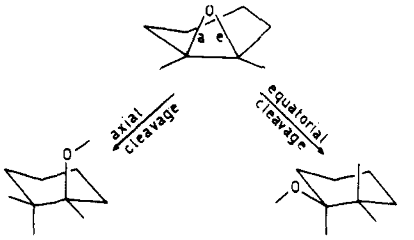
References and Notes

(1) C. A. Coulson, *Adv. Cancer Res.*, **1**, 1 (1953); A. Pullman and B. Pullman, *Adv. Cancer Res.*, **3**, 117 (1955).
(2) For recent reviews, see J. W. Daly, D. M. Jerina, and B. Witkop, *Experientia*, **28**, 1129 (1972); D. M. Jerina and J. W. Daly, *Science*, 573 (1974); P. Sims and P. L. Grouer, *Adv. Cancer Res.*, **20**, 165 (1974).
(3) J. W. Keller and C. Heidelberger, *J. Am. Chem. Soc.*, **98**, 2328 (1976); P. Yurkanis Bruice, T. C. Bruice, P. M. Dansette, H. G. Selander, H. Yagi, and D. M. Jerina, *ibid.*, **98**, 2965 (1976); D. L. Whalen and A. M. Ross, *ibid.*, **98**, 7859 (1976).
(4) See, for example, (a) C. Battistini, P. Crotti, and F. Macchia, *Tetrahedron Lett.*, 2091 (1975); (b) A. Balsamo, P. Crotti, B. Macchia, and F. Macchia, *J. Org. Chem.*, **39**, 874 (1974), and references cited therein.
(5) B. Ottar, *Acta Chem. Scand.*, **1**, 283 (1947).
(6) S. Merlino, G. Lami, B. Macchia, F. Macchia, and L. Monti, *J. Org. Chem.*, **37**, 703 (1972).
(7) (a) G. Berti, B. Macchia, and F. Macchia, *Tetrahedron*, **24**, 1755 (1968); (b) **28**, 1299 (1972).
(8) S. Winstein and N. H. Holness, *J. Am. Chem. Soc.*, **77**, 5562 (1955).
(9) E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, 1972, p 234ff.
(10) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Interscience, New York, 1965, p 47.
(11) F. R. Jensen and C. H. Bushweller, *Adv. Alicyclic Chem.*, **3**, 170 (1971).
(12) Reference 10, p 188.
(13) G. Berti, F. Bottari, B. Macchia, and F. Macchia, *Tetrahedron*, **21**, 3277 (1965).
(14) G. Berti, G. Camici, B. Macchia, F. Macchia, and L. Monti, *Tetrahedron Lett.*, 2591 (1972).
(15) It has been shown[1] that the stereoselectivities of the acid-catalyzed solvolyses of aryloxiranes are strongly dependent on the temperature and that in general a lowering in the temperature brings about an increase of the anti stereoselectivity and vice versa.
(16) C. Battistini, P. Crotti, and F. Macchia, *Gazz. Chim. Ital.*, **107**, 153 (1977).
(17) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed., Pergamon Press, Oxford, 1969, p 288.
(18) B. Macchia, F. Macchia, and L. Monti, *Gazz. Chim. Ital.*, **100**, 35 (1970).
(19) M. Tichý, *Adv. Org. Chem.*, **5**, 115 (1965).
(20) Reference 10, p 101.
(21) Following Hartshorn and Kirk,[22] we will refer to "axial cleavage" or "equatorial cleavage" of a 1,2-epoxycyclohexane as the cleavage of the epoxide ring leading to chair structures, closest to the conformation of the starting epoxy compound, in which the former epoxidic oxygen is, respectively, axial or equatorial irrespective of the position of the nucleophile which can be independently either axial or equatorial. It must be stressed that "axial cleavage" does not absolutely mean "trans diaxial" opening of the epoxide ring.[23]



(22) M. Hartshorn and D. N. Kirk, *Tetrahedron*, **21**, 1547 (1965).
(23) A. Fürst and P. A. Plattner, Abstracts of Papers, 12th International Congress of Pure and Applied Chemistry, New York, 1951, p 409.
(24) (a) G. Berti, C. Battistini, P. Crotti, M. Ferretti, and F. Macchia, *Tetrahedron*, **33**, 1629 (1977); (b) C. Battistini, P. Crotti, M. Ferretti, and F. Macchia, *J. Org. Chem.*, **42**, 4067 (1977).
(25) J. G. Buchanan and H. Z. Sable in "Selective Organic Transformations", Vol. 2, B. S. Thyagarajan, Ed., Wiley, New York, 1972, p 12.
(26) H. Kwart and T. Takeshita, *J. Am. Chem. Soc.*, **86**, 1161 (1964); J. L. Mateos, C. Perez, and H. Kwart, *Chem. Commun.*, 125 (1967).
(27) A similar conformational dependence of the product distribution was found in the boron trifluoride/ether complex catalyzed rearrangement of the same epoxides.[28]
(28) G. Berti, B. Macchia, F. Macchia, and L. Monti, *J. Chem. Soc. C*, 3371 (1971).
(29) G. Berti, G. Camici, B. Macchia, F. Macchia, and L. Monti, *Tetrahedron Lett.*, 2591 (1972).
(30) R. G. Curtis, I. Heilbron, E. R. H. Jones, and G. F. Woods, *J. Chem. Soc.*, 457 (1953).
(31) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds", 4th ed., Wiley, New York, 1956, p 255.
(32) B. Ippoliti, Doctoral Thesis in Chemistry, University of Pisa, 1970.

Acid-Catalyzed Dehydration and Acetolysis of Tertiary Methyl- and *tert*-Butylcarbinols. Empirical Force Field Treatment of *tert*-Butyl/Methyl Reactivity Ratios in Solvolysis Reactions of Alcohols and *p*-Nitrobenzoates

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Rate constants have been determined for the sulfuric acid catalyzed solvolysis in anhydrous acetic acid of 28 tertiary carbinols, 23 of which contain either a methyl or a *tert*-butyl substituent at the tertiary position. The kinetic effect of replacing Me by *t*-Bu ranges from 0.03 for alkyl(1-adamantyl)-*tert*-butylcarbinols to $10^{3.3}$ for 2-alkyl-2-adamantanols. For five systems the *t*-Bu/Me values are smaller than those found in the solvolysis of the corresponding *p*-nitrobenzoates by factors ranging from $10^{1.9}$ to $10^{4.6}$, depending on the structure. Strain energy calculations by the empirical force field method (molecular mechanics) provide a coherent interpretation of reactivity data for both alcohols and *p*-nitrobenzoates, provided that the hydrocarbon model employed for the ground state takes into account the greater steric requirements of the OPNB leaving group: OPNB is modeled by Me; OH by H. In this way self-consistent reactivity/Δ(strain) correlations are obtained for both the *t*-Bu/Me ratios and substituent effects in the 2-alkyl-2-adamantyl system. Nevertheless, the fact that the individual reactivities of disparate systems are poorly correlated by strain energy calculations limits their utility as a probe for detecting anomalous behavior in the solvolysis of *exo*- and *endo*-2-norbornyl derivatives, for example. Data for the 7-norbornyl system suggest that the carbonium ion force field, used as a model of the transition state, overestimates the importance of angle strain.

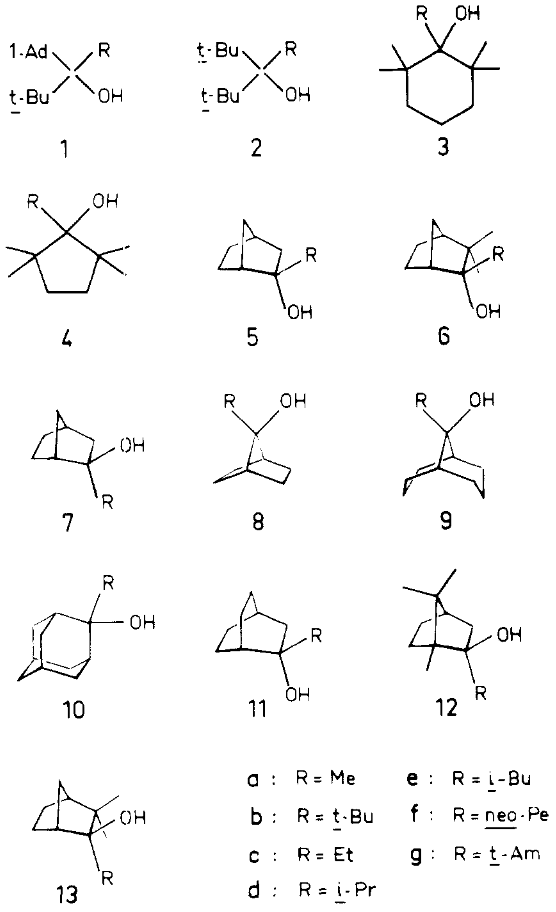
The last few years have seen a considerable development in the application of empirical force field (molecular mechanics) calculations to a variety of problems concerning structure and reactivity in systems where steric factors are of much greater importance than those of polarity or conjugation.[1] In view of the relative simplicity of handling molecules containing only carbon and hydrogen atoms and of the availability of structural and thermodynamic data, the EFF method has been the most thoroughly tested and most extensively refined as regards saturated hydrocarbons. Consequently, in the treatment of species containing heteroatoms, it is common practice to make an approximation which con-

Table I. Acid-Catalyzed Solvolysis Rates of Tertiary Alcohols in Anhydrous Acetic Acid (0.0003–0.182 M Sulfuric Acid) at 25 °C

compd	dehydration rate (s^{-1}), [H_2SO_4] 0.0003 M	0.006 M[a]	0.03 M	0.182 M	t-Bu/Me	strain energy AH	strain energy A^+	Δ(strain), kcal mol^{-1}
1a		6.91×10^{-4}	3.97×10^{-3}		0.029	22.08	21.72	0.36
1b		(2.02×10^{-5})	1.15×10^{-4}	1.83×10^{-3}		49.39	50.23	−0.84
2a		6.71×10^{-5}	3.95×10^{-4}	5.43×10^{-3}	0.070	15.04	14.20	0.84
2b		(4.82×10^{-6})	2.75×10^{-5}	3.90×10^{-4}		40.43	38.39	1.54
3a		2.08×10^{-4}	1.26×10^{-3}	1.65×10^{-2}	0.553	11.27	8.72	2.55
3b		1.10×10^{-4}	6.61×10^{-4}	1.00×10^{-2}		34.20	31.11	3.09
4a	8.79×10^{-5}	1.83×10^{-3}	1.05×10^{-2}		1.28	9.06	5.75	3.31
4b	1.07×10^{-4}	2.44×10^{-3}	1.34×10^{-2}			21.59	18.37	3.22
5a		4.56×10^{-5}	2.48×10^{-4}	1.89×10^{-3}	23.7	17.04	19.24	−2.20
5b	5.95×10^{-5}	1.09×10^{-3}	5.80×10^{-3}			20.51	20.53	−0.02
6a		7.30×10^{-5}	3.78×10^{-4}	3.06×10^{-3}	28.2	21.33	21.37	−0.04
6b	1.05×10^{-4}	1.95×10^{-3}	1.08×10^{-2}			29.38	26.83	2.55
7a	1.40×10^{-4}	2.39×10^{-3}	1.30×10^{-2}		74.3	17.90	19.24	−1.34
7b	1.04×10^{-2}	(1.96×10^{-1})				23.30	20.53	2.77
8a		(4.66×10^{-8})		2.99×10^{-6}	390	18.76	30.26	−11.50
8b		(2.38×10^{-5})	1.35×10^{-4}	1.16×10^{-3}		24.82	31.48	−6.66
9a		1.76×10^{-4}	8.69×10^{-4}	8.40×10^{-3}	1250	9.43	11.36	−1.93
9b	1.17×10^{-2}	(2.20×10^{-1})				19.46	15.40	4.06
10a		1.48×10^{-4}	9.42×10^{-4}	8.65×10^{-3}	2030	8.56	8.63	−0.07
10b	1.60×10^{-2}	(3.01×10^{-1})				16.25	12.24	4.01
10c		3.58×10^{-4}	2.10×10^{-3}			9.23	7.94	1.29
10d		1.57×10^{-4}	9.55×10^{-4}	1.19×10^{-2}		10.91	8.57	2.34
10e	5.19×10^{-5}	8.90×10^{-4}	5.43×10^{-3}			9.66	8.91	0.75
10f	1.09×10^{-4}	1.82×10^{-3}	1.07×10^{-2}			11.42	9.81	1.61
10g	2.72×10^{-2}	(5.11×10^{-1})				18.95	13.92	5.03
11a	6.44×10^{-5}	1.21×10^{-3}	6.13×10^{-3}			13.49	12.15	1.34
12a	3.53×10^{-3}	(6.64×10^{-2})				24.42	24.25	0.17
13a	1.54×10^{-3}	(2.89×10^{-2})				21.85	21.37	0.48

[a] Data in parentheses are extrapolated values.

Chart I



sists of replacing a constant fragment of the system, the leaving group in solvolysis studies, by a hydrogen atom[2] or a methyl group.[3] The justification is given by Schleyer: "our approximation is justified by the expectation that leaving group steric effects will be constant or proportional over the series examined".[2j]

This expectation is not always fulfilled. Thus, *trans, trans,trans*-perhydro-9b-phenalyl *p*-nitrobenzoate reacts about 3000 times faster at 25 °C than expected, whereas the corresponding chloride reacts normally.[4] This led to the recommendation that "whenever possible, solvolytic reactivity studies should employ chloride or similar leaving groups as opposed to esters in order to minimize F-strain effects", but for practical reasons *p*-nitrobenzoates are still the preferred substrates in solvolysis studies. Nevertheless, a simple alternative exists: alcohol dehydration in anhydrous acetic acid,[5] which satisfies the small leaving group requirement while avoiding the difficulties of chloride synthesis.

Comparison of substituent effects on *p*-nitrobenzoate and alcohol reactivities reveals marked differences in the relative rates of carbonium ion formation. The *t*-Bu/Me ratio for the formation of alkyldi-*tert*-butylcarbonium ions increases by a factor of about 750 on going from alcohol dehydration to *p*-nitrobenzoate solvolysis;[6] a somewhat smaller enhancement is observed in the 2-alkyl-2-adamantyl system.[7]

In an attempt to understand these differences we have determined *t*-Bu/Me ratios for the acid-catalyzed dehydration/acetolysis (solvolysis) of a variety of tertiary alcohols, **1–10** (Chart I). These can be usefully compared in some cases with the known *t*-Bu/Me ratios for solvolysis of their *p*-nitrobenzoates.[8] The additional structures are the highly congested systems **1–4** and the 7-norbornyl system **8**, which is particularly interesting in view of its well-known reluctance to form carbonium ions. Three other methyl derivatives,

11–13, were examined, despite the unavailability of the corresponding *tert*-butyl derivatives, since they may have a bearing on the problem of exo/endo ratios in the reactions of 2-norbornyl systems. The data for both alcohol and *p*-nitrobenzoate solvolysis are interpreted in terms of EFF calculated strain energies of the ground state and the transition state by means of suitable models.

Results and Discussion

Comparison of *t*-Bu/Me Ratios in Alcohol and *p*-Nitrobenzoate Solvolysis. Inspection of the data for alcohol and *p*-nitrobenzoate solvolysis confirms our previous observations based on systems **1** and **10** only. Firstly, when tertiary alcohols are solvolyzed in sulfuric acid–acetic acid mixtures (Table I) the dramatically large *t*-Bu/Me ratios observed in *p*-nitrobenzoate solvolysis[8,9] are reduced by factors varying between $10^{1.9}$ and $10^{4.6}$. In Brown's terminology[10a] *p*-nitrobenzoate solvolysis is a more "selective" reaction than alcohol solvolysis, i.e., more sensitive to structural changes, the replacement of a Me group by a *t*-Bu group in the present case. This is easy enough to understand. The increase in strain energy on going from a Me to a *t*-Bu substituted system will be greater for a *p*-nitrobenzoate than for an alcohol since the OPNB group has greater steric requirements than OH.[11] Consequently, if steric strain relief has any bearing on the relative reactivities, we would expect *p*-nitrobenzoate to enhance this factor. However, the fact that this enhancement operates nonuniformly leads us to think that specific leaving group steric interactions are superimposed on structural features concerned with the hydrocarbon skeleton alone.

Secondly, the highly congested alcohols **1–3** appear to contradict the established idea that solvolysis rates are enhanced by increasing the steric requirements of the alkyl groups attached to the tertiary carbon atom. In these three series the replacement of methyl by *tert*-butyl actually decreases the rate, and even in **4** only a very small enhancement occurs. Furthermore, these systems display a particularly striking trend in the *t*-Bu/Me ratios. Instead of increasing as the system becomes more strained from **4** to **1**, the *t*-Bu/Me ratio decreases steadily. To the extent that "rigidity" can be identified with strain, this result disagrees with the idea that *t*-Bu/Me ratios increase with the rigidity of the parent hydrocarbon structure.[8]

The *t*-Bu/Me ratio for the solvolysis of the *p*-nitrobenzoates of **2a** and **2b** is greater than unity (60),[6] but nevertheless surprisingly small for a highly congested and presumably rigid system. Previously we suggested that front (F)-strain relief was largely responsible for steric acceleration in *p*-nitrobenzoate solvolysis and attributed the low reactivity of the most congested alcohols to steric desolvation of the intermediate carbonium ion.[6] An alternative explanation of the latter phenomenon is that unfavorable strain energy changes are associated with the formation of the more congested carbonium ions due to the fact that C–C$^+$ bonds are normally shorter than C–C bonds.[13] This suggestion can, in principle, be tested by performing the appropriate EFF calculations.

Molecular Mechanics (EFF) Treatment of Alcohol Solvolysis Data: 2-Alkyl-2-adamantanols. Proton transfer to carbon is the rate-determining step in olefin hydration, and consequently by the principle of microscopic reversibility that for alcohol dehydration in aqueous media is carbonium ion deprotonation.[14] Kinetic isotope effects on the dehydration of **2a** in anhydrous acetic acid, on the other hand, are consistent with rate-determining heterolysis of the protonated alcohol to form a tertiary carbonium ion.[5] In systems where solvent attack is sterically hindered this carbonium ion yields alkenes via proton loss either with or without rearrangement, but in some methyl derivatives acetate is formed rather than alkene.

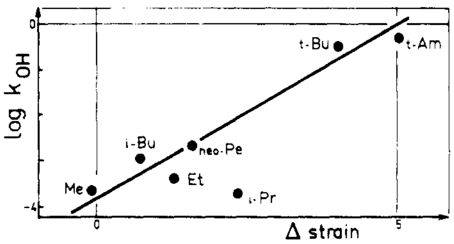


Figure 1. Correlation of 2-alkyl-2-adamantanol acid-catalyzed solvolysis rates (in s^{-1}; 0.006 M H_2SO_4 in HOAc at 25 °C) with Δ(strain) (kcal mol^{-1}).

$$\begin{tikzcd} \mathrm{AOH} \arrow[r, leftrightharpoons, "\text{fast}"'] & \mathrm{AOH_2^+} \arrow[r, "\text{slow}"'] & \mathrm{A^+} \arrow[r, "\text{fast}"'] \arrow[d] & \text{acetate} \\ & & \text{alkenes} & \end{tikzcd}$$

In the EFF approach to solvolysis, reactivity is expressed in terms of the hydrocarbon–carbonium ion[15] strain energy change; the fact that the reaction takes place in two steps is ignored. We shall make the usual assumption that the equilibrium concentration of the oxonium ion AOH_2^+ is negligibly small and focus our attention on the overall energy change, neglecting solvation energies and entropy effects, however.[17]

For alkanes several recently improved force fields are available,[18] but carbocations have only been parametrized within the framework of Schleyer's relatively simple force field.[1c,2a] Alcohols have been parametrized by Allinger,[19] but since Allinger's and Schleyer's alkane force fields differ substantially, particularly in the nonbonded interaction functions, they are not compatible. Rather than reparametrize carbocations, we have chosen therefore to work with Schleyer's 1973 force field, which has been tested on bridgehead systems with reactivities spanning 18 powers of ten as well as in studies of carbonium ion rearrangements.[20] We use the hydrocarbon AH as a surrogate for the alcohol and the carbonium ion A^+ for the transition state. The strain energies listed in Table I are in all cases those of the most stable conformation for each species.

Rate data for the 2-alkyl-2-adamantanols (**10**) are correlated by Δ(strain) fairly well, except when R = *i*-Pr (**10d**) (Figure 1). Excluding the *i*-Pr derivative,[21] the slope of the $\Delta\Delta G^{\ddagger}/\Delta$(strain) correlation is 1.02 (correlation coefficient = 0.977), which means that the effect of alkyl substituents on the dehydration rate is completely accounted for by the associated strain energy change. Although the errors introduced by the approximation implicit in the hydrocarbon model appear to cancel out rather nicely, the unit slope must nevertheless be considered fortuitous insofar as the carbonium ion parameters are based on the solvolysis rates of bridgehead bromides. Bridgehead triflates, tosylates, bromides, and chlorides all give $\Delta\Delta G^{\ddagger}/\Delta$(strain) correlations with slopes substantially less than unity.[2]

Another approximation, adopted by some authors, wherein the leaving group is replaced by a methyl group,[3] was also tested but proved to be less satisfactory. In particular, the $\Delta\Delta G^{\ddagger}/\Delta$(strain) slope was unreasonably small (0.250).

Quantitative Interpretation of the *t*-Bu/Me Ratios in Alcohol Solvolysis. When the individual solvolysis reactivities for all 28 compounds studied are plotted against Δ(strain), the correlation is at first sight not good (correlation coefficient = 0.707) (Figure 2). However, it can be seen that the points are dispersed fairly evenly around the line which correlates the 2-alkyl-2-adamantanols, with the 7-alkyl-7-norbornanols and the *exo*-2-norbornanols lying on the high side and the highly congested derivatives **2–4** (but not **1**) lying below the line.

The 7-norbornyl system **8** is notoriously unreactive in car-

Table II. Steric Energy Breakdown for 7-Alkylnorbornanes, 2-Alkyladamantanes, and the Corresponding Carbonium Ions (kcal mol^{-1})

alkane or cation	registry no.	$E\ (r)$	$E\ (\theta)$	$E\ (\phi)$	$E\ (d)$	steric energy	strain energy
7-methylnorbornane	1679-14-7	0.50	12.53	5.22	6.27	24.51	18.76
7-methyl-7-norbornyl cation	69429-68-1	1.43	22.14	8.62	3.16	35.35	30.26
7-*tert*-butylnorbornane	32640-85-0	1.19	17.25	5.61	8.58	32.63	24.81
7-*tert*-butyl-7-norbornyl cation	69429-69-2	1.56	23.69	8.42	4.95	38.62	31.48
2-methyladamantane	700-56-1	1.42	1.50	0.16	13.30	16.38	8.56
2-methyl-2-adamantyl cation	27411-03-6	1.12	1.29	2.11	11.26	15.79	8.63
2-*tert*-butyladamantane	64278-81-5	2.54	6.25	1.05	16.30	26.14	16.25
2-*tert*-butyl-2-adamantyl cation	64278-86-0	1.71	3.07	2.52	14.17	21.47	12.24

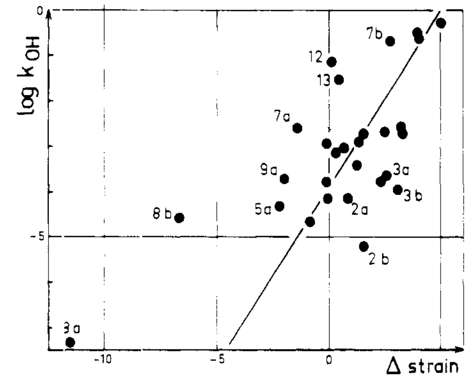


Figure 2. Correlation of the acid-catalyzed solvolysis rates of tertiary alcohols (in s^{-1}; 0.006 M H_2SO_4 in HOAc at 25 °C) with Δ(strain) (kcal mol^{-1}).

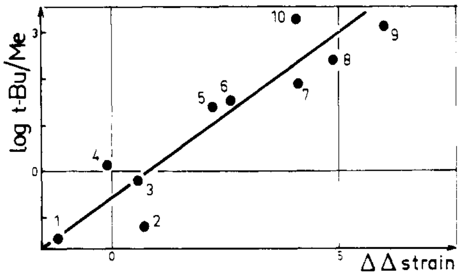


Figure 3. Correlation of *t*-Bu/Me ratios for the acid-catalyzed solvolysis of tertiary alcohols in anhydrous acetic acid with ΔΔ(strain) (kcal mol^{-1}).

bonium ion reactions.[22] Solvolysis is not facilitated by nonclassical carbonium ion formation; only the rearranged acetate and olefin are formed in the solvolysis of the tosylate of **8a**,[22d] and even the secondary brosylate, a much more likely candidate for assistance, solvolyzes with little rearrangement.[22b] Consequently, compared to the corresponding 2-adamantyl derivatives, the 7-norbornyl system is $10^{5.9}$ (secondary tosylates),[22c] $10^{5.2}$ (7- or 2-methyl chlorides),[23] or $10^{4.1}$ (7- or 2-phenyl chlorides)[24] less reactive. Similar factors are found for acid-catalyzed alcohol solvolysis (**10a**/**8a** = $10^{3.5}$; **10b**/**8b** = $10^{4.1}$).

The small angle in the 7 position (93–96° in the hydrocarbon)[1c] has long been recognized as the major contributor to this unreactivity,[22c] though quantum mechanical restrictions are also believed to play a role in destabilizing the carbonium ion intermediate.[25] In the force field treatment, since the C–C$^+$–C angle bending force constant is 4 times that of the C–C–C angle,[2a] the effect of this unusually small angle is to increase the steric energy of the carbonium ion, as is shown by the following breakdown of the steric energy contributions in the 7-norbornyl and 2-adamantyl systems (Table II). The formation of the carbonium ions in the first case leads to a considerable increase in the angle strain contribution accompanied by mutually compensating changes in the torsional and nonbonded contributions.[26] The latter phenomenon also appears in the 2-adamantyl system, but both the bond stretching and the angle strain contributions diminish when the carbonium ions are formed.

The geometry of the 7-norbornyl system must change considerably to accomodate the positive charge, the C_1–C_7–C_4 angle going from a calculated 92.0 to 112.6° and 91.5 to 111.4° for the Me and *t*-Bu derivatives, respectively,[27] but the position of **8a** and **8b** in Figure 2 suggests that Schleyer's parametrization overestimates[28] the angle strain in 7-alkyl-7-norbornyl cations by some 5–7 kcal mol^{-1}.

The deviations of the highly congested alcohols **2–4** also deserve comment. It would be unwise to assume that they are evidence for steric hindrance to solvation of the intermediate carbonium ion, especially when the most congested system, **1**, is well-correlated. Once again we are faced with the problem of force field parametrization and, in particular, of the energy function for nonbonded interactions, which is all-important here. Force fields have been optimized on the basis of data pertaining to rather small molecules; their extension to systems as crowded as **1–4** demands a certain degree of blind faith in the general validity of the energy functions and the relevant parameters. The differences in the strain energies of 1,1-di-*tert*-butylethane and tri-*tert*-butylmethane as calculated by Allinger's (12.2 and 35.5 kcal mol^{-1}) and Schleyer's (15.0 and 40.4 kcal mol^{-1}) force fields[1c] illustrate this point. By trial and error adjustment of the energy functions it would be possible to improve the correlation shown in Figure 2. This is standard practice in setting up force fields, but of course entails the *assumption* that the reactivity data are correlated by Δ(strain). Unfortunately, this is just what we are trying to test. A different approach was therefore adopted. Systematic errors in the treatment will be reduced by considering the difference between the *t*-Bu and Me derivatives. For example, according to Allinger's and Schleyer's force fields, the strain energy of tri-*tert*-butylmethane is 23.5 or 25.4 kcal mol^{-1} greater than that of 1,1-di-*tert*-butylethane, the estimates differing by only 1.9 kcal mol^{-1}, whereas the disagreement for the individual compounds is 2.8 and 4.9 kcal mol^{-1}.

When the *t*Bu/Me ratio for each system is plotted (Figure 3) against the difference in the appropriate Δ(strain) values, [Δ(strain)](*t*-Bu) – [Δ(strain)](Me), denoted ΔΔ(strain), the result is a fair correlation (correlation coefficient = 0.935) with a standard deviation of 0.8 kcal mol^{-1} in terms of strain energy.[29] The slope of this correlation (×1.36) is 0.93, which is in good agreement with that of the 2-alkyl-2-adamantanols. We conclude therefore that the relative solvolysis rates of the *t*-Bu and Me substituted tertiary carbinols are adequately explained by the associated strain energy changes. Insofar as the highly congested alcohol pairs **1–4** are included in this correlation, the explanation previously advanced,[6] that the low reactivity of the *t*-Bu derivatives is due to steric hindrance to solvation of the carbonium ion, is superfluous and can no longer be upheld. This finding answers recent criticism[16d]

Table III. *endo*- and *exo*-2-Norbornanols: Solvolysis Rates and Relative Stability (kcal mol^{-1})

compd	$\Delta G°_{exo} - \Delta G°_{endo}$ (exptl)	$\Delta G°_{exo} - \Delta G°_{endo}$ (calcd, AH)	$\Delta\Delta G^{\ddagger}$ (alc. solv.)
2-norbornanol	−1.06[a]	0.00	
2-methyl-2-norbornanol	−0.2[b]	0.86	2.3
2-*tert*-butyl-2-norbornanol	1.9[c]	2.79	3.1
2,3,3-trimethyl-2-norbornanol	(−0.5 ± 0.2)[d]	0.42	3.5
1,2-dimethyl-2-norbornanol	−0.6[b]	0.13	

[a] Reference 12. [b] Reference 12a. [c] Reference 12i. [d] Estimated from the difference between experimental and calculated values.

regarding the neglect of steric hindrance to solvation in our treatment of the 2-alkyl-2-adamantanols.[7]

Reactivities of *exo*- and *endo*-2-Alkyl-2-norbornanols. Up to now we have only considered *t*-Bu/Me ratios, but it is interesting to examine also the exo/endo ratios for the solvolysis of the 2-alkyl-2-norbornyl derivatives. The exo/endo ratios for alcohol solvolysis, 50 (**7a**/**5a**) and 175 (**7b**/**5b**), for the Me and *t*-Bu derivatives, respectively, are both smaller than the corresponding *p*-nitrobenzoate solvolysis data, 855 and 470 in 80% aqueous acetone.[12f,i] The exo/endo ratio for 2-methylcamphenilols (**13a**/**6a** = 400) is somewhat less than that reported for their acid-catalyzed heterolysis in aqueous dioxane (1200).[30]

Inspection of Figure 2 reveals that three of the *exo*-2-norbornanols (**7a**, **12**, and **13a**) are particularly out of line, all being faster than expected, while the endo isomers **5a** and **6a** are much closer to the 2-alkyl-2-adamantanol correlation. Before concluding that the exo/endo ratios are indicative of a special rate-enhancing effect in the exo isomers, we must examine more closely these results. Firstly, any attempt to rectify **8a** and **8b** by modifying the angle bending force constant will displace all of the 2-norbornanols toward the right of Figure 2 since they too suffer from angle strain. Secondly, in the strain energy calculations, the relative stability of the exo isomer is overestimated by about 0.9 kcal mol^{-1} relative to the endo since OH has been replaced by H. The data in Table III make this point clearer. When we consider the purely experimental data on rates and ground state energies, we find that the difference between the exo/endo ratio and what can be justified by $\Delta G°_{exo-endo}$ is the greatest, a factor of 1000, for the 2-methylcamphenilols **6a** and **13a**. Smaller factors, of about 100 and 10, are found for the 2-methyl- and 2-*tert*-butyl-2-norbornanols. In *p*-nitrobenzoate solvolysis also the deviation of the *tert*-butyl derivatives is less than that of the methyl epimers (1.7 and 4.2 kcal mol^{-1}, respectively).

Exo/endo ratios for alcohol solvolysis are therefore too high, but in view of parametrization uncertainties we cannot affirm that the exo isomers are too rapid nor that the endo are too slow. This point is of crucial importance to the long-standing debate regarding the origin of exo/endo ratios in 2-norbornyl systems. The current position regarding the solvolysis of tertiary *p*-nitrobenzoates is that the endo rates are slow[10c] due to steric hindrance to ionization.[31] Convincing proof that endo rates are slow, whatever the reason, is, however, lacking. The results presented here encourage us to believe that the question of exo/endo ratios in alcohol solvolysis can eventually be solved by strain energy calculations. It will be necessary, however, not only to improve the handling of the carbonium ion but also to adopt a force field which gives a more realistic picture of the relative ground state energies.

Molecular Mechanics Treatment of *p*-Nitrobenzoate Solvolysis. It has been suggested that the large steric strains arising from the rigidity of the bicyclic norbornyl structure are responsible for many of its unusual characteristics.[12j] The fact that the *t*-Bu/Me ratios for *p*-nitrobenzoate solvolysis (Table IV) are much greater in rigid bicyclic systems than in the more flexible acyclic and alicyclic systems is considered to corroborate this suggestion.[8] Against this, however, there is the observation that when alcohols are studied the same sequence of *t*-Bu/Me ratios is not obeyed and that some ex-

Table IV. Solvolysis Rates of Tertiary Carbinyl *p*-Nitrobenzoates in 80% Aqueous Acetone at 25 °C: *t*-Bu/Me Ratios

p-nitrobenzoate[a]	solv. rate, s^{-1}	*t*-Bu/Me	strain energy		Δ(strain), kcal mol^{-1}	ref
			AMe	A$^+$		
5a′	1.13×10^{-11}	39 600	18.99	19.24	−0.25	*b*
5b′	4.47×10^{-7}		29.64	20.53	9.11	*c*
6a′	2.31×10^{-11}	1 200 000	27.29	21.37	5.92	*d*
6b′	2.77×10^{-5}		47.37	26.76	20.61	*e*
7a′	1.00×10^{-8}	21 000	18.99	19.24	−0.25	*b*
7b′	2.10×10^{-4}		32.74	20.53	12.21	*f*
9a′	3.34×10^{-10}	104 000	15.65	11.36	4.29	*e*
9b′	3.48×10^{-5}		34.47	15.40	19.07	*e*
10a′	1.43×10^{-10}	240 000	13.11	8.63	4.48	*g*
10b′	3.42×10^{-5}		32.43	12.24	20.19	*g*
10c′	1.14×10^{-9}		15.91	7.94	7.97	*g*
10d′	4.97×10^{-9}		19.54	8.57	10.97	*g*
10f′	1.49×10^{-9}		27.91	9.81	8.10	*g*
14a[k]	7.45×10^{-11}	4.36	−1.44	0.00	−1.44	*h*
14b[k]	3.25×10^{-10}		7.71	7.06	0.65	*i*
15a[l]	2.11×10^{-9}	112	7.02	6.28	0.74	*j*
15b[l]	2.36×10^{-7}		14.96	7.91	7.05	*c*
16a[m]	5.48×10^{-11}	134	2.39	2.63	−0.24	*c*
16b[m]	7.35×10^{-9}		13.22	6.76	6.46	*c*
17a[n]	4.21×10^{-9}	273	9.72	7.17	2.57	*e*
17b[n]	1.15×10^{-6}		20.05	11.23	8.82	*e*

[a] *p*-nitrobenzoates of **5–7**, **9**, and **10** are primed to distinguish them from the alcohols. [b] Reference 12f. [c] Reference 8a. [d] K. Takeuchi, Ph.D. Thesis, Purdue University, 1968. [e] E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **97,** 2892 (1975). [f] Reference 12i. [g] Reference 2j. [h] H. C. Brown and W. C. Dickason, *J. Am. Chem. Soc.*, **91,** 1226 (1969). [i] H. C. Brown and E. N. Peters, *ibid.*, **95,** 2400 (1973). [j] Reference 12b. [k] **14** = alkyldimethylcarbinyl. [l] **15** = 1-alkyl-1-cyclopentyl. [m] **16** = 1-alkyl-1-cyclohexyl. [n] **17** = 1-alkyl-1-cycloheptyl.

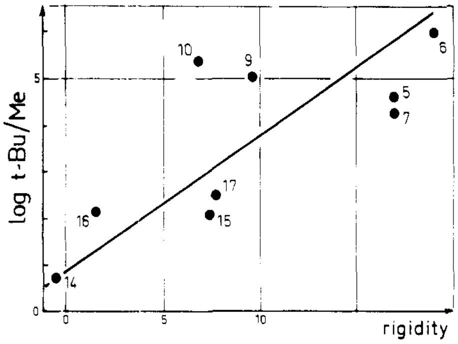


Figure 4. Correlation of the t-Bu/Me ratios for the solvolysis of tertiary carbinyl p-nitrobenzoates with the strain energy of the parent hydrocarbon ("rigidity"). Data are from ref 1c and Table IV.

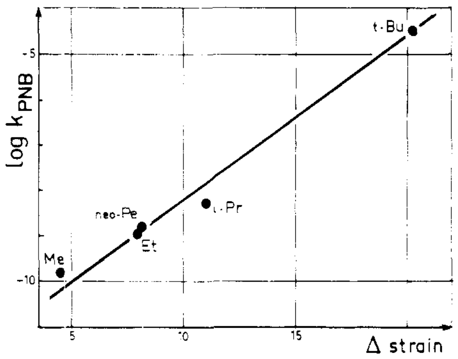


Figure 5. Correlation of the solvolysis rates of 2-alkyl-2-adamantyl p-nitrobenzoates (in s^{-1}; 80% aqueous acetone at 25 °C) with Δ(strain) (kcal mol^{-1}).

ceptionally strained systems have very low t-Bu/Me ratios. We have, therefore, attempted first to correlate p-nitrobenzoate ratios with "rigidity" and secondly to interpret them in terms of strain energy changes.

For want of a better definition of rigidity, it was taken to be expressed by the strain energy of the basic hydrocarbon skeleton, bearing neither a leaving group nor a tertiary substituent. The result, given in Figure 4, shows that a rather poor correlation (correlation coefficient = 0.771) does exist despite the evident simplicity of this idea. A much better correlation can, however, be obtained by the EFF approach.

Quantitative treatment in terms of strain energy requires first of all a suitable model. The solvolysis rates of 2-alkyl-2-adamantyl p-nitrobenzoates[2j] correlate fairly well (correlation coefficient = 0.936) with Δ(strain) for the AH–A$^+$ model,[32] but the slope of the $\Delta\Delta G^{\ddagger}/\Delta$(strain) correlation is a rather implausible 1.77. This signifies that steric acceleration is greater than can be accounted for by strain relief. Replacing OPNB by a methyl group leads to a more reasonable correlation (Figure 5) with a $\Delta\Delta G^{\ddagger}/\Delta$(strain) slope of 0.475 and better in quality to the previous one (correlation coefficient = 0.991).

When this model is applied to the t-Bu/Me ratios for p-nitrobenzoate solvolysis[8] (Figure 6), a good correlation (correlation coefficient = 0.955) is obtained with a slope of 0.502, again close to that of the 2-alkyl-2-adamantyl p-nitrobenzoates alone. As mentioned above in connection with the alcohols, no real significance can be attached to the magnitude of the slope in these correlations in view of the purely pragmatic fashion in which the carbonium ion parameters were defined[2a] and the fact that hydrocarbon models are employed for heteratomic leaving groups. More important is the internal consistency of the approach. If the hydrogen atom model is used, not only is the t-Bu/Me correlation poorer but the slope is markedly different (correlation coefficient = 0.815; $\Delta\Delta G^{\ddagger}/\Delta$(strain) = 0.826) from that of the 2-alkyl-2-adamantyl p-nitrobenzoates.

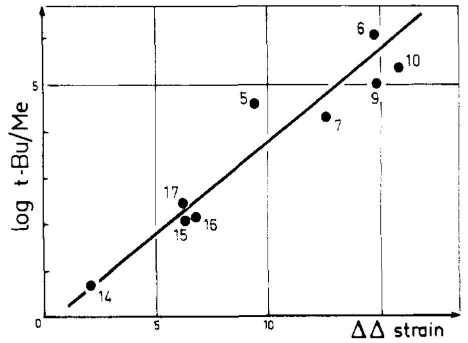


Figure 6. Correlation of t-Bu/Me ratios for the solvolysis of tertiary carbinyl p-nitrobenzoates in aqueous acetone with $\Delta\Delta$(strain) (kcal mol^{-1}).

In view of the good performance of the methyl–hydrocarbon model, we have tried to apply this same approach to the many tertiary carbinyl p-nitrobenzoates investigated by Brown and his co-workers over the last ten years[8,12b–i,33] in the hope of obtaining some information regarding the origin of exo/endo ratios.[34] The result is, however, even worse than that given in Figure 2 for the alcohols (correlation coefficient = 0.678; $\Delta\Delta G^{\ddagger}/\Delta$(strain) = 0.325) and only serves to show that the methyl group is an inadequate replica of OPNB when widely differing structures are compared individually.

Conclusions

Provided that the right model is chosen, t-Bu/Me ratios in both acid-catalyzed alcohol solvolysis and p-nitrobenzoate solvolysis can be understood in terms of the strain energy change involved in going from the ground state to the transition state. The greater steric requirement of an OPNB group is reasonably well represented by a methyl group, while a hydrogen atom serves for alcohols. The relative success of these t-Bu/Me vs. $\Delta\Delta$(strain) correlations can probably be attributed to the cancellation of intrinsically similar errors arising in calculations on closely related structures.

The hydrocarbon model performs badly when asked to correlate heterogeneous batches of tertiary carbinyl derivatives. Although specific effects could be invoked to account for certain of these deviations, it is obvious that force fields are still incapable of describing "normal" behavior with sufficient accuracy for us to discern unambiguously "abnormal" behavior. Several reasons can be advanced: alkanes are a poor substitute for alcohols and p-nitrobenzoates; the hydrocarbon force field used is one of the simplest available; the carbonium ion parameters are an ad hoc set designed to give the best correlation of bridgehead bromide reactivities for the smallest reasonable value of the C–C$^+$–C angle bending force constant; entropy and solvation effects are totally neglected.

At present, though some of these deficiencies cannot be remedied, it would seem that alcohol solvolysis, wherein the substrate contains only one heteroatom, is the reaction that is the most accessible to theoretical treatment and where significant improvements are the most likely to be achieved.

Experimental Section

Alcohol Synthesis. Most tertiary methyl and *tert*-butyl derivatives were synthesized by condensation of the corresponding alkyllithium reagents with the appropriate ketones,[35] obtained commercially or by conventional procedures. Two exceptions were the *exo*-2-norbornanols. The methyl derivative **7a** was prepared by solvolysis of the chloride obtained from the endo alcohol in a simplified Brown machine.[36] The *exo*-2-*tert*-butyl derivative **7b** was obtained by solvolysis of the *endo*-2-*tert*-butyl-2-norbornyl p-nitrobenzoate in aqueous

Table V. Summary of Physical and Microanalytical Data for New Alcohols

		calcd, %		found, %		
compd	formula	C	H	C	H	mp, °C
1a	$C_{16}H_{28}O$	81.29	11.94	81.39	12.08	96–97
1b	$C_{19}H_{34}O$	81.95	12.31	81.84	12.20	105
3b	$C_{14}H_{28}O$	79.18	13.29	79.10	13.04	118–118.5
4a	$C_{10}H_{20}O$	76.86	12.90	76.93	13.06	19.5–20.5
4b	$C_{13}H_{26}O$	78.72	13.21	78.64	13.31	103
8b	$C_{11}H_{20}O$	78.51	11.98	78.42	12.02	68–68.5
10e	$C_{14}H_{24}O$	80.71	11.61	80.71	11.76	57–58
10g	$C_{15}H_{26}O$	81.02	11.79	81.16	11.72	36

acetone as a mixture containing 4% endo alcohol,[12i] whose presence did not interfere with the kinetic measurements. Camphene hydrate (**13a**) was prepared by hydrolysis of camphene hydrochloride.[37]

(1-Adamantyl)di-*tert*-butylcarbinol (1b). This alcohol was obtained by a modification of Pearce's method for one-step alkyllithium synthesis/addition.[38] To finely chopped Li metal (0.14 g, 0.02 g-atom) in ether (15 mL) at −20 °C, under argon and with magnetic stirring, was added over 1 h a solution of di-*tert*-butyl ketone (1.42 g, 0.01 mol) and 1-bromoadamantane (2.15 g, 0.01 mol) in ether (30 mL). After completion of the addition, the cooling bath was removed and stirring was continued overnight. Chromatography on alumina (activity II–III) in petroleum ether–ether mixtures gave the desired alcohol in 44–50% yield.[39] The other products were adamantane and diadamantane.

When di-*tert*-butyl ketone was replaced by pinacolone, only a poor yield (5%) of the corresponding alcohol **1a** resulted; it was therefore prepared conventionally by the addition of MeLi to 1-adamantyl *tert*-butyl ketone.

Melting points and microanalytical data on all new alcohols are given in Table V.

Kinetic Studies. Rate constants were determined as previously described by GLC analysis on SE30, XE60, or Carbowax 20M columns.[5] Short, lightly loaded SE30 columns[40] were employed for the congested alcohols, particularly **1b** and **2b**, in order to avoid thermal decomposition during analysis.[41] Saturated linear hydrocarbons were used as internal standards.

The less congested methyl-substituted carbonium ions derived from alcohols **5a**–**13a** reacted with solvent acetic acid and eventually with water. As dehydration proceeded, the amount of water in the medium ceased to be negligible and reached a level at which reversion of the carbonium ion to the alcohol occurs significantly. This is manifested by a decrease in the reaction rate. By working with initial alcohol concentrations below 0.006 M, it was, however, possible to obtain linear first-order rate plots for at least one half-life even in the most unfavorable cases. All rate constants are based on duplicate or triplicate runs agreeing to better than 5%.

The majority of the alcohol solvolysis rates were determined in anhydrous acetic acid containing 0.006 or 0.03 M sulfuric acid. Alcohols too reactive or too unreactive to be studied under these conditions were only investigated in 0.0003 and 0.182 M solutions, respectively. Where necessary, data were extrapolated to 0.006 M by applying factors corresponding to the mean acidity dependence of the other alcohols. In the upper part of the acidity range (transfer from 0.03 to 0.182 M) there are significant variations in the factor, the higher values being generally associated with the more congested alcohols. The overall errors on extrapolated points are not likely to exceed 0.1 log units. As far as possible the *t*-Bu/Me ratios are based on data obtained at the same acidity or acidities.

Product Studies. In view of the number of compounds investigated in this study, it was impractical to carry out detailed product analyses in all cases. Some idea of the product composition can be obtained, however, by inspection of the GLC results, knowing that alkenes and acetates have retention times lower and higher, respectively, than the parent alcohols. Alcohols **1**–**4a** and **1**–**4b** gave exclusively alkenes. A complete study of **2a** has been reported elsewhere.[5] The remaining *tert*-butyl derivatives, except **6b**, gave presumably rearranged alkenes exclusively; **6b** also gave a product of higher retention time than alcohol. The methyl derivatives **5a** and **7**–**12a** gave acetates either exclusively or as the major product. These acetates had retention times identical with those of authentic samples obtained by treating the alcohols in pyridine with acetyl chloride. The methylcamphenilols **6a** and **13a** yielded predominantly alkenes.

Molecular Mechanics Calculations. Strain energies for alkanes and carbonium ions were calculated on the basis of the Engler–Andose–Schleyer 1973 force field[1c] via the Andose–Mislow program BIGSTRN or STRAIN (available from QCPE, University of Indiana, Bloomington, Indiana 47401). Pattern search minimization was assisted by a methyl group rotation routine.

Registry No.—**1a**, 69429-62-5; **1b**, 66951-98-2; **2a**, 5857-69-2; **2b**, 41902-42-5; **3a**, 29779-72-4; **3b**, 69429-63-6; **4a**, 69429-64-7; **4b**, 69429-65-8; **5a**, 3212-16-6; **5a′**, 13351-30-9; **5b**, 29339-41-1; **5b′**, 52118-14-6; **6a**, 13429-57-7; **6a′**, 13389-76-9; **6b**, 55829-60-2; **6b′**, 55836-06-1; **7a**, 3212-15-5; **7a′**, 22467-58-9; **7b**, 69429-66-9; **7b′**, 52023-06-0; **8a**, 39173-88-1; **8b**, 69429-67-0; **9a**, 33832-25-6; **9a′**, 55829-58-8; **9b**, 42928-50-7; **9b′**, 55829-59-9; **10a**, 702-98-7; **10a′**, 38432-71-2; **10b**, 38424-20-3; **10b′**, 38432-74-5; **10c**, 14648-57-8; **10c′**, 38575-67-6; **10d**, 38432-77-8; **10d′**, 38432-73-4; **10e**, 14648-58-9; **10f**, 38432-76-7; **10f′**, 38432-72-3; **10g**, 64278-80-4; **11a**, 2565-96-0; **12a**, 2371-42-8; **13a**, 13429-40-8; **14a**, 19756-72-0; **14b**, 41327-45-1; **15a**, 19013-42-4; **15b**, 52118-37-3; **16a**, 31058-46-5; **16b**, 52118-38-4; **17a**, 55829-91-9; **17b**, 55829-92-0; di-*tert*-butyl ketone, 815-24-7; 1-bromoadamantane, 768-90-1; 1-adamantyl *tert*-butyl ketone, 31482-45-8; *exo*-2-norbornanol, 497-37-0; *exo*-1,2-dimethyl-2-norbornanol, 23351-29-3; *endo*-2-norbornanol, 497-36-9; *endo*-1,2-dimethyl-2-norbornanol, 13429-45-3.

Supplementary Material Available: Table VI of solvolysis rate constants and strain energy values for alkanes and carbonium ions corresponding to *p*-nitrobenzoates featured in ref 8, 12b–i, and 33 (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Reviewed by (a) N. L. Allinger, *Adv. Phys. Org. Chem.*, **13**, 1 (1976); (b) O. Ermer, *Struct. Bonding* (*Berlin*), **27**, 161 (1976); (c) E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 8005 (1973).

(2) Solvolysis: (a) G. J. Gleicher and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **89**, 582 (1967); (b) W. G. Dauben and C. D. Poulter, *J. Org. Chem.*, **33**, 1237 (1968); (c) P. v. R. Schleyer, P R. Isele, and R. C. Bingham, *ibid.*, **33**, 1239 (1968); (d) S. A. Sherrod, R. G. Bergman, G. J. Gleicher, and D. G. Morris, *J. Am. Chem. Soc.*, **92**, 3469 (1970); (e) R. C. Bingham, W. F. Sliwinski, and P. v. R. Schleyer, *ibid.*, **92**, 3471 (1970); (f) R. C. Bingham and P. v. R. Schleyer, *ibid.*, **93**, 3189 (1971); (g) *Tetrahedron Lett.*, 23 (1971); (h) A. Karim, M. A. McKervey, E. M. Engler, and P. v. R. Schleyer, *ibid.*, 3987 (1971); (i) S. A. Sherrod, R. G. Bergman, G. J. Gleicher, and D. G. Morris, *J. Am. Chem. Soc.*, **94**, 4615 (1972); (j) J. L. Fry, E. M. Engler, and P. v. R. Schleyer, *ibid.*, **94**, 4628 (1972); (k) W. Parker, R. L. Tranter, C. I. F. Watt, L. W. K. Chang, and P. v. R. Schleyer, *ibid.*, **96**, 7121 (1974).

(3) Ester hydrolysis: (a) D. F. DeTar, *J. Am. Chem. Soc.*, **96**, 1254 (1974); (b) D. F. DeTar and C. J. Tenpas, *J. Org. Chem.*, **41**, 2009 (1976); (c) *J. Am. Chem. Soc.*, **98**, 4567 (1976); (d) *ibid.*, **98**, 7903 (1976); (e) D. F. DeTar, *ibid.*, **96**, 1255 (1974); (f) R. E. Winans and C. F. Wilcox, *ibid.*, **98**, 4281 (1976). Ketone reduction: (g) P. Müller and J. C. Perlberger, *Helv. Chim. Acta*, **59**, 1880 (1976). Alcohol oxidation: (h) P. Müller and J. C. Perlberger, *J. Am. Chem. Soc.*, **97**, 6862 (1975); (i) *ibid.*, **98**, 8407 (1976). Secondary tosylate solvolysis: (j) M. R. Smith and J. M. Harris, *J. Org. Chem.*, **43**, 3588 (1978); (k) D. Farcasiu, *ibid.*, **43**, 3878 (1978).

(4) J. Slutsky, R. C. Bingham, P. v. R. Schleyer, W. C. Dickason, and H. C. Brown, *J. Am. Chem. Soc.*, **96**, 1969 (1974).

(5) J. S. Lomas, D. S. Sagatys, and J.-E. Dubois, *Tetrahedron*, **29**, 2157 (1973).

(6) J.-E. Dubois and J. S. Lomas, *Tetrahedron Lett.*, 1791 (1973).

(7) J. S. Lomas, P. K. Luong and J.-E. Dubois, *J. Am. Chem. Soc.*, **99**, 5478 (1977).

(8) (a) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **96**, 263 (1974); (b) *ibid.*, **97**, 2892 (1975).

(9) Strictly speaking, these reactions should be compared in the same solvent, but change of solvent can only affect relative solvolysis rates to the extent that the Grunwald–Winstein *m* values and solvent nucleophilicity effects vary within the substrate series. No such variations are to be anticipated; tertiary carbinyl derivatives solvolyze uniformly via an S_N1 mechanism and should be generally immune to solvent nucleophilicity variations. In agreement with these ideas, the solvolysis rates of alkyldi-*tert*-butyl *p*-nitrobenzoates in acetic acid and aqueous dioxane[6] are linearly correlated with near unit slope.

(10) (a) H. C. Brown, "The Nonclassical Ion Problem", with comments by P. v. R. Schleyer, Plenum Press, New York, 1977, pp 115–118; (b) p 147; (c) pp 139, 149; (d) p 100.

(11) It has been stated[12a–j] that the steric requirements of a variety of common groups, including OH, Me, Ph, $MeCO_2$, and $4-NO_2C_6H_4CO_2$ (OPNB), are similar. The origin of this statement lies in the observation that the equilibrium data for 2-norbornanols[12k] and their acetates[12l] are similar and that the equilibrium epimer ratios for Me- and Ph-substituted 2-norbornanols are not very far from unity.[12a] However, the norbornane structure itself is not very demanding sterically.[10b] Differences in the steric requirements of the above groups are going to be accentuated in the more congested environment created by a *tert*-butyl group.

(12) (a) H. C. Brown and M. H. Rei, *J. Am. Chem. Soc.*, **88**, 5335 (1966); (b) H. C. Brown and W. J. Hammar, *ibid.*, **89**, 6378 (1967); (c) H. C. Brown, I. Rothberg, and D. L. Vander Jagt, *ibid.*, **89**, 6380 (1967); (d) K. Takeuchi and H. C. Brown, *ibid.*, **90**, 6216 (1968); (e) H. C. Brown and S. Ikegami, *ibid.*, **90**, 7122 (1968); (f) S. Ikegami, D. L. Vander Jagt, and H. C. Brown, *ibid.*, **90**, 7124 (1968); (g) H. C. Brown, D. L. Vander Jagt, P. v. R. Schleyer, R. C. Fort, and W. E. Watts, *ibid.*, **91**, 6848 (1969); (h) H. C. Brown and D.

L. Vander Jagt, *ibid.*, **91,** 6850 (1969); (i) E. N. Peters and H. C. Brown, *ibid.*, **96,** 265 (1974); (j) H. C. Brown, S. Ikegami, K. T. Liu, and G. L. Tritle, *ibid.*, **98,** 2531 (1976); (k) F. Wilcox, M. Sexton, and M. F. Wilcox, *J. Org. Chem.*, **28,** 1079 (1963); (l) H. L. Goering and C. B. Schewene, *J. Am. Chem. Soc.*, **87,** 3516 (1965).

(13) We are indebted to Professor P. v. R. Schleyer for this suggestion and for preliminary calculations (with D. Khoury) on **2**.

(14) (a) Reviewed by V. F. Nowlan and T. T. Tidwell, *Acc. Chem. Res.*, **10,** 252 (1977); (b) see also D. S. Noyce, D. R. Harrter, and R. M. Pollack, *J. Am. Chem. Soc.*, **90,** 3971 (1968).

(15) (a) The ρ^+ values for the dehydration of arylcarbinols are uniformly high, close to the carbonium ion value: 1,2-diphenylethanols,[14b] −4.3; *o*-tolyldi-*tert*-butylcarbinols,[16a] −4.2 (anti), −3.9 (syn); phenyldi-*tert*-butylcarbinols,[16a,b] −3.9. These data refute the recent suggestion[16c] that the differences between *t*-Bu/Me ratios in alcohols and *p*-nitrobenzoates are due to an early transition state in the former reaction. (b) The question of possible steric effects upon the preequilibrium,[16d] though interesting, is not relevant to the EFF approach.

(16) (a) J. S. Lomas and J-E. Dubois, *Tetrahedron*, **34,** 1597 (1978); (b) *Tetrahedron Lett.*, 407 (1976); (c) R. C. Badger and J. L. Fry, *J. Am. Chem. Soc.*, in press; (d) T. T. Tidwell, *Tetrahedron*, **34,** 1855 (1978).

(17) A good account of the hazards involved in trying to interpret solvolysis rates by strain energy calculations is given by N. L. Allinger and G. A. Lane, *J. Am. Chem. Soc.*, **96,** 2937 (1974).

(18) (a) N. L. Allinger, *J. Am. Chem. Soc.*, **99,** 8127 (1977); (b) L. S. Bartell, *ibid.*, **99,** 3279 (1977); (c) D. N. J. White and M. J. Bovill, *J. Chem. Soc., Perkin Trans. 2,* 1610 (1977).

(19) N. L. Allinger and D. Y. Chung, *J. Am. Chem. Soc.*, **98,** 6798 (1976).

(20) (a) E. M. Engler, M. Farcasiu, A. Sevin, J. M. Cense, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95,** 5769 (1973); (b) T. M. Gund, P. v. R. Schleyer, P. H. Gund, and W. T. Wipke, *ibid.*, **97,** 743 (1975).

(21) A possible reason for this anomaly lies in the fact that the carbonium ion of lowest energy, according to molecular mechanics, does not have the same conformation as the most stable hydrocarbon. Carbonium ion formation in this case may therefore require greater energy than is indicated by the strain energy calculation since a small additional rotational barrier has to be overcome. Nevertheless, the corresponding *p*-nitrobenzoate is well-correlated.

(22) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77,** 4183 (1955); (b) S. Winstein, F. Gadient, E. T. Stafford, and P. E. Klinedinst, *ibid.*, **80,** 5895 (1958); (c) P. v. R. Schleyer and R. D. Nicholas, *ibid.*, **83,** 182 (1961); (d) P. G. Gassman and J. M. Pascone, *ibid.*, **95,** 7801 (1973).

(23) See S. P. McManus and J. M. Harris, *J. Org. Chem.*, **42,** 1422 (1977).

(24) H. Tanida and T. Tsushima, *J. Am. Chem. Soc.*, **92,** 3397 (1970).

(25) R. Hoffmann, P. D. Mollère, and E. Heilbronner, J. Am. Chem. Soc., **95,** 4860 (1973).

(26) The steric energy components would be slightly different if a Newton–Raphson minimization procedure had been used: J. M. A. Baas, B. van de Graff, A. van Veen, and B. M. Wepster, *Tetrahedron Lett.*, 819 (1978).

(27) Internal angles are systematically smaller for *t*-Bu than for Me derivatives by 0.7–1.6° depending on the system.

(28) MINDO/3 calculations err in the other direction, finding that the 7-norbornyl cation is 3.1 kcal mol^{-1} more stable than the 2-cation: W. L. Jorgensen, private communication quoted by P. v. R. Schleyer.[10d]

(29) This approach avoids problems arising out of the eventual contribution of polar effects to the dehydration rates. Alkyl group polar effects are considered by some to be constant, whereas others maintain that Taft's σ^* scale expresses real differences in the abilities of alkyl groups to stabilize electron-deficient centers; see (a) M. Charton, *J. Am. Chem. Soc.*, **99,** 5687 (1977); (b) J. A. MacPhee and J.-E. Dubois, *Tetrahedron Lett.*, 2225 (1978).

(30) C. A. Bunton, K. Khaleeluddin, and D. Whittaker, *Tetrahedron Lett.*, 1825 (1963). For the corresponding *p*-nitrobenzoates in 60% aqueous dioxane at 50 °C, the ratio is 565.[31] That for 2-methyl-2-norbornyl *p*-nitrobenzoates under the same conditions is given as 86, a value differing by a factor of 10 from the currently accepted value in 80% aqueous acetone at 25 °C.

(31) H. C. Brown, F. J. Chloupek, and M. H. Rei, *J. Am. Chem. Soc.*, **86,** 1248 (1964).

(32) The data given as "strain engeries" in ref 2j are "steric energies" according to the more recent definition[1c] and, as such, are underestimated. Schleyer's customary force field was not, however, used in the 1972 publication.

(33) H. C. Brown and M. Ravindranathan, *J. Am. Chem. Soc.*, **100,** 1865 (1978).

(34) Details of these calculations are given in the supplementary material.

(35) Alcohols which are neither new nor discussed below are described elsewhere: **2a,** M. S. Newman, A. Arkell, and T. Fukunaga, *J. Am. Chem. Soc.*, **82,** 2498 (1960); **2b,** P. D. Bartlett and E. B. Lefferts, *ibid.*, **77,** 2804 (1955); **3a,** E. Lunt and W. R. Wragg, *J. Chem. Soc. C,* 1845 (1970); **5, 6, 9,** and **10,** ref 8b and references therein; **8a,** R. K. Bly and R. S. Bly, *J. Org. Chem.*, **28,** 3165 (1963); **11a,** W. Kraus and R. Dewald, *Justus Liebigs Ann. Chem.*, **689,** 21 (1965); **12a,** M. L. Capmau, W. Chodkiewicz, and P. Cadiot, *Tetrahedron Lett.*, 1619 (1965).

(36) H. C. Brown and M. H. Rei, *J. Org. Chem.*, **31,** 1090 (1966).

(37) H. Meerwein and K. van Emster, *Chem. Ber.*, **53,** 1815 (1920).

(38) P. J. Pearce, D. H. Richards, and N. F. Scilly, *J. Chem. Soc., Perkin Trans. 1,* 1655 (1972).

(39) This compound has also been prepared by the addition of preformed 1-AdLi to di-*tert*-butyl ketone: G. Molle, J.-E. Dubois, and P. Bauer, *Synth. Commun.*, **8,** 39 (1978).

(40) J. S. Lomas, P. K. Luong, and J.-E. Dubois, *J. Org. Chem.*, **42,** 3394 (1977).

(41) J. S. Lomas and J.-E. Dubois, *J. Org. Chem.*, **39,** 1776 (1974).

Basicity Measurements in Aqueous–Organic Solvents. 1. The 20% Ethanol–Aqueous Sulfuric Acid System

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The acidity functions H_0, H_{azo}, H_{dip}, H_{GF}, and H_A have been compared in the solvent 20% ethanol–aqueous sulfuric acid. They are all linearly related according to the $(H_X + \log c_{H^+}) = (1 - \phi_e)(H_0 + \log c_{H^+})$ relationship. The thermodynamic pK_{XH^+} values can be estimated for every base, even for those whose acidity function is unknown, by applying also in this solvent the Bunnett–Olsen equation. The protonation data of dimethyl ether and dimethyl sulfide show that the pK_{XH^+} value is not sufficient to define the protonation equilibrium of weak bases. In fact, the inversion of basicity order that occurs in going from dilute ($Me_2O > Me_2S$) to more concentrated ($Me_2S > Me_2O$) acid solutions can be accounted for only through the solvation parameter ϕ_e. Comparison of the ϕ_e values shows that the differentiation among acidity functions occurs because of differences in onium ion solvation energies, the number of hydrogen bonding sites making only a second-order contribution. For the same compound, the protonation parameters are in the mixed solvent only slightly different (pK_{XH^+} more negative, ϕ_e more positive) from those evaluated in aqueous acid solutions.

Acids in ethanol–water or dioxane–water have often been used to evaluate the basic properties of organic substrates sparingly soluble in purely aqueous media.[1] The practical importance of these systems notwithstanding, very limited attempts have been made to apply to mixed solvents the same unifying theories[2,3] that have considerably simplified the interpretation of acid–base equilibria in water. There is a general agreement[2-6] that, in water, the activity coefficients of the species involved in the protonation equilibrium of two bases X and B are linked through the following linear free-energy relationship:

$$\log (f_X f_{H^+}/f_{XH^+}) = (1 - \phi_e) \log (f_B f_{H^+}/f_{BH^+}) \qquad (1)$$

Equation 1 is easily rearranged in a form amenable to direct experimental verification by combining it with the equilibrium constant for the protonation of the base X ($XH^+ \rightleftarrows X + H^+$)

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