was also present, as was another compound giving a very high field resonance (ν 212.6) suggestive of bridgehead fluorine. The dimer and its decarbonylation product were formed in about 70% yield from quinone **17**.

Bromoheptafluorocyclopentenes 21 and 22. To a heavy-walled Pyrex ampoule (10 × 200 mm, 5 mm i.d.) was added 85 μL of dipentene; the bomb was cooled to −196 °C and evacuated. Bromotrifluoroethene (2.67 g, 16.6 mmol) and tetrafluorocyclopropene (1.62 g, 14.5 mmol, prepared by the method of Sargeant and Krespan[41]) were introduced in vacuo and the bomb was sealed. It was heated at 170 °C in a tube oven for 7 h. After cooling, the bomb was opened and all volatiles were vacuum transferred into a side-arm flask with septum. Preparative GC on a 10 ft × 0.25 in. column containing 10% SF-96 on Chromasorb-W HP at 27 °C with a helium flow of 35 mL/min yielded 1.22 g (4.47 mmol, 31%) of C_5F_7Br. Anal. Calcd. for C_5F_7Br: C, 22.01; F, 48.71; Br, 29.28. Found: C, 22.10; F, 48.52; Br, 29.06.

3-Bromoheptafluorocyclopentene (16% of total C_5F_7Br) eluted at 7.95 min; bp 71 °C; IR (vapor) 1800 ($\nu_{C=C}$), 1400, 1293, 1175 cm^{-1}; MS, *m/e* 274 (M^+), 272 (M^+), 193 ($M^+ - Br$), 143 ($C_4F_5^+$), 93 (base, $C_3F_3^+$).

4-Bromoheptafluorocyclopentene (84% of total C_5F_7Br) eluted at 9.55 min; bp 72 °C; IR (vapor) 1767 ($\nu_{C=C}$), 1384, 1255, 1173 cm^{-1}; MS, *m/e* 274 (M^+), 272 (M^+), 193 (base, $M^+ - Br$), 143 ($C_4F_5^+$), 93 ($C_3F_3^+$). The ^{19}F NMR spectra of both isomers are reported in the text.

Hexafluorocyclopentadiene (1). To a 177-mL (6 oz) Fischer-Porter glass bomb equipped with valve were added 20 mL of diglyme (freshly distilled from CaH_2), 0.11 g of zinc chloride, and 4.5 g (69 mmol) of activated[43] zinc dust. The contents were degassed in two freeze–pump–thaw cycles, and then 415 mg (1.52 mmol) of bromoheptafluorocyclopentene (84% 4-bromo and 16% 3-bromo isomer) was vacuum transferred into the bomb. The vessel was sealed, warmed to room temperature, and then immersed in a preheated 135 °C oil bath. After dropping to approximately 120 °C, the temperature was slowly raised to 140 °C and maintained there for 10 min. The bomb was removed from the bath and cooled; the more volatile components (approximately 1 mL) were transferred in vacuo to a distillation bulb. A bulb-to-bulb distillation into a flask containing 1.0 mL of *o*-dichlorobenzene yielded 245 mg (1.41 mmol, 92%) of hexafluorocyclopentadiene. The *o*-dichlorobenzene solution was used for all manipulations and storage (−25 °C) of the diene to minimize dimer formation. Gas chromatography revealed that the compound was 98% pure. GC, IR, and ^{19}F NMR data all matched those of hexafluorocyclopentadiene prepared by pyrolysis of hexafluoro-2,4-cyclohexadienone (**3**).

Acknowledgment. We thank the National Science Foundation and the Air Force Office of Scientific Research for generous financial support of this work.

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[43] Weiss, R.; Kolbl, H. *J. Am. Chem. Soc.* **1975**, *97*, 3224–3225.

Notes

Bridgehead Solvolytic Reactivity. A Unified Data Set To Test Molecular Mechanics

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Reactions at bridgehead carbon provide a unique opportunity to investigate structure/energy and structure/reactivity relationships.[1] Following earlier studies on synthesis and kinetics,[2,3] Gleicher and Schleyer[4a] applied empirical force field (molecular mechanics) calculations to correlate and predict bridgehead reactivities over 12 orders of magnitude. At this early stage in these developments, cautionary comments about the preliminary nature of the force field were made, and it was implied that the solvolysis data did not cause significant ambiguities. Later, Bingham and Schleyer[5] correlated bridgehead reactivities over 18 orders of magnitude. These pioneering studies[4,5] established molecular mechanics as a valuable method for studies of structure/reactivity relationships.

There was one very surprising feature in Bingham and Schleyer's study.[5] Separate correlation lines of substantially different slopes were calculated for chlorides, bromides, tosylates, and triflates. It was predicted that the tosylate/bromide rate ratio, typically over 1000, would be less than unity for very unreactive substrates. In a later discussion of these results, it was stated that there were "really threatening obstacles of internal return, solvation energies, nonclassical structures, etc., which plague studies of carbonium ions."[6] Thus, the emphasis appeared to have shifted from difficulties in parameterizing the force field (particularly for carbocations) to possible ambiguities in the interpretation of the solvolysis data.

More recently there has been considerable progress in mechanistic studies of solvent and leaving-group effects on S_N1 reactions.[7] We now show that consistent corrections can be made for changes in solvents and leaving groups, leading to a unified data set spanning 22 orders of magnitude in reactivity. Recent thermochemical data for carbocations in solution[8] and in the gas phase[9] will also

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[1] For reviews on bridgehead reactivity, see: (a) Fort, R. C., Jr.; Schleyer, P. v. R. *Adv. Alicyclic Chem.* **1966**, *1*, 283. (b) Rüchardt, C. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 830. (c) Fort, R. C., Jr. In "Carbonium Ions"; Olah, G. A.; Schleyer, P. v. R., Eds.; Wiley: New York, 1973; Vol. IV, Chapter 32. (d) Stirling, C. J. M. *Tetrahedron* **1985**, *41*, 1613.

[2] (a) Bartlett, P. D.; Knox, L. H. *J. Am. Chem. Soc.* **1939**, *61*, 3184. (b) Doering, W. v. E.; Levitz, M.; Sayigh, A.; Sprecher, M.; Whelan, W. P., Jr. *J. Am. Chem. Soc.* **1953**, *75*, 1008.

[3] (a) Schleyer, P. v. R.; Nicholas, R. D. *J. Am. Chem. Soc.* **1961**, *83*, 2700. (b) Wiberg, K. B.; Lowry, B. R. *J. Am. Chem. Soc.* **1963**, *85*, 3188.

[4] (a) Gleicher, G. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1967**, *89*, 582. (b) See also: Sherrod, S. A.; Bergman, R. G.; Gleicher, G. J.; Morris, D. G. *J. Am. Chem. Soc.* **1972**, *94*, 4615.

[5] Bingham, R. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 3189.

[6] Allinger, N. L.; Lane, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 2937.

[7] (a) Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5466. (b) Bentley, T. W.; Carter, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 5741. (c) Kevill, D. N.; Kamil, W. A.; Anderson, S. W. *Tetrahedron Lett.* **1982**, 4635. (d) Bunton, C. A.; Mhala, M. M.; Moffatt, J. R. *J. Org. Chem.* **1984**, *49*, 3639. (e) Creary, X.; McDonald, S. R. *J. Org. Chem.* **1985**, *50*, 474. (f) Kevill, D. N.; Anderson, S. W. *J. Org. Chem.* **1985**, *50*, 3330. (g) Bentley, T. W.; Roberts, K. *J. Org. Chem.* **1985**, *50*, 4821.

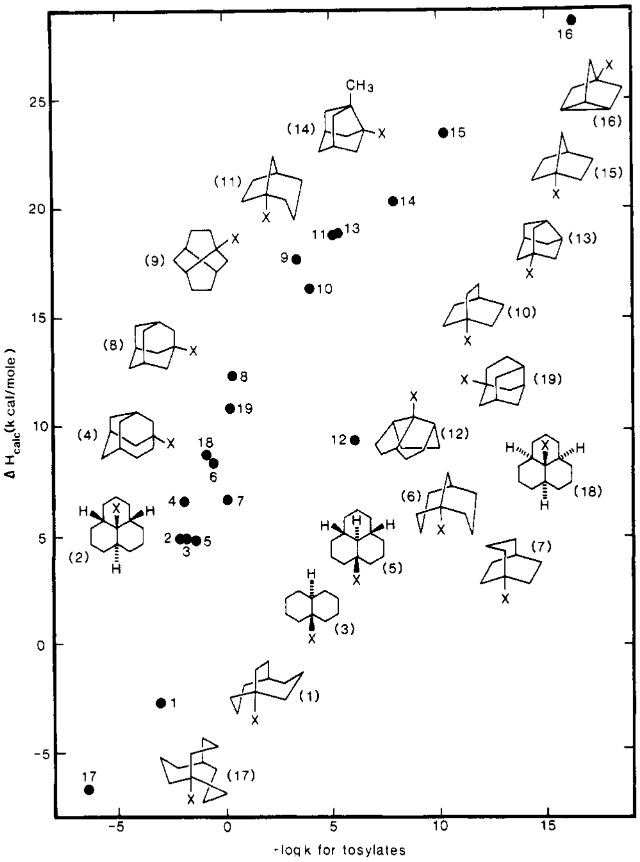

Figure 1. Correlation of the calculated change in strain energy ($RH \rightarrow R^+$) with logarithms of solvolysis rates of tosylates, strain data from ref 5 and 10, and solvolysis data from Table III. (Structures **1**–**16** are numbered as in ref 5). Slope = 1.49 ± 0.15; intercept 7.9 ± 0.9; correlation coefficient = 0.921.

be discussed. It appears that previous studies[5] have underestimated electronic effects and have overestimated angle strain and steric effects of the tosylate leaving group.

Results

The compounds (**1**–**16**, see Figure 1) are the same as those discussed previously.[5] We have added data for 1-bicyclo[3.3.3]undecyl (**17**),[10a] *trans,trans,trans*-perhydrophenalyl (**18**),[10b] and 6-protoadamantyl (**19**).[10c]

Solvent Effects on Reactivity. The rates of many S_N1 reactions depend markedly on solvent. In contrast, *relative rates* of solvolyses of different substrates *having the same leaving group* may be almost independent of solvent. A logarithmic plot of solvolytic data for 1-bicyclo[2.2.2]octyl tosylate (**10**, X = OTs) and 1-adamantyl tosylate (**8**, X = OTs) over a 10^5 range in reactivity (Figure 2) shows only a 2.4-fold change in relative rate. Although these are the only two bridgehead systems for which extensive data on solvent effects are currently available, similar results were also obtained for 1-adamantylmethylcarbinyl[7a] and 2-adamantyl[11b] tosylates. When anchimeric and nucleophilic solvent assistance is absent, the above evidence shows that relative rates are virtually independent of solvent[7a] (e.g., for solvolyses of bridgehead substrates **1**–**19**). This generalization is *not* applicable to solvolyses of cyclopropyl

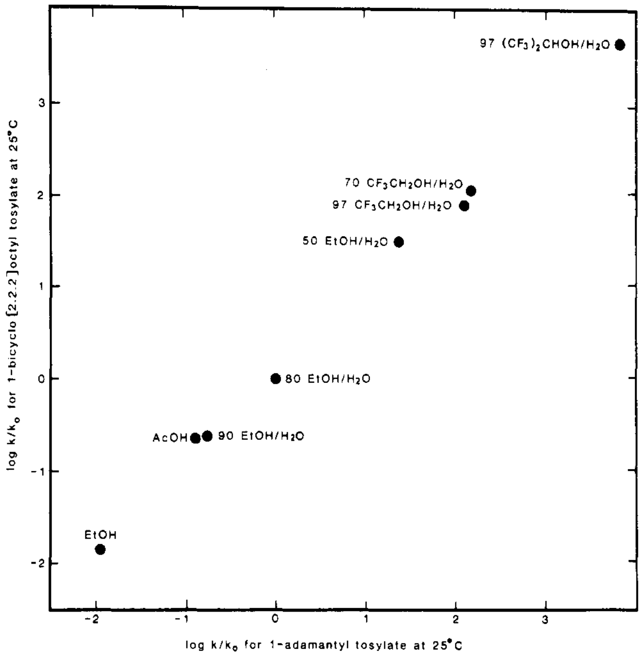

Figure 2. Correlation of logarithms of rates of solvolysis of 1-bicyclo[2.2.2]octyl tosylate (**10**, X = OTs) at 25 °C with logarithms of solvolysis rates for 1-adamantyl tosylate (**8** X = OTs) at 25 °C. Slope = 0.933 ± 0.020; intercept 0.047 ± 0.039; correlation coefficient 0.999. Data from Table III of ref 7a and Table V of ref 7g. Additional data for **8** (X = OTs) from ref 11a and for 70% CF_3CH_2OH from ref 11b, assuming OTs/OMs = 1.

Table I. Tosylate/Bromide (OTs/Br) Rate Ratios at 70 °C for 80% Ethanol/Water

	rate constants, s^{-1}		
substrate	k_{OTs}	k_{Br}	k_{OTs}/k_{Br}
8	$4.02 \times 10^{-1\,a}$	$8.3 \times 10^{-5\,b}$	
	$4.09 \times 10^{-1\,c}$	$7.6 \times 10^{-5\,d}$	5.1×10^3
9	$3.6 \times 10^{-4\,e}$	$1.41 \times 10^{-7\,f}$	2.5×10^3
10	$1.0 \times 10^{-4\,g}$	$4.0 \times 10^{-8\,g}$	2.5×10^3
15	$(4.0 \times 10^{-11})^e$	$(2.2 \times 10^{-15})^h$	(2×10^4)
			$(4 \pm 1) \times 10^{3\,i}$

[a] Reference 11a. [b] Reference 18a. [c] Reference 18b. [d] Reference 7b. [e] Calculated from data in acetic acid (ref 5) by multiplying by the average $k_{80\%\,EtOH}/k_{AcOH}$ ratio of 3.5 (see text). [f] Reference 5. [g] Reference 18c; see also ref 7a. [h] From data and assumptions given in ref 5, we calculate $k = 9.3 \times 10^{-13}$ s^{-1} in 40% ethanol/water at 70 °C, further corrected to 80% ethanol/water from the Y_{Br} value of 2.62 (ref 7b), ignoring the slight temperature dependence of Y_{Br}. [i] Recommended value (see text).

Table II. Tosylate/Triflate (OTs/OTf) Rate Ratios for Acetolysis at 70 °C

	rate constants, s^{-1}		
substrate	k_{OTs}	k_{OTf}	k_{OTs}/k_{OTf}
13	$(3.13 \times 10^{-7})^a$	$2.96 \times 10^{-2\,b}$	(1.1×10^{-5})
14	$3.40 \times 10^{-9\,b}$	$9.03 \times 10^{-5\,b}$	3.8×10^{-5}
15	$1.15 \times 10^{-11\,b}$	$6.52 \times 10^{-8\,b}$	1.8×10^{-4}
7-norbornyl	$2.1 \times 10^{-11\,c}$	$1.09 \times 10^{-6\,d}$	
		$9.94 \times 10^{-7\,e}$	2.1×10^{-5}
2-adamantyl	$3.4 \times 10^{-6\,f}$	$1.0 \times 10^{-1\,g}$	3.4×10^{-5}
			$6 \times 10^{-5 \pm 0.5\,h}$

[a] Reference 14; this result appears to be anomalously low (ca. 4-fold)—see section in text on solvent effects. [b] Reference 5. [c] Reference 20a. [d] Reference 20b. [e] Reference 7e. [f] Reference 20c. [g] Reference 7f. [h] Recommended range (see text).

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(8) Arnett, E. M.; Petro, C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 522.

(9) (a) Staley, R. H.; Wieting, R. D.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 5964. (b) Houriet, R.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 951. (c) Sharma, R. B.; Sen Sharma, D. K.; Hiraoka, K.; Kebarle, P. *J. Am. Chem. Soc.* **1985**, *107*, 3747.

(10) (a) Parker, W.; Tranter, R. L.; Watt, C. I. F.; Chang, L. W. K.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 7121. (b) Slutsky, J.; Bingham, R. C.; Schleyer, P. v. R.; Dickason, W. C.; Brown, H. C. *J. Am. Chem. Soc.* **1974**, *96*, 1969. (c) Karim, A.; McKervey, M. A.; Engler, E. M.; Schleyer, P. v. R. *Tetrahedron Lett.* **1971**, 3987.

(11) (a) Kevill, D. N.; Kolwyck, K. C.; Weitl, F. L. *J. Am. Chem. Soc.* **1970**, *92*, 7300. (b) Bentley, T. W.; Carter, G. E. *J. Org. Chem.* **1983**, *48*, 579.

Table III. Solvolytic Kinetic Data at 70 °C and Calculated Strain Energies (ΔH) for Bridgehead Reactivity

substrate[a]						
	X	k, s^{-1} [b]	solvent	correction factor[c]	k, s^{-1} [d]	ΔH[b]
1	Cl	7.33×10^{-3}	80% EtOH	1.6×10^{5}	1.2×10^{3}	−2.8
2	Cl	7.63×10^{-4}	80% EtOH	1.6×10^{5}	1.2×10^{2}	4.8
3	Cl[e]	5.68×10^{-4}	80% EtOH	1.6×10^{5}	9.1×10^{1}	4.8
4	Br[f]	2.36×10^{-2}	80% EtOH	4×10^{3}	9.4×10^{1}	6.5
5	Cl	1.95×10^{-4}	80% EtOH	1.6×10^{5}	3.1×10^{1}	4.7
6	Br[g]	8.10×10^{-4}	80% EtOH	4×10^{3}	3.2	8.3
7	Br	1.87×10^{-4}	80% EtOH	4×10^{3}	7.5×10^{-1}	6.6
8	OTs	4.02×10^{-1}	80% EtOH		4.0×10^{-1}	12.3
9	OTs	1.02×10^{-4}	HOAc	3.5	3.6×10^{-4}	17.6
10	OTs	1.00×10^{-4}	80% EtOH		1.0×10^{-4}	16.3
11	OTs	1.93×10^{-6}	HOAc	3.5	6.8×10^{-6}	18.7
12	OTs[h]	6.86×10^{-7}	80% EtOH		6.9×10^{-7}	9.3
13	OTs	5.19×10^{-6}	80% EtOH		5.2×10^{-6}	18.8
14	OTs	1.12×10^{-8}	80% EtOH		1.1×10^{-8}	20.3
15	OTs	1.15×10^{-11}	HOAc	3.5	4.0×10^{-11}	23.5
16	OTf[i]	7.6×10^{-11}	50% EtOH	4.6×10^{-7}	3.5×10^{-17}	28.5
17	Cl[j]	17.4	80% EtOH	1.6×10^{5}	2.8×10^{6}	−6.8
18	Cl[k]	4.36×10^{-5}	80% EtOH	1.6×10^{5}	7.0[l]	8.6
19	Br[m]	1.50×10^{-4}	80% EtOH	4×10^{3}	6.0×10^{-1}	10.8

[a] Structures shown in Figure 1. [b] Reference 5, unless stated otherwise; units of ΔH are kcal/mol. [c] Assuming $k_{Br}/k_{Cl} = 40$ (see ref 17); $k_{OTs}/k_{Br} = 4 \times 10^{3}$ (Table I); hence $k_{OTs}/k_{Cl} = 1.6 \times 10^{5}$; for acetolysis OTs/OTf = 6×10^{-5} (Table II); solvent correction $k_{80\%\ EtOH}/k_{AcOH} = 3.5$ (see text). [d] Final calculated rate constant for solvolyses of tosylates in 80% ethanol/water. [e] Reference 21a. [f] See also ref 21b. [g] See also ref 21c. [h] Reference 5 quotes a rate constant of 8.86×10^{-7} s^{-1}, which appears to be a typographical error. [i] Reference 21d; data for acetolysis estimated by dividing by 460, the solvent dependence of 2-adamantyl triflate at 70 °C (ref 7f and 7g). [j] Data from ref 10a. [k] Data from ref 10b. [l] This result ignores the likely possibility that solvolysis of the tosylate will, like the *p*-nitrobenzoate,[10b] be accelerated by F-strain effects. [m] Data from ref 10c.

tosylate (ring opening occurs[12]) or to solvolyses of simple secondary systems that are susceptible to nucleophilic solvent assistance: e.g., the relative rates of solvolyses of 2-propyl and 2-adamantyl tosylates vary almost 10^5-fold from ethanol to 97% hexafluoroisopropyl alcohol/water (HFIP),[7a] the range of solvents shown in Figure 2.

Further evidence for the consistency of solvent effects on bridgehead reactivity is the linear relationship of unit slope established between logarithms of solvolysis rates of tosylates **8**, **10**, **12**, and **14** in 80% ethanol/water and in acetic acid at 70 °C;[13a] the relative rates ($k_{80\%\ EtOH}/k_{AcOH}$) at 70 °C are as follows: **8**, 4.0; **10**, 4.0;[13b] **12**, 3.0; **14**, 3.3; i.e., 3.5 ± 0.5. An exception is the noradamantyl system (**13**),[5,14] which gives an anomalously high $k_{80\%\ EtOH}/k_{AcOH}$ ratio of 16.6 as well as an anomalously low k_{OTf}/k_{OTs} ratio in acetic acid (Table II). Hence the extrapolated rate constant for acetolysis of **13** (X = OTs) may be about 4-fold too high, perhaps in part because the data were obtained conductimetrically[14] (less reliable for acetolysis[5,15]). Data for acetolysis of tosylates **9**, **11**, **15**, and **16** have been converted to data for reaction in 80% ethanol/water (Table III), so that kinetic data in this one solvent are available for all substrates (**1**–**19**).

Conversion Factors for Changes in Leaving Group. Because relative rates of S_N1 reactions of adamantyl systems vary about 10^2-fold with changes in leaving group,[7g] we will restrict comparisons to one leaving group (tosylate). Data obtained at other temperatures will be extrapolated by using the Arrhenius equation—for long extrapolations, this procedure could introduce large errors (e.g., up to 10-fold in rate[4b]). Even with long temperature extrapolations a vast range of reactivity cannot be covered, so conversion factors for changes in leaving group are also required.

A conversion factor for bromides and chlorides ($k_{Br}/k_{Cl} = 40 \pm 10$) can readily be obtained from Bingham and Schleyer's data set.[5,17]

Tosylate/bromide rate ratios for compounds **8**–**10** (Table I) show a variation from 2.5×10^3 to 5.1×10^3, but in each case one of the pairs of rate constants was extrapolated from data at other temperatures. All such extrapolations are likely to produce high rate constants because of curvature of the Arrhenius plots.[4b,19] For the adamantyl system (**8**) data for the tosylate was extrapolated to 70 °C from below 35 °C, and hence the OTs/Br rate ratio is probably too large. For the twistyl (**9**) and 1-bicyclo[2.2.2]octyl (**10**) systems, data for the bromides were extrapolated to 70 °C from above 125 °C; hence the corresponding OTs/Br values are probably too low. Therefore the available experimental evidence is consistent with a OTs/Br rate ratio of $(4 \pm 1) \times 10^3$. Combining this with the Br/Cl rate ratio of 40 ± 10 gives a OTs/Cl rate ratio of $(16 \pm 8) \times 10^4$.

Bingham and Schleyer's data set shows a 16-fold range of OTs/OTf rate ratios from 1.1×10^{-5} to 1.8×10^{-4} (Table II). However, the rate data for acetolysis of **13** (X = OTs) may be anomalously low (see above). Relatively consistent OTs/OTf ratios are obtained for **14**, 2-adamantyl, and 7-norbornyl (Table II), but the range of acceptable values is $6 \times 10^{-5 \pm 0.5}$; this ratio is required only for the nortricyclyl system (**16**) in the final set of data (Table III). Variations in the OTs/OTf rate ratios (Table II) probably represent considerable experimental uncertainties rather than a

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[12] Schleyer, P. v. R.; Sliwinski, W. F.; Van Dine, G. W.; Schöllkopf, U.; Paust, J.; Fellenberger, K. *J. Am. Chem. Soc.* **1972**, *94*, 125.

[13] (a) See Figure 6 of ref 5. (b) Data for acetolysis from ref 13c. (c) Rhodes, Y. E.; Difate, V. G. *J. Am. Chem. Soc.* **1972**, *94*, 7582.

[14] Wishnok, J. S.; Schleyer, P. v. R.; Funke, E.; Pandit, G. D.; Williams, R. O.; Nickon, A. *J. Org. Chem.* **1973**, *38*, 539.

[15] The importance of additional experimental errors can be further emphasised by three independent rate constants (not conductimetric) for acetolysis of 1-adamantyl tosylate (**8**, X = OTs) at 25 °C (10^4k = 5.86,[3a] 4.36,[16a] and 5.15[16b] s^{-1}).

[16] (a) Sinnott, M. L.; Whiting, M. C. *J. Chem. Soc. B* **1971**, 965. (b) Ree, B. R.; Martin, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 1660.

[17] For compound **4** at 70 °C, k_{Br}/k_{Cl} = 46; other values are as follows: **6**, 32; **7**, 40; **8**, 34 (our independent value at 70 °C is 31[7b]); **9**, 47.

[18] (a) Raber, D. J.; Bingham, R. C.; Harris, J. M.; Fry, J. L.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 5977. (b) Grob, C. A.; Schaub, B. *Helv. Chim. Acta* **1982**, *65*, 1720. (c) Grob, C. A. Kostka, K.; Kuhnen, F. *Helv. Chim. Acta* **1970**, *53*, 608.

[19] Bentley, T. W.; Carter, G. E. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 1633.

marked dependence on structure; even S_N2 acetolyses of methyl and ethyl sulfonates show similar OTs/OTf rate ratios to the above values (Table II).[20b] Because acetolyses of triflates have significantly lower $\Delta H^{\ddagger}$ values compared with tosylates (by 3–5 kcal/mol[5,7g]), OTs/OTf rate ratios are more temperature dependent than Br/Cl and OTs/Br rate ratios.

From the above data, we can unify the data set for the compounds **1**–**19**—see Table III. A plot of the change in strain energy ($RH \rightarrow R^+$, predicted from molecular mechanics[5]) against logarithms of solvolysis rate constants is shown in Figure 1.

Discussion

Should Separate Correlations Be Made for Each Leaving Group? The slope of a correlation line for *all* substrates (Figure 1) is 1.49 ± 0.15 kcal/mol/log unit. The previously reported[5] slopes are for triflates (0.92), tosylates (1.11), bromides (2.44), and chlorides (3.12). This led to the remarkable prediction that k_{OTs}/k_{Br} would be less than unity for 1-norbornyl (**15**).[5] Our estimates (Table I) and independent kinetic evidence[22] show that this prediction is incorrect. The effect of pinning back the CH_2 bridges of **15** is much less than was previously suggested.[5,23] While relief of F-strain in tertiary tosylates accounts for the high OTs/Br rate ratios (compared with secondary systems),[5] there appear to be no significant *variations* in relief of F-strain during ionization of typical tertiary tosylates, e.g., solvolyses of 3-substituted 1-adamantyl tosylates,[18b] in which the tosylate group must be in the same steric environment, show a similar range of k_{OTs}/k_{Br} values to those in Table I. Available experimental evidence is consistent with almost constant Br/Cl[17] and OTs/OTf (Table II) rate ratios, so one correlation line for all substrates can be justified.[24]

The slope of our correlation (Figure 1) corresponds to an energy change of 1.05 ± 0.11 kcal/mol in the solvolysis for every 1.0 kcal/mol of predicted change in strain. This implies essentially complete carbocation character in the transition state, in satisfactory agreement with an independent estimate of 0.89 based on heats of ionization of alkyl halides.[8] However, there is much more scatter in these results (Figure 1) than was thought previously,[5] and deviations from the separate correlation lines (e.g., for the highly deviating compound **12**[5]) may not be meaningful.[25,26]

Absence of Mechanistic Changes. Bridgehead systems were originally chosen for their uniformity of solvolytic mechanism,[4a] and more recent work[7,11] firmly supports this choice. When rearside nucleophilic attack is prevented or inhibited, it appears that a high degree of cleavage of the C-leaving group bond is necessary before nucleophilic attack can occur. Such charge development does not appear to vary significantly for different substrates.[8,28] The cationic intermediates formed during solvolyses of 1- and 2-adamantyl chloride react unselectively with azide and water.[29] Less reactive bridgehead systems probably form even less stable intermediates or react by concerted ionic processes. There appears to be little scope for mechanistic change, except no reaction at all! A recent comparison of solvolyses of 2-adamantyl perchlorate with more nucleophilic leaving groups (e.g., chlorides, bromides, and tosylates) provided no indications of substantial ion pair return.[7g]

Electronic Effects. Studies of diadamantyl bromides led to the inclusion of a correction term for the electronic effects of β-alkyl substitution.[30a] However, there also appear to be electronic effects of the ring carbon atoms,[4a] which are excluded from the force field;[5] e.g., the 1-adamantyl cation is more stable than the *tert*-butyl cation in the gas phase,[9] paralleling studies of stable ions in solution and of S_N1 reactivity.[7b,8] Also, electron withdrawal by a cyclopropane ring may contribute 100-fold to the low reactivity of **16**.[31] The relative magnitudes of stabilization by long-range electronic effects and of destabilization by angle strain[32] need to be reevaluated.

To summarize, the results in Table III provide a unique data set, to which more recent data could be added[4b,13c,30a,33] and which is relatively free from mechanistic complexity. The data test and challenge current and developing theoretical approaches to structure/reactivity relationships.

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(20) (a) Winstein, S.; Shatavsky, M.; Norton, C.; Woodward, R. B. *J. Am. Chem. Soc.* **1955**, *77*, 4183. (b) Su, T. M.; Sliwinski, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1969**, *91*, 5386. (c) Schleyer, P. v. R.; Fry, J. L.; Lam, L. K. M.; Lancelot, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 2542.

(21) (a) Becker, K. B.; Boschung, A. F.; Geisel, M.; Grob, C. A. *Helv. Chim. Acta* **1973**, *56*, 2747. (b) Mergelsberg, I.; Rüchardt, C. *Tetrahedron Lett.* **1982**, *23*, 1809. (c) Quinn, C. B.; Wiseman, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 1342. (d) Bingham, R. C.; Sliwinski, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 3471.

(22) (a) 1-norbornyl bromide (**15**, X = Br) underwent no detectable reaction in HFIP at 120 °C, when a rate constant of $1.3 \times 10^{-7}\ s^{-1}$ was determined for another bridgehead system under the same conditions.[22b] Hence we estimate $k \leq 10^{-9}\ s^{-1}$ at 120 °C in HFIP and $k \leq 10^{-11}\ s^{-1}$ at 70 °C (if $\Delta H^{\ddagger} \geq 24$ kcal/mol). Data for **15** (X = OTs) in acetic acid (Table III) allows an estimate of $k = 10^{-8}\ s^{-1}$ for reaction in HFIP at 70 °C, assuming that solvolyses of **15** (X = OTs) show the same solvent dependence as 2-adamantyl tosylate at 70 °C.[7a,20c] Hence k_{OTs}/k_{Br} for **15** in HFIP at 70 °C exceeds 10^3. (b) Mergelsberg, I.; Langhals, H.; Rüchardt, C. *Chem. Ber.* **1983**, *116*, 360.

(23) (a) This conclusion is supported by dynamic NMR studies of the rotational barriers in **8**, **10**, and **15**, X = $C(CH_3)_2Cl$.[23b] (b) Anderson, J. E.; Pearson, H.; Rawson, D. I. *J. Am. Chem. Soc.* **1985**, *107*, 1446.

(24) (a) In exceptional circumstances (e.g., solvolyses of the *p*-nitrobenzoate of **18**), F-strain contributes substantially to leaving-group effects.[10b] Electronic effects will also contribute, if varied over a wide range,[24b] but these effects will be very similar for bridgehead solvolyses. (b) Harris, J. M.; Shafer, S. G.; Moffatt, J. R.; Becker, A. R. *J. Am. Chem. Soc.* **1981**, *101*, 3295.

(25) If the value of change in strain for *tert*-butyl (ΔH = 2.85 kcal/mol) from the initial study[4a] is combined with our evidence[7b] that an S_N1 solvolysis of *tert*-butyl chloride would proceed at approximately the same rate as solvolysis of 1-adamantyl chloride (**8**, X = Cl) then *tert*-butyl would fit close to a line (see Figure 1) through data points for compounds **17**, **12**, and **16**.

(26) After this manuscript had been submitted for publication, a preprint was sent to P. Müller, who notified us of his recent work on a revised force field for tertiary carbocations. These results[27] (based solely on calculations) provide strong *independent* support for our conclusions (based solely on the experimental solvolytic rate constants). Particularly significant is that compound **12** behaves normally in Müller's correlations, which show the same slope for halides and tosylates.

(27) (a) Müller, P.; Blanc, J.; Mareda, J. *Chimia* **1984**, *38* (11), 389. (b) Müller, P.; Blanc, J.; Mareda, J. *Helv. Chim. Acta*, submitted for publication.

(28) Kevill, D. N.; Kolwyck, K. C.; Shold, D. M.; Kim, C. *J. Am. Chem. Soc.* **1973**, *95*, 6022.

(29) Ta-Shma, R.; Rappoport, Z. *J. Am. Chem. Soc.* **1983**, *105*, 6082.

(30) (a) Gund, T. M.; Schleyer, P. v. R.; Unruh, G. D.; Gleicher, G. J. *J. Org. Chem.* **1974**, *39*, 2995. (b) See also: Engler, E. M.; Farcasiu, M.; Sevin, A.; Cense, J. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 5769.

(31) Chenier, P. J.; McClure, J. R.; Golembeski, D. J. *J. Org. Chem.* **1978**, *43*, 4306.

(32) Lomas, J. S.; Luong, P. K.; Dubois, J. E. *J. Org. Chem.* **1979**, *44*, 1647.

(33) (a) Osawa, E.; Engler, E. M.; Godleski, S. A.; Inamoto, Y.; Kent, G. J.; Kausch, M.; Schleyer, P. v. R. *J. Org. Chem.* **1980**, *45*, 984. (b) Andersen, B.; Schallner, O.; de Meijere, A. *J. Am. Chem. Soc.* **1975**, *97*, 3521. (c) de Meijere, A.; Schallner, O.; Weitemeyer, C.; Spielmann, W. *Chem. Ber.* **1979**, *112*, 908. (d) Rüchardt, C.; Golzke, V.; Range, G. *Chem. Ber.* **1981**, *114*, 2769.