II. By definition

$$D = (k_6'K_A + k_9'K_B + k_8K_C)K_BK_a + k_7'K_CK_aK_A \simeq k_6'K_AK_BK_a + k_7'K_CK_aK_A \quad \text{(iv)}$$

for it can be shown by an approximate estimation that $(k_9'K_B + k_8K_C)K_BK_a$ will not contribute more than ~4% to the observed value of D. The lower limit of the obtained α (0.50) was used in the estimation of k_6' and k_7'.

The calculation of k_5' from E was carried out as in eq v because an approximate estimate has revealed that the

$$E = (k_6K_A + k_9K_B)K_B + (k_5'K_a + k_7K_C)K_A \text{ or } E \simeq k_5'K_aK_A \quad \text{(v)}$$

contribution due to $(k_6K_A + k_9K_B)K_B + k_7K_CK_A$ to E should not be more than ~3.5%. Equation v was used for calculation of k_5'.

Registry No. *m*-AMSA, 51264-14-3; L-cysteine, 52-90-4; glutathione, 70-18-8; *N*-acetylcysteine, 616-91-1; 2-mercaptoethanol, 60-24-2; cysteamine, 60-23-1.

Reactivity of Geometrically Constrained Cyclopropylcarbinyl and Homoallyl Substrates. Solvolysis of 2,4-Dehydro-5-homoadamantyl and 2-Homoadamant-4-enyl Derivatives

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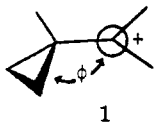
Received February 4, 1982

Solvolysis of 5-*endo*-2,4-dehydrohomoadamantyl 3,5-dinitrobenzoate (**5**) or 2-*exo*-chloro-4-homoadamantene (**6**) in buffered 70% aqueous acetone gives a very similar mixture of products by way of an apparent common intermediate. The formation of 5-*endo*-hydroxy-2,4-dehydrohomoadamantane as the major reaction product suggests that this species is a nonplanar 2,4-dehydro-5-homoadamantyl cation. When compared to the kinetic behavior of structurally analogous derivatives which react with unassisted ionization, both **5** and **6** show large solvolytic rate enhancements. The unusually large acceleration for **6** seems to be a consequence of the particular stereoelectronic arrangement of the double bond and the leaving group in this compound. In contrast to these results, 2-*endo*-homoadamant-4-enyl tosylate (**7**) solvolyzes 11 times more slowly than its saturated analogue to give a mixture of 2-*endo*- and 2-*exo*-hydroxyhomoadamant-4-ene. Since the solvolysis of **7** occurs by a k_c process, this may provide the best available measure of the inductive destabilization of a cationic center by a homoallylic double bond.

The rapid interconversion of cyclopropylcarbinyl, cyclobutyl, and homoallyl derivatives in solvolytic systems has attracted considerable attention.[4] As a result of both experimental studies and theoretical calculations, it is clear that the "bisected" conformation (**1**) of a cyclopropylcarbinyl cation is significantly energetically favored over the "perpendicular" conformation (**2**).[4] Recently, it has been demonstrated that a cyclopropylcarbinyl cation is also stabilized when the conformation of the system is locked by structural constraints at an intermediate position between bisected and perpendicular.[5] Indeed, the change in energy of a cyclopropylcarbinyl cation upon rotation of the cation center seems to follow a function that is very similar to a $\cos^2 \phi$ relationship (with ϕ being the angle of rotation).[5] In view of these observations, we were interested in examining the solvolytic generation of the 2,4-dehydro-5-homoadmantyl cation (**3**) and comparing its



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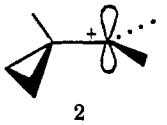

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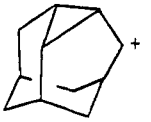

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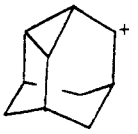

4

behavior with that of the 8,9-dehydro-2-adamantyl cation (**4**) which is constrained to the bisected conformation (ϕ = 0°). If the solvolysis of 2-adamantyl tosylate is used as a model for the localized cation **4**, then the rate enhancement associated with the assisted formation of a cation from 8,9-dehydro-2-adamantyl tosylate in acetolysis at 25 °C is 2.5×10^8.[6] An examination of Dreiding molecular models shows that for such an idealized representation of **3** the dihedral angle ϕ between the axis of the vacant p orbital at C-5 and the adjacent cyclopropyl moiety should be about 30°. Thus, it can be anticipated that ion **3** will experience only some of the cyclopropyl stabilization effective in **4**.

Ions **3** and **4** have been studied previously under stable ion conditions by NMR spectroscopy.[7,8] Ion **3** is static at

(1) University of Alabama in Huntsville.
(2) University of Delaware.
(3) Recipient of a Camille and Henry Dreyfus Teacher-Scholar Grant Award, 1976–1981.
(4) For reviews see: (a) Wiberg, K. B.; Hess, B. A., Jr.; Ashe, A. J., III "Carbonium Ions", Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, Chapter 26. (b) Richey, G. *Ibid.* Chapter 25. (c) Story, P. R.; Clark, P. R., Jr. *Ibid.* Chapter 23. (d) Haywood-Farmer, J. *Chem. Rev.* **1974**, *74*, 315–350. (e) Brown, H. C. "The Nonclassical Ion Problem", Plenum Press: New York, 1977; Chapter 5.
(5) de Meijere, A.; Schallner, O.; Weitemeyer, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *84*, 56–57. Rhodes, Y. E.; DiFate, V. G. *J. Am. Chem. Soc.* **1972**, *94*, 7582–7583. Andersen, B.; Schallner, O.; de Meijere, A. *Ibid.* **1975**, *97*, 3521–3522. de Meijere, A.; Schallner, O.; Weitemeyer, C.; Spielmann, W. *Chem. Ber.* **1979**, *112*, 908–935.
(6) Baldwin, J. E.; Foglesong, W. D. *J. Am. Chem. Soc.* **1968**, *90*, 4303–4310.

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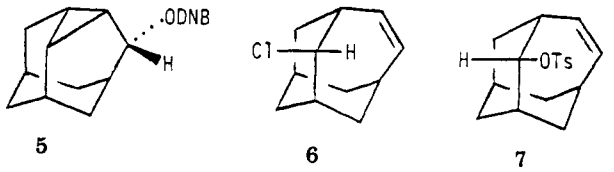
−120 °C.[7] Upon warming to −60 °C, it undergoes a degenerate cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement that is fast on the NMR time scale. In contrast,

under stable ion conditions 4 undergoes a threefold degenerate cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement that is fast on the NMR time scale even at −130 °C.[8] By the criterion of the total ^{13}C chemical shift difference between a carbocation and its corresponding neutral hydrocarbon, both 3 and 4 are classical cations.[9]

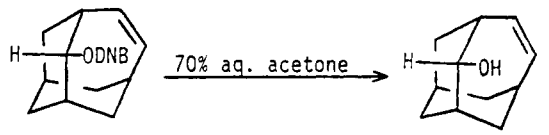
Results and Discussion

Synthesis of Starting Materials. In this study we have investigated the solvolytic behavior of 5-*endo*-2,4-dehydrohomoadamantyl 3,5-dinitrobenzoate (**5**), 2-*exo*-



5 **6** **7**

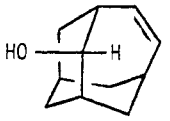
chloro-4-homoadamantene (**6**), and 2-*endo*-homoadamant-4-enyl tosylate (**7**). Initially we intended to use 3,5-dinitrobenzoate derivatives for all of the substrates. However, the formation of 2-*endo*-hydroxy-4-homoadamantene[10] (**9**) as the only product in the reaction of the



8 **9**

corresponding 3,5-dinitrobenzoate **8** in 70% aqueous acetone suggested that the intended solvolysis was being superceded by ester hydrolysis. This was established to be the case by carrying out the reaction with ^{18}O-labeled water. Treatment of **8** under these conditions gave **9** which contained no ^{18}O. This system ultimately proved to be sufficiently unreactive so that tosylate **7** could be readily prepared from **9**.

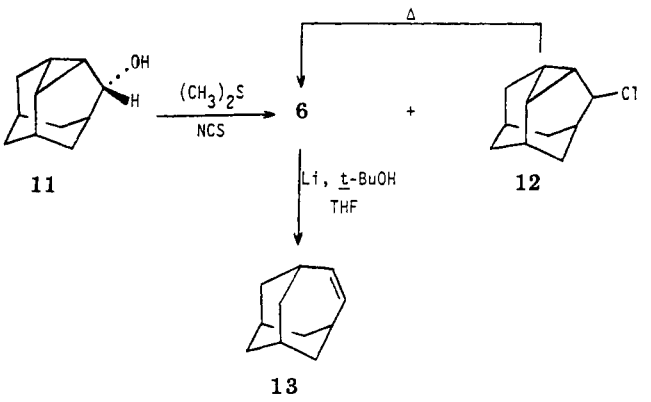
In view of the behavior of **8**, we were concerned that ester hydrolysis of the 3,5-dinitrobenzoate derivative of 2-*exo*-hydroxy-4-homoadamantene[10] (**10**) might also be



10

competitive with its solvolysis.[11] Since the tosylate of **10**

Scheme I



11 **12** **13**

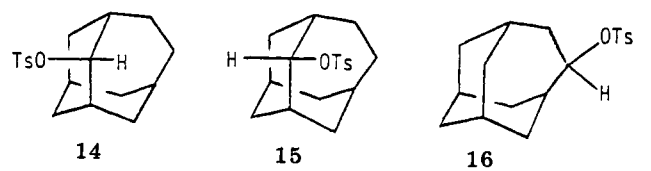
Table I. Product Compositions from the Solvolysis of Compounds 5–7 in 70% Aqueous Acetone Buffered with Lutidine[a]

		composition, %				
					unidentified isomers	
compd	temp, °C	9	10	11	A	B
5	25	0	8	87	5	0
6	75	0	12	83	5	0
7	100	39	51	0	0	10

[a] Determined by GC/MS. Products comprising less than 5% of the product mixture are not included.

was too reactive to prepare, chloride **6** was synthesized. Treatment of 5-*endo*-hydroxy-2,4-dehydrohomoadamantane[10] (**11**) with the 1:1 complex of methyl sulfide and *N*-chlorosuccinimide in methylene chloride[12] provided a 1.7:1 mixture of **6** and 5-chloro-2,4-dehydrohomoadamantane (**12**) in 93% yield (Scheme I). In the course of GLC purification, **12** isomerized to **6**. The carbon skeleton of **6** was established by reduction of **6** with lithium–tetrahydrofuran–*tert*-butyl alcohol[13] to give the known hydrocarbon 4-homoadamantene[14] (**13**). The stereochemistry of the chloro substituent in **6** follows from the characteristic splitting pattern of the C-2 *endo*-hydrogen.[10]

Kinetic and Product Studies. The results of the rate and product studies for the solvolysis of compounds **5–7** are summarized in Tables I–III. For comparative purposes we have also determined the rates of solvolysis for the 2-*exo*- and 2-*endo*-homoadamantyl tosylates, **14** and **15**, respectively. A detailed study on the acetolysis of 4-



14 **15** **16**

homoadamantyl tosylate (**16**) has been reported previously.[14]

By inspection, it is apparent that the product mixtures formed from **5** and **6** are very similar (Table I). This

(7) Olah, G. A.; Liang, G.; Babiak, K. A.; Morgan, T. K., Jr.; Murray, R. K., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 576–580.
(8) Olah, G. A.; Liang, G.; Babiak, K. A.; Ford, T. M.; Goff, D. L.; Morgan, T. K., Jr.; Murray, R. K., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 1494–1500.
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(10) Murray, R. K., Jr.; Babiak, K. A.; Morgan, T. K., Jr. *J. Org. Chem.* **1975**, *40*, 2463–2468.
(11) Treatment of the 3,5-dinitrobenzoate derivative of **10** under the same set of reaction conditions employed for the solvolysis of **5–7** provides **10** and **11** as the only volatile products in a relative ratio of 94:6.
(12) Corey, E. J.; Kim, C. U.; Takeda, M. *Tetrahedron Lett.* **1972**, 4339–4342.
(13) Bruck, P.; Thompson, D.; Winstein, S. *Chem. Ind. (London)* **1960**, 405–406.
(14) Norlander, J. E.; Hamilton, J. B., Jr.; Wu, F. Y.-H.; Jindal, S. P.; Gruetzmacher, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 6658–6669. See also: Schleyer, P. v. R.; Funke, E.; Liggero, S. H. *Ibid.* **1969**, *91*, 3965–3967.

Table II. First-Order Rate Constants for the Solvolysis of Homoadamantyl Derivatives[a]

compd	temp, °C	k, s^{-1} 70% aqueous acetone	70% aqueous ethanol	60% aqueous ethanol
5	100	3.35×10^{-4}		
6	75	8.31×10^{-4}		
	50	1.16×10^{-4}		
	100[b]	4.61×10^{-3}		
7	100	8.30×10^{-5}	3.35×10^{-4}	
	75	5.94×10^{-6}	1.66×10^{-5}	
	25[b]	8.20×10^{-9}	9.14×10^{-9}	
14	100[b]	9.17×10^{-3}	5.63×10^{-2}	
	75	1.09×10^{-3}		
	50	9.46×10^{-5}	3.87×10^{-4}	
	35	1.98×10^{-5}		
	25	5.46×10^{-6} [b]	1.73×10^{-5}	3.84×10^{-5}
15	100[b]	9.14×10^{-4}	4.19×10^{-3}	8.01×10^{-3}
	75	1.06×10^{-4}	4.29×10^{-4}	9.57×10^{-4}
	50	9.21×10^{-6}	3.17×10^{-5}	8.32×10^{-5}

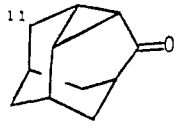
[a] All solvents are volume percent. Error limits are all within 5%. [b] Calculated from rates at other temperatures.

Table III. First-Order Rate Constants and Solvolysis Rates for Homoadamantyl Tosylates in 70% Aqueous Acetone at 100 °C

compd	k, s^{-1}	k_{rel}
7	8.30×10^{-5}	1
14	9.17×10^{-3}	110
15	9.14×10^{-4}	11
19[a]	1×10^{5}	1×10^{9}
20[a]	2×10^{3}	3×10^{7}

[a] Calculated by using an OTs/Cl ratio of 5×10^5 and an OTs/ODNB ratio of 3×10^8 (see Experimental Section for the derivation of these ratios).

suggests that each of these kinetically controlled reactions proceeds by a common cationic intermediate. Our results do not permit a definitive assignment of structure to the cationic intermediate in these reactions. However, in light of the many reported studies concerning the solvolysis of cyclopropylcarbinyl and homoallyl derivatives[4] and in view of the nature of the ion formed from alcohols 10 and 11 under stable-ion conditions,[7] it is reasonable to consider that these solvolyses are proceeding via the 2,4-dehydro-5-homoadamantyl cation (3). In this regard it is particularly noteworthy that the major product isolated from the solvolysis of 5 and 6 is the endo alcohol 11. This is the same product that results from the sodium borohydride reduction of 2,4-dehydro-5-homoadamantanone (17).[10] An



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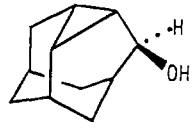

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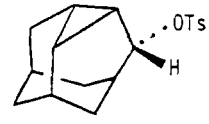
examination of molecular models shows that attack at the carbonyl carbon in 17 across the face of the seven-membered ring (i.e., endo attack) should be significantly impeded by the *endo*-hydrogen at C-11. By contrast, there is no apparent steric hindrance to attack at the carbonyl carbon in 17 across the face of the six-membered ring (i.e., exo attack). Consequently, we might well expect that capture of 3 by water should give exo alcohol 18 rather than the observed endo alcohol 11. Several other polycyclic cyclopropylcarbinyl cationic intermediates are also known to undergo anomalous endo attack by solvent.[15] Bach has accounted for this behavior by providing theoretical evidence that such reactions occur by nonplanar cyclopropylcarbinyl cations.[15] This is a result of rehybridization of the cationic center in the transition state to attain the best balance between the increase in energy accompanying the out-of-plane deformation of the cationic center and the decrease in energy associated with cyclopropylcarbinyl stabilization. In all of the cases examined, this results in an out-of-plane bend of the C–H bond at the cationic center toward the exo face.[15] On the basis of stereoelectronic considerations, interaction of the cationic center with solvent molecules is then expected to occur preferentially with the more directed lobe of the vacant p orbital, i.e., on the endo face of the cationic center, and thus 3 can give 11.

When compared to the kinetic behavior of structurally analogous "saturated" derivatives (Table III), both 5 and 6 show large rate enhancements in these solvolytic reactions. The acetolysis of 4-homoadamantyl tosylate (16) seems to take place by a mechanism involving meager nucleophilic solvent assistance and occurs at 25 °C at a rate of 1.35×10^{-5} s^{-1}.[14] The acetolysis rate of 5-*endo*-2,4-dehydrohomoadamantyl tosylate (19) at 25 °C can be



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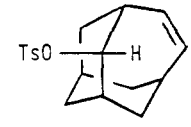

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estimated from the solvolysis rate of 5 in 70% aqueous acetone at 100 °C as 2.5×10^{-1} s^{-1}.[16] Consequently, the rate enhancement associated with the formation of ion 3 under these conditions is approximately 2×10^4. Although this rate acceleration is not nearly as large as that observed for the formation of the 8,9-dehydro-2-adamantyl cation under comparable solvolytic conditions (2.5×10^8),[6] it is consistent with the geometry of 3 whose rigid carbon skeleton requires significant distortion of the cyclopropylcarbinyl cation moiety from the ideal bisected conformation.[4,5]

The largest reported rate acceleration in the solvolysis of any homoallyl derivative (when compared to the cor-

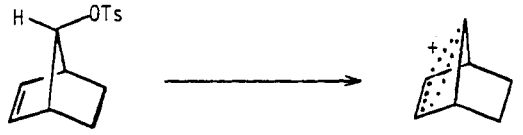
(15) Bach, R. D.; Siefert, J. H.; Tribble, M. T.; Greengard, R. A.; LeBel, N. A. *J. Am. Chem. Soc.* **1973**, *95*, 8182–8184. Bach, R. D.; Blanchette, P. E. *Ibid.* **1979**, *101*, 46–50.

(16) The acetolysis rate at 25 °C for tosylate 19 can be estimated from the measured rate of solvolysis of 5 in 70% aqueous acetone at 100 °C by correcting for the changes in leaving group (OTs/ODNB ratio of 3×10^8; see experimental section), temperature (25 °C/100 °C ratio of 10^{-3}), and solvent ($m = 0.8$ by the Grunwald-Winstein equation for a change from 70% aqueous acetone to acetic acid).

Table IV. Winstein-Grunwald m Values Calculated from Data in Table I

compd	temp, °C	m
7	75	0.96
14	25	0.86
15	25	0.99
	50	0.96
	75	0.95

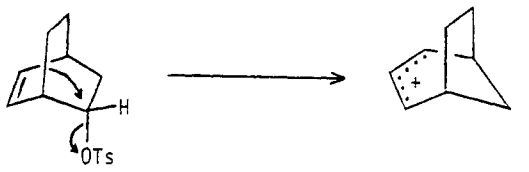
responding saturated compound) is the factor of about 10^{11} in the acetolysis of 7-*anti*-norbornenyl tosylate (**21**).[17] This



21 **22**

behavior has been attributed to the symmetrical placement of the double bond in **21** which permits formation of the bishomocyclopropenium ion **22**. On the other hand, relatively small rate accelerations are generally characteristic of homoallyl systems in which the double bond is unsymmetrically disposed with respect to the carbon atom bearing the leaving group.[4c,18] Consequently, it is striking that 2-*exo*-homoadamant-4-enyl tosylate (**20**) is calculated to solvolyze approximately 3×10^5 times faster than the corresponding saturated tosylate **14** and 3×10^7 times faster than the corresponding endo unsaturated tosylate **7**. Since the m value for **14** (Table IV) deviates significantly from unity, it follows that **14** is reacting by kinetic assistance either through neighboring carbon participation or from solvent nucleophiles.[19] Thus, **14** does not provide a good k_c model[20] for estimating the magnitude of assistance provided by the double bond in the solvolysis of **20**. However, **7** clearly appears to be reacting by a k_c mechanism (see below), and so the best estimate of the acceleration by the double bond in the solvolysis of **20** is obtained by comparison with **7**. An examination of a molecular model of the 2-homoadamant-4-enyl cation shows that the vacant p orbital at C-2 is directed between the p orbitals of the double bond and suggests that it overlaps more strongly with the p orbital at C-4. Thus, the enhanced homoallylic participation found in the solvolysis of **6** appears to be a consequence of the stereoelectronic arrangement of the double bond and the leaving group.

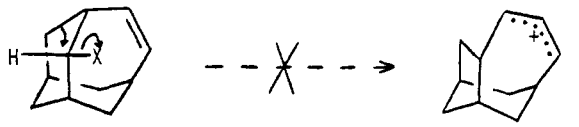
In contrast to **5** and **6**, *endo*-tosylate **7** reacts more slowly under comparable conditions than the saturated model **15** (Table III) and gives a mixture of both *endo*- and *exo*-homoadamant-4-en-2-ols as reaction products (Table I). These results suggest that the solvolysis of **7** is occurring with unassisted ionization (a k_c process[20]). This conclusion is further supported by the observation that the m values for **7** and **15** are close to unity (Table IV), in accord with expectations for a k_c process.[20] Double bond participation does not occur in the reaction of **7** because the rigid skeleton of **7** prevents the π electrons from interacting with the back side of the developing p orbital at the cationic center. Thus, the reactivity of **7** is dominated by the electron-withdrawing inductive effect of the double bond.[21-23] The inductive effect of an allylic double bond on a cationic center is known to lead to a rate reduction of approximately 10^4.[4c,21-23] No such estimate is currently available for the inductive destabilization of a cation by a homoallylic double bond. Indeed, it is generally the case that the syn derivative of a bicyclic β,γ-unsaturated alcohol reacts faster than the corresponding saturated analogue under a comparable set of solvolytic conditions. For example, k_{unsat}/k_{sat} is 5 for **23**[24] and 10^4 for **24**.[25] Of course,



23

24

in these cases the syn unsaturated compound can undergo σ participation with ionization to produce an allyl cation. Presumably such assistance does not occur in the ionization of **7** because of the increase in strain energy that would be required to form **25**. Consequently, the rate ratio of



7 **25**

7 to **15** of 0.1 may provide the best available measure of the inductive destabilization of a cationic center by a homoallylic double bond.

The generation of significant amounts of both **9** and **10** in the solvolysis of **7** suggests that product formation in this reaction may occur from a solvent-separated ion pair (**26**). Such an intermediate could be formed in a k_c process

$$7 \rightarrow R^+||^-OTs \rightarrow 9 + 10$$
26

and could give products with both retention and inversion of stereochemistry, i.e., **9** and **10**, respectively. This behavior would be consistent with other observations concerning the stereochemistry of product formation from solvent-separated ion pairs.[26]

Experimental Section

Melting points were obtained in sealed capillary tubes by using a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were obtained on Perkin-Elmer 180 and 337

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spectrophotometers. Proton magnetic resonance spectra were recorded with a Perkin-Elmer R-12B 60-MHz spectrometer and are referenced to an internal standard of tetramethylsilane. GC/MS was carried out on an HP 5985 mass spectrometer interfaced with an HP 5840 gas chromatograph. Elemental analyses were performed by Micro-Analysis, Inc., Wilmington, DE.

5-*endo*-2,4-Dehydrohomoadamantyl 3,5-Dinitrobenzoate (5). 3,5-Dinitrobenzoyl chloride (1.547 g, 6.7 mmol) was added to a solution of 5-*endo*-hydroxy-2,4-dehydrohomoadamantane[10] (**11**; 1.000 g, 6.1 mmol) in dry pyridine (25 mL). the solution was stirred at 80 °C for 1 h and then poured into 75 mL of ice water. The resulting precipitate was filtered, washed with several small portions of water, and dissolved in chloroform (100 mL). This solution was washed with saturated aqueous sodium bicarbonate (3 × 25 mL) and then dried over anhydrous magnesium sulfate. Evaporation of the solvent under reduced pressure provided a solid residue which was recrystallized twice from chloroform–ethanol to give 1.49 g (68% yield) of **5** as a white solid: mp 169–170 °C; ^{1}H NMR ($CDCl_3$) δ 9.29 (m, 3 H, aromatic protons), 5.93 (t, J = 6 Hz, 1 H, CHODNB), 2.6–0.9 (br m, 14 H); IR (CCl_4) 3105, 2925, 2850, 1730, 1630, 1550, 1460, 1340, 1275, 1165, 960 cm^{-1}.

Anal. Calcd for $C_{18}H_{18}N_2O_6$: C, 60.33; H, 5.06; N, 7.82. Found: C, 60.32; H, 5.20; N, 7.93.

2-*exo*-Chloro-4-homoadamantene (6). Dimethyl sulfide (170 mg, 2.7 mmol) was added to a stirred solution of *N*-chlorosuccinimide (335 mg, 2.5 mmol) in anhydrous methylene chloride (10 mL) at −20 °C under nitrogen.[12] The resulting precipitate slowly dissolved as a solution of **11**[10] (375 mg, 2.3 mmol) in methylene chloride (1 mL) was added. The reaction mixture was stirred for 1 h at 0 °C and then for 2 h at room temperature at which point it was poured into 50 mL of ice-cold brine. The resulting layers were separated, and the aqueous phase was extracted with ether (2 × 25 mL). The organic extracts were combined and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure provided 415 mg (93% yield) of a white solid which was shown by ^{1}H NMR analysis to be a 1.7:1 mixture of **6** and 5-chloro-2,4-dehydrohomoadamantane (**27**), respectively. In the course of GLC purification (10 ft × 0.25 in. DC-550 column, 200 °C), **27** was isomerized to **6** so that pure **6** was obtained as a white solid: mp 146–152 °C; ^{1}H NMR (CCl_4) δ 6.45–5.75 (m, 2 H, CH=CH), 4.38 (br s, 1 H, CHCl), 2.83–1.33 (m, 12 H); IR (CCl_4) 3030, 2925, 2850, 1450, 1430, 1335, 1230, 1220, 1115, 1085, 1055, 940, 930, 910 cm^{-1}.

Anal. Calcd for $C_{11}H_{15}Cl$: C, 72.32; H, 8.28. Found: C, 72.23; H, 8.12.

4-Homoadamantene (13). Freshly cut lithium (70 mg, 10.0 mmol) was added to a stirred solution of **6** (20 mg, 0.11 mmol) in tetrahydrofuran (10 mL) and *tert*-butyl alcohol (2 mL). The reaction mixture was maintained at room temperature under nitrogen and stirred for 4 h. At this point water (20 mL) was added, and stirring was continued for an additional 30 min. The mixture was then extracted with ether (3 × 15 mL), and the combined extracts were dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave a colorless oil which GLC analysis (10 ft × 0.25 in. DC-550 column, 170 °C) showed was homogeneous. Olefin **13** was isolated by GLC (above conditions) and was identified by comparison of its infrared spectrum with that of an authentic sample prepared by an alternative route.[14]

2-*endo*-Homoadamant-4-enyl *p*-Toluenesulfonate (7). Freshly recrystallized *p*-toluenesulfonyl chloride (1.395 g, 7.3 mmol) was added to a solution of 2-*endo*-hydroxy-4-homoadamantene[10] (**9**; 600 mg, 3.66 mmol) in dry pyridine (8 mL) which was maintained at 0 °C. The resulting solution was stored at 0 °C for several days. When it appeared that no more pyridine hydrochloride was precipitating, the entire mixture was poured with stirring into ice–water (50 mL). The resulting white precipitate was filtered, washed with water, and then dried in vacuo at room temperature. Recrystallization of this material from a minimal amount of petroleum ether provided 717 mg (62% yield) of **7** as a white solid: mp 80–81 °C; ^{1}H NMR ($CDCl_3$) δ 8.00 (d, J = 8 Hz, 2 H, aromatic protons), 7.48 (d, J = 8 Hz, 2 H, aromatic protons), 6.29 (dd, J = 10, 8.5 Hz, 1 H, CH=CH at C-5), 5.74 (dd, J = 10, 8.5 Hz, 1 H, CH=CH at C-4), 4.83 (t, J = 5 Hz, 1 H, CHOTs), 2.80–1.27 (m, 15 H, containing CH_3 signal at δ 2.47); IR (CCl_4) 3030, 2920, 2855, 1600, 1460, 1440, 1365, 1290, 1180, 1100 cm^{-1}.

Anal. Calcd for $C_{18}H_{22}O_3S$: C, 67.90; H, 6.96; S, 10.07. Found: C, 68.05; H, 7.10; S, 10.11.

2-*exo*-Homoadamantyl *p*-Toluenesulfonate (14). Treatment of 2-*exo*-hydroxyhomoadamantane[10] (560 mg, 3.4 mmol) with *p*-toluenesulfonyl chloride (1.286 g, 6.7 mmol) in dry pyridine (8 mL) by the procedure described for **9** → **7** gave 737 mg (68% yield) of **14** as a white solid: mp 96–97.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.93 (d, J = 8 Hz, 2 H, aromatic protons), 7.42 (d, J = 8 Hz, 2 H, aromatic protons), 4.52 (s, 1 H, CHOTs), 2.67–0.97 (m, 19 H, containing CH_3 signal at δ 2.47); IR (CCl_4) 2925, 2910, 2860, 1600, 1460, 1370, 1190, 1180, 1100 cm^{-1}.

Anal. Calcd for $C_{18}H_{24}O_3S$: C, 67.47; H, 7.55; S, 10.01. Found: C, 67.63; H, 7.32; S, 9.99.

2-*endo*-Homoadamantyl *p*-Toluenesulfonate (15). Treatment of 2-*endo*-hydroxyhomoadamantane[10] (452 mg, 2.7 mmol) with *p*-toluenesulfonyl chloride (1.039 g, 5.45 mmol) in dry pyridine (6 mL) by the procedure described for **9** → **7** afforded 494 mg (57% yield) of **15** as a white solid: mp 66.5–68.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.96 (d, J = 8 Hz, 2 H, aromatic protons), 7.42 (d, J = 8 Hz, 2 H, aromatic protons), 4.87 (t, J = 5 Hz, 1 H, CHOTs), 2.69–1.19 (m, 19 H, containing CH_3 signal at δ 2.47); IR (CCl_4) 2910, 2855, 1600, 1450, 1365, 1190, 1180, 1100 cm^{-1}.

Anal. Calcd for $C_{18}H_{24}O_3S$: C, 67.47; H, 7.55; S, 10.01. Found: C, 67.43; H, 7.56; S, 9.96.

Kinetic Methods. Rates were determined conductometrically according to reported procedures.[19] The solvents for these studies were purified as previously described.[19]

Product Analyses. The products were identified by the comparison of their GC retention times and mass spectra with those of authentic samples by means of a GC/MS system. The presence of two small peaks in the GC trace of the solvolysate from **6** and one small peak in the GC trace of the solvolysate from **7** were ignored in calculating the relative ratio of products (Table I). In each case these peaks constituted less than 3% of the total volatile products.

Leaving Group Ratios. The OTs/Cl ratio of 5 × 10^5 in Table II is that reported for tertiary derivatives.[27] We have used this ratio because it is derived from substrates which are known to react by a k_c mechanism. The rates for the solvolysis of several tertiary chlorides in 80% ethanol and the corresponding *p*-nitrobenzoates in 80% acetone have appeared.[28] Averaging these values gives a Cl/OPNB ratio of 3.5 × 10^4. Assumption of an m value of 0.8 to correct this ratio for the difference in solvents provides a Cl/OPNB ratio of 1 × 10^4. The product of these OTs/Cl and Cl/OPNB ratios gives an OTs/OPNB ratio of 5 × 10^9. Since the ODNB/OPNB ratio is 16.0,[29] it follows that the OTs/ODNB ratio is 3 × 10^8. Relative to the assumptions involved in the calculation of this value, it should be noted that the OTs/ODNB conversion factor is only being used here to compare systems in which there is such a large rate difference that an error in the conversion factor of several orders of magnitude would be of little consequence.

Acknowledgment. We are grateful to Dr. Charles D. Duncan of the University of Alabama in Birmingham for his assistance in the GC/MS identification of the solvolytic products. Acknowledgment is made to the University of Delaware Research Foundation and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. **5**, 81523-08-2; **6**, 81523-09-3; **7**, 81523-10-6; **9**, 55659-66-0; **10**, 55638-04-5; **11**, 55638-03-4; **12**, 81523-11-7; **13**, 24669-57-6; **14**, 66687-78-3; **15**, 66748-94-5; **19**, 81523-12-8; **20**, 81570-99-2; 2-*exo*-hydroxyhomoadamantane, 55638-08-9; 2-*endo*-hydroxyhomoadamantane, 55659-65-9.

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