and then the reaction mixture was poured onto 3 L of crushed ice. The organic layer was separated and the aqueous layer extracted three times with chloroform. Three more runs were carried out on the same scale with a total of 8.0 g (48 mmol) of 2-methyl-2-hydroxyadamantane. The combined extract was washed with water and the solvent evaporated. The solid residue was recrystallized from *n*-hexane and then from aqueous methanol to give 2.9 g (32%) of pillar-like crystals of 6, mp 138.5–140.5 °C. An analytical sample, mp 146.5–148.5 °C, was obtained after three more recrystallizations from aqueous methanol: ^{1}H NMR (CCl$_4$) δ 12.2 (s, COOH), 2.3–1.0 (m, 14 H), 1.36 (s, CH$_3$); IR 1693 cm^{-1}. Anal. (C$_{12}$H$_{18}$O$_2$) C, H.

2-Methyltetracyclo[6.4.0.0^{4,12}.0^{5,9}]dodecan-3-one (7). In a 25-mL round-bottom flask, 2.48 g (12.8 mmol) of 2-(2-methyladamantyl)carboxylic acid (6) and 5 mL of thionyl chloride were heated under reflux and stirred for 0.5 h. Most of the excess thionyl chloride was removed in vacuo. After the addition of 10 mL of anhydrous benzene to the residue, benzene was distilled to remove any trace of thionyl chloride. The colorless residual oil crystallized to give long needles. Treatment of the acid chloride with a 1.3 M excess with diazomethane in ether (dried with KOH pellets[49]) gave the desired diazo ketone (7, $\nu_{N=N}$ 2100, $\nu_{C=O}$ 1640 cm^{-1}) still mixed with unreacted acid chloride ($\nu_{C=O}$ 1790 cm^{-1}). The crude diazo ketone was dissolved in 300 mL of dry toluene. The solution was filtered, cooled below −30 °C, and dropped very slowly during the course of 8 h into a refluxing suspension of 15.4 g of anhydrous cupric sulfate in 500 mL of dry toluene with vigorous stirring.[50] After the addition was complete, stirring under reflux was continued for 3 h. The cupric sulfate was removed by filtration, and the filtrate was washed with water and extracted with 10% NaOH solution. The alkaline extract was acidified with concentrated HCl to precipitate 0.77 g (31%) of unreacted carboxylic acid (6), mp 141–142.5 °C. The filtrate was washed again with water and dried with sodium sulfate, and the solvent was evaporated to leave 1.62 g of colored oil, of which 78% was a single product from GLC analysis. The crude yield of ketone 8 was 75% based on the amount of 6 actually converted. An analytical sample was obtained by preparative GLC on a 6 mm × 6 m Silicone DC 550 column, followed by sublimation of the material collected and recrystallization from methanol, mp 174–7 °C; ^{1}H NMR (CCl$_4$) δ 2.5–1.3 (m with characteristic peaks at 2.19, 2.12, 1.84, 15 H), 1.01 (s, CH$_3$); IR (KBr) 1747, 1458, 1200, 1049 cm^{-1}; mass spectrum, m/e 190 (M$^+$, 90%), 162 (M$^+$ − CO, 91%), 121 (38%), 106 (25%), 93 (100%), 92 (75%), 91 (62%). Anal. Calcd for C$_{13}$H$_{18}$O: C, 82.05; H, 9.53. Found: C, 81.24; H, 9.43.

2-Methylethanoadamantane (2-Me-1) from 8. Crude ketone (8, 1.29 g) was heated with 8 mL of 95% triethanolamine, 2 g of KOH, and 1.5 mL of 85% hydrazine at 140 °C for 4 h. Then the temperature was raised to 195 °C by allowing the water to distill during 4 h. After the solution was cooled, the reaction mixture was acidified by the addition of 10 mL of concentrated HCl, diluted with 50 mL of water, and extracted three times with ether. The combined extract was washed with water and dried, and the solvent evaporated to give 0.93 g of lightly colored oil. Direct sublimation under vacuum gave 0.34 g of white crystals. GLC analysis revealed a purity of 92% for this product; thus the crude yield of 2-Me-1 was 34%. An analytical sample was obtained by preparative GLC on 6 mm × 1 m Silicone DC 550 at 98 °C, followed by vacuum sublimation, mp 153–5 °C (sealed tube); ^{1}H NMR (CCl$_4$) δ 2.3–1.2 (m with prominent peaks at 1.75, 1.52, 1.46, 17 H), 1.0 (s, CH$_3$); mass spectrum, m/e 176 (M$^+$, 100%), 161 (M$^+$

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(49) de Boer, T. J.; Backer, H. J. "Organic Syntheses", Collective Vol. 2; Wiley: New York, 1963; p 250.

(50) (a) Wenkert, E.; Mylari, B. L.; Davis, L. L. *J. Am. Chem. Soc.* **1968**, *90*, 3870. (b) Reference 2.

	GLC retention time, min		composition, %	
	Carbowax 20M[a]	Silicone DC 550[b]	58 °C[c]	3 °C[c,d]
6-OH-1	124	159	33	46
1-OH-1	136	172	67	52

[a] 6 mm × 6 m, 145 °C. He 17.5 kg/cm². [b] 6 mm × 9 m, 165 °C. He 16 kg/cm². [c] Temperature of bromination reaction. [d] 2% of an unknown component having a retention time of 148 min on Carbowax 20M also was present.

− CH₃, 80%), 147 (16%), 133 (33%), 91 (59%), 79 (79%). Anal. (C₁₃H₂₀) C, H.

Hydroxyethanoadamantanes. The monobromide mixtures were hydrolyzed by the method of Geluk and Schlatmann.[51] The crystalline, mixed bromide (3.4 g), obtained by heating 1 with liquid bromine, was heated in 5 mL of 0.69 N HCl and 4 mL of dimethylformamide at 105 °C with stirring for 0.5 h. After the solution was cooled, the reaction mixture was diluted with 30 mL of water and the pasty precipitates were pressed onto a porcelain plate overnight. Sublimation in vacuo gave 1.9 g (crude yield 76%) of glassy crystals; IR 3320 cm⁻¹ (br). This mixture, as well as that obtained similarly from the product of bromination at 3 °C consists of 6-OH-1 and 1-OH-1.

The alcohols were separated by preparative GLC under the conditions specified in Table V. Poor separation necessitated repeated passes in order to obtain satisfactory purity.

6-OH-1: glass transition temperature (T_g) ∼140 °C; mp ∼210 °C; high-dilution IR (CCl₄) 3622, 3608 cm⁻¹; ¹H NMR (Eu(fod)₃[25] was used) δ 1.94 (d, J = 3 Hz, 2 H), 1.93 (m, 4 H), 1.8–1.5 (m, 9 H), 1.41 (d, J = 12 Hz, 1 H), 1.19 (d, J = 12 Hz, 1 H), 0.8 (br s, OH); mass spectrum, m/e 178 (M⁺, 68%), 160 (M⁺ − 18, 95%), 108 (86%), 107 (72%), 95 (base peak). Anal. (C₁₂H₁₈O) C, H.

1-OH-1: T_g ∼140 °C; mp ∼230 °C; high dilution IR (CCl₄) 3606 cm⁻¹; ¹H NMR δ 2.1–1.0 (m); mass spectrum, m/e 178 (M⁺, 15%), 95 (base peak). Anal. (C₁₂H₁₈O), C, H.

(51) Geluk, H. W.; Schlatmann, J. L. M. A. *Tetrahedron* **1968**, *24*, 5361.

6-Bromoethanoadamantane from 6-OH-1. A suspension of 33.5 mg of purifed and well-pulverized 6-OH-1 in 4 mL of 47% hydrobromic acid was sealed in a test tube and heated at 100 °C for 2 h with occasional shaking. The reaction mixture was poured into water and extracted with ether. The combined ether solution was washed with water, dried with calcium chloride, and evaporated. The solid residue remaining was sublimed in vacuo to give 37.5 mg (83%) of white, ill-formed crystals, mp 127–130 °C; ¹H NMR δ 2.56 (d, J = 2 Hz, 2 H), 2.5–1.2 (m with a prominent peak at 1.80); mass spectrum m/e 161 (M⁺ − Br). Anal. (C₁₂H₁₇Br) C, H, Br.

1-Bromoethanoadamantane from 1-OH-1 was prepared as above from 92.5 mg of 1-OH-1. The pure bromide (88.9 mg, 66.5%) melted at 121–125 °C; its mass spectrum was superimposable with that of 6-Br-1. Anal. (C₁₂H₁₇Br) C, H, Br.

6-Methylethanoadamantane from 6-Br-1. Pure 6-Br-1 (128 mg) was treated with methyl Grignard reagent as described above. The product (76 mg, 80%) had the same GLC retention time and ¹H NMR spectrum as the sample of 6-Me-1 described above.

1-Methylethanoadamantane from 1-Br-1. The reaction was carried out on 3 mg of 1-Br-1. The product had the same GLC retention time as the sample of 1-Me-1 obtained previously.

Base-Catalyzed Deuterium Exchange of 6,6-Dimethylfulvene[1]
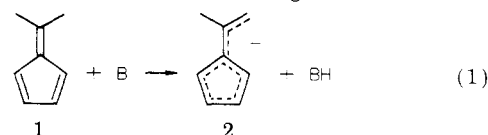
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The kinetics of the deuterium exchange of 6,6-dimethylfulvene have been studied in the presence of sodium methoxide–methanol-*d* and potassium *tert*-butoxide–*tert*-butyl alcohol-*d*. The rate of disappearance of undeuterated starting material was followed by mass spectral measurements. The rate of introduction of deuterium into the methyl groups and into the ring was followed by ¹H NMR. The rates of methyl exchange and ring exchange were of the same order of magnitude. The reaction of *tert*-butyl alcohol-*d* was speeded by addition of cryptate (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane). The occurrence of methyl exchange establishes a deprotonation mechanism (Scheme I) in both solvents. The greater rate in *tert*-butyl alcohol-*d* than in methanol-*d* is evidence that an addition–elimination mechanism for ring exchange is not important in *tert*-butyl alcohol-*d* solution, but its importance in methanol-*d* cannot be proven or disproven.

To better understand the preferred positions of reaction of mesomeric species, we earlier studied the protonation of the anion **2** produced by deprotonation of 6,6-di-

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methylfulvene (**1**).[2,3]   Anion **2** was generated almost

$$\text{1} + \text{B} \longrightarrow \text{2} + \text{BH} \qquad (1)$$

quantitatively by reaction of **1** with potassium *tert*-but-