Table I. Proton Chemical Shifts and Coupling Constants for Cyclohexane, **2**[a]

	Proton chemical shifts[b]		Proton coupling constants				
				trans		*cis*	
Spectrum	Equatorial (E)	Axial (A)	Geminal	a,a	e,e	a,e	^{13}C–H
AA′BB′ (−103°)[c]	96.96	68.20	−13.05	13.12	2.96	3.65	
^{13}C–H satellite (38°)[d]	83.92[e]		*f*	8.07[g]		3.73	125.00[h]

[a] In cycles per second. The tabulated parameters are considered accurate to 0.05 cps. The probable errors for the parameters, that arise from the least squares analysis, fall between 0.01 and 0.02 cps. [b] Cycles per second downfield from TMS at 60 Mcps. [c] 5% of **2** in CS_2 (mole/mole). [d] Neat **2**. [e] $^1/_2(\nu_a + \nu_e)$. [f] Not accurately determined from the analysis. [g] $^1/_2(J_{a,a} + J_{e,e})$. [h] Neither the least-squares frequency fit nor the relative transition intensities are affected significantly by varying $J_{^{13}C-C-H}$ between 10 and −10 cps.

Analysis of the deuterium decoupled ^{13}C–H (natural abundance) satellite spectrum of neat **2** at 38° (see Figure 2) verified the AA′BB′ spectral analysis. The low-field ^{13}C–H satellites were shifted from the $C_6D_8H_4$ band 0.28 cps less than were the corresponding high-field ones. This shift gives an isotope shift of −0.14 ± 0.05 cps for the proton bonded to ^{13}C. A comparable result has been reported for the ^{13}C–H satellites of benzene.[9] Ten $C_6D_8H_4$ side-band calibrated spectra were determined and the averaged[6] transition frequencies used for an approximate AA′XX′ ($^{13}CH_AH_{A'}$-$CH_XH_{X'}$) analysis.[7] The solution parameters obtained therefrom were refined by analyzing[8] the spectrum as arising from an AA′A″A‴X system (X = ^{13}C nucleus). The resulting parameters are given in Table I.

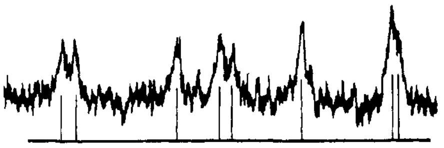

Figure 2. Low-field half of the deuterium-decoupled ^{13}C–H satellite spectrum of neat **2** at 38°. The total width of the spectrum is 12.1 cps. The bottom stick spectrum is the computed one.

The theoretical relationship between dihedral angles (ϕ) and vicinal proton couplings in saturated systems is given[10] by

$$J = A(\cos^2 \phi + n \cos \phi)$$

If ϕ is taken as the angle shown in **3**, the following set of three equations in four unknowns can be written. Solution of these equations using the values obtained

$$J_{a,a} = A[\cos^2 (\omega + \phi) + n \cos (\omega + \phi)]$$

$$J_{e,e} = A[\cos^2 (\omega - \phi) + n \cos (\omega - \phi)]$$

$$J_{a,e} = A(\cos^2 \phi + n \cos \phi)$$

for the vicinal proton couplings in **2** at −103° gives for $\omega = 120°$: $A = 13.13$, $n = 0.00$, and $\phi = 58.2°$; and for $\omega = 118°$: $A = 12.95$, $n = -0.02$, and $\phi = 57.2°$. The latter solution probably is the most reliable, as the H–C–H bond angles in cyclohexane are smaller than the tetrahedral value.[11] The value of ϕ of about 57° should be compared with that of about 55° as estimated[12] from electron diffraction data[11] on cyclohexane.

Acknowledgment. We appreciate support of this work by the National Science Foundation (Grant GP-8315).

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(9) J. M. Read, Jr., R. E. Mayo, and J. H. Goldstein, *J. Mol. Spectrosc.*, **22**, 419 (1967).

(10) M. Barfield and D. M. Grant, *Advan. Magnetic Resonance*, **1**, 149 (1965).

(11) M. Davis and O. Hassel, *Acta Chem. Scand.*, **17**, 1181 (1963); E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1965, p 455.

(12) R. A. Wohl, *Chimia*, **18**, 219 (1964).

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Intramolecular 1,3-Proton Transfers during Isofluorene–Fluorene Isomerization

Sir:

The substantial intramolecular components of 1,3- and 1,5-proton transfers in conjugated unsaturated systems catalyzed by strong bases in weakly acid solvents have been well documented by Cram, Schriesheim, and others.[1] Cram's approach is exemplified by the allylic rearrangement of 3-phenyl-1-butene to the more stable isomeric 2-phenyl-2-butenes, catalyzed by potassium *t*-butoxide in *t*-butyl alcohol. With a deuterium label in either the substrate (at C_3) or solvent (t-C_4H_9-OD) deuterium loss or incorporation into product was followed in order to measure intermolecularity.[1] Formation and rapid collapse of hydrogen-bonded delocalized carbanions, during which exchange of the bonding alcohol molecule with surrounding solvent does not occur, has been invoked to account for the frequently noted high degree of intramolecularity.[1] We now wish to report the overwhelming intramolecular nature of a 1,3-proton transfer carried out in strongly acidic trifluoroacetic acid (TFA), wherein trifluoroacetate is the strongest base available.[2] The systems

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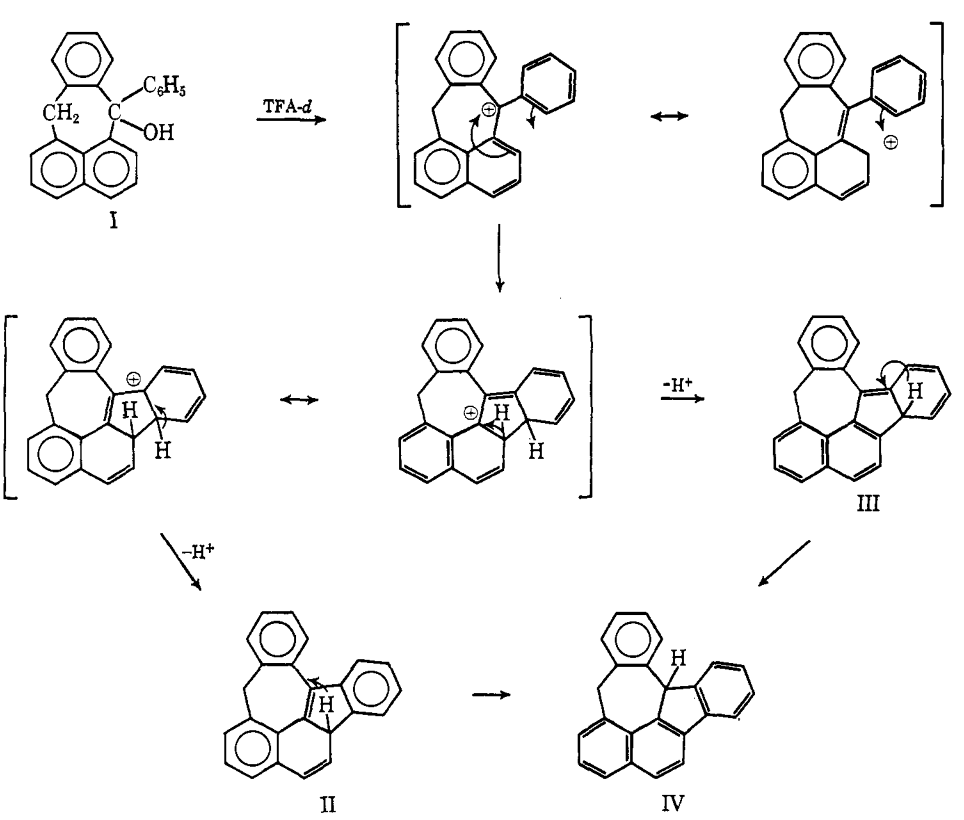
(1) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, Chapter 5.

(2) A concerted uncatalyzed 1,3-electrocyclic hydrogen shift would have to be antarafacial, according to the Woodward–Hoffmann rules (R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968)) which is obviously impossible in our systems. On the other hand, our rearrangements could also come about by a series of 1,5-suprafacial hydrogen shifts. We cannot rigorously disprove this possibility, but it is not consistent with the variation in k_{intra}/k_{inter} for cyclization of VI when deuterium is in the substrate as compared with solvent (less intermolecular protonation), nor with the apparent catalytic effect of added sodium trifluoroacetate.[3a]

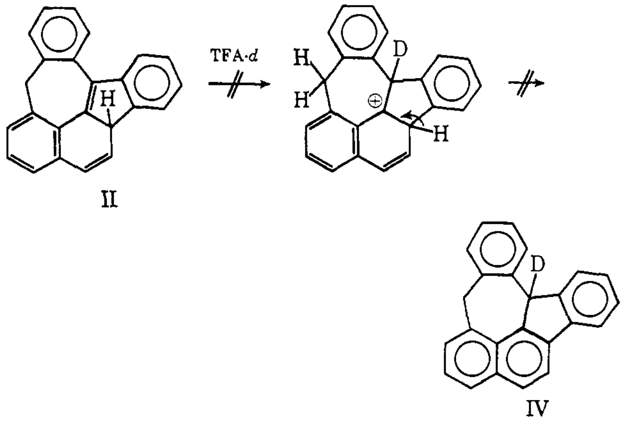
(3) (a) Qualitative evidence for base catalysis was obtained with VI, which gave essentially no 9-phenyl-1,2-benzfluorene (VII) in refluxing trifluoroacetic anhydride during 6 hr, whereas addition of 2 equiv of sodium trifluoroacetate in an otherwise comparable experiment produced 65% of VII. In highly ionized TFA itself, the greatest yield of VII (~100%) resulted. The increased yields in these reactions roughly parallel the higher concentrations of trifluoroacetate in the medium. Ad-

Scheme I

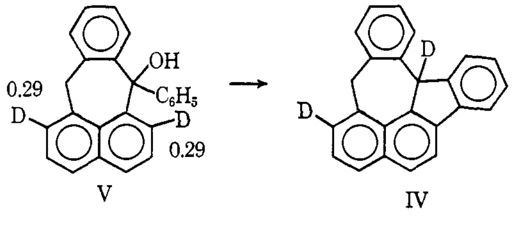


we discuss are derivatives of isofluorene,[3b] which are formed during acidic cyclodehydration of certain triaryl cations to fluorenes.[4] Although some attention has been focused on the cyclization step[4] (*e.g.*, leading to II or III), little has been reported concerning the mechanism of aromatization (*e.g.*, II or III → IV; Scheme I). As we noted earlier,[5] 7-phenyl-7-hydroxy-7,12-dihydropleiadene (I) instantly forms a colored carbonium ion on dissolution in various acids (*e.g.*, TFA, formic acid); colorless 1,12-(*o*-phenylene)-7,12-dihydropleiadene precipitates rapidly (30–60 sec) in virtually quantitative yield.[5a] Initially, we presumed that intermediate II[6] would undergo protonation by TFA, followed by base-catalyzed deprotonation (as shown in Scheme II). Accordingly, we were surprised to find essentially no deuterium[7] in IV after cyclizing I in TFA-*d*.[8] This finding was followed by the observation that 7-(phenyl-d_5)-7-hydroxy-7,12-dihydropleiadene cyclized in TFA to give IV again with no detectable C_{12}–D.[7,9] Thus III can be eliminated as the isofluorene precursor of IV. Verification that II

Scheme II



intervenes *en route* to IV was gained from specifically deuterated I[10] (V), which cyclized in TFA to give IV



with ≥96% deuterium retention (mass spectrometry). Nmr analysis[7] confirmed that the C_{12}–H signal in IV was diminished in intensity corresponding to *ca.* 0.3 D.

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mittedly there is also some variation in ionic strength, solvent polarity, etc., in these runs. (b) A similar tautomer of indene has been shown to intervene in the Diels-Alder reaction with maleic anhydride: J. A. Berson and G. B. Aspelin, *Tetrahedron*, 20, 2697 (1964).

(4) L. R. C. Barclay in "Friedel-Crafts and Related Reactions," Vol. 3, Part 2, Interscience Publishers, New York, N. Y., 1964, pp 843–847.

(5) (a) P. T. Lansbury, J. F. Bieron, and A. J. Lacher, *J. Am. Chem. Soc.*, **88**, 1482 (1966): (b) P. T. Lansbury, J. B. Bieber, F. D. Saeva, and K. R. Fountain, *ibid.*, in press.

(6) A similar argument can be made for III → IV.

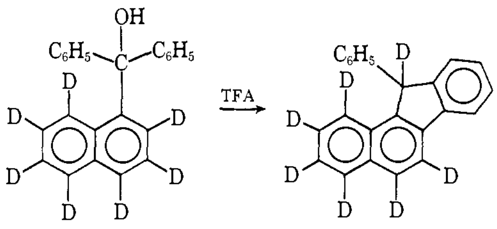
(7) By integration of the nmr signals of the aliphatic protons which appear at 3.9 and 4.9 ppm (C_7–H) and 5.7 ppm (C_{12}–H); the latter signal integrated for *ca.* one proton when deuterium was in the solvent. The aromatic region also showed the requisite 13 protons.

(8) Typically, 0.2–1 g quantities of substrate I or VI were refluxed in *ca.* 10–25 ml of solvent (TFA or the anhydride). IV was isolated by filtering the cooled reaction mixture, whereas VII was obtained by quenching the reaction in ice water prior to filtration and recrystallization.

(9) We are indebted to Dr. Franklin D. Saeva for this experiment.

(10) 7,12-Dihydropleiadene-1-*d* (containing 0.58 D) was prepared by reducing 1-chloro-7,12-dihydropleiadene with deuterated hydrazine and Pd–C (M.P. Cava and R. H. Schlessinger, *Tetrahedron*, **21**, 3073 (1965)); the former was oxidized selectively (P. T. Lansbury and F. D. Saeva, *J. Am. Chem. Soc.*, **89**, 1890 (1967)) to 7(12H)-pleiadone (with 0.58 D equally divided between C_1 and C_6), which was in turn converted to I.[5a]

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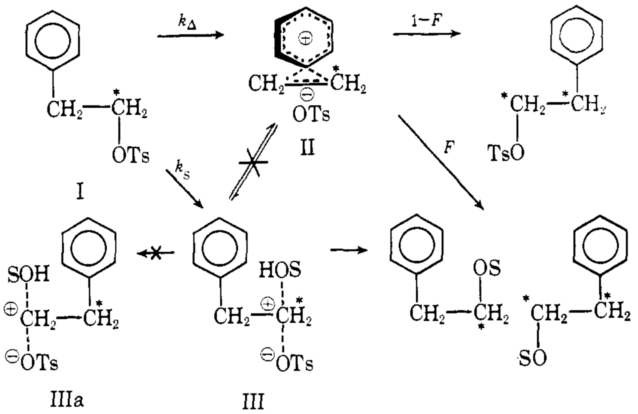
Correlation of k_Δ and k_s in Solvolysis of 2-Phenylethyl Toluenesulfonate[1]

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*-RO-$COCF_3$).



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).