sulfuric acid at 25° ^{18}O exchange, found only at the benzhydryl oxygen, was 50% complete in 5 min, conditions under which no detectable rearrangement reaction occurs.

The Neopentyl System. The neopentyl system is one that appears *per se* much more likely to involve methyl participation. Table II lists observed rate constants for solvolysis of α-methylneopentyl brosylate and its γ-d_9 derivative (93.7% isotopically pure). There is practically no isotope effect, even in the weakly basic 95% trifluoroacetic acid, which should favor the direct formation of the intrinsically more stable rearranged tertiary carbonium ion.[9,10] Insofar as rate-controlling synchronous methyl migration might be expected to give the same sort of appreciable positive kinetic isotope effect as found above for a rate-controlling nonsynchronous methyl migration, the results would indicate that methyl migration occurs after the rate-controlling step. However, this is yet to be fully determined by a comparison of kinetic isotope effects *and* product ratios, now being carried out on γ-deuterated neopentyl p-nitrobenzenesulfonates.

(9) V. J. Shiner, Jr., R. Fisher, and W. Dowd, *J. Am. Chem. Soc.*, **91**, 7748 (1969), report $k_H/k_{\gamma\text{-}d_9}$ values very slightly greater than unity in three solvents. On this and other evidence, they have independently concluded that rearrangement follows rate-controlling ion pair formation. We are grateful to Professor Shiner for communication of this work prior to publication.

(10) For solvolysis of γ-deuterated alkyl methanesulfonates in water, Robertson reports k_H/k_D: neopentyl (1.017), isobutyl (0.968), and propyl (0.924).[11]

(11) M. J. Blandmer and R. E. Robertson, *Can. J. Chem.*, **42**, 2137 (1964); K. T. Leffek, J. A. Llewellyn, and R. E. Robertson, *J. Am. Chem. Soc.*, **82**, 6315 (1960).

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Enhancement of Solvolysis Rates by Wagner–Meerwein Rearrangements of Ion Pairs

Sir:

The detection of a large ratio of ion-pair return to solvolysis for isopropyl cation–brosylate tight ion pairs in trifluoroacetic acid (TFA) at 25°[1] emphasizes the necessity to estimate ionization rates *in the absence of internal return* in order to distinguish between acceleration due to participation in ionization and acceleration due to participation *after* ionization. We wish to propose that 3,3-dimethyl-2-butyl ("pinacolyl") brosylate is a useful reference compound to estimate unassisted ionization rates of secondary brosylates in the absence of return.

t-Butylethylene (0.1 M) in trifluoroacetic acid at 12° reacts with p-bromobenzenesulfonic acid (HOBs, 0.125 M) so rapidly that within 20 sec after mixing the nmr spectrum shows no proton resonances except those due to (rearranged) 2,3-dimethyl-2-butyl trifluoroacetate. No pinacolyl brosylate is detected even though its half-life under these conditions is ~16 sec. t-Butylethylene reacts with trifluoroacetic acid at 25° with a first-order rate constant some ten times that of propene; only a few per cent of unrearranged secondary ester is produced. These results are consistent with the pinacolyl cation rearranging to the 2,3-dimethyl-2-butyl cation in the tight ion pair in TFA faster than it combines with the brosylate counterion. Thus, in the trifluoroacetolysis of pinacolyl brosylate the formation of the tight ion pair is rate determining while with isopropyl brosylate the *dissociation* of the tight ion pair is rate determining. This explains why the pinacolyl compound solvolyzes ~2800 times faster than isopropyl brosylate in TFA. This acceleration is not due to participation in ionization since, as reported above, the addition of trifluoroacetic acid to the corresponding alkene is only accelerated by a factor of about 10 as expected from a normal inductive effect. The fact that the products are almost exclusively those of Wagner–Meerwein rearrangement confirms that, as expected, these electrophilic additions involve carbonium ion type intermediates. The deuterium isotope effects for the solvolysis of pinacolyl brosylate in trifluoroethanol–water and ethanol–water solvents (Table I) also indicate that ionization without participation is the rate-determining step.

Table I. Deuterium Effects in Solvolysis of 3,3-Dimethyl-2-butyl Brosylates at 25°[a]

Solvent[b]	$k_H/k_{\alpha\text{-}d}$	$k_H/k_{\beta\text{-}d_3}$	$k_H/k_{\gamma\text{-}d_9}$
97 T	1.153	1.188	1.011
70 T	1.152	1.205	
50 E	1.159	1.205	1.003

[a] From rates determined conductometrically. [b] 97 T is 97% trifluoroethanol–3% water; 50 E is 50 vol % ethanol–50 vol % water, etc.

The α-d and β-d_3 effects are not strongly solvent dependent and are both smaller than the limiting values[1,2] of 1.22 and 1.46, consistent with some nucleophilic attachment of the leaving group in the transition state. The γ-d_9 effect is very small, indicating that there is no migration of the methyl group in the rate-determining step.[3]

Table II. Solvolysis Rate Constants[a] for Isopropyl ($k_{i\text{-Pr}}$) and 3,3-Dimethyl-2-butyl (k_{Pin}) Brosylates

Solvent[b]	$k_{i\text{-Pr}}$	k_{Pin}	$k_{i\text{-Pr}}/k_{\text{Pin}}$	$k_H/k_{i\text{-P-}\alpha\text{-}d}$
TFA	1.5[c]	4200[d]	0.00036	1.22[e]
97 T	0.1075	7.98	0.026	1.16
70 T	1.41	10.64	0.107	1.140
50 T	1.833	16.56	0.172	1.122
50 E	7.20	10.11	0.714	1.114
80 E	1.447	0.6357	2.27	1.098
90 E	0.636	0.190[f]	3.35	1.083

[a] Units of 10^{-5} sec^{-1} at 25° determined conductometrically. [b] See footnote *b*, Table I. [c] Estimated for 12° by extrapolation from the rate at 25°. [d] Value determined by nmr at 12°. [e] Value at 25° from ref 2. [f] Estimated from a plot of log k *vs.* Y.

The smaller isotope effects for isopropyl brosylate solvolysis in TFE–water solvents (Table II) can be

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(1) V. J. Shiner, Jr., and W. Dowd, *J. Amer. Chem. Soc.*, **91**, 6528 (1969).

(2) A. Streitwieser, Jr., and G. A. Dafforn, *Tetrahedron Letters*, 1263 (1969).

(3) Professor W. M. Schubert and P. N. LeFevre have also independently observed the absence of a significant γ-d_9 effect in the 50% aqueous ethanolysis and the 95% aqueous trifluoroacetolysis of pinacolyl brosylate and have also interpreted this as indicating the absence of participation in ionization.[4] We are grateful to Professor Schubert for the communication of these results prior to publication.

(4) P. H. LeFevre, Ph.D. Thesis, University of Washington, 1968; W. M. Schubert and P. H. LeFevre, *J. Amer. Chem. Soc.*, **91**, 7746 (1969).

Table III. Solvolysis Rates of Alkyl Brosylates Relative to Pinacolyl Brosylate at 25°

Alkyl brosylate	Solvent[a] 70 E	70 T	97 T	HOAC	HCOOH	TFA
Isopropyl	1.47[n]	0.11	0.025	0.344[b]	0.071[b]	0.00036[c]
sec-Butyl	2.1[n]	0.25[d]	0.07[n]	0.79[b]	0.177[b]	0.0021[c,l]
3-Methyl-2-butyl		1[d]	0.61[d]	2.1[b]	1[b]	
Cyclopentyl	16[e]			9.03[f]	0.91[m]	0.094[c,m]
Cyclohexyl	0.64[n]	0.14[g]	0.056[n]	0.246[h]	0.12[h]	0.0128[c,g]
exo-Norbornyl	153[i]			128[j]		
3-Phenyl-2-butyl				0.341[b,k,o]	0.43[b,k,p]	0.13[c,k,l]

[a] E = per cent ethanol as volume per cent in ethanol–water mixtures; T = per cent trifluoroethanol as weight per cent in trifluoroethanol–water mixtures; HOAC = acetic acid; TFA = trifluoroacetic acid. [b] S. Winstein and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1120 (1952). [c] Reference 1. [d] Dr. M. A. Kessick, unpublished results. [e] Private communication from Professor J. O. Stoffer. [f] H. C. Brown and G. Ham, *J. Am. Chem. Soc.*, **78**, 2735 (1956). [g] W. Dowd, unpublished results. [h] S. Winstein, *et al.*, *J. Am. Chem. Soc.*, **74**, 1127 (1952). [i] Value refers to 80 E; private communication from Professor B. L. Murr, Jr. [j] S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1154 (1952). [k] J. A. Thompson and D. J. Cram, *ibid.*, **91**, 1778 (1969). [l] P. E. Peterson, *et al.*, *ibid.*, **87**, 5169 (1965). [m] D. D. Roberts and W. Hendrickson, *J. Org. Chem.*, **34**, 2415 (1969). [n] R. D. Fisher, unpublished results. [o] S. Winstein, *et al.*, *J. Am. Chem. Soc.*, **74**, 1113 (1952). [p] S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2165 (1952).

explained on the basis of some nuceophilic attachment in the transition state either of the leaving group or the incoming group, depending on whether formation of or nucleophilic attack on the tight ion pair is determining. In solvents which show rate ratios for isopropyl brosylate to pinacolyl brosylate between 0.2 and 0.1 the formation of the tight isopropyl cation–brosylate ion pairs is probably largely rate determining, with nucleophilic attack on them being fast. The $k_{i\text{-Pr}}/k_{\text{Pin}}$ ionization rate ratio is expected to be somewhat solvent dependent because of steric inhibition of solvation or solvent enhancement of hyperconjugation.[5,6] However, in 50, 80, and 90 vol % ethanol–water solvent the α-d effect is sufficiently low to indicate a significant S$_N$2 component, consistent with the larger solvolytic rate ratios.

In Table III are listed some solvolysis rates of several secondary brosylates relative to pinacolyl brosylate in various solvents. The number of β-alkyl groups varies from 0 to 3 so the inductive effect on the rates may contribute a factor from 0.5 to 0.1. However, rate ratios less than about 0.1 definitely indicate significant internal return, and those higher than 1 indicate the dominance of some cause of acceleration such as internal strain energy release, S$_N$2 attack, or participation in ionization.

In this analysis, *exo*-norbornyl brosylate shows significant acceleration to ionization as does the 3-phenyl-2-butyl brosylate if an appreciably retarding inductive effect is attributed to the phenyl ring. 3-Methyl-2-butyl brosylate is borderline and cyclohexyl brosylate is not accelerated. Of course, a compound could show both acceleration to ionization *and* internal return as *exo*-norbornyl and 3-phenyl-2-butyl brosylates apparently do. The actual acceleration of ionization is then correspondingly larger than the rate ratio relative to pinacolyl brosylate. Cyclopentyl *ionization* is probably accelerated, as indicated by the faster relative solvolysis rate in ethanol–water and acetic acid; the lower solvolysis rate in trifluoroacetic acid is probably due, as in the case of isopropyl brosylate, to an increasing proportion of internal return in the solvent of low nucleophilicity and low dielectric constant.

The rate ratios for isopropyl brosylate relative to pinacolyl brosylate in acetic (0.344) and formic (0.071) acids indicate relatively little internal return for the isopropyl compound in these solvents; these reactions must, therefore, largely involve rate-determining formation of the tight ion pair followed by rapid solvent nucleophilic attack or possibly, in the case of formic acid, rapid dissociation. Attack by formic acid appears slower (more internal return, smaller ratio) than attack by acetic acid, as expected, but, surprisingly, both carboxylic acids seem to be more effective in reducing internal return than trifluoroethanol. Other reports[7] indicate that trifluoroethanol may be a poorer nucleophile than acetic acid.

(5) W. M. Schubert and W. A. Sweeney, *J. Org. Chem.*, **21**, 119 (1956); D. F. Gurka and W. M. Schubert *J. Org. Chem.*, **31**, 3416 (1966).

(6) V. J. Shiner, Jr., and C. J. Verbanic, *J. Am. Chem. Soc.*, **79**, 369 (1957).

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(7) W. S. Trahanovsky and M. P. Doyle, *Tetrahedron Letters*, 2155 (1968).

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Structure and Stereochemistry of a Cobalt(III)–Diethylenetriaminepentaacetic Acid Complex

Sir:

The literature abounds with reports of metal–diethylenetriaminepentaacetic acid (DTPA) complexes (H_5-DTPA = $(HO_2CCH_2)_2NCH_2CH_2N(CH_2CO_2H)CH_2CH_2$-$N(CH_2CO_2H)_2$), and it is well known that the potentially octadentate DTPA ligand forms very stable complexes with many metal ions.[1] However, this earlier work has revealed little information, apart from their stoichiometries, about the structures and stereochemistries of these complexes in solution. For most DTPA complexes many geometrical isomers are possible. We have recently isolated a cobalt(III)–DTPA complex[2] and have determined its structure (and stereochemistry)

(1) For example, see L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964, p 693.

(2) Several Co(III)–DTPA complexes have been isolated and a full description of these will be reported subsequently.