Bridgehead Carbocations: Correlation Between MP2/6-31G* Cation Energies of Some Caged Cations and the Solvolysis Rates of Their Precursor Triflates

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Synthesis of the series of caged systems, 4-homocubyl triflate (**7**), 1-homocubyl triflate (**10**), 6-tricyclo-$[3.1.1.0^{3,6}]$heptyl (norcubyl) triflate (**11**), and 6-tricyclo$[3.2.1.0^{3,6}]$octyl triflate (**12**) together with 1-norbornyl triflate (**9**) is described. Examination of their behavior under solvolysis conditions in 80% ethanol shows that in each case ionization occurs to give the corresponding bridgehead cation and that there is an enormous difference in reactivity between the triflates. A linear correlation is observed when the logarithm of the ionization rates of the triflates **7** and **9−12** as well as that of cubyl triflate (**8**) are plotted against the MP2-derived energies of the corresponding bridgehead cations.

Introduction

Recent literature reports[1−7] confirm the ongoing interest in the chemistry of caged carbocations. In a recent study[8] concerned with fluorodeiodination of a number of bridgehead iodides by xenon difluoride in dichloromethane, a reaction which proceeds via the bridgehead cation, it was noted that in several cases the fluorides were contaminated with significant quantities of the corresponding chloride. We considered it appropriate to evaluate[4b,c] the relative energies of the intermediates involved in the fluorination reactions, viz., the 4-homocubyl, 1-homocubyl, 6-tricyclo$[3.1.1.0^{3,6}]$heptyl (6-norcubyl) and 6-tricyclo$[3.2.1.0.^{3,6}]$octyl cations (**1** and **4−6**) particularly those cations (**4−6**) which were less discriminating and therefore thought to be of higher energy. The cation stabilities were determined[4b] at the MP2/6-31G*//RHF/3−21G *ab initio* level employing the isodesmic equation (eq 1) as described by Hrovat and Borden[7] who

$$\mathrm{RH} + t\text{-}\mathrm{Bu}^+ \rightarrow \mathrm{R}^+ + t\text{-}\mathrm{BuH} \qquad (1)$$

had previously determined the energies for the related species **2** and **3** in this way. The complete set of data is collected in Table 1, inspection of which reveals that the relative order of stability of the cations is found to be **1** > **2** > **3** > **4** > **5** > **6**.

Interestingly, although all of the polycyclic carbocations **1**, **2**, and **4−6** contain at least one cyclobutyl cation fragment, it can be seen that their thermodynamic stabilities cover a substantial range. For example, both the nonclassical 4-homocubyl and cubyl cations (**1** and **2**) are of much lower energy than the closely related 1-homocubyl and 6-tricyclo$[3.2.1.0^{3,6}]$octyl classical cations (**4** and **6**).

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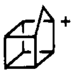

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Some time ago Schleyer and his associates[9] demonstrated that bridgehead reactivity could be placed on a quantitative basis by establishing the existence of an inverse linear correlation between the logarithms of the solvolysis rates of bridgehead compounds and the MM2-calculated strain energies of the bridgehead cations. Over the years the molecular mechanics calculations have undergone considerable refinement, particularly by Müller and his co-workers,[1,10] so that caged systems such as the cubyl and 4-homocubyl cations can be accommodated readily by the use of updated force-field parameters appropriate to the cyclobutyl cation. In accordance with predictions based upon the results of the MM2[1] and *ab initio*[4b,c] calculations, it is not surprising that cubyl triflate (**8**) solvolyzes much more rapidly than originally expected and many orders of magnitude faster than 1-norbornyl triflate (**9**). 4-Homocubyl bromide also displays "enhanced" solvolytic reactivity[11] in agreement with the results of the strain energy calculations[1].

Solvolytic data for the systems **10−12** were unavailable at that time, and these substrates could not therefore be included in the above strain/reactivity comparisons. Interestingly, an ICR study[4d] of the relative energies of a series of bridgehead cations (R_1^+) determined by

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Table 1. Kinetic Data for Solvolysis of the Caged Triflates 7–12[a] and the MP2 Energies of the Corresponding Bridgehead Cations 1–6

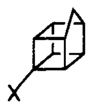
triflate	temp (°C)	$k \times 10^7$ (s^{-1})[a]	rel k	cation MP2 energy[b] (kcal mol^{-1})
4-homocubyl (**7**)	32	645		
4-homocubyl	38	1428		
4-homocubyl	44	3492		
4-homocubyl	50	5703		
4-homocubyl	57	15422		
4-homocubyl	135[c]	2.13×10^7	5.97×10^6	5.2
cubyl (**8**)[d]			2.10×10^6	7.6
1-norbornyl (**9**)	79.7	29.8		
	95.3	164		
	110	688		
	135[c]	6540	1832	14.9
1-homocubyl (**10**)	95.3	10.7		
1-homocubyl	110	50.2		
1-homocubyl	135	636	178	19.2
6-tricyclo[3.1.1.0^{3,6}]-heptyl (**11**)	135	1002	281	20.8
6-tricyclo[3.2.1.0^{3,6}]-octyl (**12**)	135	3.57	1	22.7

[a] Errors are 1% at the 95% confidence interval via standard single variable regression; rate constants are the average of duplicate measurements. [b] Data from reference 4b. [c] Extrapolated. [d] Data for the cubyl system taken from reference 1.

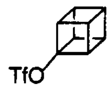
examination of the exchange process below using 2-*exo*-bromonorbornane (RBr) as a reference:

$$R_1Br + R^+ \rightarrow R_1^+ + RBr$$

was found to give a lower value for the heterolytic bond dissociation energy, $D°(R^+{-}Br)$, for 6-bromonorcubane than for bromocubane. This feature was supported by an MM2 strain-energy assessment of the solvolytic behavior of 6-bromonorcubane suggesting it to be *ca.* 10 times more reactive than bromocubane. On the other hand, it was predicted[4a,b] on the basis of the cation *ab initio* energies that 4-homocubyl triflate (**7**) and cubyl triflate (**8**) should solvolyze considerably faster than the related triflates **10–12**. In order to provide a test of these predictions we have synthesized and examined the solvolytic behavior of 4-homocubyl triflate (**7**), 1-homocubyl triflate (**10**), 6-norcubyl triflate (**11**), and 6-tricyclo[3.2.1.0^{3,6}]octyl triflate (**12**). We now wish to disclose the results of our investigation.



7, X=OTf
17, X=OH
21, X=OEt



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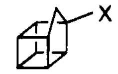
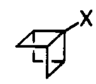
9, X=OTf
13, X=OH
16, X=OEt

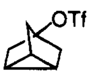


10, X=OTf
14, X=OH
19, X=OEt



11, X=OTf
18, X=OH
22, X=OMe

12, X=OTf
15, X=OH
20, X=OEt



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Results and Discussion

Details of the solvolysis of 1-norbornyl triflate (**9**) have been reported previously,[9a] but we felt it desirable to reexamine **9** under the conditions employed in this work. Similarly, although Rüchardt and his collaborators[11] have measured the rate constant for ionization of 4-bromohomocubane in hexafluoro-2-isopropanol and the data have been normalized by Müller[1] to provide the corresponding information for 80% ethanol, we preferred to determine the kinetics of reaction of 4-homocubyl triflate (**7**) under our conditions in order to allow direct comparison with the other substrates. The triflates **7**, **9**, and **11** were synthesized by treatment of the corresponding iodides with iodosobenzene/trimethylsilyl triflate by employing the procedure described recently by Moriarty and co-workers.[12] Further quantities of **9** as well as the remaining substrates **10** and **12** were obtained from the corresponding alcohols (**13–15**) by standard treatment with triflic anhydride and pyridine.

Identification of the products of solvolysis was undertaken to determine whether the caged triflates ionized to give the corresponding cation or whether ionization was accompanied by rearrangement. We did not examine the solvolysis products derived from 1-norbornyl triflate (**9**) because Schleyer and his associates[9a] have shown these to consist of a mixture of the corresponding alcohol **13** and ether **16** exclusively, thus establishing the intermediacy of the 1-norbornyl cation (**3**) in this case. We were aware of the possibility that, by analogy with cubanol[13] and 4-homocubanol (**17**)[11] which are known to ring-open readily under mildy basic conditions, 6-norcubanol (**18**) would be labile under the solvolytic conditions employed. It was not surprising to discover, therefore, that whereas the product of solvolysis of triflate **10** in 80% ethanol consisted of a mixture of the corresponding alcohol and ethyl ether **14** and **19**, and that of tosylate **12** a mixture of **15** and **19**, respectively, only the ether **21** was identified in the mixture of products arising from 4-homocubyl triflate (**7**); a complex mixture was obtained from 6-norcubyl triflate (**11**) under these conditions. In nonaqueous alcoholic media, however, both triflates **7** and **11** solvolyzed to give excellent yields of the corresponding ethers **21** and **22**, respectively. Thus, the reactions of all triflates under study proceed cleanly to give the corresponding bridgehead cation without rearrangement.

For the kinetic studies, reaction rates were determined in 80% ethanol buffered with triethylamine (1 equiv). Rates were monitored over three half-lives; the extent of reaction was followed conveniently by integration of the ^{19}F signals of the covalent triflate and the ionic triflate produced using the ^{19}F NMR procedure described recently by Creary and Wang.[14] This is an attractive procedure because it requires only very small quantities (*ca.* 5mg) of material for each kinetic run, and it possesses the added advantage that both the rate of disappearance of reactant and the rate of appearance of product can be monitored. Indeed, our experience is that standard single variable regressional analysis of the data so obtained gave excellent linear plots of ln k against T ($0.99 < r^2 < 1.00$) over the range of temperatures employed, consistent with the operation of first order processes in all cases.

The solvolytic rate constants for triflates **7** and **9–12** are averaged values of duplicate runs for which the agreement is ±1.5%; the data are assembled in Table 1. It can be seen that, in agreement with theoretical predictions,[4b] the substrates **10–12** are remarkably sluggish toward ionization; indeed, they represent some of

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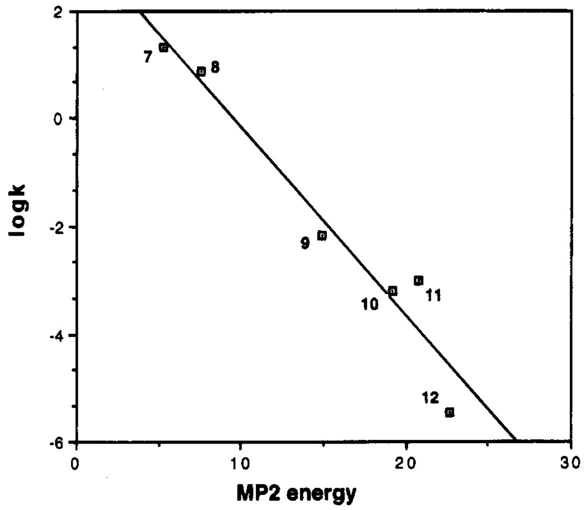

Figure 1. Plot (r^2 = 0.95) of the MP2 energies (kcal mol^{-1}) of the cations **1**–**6** against log *k* of the relative rates of solvolysis of their precursor triflates **7**–**12**.

the most unreactive substrates known.[4a] 4-Homocubyl triflate (**7**), for example, undergoes solvolyses almost 10^5 times faster than its isomer **10**, and *ca.* 10^7 times as fast as 6-tricyclo[3.2.1.0^{3,6}]octyl triflate (**12**). It is noteworthy that the caged system **12** is second only to the related triflate **23**[9a] in terms of its extreme reluctance toward ionization. The difference in reactivity between these substances had rather interesting implications in the way they could be handled. For example, whereas the triflates **10**–**12** could actually be purified by distillation, 4-homocubyl triflate (**7**) was so reactive it largely decomposed during attempts to purify it by column chromatography.

The plot of the logarithm of the relative rates of solvolysis of **7** and **9**–**12** as well as that reported[15] for **8**[5,6] against the respective MP2/6-31G* energies, is reproduced in Figure 1. Attention is drawn to the good correlation (r^2 = 0.95) observed between log *k* and the cation MP2 energies. Interestingly, an improvement in the fit (r^2 = 0.98) can be achieved if the point for 6-norcubyl triflate (**11**) is excluded from the plot; however, this may not be justified considering that the average error associated with the calculated energies is likely to be as high as the energy difference between **10** and **11** on the one hand, and **11** and **12** on the other.

In summary, these observations demonstrate the consistency of the correlation between the solvolytic rates of the series of bridgehead caged triflates **7**–**12** and the *ab initio* energies of their corresponding bridgehead cations.

Experimental Section

For the kinetic studies, rates were determined in 80% ethanol buffered with triethylamine (1 equiv). The extent of reaction was followed by integration of the ^{19}F signals of covalent triflate and the ionic triflate produced, using the ^{19}F NMR procedure described recently by Creary and Wang.[14] 4-Iodohomocubane,[4b] 6-iodonorcubane,[4b] 6-tricyclo[3.2.1.0^{3,6}]octanol,[13] 1-norbornanol,[16] and (hydroxymethyl)cubane[17] were prepared according to the designated literature procedures.

4-Homocubyl Triflate (7). The procedure described by Moriarity and co-workers[12] was employed. A mixture of 4-iodohomocubane (0.75 g, 3 mmol), iodosobenzene (1.98 g, 9 mmol), and trimethylsilyl triflate (2.0 g, 9 mmol) was stirred at room temperature until most of the iodosobenzene had dissolved (*ca.* 1 h). The mixture was washed with water and then dried (Na_2SO_4) and concentrated. Chromatography (silica gel) of the residue and distillation of the pentane fraction afforded 4-homocubyl triflate (**7**) (110 mg, 15%): ^1H NMR ($CDCl_3$) δ 1.8 (s, 2H); 3.2–3.8 (m, 7H); ^{13}C NMR ($CDCl_3$) δ 39.59, 41.41, 41.47, 46.08, 50.63, 53.49, 90.76, 118.12 (q, *J* = 319.2 Hz); HRMS calcd for $C_{10}H_9F_3O_3S$ ($M^+ - CF_3O_2S$) 133.0653, found 133.0716.

1-Norbornyl Triflate (9). Method A. Triflic anhydride (3.1 g, 11 mmol) was added dropwise with stirring to a solution of 1-norbornanol (0.73 g, 6.5 mmol) in dichloromethane (30 mL) containing pyridine (1 g, 12 mmol) at −10 °C and protected from moisture. After addition, stirring was continued for a further 3 h after which the mixture was allowed to warm to room temperature and then added to ice-cold dilute HCl. Standard workup gave the crude product which was purified by flash chromatography (silica gel/pentane). Distillation (Kugelrohr: 95 °C/1 mm) afforded 1-norbornyl triflate (**9**) (1.3 g, 82%): ^1H NMR ($CDCl_3$) δ 1.45–2.35, m; ^{13}C NMR ($CDCl_3$) δ 29.57; 32.39; 33.03; 41.86; 101.56; 118.29 (q, *J* = 319.2 Hz). Anal. Calcd for $C_8H_{11}F_3O_3S$: C, 39.1; H, 4.5. Found: C, 38.8; H, 4.6.

Method B. Treatment of 1-iodonorbornane with iodosobenzene/trimethylsilyl triflate as described above in the synthesis of **7** afforded the title triflate **9** in 64% yield.

1-Homocubyl Triflate (10). A solution of (hydroxymethyl)cubane (1.2 g, 9 mmol) in a mixture of 50% H_2SO_4 (10 mL) and 1,2-dimethoxyethane (15 mL) was heated at 80 °C for 18 h. After the volatile components were removed under vacuum, the residue was extracted with ether, and the extracts were washed successively with water and saturated sodium bicarbonate solution. After being dried ($MgSO_4$) and concentrated the residue was sublimed to give 1-homocubanol (**14**) (1.1 g, 92%): ^1H NMR ($CDCl_3$) δ 1.82 (d, *J* = 7.6 Hz, 2H), 2.6–2.9 (m, 1H), 3.0–3.5 (m, 7H); ^{13}C NMR ($CDCl_3$) δ 40.82, 40.84, 41.31, 44.40, 47.72, 48.20, 89.65. Anal. Calcd for $C_9H_{10}O$: C, 80.4; H, 7.5. Found: C, 80.3; H, 7.6. The alcohol (0.76 g, 5.6 mmol) was treated with triflic anhydride as described for the preparation of **9** to give 1-homocubyl triflate (**10**) (1.32 g, 88%): bp 105 °C/0.2 mm; ^1H NMR ($CDCl_3$) δ 2.55 (s, 2H), 3.40–3.35 (m, 7H); ^{13}C NMR ($CDCl_3$) δ 38.75, 40.11, 41.95, 43.95, 45.71, 46.74, 103.65, 118.02 (q, *J* = 319.2 Hz). Anal. Calcd for $C_{10}H_9F_3O_3S$: C, 45.1; H, 3.4. Found: C, 44.8; H, 3.2

6-Norcubyl Triflate (11). 6-Iodonorcubane (0.35 g, 1.6 mmol) was treated with a mixture of iodosobenzene and trimethylsilyl triflate as described above for the preparation of **7**. Distillation (Kugelrohr: 90 °C/0.2mm) of the product yielded 6-norcubyl triflate (**11**) (0.2 g, 52%): ^1H NMR ($CDCl_3$) δ 2.0–2.3 (m, 3H), 2.8–3.4 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 33.85, 43.82, 97.20, 118.28 (q, *J* = 319.2 Hz). Anal. Calcd for $C_8H_9F_3O_3S$: C, 39.7; H, 3.75. Found: C, 39.5; H, 4.0.

6-Tricyclo[3.2.1.0^{3,6}]octyl Triflate (12). 6-Tricyclo[3.2.1.0^{3,6}]octanol (0.35 g, 2.8 mmol) was treated with triflic anhydride as outlined above. Distillation (Kugelrohr: 45 °C/0.1mm) of the crude product yielded the title triflate **12** (0.52 g, 72%): ^1H NMR ($CDCl_3$) δ 1.42 (d, *J* = 7.2 Hz, 1H), 1.80 (d, 7.2 Hz, 2H), 2.00–2.75 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 34.73, 35.75, 37.90, 38.38, 42.24, 105.64, 117.63 (q, *J* = 319.2 Hz). Anal. Calcd for $C_9H_{11}F_3O_3S$: C, 42.2; H, 4.3. Found: C, 42.0; H, 4.4.

Solvolysis of 4-Homocubyl Triflate (7). (i) In aqueous ethanol. The triflate **7** and triethylamine (1.1 equiv) were warmed in 80% ethanol at 45 °C for 24 h, after which the mixture was diluted with water and extracted thoroughly with dichloromethane. GC and ^{13}C NMR analysis of the crude product showed it to consist of a mixture of several components, the major one of which was identified as 4-ethoxyhomocubane (**21**) by spectral and GC comparison with an authentic specimen prepared below.

(ii) In ethanol. A solution of 4-homocubyl triflate (**7**) and triethylamine (1.1 equiv) in ethanol was heated at 50 °C for 24 h. The solution was concentrated under vacuum and the

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(15) Normalized to standard conditions by Müller and his associates (ref 1).

(16) Poindexter, G. S.; Kropp, P. J. *J. Org. Chem.* **1976**, *41*, 1215.

(17) Eaton, P. E.; Yip, Y. C. *J. Am. Chem. Soc.* **1991**, *113*, 7692.

residue extracted with dichloromethane to yield 4-ethoxyhomocubane (**21**) (78% yield): ^{1}H NMR (CD_2Cl_2) δ 1.16 (t, J = 6.5 Hz, 3H), 1.68 (bs, 2H), 2.95–3.48 (m, 7H), 3.36 (q, J = 6.5 Hz, 2H) (lit.[18] ^{1}H NMR); ^{13}C NMR (CD_2Cl_2) δ 14.97, 37.91, 40.50, 42.17, 45.54, 47.69, 49.79, 59.66, 84.30.

Solvolysis of 1-Homocubyl Triflate (10). A solution of the triflate **10** and triethylamine (1.1 equiv) in 80% ethanol was heated at 135 °C for 50 h before being worked up as described above. The product, shown by GC and ^{13}C NMR analysis to consist two components in a 4:3 ratio, was chromatographed (silica gel) affording (i) (pentane eluent) 1-ethoxyhomocubane (**19**): ^{1}H NMR ($CDCl_3$) δ 1.27 (t, J = 7.0 Hz, 3H), 1.80 (d, J = 0.6 Hz, 2H), 3.05–3.35 (m, 7H), 3.69 (q, J = 7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 16.00, 40.50, 41.07, 41.86, 43.84, 44.56, 44.98, 61.51, 94.63. Anal. Calcd for $C_{11}H_{14}O$: C, 81.4; H, 8.7. Found: C, 81.7; H, 8.8; and (ii) (ether eluent) 1-homocubanol (**14**).

Solvolysis of 6-Norcubyl Triflate (11). (i) In aqueous ethanol. The triflate **11** was heated at 135 °C for 24 h in 80% ethanol containing triethylamine (1.1 equiv) and then processed as described above. GC/MS and ^{13}C NMR analysis of the product showed the presence of several unidentified components.

(ii) In methanol. A solution of the triflate **11** and triethylamine (1.1 equiv) in methanol was heated at 135 °C for 3 days before being concentrated and extracted with $CFCl_3$. Removal of the solvent left a residue which was shown (GC/MS, NMR) to be essentially pure 6-methoxynorcubane (**22**) (75% yield): ^{1}H NMR (CD_2Cl_2) δ 2.08 (d, J = 2.5 Hz, 3H), 2.66–2.70 (m, 3H), 2.92–2.98 (m, 3H), 3.30 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 33.67, 40.02, 53.07, 93.98. HRMS calcd for $C_8H_{12}O$: 124.0888, found 124.0886.

Solvolysis of 6-Tricyclo[3.2.1.0^{3,6}]octyl Triflate (12). A solution of the triflate **12** and triethylamine (1.1 equiv) in 80% ethanol was heated at 135 °C for 42 days before being worked up as described above. GC/MS and ^{13}C NMR analysis of the product showed it to consist of a mixture of two components. Chromatography (silica gel) of the product gave (i) (pentane eluent) 6-ethoxytricyclo[3.2.1.0^{3,6}]octane (**20**): ^{1}H NMR ($CDCl_3$) δ 1.27 (t, J = 7.0 Hz, 3H), 1.32–2.58 (m, 11H), 3.53 (q, J = 7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 15.95, 35.62, 36.13, 36.45, 39.37, 40.84, 61.69, 94.94; mass spectrum m/z (relative intensity) 152 (M^+) (9), 123 (68), 110 (53), 95 (55), 82 (100); and (ii) (ether eluent) 6-tricyclo[3.2.1.0^{3,6}]octanol (**15**).

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