

complete reaction, the mixture was oxidized. NaOH solution (3 M, 6 ml, large excess) was injected into the flask followed by H_2O_2 (30% solution, 6 ml, excess), which was added dropwise over 15–25 min. (More rigorous conditions, 1 h at 50 °C, were utilized for the more hindered derivatives, such as *B*-thexyl-9-BBN.)

The mixture was stirred for an additional 1.0–1.5 h, then the water layer was saturated with K_2CO_3 (anhyd) and the THF layer was separated and dried (MgSO_4 , anhyd). The water layer was extracted with two 15-ml portions of diethyl ether, which were dried (MgSO_4 , anhyd) and combined with the first extract. GLC analysis was carried out on a Varian 1200 Aerograph ($\frac{1}{8}$ in. \times 12 ft 10% SE-30 on 100–120 mesh Varaport 30) and/or Hewlett-Packard 5750 ($\frac{1}{4}$ in. \times 6 ft 10% SE-30 on Chromosorb W). The alcohol/internal standard ratios were determined.

References and Notes

- (1) (a) Graduate research assistant on Grant GM 10937 of the National Institutes of Health; (b) Graduate research assistant on Grant GP-6942X of the National Science Foundation.
- (2) E. F. Knights and H. C. Brown, *J. Am. Chem. Soc.*, **90**, 5250 (1968).
- (3) H. C. Brown, E. F. Knights, and C. G. Scouten, *J. Am. Chem. Soc.*, **96**, 7765 (1974).

- (4) Blank runs were performed using known olefin/octane ratios to ensure the reliability of the procedure.
- (5) C. K. Ingold and F. R. Shaw, *J. Chem. Soc.*, 2818 (1927).
- (6) Table I shows six relative rate values were obtained by both procedures. The actual experiment numbers were identical to within $\pm 2\%$.
- (7) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 3222 (1960).
- (8) H. C. Brown and A. W. Moerikofer, *J. Am. Chem. Soc.*, **83**, 3417 (1961).
- (9) R. B. Turner and W. R. Meador, *J. Am. Chem. Soc.*, **79**, 4133 (1957).
- (10) The values reported for the rate constants for the reaction of disiamylborane with cycloheptene and cyclooctene, Table III of H. C. Brown and A. W. Moerikofer, *J. Am. Chem. Soc.*, **85**, 2063 (1963), should be corrected as follows:

	Rel reactivity	k_2 , 10^{-4} l. $\text{mol}^{-1} \text{s}^{-1}$
Cycloheptene	7	72
Cyclooctene	26	266

In this same table *cis*- and *trans*-2,4-dimethyl-2-pentene should read *cis*- and *trans*-2,5-dimethyl-3-hexene.

- (11) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **95**, 2397 (1973).
- (12) 9-BBN is available from the Aldrich Chemical Co., Milwaukee, Wisc.
- (13) R. C. Woodward and P. S. Skell, *J. Am. Chem. Soc.*, **81**, 2542 (1959).
- (14) The ketone was converted to the tertiary alcohol using the procedure of J. D. Buhler, *J. Org. Chem.*, **38**, 904 (1973). The tertiary alcohol was then dehydrated to the desired olefin by using a catalytic amount of iodine and distilled through a 20-cm Widmer column.

Solvolysis of 1-Substituted-2-adamantyl Sulfonates. Bridging or No Bridging?

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Abstract: The solvolysis rates (50% ethanol) of 2-adamantyl tresylate (**1a**-OTres, Tres = $\text{CF}_3\text{CH}_2\text{SO}_2^-$) and deactivated substrates 1-carbomethoxy (**1g**-OTres) and 1-cyano-2-adamantyl tresylate (**1h**-OTres) are correlated with σ^* constants by a straight line of slope $\rho^* = -4.09$ ($r = 0.9986$) at 25 °C. A small amount (6%) of rearranged product is obtained from **1g**, while **1h** gives 38% rearranged product (for which the 8-cyano-4-*exo*-protoadamantanol structure is established). The extent of rearrangement for **1h** is one-third larger than that for 1-methyl-2-adamantyl substrate (**1b**), which solvolyzes 14–40 times faster than **1a**. It has been concluded previously that ionization of **1b** is anchimerically assisted. On this basis, a rate-product correlation requires that ionization of **1h** be even more so. However, considering all effects upon rate, anchimeric assistance in **1b** must be at best marginal, the possible extent of stabilization by bridging being less than 1 kcal/mol. An equally satisfactory model can be based on the assumption that σ bridging is absent in the solvolysis of these substrates, but ionization is limiting (k_c) and rearrangement takes place subsequently. Other findings which can be used as arguments for a σ -bridged intermediate in the solvolysis of **1b** are examined critically. It is concluded that the existing data do not permit a definite decision to be made for one of the two models (marginal acceleration by σ bridging or no σ bridging).

The 2-adamantyl system (**1a**) is exceptional among *sec*-alkyl substrates, since it solvolyzes by a limiting² (k_c) mechanism, with little or no solvent (k_s) or anchimeric (k_A) participation.^{3,4} A 1-methyl group (as in **1b**) increases the rate of solvolysis by a factor of 14–38 over **1a** and leads to significant amounts (28%) of the rearranged product 4-methyl-4-*exo*-protoadamantanol (**2a**-OH) and some olefin.⁵ The same reaction products (with minor variations in distribution) are formed from the protoadamantyl precursors, **2a**-ODNB and **2b**-OTs.⁵ The rate enhancement and extent of rearrangement are even more important for the higher 1-alkyl derivatives (**1c**–**f**-OTs).^{5b} This fact, together with other mechanistic criteria (vide infra), led to the conclusion that solvolyses of **1b**–**f** involve the σ -bridged ions **3a** as intermediates.⁵ We undertook to test this conclusion and to evaluate quantitatively the acceleration by bridging in **1b** by an established procedure,⁶ namely by studying the solvolysis rates of 2-adamantyl sulfonates with representative deactivating groups in the 1 position (**1g**, **h**), thereby establishing the magnitude of acceleration in **1a** through the deviation from a Hammett–Taft plot.⁶

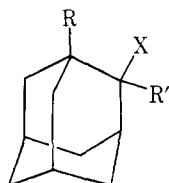
The required alcohols,⁷ 1-carbomethoxy- (**1g**-OH) and 1-cyano-2-adamantanol (**1h**-OH) were obtained from protoadamantanone⁸ (**2c**) via the epoxide **2d**, which in acidic medium gave the diol **li**. Chromic acid oxidation of **li** gave 1-carboxy-2-adamantanone (**1**, R = COOH; R', X = O),⁹ from which **1g** and **1h** were obtained by standard procedures (see Experimental Section). The tresylates of **1a**, **b**, **g**, **h** (X = $\text{CF}_3\text{CH}_2\text{SO}_2\text{O}$, OTres) were prepared^{8b,10} and solvolyzed. The rates are given in Table I.¹¹ The rates for **1a**-OTres, **1g**-OTres, and **1h**-OTres were plotted¹³ against the σ^* values,¹⁴ giving a straight line (line A in Figure 1) with the slope $\rho^* = -4.09$ (correlation coefficient $r = 0.9986$) at 25 °C. As foreseen, the rate for the 1-methyl-2-adamantyl tresylate (**1b**-OTres) exhibits an upward deviation.

The solvolysis products (in 60% acetone⁵) were analyzed by GLC–mass spectrometry. Besides the expected alcohol (**1g**-OH and **1h**-OH, respectively) an isomeric alcohol was found in a small amount (6%) for **1g**, but in an important amount (38%) for **1h**. The mass spectra of these indicated the protoadamantanol structure **2e** and **2f**, respectively. Also, the

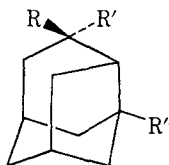
Table I. Solvolysis of 2-Adamantyl Sulfonates in 50% Ethanol^{a,b}

Sulfonate ester	$k_1, s^{-1} (t^0)$	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu
1a -OTres ^c	8.56×10^{-5} (25), ^{d,e} 8.80×10^{-5} (25.20), 1.83×10^{-3} (48.90), 3.48×10^{-1} (100) ^d	23.8	2.8
1b -OTres	1.02×10^{-4} (0.10), 3.38×10^{-3} (24.95), 3.40×10^{-3} (25), ^d 8.04 (100) ^d	22.2	4.7
1g -OTs	2.03×10^{-9} (25), ^d 2.53×10^{-6} (75.61), 3.96×10^{-5} (100), ^d 4.01×10^{-5} (100.11)	28.5	-2.9
1g -OTres	2.92×10^{-7} (25), ^d 2.18×10^{-4} (75.57), 2.82×10^{-3} (100), ^d 2.96×10^{-3} (100.49)	26.4	0.1
1h -OTres ^f	6.55×10^{-10} (25), ^d 1.40×10^{-5} (99.60), 1.46×10^{-5} (100), ^d 1.3×10^{-4} (121.60) ^g	28.9	-3.8

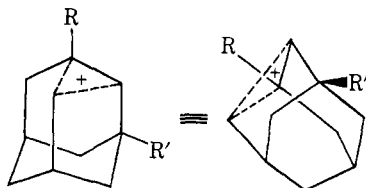
^a Determined conductometrically. ^b Duplicate runs. ^c For comparison, the values for **1a**-OTs are:^{3c} 7.70×10^{-7} (25), 4.30×10^{-3} (100), $\Delta H^\ddagger = 24.8$, $\Delta S^\ddagger = -3.4$. ^d Calculated from values at other temperatures. ^e Literature: 8.17×10^{-5} (25), V. J. Shiner, Jr. and R. D. Fisher, *J. Am. Chem. Soc.*, **93**, 2553 (1971). ^f Buffered with 0.005 M 2,6-lutidine. ^g Three runs; the highest deviation of a run from the average was 15%.



- 1a**, R = R' = H; X = OH (OTs) (OTres) (Br)
b, R = Me; R' = H
c, R = Et; R' = H
d, R = *i*-Pr; R' = H
e, R = cyclopropyl; R' = H
f, R = *t*-Bu; R' = H
g, R = COOMe; R' = H
h, R = CN; R' = H
i, R = CH₂OH; R' = H; X = OH
j, R = R' = Me
k, R = H; R' = Me



- 2a**, R = Me; R' = OH (ODNB); R'' = H
b, R = OH (OTs); R' = Me; R'' = H
c, R, R' = O; R'' = H
d, R, R' = CH₂; R'' = H
e, R = H; R' = OH; R'' = COOMe
f, R = H; R' = OH; R'' = CN
g, R = R'' = H; R' = OH (ODNB)
h, R = OH (OTs); R' = R'' = H



- 3a**, R = alkyl; R' = H
b, R = H; R' = CN

rearranged product from **1h** could be unambiguously identified as 8-cyano-4-*exo*-protoadamantanol (**2f**) by NMR with Eu-shift reagent.¹⁵ No other rearranged product from **1h** was evidenced by GLC on silicon SE-30 or Carbowax 20M columns. Thus, an interesting feature is the observation that the solvolysis of strongly deactivated **1h** is accompanied by the formation of a large amount of rearranged product, even larger than in the 1-methyl-2-adamantyl derivative **1b**.

Two extreme viewpoints can be taken in an attempt to rationalize the present and earlier^{5,8b} results. The first approach considers the σ -bridged ions **3** as playing a determining role in the solvolysis of **1b-f**; the second considers nonbridged ions,

as proposed for the parent compound, **1a**.³ The present discussion will adopt successively the two views; a case will be built on each premise and the conclusions arrived at will be analyzed for consistency with the facts known about the chemistry of **1**.

1. The rate enhancement and formation of rearranged product are the result of the formation of bridged ion **3a** on ionization of **1b**. A basic tenet of the bridged-ion concept is that in a given system there is a direct relationship between the rate increase and the amount of rearranged product formed in solvolysis.⁶ Accordingly, for 2-adamantyl systems, the acceleration by σ bridging, shown^{3,5c} to be virtually negligible in **1a** (0.4% rearranged product), is small in **1g** (6% rearranged product) but important in **1b** (28% rearranged alcohol, 2% olefin), and even more important in **1h** (38% rearranged alcohol). In the case of **1b** the driving force for σ participation is attributed to the difference in the electron-donating ability of Me (R in **3a**) and H (R' in **3a**), whereas the bridging in **3b** is attributed to the corresponding difference between H (R in **3b**) and CN (R' in **3b**), with H now being the better stabilizer for the positive charge than CN. Based on the amount of rearranged product, it can be concluded that ionization of the cyano compound benefits significantly from σ bridging, possibly more than the ionization of the methyl compound **1b**. Therefore, the measured solvolysis rate for **1h** is not determined by the inductive effect of the cyano group alone, but is faster due to the postulated anchimeric assistance. Then, if a $\rho^*\sigma^*$ plot representing the "purely inductive" effect of 1 substituents could be drawn, the point for **1h**-OTres should deviate upward, perhaps more than the point for **1b**-OTres. Of course, that line should pass through the point for **1a** (R = H, virtually no bridging). An illustration is offered by line B in Figure 1.¹⁶ It can be seen that the upward deviation of the point for **1b** (R = Me) from line B is smaller than from line A, which was not very large to begin with. In energy terms, the upward deviation of the point for **1b** from line B (i.e., the stabilization provided by bridging) is rather small.¹⁷ At the same time, for a line like B the point for 1-carbomethoxy derivative **1g** deviates upward by about as much as the point for **1b** (0.9 log units), while the bridging assistance for **1g** should be minor (ca. 6% rearrangement). One way to solve this contradiction is by admitting an accelerating steric effect¹⁸ as responsible for most of the deviation found for **1g**. This is easily rationalized as a repulsive interaction between the β substituent and the leaving group, which is relieved on ionization. However, if in **1** a β substituent does have an accelerating steric effect upon the solvolysis rate, such an effect (conceivably smaller than that of the carbomethoxy group) should be exhibited by the methyl group of **1b** as well. It was already established that β -methyl substituents produce large rate enhancements in rigid polycyclic systems.¹⁹ As a model for our case, steric destabilizing interaction was found for 1,2-dimethyladamantane by force-field calculations.²⁰

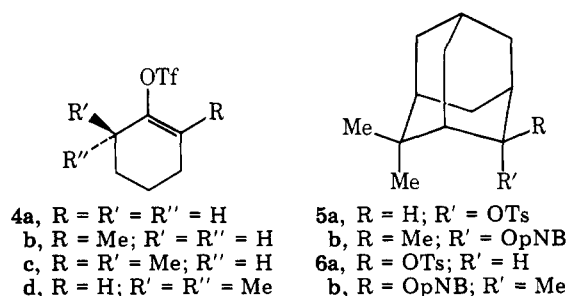
A consequence of existence of such a steric effect in **1b** is that the maximum possible stabilization by bridging in this system cannot represent more than a fraction of a kilocalorie. Thus, even by accepting the bridged ion as an intermediate in the solvolysis of **1b** sulfonates, we must conclude that the energy gain (stabilization) offered by bridging is barely significant. It is then unlikely that such a minor contribution could have such a profound effect upon the solvolysis of **1b**, determining, in fact, all of its chemistry.^{5,8b} This point will be discussed below.

II. The second line of reasoning rests on the assumption that ions **3** are *not* intermediates in the ionization of **1b-f** and **1h**, but solvolysis is in all cases a limiting² (k_c) process, as proposed for the parent compound **1a**,³ with the rearrangement taking place after ionization. To hold this view, it is necessary to provide alternative explanations for the experimental observations which were previously attributed to σ participation.⁵

The first such finding was the rate enhancement by a β -methyl group ($k_{1b}/k_{1a} = 14-38$), which appears large when compared with "normal" inductive and steric effects for such a group.⁵ However, in none of the "normal" systems is the β -methyl group *conformationally locked*, as it is in **1b**. Such examples are known,¹⁹ and one more case may be described here. Thus, the cyclohexenyl triflates **4a-d** exhibit relative solvolysis rates of 1:10:155:950.²¹ An enhanced inductive effect was proposed for such systems.²¹ In addition, a rate enhancement arising from relief of steric strain in the starting material could also be a factor. Clearly, such a steric interaction between the methyl group and the leaving group X could be of considerable importance in **1b**.²⁰

A second consideration is the diminished effect on an α -methyl group upon the solvolysis rate in this system.^{5c} The ratio $k_{\alpha\text{-Me}}/k_H$ (i.e., k_{1j}/k_{1b}) is 10^6 instead of the expected^{3b} $10^{7.5}$. A logical analysis²² shows that such a variation does not establish the presence of σ participation. A structural factor which does not affect the rate of secondary substrates, but lowers the rate of the tertiary ones will produce the same effect, i.e., a decrease in the $k_{\alpha\text{-Me}}/k_H$ ratio. Thus, since ionization of **1j** brings the two methyl groups in an eclipsed conformation, the extra strain energy may be quite sufficient to account for the lower value of $k_{\alpha\text{-Me}}/k_H$ in this system.²³

In agreement with this view, variations of the $k_{\alpha\text{-Me}}/k_H$ ratio which cannot be ascribed to variations in solvent assistance and/or σ bridging are found in other systems as well. Thus, the $k_{\alpha\text{-Me}}/k_H$ ratio for **5** (i.e., k_{5b}/k_{5a}) is lower by a factor of 13



(at 25 °C) than k_{1k}/k_{1a} , while the ratio k_{6b}/k_{6a} is 275 times higher than k_{1k}/k_{1a} (at 75 °C).²⁴ In the 2-*exo*-norbornyl series, a 7,7-dimethyl substitution decreases $k_{\alpha\text{-Me}}/k_H$ by $10^{2.6}$, while a 6,6-dimethyl substitution increases $k_{\alpha\text{-Me}}/k_H$ by $10^{3.7}$ over the parent system.^{24,25} It is also noteworthy that $k_{\alpha\text{-Me}}/k_H$ for the *endo*-protoadamantyl series (k_{2b}/k_{2h}) is slightly higher than the limiting value, although some σ participation in the solvolysis of the secondary substrate (**2h**) was deduced from other type of arguments.^{5c,8b} This strengthens our view that the variations of the $k_{\alpha\text{-Me}}/k_H$ in these systems originate in steric interactions. Therefore, the $k_{\alpha\text{-Me}}/k_H$ ratio is not a reliable criterion for σ bridging in complex systems.²⁶

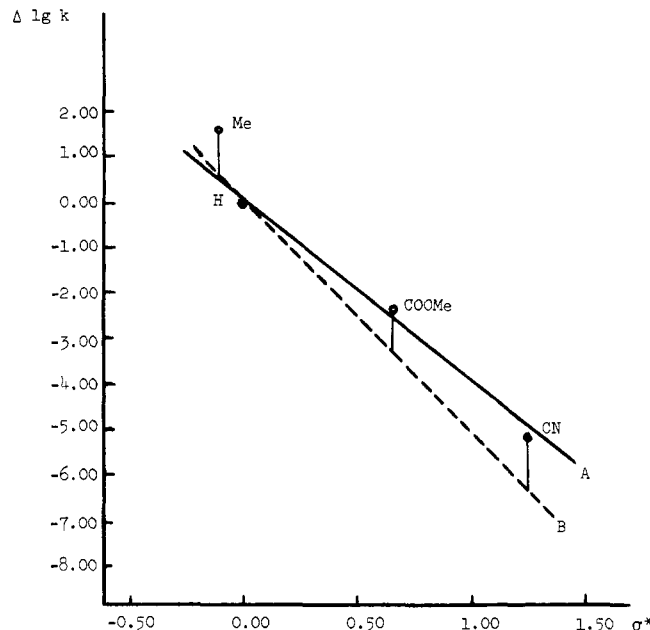
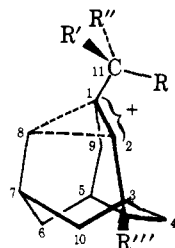


Figure 1. $\rho^*\sigma^*$ correlation of solvolysis rates of 1-substituted-2-adamantyl triflates: A, experimental values (cyano compound solvolyzes without σ participation); B, position of the line if the cyano compound solvolyzes with σ participation.

Another possible argument for bridging in 4-*exo*-protoadamantyl substrates is the decrease^{5c} in $k_{\text{exo}}/k_{\text{endo}}$ ratio in going from secondary (k_{2g}/k_{2h}) to tertiary 4-protoadamantyl derivatives (k_{2a}/k_{2b}). Again, logical analysis shows this is not an independent argument, but follows directly from the variations in $k_{\alpha\text{-Me}}/k_H$ for the two epimers (decreased for *exo*, increased for *endo*) discussed above.

The next argument to be considered is the effect of a second β -methyl group (as in 1,3-dimethyl-2-adamantyl) upon the solvolysis rate. In principle,^{5d} in the absence of σ participation the effect of two methyl groups should be multiplicative ($\text{Eff}_{2\text{Me}} = [\text{Eff}_{\text{Me}}]^2$), while in the presence of participation it should be additive ($\text{Eff}_{2\text{Me}} = 2\text{Eff}_{\text{Me}} - 1$). The experimental result is nearer to the additive model (slightly higher).^{5d} However, in practice, for multiple substitution a diminution of the substituent effect per substituent added is observed.²⁷ This diminution brings experimental results theoretically expected to follow the multiplicative model nearer to the additive model. For example, in the series $(\text{Me}_2\text{CH})_3\text{CX}$, $(\text{Me}_2\text{CH})_2\text{-CXCM}_3$, $\text{Me}_2\text{CHCX}(\text{CMe}_3)_2$, $(\text{Me}_3\text{C})_3\text{CX}$ (X = OpNB), the relative rates are 1, 8.54, 8.26, 33.5,²⁸ respectively, nearer to the additive model (1, 8.54, 16, 25) than to the multiplicative model (1, 8.54, 73, 620). There are also other examples.^{27,29}

Finally, the product composition can be rationalized in terms other than the intermediacy of **3a**. Thus, exclusive formation of the *exo* alcohol **2a-OH**, with no detectable amount of the epimer **2b-OH**,⁵ is compatible with the 4-methyl-4-protoadamantyl cation in the "classical" formulation, the *endo* side of which is more sterically hindered than the *exo* side. Also, formation of the same product mixture from **1b-OTs**, **2a-ODNB**, and **2b-ODNB** can be rationalized by a rapidly equilibrating pair of isomeric ions.³⁰ On the other hand, bridging should increase the distance C1-C8 and decrease the distance C2-C8, thus tilting the C1-C11 bond toward C4 (as in **7**). This should hinder the attack at C1 moderately in **7a-c**, but more severely in **7d**. Therefore, a drop in the amount of protoadamantanol produced should be observed from **1f**, which is not the case. Moreover, for the 1,3-dimethyl-2-adamantyl system, the bridged ion **7e** should give about the same amount of rearranged product as the 1-methyl derivative **7a**, while the



- 7a, R = R' = R'' = H; R''' = H
 b, R = R' = H; R'' = Me, R''' = H
 c, R = H, R' = R'' = Me; R''' = H
 d, R = R' = R'' = Me; R''' = H
 e, R = R' = R'' = H; R''' = Me

nonbridged, equilibrating ions should give about twice as much, as, indeed, it was found.^{8b}

Conclusions

From this analysis, all the kinetic and product data can be rationalized without assuming the intervention of σ -bridged ("nonclassical") ions as intermediates in the solvolysis of 1-substituted-2-adamantyl substrates. None of the data require σ bridging, although they are generally compatible with it. The rate enhancements and the formation of rearranged products observed from such substrates are then not physically related, so that the rearrangement can take place following ionization. On the other hand, the data can be rationalized by accepting a minimal σ participation in the solvolysis of **1b** (cf. **3a**). In this case, the 2-adamantyl substrates with strongly electron-withdrawing substituents in the 1 position should exhibit a somewhat stronger bridging (cf. **3b**). Such a minor assistance cannot influence the chemistry of **1b** as deeply as it appeared to do at first, but alternative explanations can be found. In order to make a definite choice between the two possibilities, other evidences should be found.^{31,32}

In this paper, the arguments for σ -bridged structures in this system and related systems have been considered. It has been pointed out that some of these arguments are circular in nature and should not be considered as unambiguous proofs for the existence of σ -bridged structures.

Experimental Section³³

General. Melting points (Mettler FPI apparatus) are uncorrected. Elemental analyses were performed by Hoffmann-La Roche, Inc. The NMR spectra were taken at 60 MHz (Varian A-60 instrument). Mass spectra (AEI-MS9 instrument) and GLC-mass spectra (E.I. DuPont 21-490 instrument) were done at 70 eV.

4-Epoxyethyleneprotoadamantane (2d). 4-Protoadamantanone^{8a} (1.0 g) was treated with dimethylsulfoxonium methylide (from 1.78 g of trimethylsulfoxonium iodide and 0.5 g of 41% sodium hydride) in Me₂SO (15 ml) as described³⁴ for 3 h at 25 °C and 8 h at 50–55 °C. After workup,³⁴ 0.924 g (84% yield) of an oil was obtained: ir 3008 cm⁻¹; NMR (CCl₄) 2.42 (s, 2 H, OCH₂), 2.68–0.67 (complex, 14 H) ppm.

1-Hydroxymethyl-2-adamantanol (1i). The crude epoxide (**2d**) in acetone (15 ml) and 0.086 M aqueous sulfuric acid (15 ml) was boiled under reflux for 75 min. After neutralization (Na₂CO₃), evaporation of acetone, and saturation with NaCl, the solution was extracted with pentane, then with benzene. The benzene extract gave 0.481 g of **1i**. The residue from the pentane extract was chromatographed on silica gel (15 g), eluting some impurities with benzene, then the product was eluted with benzene-methanol (95:5): combined yield 0.621 g (60%) **1i**, mp 170–173 °C (after sublimation at 130 °C (0.3 mm));³⁵ NMR (CDCl₃) 3.83 (br s, 1 H, CHO), 3.38 (s, 2 H, CH₂O), 3.35 (br, 2 H, OH), 2.38–0.98 (complex, 13 H) ppm.

1-Carboxyadamantan-2-one. To an acetone solution (10 ml) of **1i** (0.33 g), Jones reagent³⁴ (5 ml) was added during 40 min at 10–15 °C. After 4 h of stirring at 15–25 °C, methanol (1 ml), then water (10 ml) was added, and the acetone was distilled off. A standard workup³⁴ gave 0.215 g (60% yield) of material identical with an authentic sample.⁹

Methyl 2-Adamantanol-1-carboxylate (1g-OH). A solution of 1-carbomethoxy-2-adamantanone (1.0 g) in methanol (14 ml) cooled at 0 °C, was treated with NaBH₄ (0.19 g) for 4 h at 0°, then acidified with diluted HCl to pH 5–6, saturated with NaCl, extracted with ether, and dried (Na₂SO₄). The residue from the ether solution was chromatographed on silica gel (110 g). Elution with benzene-ether (9:1) gave, after some impurities, pure **1g-OH** (0.63 g, 62% yield;³⁵ mp 38.8–40.7 °C (after distillation at 104–108 °C (0.15 mm)); ir (neat) 3470, 1730, 1245, 1081, 1050 cm⁻¹; NMR (CCl₄) 4.03 (br s, 1 H, CHO), 3.67 (s, 3 H, OCH₃), 2.45–1.18 (complex, 13 H) ppm; mass spectrum³⁶ 210 (M⁺) (97), 192 (44), 182 (100), 178 (59), 151 (46), 150 (94), 133 (35), 101 (32), 93 (29), 91 (57), 81 (30), 80 (37), 79 (45), 77 (25), 67 (32), 55 (28), 41 (38).

1-Cyanoadamantan-2-one. 1-Carboxyadamantan-2-one (1.7 g) was treated with SOCl₂ (6 ml) for 8 h at 55 °C and for 1 h at 85 °C. The excess of SOCl₂ was distilled off, and the residue diluted with dry ether was poured onto a saturated solution of ammonia in dry THF. The solvent was evaporated, the residue was treated with ice water, filtered, washed twice with water, and dried under vacuum to give 1.337 g (79% yield) of amide: ir (KBr disk) 3415, 3330, 3280, 3185, 2920, 2850, 1719, 1662, 1613, 1448, 1382, 1055 cm⁻¹. The amide (1.3 g) was refluxed in SOCl₂ (6 ml) for 6 h. The excess SOCl₂ was evaporated and the part of the residue soluble both in CHCl₃ and benzene was chromatographed on silica gel (51 g). Elution with benzene gave (after some impurities) 0.644 g (54.5% yield) of 1-cyano-2-adamantanone: mp 204.4–205.5 °C (from heptane);³⁵ ir 2240, 1730 cm⁻¹; NMR (CDCl₃) 2.73 (br s, 1 H), 2.35 (br s, 4 H), 2.25–1.75 (br, 8 H) ppm.

2-Hydroxyadamantane-1-carbonitrile (1h-OH). The cyano ketone (0.62 g) was treated with NaBH₄ (0.085 g) in dimethylformamide for 1 h at 0 °C and for 22 h at 20 °C. After neutralization (dilute HCl) the solvent was evaporated at 40 °C, water was added, and the product was extracted with a benzene-ether mixture. The residue from the dried (Na₂SO₄) organic solution was recrystallized from heptane, giving 0.566 g (90.5% yield) of **1h-OH**: mp 218–219 °C;³⁵ ir (KBr disk) 3400, 2890, 2840, 2220, 1450, 1100, 1053, 1034 (sh) cm⁻¹; NMR (CDCl₃) 3.98 (br s, 1 H, CHO), 2.50–1.50 (complex, 14 H) ppm; mass spectrum³⁶ 177 (M⁺) (24), 149 (100), 130 (27), 80 (28), 69 (73).

Sulfonate Esters.³⁵ The new tresylates **1b-OTres** (liquid), **1g-OTres** (liquid), **1h-OTres** (mp 178–180 °C), the tosylate **1g-OTs** (mp 96.5–97.5 °C), and the known¹⁰ tresylate **1a-OTres** were synthesized by standard procedures,^{5c,d,8b,10} and recrystallized from pentane at –78 °C.

Solvolysis rates were determined conductometrically, as described.^{5b-d,8b}

Solvolysis Products. (a) **From 1g-OTres.** The main product (94%) was **1g-OH**. The minor product (6%, longer retention time on a 5% Carbowax 1.5 m × 3 mm o.d. column) had the mass spectrum³⁶ 210 (M⁺) (7), 192 (100), 160 (20), 133 (40), 93 (24), 91 (69), 79 (41), 59 (20), 45 (80), 41 (34). (b) **From 1h-OTres.** The main product (**1h-OH**, 62%) and the minor product (38%) were best separated on a OV-1 silicon column, 1.5 m × 3 mm o.d., at 130 °C. The second product, **2f**, had the mass spectrum³⁶ 177 (M⁺) (2), 159 (100), 118 (22), 117 (56), 104 (22), 92 (23), 91 (22), 80 (31), 79 (21), 67 (20), 55 (25), 41 (42).

Isolation of 2f. The tresylate **1h-OTres** (1.0 g) in 60% acetone (30 ml) was heated for 15 h at 125 °C in a sealed ampule. After cooling, water (60 ml) was added and the product was extracted five times with ether (20 ml each). The combined ether solution, after washing with aqueous NaCO₃H and drying (Na₂SO₄) left 0.7 g of a residue, 0.25 g of which was chromatographed on silica gel (130 g), using benzene-ethyl acetate (4:1) as eluent. After 0.14 g of **1h-OH**, 0.09 g of **2f** was eluted: mp 231–232 °C;³⁵ ir (KBr disk) 3390, 2920, 2875, 2230 cm⁻¹; NMR (CDCl₃) 4.27 (1 H, CHO), 3.30–1.10 (complex, 14 H) ppm.

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- (14) The σ^* values were taken from P. R. Wells, "Linear Free-Energy Relationships", Academic Press, London, 1968, p 38.
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- (16) We have no sure way to determine accurately the line B in Figure 1, but the "purely inductive effect" line cannot be much different from the one drawn ($\rho^* = -5.1$, deviation for **1b** ca. 1.0 log unit, deviation for **1h** ca. 1.3 log units). A minor change of position of line B would not alter the conclusions.
- (17) At variance with other substrates (e.g., the β -arylalkyl system) solvolysis of **1b** is not visualized as a competition between two discrete pathways, solvent assisted and anchimerically assisted.⁵ When such a competition exists, a small *measured* acceleration represents an important stabilization by bridging, since this had to overcome an already strong solvent assistance. Thus, in acetic acid, the solvent assists the ionization of a normal secondary substrate by a factor of more than 2000,^{3c} whence a measured acceleration of, say, five over the value expected based on the inductive effects of substituents represents an assistance worth 10^4 in rate. Any correction for steric effects of substituents is small compared to this value, and the stabilization by bridging is important.⁶ On the other hand, for **1b**, the (already small) value of 1.0 log unit represents the *total* acceleration; any steric (or other) effect will cut into this value, leaving a very small energy gain attributable to bridging.
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- (20) Comparison of strain energies calculated for adamantane, 1-methyl-, 2-methyl-, and 1,2-dimethyladamantane (E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 8005 (1973); E. M. Engler, Ph.D. Thesis, Princeton University, 1973) indicates the strain due to the interaction between the two methyl groups of the latter amounts to at least 1 kcal/mol.
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- (23) As an example, ab initio calculations indicate the 2-methyl-2-butyl cation with the two methyl groups eclipsed is 4.42 kcal/mol less stable than its rotamer with the two groups in a skew conformation. For the secondary cation (2-butyl) the difference (H eclipsing Me vs. skew) is only 2.16 kcal/mol (L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94**, 5935 (1972)). The calculations refer to ions in the gas phase. However, it was shown (P. v. R. Schleyer, in "Reaction Transition States", J. E. Dubois, Ed., Gordon and Breach, New York, N.Y., 1972, p 197, 207) that energy differences between carbocations are practically the same in the gas phase, super acid, or solvolytic media.
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- (26) Similarly, for the di-*tert*-butylcarbonyl system a modest acceleration due to σ bridging was proposed, based on the $k_{\alpha\text{-Me}}/k_H$ criterion (S. H. Liggero, J. J. Harper, P. v. R. Schleyer, A. P. Krapcho, and D. E. Dorn, *J. Am. Chem. Soc.*, **92**, 3789 (1970)). In view of the above considerations this conclusion appears doubtful.
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- (31) For instance, the study of optically active substrates.⁶
- (32) After submission of the manuscript, Professor P. v. R. Schleyer (personal communication) informed us that the ¹³C NMR spectrum of 1,3,5,7-tetramethyl-2-adamantyl cation can be rationalized as representing a set of rapidly equilibrating bridged ions. However, the rearrangement of the 1,3,5,7-tetramethyl-2-adamantyl cation into the 1,2,5,7-tetramethyl-2-adamantyl cation in super acid was rationalized as involving "open", nonbridged ions.^{5d}
- (33) The experiments presented here were done in collaboration with Dr. D. Lenoir. As Dr. Lenoir's interpretation of the data differs from that of the present author, the former is presenting his interpretation and results separately: *Chem. Ber.*, in press.
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