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Substituent Effects of Alkoxy and Amino Groups Directly Bonded to Cationic Carbon in the Perpendicularly Twisted Geometry. 2-Oxa- and 2-Aza-1-adamantyl Tosylates[1]

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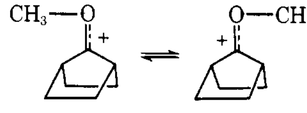
Abstract: In order to provide evidence on the possibility of resonance stabilization of carbocations by α-alkoxy and α-amino substituents which are constrained to the perpendicular geometry (90° twisted from the optimum parallel geometry in which the lone pair p orbital is parallel to the vacant p orbital), we have prepared a series of analogues of adamantyl tosylate in which the methylene group at C-2 has been replaced by an oxygen or an *N*-methyl group. (Some of the tosylates contain a cyano substituent at C-3.) Relative rates of solvolysis in 80% aqueous ethanol at 25° are: for the 2-oxa-3-cyano, 7.43×10^{-8}; for the 2-methyl-2-aza-3-cyano, 3.56×10^{-2}; for the 3-cyano, 9.97×10^{-5}; for the 2-oxa, 3.68×10^{-3}; and for unsubstituted adamantyl tosylate, 1. These data were considered along with earlier data on solvolysis of adamantyl tosylates in which a methylene group at position 2 was replaced by a cyclopropylidene group, 4.93×10^{-3}, an ethenylidene group, 4.23×10^{-5}, or an isopropylidene group, 2.68. The rate constants are correlated with $\sigma_{\mathrm{eff}} = \sigma_{\mathrm{I}} + \delta\sigma_{\mathrm{R}}^{+}$ with the fractional contribution of resonance, δ, being varied to maximize the correlation coefficient. In the geometry of the adamantyl system, the resonance stabilization of a 1 cation by a 2 substituent is 0.18–0.29 of the maximum resonance stabilization for an unconstrained substituent. The implications of this finding are discussed in terms of hyperconjugative resonance interactions in the perpendicularly twisted geometry. In the perpendicular geometry, carbocation stabilization by electron-donating resonance from filled skeletal orbitals with heteroatom p_x and p_z character is concluded to be 0.18–0.29 as large as that resulting from electron donation from the p_y lone pair in the parallel geometry.

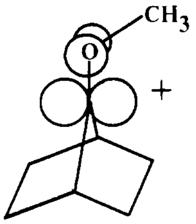
A substituent directly bonded to a carbon which is developing positive charge in an ionization reaction can influence the rate of the reaction by donating or withdrawing electrons from the reaction center by (a) a resonance effect or (b) a polar effect, with the latter often discussed in terms of a composite of field (through-space) effects and inductive (through-bond) effects. Much effort has recently been devoted to the differentiation[2] and quantitative understanding of field effects[3] and inductive effects.[4]

The angular dependence of resonance interactions, particularly the steric inhibition of resonance, has been the object of long-term interest[5] to organic chemists. The availability of NMR methods to measure energy barriers to internal rotations has provided a major impetus to studies of such angular dependence. The carbon–oxygen double bond character in α-alkoxycarbinyl cations[6,7,8] is reflected in a barrier to rotation (ΔG^*) of 18.4 kcal/mol at 82° for cation **1**,[8,9] for example.



1 ("parallel")

This barrier to rotation represents the difference in energy between the conformations which maximize double bond character, such as the two pictured structures for **1** in which the vacant p orbital on carbon and the lone-pair p orbital on oxygen are parallel, and those which minimize it, such as transition state **2** for rotation about the C–O bond in which the two pertinent p orbitals are perpendicular.

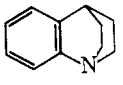


2 ("perpendicular")

The "perpendicular" conformer **2** is,[8] as anticipated, of higher energy than "parallel" conformer **1**, but the question of the importance of residual resonance stabilization in the perpendicular geometry is highlighted by studies such as the ab initio calculation of Hehre, Radom, and Pople[10] on phenol. Even in the perpendicular conformation, charge is donated, notably to the ortho and para positions of the ring, by an amount (total π-charge donation, 0.049) which is an appreciable fraction of that seen in the parallel conformation (0.102).

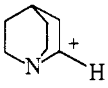
The much studied restriction of rotation (rotational barrier in the range 20 to 30 kcal/mol) about the C–N bonds of amides[11] and amidinium ions[12] reflects a degree of double bond character which is greatly intensified (up to 70–80 kcal/mol)[13] in compounds such as the methyleneimmonium ion.

The synthesis of compounds in which structural features severely attenuate usual resonance interactions has resulted in many cases of strikingly altered reactivity. For example, aniline **3** shows[14] enhanced basicity at nitrogen (pK 7.79) and decreased reactivity in electrophilic substitution at carbon, with electrophilic attack being favored meta to the amino substituent[15] (para to the alkyl substituent) of **3**.



3

Other studies[16] of the azabicyclo[2.2.2]octanes suggest that C–N π bonding involving a bridgehead atom as in **4** or **5** is still important. Ionizations to give **4** or **5** are observed qualitatively to be considerably faster than those leading to the carbon analogues.



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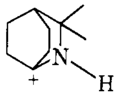
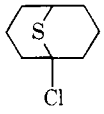
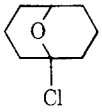
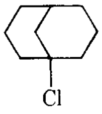


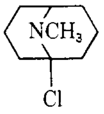
5

Related studies from Wiseman's laboratories,[17] reported during the course of our work, have utilized the geometry of the bicyclo[3.3.1]nonane ring system in compounds **6–9** to inhibit resonance stabilization of a developing bridgehead cation. Relative rates of solvolysis again show the nitrogen substituted compound, **9**, to be faster than carbon analogue **8** (by a factor of ca. 10^7 in this case), with the oxygen (**7**) and sulfur (**6**) analogues being slower than **8** by factors of ca. 3 and 93, respectively.



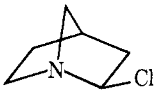






	6	**7**	**8**	**9**
$k_{\rm rel}$	1	30	93	7.5×10^8

In the cases discussed above, the α-amino substituent, even with its resonance interactions sterically inhibited, was found to accelerate the ionization, relative to the analogous carbon-substituted compound. Only in the case of the much more rigid bicyclo[2.2.1]heptane system has an α-amino substituent been found[18] to decelerate an ionization. The methanolyses (25°) of **10** and two C-methylated analogues show factors of 2 to 20 of deceleration attributable to the bridgehead nitrogen-substituent effect.



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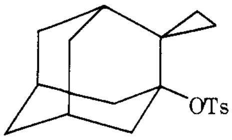
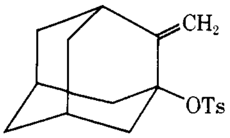
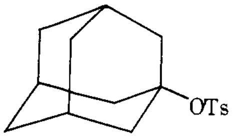
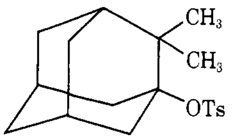
The adamantyl ring system has also been used to constrain α substituents in the perpendicular geometry. Ree and Martin[19] studied solvolysis rates for tosylates **11–14**





	11	**12**
$k_{\rm rel}$, 45°	6.5×10^{-3}	8.8×10^{-5}

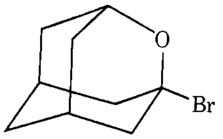




	13	**14**
$k_{\rm rel}$, 45°,	1.0	2.3

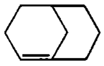
and rationalized the observed inertness of the allylic and cyclopropylcarbinyl tosylates in terms of a steric inhibition of resonance, which allows the dominant contributions of usually masked inductive effects to determine the order of rates.[20]

Steric inhibition of resonance is also seen in the report by Stetter, Tacke, and Gartner[21] that 2-oxa-1-adamantyl bromide (**15**) solvolyses more slowly than 1-adamantyl bromide by a factor of 7 at 25°.



15

The additional one-carbon bridge, which converts the bicyclo[3.3.1]nonane ring system into that of adamantane, imparts much greater rigidity to the system, making it more difficult to deform the molecular skeleton to avoid the electronically unfavored perpendicular geometry in **11–15** and their analogue. This may be reflected in the order of stabilities seen for certain bridgehead olefins.[22] The (Z) isomer of olefin **16** is reasonably stable,[17b,23] while evidence for adamantene[24] (**17**) like that for 1-norbornene[25] (**18**) is based upon experiments designed to trap the transient intermediate olefin. Wiseman has pointed out[26] that the isomer of **16**, which is the closer analogue of **17**, would be the unknown (E) isomer or perhaps the isomer with the double bond in the one-carbon bridge, which is also unknown. This line of evidence for greater rigidity in the adamantyl ring system, compared with that in bicyclononyl nucleus, is therefore not compelling even though the conclusion is intuitively attractive.



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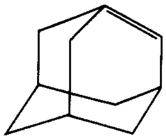

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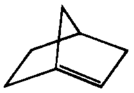


18

The goal of this research was to use the geometrical constraints of the adamantyl system to probe the effects of oxygen- and nitrogen-centered α substituents in the perpendicularly twisted conformations.

Experimental Section

All new compounds gave elemental analyses (C, H, N, and S) within 0.3% of the theoretical values unless otherwise noted.

Bicyclo[1,3,3]nonane-3,7-dione (19). The multistep synthesis of Stetter et al.[27] gave **19** with an overall yield of 24%. The following more facile synthesis was developed to make **19** more easily available.

Hydrogenation of 200 ml of dicyclopentadiene (186 g) in 350 ml of absolute ethanol was carried out in a Pyrex glass liner at 1000 psi pressure for 30 min using Grade 28 Raney nickel (W. R. Grace and Co.). The catalyst was filtered, and tetrahydrodicyclopentadiene was obtained by crystallizing from ethanol at −20° (180 g, 86%).

Adamantane was made by stirring 500 g of molten tetrahydrodicyclopentadiene with 500 g of anhydrous $AlCl_3$ for 1 h.[28a] The mixture was poured onto ice, and 133 g of adamantane (27%) was collected by filtration.

1,3-Dibromoadamantane was made by the procedure of Talaty, Cancienne, and Dupuy[28b] from adamantane. Heating the 1,3-dibromoadamantane with 0.5 M NaOH in 50% aqueous dioxane for 18 h in a sealed tube at 180° produced the 3-methylenebicyclo[1,3,3]nonan-7-one.[28c] Ozonolysis by the method of Stetter[27] gave **19** with an overall yield of 43% from adamantane.

3-Cyano-2-oxa-1-adamantol (21) was prepared by a general method for the preparation of cyanohydrins.[29] To 1.72 g of **19** (13.3 mmol) in 15 ml of dichloroethane was added 19 mmol of NaCN (2.2 ml of a solution of 5 g of NaCN in 12 ml of water), and the mixture was stirred for 30 min. Over a 2-h period, 4.6 ml of 40% aqueous H_2SO_4 was added. The aqueous solution was extracted with dichloroethane, the extract was dried ($MgSO_4$), and the solvent removed in vacuo. The resulting compound was recrystallized from chloroform–pentane and sublimed at 140° (1.0 Torr) to give colorless crystals (1.67 g, 82.5%): mp 150–151° (sealed tube); ir ($CHCl_3$) 3440, 2250 (w, C≡N), 1120, 1050 cm^{-1}; NMR ($CDCl_3$) δ 3.36 (s, 0.8, OH), 2.47 (s, 2.1, O-C-C-CH), 2.24 and 1.95 (d of d, 4.3, N≡C-C-CH_2, J = 12.3 Hz), 1.87 (s, 3.8, HO-C-CH_2), 1.81 (s, 1.9, O-C-C-C-CH_2); mass spectrum (70 eV) m/e (rel intensity) 179 (96.0, $M\cdot^+$), 161 (33.5, $M\cdot^+ - H_2O$), 152 (21.4, $M\cdot^+$ − HCN), 68 (100).

3-Cyano-2-oxa-1-adamantyl *p*-Toluenesulfonate (23). In accord with the procedure of Wilt,[30] 0.28 g of **21** (1.59 mmol) was dissolved in 1 ml of $CHCl_3$. *p*-Toluenesulfinyl chloride (0.30 g, 1.74 mmol) was added at 0° followed by 0.14 ml (1.81 mmol) of pyridine. This was allowed to warm slowly to room temperature, and no attempt was made to isolate the sulfinate ester. After 2 h the solution was cooled to −74°, and 9 ml of 0.204 M RuO_4 in $CHCl_3$ was added.[19] The reaction mixture immediately turned black as RuO_2 was formed. After 1 h the mixture was slowly warmed to room temperature, and CH_3OH was added to reduce the excess RuO_4. The solution was concentrated and passed through a layer of alumina to remove the RuO_2. The solvent was removed in vacuo and the product recrystallized from CCl_4 to give 0.25 g (47%) of a crystalline solid: mp 133–134.5°; ir ($CHCl_3$) 2250 (very weak, C≡N), 1365, 1180, 1140 cm^{-1}; NMR ($CDCl_3$) δ 7.85 and 7.30 (d of d, 4.0, aromatic, J = 8.0 Hz), 2.46 (s, 4.8, Ar-CH_3 and O-C-C-CH), 2.32 and 2.06 (d of d, 4.0, TsO-C-CH_2, J = 11.5 Hz), 2.18 and 1.89 (d of d, 3.9, N≡C-C-CH_2, J = 14.2 Hz), 1.79 (s, 1.7, O-C-C-C-CH_2); mass spectrum (70 eV) m/e (rel intensity) 333 (4.9, $M\cdot^+$), 178 (23.4, $M\cdot^+ - SO_2C_7H_7$), 162 (7.4, $M\cdot^+$ − OTs), 155 (100), 91 (84.7).

3-Cyano-2-oxa-1-adamantyl Triflate. To 0.65 g (3.6 mmol) of **21** in 5 ml of $CHCl_3$ was added 1.80 ml (10.8 mmol) of trifluoromethanesulfonic acid anhydride (95%).[31] Then at 0° 1.1 ml (13.7 mmol) of pyridine was slowly added. A very exothermic reaction occurred with the formation of a white precipitate, which dissolved as more pyridine was added. The solution was passed through a short column of alumina to remove the pyridine, and the solvent was removed in vacuo. The product was recrystallized from CCl_4 to give a slightly hygroscopic crystalline product (0.6734 g, 60%): mp 94.5–97.5°; ir ($CHCl_3$) 1415, 1140 cm^{-1} (no observable C≡N stretch); NMR ($CDCl_3$) δ −70 (CF_3, ppm from $CFCl_3$), 2.60 (s, 2.2, O-C-C-CH), 2.40 and 2.13 (d of d, 4.1, TfO-C-CH_2, J = 11.9 Hz), 2.33 and 2.01 (d of d, 4.2, N≡C-C-CH_2, J = 13.1 Hz), 1.85 (s, 2.1, O-C-C-C-CH_2); mass spectrum (70 eV) m/e (rel intensity) 311 (18.1, $M\cdot^+$), 178 (21.0, $M\cdot^+ - SO_2CF_3$), 162 (40.4, $M\cdot^+$ − OTf), 68 (100).

3-Cyano-2-oxa-1-ethoxyadamantane. Under a nitrogen atmosphere, 0.71 g (2.3 mmol) of 3-cyano-2-oxa-1-adamantyl triflate and 0.2 ml (2.5 mmol) of pyridine were added to 35 ml of ethanol. The solution was stirred at room temperature for 24 h, and the solvent was then removed in vacuo. The product was recrystallized from an ether–pentane solution and then sublimed at 0.1 Torr and 70° to give 0.32 g (67%) of a white crystalline solid: mp 78–80°; ir ($CHCl_3$) 2228, 1445, 1378, 1185, 1140, 1073, 1002, 979 cm^{-1}; NMR ($CDCl_3$) δ 3.71 (q, 1.7, O-CH_2-CH_3, J = 7.1 Hz), 2.42 (s, 1.9, O-C-C-CH), 2.18 and 1.90 (d of d, 4.2, N≡C-C-CH_2, J = 12.3 Hz), 2.00 and 1.66 (d of d, 4.2, CH_3CH_2O-C-CH_2, J = 11.9 Hz), 1.79 (s, 1.7, O-C-C-C-CH_2), 1.21 (t, 2.7, O-CH_2-CH_3, J = 7.1 Hz); mass spectrum (70 eV) m/e (rel intensity) 207 (86.1, $M\cdot^+$), 178 (5.9, $M\cdot^+$ − Et), 162 (12.0, $M\cdot^+$ − OEt), 139 (100).

3-Cyano-2-aza-1-adamantanol. In a 35-ml tube was sealed 2.00 g of **19** (13.1 mmol), 1.00 g of NaCN (20.3 mmol), 0.76 g of NH_4Cl (14.3 mmol), and sufficient liquid NH_3 to make 25 ml. The mixture was heated at 50° for 2 days after which the tube was opened. Sublimation from the inorganic salts at 150° (0.1 Torr) gave 1.98 g (84%) of product, mp 209–211.5° dec, which, even after repeated sublimation and recrystallizations from THF, failed to give acceptable elemental analyses: ir (KBr) 3280 (sharp), 3180 (broad), 2940, 2250, 1600 (weak), 1340, 1180 cm^{-1}; mass spectrum (70 eV) m/e (rel intensity) 178 (42.1 $M\cdot^+$), 177 (100.0, $M\cdot^+$ − H), 121 (86.1), 110 (74.8).

***N*-Methyl-3-cyano-2-aza-1-adamantanol (20). Method A.** By the procedure of Kaluszyner et al.[32] 1.56 g (8.7 mmol) of 3-cyano-2-aza-1-adamantanol, 23.4 mmol of an 88% aqueous solution of formic acid, and 2.0 ml (24.6 mmol) of a 37% aqueous solution of formaldehyde were stirred at 0° for 0.5 h and then at room temperature for 8 h. The solution was made basic (pH 10) with 2 M NaOH and extracted with $CHCl_3$. The solution was dried over $MgSO_4$ and the solvent removed in vacuo. The resulting crystals were recrystallized from pentane–ether and sublimed to form 0.72 g (43%) of **20**: mp 125–143° dec; ir ($CHCl_3$) 3580 (sharp), 2940, 2240, 1450, 1370 cm^{-1}; NMR ($CDCl_3$) δ 2.62 (s, 3.0, N-CH_3), 2.33 and 1.81 (d of d, 2.0 and 2.4, N≡C-C-CH_2, J = 11.8 Hz), 2.31 (s, 1.9, N≡C-C-C-CH), 1.95 and 1.63 (d of d, 2.2 and 1.9, HO-C-CH_2, J = 11.9 Hz), 1.71 (s, 1.6, N≡C-C-C-C-CH_2); mass spectrum (70 eV) m/e (rel intensity) 192 (48.0, $M\cdot^+$), 191 (57.4, $M\cdot^+$ − H), 177 (9.8, $M\cdot^+ - CH_3$), 135 (100.0), 124 (80.4).

Method B. In a 35-ml tube was sealed 1.54 g of **19** (10.1 mmol), 4.5 g of Et_4NCN[33] (28.8 mmol), 0.80 g of NH_4Cl (15.4 mmol) and sufficient liquid CH_3NH_2 to make 25 ml. The mixture was heated at 60° for 2 days after which the tube was opened, and the liquid CH_3NH_2 was boiled off. The material remaining was heated at 50° and 0.1 Torr to sublime an impurity. The bath temperature was then raised to 120° and 1.15 g (60%) of **20** was obtained.

***N*-Methyl-3-cyano-2-aza-1-adamantyl *p*-toluenesulfonate (24)** was prepared by the same procedure as described for **23.** The product was recrystallized from ether–pentane to give 54% of a crystalline solid: mp 105–107°; ir ($CHCl_3$) 2940, 2240, 1335, 1190, 1180, 935, 873 cm^{-1}; NMR ($CDCl_3$) δ 7.80 and 7.34 (d of d, 3.9, aromatic, J = 9.0 Hz), 2.64 (s, 3.1, N-CH_3), 2.44 (s, 3.6, Ar-CH_3), 2.35 (m, 7.2), 1.81 (d, 1.9, J = 13.2 Hz), 1.74 (s, 1.9, N-C-C-C-CH_2); mass spectrum (10 eV) m/e (rel intensity) 346 (35.5, $M\cdot^+$), 191 (18.4, $M\cdot^+ - SO_2C_7H_7$), 132 (30.8), 74 (89.9), 59.1 (100).

***N*-Methyl-3-cyano-2-aza-1-ethoxyadamantane.** To 5 ml of ethanol was added 0.19 g (0.54 mmol) of **24** and 0.08 ml of Et_3N. The solution was stirred at 60° for 24 h. The solvent was removed in vacuo and the product was recrystallized from an ether–pentane solution to give 0.09 g (79%) of a white crystalline solid: mp 64–66°; ir ($CHCl_3$) 2940, 2242, 1180, 1068, 1005 cm^{-1}; NMR ($CDCl_3$) δ 3.56 (q, OCH_2CH_3, 1.8, $J = 7.0$ Hz), 2.48 (s, N-CH_3, 2.9), 2.30 and 1.79 (d of d, 4.1, $N\equiv C-C-CH_2$, $J = 11.8$ Hz), 2.28 (s, N-C-C-CH, 1.9), 2.06 and 1.46 (d of d, 4.3, O-C-CH_2, $J = 12.0$ Hz), 1.71 (s, N-C-C-C-CH_2, 2.0), 1.17 (t, 2.9, OCH_2CH_3, $J = 7.0$ Hz); mass spectrum (70 eV) m/e (rel intensity) 220 (47.5, M·$^+$), 205 (s.7, M·$^+$ − CH_3), 191 (100.0, M·$^+$ − Et), 163 (45.3), 135 (39.8).

3-Cyano-1-adamantanol (22). To 7.20 g (30.0 mmol) of 3-bromo-1-cyanoadamantane (prepared by the method of Applequist, Rivers, and Applequist)[34] in 180 ml of 75% aqueous tetrahydrofuran was added 10 g of $AgNO_3$ in 20 ml of water. The mixture was boiled for 10 h, cooled to room temperature, and extracted with ether. The extract was dried over $MgSO_4$ and the ether removed in vacuo. The resulting oil was recrystallized from pentane-chloroform to give crystalline **22** (4.02 g, 75.6%): mp 209.5–211.5° (sealed tube); ir ($CHCl_3$) 3450, 2920, 2240 cm^{-1}; NMR ($CDCl_3$) δ 2.30 (s, 2.2, HO-C-C-CH), 2.00 (s, 2.2, HO-C-CH_2-C-$C\equiv N$), 1.94 and 1.95 (2s, 5.4, $N\equiv C-C-CH_2$ and at 1.94, OH), 1.74 (unresolved doublet, 3.8, HO-C-CH_2), 1.64 (s, 1.8, $N\equiv C-C-C-C-CH_2$); mass spectrum (70 eV) m/e (rel intensity) 177 (31.2, M·$^+$), 120 (96.7), 95 (100).

3-Cyano-1-adamantyl *p*-Toluenesulfonate (25). Carbinol **22**, 1.97 g (11.1 mmol), 6.04 g (31.6 mmol) of tosyl chloride, 3.7 ml (46 mmol) of pyridine, and 50 ml of $CHCl_3$ were stirred at 55° for 15 days. The mixture was washed with cold dilute HCl, then with cold dilute NaOH. The $CHCl_3$ was then dried over $MgSO_4$, and the solvent was removed in vacuo. Recrystallization from ether gave 1.55 g (42%) of **25**: mp 107–108.5°; ir ($CHCl_3$) 2220 ($C\equiv N$), 1350, 1180, 925 cm^{-1}; NMR ($CDCl_3$) δ 7.80 and 7.35 (d of d, 4.0, aromatic, $J = 8.4$ Hz), 2.45 (s, 2.9, Ar-CH_3), 2.42 (s, 2.1, TsO-C-CH_2-C-$C\equiv N$), 2.33 (s, 2.1, $N\equiv C-C-C-CH$), 2.17 (s, 3.7, TsO-C-CH_2), 1.97 (s, 3.8, $N\equiv C-C-CH_2$), 1.64 (s, 2.1, $N\equiv C-C-C-C-CH_2$); mass spectrum (70 eV) m/e (rel intensity) 331 (21.2, M·$^+$), 160 (99.8, M·$^+$ − OTs), 159 (100, M·$^+$ − HOTs), 93 (35.5), 91 (60.1).

1-Ethoxy-3-cyanoadamantane. Under a nitrogen atmosphere, 0.27 g (1.1 mmol) of 3-bromo-1-cyanoadamantane, 0.33 g (1.7 mmol) of $AgBF_4$, and 0.14 ml (1.7 mmol) of pyridine were added to 10 ml of ethanol and stirred for 5 days at 55°. The product was recrystallized from an ether–pentane solution and sublimed at 0.1 Torr and 50° to give 0.13 g (63%) of a white crystalline solid: mp 61–65°; ir ($CHCl_3$) 2940, 2250 ($C\equiv N$), 1185, 1070, 1000 cm^{-1}; NMR ($CDCl_3$) δ 3.49 (q, 1.6, OCH_2CH_3, $J = 7.3$ Hz), 2.42 (s, 2.1, $N\equiv C-C-C-CH$), 2.02 (s, 2.1, $N\equiv C-C-CH_2-C-OCH_2CH_3$), 1.95 (unresolved doublet, 4.1, $N\equiv C-C-CH_2$), 1.76 (unresolved doublet, 3.5, $CH_3CH_2O-C-CH_2$), 1.63 (s, 2.2, $N\equiv C-C-C-C-CH_2$), 1.17 (t, 2.5, OCH_2CH_3, $J = 7.3$ Hz); mass spectrum (70 eV) m/e (rel intensity) 205 (55.0, M·$^+$), 160 (31.0, M·$^+$ − CH_3), 148 (97.2), 123 (100), 120 (53.4).

2-Oxa-1-adamantyl *p*-toluenesulfonate (26) was prepared from 2-oxa-1-adamantanol by the same method as that described above for **23** to give, after recrystallization from ether pentane, 45% of **26**: mp 87–92°; ir ($CHCl_3$) 2950, 1360, 1180, 1075, 950, 915, 890, 840 cm^{-1}; NMR ($CDCl_3$) δ 7.85 and 7.29 (d of d, 3.5, aromatic, $J = 8.2$ Hz), 4.37 (s, 0.8, O-CH), 2.42 (s, 3.0, Ar-CH_3), 2.32 and 2.08 (d of d, 4.3, TsO-C-CH_2, $J = 11.5$ Hz), 1.98 and 1.54 (d of d, 3.9, O-CH-CH_2, $J = 12.8$ Hz), 1.78 (s, 2.2, O-C-C-C-CH_2); mass spectrum (70 eV) m/e (rel intensity) 308 (28.2, M·$^+$), 155 (34.2), 137 (33.7, M·$^+$ − OTs), 136 (31.7, M·$^+$ − HOTs), 91 (100).

2-Oxa-1-ethoxyadamantane. To 5 ml of ethanol was added 0.38 g (1.2 mmol) of **26** and 0.11 ml (1.3 mmol) of pyridine. The mixture was stirred at 60° for 48 h. The solvent was removed in vacuo, and the resulting liquid was distilled at 80° and 0.5 Torr to give 0.10 g (43%) of a colorless liquid: ir ($CHCl_3$) 2920, 1115, 1090, cm^{-1}; NMR ($CDCl_3$) δ 4.26 (s, 1.0, O-CH), 3.68 (q, 1.9, O-CH_2CH_3, $J = 7.1$ Hz), 2.29 (s, 1.8, O-C-C-CH), 2.3–1.7 (m, 7.3), 1.60 (m, 2.1), 1.48 (m, 0.9), 1.20 (t, 3.1, O-CH_2-CH_3, $J = 7.1$ Hz); mass spectrum (70 eV) m/e (rel intensity) 182 (99.9, M·$^+$), 153 (11.3), 137 (16.2, M·$^+$ − OEt), 136 (30.4, M·$^+$ − HOEt), 114 (100), 94 (77.1), high-resolution peak matching m/e 182.1308 (calcd for $C_{11}H_{18}O_2$, 182.1307).

1-Ethoxyadamantane. Under a nitrogen atmosphere 0.62 g (4.1 mmol) of 1-adamantanol, 0.37 ml (4.5 mmol) of 2,2,2-trifluoroethanesulfonyl chloride, and 0.63 ml (4.5 mmol) of triethylamine were stirred in 5 ml of CH_2Cl_2. After 30 min, 10 ml of ethanol was added, and the solution was stirred for 12 h. The solvent was removed in vacuo and the resulting oil was distilled at 80° and 0.5 Torr to give 0.2 g of a clear liquid (27%): bp 110–111°; ir ($CHCl_3$) 2920, 1110, 1090 cm^{-1}; NMR ($CDCl_3$) δ 3.46 (q, 1.8, OCH_2CH_3, $J = 7.1$ Hz), 2.13 (s, 3.1, $CH_3CH_2O-C-C-CH$), 1.75 (unresolved AB doublet, 5.8, $CH_3CH_2O-C-CH_2$), 1.62 (unresolved AB doublet, 6.1, $CH_3CH_2O-C-C-C-CH_2$), 1.16 (t, 3.2, OCH_2CH_3, $J = 7.1$ Hz); mass spectrum (70 eV) m/e (rel intensity) 180 (29.7, M·$^+$), 135 (22.7, M·$^+$ − OEt), 123 (100), 95 (45.8), high-resolution peak matching m/e 180.1516 (calcd for $C_{12}H_{20}O$, 180.1514).

***N*,*N*-Dimethyl-3-cyano-2-aza-1-*p*-toluenesulfonyloxyadamantane Fluorosulfonate (27).** A sample of 0.14 g (0.40 mmol) of **24**, 0.30 ml (0.48 mmol) of methyl fluorosulfonate, and 3 ml of $CHCl_3$ was stirred for 5 h at 50°. The resulting crystals were recrystallized from an acetonitrile-ether solution to give 0.06 g (32%) of **27**: mp 158–167°; ir (KBr) 3480 (broad), 1290, 1200, 850, 710 cm^{-1}; NMR (80% CD_3CD_2OD-D_2O) δ 7.95 and 7.56 (d of d, 4.3, aromatic, $J = 9.0$ Hz), 3.48 (s, 5.7 N-CH_3), 1.54–1.32 (m, 12.8, superposed s at 1.49, Ar-CH_3), 0.92 (s, 2.2, N-C-C-C-CH_2); field desorption mass spectrum (12 mA), m/e (rel intensity) 362 (25, M·$^+$ + H), 361 (100, M·$^+$), 346 (10, M·$^+$ − CH_3), 172 (50, TsOH).

Kinetic Experiments

Commercial ethanol was purified by distillation. Following the procedure of Fainberg and Winstein,[35] 80% ethanol-water was prepared using four volumes of ethanol to one volume of water at 25°. A 0.02 M solution of sodium hydroxide in 80% ethanol–water was standardized against potassium acid phthalate and stored under nitrogen. For the sealed tube kinetic runs, a standard 0.015 M solution of *N*,*N*-dimethylbenzylamine in 80% ethanol-water was used as reaction medium.

All low-temperature solvolysis runs were conducted in solutions 0.02 M in sodium perchlorate. The rate constants were determined by continuous titration of the liberated *p*-toluenesulfonic acid with 0.02 M sodium hydroxide. A recording pH-stat equipped with a combination glass–silver|silver chloride electrode was used for the kinetic runs below 75°.

In a typical solvolysis experiment, approximately 0.04 mmol of the desired tosylate was weighed out into a solvolysis tube fitted with a side arm for the electrode and a side arm for the titrant delivery tube. A magnetic stirring bar and 6 ml of 0.02 M sodium perchlorate in 80% ethanol-water were added, and the tube was equilibrated at bath temperature with magnetic stirring. For solvolysis runs below room temperature, the solvolysis tube with the tosylate was precooled in a −20° freezer, and then cold sodium perchlorate solution was added. The electrode was cooled in an ice bath before inserting into the cold reaction mixture. Zero points were taken about 1 min after admitting the sample.

For runs above 75°, enough tosylate was dissolved in 0.015 M *N*,*N*-dimethylbenzylamine in 80% ethanol-water to make 0.01 M solutions. Approximately 1.2-ml aliquots of these solution were sealed in tubes and heated in a constant temperature bath. At selected intervals, a tube was removed and the reaction quenched by cooling the tube to 0°. Exactly measured 1-ml aliquots were back-titrated with 0.01 M hydrochloric acid using a Methyl Red indicator.

All rate constants were calculated directly from raw data using an unweighted least-squares program which was also equipped to change the experimental infinity value in increments of ±1% to minimize the percent standard deviation of slope.

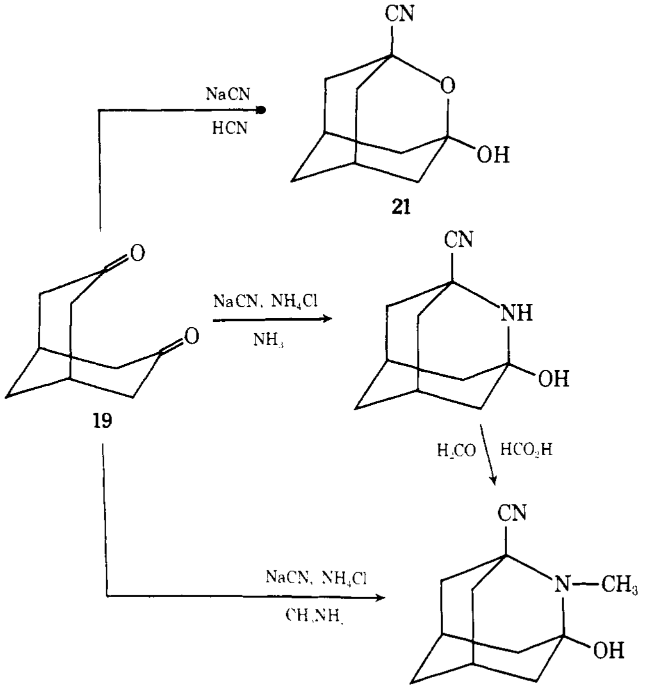
Product Studies

A completed solvolysis run of each tosylate was analyzed on a 2.0 ft × 0.25 in. glass GLC column packed with 20% SE-30 on Anakrom ABS. The retention times of the solvolysis products were identical to those of the authentic alcohols and ethers expected. The yields of the solvolysis products were determined quantitatively by the addition of an internal standard to the completed solvolysis runs.

The solvolysis products were also analyzed by GLC-mass spectrometry. A completed solvolysis run was extracted with ether using a liquid-liquid micro-extractor. The ether solution was then dried with $MgSO_4$ and the solvent removed in vacuo. The residue was taken up with dry ether, and the products were analyzed using a Varian-MAT 311A double-focusing mass spectrometer equipped with an Aerograph 2700 G. C. two-stage Biemann-Watson separator system. Spectra obtained from the solvolysis products were identical to those of the corresponding alcohols and ethers with the exception of **20**, **21**, and **22** which decomposed in the separator system. These alcohols were converted to the trimethylsilyl ethers by treating the samples with TRI-SIL (Pierce Chemical Co.). The parent mass spectrometer peaks for the resulting samples corresponded to the molecular weight of the respective trimethylsilyl ethers of **20**, **21**, and **22**.

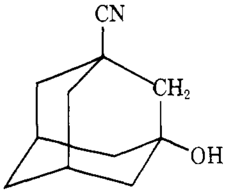
Results

Syntheses. Dione **19** was originally prepared from adamantane-1-carboxylic acid by Stetter[27] using a five-step process. In this work an alternative[28] three-step synthesis of **19** (overall 43% yield from adamantane) was developed to facilitate large-scale preparations leading by the indicated routes to alcohols **20** and **21**.

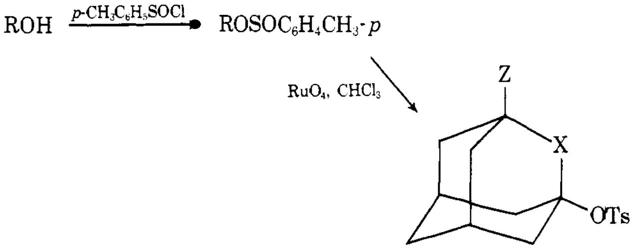


Anticipating very low-solvolytic reactivation for derivatives of **21** in acetic acid, we originally intended to study the more reactive[36a] trifluoromethane sulfonates. While that from **21** was easily prepared, we were unable to isolate the more reactive triflate from **22**.

We therefore decided to use the less reactive tosylates in the better ionizing medium, 80% aqueous ethanol. Tosylates **23**–**26** and **13** were prepared by the method of Ree and Martin[19] by ruthenium tetroxide oxidation of the easily formed *p*-toluenesulfinate esters.[36b]



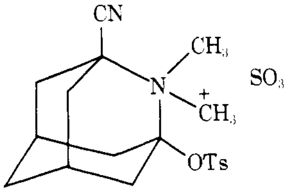
22



13, X = CH_2; Z = H
23, X = O; Z = CN
24, X = NCH_3; Z = CN
25, X = CH_2; Z = CN
26, X = O; Z = H

Rate Studies. The solvolysis rates for tosylates **13**, **24**, **25**, and **26** were followed at constant pH and ionic strength by continuous titration of the liberated *p*-toluenesulfonic acid with 0.02 M sodium hydroxide in 80% ethanol-water. For the solvolysis runs above 75° (all runs for **23** and one run for **25**), sealed tubes containing tosylate solutions buffered with 0.015 *N*,*N*-dimethylbenzylamine were used.

All compounds gave normal first-order rate plots using the experimental infinity titers. However, the infinity titers for **24** were about 15–25% lower than the theoretical value. The pH setting of the pH meter was varied from pH 3 to 10 (near the extremes of the vertical section of the titration curve for the acid in this medium) to determine the effect of acidity on the solvolysis of **24**. At the lowest pH settings, the total titer was 60% of the theoretical titer, and at the highest pH setting, the total titer was 110% of the theoretical titer. This disparity between the total titer and the theoretical titer is attributed to some decomposition of alcohol **20** to give **19**, methylamine, and hydrogen cyanide. To ensure that the conjugate acid of **24** was not reacting with solvent in an unexpected manner before ionization of the *p*-toluenesulfonate, a model compound, **27**, was studied. Under normal reaction conditions and times at 45° no reaction was observed by NMR, and even after heating at 75° for 5 days no loss of starting material was observed.

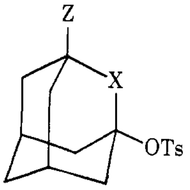


27

The rates of solvolysis of **24** at 45° followed at different settings of the pH-stat are shown in Table I. Activation parameters, solvolysis rates at various temperatures, and relative rates at 25° are also listed in Table I for the series of compounds studied. In addition, the rates calculated for the three tosylates studied by Ree and Martin, **11**, **12**, and **14**, at 25° in 80% ethanol-water are listed with the pertinent activation parameters.

Product Studies. The solvolysis products listed in Table II were determined quantitatively by gas chromatography, using an internal standard. The total observed yields of volatile products were consistently greater than 90%. Products were isolated from completed solvolysis runs and compared

Table I. Solvolysis of Tosylates in 80% Ethanol–Water



Compound (X, Z)	Temp, °C ±0.05°	k, s^{-1}	ΔH^*, kcal/mol	ΔS^*, eu	$k_{rel}^{25°}$
23[a] (O, CN)	120.00	$(2.97 \pm 0.03) \times 10^{-6}$			
	105.00	$(6.44 \pm 0.12) \times 10^{-6}$	26.6 ± 1.1	−12.4 ± 2.3	7.43×10^{-8}
	90.00	$(1.65 \pm 0.03) \times 10^{-6}$			
24[b] (NCH_3, CN)	45.00[c]	$(1.51 \pm 0.08) \times 10^{-3}$			
	45.00[d]	$(1.44 \pm 0.005) \times 10^{-3}$			
	45.00[e]	$(1.71 \pm 0.006) \times 10^{-3}$			
	45.00	$(1.89 \pm 0.01) \times 10^{-3}$	20.9 ± 0.7	−5.4 ± 2.0	3.56×10^{-2}
	30.00	$(4.09 \pm 0.02) \times 10^{-4}$			
	15.00	$(5.54 \pm 0.02) \times 10^{-5}$			
25 (CH_2, CN)	84.7[a]	$(3.20 \pm 0.03) \times 10^{-4}$			
	75.22[b]	$(1.38 \pm 0.005) \times 10^{-4}$			
	70.13[b]	$(8.87 \pm 0.02) \times 10^{-5}$	21.9 ± 0.4	−13.5 ± 1.0	9.97×10^{-5}
	65.05[b]	$(5.50 \pm 0.02) \times 10^{-5}$			
	54.88[b]	$(3.10 \pm 0.005) \times 10^{-5}$			
26 (O, H)	60.00	$(1.27 \pm 0.001) \times 10^{-3}$			
	60.00	$(1.25 \pm 0.002) \times 10^{-3}$	22.3 ± 0.4	−5.1 ± 1.1	3.68×10^{-3}
	45.00	$(2.24 \pm 0.009) \times 10^{-4}$			
	30.00	$(4.14 \pm 0.01) \times 10^{-5}$			
13[b] (CH_2, H)	25.00	$(5.73 \pm 0.02) \times 10^{-3}$			
	20.00	$(3.55 \pm 0.03) \times 10^{-3}$			
	15.00	$(1.80 \pm 0.004) \times 10^{-3}$	20.5 ± 0.4	0.1 ± 1.4	1.00
	15.00	$(1.89 \pm 0.006) \times 10^{-3}$			
	10.00	$(9.29 \pm 0.02) \times 10^{-4}$			
	2.00	$(3.06 \pm 0.006) \times 10^{-4}$			
11 (C◁, H)	25.00[f]	2.82×10^{-5}	23.3 ± 1.1	−5.0 ± 5.4	4.93×10^{-3}
	25.00[f,g]	$[2.13 \times 10^{-3}]$			$[3.71 \times 10^{-1}]$
12 ($C{=}CH_2$, H)	25.00[f]	2.42×10^{-7}	26.7 ± 0.8	−3.0 ± 2.3	4.23×10^{-5}
	25.00[f,g]	$[1.08 \times 10^{-4}]$			$[1.88 \times 10^{-2}]$
14 (CMe_2, H)	25.00[f]	1.54×10^{-2}	19.0 ± 0.2	−7.0 ± 0.6	2.68

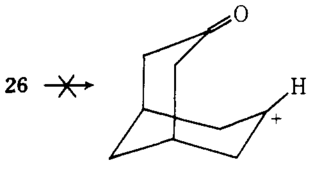
[a] 0.015 M *N,N*-dimethylbenzylamine. [b] 0.02 M $NaClO_4$. [c] Run at pH setting of 4. [d] Run at pH setting of 5.5. [e] Run at pH setting of 10. [f] Calculated from data from ref 19; corrected for changes in solvent ionizing power using the method of E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948). [g] Corrected for strain effects, see text.

Table II. Products from the Solvolyses of Tosylates and Bromides in 80% Ethanol–Water

Compd	Temp, °C	Theoretical yield, mol × 10^6	Alcohol, mol × 10^6	Ethyl ether, mol × 10^6	% alcohol	% ether	Alcohol/ether
23	120	9.0	5.3	3.3	59	37	1.6
24	45	56	38[a]	13	68[a]	23	3.0
25	80	9.1	6.5	2.9	71	32	2.2
26	60	32	18	12	56	38	1.5
13	25	34	20.4	10.5	60	31	1.9
13[b]	25				71	29	2.4
13-Br[c]	60				60.	40	1.5
13-Br[d]	75				49	51	1.0

[a] Includes 2 × 10^{-6} mol of **19**. [b] D. N. Kevill, K. C. Kolwyck, and F. L. Weitl, *J. Am. Chem. Soc.*, **92**, 7300 (1970); percentages determined by NMR integration. [c] J. MacMillen and R. J. Pryce, *J. Chem. Soc. B*, 337 (1970). [d] J. M. Harris, D. J. Raber, R. E. Hall, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **92**, 5729 (1970).

to authentic samples by GLC-mass spectrometry. The mass spectra of the products were identical with those of the expected ethers and alcohols except for alcohols, **20**, **21**, and **22**, which decomposed in the separator system of the mass spectrometer. These products were converted to the trimethylsilyl ethers, and the parent mass spectrometer peaks for the resulting samples corresponded to the molecular weight of the respective trimethylsilyl ethers of **20–22**.



The possibility that ring opening was occurring during the solvolysis of **26**, with the formation of the intermediate secondary alkyl cation rather than a possibly less stable perpendicular α-alkoxy cation, was eliminated by the following observations. Products expected from the secondary alkyl cation were not observed, and the observed ratio of alcohol to ether (Table II) was not significantly different from the ratios found for the solvolyses of the other tosylates studied. A comparison of the spread of relative rates for **25** and **23** (7.5 × 10^{-4}) with that for **13** and **26** (3.7 × 10^{-3}) shows a difference of a factor less than five, providing no evidence for the fragmentation process pictured above for **26**.

Discussion

The geometry-imposed perpendicular twist of the lone-pair p orbital of a 2-heteroatom, relative to the vacant p orbital of a 1-adamantyl cation, would be expected to minimize the resonance stabilization of such a species. This might lead one to expect an order of rates for the tosylate solvolyses studied here which would reflect the inductive order, $CH_2 > NCH_3 > O$. In fact, the order is $NCH_3 > CH_2 > O$, requiring the operation of influences on rate other than simple inductive effects.

In addition to the inductive effect, three other possible influences of the α-heteroatom on rates of ionization of the tosylates of this study deserve comment: (a) the cation may be stabilized to varying degrees by resonance interaction with bonding or nonbonding electrons associated with the heteroatom despite the unfavorable geometry for such interactions, (b) the difference in strain between ground state and transition state may vary with the heteroatom to a kinetically significant degree, and (c) the transmission of the polar inductive effect of the C≡N substituent at the 3 position may be significantly different for the 2-oxa-, the 2-aza-, and unsubstituted adamantyl systems.

Both experimental and theoretical bases exist for the separation of polar and resonance effects using a modified Hammett $\sigma = \sigma_R + \sigma_I$.[2g,37-39] The polar substituent constant given the symbol σ_I is widely accepted as a measure of the polar contribution of a substituent on a reaction site. It is intimately related to the σ^* substituent constant[4b,37] which is derived from systems in which the substituent is insulated from the reaction center by CH_2 groups which make direct resonance interactions impossible. The resonance substituent effect is reflected in the constant σ_R. While attempts have been made to establish a single constant to correlate resonance substituent effects,[39] theoretical and experimental evidence suggests that σ_R varies with the electrical demands of the reaction site.[4c,37] For the resonance effects of a substituent directly bonded to a carbocationic center it is appropriate to use the $\sigma_R{}^+$ constants originally based on $\sigma_p{}^+$ values[37,40] for the rates of solvolysis of para-substituted *tert*-cumyl chlorides. In order to quantify any possible resonance contribution in the solvolysis of **13** and **23–26**, an effective substituent constant, σ_{eff} was defined

$$\sigma_{eff} \equiv \sigma_I + \delta\sigma_R{}^+$$

which incorporated the entire polar contribution of the substituent, σ_I, and a fraction, δ, of the resonance contribution, $\sigma_R{}^+$.[2g,37-39]

The appropriate values for σ_I and $\sigma_R{}^+$ in the series of compounds studied are listed in Table III taking the ethyl group as the appropriate model for the CH_2 substituent at the 2 position in **13** and **25**, the methoxy group for the ether oxygen substituent in **23** and **26**, the dimethylamino group for the $N-CH_3$ substituent of **24**, the cyclopropyl group for the cyclopropylidene group of **11**, the vinyl group for the vinylidene substituent of **12**, and the *tert*-butyl group for the $C(CH_3)_2$ substituent of **14**.

An iterative least-squares program was developed which varied δ in increments of 0.005 to maximize the correlation coefficient, *r*, of the plot of log *k* vs. σ_{eff}, with respect to δ. For the three cyano-substituted tosylates, **23–25**, the best value of δ was found to be 0.175 with $\rho = -16.8$. An effective Δσ for the 3-cyano substituent was chosen to place the point for **13** on the line thus determined.

$$\Delta\sigma_{CN} \equiv \sigma_{25} - \sigma_{13} = 0.24$$

This value for σ_{X-C-CN}, 0.24, when compared with the σ_{CN} value of 0.56 (Table III), corresponds to an attenuation of the inductive electron-withdrawing effect of the cyano substituent transmitted through a two-atom chain by a factor of ⅔ per atom. This is considerably larger than the traditionally accepted[4] fall-off factor of $^1/_{2.8}$. Referee I has reminded us of other experimental evidence more in keeping with a larger value of this fall-off factor.[41] Cyanoamine pK_a values[42] vary by a factor of ½ per methylene group separating the substituent from the substituent. Reactions forming adamantyl cations[43] show a substituent effect which falls off more slowly than the $^1/_{2.8}$ factor. Systematic kinetic studies of carbonium ion formation by olefin protonation[44] and by tosylate trifluoroacetolysis,[45] as well as calculations of carbonium ion stability,[46] have produced data more consistent with a fall-off factor of ⅔ per CH_2 group. Our result is consistent with this latter estimate for the fall-off factor and therefore appears not to require any ad hoc explanations based on the strained geometry of the adamantyl cation.[47]

Table III. Substituent Constants

Compd	Model substituent	σ_I	$\sigma_R{}^+$
23	CH_3O	0.51^a (0.27^b)	-1.02^b
24	$(CH_3)_2N$	0.30^a (0.06^b)	-1.75^b
25	CH_3CH_2	0.18^a (-0.055^c)	-0.24^d
26	CH_3O	0.27^b	-1.02^b
13	CH_3CH_2	-0.055^c	-0.24^d
14	$(CH_3)_3C$	-0.074^c	-0.18^d
11	Cyclo-C_3H_5	0.01^e	-0.45^f
12	$H_2C{=}CH$	0.05^g	-0.21^g
	CN	0.56^b	
	$NCCH_2$	0.24^h	
	CH_3S	0.23^b	-0.83^i

[a] Value assuming $\sigma_{XCCN} = 0.24$; see text for discussion. [b] Reference 37. [c] R. W. Taft and I. C. Lewis, *Tetrahedron*, 5, 210 (1959). [d] Calculated from data of H. C. Brown, J. D. Brody, M. Grayson, and W. H. Bonner, *J. Am. Chem. Soc.*, 79, 1897 (1957); $\sigma_p{}^+$ for $CH_3CH_2 = -0.291$, $(CH_3)_3C = -0.250$. [e] Reference 19. [f] An average of the values calculated from the following references: L. B. Jones and V. K. Jones, *Tetrahedron Lett.*, 1493 (1966), $\sigma_p{}^+ = -0.41$; L. B. Jones and S. S. Eng, *ibid.*, 1431 (1968), $\sigma_p{}^+ = -0.439$; R. C. Hahn, T. F. Corbin, and H. Shechter, *J. Am. Chem. Soc.*, **90**, 3404 (1968), $\sigma_p{}^+ = -0.462$; D. H. Man and J. B. Stothers, *Can. J. Chem.*, **45**, 225 (1967), $\sigma_p{}^+ = -0.45$; reference 19, $\sigma_R{}^+ = -0.47$. [g] Reference 2g. [h] Reference 4c. [i] Calculated from data of reference 40b; $\sigma_p{}^+$ for $CH_3S = -0.604$.

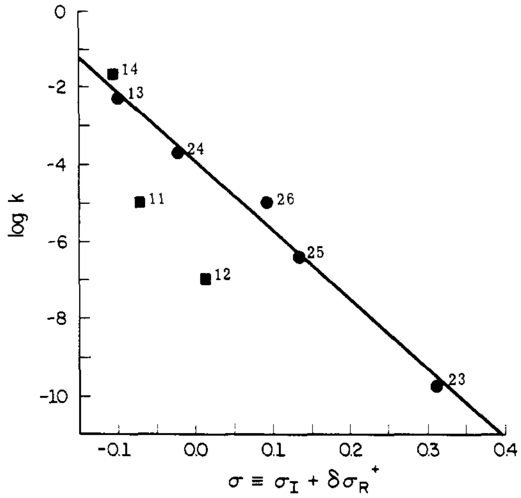


Figure 1. Hammett plot for the solvolyses of **13** and **23–26** in 80% ethanol–water at 25°. Points (■) for the acetolysis, corrected for solvent, of **30**, **27**, and **28** from Ree and Martin[19] are not included in the calculation of the least-squares line. ($\delta = 0.175$, $\rho = 16.8$, $r = 0.995$. If the points from ref 19 are included, $\delta = 0.215$, $\rho = -15.7$, $r = 0.902$.)

Figure 1 shows the graph obtained when all five tosylates of this study, **13** and **23–26**, are considered. The use of the $\Delta\sigma_{CN}$ value derived from the carbon system of **13** and **25**

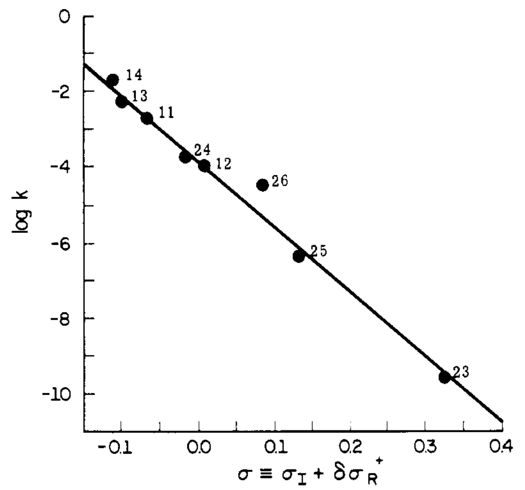
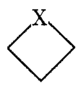


Figure 2. Hammett plot for the solvolyses of **23–26**, **13**, and **14**, plus points for **11** and **12** which have been corrected for strain (see text), in 80% ethanol-water at 25° ($\delta = 0.180$, $\rho = 16.9$, $r = 0.995$).

for the oxa analogue, **23**, places the point for **23** very near the line in Figure 1. The transmission[48] of the cyano inductive effect through an oxygen bridge is very similar to that through a methylene bridge. Errors introduced by our use of a single $\Delta\sigma_{CN}$ value are therefore likely to be minimal.

At the transition state for the solvolysis of adamantyl tosylates, the tertiary carbon at the reaction center goes toward planarity forcing a reduction of the endocyclic angle at the 2 position from the tetrahedral value which it can assume in the ground state. This would not be a factor in determining the order of rates of reaction if the bending force constants for the atoms at the 2 position were constant across the series. A case can be made that this is approximately true for the tosylates of Figure 1 except for **11** and **12.** A comparison of the total strain energy in the four-membered ring compounds **28a–e** can provide a hint as to the relative effects of strain on the rates of reaction of the series of tosylates.



28a, X = CH_2
b, X = O
c, X = NH
d, X = $C{=}CH_2$
e, X = cyclo-$C(CH_2)_2$

The near constancy of strain in **28a** (26.2 kcal/mol),[49] **28b** (25.7 kcal/mol),[49] and **28c** (26.2 kcal/mol)[49] suggests the increase in strain at the 2 positions, for the tosylates with CH_2 (**13** and **25**), O (**23** and **26**), and N (**24**) at this position, might be expected to contribute roughly equally to the depression of the rate of ionization. On the other hand, the vinylidene group and the cyclopropylidene group introduce appreciably greater strain in **28d** (28.8 kcal/mol)[50] and **28e** (ca. 34 kcal/mol),[51] suggesting that the deviation of the points for **11** and **12** from the line of Figure 1 might reflect the greater importance of angle strain on going to the transition states for these two tosylates. When we view the entire range of substituents plotted in Figure 1 we are therefore led to agree with the conclusion of Sherrod, Bergman, Gleicher, and Morris[20] that the ionizations **11** and **12** are slowed by this effect more than those of **13** and **14.** Gleicher and Bergman[52] have used molecular mechanics to calculate a strain increase on going from ground to transition state 2.75 kcal/mol greater for **11** than for **13** and 3.6 kcal/mol greater for **12** than for **13.** If we assume all other tosylates to show a strain effect equal to that for **13,** we can correct the rates for **11** and **12** using the calculated[52] values for strain quoted above. These values for rates of solvolysis of **11** and **12,** corrected for differential strain effects, are listed in brackets in Table I and are used in obtaining the plot of Figure 2. The correlation coefficient for the plot of Figure 2 was maximized at 0.995 for a value of δ of 0.18 and a ρ of -16.9.

Application of the same procedure to the data from Wiseman's laboratory[17] on the solvolysis of the four bridgehead chlorides **6–9** in the bicyclo[3.3.1]nonyl system, using values for σ_I and $\sigma_R{}^+$ for the model substituents listed in Table III, led to a very satisfactory correlation, $r = 0.994$. The optimum value for δ proved to be 0.35, leading to a ρ (-17.0) essentially identical with that derived for the adamantyl tosylates of this study (-16.9).

The finding that the bicyclo[3.3.1]nonyl ring system allows a greater fractional contribution of resonance stabilization of a bridgehead cation by an α-heteroatomic substituent (35% of that for a geometrically unconstrained substituent) than does the adamantyl system (18% of $\sigma_R{}^+$) is not surprising in view of the greater flexibility of the former system, which is obvious from an examination of molecular models. This flexibility could clearly allow a molecular distortion in the cations from **6** to **9** to relieve the orthogonality of the two interacting p orbitals. A similar twisting about the C-1–C-2 bond in the adamantyl system would appear to be much more costly in strain energy.

The degree of twist which would be required can be calculated if one adopts the commonly accepted[53] postulate that the resonance energy, E, varies with $\cos^2\theta$, where θ is the angle between two interacting p orbitals on adjacent atoms.[54]

$$E_\theta = E_{90°} - (E_{90°} - E_{0°})\cos^2\theta$$

If one assumes the resonance energy in the perpendicular geometry ($E_{90°}$) to be zero, the value of θ which is required to explain the fractional resonance contributions derived above is 65° for the adamantyl tosylates and 54° for the bicyclononyl chlorides. While a 36° twisting from the geometrically preferred perpendicular geometry is conceivable for the bicyclononyl system, a 25° twisting of the bond joining positions 1 and 2 of the adamantyl system seems clearly impossible.[57] We therefore favor the alternative explanation which suggests that the 18% of $\sigma_R{}^+$ used to correlate the rates of this study is very near the residual resonance interaction in the perpendicular geometry.[58]

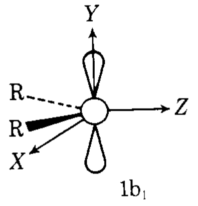
If one adopts the view that the resonance contributions to stabilization of the adamantyl cations of this study approximate those which would be expected for the exactly perpendicular geometry, it becomes necessary to reevaluate the assumption, common to all the above calculations, that the fractional resonance contribution of a series of substituents in a given geometry will be constant across the series.

Photoelectron spectroscopy[60] provides a method for determining energies of occupied orbitals which have large contributions from heteroatom atomic orbitals. For example, the three highest energy occupied orbitals in dialkyl ethers, those with $1b_1$, a_1, and b_2 symmetry, have large contributions from the oxygen 2p atomic orbitals pictured in **29a, 29b,** and **29c,** respectively. The highest energy orbital (see Table IV), essentially the lone pair p_y orbital,[61] is of the proper symmetry to interact with the unoccupied p orbital of an α-carbocationic center in the parallel geometry. In the perpendicular geometry, the vacant p orbital is orthogonal to the p_y orbital and can interact only with the two lower energy filled skeletal orbitals with oxygen p_z and p_x character (a_1, **29b,** and b_2, **20c**).[62] Electron donation from

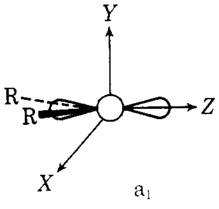
Table IV. Vertical Ionization Potentials for the Three Highest Energy Orbitals as Determined by Photoelectron Spectroscopy

Compound	Ionization potentials, eV		
$(CH_3)_2O$[a]	10.0	11.9	13.4
$(CH_3)_2S$[a]	8.7	11.3	12.7
$(CH_3)_3N$[b]	8.5	12.4	12.4
$(CH_2)_5O$[c]	9.5	(10.9)	(11.5)
$(CH_2)_5S$[d]	8.6	11.2	12.6
$(CH_2)_5N—CH_3$[e]	8.3	10.6	10.6
$(CH_2)_4N—CH_3$[e]	8.4	11.2	11.2
$(CH_2)_3N—H$[e]	9.0	11.5	11.5
$CH_3CH_2CH_3$[f]	12.7	12.1	11.5
$(CH_3)_4C$[f]	11.3	11.3	11.3

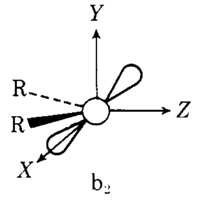
[a] S. Cradock and R. H. Whiteford, *J. Chem. Soc., Faraday Trans. 2*, **68**, 281 (1972). [b] A. B. Cornford, D. C. Frost, F. G. Herring, and C. A. McDonell, *Can. J. Chem.*, 49, 1135 (1971). [c] D. A. Sweigart and D. W. Turner, *J. Am. Chem. Soc.*, **94**, 5599 (1972); the second and third highest atomic orbitals estimated for published photoelectron spectra. [d] D. C. Frost, F. G. Herring, C. A. McDowell, and R. A. N. McLean, *J. Phys. Chem.*, 76, 1030 (1972). [e] K. Yoshikana, M. Hashimoto, and I. Morishima, *J. Am. Chem. Soc.*, 96, 288 (1974). [f] Reference 59.



29a



29b



29c

these orbitals to a vacant p orbital on an α-carbocationic center in the perpendicular geometry will, because of their lower energy, be less important than the donation from the p_y lone-pair orbital which is important in the parallel geometry, and the difference in energy of the π bonding in the two geometries will reflect the difference in energy of the oxygen-centered orbitals which are of proper symmetry to interact in the two geometries. The three highest energy orbitals for amines and sulfides are also those with large contributions from heteroatom atomic orbitals and have symmetries analogous to those discussed above for ethers. In every case the parallel geometry of the carbocation allows π bonding involving the highest energy filled orbital with the perpendicular geometry allowing interactions with the two next lower energy orbitals. To the extent that the difference in energy between the highest energy orbital and the next two is constant for the O, S, and N analogues, the assumption that δ is constant across the series is a reasonable one. The ordering of energy levels for the cyclopropylidene substituent of **11** is also appropriate to justify the assumption of a constant δ.[63] On the other hand, the highest energy orbitals for propane (as a model for the methylene substituent of **13**) are reversed with the highest energy orbital being of proper symmetry for the hyperconjugative delocalization of electrons in the perpendicular geometry of the adamantyl cation.[64] The analogous orbitals in neopentane, as a model for **14**, are degenerate.

It therefore seemed desirable to revise the method described above for the correlation of rates with substituent constants to allow the full contribution of σ_R^+ for the methylene and isopropylidene substituted compounds (**13** and **14** in the adamantyl series and **8** in the bicyclononyl series) and assuming a constant δ for other members of the series. With this approach the correlation of Figure 3 was obtained. This shows, for the adamantyl series, a correlation with $r = 0.952$, $\delta = 0.29$, and $\rho = -13.1$. A similar correlation in the bicyclononyl series gives $r = 0.997$, $\delta = 0.495$, and $\rho = -13.7$. While the correlation is not quite as good with this set of assumptions as with the earlier set (r value 0.952 vs. 0.995 for the assumption of a common δ across the series of adamantyl analogues), it is probably more nearly correct. We would therefore conclude, within this framework of assumptions, that the resonance stabilization for the perpendicular heteroatomic substituents of this study is 0.29 as large as that in the parallel geometry.

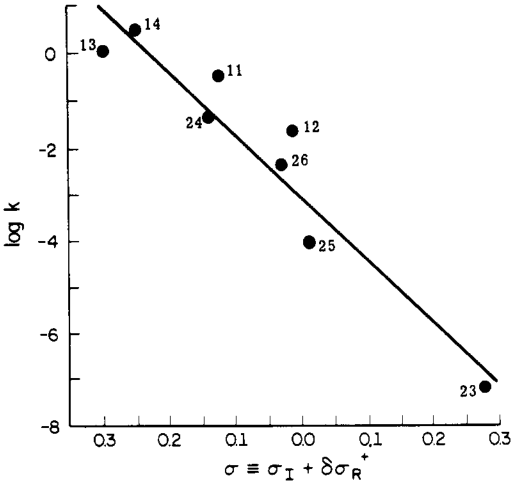


Figure 3. Hammett plot for the solvolyses of **23–26**, **13**, and **14**, plus points for **11** and **12**, which have been corrected for strain (see text), in 80% ethanol–water at 25° using δ = 1 for the CH_2 and CMe_2 substituents and δ = 0.29 (the value which maximizes r) for all other substituents ($\rho = -13.1$, $r = 0.952$).

The expected difference in rates of ionizations leading to perpendicular and parallel α-substituted carbocations can be calculated from the equation

$$\log\left(\frac{k_{\parallel}}{k_{\perp}}\right) = \log\left[k_{(\delta=1.0)}/k_{(\delta=0.29)}\right] = \rho(0.71\sigma_R^+)$$

Using the value of $\rho = -13.1$ and the substituent constants of Table III, we can calculate a rate difference of 10^{16} for the two extreme geometries of an α-dimethylaminocarbinyl cation. This is consistent with the observation that most α-aminoalkyl halides are ionic.[65] Only six covalent α-aminoalkyl chlorides[16-18,21] and one α-aminoalkyl tosylate[18] have to our knowledge been reported, and these, like **24**, owe their existence as covalent species to the steric inhibition of resonance interactions in rigid ring systems.

The rate difference calculated for the α-methoxycarbinyl cation is ca. 10^{10}, corresponding to an activation energy difference of approximately 14 kcal/mol at 25°. This value is comparable to the rotational barrier (18.4 kcal/mol) observed by Lustgarten, Brookhart, and Winstein[8] for the methoxy substituent in **1**.

The 10^{10} rate difference calculated can also be compared to estimated differences in rates of solvolysis for suitable α-alkoxycarbinyl cation precursors. The ratio $(k_O/k_{CH_2})_\perp$ is approximated by $k_{26}/k_{13} = 1/300$ or $k_{23}/k_{25} = 1/1300$, a value of about 10^{-3}. The ratio $(k_O/k_{CH_2})_\parallel$ is less easily estimated but can be approached by comparing an extrapolated rate constant for the solvolysis of 2-methoxy-2-chloropropane with that for *tert*-butyl chloride.[35] The rate constant for the ethanolysis at 0° of chloromethyl methyl ether is 1.4×10^{-2} s and that for 1-methoxy-1-chloroethane is estimated to be more than 10^2 faster.[66] The further increase in rate for the further substitution of methyl for the final α-hydrogen to give 2-methyl-2-chloropropane can be estimated by comparing the basicities of benzaldehyde (pK_a −7.5) and acetophenone (pK_a −6.4).[67] The factor of 10 increase in rate expected for the introduction of the second methyl group allows us to estimate the rate constant for the ethanolysis of 2-methoxy-2-chloropropane at 0° to be somewhat greater than 10 s^{-1}. Under these conditions, *tert*-butyl chloride solvolyzes with $k = 10^{-9}$ s^{-1}.[35] The ratio $(k_O/k_{CH_2})_\parallel$ is therefore estimated to be somewhat greater than 10^{10}. One can then estimate that the value of the ratio

$$\frac{(k_O/k_{CH_2})_\parallel}{(k_O/k_{CH_2})_\perp} \geq 10^{13}$$

This corresponds to an energy difference of >17 kcal/mol between transition states leading to parallel and perpendicular α-alkoxycarbinyl cations in reasonable agreement with the 14 kcal/mol calculated assuming $\delta = 0.29$.

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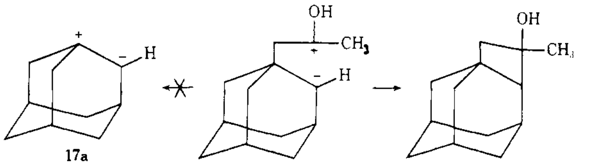

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Anionic Rearrangement of 7-Norbornadienol: a 1,3-Sigmatropic Shift

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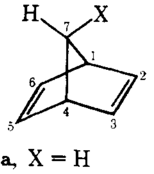
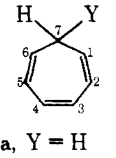
Abstract: The major factors influencing rearrangement of 7-acetoxynorbornadiene to tropyl derivatives have been elucidated. 7-Acetoxynorbornadiene undergoes saponification to 7-norbornadienol which, in turn, via base catalysis, rearranges rapidly to the tropyl skeleton. Lack of deuterium incorporation in the product when the rearrangement was run in CH_3OD seemed to eliminate a "free" carbanion as a mechanistic possibility. Rearrangement of 7-deuterio-7-norbornadienol exclusively to 7-deuteriotropyl oxide clearly demonstrated that the bridge carbon, C-7, migrated intact with its deuterium and oxygen to the final tropyl skeleton. The rearrangement has been rationalized in terms of a 1,3-sigmatropic shift with inversion to a norcaradiene intermediate which in turn undergoes a symmetry-allowed disrotatory ring opening to product. The formation of tropyl products has been rationalized in terms of the proposed mechanism. The relationship of a very low enthalpy of activation (for rearrangement) and a rate acceleration due to oxide formation of 7-norbornadienol is discussed in terms of rearrangement via a 1,3-sigmatropic shift.

The isomerization of norbornadiene (**1a,** X = H) to cycloheptatriene (**2a**) takes place under relatively severe thermal conditions (452°);[2] however, 7-alkoxy (**1b,** X = OR) and 7-phenyl (**1c,** $X = C_6H_5$) substituted norbornadienes undergo a more facile (170 °) thermal rearrangement to the corresponding tropyl derivatives.[3] A similar reaction involving conversion of a norbornadiene system into a cycloheptatriene, occurring under milder conditions, was observed in the reduction of 7-acetoxynorbornadiene (**1d,** $X = OCOCH_3$) with lithium aluminum hydride in tetrahydrofuran.[4] The product obtained in this case using lithium aluminum deuteride was 1-deuteriocycloheptatriene (**2a,** Y = D).



1a, X = H
b, X = OR
c, $X = C_6H_5$
d, $X = OCOCH_3$
e, X = OH

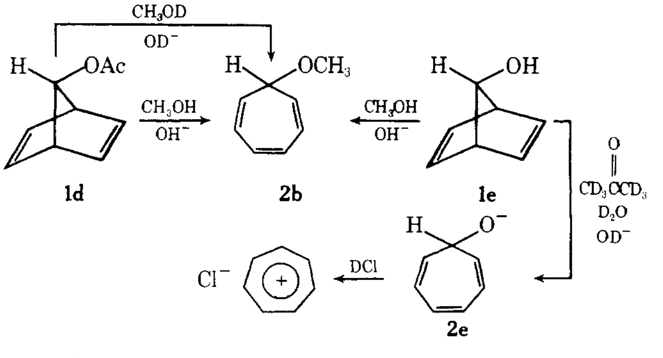


2a, Y = H
b, $Y = OCH_3$
c, $Y = C_6H_5$
d, $Y = OCOCH_3$
e, Y = OH
f, $Y = OC_6H_5$

Story[5] reported that attempted preparations of 7-norbornadienol (**1e**) by either acid- or base-catalyzed hydrolysis of the corresponding ester (**1d**) were unsuccessful, leading to complicated product mixtures. 7-Norbornadienol is known to be slowly converted to tropylium ion under strongly acidic conditions (fluorosulfonic acid, $k = 6.2 \times 10^{-4}\ s^{-1}$ at 47°) presumably via the intermediacy of the 7-norbornadienyl cation,[6] but failure to isolate (**1e**) under basic conditions does not support these conclusions.

In an earlier investigation of this rearrangement,[7] it was found that upon repeating Story's[5] work on the base-catalyzed reaction of 7-acetoxynorbornadiene (**1d**) in methanol, methyl tropyl ether[8] (**2b**) was isolated. Indeed, as shown in Scheme I, methyl tropyl ether (**2b**) is also formed by reaction of 7-norbornadienol (**1e**) with *catalytic* quantities of base in the presence of methanol. The course of these rearrangements is readily followed by NMR spectroscopy since

Scheme I



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