was transferred under nitrogen to the irradiation tube and diluted to 500 mL. The nitrogen was bubbled through the mixture for 30 min, and then irradiation took place for 6 h. Filtration followed by evaporation and chromatography on silica-H with 10% acetone in petroleum ether as eluent was the usual workup procedure.

I. In this case 1.35 g of white solid was isolated from the irradiation mixture, 0.5 g of which were identified as starting material. The weight of the residue after evaporation was 1.4 g. Dimethyl allylphosphonate (XVI)[21] was isolated in 70% yield (1.05 g): NMR δ 2.48 (J_{PH} = 22 Hz, J_{HH} = 7 Hz), 3.65 (J_{PH} = 11 Hz), 5.13 (m), 5.70 (m).

II. In this case 1.14 g of white solid identified as sodium *p*-toluenesulfinate (XIV) was isolated from the irradiation mixture (70%). From the residue after evaporation (3.01 g) 0.544 g (19.7%) of phosphorus-containing organic materials could be isolated: dimethyl β,β-diphenylvinylphosphonate (XVII; 0.134 g, 25% of the above mixture), dimethyl *cis*-stilbenephosphonate (XVIII; 0.207 g, 38%), dimethyl *trans*-stilbenephosphonate (XIX; 0.204 g, 37%). Compound XVII was compared with an authentic sample prepared from the known acid:[23] NMR δ 3.37 (J_{PH} = 11 Hz), 6.09 (J_{PH} = 14 Hz), 7.20 (m), 7.29 (m); MS *m/e* 288 (M^+).

III. In this case 2.85 g (67%) of the starting material could be isolated from the irradiation mixture. The residue after evaporation (1.7 g, 36%) was chromatographed to give dimethyl 9-phenanthrenylphosphonate (XX; 0.97 g, 53% of the above mixture) which was compared with an authentic sample prepared by esterification of the corresponding acid[24] with CH_2N_2 in ether [NMR δ 3.79 (J_{PH} = 11 Hz), 7.57 (m), 8.53 (m)] together with 1-(dimethoxyphosphonyl)methylenedibenzocyclopentene (XXI): 0.73 g (43%); NMR δ 3.51 (J_{PH} = 11 Hz), 5.19 (J_{PH} = 30 Hz), 7.32 (m), 7.79 (m), 8.53 (m); MS *m/e* 286 (M^+).

Registry No. I, 71265-00-4; I sodium salt, 71265-01-5; II, 71265-02-6; II sodium salt, 71265-03-7; III, 71265-04-8; III sodium salt, 71265-05-9; IV, 71265-06-0; VI, 71302-35-7; VIII, 103-19-5; IX, 2943-42-2; X, 3185-99-7; XI, 3900-79-6; XIV, 71161-92-7; XVI, 757-54-0; XVII, 71265-07-1; XVIII, 71265-08-2; XIX, 71265-09-3; XX, 71265-10-6; XXI, 71265-11-7; dimethyl α-acetylmethylphosphonate, 4202-14-6; *p*-toluenesulfonyl hydrazide, 1576-35-8; β,β-diphenylepoxyethylphosphonate, 71265-12-8; dimethyl α-formyldiphenylmethylphosphonate, 22894-34-4; benzophenone, 119-61-9; fluorenone, 486-25-9; dimethyl chloromethylphosphonate, 6346-15-2.

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Ethanolysis of 1-Chloro-2-azaadamantanes[1]

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Solvolyses of 1-chloro-2-azaadamantanes (**1b** and **1c**) in ethanolic solution follow first-order kinetics. Reaction proceeds via an S_N1 mechanism. The solvolysis is accelerated by a factor of 10^3–10^4 relative to 1-chloroadamantane, due to stabilization of the bridgehead carbonium ion by the lone pair on adjacent nitrogen. Addition of ethanol to the bridgehead cation with subsequent loss of a proton yields 1-ethoxy-2-azaadamantanes (**1j** and **1k**). Results are compared with published data for other ring systems.

Since 1939, considerable attention has been devoted to solvolytic reactions involving bridgehead carbonium ions in bi- and tricyclic ring skeletons. This research has resulted in important contributions to mechanistic organic chemistry. Some excellent reviews are available.[3,4] In recent years, there has been a surge of activity with such systems modified by substitution of a heteroatom in the ring structure adjacent to the bridgehead.[5-11] However, only two papers have been concerned with heteroadamantanes. The solvolysis rate of 1-bromo-2-oxaadamantane (**1e**) was determined and compared with that of 1-bromoadamantane (**1d**).[5] The corresponding tosylates **1g** and **1f** have also been solvolyzed.[7] Although a more extensive study was made of 2-hetero-3-cyano-1-adamantyl tosylates (**2**), the presence of the cyano group complicates comparison with solvolytic data from related compounds.[7]

In the present study, we report on the solvolytic behavior of 1-chloro-2-azaadamantanes (**1b** and **1c**) and explore the possibility of base-promoted elimination in the case of **1b**. Results are compared with literature data for the solvolyses of related adamantane substrates (**1** and **2**), as well as for bicyclo[2.2.2]octyl (**3**),[9] bicyclo[3.3.1]nonyl (**4**),[10] and homoadamantyl (**5**)[11] systems.

Results and Discussion

Chlorides **1b** and **1c** were prepared according to published procedures.[5,6] In most cases, the ethanolysis reaction was followed by "rapid intermittent titration" of the hydrogen chloride generated in the reaction. Little or no

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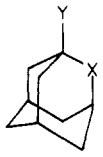
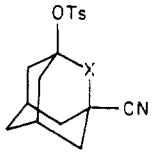
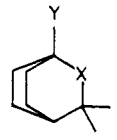


1a, X = CH_2, Y = Cl
b, X = NH, Y = Cl
c, X = NCH_3, Y = Cl
d, X = CH_2, Y = Br
e, X = O, Y = Br
f, X = CH_2, Y = OTs

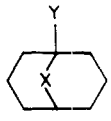
g, X = O, Y = OTs
h, X = NH, Y = OH
i, X = NCH_3, Y = OH
j, X = NH, Y = OC_2H_5
k, X = NCH_3, Y = OC_2H_5



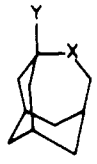
2a, X = CH_2
b, X = NCH_3
c, X = O



3a, X = CH_2, Y = Cl
b, X = NH, Y = Cl
c, X = CH_2, Y = Br



4a, X = CH_2, Y = Cl
b, X = NCH_3, Y = Cl
c, X = O, Y = Cl
d, X = CH_2, Y = Br



5a, X = CH_2, Y = Cl
b, X = NH, Y = SC_2H_5
c, X = NCH_3, Y = SC_2H_5
d, X = NCH_3, Y = Cl
e, X = CH_2, Y = Br

salt effect was detected within the precision of the experiments in runs made in the presence of a low concentration of added NaCl (saturated solution, ca. 0.01 M)[13] or $NaClO_4$ (0.0087 M). Rate constants were calculated from data collected during the first 1 to 3 half-lives, although in some cases the first-order plots were linear to as much as 95% reaction. Observed rate constants are listed in Table I. Consistent with the expected S_N1 mechanism (Scheme I), the rate constant showed a positive salt effect with sodium perchlorate (0.2 and 1.44 M), increased in aqueous ethanol (m = 0.84), and was insensitive to a fivefold increase in substrate concentration. In the more dilute salt solutions and at salt concentrations generated during reaction by the titration procedure, neither a normal salt effect nor a common ion effect of chloride ion should affect the observed rates appreciably.[14] Ethyl ethers **1j** and **1k** were isolated as the reaction products.

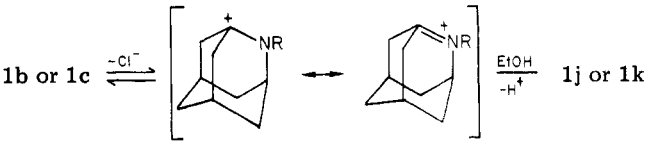
The *N*-methyl substituent in **1c** produced a 15-fold *decrease* in the solvolysis rate relative to **1b** (Table I). The normal qualitative expectation of greater electron release by methyl vs. hydrogen would have predicted instead that the rate should be increased. In a different system where nitrogen is called upon to stabilize a positive charge, N-methylation of pyrroles slightly increases the rate of coupling with diazonium ions.[15] In terms of LFE substituent constants,[16] it also appears that N-methylation increases nitrogen's tendency to release electrons by

Table I. Ethanolysis of 1-Chloro-2-azaadamantane (1b) and 1-Chloro-2-methyl-2-azaadamantane (1c)[a]

T, °C[b]	solute	compd	10^6k,[c] s^{-1}
75	0.01 M NaCl	1b	151
70	*d*	1b	98.5 ± 6
70	0.2 M $NaClO_4$	1b	176
70	1.44 M $NaClO_4$	1b	750
70	1.44 M $NaOC_2H_5$	1b	170[e]
65	0.01 M NaCl	1b	52.7
60	0.01 M NaCl	1b	29.2
50	0.01 M NaCl	1b	8.2
50[f]	0.01 M NaCl	1b	89 ± 5
50[g]	0.01 M NaCl	1b	381 ± 14
25[h]	0.01 M NaCl	1b	0.27
70	0.01 M NaCl	1c[i]	6.7

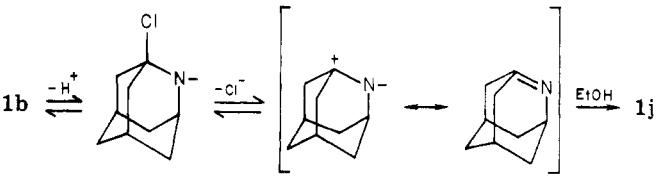
[a] Unless otherwise indicated, data are for solvolysis of substrate present initially at about 6×10^{-3} M concentration in absolute ethanol and followed by rapid intermittent titration. Standard deviations within a run were calculated to be 1% or less in all cases, but repeatability between runs was closer to ±5%. [b] ±0.1 °C. [c] Standard deviations are shown for replicate runs. [d] Average of runs with no added salt (10^6k = 94.9), 0.0087 M $NaClO_4$ (96.4) and 0.01 M NaCl with substrate concentration 6×10^{-3} M (107) and 2.9×10^{-2} M (95.5). The latter run was also followed by GLC (10^6k = 94.3). [e] Analyzed by NMR; ±10%. [f] 90% ethanol (v/v). [g] 80% ethanol (v/v). [h] Extrapolated from higher temperatures; $\Delta H^{\ddagger}$ = 26.6 ± 0.1 kcal/mol; $\Delta S^{\ddagger}$ = 0.6 ± 0.8 eu. [i] Substrate concentration, 1.4×10^{-2} M; temperature ±0.5 °C.

Scheme I



R = H or CH_3

Scheme II



resonance (σ_{para} = −0.83 and −0.66; σ_R^+ = −1.75 and −1.61; R = −0.92 and −0.51, respectively, for NMe_2 and NH_2). Although the influence of N-methylation is less clear-cut on the inductive effect of nitrogen (e.g., σ_I = +0.06 and +0.12; $\tilde{f}$ = +0.10 and +0.02 for NMe_2 and NH_2), it appears that the observed rate decrease is the opposite of what would be expected both qualitatively and quantitatively for the electronic effect of methyl substitution on the rate.

We feel that the major contribution to the rate decrease on N-methylation arises from steric interference with resonance stabilization of the carbonium ion. The limited overlap of the filled nitrogen lone-pair orbital with the vacant carbonium ion orbital is dependent upon the geometry at nitrogen. Interference with the *N*-methyl group by methylene groups of the tricyclic framework should oppose any distortions which would increase overlap between these orbitals. Differences in solvation at the partially positive nitrogen might also be important. The NH group in the carbonium ion from **1b** may hydrogen bond to solvent, while the *N*-methyl of **1c** may hinder solvation. The well-known irregularities in basicities of amines are believed to originate from competing inductive and hydrogen-bonding effects; in a σ^* correlation, this results in secondary amines falling on a correlation line

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Table II. Comparison of Solvolysis Rates of Bridgehead Substrates in Various Bi- and Tricyclic Ring Systems

ring system[a] Y =	conditions	X[a]	k, s^{-1}	k(rel),[b] s^{-1}	k(rel),[c] s^{-1} X = CH_2	k(rel),[d] s^{-1} X = NR
3, Cl	70% dioxane, 52 °C	CH_2[e]	8×10^{-11}	(1)	1.1×10^{-3}	
		NH[f]	3.7×10^{-4}	5×10^{6}		36
1, Br	80% EtOH, 25 °C	CH_2[g]	5.1×10^{-7}	(1)	(1)	
		O[h]	6.3×10^{-8}	0.12		
1, OTs	80% EtOH, 25 °C	CH_2[i]	5.73×10^{-3}	(1)		
		O[i]	2.1×10^{-5}	0.0037		
1, Cl	EtOH, 25 °C	CH_2[j]	3×10^{-11}	(1)		
		NH[k]	2.7×10^{-7}	9000		15
		NCH_3[k]	2×10^{-8}	700		(1)
2, OTs	80% EtOH, 25 °C	CH_2[i]	5.71×10^{-7}	(1)	1×10^{-4}	
		NCH_3[i]	2.04×10^{-4}	357		5×10^{-5} [l]
		O[i]	4.25×10^{-10}	7.4×10^{-4}		
4, Cl	96% EtOH, 29 °C	CH_2[m]	3.6×10^{-9}	(1)	1.1×10^{1}	
		NCH_3[m]	2.9×10^{-2}	8×10^{6}		2×10^{4}
		O[m]	1.2×10^{-9}	0.32		
		S[m]	4×10^{-11}	0.011		
5, Cl	EtOH, 25 °C	CH_2[n]	3.2×10^{-8}	(1)	3.3×10^{2}	
		NCH_3[o]	4×10^{6}	10^{14}		$\sim 10^{14}$

[a] Y = leaving group; X = ring segment adjacent to bridgehead; 3-cyano-1-adamantyl is treated as a separate ring system. [b] Relative rates for various X moieties within the ring system. [c] Relative rates for different ring systems in 80% ethanol, 70 °C, Y = Br, ref 21. [d] Relative rates for different aza ring systems, 100% ethanol, 25 °C, Y = Cl, extrapolated if necessary from other temperatures, solvent, or leaving groups. [e] See ref 24. [f] Reference 9; the observed rate in ethanol at 52 °C relative to the interpolated rate of **1c** was used in the last column. [g] D. J. Raber, R. C. Bingham, J. M. Harris, J. L. Fry, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 5977 (1970). [h] Reference 5. [i] Reference 7. [j] Estimated from ref 21 and P. v. R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 2700 (1961), in 80% ethanol, assuming $m = 1.20$ (see footnote *g*). [k] Present work; relative rates for X = NCH_3 vs. X = NH assumed equal at 25 and 70 °C. An independent value of $k_{rel} = 1.6 \times 10^3$ for **1b** in 80% ethanol at 50 °C may be obtained by comparing data of Table I with a rate constant for **1a** extrapolated from data in ref 21. [l] Estimated ignoring possible leaving group effects. [m] Reference 10. [n] Estimated from ref 21 and H. Stetter and P. Goebel, *Chem. Ber.*, **96**, 550 (1963), using $m = 1.0$. [o] Reference 11.

about 2.5 pK units more basic than the line for tertiary amines.[17]

In earlier work with compounds **3b** and **5b**, a base-promoted elimination–addition mechanism was proposed to rationalize a sizable rate increase in basic solution.[9,11] The possibility of a similar mechanism (Scheme II) in the present system was investigated by a study of the reaction in ethanolic sodium ethoxide solution. Kinetics were followed by extraction of reaction aliquots and NMR analysis of the resulting mixtures of **1b** and **1j**. A similar technique has been used to study the behavior of **5b** in basic solution.[11] With **1b**, the reaction rate in 1.44 M sodium ethoxide was increased by a factor of only about 1.7 relative to neutral ethanol. The modest size of the effect and the substantially larger rate enhancement produced by sodium perchlorate (Table I) suggest that most or perhaps all of the observed increase arises from a salt effect, rather than from the pathway in Scheme II. The relative magnitudes of the perchlorate and alkoxide salt effects appear consistent with published studies.[14]

The virtual absence of a base-promoted elimination–addition route with **1b** stands in marked contrast to results reported in the azahomoadamantyl (**5b**)[11] and bicyclo[2.2.2]octyl (**3b**)[9] systems. In the latter case, a 10^2-fold rate enhancement was estimated in 2.5 M sodium ethoxide, based on gas chromatographic analysis of solutions in which 90–95% of reaction had apparently occurred after short periods of heating. In the present work with **1b**, we obtained identical results, using the GLC and titrimetric analytical techniques on a run in neutral solution (Table I, footnote *d*). However, with the strongly basic medium, GLC analysis gave erratic results (probably as a result of reaction in the GLC injection port), indicating in most analyses an extent of reaction greater than 75% and differing from the NMR data. It is possible that the earlier results[9] were in error due to similar problems with the GLC analytical method. If so, it is reasonable that an elimination–addition pathway should be important for **5b** but not for **1b** or **3b**, since a bridgehead double bond in the former is less strained.[18] The poorer leaving group in **5b** (SC_2H_5)[11] might also favor elimination–addition.

The present results provide a comparison of the effects of 2-aza and 2-oxa substitution on the solvolysis of 1-adamantyl derivatives and, in addition, a comparison with other ring systems (Table II). 2-Aza substitution has a pronounced accelerating effect (10^3–10^4) on the solvolysis of 1-chloroadamantane. Since the electron-withdrawing inductive influence of an adjacent nitrogen has been estimated to produce a retardation of roughly 10^{-4} to 10^{-6} in solvolysis in a somewhat different ring system,[19] even the rather restricted overlap between the lone-pair orbital of the nitrogen and the vacant carbonium ion orbital may be responsible for a resonance effect of 10^7–10^{10} on the rate. With 2-oxa substitution, the inductive effect of the oxygen dominates, although there is some uncertainty as to the net magnitude.[20] (For bromides **1d** and **1e**, a decrease by a factor of 0.12 to 0.54 was reported,[5] whereas for tosylates **1f** and **1g**, the observed factor[7] was 3.7×10^{-3}.) 3-Cyano substitution[7] in **2** decreases rates by about four powers of ten via the electron-withdrawing inductive effect, but the 2-aza and 2-oxa substitution effects remain remarkably similar to the ratios found for **1b**/**1a** and **1g**/**1f**, respectively. Inductive electron withdrawal by the cyano group might be expected to decrease the ability of the nitrogen

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(20) The difference in the oxa effect between bromide and tosylate solvolyses may be real, possibly reflecting the difference in relief of ground-state strain in sulfonate and halide solvolyses.[21] The difference might also be an artifact, since the bromide solvolyses were followed for only a fraction of a half-life.[5]

and oxygen of **2b** and **2c** to stabilize a carbonium ion by resonance electron release. The observed relative rates are consistent with a small influence of this type.

Variations in solvent, leaving group, and temperature combine to introduce some uncertainties into the comparisons between different ring systems. However, it does not appear that these uncertainties are great enough to change the overall picture. The chloride to bromide rate ratio is relatively insensitive to structural changes, and solvent effects are similar in a variety of bridgehead solvolyses.[21] The selectivity is greater at lower temperatures, but changes over the range studied are not great. In Table II, a number of comparisons are set forth. Within a specific ring system, the effects of aza, oxa, and thia substitution are tabulated for the solvent and temperature of the original work (or extrapolated to a common temperature, if necessary). Relative rates of the parent carbocyclic bromides are given as a measure of the inherent difficulty of generating a bridgehead carbonium ion (largely as a consequence of "bridgehead strain" which opposes planarity at the cationic center[21,22]). Solvolysis rates of the various aza-substituted chlorides are also compared.

In the absence of geometric constraint, resonance stabilization of a carbonium ion center by nitrogen heavily outweighs inductive destabilization, with the consequence that α-haloamines are generally ionic.[23] In bi- or tricyclic ring systems, alignment of the nitrogen lone pair and the carbonium ion p orbitals is restricted, thereby decreasing overlap. Further reduction of overlap should result from nonplanarity of the bridgehead cation in a strained ring system, since this reduces the p character of the vacant orbital. Other factors which may have a less important influence on solvolysis rates could include changes in hybridization and electronegativity at nitrogen or oxygen due to ring strain or modification of ring strain by the presence of a heteroatom possessing bond angles and bond lengths which differ from those of CH_2. We intend to explore the importance of the several factors via molecular orbital calculations.

For the systems presented in Table II, the largest rate enhancement by nitrogen and the greatest overall rate are found for the 4-aza-3-homoadamantyl system (**5**). In this case, the solvolysis rate of the carbocyclic analogue indicates relatively little bridgehead strain,[21,22] and a fairly favorable geometry for π overlap may be achieved without a great deal of distortion. The other three ring systems (**1**, **3**, and **4**) exhibit similar geometries in the vicinity of the bridgehead. All are nearly tetrahedral, and the bond to leaving group Y has a staggered arrangement relative to the orbitals (or bonds) on the X group.[22] Carbocyclic solvolysis rates decrease in the order **5** > **4** > **1** > **3**, as a result of decreasing ease in attaining planar bridgehead geometry.[21] However, in the bicyclo[2.2.2]octyl system, aza substitution increases the solvolysis rate considerably more than in the adamantyl one (**1b** or **1c**) and nearly as much as in **4b**. Examination of models suggests a rationalization. Although the bicyclo[2.2.2]octyl framework is relatively inflexible to distortions which flatten the bridgehead (in part due to C_1–C_4 repulsion[22]), it is fairly flexible to a twisting action which increases π overlap (and partial double bonding) between carbon and nitrogen. Indeed, such twisting is favored by relief of torsional strain in the ethylene bridges; for instance, the parent hydrocarbon has a broad potential well, with little energy difference over considerable angles of twist.[22b] In contrast, with the adamantane model the twisting distortion encounters more resistance, so that less effective overlap may be achieved.

Experimental Section

Commercial materials were used without purification except for ethanol (See Kinetic Procedures). Infrared spectra were obtained on a Beckman IR8 spectrophotometer, NMR spectra on Varian T60 and CFT-20 instruments, mass spectra on a Hitachi Perkin-Elmer RMU-6E spectrometer, and GLC analyses on a Varian Aerograph 1800 instrument with a 6 ft × 0.25 in. 10% Carbowax 20 M on Chromosorb W column.

1-Chloro-2-azaadamantane (1b). Chlorination of the alcohol **1h** was carried out according to Stetter:[5] yield 88% (lit.[5] yield 92%); mp 97–98 °C (lit.[5] mp 101–102 °C); IR (KBr) 3250, 2920, 2860, 1460, 1440, 1090, 1030, 950, 900, 805, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.33 (s, NHC**H**), 2.20–1.50 (m).

1-Chloro-2-methyl-2-azaadamantane (1c). Chlorination of alcohol **1i** afforded **1c** in 49% yield (lit.[5] yield 87%) as a distillable oil (lit.:[5] oil solidified at 20 °C, bp 124–125 °C (13 mm)); IR (NaCl) 2950, 2850, 2810, 1450, 1150, 1030, 960, 945, 895, 835, 750, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.15 (s, NCH_3CH), 2.66 (s, NCH_3), 2.60–1.30 (m); ^{13}C NMR ($CDCl_3$) δ (position) 87.21 (1), 58.44 (3), 43.45 (8, 9), 37.89 (NCH_3), 35.50 (6), 31.54 (4, 10), 31.30 (5, 7) (lit.[27] 86.8 (1), 58.2 (3), 43.3 (8, 9), 37.7 (NCH_3), 35.4 (6), 31.4 (4, 10), 31.2 (5, 7)).

1-Ethoxy-2-azaadamantane (1j). Extraction of combined solvolysis products from **1b** with CH_2Cl_2 afforded after drying and evaporation of solvent a yellow oil: IR (NaCl) 2920, 2860, 1440, 1420, 1110, 1075, 840, 650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.50 (q, J = 7 Hz, CH_2), 3.20 (s, NCH), 2.30–1.50 (m), 1.10 (t, J = 7 Hz CH_3); ^{13}C NMR ($CDCl_3$) δ (position) 82.64 (1), 55.14 (CH_2), 50.27 (3), 41.49 (8, 9), 36.37 (4, 10), 36.07 (6), 29.91 (5, 7), 16.31 (CH_3); mass spectrum m/e (relative intensity) 110 (68), 124 (17), 138 (100), 139 (12), 150 (6), 152 (6.5), 166 (15), 167 (14), 180 (10), M^+· 195 (31).

Anal. Calcd for $C_{11}H_{19}NO$: C, 72.88; H, 10.56; N, 7.73. Found: C, 72.73; H, 10.87; N, 7.33.

1-Ethoxy-2-methyl-2-azaadamantane (1k). Extraction of the solvolysis products from **1c** afforded a yellow oil: IR (NaCl) 2930, 2860, 2810, 1450, 1170, 1090, 1045, 980 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.57 (q, J = 7 Hz, CH_2), 3.05 (s, NCH_3CH), 2.35 (s, NCH_3), 2.40–0.80 (m), 1.00 (t, J = 7 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ (position) 84.67 (1), 56.92 (3), 54.50 (CH_2), 37.01 (8, 9), 36.68 (6), 34.91 (NCH_3), 32.20 (4, 10), 30.38 (5, 7), 29.84 (?), 15.78 (CH_3); mass spectrum m/e (rel intensity) 93 (31), 110 (39), 124 (100), 125 (40), 136 (17), 138 (16), 152 (36), 153 (12), 166 (17), M^+· 181 (25).

Kinetic Procedures. Ethanol was purified according to Perrin[28] by refluxing with magnesium and distilling. Ethanolic sodium ethoxide was prepared by adding freshly cut sodium to ethanol and standardizing the solution against potassium hydrogen phthalate with phenol red as indicator. A weighed sample of substrate was added to pre-equilibrated solvent containing phenol red indicator. Standard base solution was added to make the

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(24) In an earlier paper,[9] the effect of aza substitution in **3b** was estimated, using for comparison a rate constant for **3c** extrapolated from data at higher temperatures.[25] It now appears that these data for **3c** were inaccurate.[26] From activation parameters tabulated in ref 4, the rate constant for **3c** in 70% dioxan at 52 °C is calculated to be 3×10^{-9} s^{-1}. By use of an average k_{Br}/k_{Cl} ratio of 40 for bridgehead halides,[21] the rate constant for **3a** is estimated as 8×10^{-11} s^{-1}. The solvolysis rate constant for **3c** in 80% ethanol at 70 °C was taken as twice that of the parent 1-bromobicyclo[2.2.2]octane.[21,26]

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reaction mixture basic, and the time was recorded when the indicator changed back to the acidic form. Repetition of this process gave between 10 and 34 points through the course of the reaction. Reactions were followed for up to 8–10 half-lives; however, only the first 1–3 half-lives were taken for calculations. The titrant volume at 8–10 half-lives was taken as the infinity titer.

GLC analyses were carried out by injection of reaction solution samples on the instument indicated above (flow rate 60–100 mL/min, and injector, column, and detector temperatures ~230, 180, and 260 °C). Integration was by "cut and weigh", with adamantane as an internal standard.

In a reaction followed by NMR, aliquots of reaction solution were added to a mixture of methylene chloride and aqueous sodium bicarbonate. After additional extraction with methylene chloride, the organic layer was washed, dried, and evaporated under vacuum, and the residue was analyzed by NMR in deuteriochloroform. The extent of reaction was determined by comparison of the integral of the signal for CH_2O protons with that for the N–CH protons of both reactant and product.

Rate constants and activation parameters were calculated, using a least-squares program on a Wang 700 calculator.

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Registry No. **1a**, 935-56-8; **1b**, 3632-95-9; **1c**, 3148-17-2; **1d**, 768-90-1; **1e**, 3049-61-4; **1f**, 16200-57-0; **1g**, 58373-13-0; **1h**, 3015-19-8; **1i**, 3015-18-7; **1j**, 71265-13-9; **1k**, 71265-14-0; **2a**, 59223-60-8; **2b**, 59223-59-5; **2c**, 59223-58-4; **3a**, 57422-54-5; **3b**, 40213-45-4; **3c**, 57422-55-6; **4a**, 15158-55-1; **4b**, 51209-45-1; **4c**, 40164-34-9; 4 (Y = Cl, X = S), 71265-15-1; **5a**, 27011-47-8; **5d**, 71265-16-2.

Synthesis of Adamantane Derivatives. 47.[1] Photochemical Synthesis of 4-Azahomoadamant-4-enes and Further Studies on Their Reactivity in Some Cycloadditions

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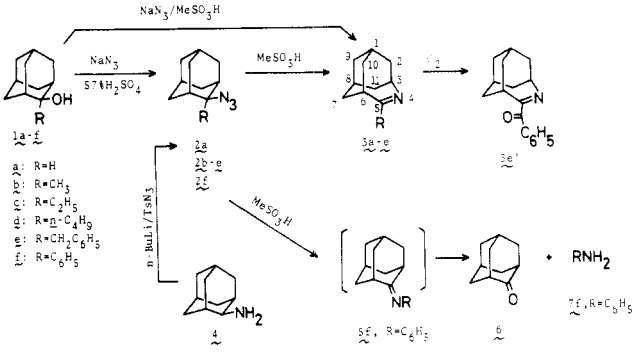
Direct photolysis of 2-azidoadamantanes (**2a,b,e,f**) in cyclohexane and/or in benzene afforded predominantly ring-expanded 4-azahomoadamant-4-enes (**3a,b,e,f**) and *N*-adamantylideneamines (**5a,b,e,f**) resulting from migration of H or a nonring carbon atom as minor products. The benzyl derivative **3e** was particularly air-sensitive and was isolated as the 5-benzoyl derivative **3e'**. The ^{13}C NMR spectra of **3a,b,e',f** are reported. The reactions of imines **3** with diphenylketene, benzonitrile oxide, diphenylnitrilimine, and tosylmethyl isocyanide afforded the corresponding cycloadducts **11**, **14a–c**, **15a,b**, and **17**, respectively.

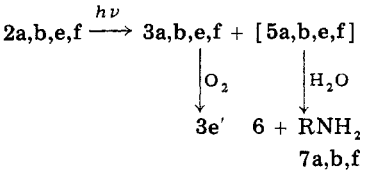
We have recently reported[2,3] that 2-azidoadamantanes **2b–f** and 4-azahomoadamant-4-enes **3a–e** are obtained in good yields from the corresponding 2-hydroxyadamantanes **1a–f** by treatment with sodium azide in 57% H_2SO_4 and in CH_3SO_3H, respectively (Scheme I). The parent **2a** could not be prepared by this simple method but was obtained by the diazo-transfer method[4] from 2-aminoadamantane (**4**). In contrast, rearrangement of **2f**, readily obtainable from **1f**, gave only adamantanone (**6**) and aniline (**7**), products of phenyl migration.

To extend these studies, we have examined the photolysis of 2-azidoadamantanes as a possible route to 4-azahomoadamant-4-enes. In this paper, we describe the results of photolysis of **2a,b,e,f**, which provided a better method for synthesis of **3f**. The carbon-13 nuclear magnetic resonance spectra of **3a,b,e',f** and cycloadditions of **3a,b,f** with ketenes and 1,3-dipoles are also reported.

Scheme I



Scheme II



Results and Discussion

Photolysis of 2-Azidoadamantanes. The photolysis of bridgehead azides such as 1-azidonorbornane,[5] 1-azidoadamantane,[6] and 1-azidotriptycene[7] is an elegant method for generation of the corresponding bridgehead imines. However, photolysis of azide derivatives at nonbridgehead positions of bi- and tricyclic compounds such as 2-azidoadamantanes has not been investigated extensively. Results of photolysis of **2a,b,e,f** in cyclohexane and/or in benzene are summarized in Scheme II and Table I. For all azides examined, preferential formation of the ring-expanded 4-azahomoadamant-4-enes **3** rather than imine **5**, the H or substituent migration product, was observed. Imines **5a**, **5b**,[8] and **5f**[9] were unstable in the

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