the cold to give a solid residue. Recrystallization from ether-hexane in the cold gave 45 mg (42%) of **4b** as white, well-formed crystals: mp 75 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.76 (2 H, A of AB q, J = 9 Hz), 7.25 (2 H, B of AB q, J = 9 Hz), 3.41 (2 H, m), 2.40 (5 H, m), 1.73 (3 H, s), 1.50 (4 H, m); ^{13}C NMR ($CDCl_3$) δ 129.4, 126.8, 55.1, 45.2, 24.0, 18.1. Although this material could be stored safely at -30 °C, it slowly decomposed at room temperature and underwent extensive fragmentation on attempted analysis by mass spectroscopy. Therefore neither an elemental analysis nor an exact mass molecular weight was obtained for **4b**. Upon solvolysis in 90:10 v/v acetone-water buffered with 0.01 M 2,6-lutidine, **4b** liberated 100 ± 2% of the theoretical amount of *p*-toluenesulfonic acid.

Kinetic Procedure. Solvolyses were run in 90% acetone-10% water (v/v) containing 0.01 M 2,6-lutidine. Rates were determined conductometrically. The conductivity cell could be sealed by a high-vacuum stopcock equipped with O-rings that permitted measurements above the normal boiling point of acetone. The runs at 45 °C and lower were made by adding the substrate to the solvent in a thermally preequilibrated cell.

Product Studies of 3b. Preparative solvolysis of 0.168 g of **3b** in 90:10 (v/v) acetone-water followed by removal of the solvent gave a residue to which water was added. The organic products were extracted with methylene chloride and chromatographed on 15 g of activity III basic alumina. Elution with 50% ether-50% hexane gave 0.095 g (57%) of 1-methyltricyclo[3.3.0.0^{2,8}]oct-*endo*-4-yl *p*-nitrobenzoate (**16**) as a white solid after recrystallization from ether-hexane: mp 104-105 °C (lit.[5] mp 100-101 °C); ^{1}H NMR ($CDCl_3$) δ 8.19 (4 H, br s), 5.34 (1 H, br q, J = 7 Hz),[15] 2.7-2.4 (2 H, m), 1.36 (3 H, s), 2.4-0.7 (7 H, br m); mass spectrum 287.1135, calcd for $C_{16}H_{17}NO_4$ 287.1156.

Anal. Calcd for $C_{16}H_{17}NO_4$: C, 66.88; H, 5.97; N, 4.88. Found: C, 66.86; H, 6.20; N, 5.00.

Further elution yielded 26.5 mg (33%) of 1-methyltricyclo-[3.3.0.0^{2,8}]octan-*endo*-4-ol (**17**)[5] as a clear, colorless oil which was homogeneous by GLC analysis: ^{1}H NMR ($CDCl_3$) δ 4.32 (1 H, br q, J = 6 Hz), 2.5-0.7 (9 H, m), 1.30 (3 H, s); mass spectrum 138.1054, calcd for $C_9H_{14}O$ 138.1044.

When **7** was dissolved in ether and treated with a small amount of 10% perchloric acid for 10 min at room temperature, it was completely converted to **17**.

Product Studies of 4a. A solution of 0.172 g of **4a** and 0.070 g of 2,6-lutidine in 4.0 mL of 90% acetone-10% water (v/v) was heated at 95-100 °C for 3.5 h in a sealed ampoule. Workup involved removal of the solvent under reduced pressure, extraction of the product with methylene chloride, and drying over anhydrous magnesium sulfate. Filtration followed by removal of the solvent under reduced pressure gave 0.080 g of a 4:1 mixture of **18** and **12** which was contaminated by a small amount of 2,6-lutidine (as determined by NMR analysis). Preparative HPLC on porosil with ethyl acetate as eluant gave pure **18**: ^{1}H NMR ($CDCl_3$) δ 4.91 (1 H, s, $H_{4\text{-endo}}$),[16] 4.01 (1 H, br t, J = 6 Hz), 2.70 (1 H, br m), 2.30 (1 H, t, J = 6 Hz), 2.1-1.2 (5 H, complex m); ^{13}C NMR ($CDCl_3$) δ 109.6, 64.3, 50.3, 35.5, 29.8, 26.3, 25.7, 22.1; mass spectrum 126.0679, calcd for $C_7H_{10}O_2$ 126.0678.[17]

Lanthanide Shift Study of 18. The slopes obtained for **18** were as follows: H_1, 10.5; H_2, 20.73; H_4, 28.30; H_5, 11.90; H_6, H_7, H_8 (5 H total), ca. 6.5.

Product Studies of 4b. The solvolysis of 67 mg of **4b** in 90% acetone-10% water (v/v) was carried out for 10 half-lives to give 34.7 mg of material which consisted of only **14** contaminated by trace amounts of acetone and methylene chloride. Integration of the ^{1}H NMR sample vs. an internal standard indicated a yield of 97 ± 10% of **14**. No trace of the ring-opened product could be detected by NMR.

Acknowledgment. We are indebted to the National Science Foundation for Grant CHE78-10231 and CHE81-14772, which supported this investigation.

Registry No. 3a, 16384-95-5; **3b**, 83153-08-6; **4a**, 83153-09-7; **4b**, 83153-10-0; **5**, 14224-86-3; **6**, 38310-50-8; **7**, 83198-89-4; **9**, 74816-10-7; **10**, 83153-11-1; **11**, 83198-87-2; **12**, 83198-88-3; **14**, 83153-12-2; **16**, 38310-53-1; **17**, 38310-52-0; **18**, 83153-13-3.

(15) This peak could also be described as a doublet of doublets with $J_{H_{4\text{-ex}}-H_5}$ = $J_{H_{4\text{-ex}}-H_3}$ = ca. 7 Hz. It has been well established that a hydrogen in the exo position at C_4 couples to the bridgehead hydrogen at C_5 with a J = 6-7 Hz while the corresponding hydrogen in the endo position at C_4 has J = 0 Hz.[1,5,12] See also: Buckeridge, R. G.; Frayne, K. J.; Johnson, B. L. *Aust. J. Chem.* **1965**, *28*, 1311.

(16) The singlet nature of this absorption requires that the hydroxyl group be in the exo position.[15]

(17) Compound **18** was quite unstable, and much of the material was lost on a single pass through an HPLC. No attempt was made to obtain an elemental analysis.

Synthesis and Solvolysis of Sulfonate Esters of 3-Phenyl-3-aza-*endo*-tricyclo[3.2.1.0^{2,4}]octan-*anti*-8-ols. Identification of the Carbon-Carbon Bond of Aziridines as a Powerful Neighboring Group in Solvolysis Reactions

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Abstract: 3-Phenyl-3-aza-*endo*-tricyclo[3.2.1.0^{2,4}]octan-*anti*-8-ol and *syn*-8-methyl-3-phenyl-3-aza-*endo*-tricyclo[3.2.1.0^{2,4}]-octan-*anti*-8-ol have been synthesized and converted to the corresponding *p*-toluenesulfonate esters. Solvolysis of these two sulfonates in acetone-water buffered with 2,6-lutidine gave an α-methyl/hydrogen rate ratio of 1.0 × 10^3. This established that the carbon-carbon bond of aziridines can be a powerful neighboring group in solvolysis reactions when properly oriented. In an absolute rate comparison, 3-phenyl-3-aza-*endo*-tricyclo[3.2.1.0^{2,4}]oct-*anti*-8-yl *p*-toluenesulfonate solvolyzes about 10^9 times faster than bicyclo[2.2.1]hept-7-yl *p*-toluenesulfonate. Product studies were carried out.

We have demonstrated that α-methyl/hydrogen rate ratios are a very useful measure of the presence of neighboring group participation by the carbon-carbon bonds of cyclopropanes and of epoxides.[1,2] We were particularly intrigued by the observation

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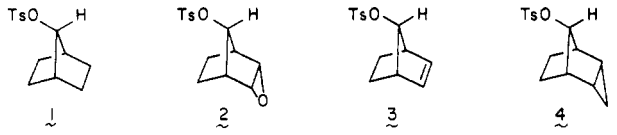
that the 3-oxa-*endo*-tricyclo[3.2.1.0^{2,4}]oct-8-*anti*-yl system (**2**)



	1	2	3	4
k_{rel}	1	10^8	10^{11}	10^{14}

appears to solvolyze with neighboring group participation comparable to that of the double bond of **3**.[3] In view of the powerful neighboring group participation of the epoxide carbon–carbon bond in **2** and of the cyclopropane carbon–carbon bond in **4**, we explored the role of the aziridine carbon–carbon bond in the stabilization of incipient carbonium ion centers.

A major problem associated with establishing the effectiveness of the carbon–carbon bond of an aziridine as a neighboring group was the synthesis of an appropriate rigid substrate. Ideally, the most desirable system for such a study would be the sulfonate esters of N-substituted 3-aza-*endo*-tricyclo[3.2.1.0^{2,4}]octan-*anti*-8-ols. The syntheses of the appropriate derivatives started with 7,7-dimethoxybicyclo[2.2.1]hept-2-ene (**5**, Scheme I),[4,5] which on transketalization with 0.66 equiv of 2,2,2-tribromoethanol in the presence of *p*-toluenesulfonic acid gave an 82% yield of a 1:1 mixture of the two epimers of **6**. Treatment of **6** with 3 equiv of phenyl azide at 50–60 °C in the dark for 15 h gave 64% of the exo-triazoline **7**, which was predominately the stereoisomer with the methoxyl function syn to the triazoline. Three recrystallizations from hexane–chloroform gave the pure stereoisomer **7**, mp 182.5–183.5 °C. This material showed a single methoxyl group in the ^{1}H NMR at δ 3.11 and H_A and H_B appeared at δ 3.80 and 4.63, respectively, as doublets with J = 11 Hz. The absence of coupling to the bridgehead protons established the exo stereochemistry of the triazoline.[5] Thermolysis of **7** at 165–170 °C in Decalin for 90 min gave 44% of **8**, mp 148–149 °C. The endo stereochemistry of the aziridine moiety was established by the coupling of the hydrogen on the aziridinyl ring with the bridgehead protons; δ 2.85 (2 H, t, J = 2 Hz). Photolysis of **7** gave the epimeric exo aziridine, which had these protons at δ 2.55 (2 H, s). For a discussion of the mechanism of the thermolysis of **7** see our earlier work and references contained therein.[5] Electrochemical reduction of **8** (500 mg, 1 mmol) at −1.50 V (200 C) in dimethylformamide containing tetra-*n*-butylammonium perchlorate as electrolyte gave 400 mg of a mixture of **9** and partially debrominated analogue(s) of **8**. Careful chromatography on alumina permitted the isolation of pure **9**. Sodium borohydride reduction of **9** gave 93% of **10** as a slightly yellow solid, which on recrystallization gave colorless crystals, mp 152.0–152.5 °C. When the isolation of **9** was omitted, the two-step process converted **8** into **10** in 36% overall yield. The stereochemistry of the hydroxyl function of **10** was established on the basis of a lanthanide shift reagent study.

Treatment of **10** with *p*-toluenesulfonyl chloride in pyridine gave 38% of pure **11**. The tertiary alcohol **12** was prepared from **8** in a two-step process, which involved the addition of methyllithium to the crude reduction product mixture, in 46% overall yield.[6]

Scheme I

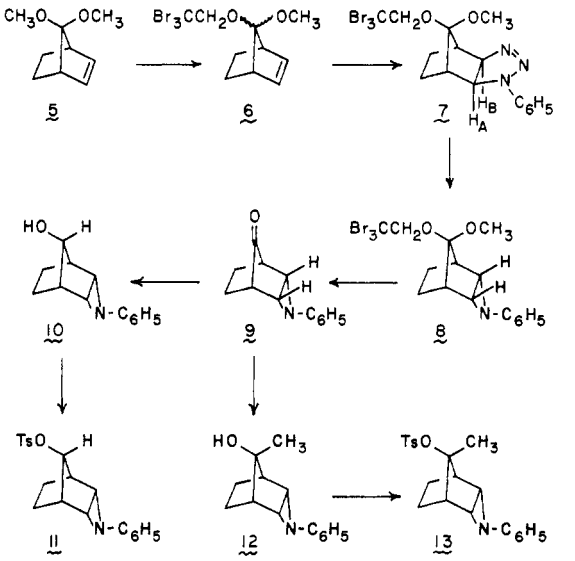


Table I. Rates of Solvolysis of 3-Phenyl-3-aza-*endo*-tricyclo[3.2.1.0^{2,4}]octan-*anti*-8-ol and *syn*-8-Methyl-3-phenyl-3-aza-*endo*-tricyclo[3.2.1.0^{2,4}]octan-*anti*-8-ol *p*-Toluenesulfonate Esters in 90:10 (v/v) Acetone–Water Buffered with 0.01 M 2,6-Lutidine

compd	temp, ±0.05 °C	rate, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
11	95.00	(5.22 ± 0.11) × 10^{-3}		
	80.00	(1.39 ± 0.01) × 10^{-3}	22.6 ± 0.2	−7.9 ± 0.5
	65.00	(3.04 ± 0.02) × 10^{-4}		
	25.00[a]	2.90 × 10^{-6}		
13	30.00	(1.75 ± 0.01) × 10^{-2}		
	15.00	(3.39 ± 0.03) × 10^{-3}	18.9 ± 0.1	−4.3 ± 0.5
	0.00	(5.06 ± 0.03) × 10^{-4}		
	25.00[a]	1.04 × 10^{-2}		
	95.00[a]	5.41		

[a] Extrapolated from other temperatures.

Treatment of **12** with 2 equiv of *n*-butyllithium followed by 2 equiv of *p*-toluenesulfonyl chloride gave 49% of **13**.

Solvolytic Studies

As shown in Table I, solvolysis of **11** in 90% acetone–water buffered with 2,6-lutidine gave $k_{95°C}$ = (5.22 ± 0.11) × 10^{-3} s^{-1}, $\Delta H^{\ddagger}$ = 22.6 ± 0.2 kcal/mol, and $\Delta S^{\ddagger}$ = −7.9 ± 0.5 eu. Similar solvolysis of **13** gave $k_{95°C}$ = 5.41 s^{-1}, $\Delta H^{\ddagger}$ = 18.9 ± 0.1 kcal/mol, and $\Delta S^{\ddagger}$ = −4.3 ± 0.5 eu. At 95 °C, the α-methyl/hydrogen rate ratio was 1036. This ratio can be compared with that of other closely related systems. For instance, α-CH$_3$/H rate ratios are as follows: **1**, 1.3 × 10^8; **2**, 1.5 × 10^3; **3**,[7] 7.6 × 10^3; **4**, 3.1 × 10^1. Thus, on the basis of a comparison of α-CH$_3$/H rate ratios, *the carbon–carbon bond of the aziridinyl moiety of* ***11*** *is comparable as a neighboring group in solvolysis reactions to the double bond of* ***3*** *and to the epoxide ring of* ***2***. However, it is not as powerful as the carbon–carbon bond of the cyclopropyl ring of **4**. In an absolute sense, **11** solvolyzes 7 times faster than **2**, and **13** solvolyzes 5 times faster than *syn*-8-methyl-3-oxa-*endo*-tricyclo[3.2.1.0^{2,4}]oct-*anti*-8-yl *p*-toluenesulfonate.

Product analysis of the solvolytic reaction of **11** yielded 92% of an oil that exhibited a single spot on thin-layer chromatography and gave relatively clean spectra. No trace of **10** could be detected. This material showed no hydroxyl stretch in the IR but did exhibit a strong carbonyl band at 1714 cm^{-1}. The exact mass molecular weight calculated for $C_{16}H_{19}NO$ was 241.1467 (found 241.1478). Thus, instead of adding a hydroxyl group, the product had in-

(1) Gassman, P. G.; Schaffhausen, J. G.; Raynolds, P. W. *J Am. Chem. Soc.*, preceding article in this issue.

(2) Lustgarten, R. K.; Lhomme, J.; Winstein, S. *J. Org. Chem.* **1972**, *37*, 1075. Tanida, H.; Hata, Y.; Ikegami, S.; Ishitobi, H. *J. Am. Chem. Soc.* **1967**, *89*, 2928. Tanida, H. *Acc. Chem. Res.* **1968**, *1*, 239. Gassman, P. G.; Pascone, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 7801.

(3) α-Methyl/hydrogen rate ratios of 10^8, 10^3, 10^3, and 10^1 were observed for **1**, **2**, **3**, and **4**, respectively.[1,2]

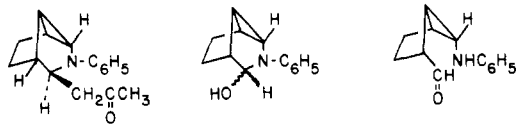
(4) Gassman, P. G.; Marshall, J. L. "Organic Synthesis"; Wiley: New York, 1973; Collect. Vol. V, p 424.

(5) For a discussion of unsuccessful synthetic approaches to the desired tricyclic system see: Gassman, P. G.; Schaffhausen, J. G. *J. Org. Chem.* **1978**, *43*, 3214.

(6) The crude product melted at 193–195 °C. An analytical sample melted at 196–198 °C. The stereochemistry of the hydroxyl function was established by a lanthanide shift reagent study. It is interesting to note that the addition of methyllithium to **9** occurs from a direction opposite to that observed with tricyclo[3.2.1.0^{2,4}]octan-8-one.[1] We have no rationale for this behavior other than that the electronic effect of the aziridine must be very different from that of the cyclopropane moiety.

(7) As discussed in the preceeding paper,[1] the α-CH$_3$/H rate ratio for **3** can vary from 44 to 7.6 × 10^3, depending on the literature value chosen in making the necessary extrapolations.[2]

corporated acetone. The structure **14** was assigned on the basis



14 **15** **16**

of the following: ^{1}H NMR ($CDCl_3$) δ 7.38–6.45 (5 H, complex m), 3.80 (1 H, br t, J = 6 Hz), 3.00 (1 H, br t, J = 6 Hz), 2.80–1.00 (12 H, complex m containing a sharp methyl singlet at 2.17); ^{13}C NMR ($CDCl_3$) δ 129.1 (2), 115.6 (2), 111.1, 69.4, 50.0, 47.6, 44.5, 39.6, 31.1, 30.0, 27.9, 23.1. The carbonyl carbon and the quaternary aromatic carbon were not located. It should be stressed that this is a tentative assignment of structure. The formation of **14** could be rationalized by the initial formation of **15** (for analogy see ref 1) followed by opening of **15** to give **16**. Aldol condensation of **16** with acetone would give an α,β-unsaturated ketone, which on intramolecular Michael addition of the amine function would give **14**.

The tertiary *p*-toluenesulfonate **13** gave a complex mixture of products on solvolysis that contained at least four components. The starting alcohol **12** was identified as one of the products. The other products were extremely unstable and decomposed upon various attempts at separation and purification.

In summary, we have demonstrated that the carbon–carbon bond of an aziridine can act as an extremely powerful neighboring group when properly oriented.

Experimental Section[8]

7,7-Dimethoxybicyclo[2.2.1]hept-2-ene (5). The ketal **5** was prepared according to the literature procedure.[4]

7-(2,2,2-Tribromoethoxy)-7-methoxybicyclo[2.2.1]hept-2-ene (6). A mixture of 20.0 g (130 mmol) of **5**, 24.5 g (86 mmol) of 2,2,2-tribromoethanol, and 0.6 g of *p*-toluenesulfonic acid in benzene was refluxed in a flask equipped with a Dean–Stark trap. After several hours, IR analysis indicated only residual amounts of methanol in the azeotroped benzene. The reaction mixture was cooled, stirred for 0.5 h with solid sodium carbonate, filtered, and concentrated to yield a dark residue (43.5 g). Chromatography on 200 g of neutral alumina with benzene gave a yellow oil containing a mixture of **5** and **6**. This oil was concentrated under vacuum (0.1 mmHg) for several hours and then distilled under high vacuum to give 28.72 g (82%) of **6** as a pale yellow oil, bp 115–138 °C (1×10^{-5} mmHg). This oil crystallized after storage in a refrigerator for 1 week. Three sublimations (40 °C, 0.3 mmHg) gave an analytical sample: mp 48–50 °C; IR (potassium bromide) 2970, 2930, 2860, 2820, 1450, 1305, 1290, 1190, 1180, 1140 (db), 1105, 1083, 1045, 1030, 967, 777, 770, 710, 699, 670, 630, 570, 510, 360 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.10 (2 H, m), 4.15 and 4.08 (2 H, 2 s), 3.38 and 3.30 (3 H, 2 s), 2.85 (2 H, m), 1.5–2.2 (2 H, m), 0.85–1.20 (2 H, m).

The compound eluted as one peak in GLC analysis (6 ft × 1/4 in. 10% DC 200 on 60/80 Chrom W column at 160 °C), NMR integration of the singlets at δ 4.15 and 4.08 as well as δ 3.38 and 3.30 indicated a syn:anti ratio of nearly 1:1.

Anal. Calcd for $C_{10}H_{13}Br_3O_2$: C, 29.66; H, 3.24. Found: C, 29.67; H, 3.25.

An alternate method for purification was also developed that was simpler and nearly comparable in yield. Treatment of 45.0 g (290 mmol) of **5**, 55.0 g (190 mmol) of 2,2,2-tribromoethanol, and 1.3 g of *p*-toluenesulfonic acid under the same conditions (reflux time extended to 18 h) followed by chromatography on 400 g of alumina with benzene–hexane (1:1) gave an oil. Concentration of this oil under vacuum (0.03 mmHg) gave 79 g of **6** as a semisolid. This material was dissolved in hexane, treated with Norit, filtered, concentrated to a small volume, and cooled to −5 °C to give 55.6 g (71%) of **6** after filtration. The off-white solid obtained in this manner was of adequate purity for further synthetic use.

3-Phenyl-10-(2,2,2-tribromoethoxy)-10-methoxy-3,4,5-triaza-*exo*-tricyclo[5.2.1.0^{2,6}]dec-4-ene (7). A mixture of 20.2 g (49.8 mmol) of **6** and 20.0 g (168 mmol) of phenyl azide was heated at 50–60 °C in the dark for 15 h. Dilution with hexane and storage in a freezer for several days caused precipitation of **7**. Filtration afforded 16.6 g (64%) of **7** as an off-white solid.[9] Three recrystallizations from hexane–chloroform gave an analytical sample: mp 182.5–183.5 °C dec; IR (potassium bromide) 2980, 2940, 2920, 2880, 2860, 2840, 1605, 1495, 1368, 1232, 1205, 1158, 1108, 1086, 1050, 1015 (db), 997, 910, 784, 753, 692, 677, 638 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.20 (5 H, br s), 4.63 (1 H, d, J = 11 Hz), 4.05 (2 H, s), 3.80 (1 H, d, J = 11 Hz), 3.11 (3 H, s), 2.85 (1 H, m), 2.60 (1 H, m), 1.2–2.4 (4 H, m).

Anal. Calcd for $C_{16}H_{18}Br_3N_3O_2$: C, 36.67; H, 3.46; N, 8.02. Found: *C, 36.82; H, 3.54; N, 8.01.*

Thermolysis of 7. Preparation of 3-Phenyl-8-(2,2,2-tribromoethoxy)-8-methoxy-3-aza-*endo*-tricyclo[3.2.1.0^{2,4}]octane (8). A suspension of 9.32 g (17.8 mmol) of **7** in Decalin (100 mL) and 0.6 g of ground glass was heated at 165–170 °C for 90 min. The dark solution was then cooled and the Decalin removed by distillation [40 °C (1 mmHg)]. The residue was chromatographed on 150 g of neutral alumina with benzene–hexane (4:1) to give 3.93 g (44%) of **8** (after recrystallization from hexane) as a colorless solid. Two further recrystallizations gave an analytical sample: mp 148–149 °C; IR (potassium bromide) 3150, 2990, 2970, 2940, 1600, 1490, 1452, 1367, 1316, 1291, 1267, 1221, 1142, 1109, 1089, 1060, 951, 794, 764, 747, 692, 633 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.8–7.4 (5 H, m), 4.22 (2 H, s), 3.47 (3 H, s), 2.85 (2 H, t, J = 2 Hz), 2.5 (2 H, m), 1.7 (4 H, m).

Anal. Calcd for $C_{16}H_{18}Br_3NO_2$: C, 38.74; H, 3.66; N, 2.82. Found: C, 38.96; H, 3.76; N, 2.85.

Electrochemical Reduction of 8. Preparation of 3-Phenyl-3-aza-*endo*-tricyclo[3.2.1.0^{2,4}]octan-8-one (9) and Isolation of 3-Phenyl-8-(2,2-dibromoethoxy)-8-methoxy-3-aza-*endo*-tricyclo[3.2.1.0^{2,4}]octane (17). Reduction of 500 mg (1 mmol) of **8** at −1.50 to −1.30 V (200 C; 193 C = 2 equiv) in dimethylformamide–tetra-*n*-butylammonium perchlorate gave 400 mg of a yellow oil. Preparative TLC of this residue (in two portions) on alumina with benzene–hexane (1:1) gave two products with **17** eluting first and **9** eluting second. An analytical sample of **9** was obtained by preparative VPC (on a 6 ft × 1/4 in. 10% DC 200 on 60/80 Chrom W column at 165 °C) as a pale yellow oil: IR ($CDCl_3$ solution) 2950, 1850, 1780, 1730, 1600, 1490, 1460, 1360, 1275 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.8–7.5 (5 H, m), 2.87 (2 H, t, J = 2 Hz), 2.42 (2 H, m), 1.72 (4 H, br s).

Anal. Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03. Found: C, 78.07; H, 6.85; N, 7.00.

The dibromoketal **17** was identified by its ^{1}H NMR spectrum: ($CDCl_3$) δ 6.8–7.5 (5 H, m), 5.70 (1 H, t, J = 6 Hz), 4.00 (2 H, d, J = 6 Hz), 3.37 (3 H, s), 2.80 (2 H, t, J = 2 Hz), 2.4 (2 H, m), 1.7 (4 H, br s). Compound **17** was isolated as an oil which crystallized on cooling to −5 °C.

3-Phenyl-3-aza-*endo*-tricyclo[3.2.1.0^{2,4}]octan-*anti*-8-ol (10). To a stirred solution of 75 mg of sodium borohydride in 10 mL of absolute ethanol at 0–5 °C was added 102 mg of **9** in 4 mL of absolute ethanol dropwise over a 0.5-h period. The reaction mixture was stirred for 18 h and diluted with 30 mL of water and 30 mL of ether. The layers were separated, the aqueous phase was reextracted with ether, and the combined organic extracts were washed with brine and dried over anhydrous magnesium sulfate. After filtration and removal of the solvent under reduced pressure, 96 mg (93%) of crystalline **10** was obtained. Three recrystallizatios from 60–70 °C petroleum ether gave analytically pure material: mp 152.0–152.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.4–6.7 (5 H, complex m), 3.97 (1 H, t), 2.60 (2 H, t), 2.31 (2 H, br s), 1.88 (1 H, br s), 1.59 (4 H, br s); ^{13}C NMR ($CDCl_3$) δ 128.79, 124.59, 121.57, 120.39, 85.27, 42.46, 41.40, 23.83.

Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.71; H, 7.53; N, 7.04.

Direct Conversion of 8 to 10. The crude product mixture obtained from the electrochemical reduction of 1.00 g of **8** was dissolved in absolute ethanol, and a small amount of insoluble material was removed by filtration. To this solution was added 0.05 g of sodium borohydride, and the reaction mixture was stirred for 0.5 h. The solvent was removed under reduced pressure, and the residue was partitioned between chloroform and water. The organic layer was dried over anhydrous sodium sulfate and filtered, and the solvent was removed under reduced pressure to yield an oil which crystallized from methylcyclohexane to give 0.147 g (36%) of **10**, mp 142–148 °C.

Lanthanide Shift Reagent Study of 10. Lanthanide shift reagent studies were carried out by using europium tris(1,1,1,2,2,3,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate) [Eu(fod)$_3$]. Chemical shifts vs. [LSR]/[alcohol] ratios were plotted, and the slopes were determined.

(8) Melting points and boiling points are uncorrected. ^{1}H NMR spectra were recorded on either a Varian HFT-80 or a Hitachi Perkin-Elmer R24B nuclear magnetic resonance spectrometer. ^{13}C NMR spectra were recorded on a Varian CFT-20 nuclear magnetic resonance spectrometer. All chemical shifts are reported relative to tetramethylsilane. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

(9) This material was primarily **7**. It was contaminated with a small amount of the material which was epimeric at C-8.

The observed slopes for **10** were as follows: H_1, 5.78; H_2, 2.29; $H_{6\text{-exo}}$, 7.58; $H_{6\text{-endo}}$, 3.87; H_8, 11.37.

3-Phenyl-3-aza-*endo*-tricyclo[3.2.1.0^{2,4}]oct-*anti*-8-yl *p*-Toluenesulfonate (11). A solution of 0.123 g of **10** and 0.615 g of *p*-toluenesulfonyl chloride in 5 mL of pyridine was stirred at 25 °C for 13 h, diluted with water, and extracted with methylene chloride. The organic phase was dried over anhydrous sodium sulfate and filtered, and the solvent was removed under reduced pressure. Recrystallization of the residue from ether–hexane gave 0.083 g (38%) of **11**: mp 123–125 °C; ^{1}H NMR ($CDCl_3$) δ 7.80 (2 H, d, J = 9 Hz), 7.5–6.6 (7 H, complex m), 4.42 (1 H, br s), 2.52 (2 H, br s), 2.44 (3 H, s), 1.53 (4 H, br s); mass spectrum 355.1239, calcd for $C_{20}H_{21}NO_3S$ 355.1239.

Anal. Calcd for $C_{20}H_{21}NO_3S$: C, 67.58; H, 5.96. Found: C, 67.47; H, 6.03.

***syn*-8-Methyl-3-phenyl-3-aza-*endo*-tricyclo[3.2.1.0^{2,4}]octan-*anti*-8-ol (12).** The crude product mixture obtained from the electrochemical reduction of 1.05 g of **8** (vide supra) was dissolved in 20 mL of tetrahydrofuran, and 3 mL of 1.4 M methyllithium was added at −60 °C. The reaction mixture was stirred at −60 °C for 10 min and then allowed to warm to 25 °C over a 1-h period. Ammonium chloride (0.5 g) was added, the solvent was removed under reduced pressure, and the residue was extracted with methylene chloride. Addition of methylcyclohexane resulted in the precipitation of 0.210 g (46%) of **12** as light brown crystals, mp 193–195 °C. Recrystallization followed by sublimation gave analytically pure material: mp 196–198 °C; ^{1}H NMR ($CDCl_3$) δ 7.3–6.7 (5 H, m), 2.68 (2 H, br s), 2.00 (2 H, br s), 1.67 (4 H, br s), 1.49 (3 H, s); ^{13}C NMR δ 153.5, 128.7, 121.5, 120.2, 93.1, 45.2, 44.5, 25.4, 20.3.

Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 78.09; H, 7.82; N, 6.53.

Lanthanide Shift Reagent Study of 12. The observed slopes were as follows: H_1, 9.20; H_2, 4.18; $H_{6\text{-exo}}$, 9.49; $H_{6\text{-endo}}$, 4.92; H_{CH_3}, 10.87.

***syn*-8-Methyl-3-phenyl-3-aza-*endo*-tricyclo[3.2.1.0^{2,4}]oct-*anti*-8-yl *p*-Toluenesulfonate (13).** A solution of 85 mg of **12** in 2 mL of tetrahydrofuran was treated with 0.33 mL of 2.4 M *n*-butyllithium in hexane at −60 °C. After 10 min, 150 mg of *p*-toluenesulfonyl chloride was added rapidly under a nitrogen atmosphere. The reaction mixture was allowed to warm to 0 °C and stirred at that temperature for 2 h. The reaction mixture was then added to 20 mL of cold methylene chloride (<0 °C), and this organic solution was washed with 20 mL of cold, saturated sodium bicarbonate solution. The organic solution was filtered through a cone of anhydrous calcium sulfate, and the solvent was removed at ca. 0 °C under reduced pressure. The residue was dissolved in 3 mL of cold ether and filtered through a plug of glass wool to remove a small amount of white solid. The addition of 3 mL of methylcyclohexane followed by reduction in the volume to 2 mL (with a stream of nitrogen) resulted in the precipitation of 71 mg (49%) of **13** as a faintly pink solid. This material was stable at −30 °C, but decomposed at room temperature; mp 80–85 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.70 (2 H, A of an AB q, J = 8 Hz), 7.40–6.60 (7 H, m), 2.62 (4 H, br s), 2.41 (3 H, s), 1.75 (3 H, s), 1.62 (4 H, br s).[10]

Kinetic Procedure. Solvolyses were run in 90% acetone–10% water (v/v) containing 0.01 M 2,6-lutidine as buffer. Rates were determined conductimetrically. The conductivity cell was fitted with a high-vacuum stopcock equipped with O-rings in order that rates could be measured above the normal boiling point of acetone. The runs at 45 °C and below were made by adding the substrate to the solvent in a thermally preequilibrated cell.

Product Studies for the Solvolysis of 11. A solution of 85 mg of **11** and 28 mg of 2,6-lutidine in 3 mL of 90% acetone–10% water was heated at 95–100 °C for 45 min. The solvent was removed under a stream of nitrogen and the residue extracted with ether. The organic phase was dried over anhydrous magnesium sulfate and filtered, and the solvent removed under high vacuum to yield 53.5 mg (92%) of a yellow oil. Gas chromatography, high-pressure liquid chromatography (both normal and reverse phase), and silica gel chromatography resulted in the decomposition of the product. However, thin-layer chromatography indicated a single component, and spectral data indicated a high degree of purity. Chromatography on activity III basic alumina resulted in minor decomposition, but the product obtained had spectral properties identical with the sample placed on the column. The spectral properties were only consistent with the product having structure **14**: ^{1}H NMR ($CDCl_3$) δ 7.38–6.45 (5 H, complex m), 3.80 (1 H, br t, J = 6 Hz), 3.00 (1 H, br t, J = 6 Hz), 2.80–1.00 (12 H, complex m containing a sharp methyl singlet at 2.17); ^{13}C NMR ($CDCl_3$) δ 129.1 (2), 115.6 (2), 111.1, 69.4, 50.0, 47.6, 44.5, 39.6, 31.1, 30.0, 27.9, 23.1 (the carbonyl carbon and the quaternary aromatic carbon were not located); IR (neat) 1714, 1600, 1500, 1385, 1348, 740, 688 cm^{-1}; mass spectrum 241.1478, calcd for $C_{16}H_{19}NO$ 241.1467.

Product Studies for the Solvolysis of 13. Product studies for the solvolysis of the tertiary *p*-toluenesulfonate **13** showed a complex mixture containing at least four components. The starting tertiary alcohol **12** was identified as one of the components; the remaining products were extremely unstable and decomposed upon various attempts at purification. ^{1}H NMR studies of the crude product mixture showed signals at δ 4.85 (d, J = 6 Hz) and 4.80 (s), which would be consistent with the presence of the C_1-methylated version of the two epimers of **15**. ^{13}C NMR signals at δ 101.5 and 100.1 are also consistent with this hypothesis.[10]

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Registry No. 5, 875-04-7; *syn*-**6**, 83136-09-8; *anti*-**6**, 83136-17-8; **7**, 83136-10-1; **8**, 83136-11-2; **9**, 83198-44-1; **10**, 83198-45-2; **11**, 83136-12-3; **12**, 83136-13-4; **13**, 83136-14-5; **14**, 83136-15-6; **17**, 83136-16-7.

(10) Because of the limited stability of **13**, an elemental analysis was not obtained. Extensive fragmentation prevented us from obtaining an exact mass molecular weight.