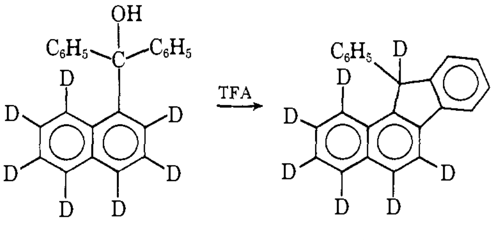
Similar studies with diphenyl-α-naphthylcarbinol (VI)[11] which cyclizes quantitatively in refluxing TFA-*d* to 9-phenyl-1,2-benzfluorene[12] (VII) only after *ca.* 6 hr demonstrated that the final isomerization was ≥92% intramolecular (by nmr integration of the C_9-methine and aromatic proton signals, and also by mass spectrometry[13]). The intermediacy of an isofluorene analogous to II was verified by noting that diphenyl-α-(naphthyl-d_7)carbinol cyclized and rearranged in TFA with at least 60% deuterium shift to C_9 in VII. The decrease in intramolecularity when deuterium is in the substrate rather than solvent parallels Cram's results with 3-phenyl-1-butene-3-*d*.[1]



The above experiments suggest that 1,3-hydrogen transfer in the isofluorene–fluorene isomerization can be accomplished by trifluoroacetate,[3a] in spite of the opportunity for intermolecular pathways such as depicted in Scheme II.[14] Apparently hydrogen-bonded delocalized carbanions, from ionization of the isofluorenes, collapse before exchange with neighboring solvent molecules.[1] This appears reasonable, since the latter would probably not closely interact with the nonpolar hydrocarbon acid.

Additional examples of the generation and fate of isofluorenes during cationic cyclizations to fluorene derivatives and further mechanistic details will be presented in our complete paper.

Acknowledgment. We are grateful to the U. S. Army Research Office (Durham) for partial support and to Dr. Norman R. Mancuso of Massachusetts Institute of Technology for the mass spectral analyses.

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[11] S. T. Bowden, W. L. Clarke, and W. E. Harris, *J. Chem. Soc.*, 874 (1940).

[12] A. Guyot and A. Kovache, *Compt. Rend.*, **155**, 838 (1912).

[13] Some polydeuterated species were present in small amount, since the prolonged reaction time for VI apparently allowed some aryl H–D exchange.

[14] Our labeling results could be explained if initial protonation of II occurred instead at the 1 position of the naphthalene, followed by exclusive 1,3-hydride shift of the rearranging hydrogen (rather than the more probable 1,2 shift) before deprotonation. We regard this possibility as highly improbable, especially upon inspecting molecular models.

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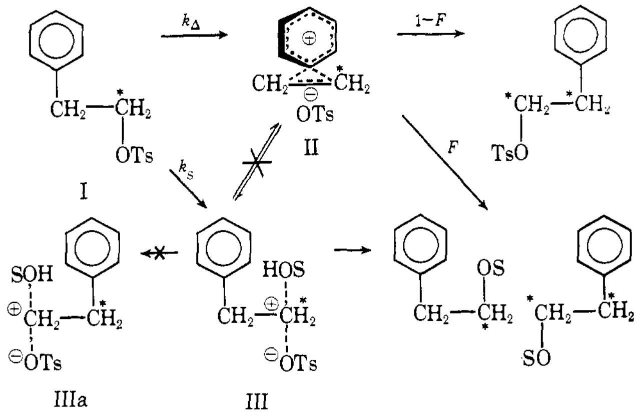
Correlation of k_Δ and k_s in Solvolysis of 2-Phenylethyl Toluenesulfonate[1]

Sir:

For some years we have discussed solvolysis of 2-phenyl-1-ethyl OTs (PhEtOTs) and related systems[2] which are marginal with respect to neighboring phenyl participation in terms of a competition between anchimerically unassisted ionization (k_s) and anchimerically assisted ionization (k_Δ). The latter leads to the "nonclassical" phenyl-bridged or "ethylene phenonium"[3] cation. The two modes of ionization are associated with characteristically different $\Delta S^{\ddagger}$,[2c] β-D isotope effects,[4] phenyl substituent effects, and response to solvent nucleophilicity and ionizing power. From kinetic criteria the k_Δ/k_s ratio in solvolysis of PhEtOTs is judged[2b,c] to be low in EtOH and AcOH and substantial in HCOOH. For 2-*p*-anisyl-1-ethyl OTs (AnEtOTs), with a *p*-MeO group accelerating k_Δ substantially and k_s only slightly, the kinetic criteria[2c] indicate k_Δ/k_s is *ca.* 1 in EtOH and high in both AcOH and HCOOH. In typical solvolysis of such simple primary systems leakage between intermediate III associated with k_s and the bridged ion II or the rearranged open ion IIIa is negligible, so that product composition[2d,5] (or product stereochemistry) from suitably labeled starting material seems to be well correlated with the proportions of k_Δ and k_s.

In our earlier work, EtOH, AcOH, and HCOOH proved to be instructive and useful solvents, with the sequence of k_Δ/k_s ratios in solvolysis of marginal 2-phenylethyl systems being EtOH < AcOH < HCOOH. Quite recently, CF_3COOH, with its very low nucleophilicity and relatively high ionizing power, has become an important solvolyzing solvent which gives rise to k_Δ/k_s ratios much higher than in HCOOH. Thus, Nordlander[6a] has observed that PhEtOTs solvolyzes more than a thousand times as rapidly as does EtOTs in CF_3COOH and leads to completely scrambled product. Consistently, Snyder[6b] has shown that the stereochemical result of such trifluoroacetolysis of 1,2-dideuterio-PhEtOTs leads to complete retention of configuration in the product (*threo*-ROTs → *threo*-$ROCOCF_3$).



An interesting and crucial test of the above mechanistic analysis of the solvolysis of PhEtOTs may be based on the quantitative trends shown by the derived k_Δ and k_s values as solvent is varied. On the basis of the mechanistic significance assigned to k_Δ, we should ex-

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[1] Research sponsored by the National Science Foundation.

[2] S. Winstein, *et al.*: (a) *Bull Soc. Chim. Fr.*, **18**, 55 (1951); (b) *J. Amer. Chem. Soc.*, **75**, 147 (1953); (c) *ibid.*, **78**, 4801 (1956); (d) *Helv. Chim. Acta*, **41**, 807 (1958); (e) *J. Amer. Chem. Soc.*, **86**, 2071 (1964); (f) *ibid.*, **87**, 3504 (1965).

[3] (a) D. J. Cram, *ibid.*, 71, 3863 (1949); (b) D. J. Cram, *ibid.*, **86**, 3767 (1964); (c) D. J. Cram and J. A. Thompson, *ibid.*, **89**, 6766 (1967).

[4] (a) W. H. Saunders, *et al.*, *ibid.*, **80**, 242 (1958); (b) *ibid.*, **82**, 3586 (1960).

[5] C. C. Lee, *et al.*, *Can. J. Chem.*, **35**, 1417 (1957); *Tetrahedron*, **7**, 206 (1959).

[6] (a) J. E. Nordlander and W. G. Deadman, *Tetrahedron Lett.*, 4409 (1967), *J. Amer. Chem. Soc.*, **90**, 1590 (1968); (b) R. J. Jablonski and E. I. Snyder, *Tetrahedron Lett.*, 1103 (1968).

pect a quantitative correlation of k_Δ values with solvolysis rates (k_t) of neophyl OTs,[7] for which it is agreed[8] that ionization occurs with phenyl participation at a rate equal to k_t and dependent on solvent ionizing power but not nucleophilicity. On the other hand, the k_s process should depend on a blend of nucleophilicity and ionizing power for which the simple primary ethyl tosylate (EtOTs) should be a rather good model. Thus, k_s would be expected to correlate rather well with k_t values for EtOTs. We are now able to report the results of this kind of analysis for solvolysis of PhEtOTs in EtOH, AcOH, HCOOH, and CF_3COOH.

In Table I are listed solvolysis rate constants (k_t) for PhEtOTs, as well as for EtOTs and neophyl OTs, in all four solvents. In Table II are listed k_Δ and k_s values for PhEtOTs. In EtOH and HCOOH, these are based on k_t and Lee's observations on scrambling during solvolysis of labeled material.[5] In AcOH, they are based on Coke's recent elegant determination[9a] of F, k_Δ, and k_s, where $(1 - F)$ represents the fraction of ion pair return associated with the k_Δ process. Assuming Fk_Δ leads to retention of configuration and k_s to inversion, Snyder[9b] has observed good agreement between Coke's rearrangement results and his own observations on stereochemistry of acetolysis of PhEtOTs. In CF_3COOH, as is clear from Tables I and II, we observe quite extensive ion-pair return during solvolysis of $C_6H_5CD_2OTs$, the ionization rate constant (k_Δ) being *ca.* 2.9 times k_t (F = *ca.* 0.35).

Table I. Some Solvolysis Rates (k_t) at 75.0° (0.01 M ROTs)

Solvent	10^6k, sec^{-1} Neophyl OTs	EtOTs	PhEtOTs	PhEt/Et
EtOH	5.23	29.8[e]	7.08[d]	0.24
AcOH	20.0[7a]	0.772[e]	0.288[d]	0.37
HCOOH	3000[b]	18.9[e]	39.4[d]	2.1
CF_3COOH	1.12×10^5 [c]	0.226	401[a]	1770

[a] 401 ± 22 (lit.[6a] 322); k_t for $C_6H_5CH_2CD_2OTs$, 316 ± 13, lower by a factor of 1.27. [b] Extrapolated from values of 2.3×10^{-4} sec^{-1} at 50.0° and 1.16×10^{-5} sec^{-1} at 25.0°. [c] Extrapolated from values of 1.00×10^{-3} sec^{-1} at 25.0° and 4.97×10^{-5} sec^{-1} at 0.0°. [d] S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *J. Amer. Chem. Soc.*, **75**, 147 (1953). [e] S. Winstein and H. Marshall, *ibid.*, **74**, 1120 (1952).

As is evident from Figure 1, log k_t for PhEtOTs is not linear in log k for the neophyl ester. As expected, however, a good linear free energy correlation exists between log k_Δ for PhEtOTs and log k for the neophyl analog. The slope of the least-squares line is 1.02, this line reproducing the four k_Δ points with a mean deviation of 0.050 log unit. Similarly, it is seen in Figure 2 that a linear free energy correlation exists between log k_s for PhEtOTs and log k for EtOTs. The slope of the least-squares line is 0.987 and this line reproduces the AcOH, HCO_2H, and EtOH points with a mean deviation of 0.018 log unit. With the aid of this line an extrapolated value of 5×10^{-8} sec^{-1} may be obtained for k_s of PhEtOTs in CF_3COOH, (k_Δ/k_s) being 23,000 in this solvent.

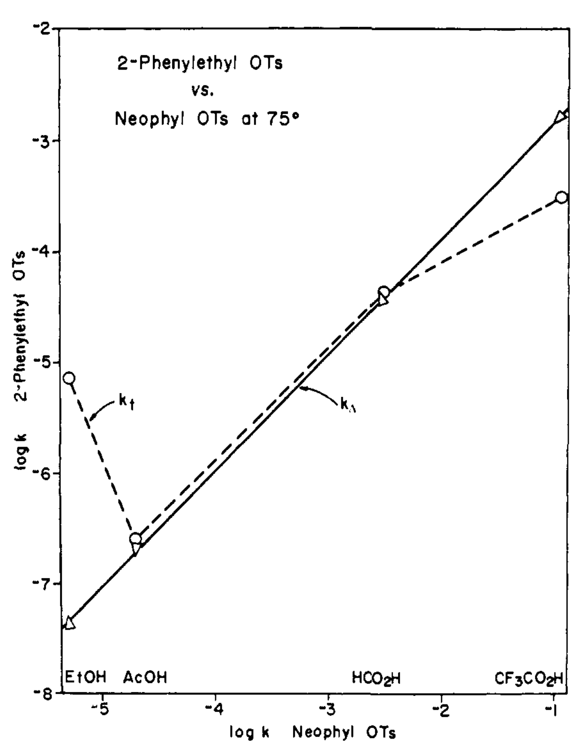

Figure 1.

Table II. k_Δ and k_s Values in Solvolysis of $C_6H_5CH_2CH_2OTs$ at 75.0°

Solvent	10^6k_Δ, sec^{-1}	10^6k_s, sec^{-1}	k_Δ/k_s
EtOH	0.042[a]	7.04	0.006
AcOH	0.215[b]	0.186[c]	1.2
HCOOH	35.4[d]	3.94	9
CF_3COOH	1160[e]	(0.05)[f]	23,000

[a] 0.6%[5] of 7.08. [b] Extrapolated from Coke's values[9a] of 1.29×10^{-5} sec^{-1} at 115° and 1.18×10^{-6} sec^{-1} at 90°. [c] Extrapolated from Coke's values[9a] of 7.93×10^{-6} sec^{-1} at 115° and 8.92×10^{-7} sec^{-1} at 90°. [d] 90%[5] of 39.4. [e] Based on value of $(9.12 \pm 0.16) \times 10^{-4}$ sec^{-1} for the total scrambling rate constant determined by nmr on 0.4 M $C_6H_5CH_2CD_2OTs$ from the decrease of the area of combined β-proton signals in the ROTs (δ 2.55 ppm) and the $ROCOCF_3$ (δ 2.67 ppm) from that for two protons to one; this value multiplied by 1.27 for the assumed isotope effect. [f] Value from plot of log k_s *vs.* log k_t for EtOTs in Figure 2.

The present results obviously support the description of PhEtOTs solvolysis on the basis of discrete k_Δ and k_s processes. As far as data are available, the correlation of k_Δ with k_t for neophyl OTs is also successful for 2-*p*-anisylethyl,[2d,10a,d] 1-phenyl-2-propyl,[10c,d,11] and

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(7) (a) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2763 (1956); (b) R. Heck and S. Winstein, *ibid.*, **79**, 3432 (1957); (c) A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1608 (1957).

(8) H. C. Brown, *et al.*: (a) Special Publication No. 16, The Chemical Society, London, 1962, p 140; (b) *J. Amer. Chem. Soc.*, **87**, 1280 (1965); (c) *ibid.*, **87**, 2137 (1965); (d) *ibid.*, **89**, 370 (1967); (e) *ibid.*, **90**, 2082 (1968).

(9) (a) J. L. Coke, *et al.*, *ibid.*, in press; we are indebted to Dr. Coke for discussion and information prior to publication; (b) E. I. Snyder, private communication.

(10) (a) S. Winstein, James Flack Norris Award Address, 153rd National Meeting of the American Chemical Society, Miami, Fla., April 1967; (b) S. Winstein and K. C. Schreiber, *J. Amer. Chem. Soc.*, **74**, 2165 (1952); (c) S. Winstein, *et al.*, *ibid.*, **74**, 1140 (1952); S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2171 (1952); (d) A. Diaz, unpublished work.

(11) We have learned from Professor Paul Schleyer of Princeton University that our picture for solvolysis of this system has been confirmed in his laboratory. By estimation of k_s from a $\rho\sigma$ line for electron-attracting substituents which make k_Δ negligible, $k_\Delta F$ for the unsubstituted 1-phenyl-2-propyl system can be evaluated as that part of the solvolysis rate in excess of k_s. His results for acetolysis and formolysis agree with our reported stereochemical results[10c] on the assumption that k_s leads to inversion and k_Δ leads to retention. See C. G.

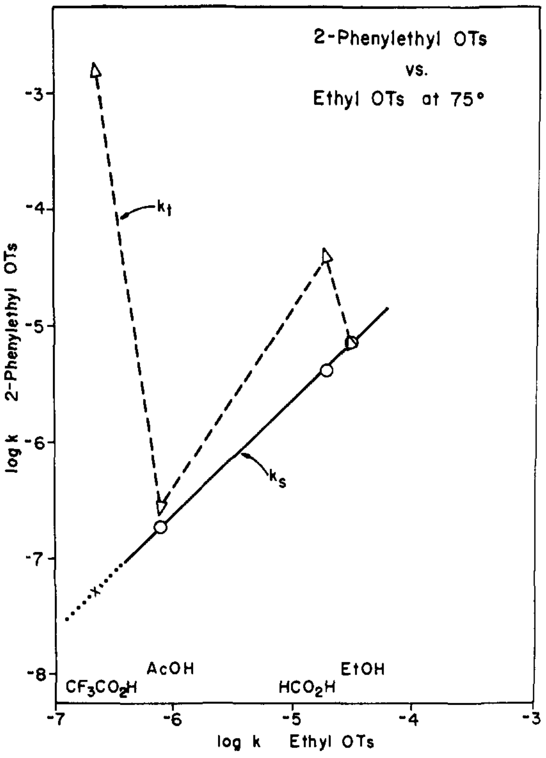

Figure 2.

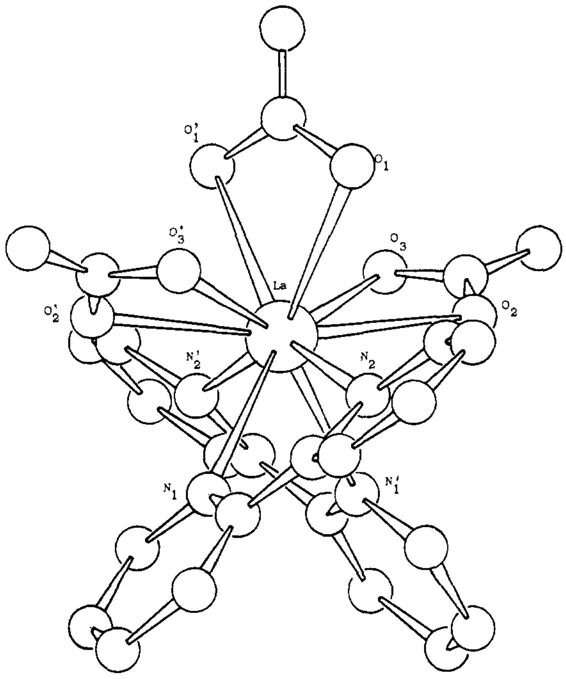

Figure 1. A perspective drawing of the $La(NO_3)_3 \cdot 2$bipyridyl molecule, viewed down the x axis of the orthorhombic unit cell.

threo-3-phenyl-2-butyl[3,10a,b,d] toluenesulfonate. The same general picture of competing k_Δ and k_s routes, with little or no leakage between them, and with (k_Δ/k_s) dependent on structure and solvent, applies generally to the simple primary and secondary β-arylalkyl systems.

Quite a different description of the solvolysis of the above systems has been evolved by Brown.[8] Without recognizing competing k_Δ and k_s processes in his discussion, his treatments of rates, phenyl substituent effects, solvent effects, and stereochemistry are unacceptable, in our opinion. Also, we believe that this failure to recognize relatively discrete k_Δ and k_s processes is the chief cause of his two great "anomalies in current carbonium ion theory." [8]

Lancelot and P. von R. Schleyer, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 9–13, 1968, Paper ORGN-40.

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The Stereochemistry of Decacoordination. The Molecular Structure of Bis(bipyridyl)lanthanum Nitrate

Sir:

As part of a program of study of the geometry of the coordination polyhedra in complex compounds of the lanthanides, we have determined the crystal and molecular structure of an adduct of lanthanum nitrate with 2,2′-bipyridyl, formulated as $La(NO_3)_3 \cdot 2$bipy. This particular molecule was chosen for study because the presence of a higher coordination number than eight was suspected if the capacity of the nitrate ions to act as bidentate ligands was utilized; and in addition, since only bidentate chelating ligands are involved, it was thought that information on the preferred ground-state geometry for decacoordination might be forthcoming from such an analysis. The only discrete molecular complex in which decacoordination has been rigorously established thus far is $La(H_2O)_4HA \cdot 3H_2O$, where H_4A is ethylenediaminetetraacetic acid.[1] Here, the geometry of the coordination polyhedron is determined primarily by the constraints of the chelating ligand.

Crystals suitable for X-ray analysis were prepared as described by Hart and Laming[2] and were found to belong to the orthorhombic system, space group Pbcn, with four molecules in the unit cell. From intensity data collected on a General Electric manual diffractometer, utilizing Mo Kα radiation in the moving crystal–moving counter technique, we have determined the molecular structure by the usual sequence of Patterson, Fourier, and least-squares calculations. The residual for 1514 reflections after two cycles of refinement, with anisotropic thermal parameters for the metal atom, and isotropic parameters for the light atoms, stands at 0.11 (0.078 for the nonzero data), and refinement is continuing.

From the illustration of the molecular structure given in Figure 1, it can be seen that the metal atom is in fact ten-coordinate, all three nitrate ligands being bidentate. The coordination polyhedron and the molecule are required to possess C_2 symmetry. The three metal–

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(1) M. D. Lind, B. Lee, and J. L. Hoard, *J. Amer. Chem. Soc.*, 87, 1611 (1965). A referee has drawn our attention to the fact that, during a recent symposium, Professor Hoard pointed out that the coordination polyhedron in this molecule approximates the bicapped square antiprism.

(2) F. A. Hart and F. P. Laming, *J. Inorg. Nucl. Chem.*, 27, 1825 (1965).