the loss of some delocalization energy at the transition state.

Acknowledgment. We thank Professor Ritchie for informing us of his results and for helpful discussions. This work was supported, in part, by the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation.

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Proton Transfers in Dipolar Aprotic Solvents. II. Transfer from 9-Methylfluorene to 4,5-Methylenephenanthryl Anion in Dimethyl Sulfoxide Solution

Sir:

We wish to report the observation of a strikingly fast proton-transfer reaction from a hydrocarbon to a carbanion in dimethyl sulfoxide (DMSO) solution. We have found that 9-methylfluorene has a pK_a of 19.7 in DMSO, and that 4,5-methylenephenanthrene has a pK_a of 20.0 in the same solvent.[1] In view of our earlier suggestion concerning the rapidity of proton-transfer reactions in nonhydroxylic solvents,[2] it appeared of interest to measure the rate of transfer between the hydrocarbon, 9-methylfluorene, and the carbanion, 4,5-methylenephenanthryl anion, in DMSO, Certainly, if one is to find a slow proton transfer, this reaction would be expected to provide a counterexample to the previously studied cases.

A solution of 4,5-methylenephenanthryl anion in DMSO was prepared by potentiometric titration of a solution of *ca.* 5×10^{-4} *M* hydrocarbon with a solution of potassium *t*-butoxide in DMSO.[1] The solvent used was purified by the technique described in a separate paper and contained less than 5×10^{-6} *M* acidic or basic impurities and less than 10 ppm of water.

The solution of the anion was mixed with a solution of *ca.* 10^{-2} *M* 9-methylfluorene in a stop-flow apparatus,[3] and the reaction was followed either by observation of the disappearance of the absorption of the solution at 513 mμ due to the 4,5-methylenephenanthryl anion or the appearance of the absorption of the solution at 388 mμ due to the 9-methylfluorenyl anion. Rate constants calculated from the two different observations agreed within 10%. The reaction was found to be accurately second order, first order in both hydrocarbon and carbanion, and a rate constant of 1.4×10^3 M^{-1} sec^{-1} at 25.0° was obtained. A study of the reaction of 9-methylfluorene-9-*d* allowed the determination of the isotope effect on the rate. A value of $k_H/k_D = 4.2$ at 25.0° was found.

The observed reaction is most reasonably formulated as the direct proton transfer from the hydrocarbon to the carbanion. Alternative mechanisms involving indirect transfer, such as eq 1,

$$P^- + RH \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} PH + R^- \qquad (1a)$$

$$F^- + RH \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} FH + R^- \qquad (1b)$$

where PH is 4,5-methylenephenanthrene, FH is 9-methylfluorene, and RH is either solvent, *t*-butyl alcohol, or water, can reasonably be ruled out on several bases. If mechanism 1 were operative, second-order kinetics and a primary isotope effect would be observed only if step 1b were rate determining (*i.e.*, if k_{-1}(PH) > k_{-2}(FH)). This is very unlikely since (PH) is always much less than (FH) and k_{-1} is expected to be nearly equal to k_{-2}.

By methods similar to those described above, we have also observed the reaction of benzoic acid with 9-methylfluorenyl anion in DMSO solution. At a concentration of 2.9×10^{-4} *M* anion and 4.4×10^{-4} *M* benzoic acid, the reaction is complete before the solution reaches the observation chamber of the stop flow. We estimate a lower limit on the rate constant for this reaction of 10^6 M^{-1} sec^{-1}.

The rate constant observed in the present study is *ca.* 5×10^3 greater than that found by Brauman[4] for the similar reaction of proton transfer between fluorene and its lithium salt in DMSO. Several factors could reasonably be responsible for the discrepancy. At the concentrations of *ca.* 0.5 *M* used in the nmr study, ion pairing must certainly be present. If the ion pairs are less reactive than the free ions by several orders of magnitude, as is not unreasonable,[5] or if only free ions are involved in the reaction, the smaller rate constant is understandable.

In any case, the very fast proton transfers observed in DMSO provide strong evidence for the importance of solvent reorganization in drastically reducing the rates of reactions in hydroxylic solvents.

Acknowledgments. We wish to express our appreciation to Dr. Brauman for making the results of his work available to us prior to publication and for agreeing to simultaneous publication of our results. This work was supported by a grant from the Public Health Service (NIH GM-12832).

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(1) C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, **89**, 1721 (1967).

(2) C. D. Ritchie and R. E. Uschold, *ibid.*, **86**, 4488 (1964).

(3) C. D. Ritchie, G. A. Skinner, and V. G. Badding, *ibid.*, in press.

(4) J. I. Brauman, D. F. McMillen, and Y. Kanazawa, *J. Am. Chem. Soc.*, 89, 1728 (1967).

(5) See, for example, T. E. Hogen-Esch and J. Smid, *ibid.*, 88, 307 (1966).

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γ-Deuterium Isotope Effects on the Solvolyses of Norbornyl Brosylates[1,2]

Sir:

We have measured the average kinetic isotope effects through three half-lives on the solvolysis (k_t) of *exo*-norbornyl-6-*exo-d* brosylate (6-*exo-d*-I), *exo*-norbornyl-6-*endo-d* brosylate (6-*endo-d*-I), *endo*-norbornyl-6-*exo-d* brosylate (6-*exo-d*-II), and *endo*-norbornyl-6-*endo-d*

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(1) This work was supported by the National Science Foundation and by the Petroleum Research Fund, administered by the American Chemical Society.

(2) For earlier work on isotope effects in the norbornyl system, see (a) S. Borčić, V. Belanic-Lipovac, and D. E. Sunko, *Croat. Chem. Acta*, **33**, 35 (1961); (b) C. C. Lee and E. W. C. Wong, *J. Am. Chem. Soc.*, **86**, 2752 (1964); *Can. J. Chem.*, **43**, 2254 (1965); *Tetrahedron*, **21**, 539 (1965); (c) J. P. Schaefer and D. S. Weinberg, *Tetrahedron Letters*, **2491** (1965); (d) K. Humski, S. Borčić, and D. E. Sunko, *Croat. Chem. Acta*, 37, 3 (1965).

Table I. Kinetic Isotope Effects (k_H/k_D) on the Solvolyses of 6-*d*-Norbornyl Brosylates[a]

Solvent	6-*exo*-*d*-I	6-*endo*-*d*-I	6-*exo*-*d*-II	6-*endo*-*d*-II
KOAc–HOAc	1.09 ± 0.03[b]	1.11 ± 0.01[b]	0.98 ± 0.01[c]	0.99 ± 0.02[c]
80% ethanol	1.09 ± 0.01[b]	1.11 ± 0.01[b]	1.00 ± 0.02[d]	0.97 ± 0.01[d]

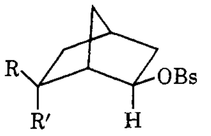
[a] Observed isotope effects have been corrected to isotopic purity. In no case was the correction greater than +0.02. Rates were measured spectrophotometrically [G. C. Swain and C. R. Morgan, *J. Org. Chem.*, **29**, 2097 (1964)]. [b] 24.9°. [c] 70.1°. [d] 49.1°.

Table II. Expected Behavior of $\overline{(k_H/k_D)}_t$ for Maximum Scrambling and Various Assumed Isotope Effects at C-6, C-6′, C-2, and C-1

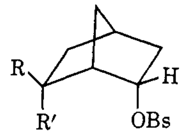
	Assumed isotope effect at				Calculated average isotope effects after *n* half-lives,[a]		
Entry	C-6	C-6′	C-2	C-1	1	3	∞
			Acetolysis (k_α/k_t = 4.6)				
1	1.00	1.00	1.20	1.00	1.030	1.040	1.042
2	1.00	1.00	1.20	1.10	1.045	1.061	1.069
3	1.10	1.10	1.20	1.00	1.100	1.100	1.100
4	1.10	1.10	1.15	1.05	1.100	1.100	1.100
			80% Ethanol (k_α/k_t = 1.53 ± 0.13)[b]				
5	1.00	1.00	1.20	1.00	1.008	1.019	1.042
6	1.00	1.00	1.20	1.10	1.015	1.030	1.069
7	1.10	1.00	1.20	1.10	1.100[c]	1.100[c]	1.100[c]
8	1.10	1.00	1.20	1.10	1.017[d]	1.040[d]	1.100[d]

[a] Values given are applicable starting with either 6-*exo*-*d*-I or 6-*endo*-*d*-I unless otherwise noted. [b] The conclusions are not altered by a 30% change in k_α/k_t. [c] Value starting with 6-*exo*-*d*-I. [d] Value starting with 6-*endo*-*d*-I.

brosylate (6-*endo*-*d*-II) in acetic acid–potassium acetate[3] and in 80% aqueous ethanol.[4] The polarimetric (k_α) and solvolytic (k_t) rates have also been determined for *exo*-norbornyl brosylate in 80% aqueous ethanol to interpret the isotope effect data fully.[6] Analysis of the data (Table I) reveals an appreciable isotope effect (k_H/k_D = 1.10 ± 0.02) for D at C-6 on the solvolysis of 6-*exo*-*d*-I and 6-*endo*-*d*-I but a negligible or slightly inverse isotope effect (k_H/k_D = 0.99 ± 0.02) for D at C-6 on the solvolysis (and hence on the ionization) of 6-*exo*-*d*-II and 6-*endo*-*d*-II.[7]



I, 6-*exo*-*d* (R = D, R′ = H)
6-*endo*-*d* (R = H, R′ = D)



II, 6-*exo*-*d* (R = D, R′ = H)
6-*endo*-*d* (R = H, R′ = D)

For an *exo*-brosylate initially labeled at one site, isotopic scrambling[8] due to internal return[6] is taken into account as follows. The instantaneous rate constant at time *t*, $(k_D)_t$, for *solvolysis* of a mixture of isotopic species is given by eq 1, in which k_{Di}, the rate constant for solvolysis of brosylate deuterated at

$$(k_D)_t = f_1k_{D1} + f_2k_{D2} + f_6k_{D6} + f_6{}'k_{D6'} \qquad (1)$$

C-*i* (k_{D6} for 6-*exo*-*d*-I and $k_{D6'}$ for *endo*-*d*-*I*) is composed of the rate constant for ionization multiplied by the fraction of intimate ion pairs that suffers dissociation.[6b] The f_i are time-dependent fractions of each of the deuterated brosylates. Division by k_H (solvolytic rate constant for the undeuterated species) gives the inverse of the isotope effect at time *t* (eq 2).

$$\left(\frac{k_D}{k_H}\right)_t = f_1\left(\frac{k_{D1}}{k_H}\right) + f_2\left(\frac{k_{D2}}{k_H}\right) + f_6\left(\frac{k_{D6}}{k_H}\right) + f_{6'}\left(\frac{k_{D6'}}{k_H}\right) \qquad (2)$$

That the measured k_H/k_D values for the *exo*-brosylates (I) could not have resulted from an isotope effect solely at C-2 may be shown (*e.g.*, for 6-*exo*-*d*-I) if one considers the extreme case that ionization results in complete scrambling of D over positions C-1, C-2, C-6, and C-6′.[9] The f_i are computed from eq 3, which was derived by Winstein and Trifan.[6a] The fraction of 6-*exo*-*d*-I that has not yet ionized at time *t* is *P*, and

$$P = e^{-(k\alpha - k_t)t} \qquad (3)$$

$P + [(1 - P)/4]$ is the fraction of 6-*exo*-*d*-I in remaining brosylate. The fractions of 6-*endo*-*d*-I, 1-*d*-I, and 2-*d*-I are each $(1 - P)/4$.

By substituting these f_i into eq 2, inverting, and integrating, we can calculate the average value of $\overline{(k_H/k_D)}_t$ during the period of kinetic observation $t_1 \rightarrow t_2$ (eq 4, where $A = k_{D6}$; $B = k_{D1} + k_{D2} + k_{D6'}$).[10]

Using for k_H/k_{D2} the maximum value ever reported for an α-isotope effect (k_H/k_{D2} = 1.20 observed by Lee

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(3) J. M. Jerkunica, S. Borčić, and D. E. Sunko [*J. Am. Chem. Soc.*, **89**, 1732 (1967)] have independently examined acetolysis with similar results using different kinetic methods. We are grateful to Dr. Borčić for keeping us informed of their work.

(4) The 6-*d*-norborneols were prepared by reduction of stereospecifically labeled 6-*d*-norcamphors, which were obtained by homoketonizations.[5] Control experiments showed no change in stereochemistry or loss of D in reduction and purification procedures. The two *endo*-*d*-alcohols contained 86.6% d_1 and 13.4% d_0 at C-6 and were at least 90% stereochemically pure *endo*-*d*. The two *exo*-*d*-alcohols contained 89.7% d_1 and 10.3% d_0 at C-6 and were at least 94.5% stereochemically pure *exo*-*d* (A. Nickon and N. Werstiuk, unpublished results).

(5) (a) A. Nickon, J. H. Hammons, J. L. Lambert, and R. O. Williams, *J. Am. Chem. Soc.*, **85**, 3713 (1963); (b) A. Nickon, J. L. Lambert, R. O. Williams, and N. H. Werstiuk, *ibid.*, **88**, 3354 (1966).

(6) (a) S. Winstein and K. S. Trifan, *ibid.*, **74**, 1147, 1154 (1952); (b) S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958).

(7) The conclusions require no assumptions concerning mechanism of force constant weakening in the transition state.

(8) J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **76**, 4501 (1954); C. C. Lee and L. K. M. Lam, *ibid.*, **88**, 2831, 5355 (1966).

(9) We justifiably neglect scrambling to C-3 and to the more remote C-4, C-5, and C-7 positions in our estimate of the *upper* limit of $\overline{(k_H/k_D)}_t$. The isotope effects at these positions are necessarily considerably less than that at C-2, and the sum of the scrambling to these positions is only 6.8% in the *product*.[8]

(10) We reckon that scrambling commences at the instant of mixing (t = 0) and continues through the entire period ($t = 0 \rightarrow t_1$) preceding kinetic observation.

$$\overline{\left(\frac{k_{\mathrm{H}}}{k_{\mathrm{D}}}\right)}_t = \frac{1}{(t_2 - t_1)}\int_{t_1}^{t_2}\left(\frac{k_{\mathrm{H}}}{k_{\mathrm{D}}}\right)_t \mathrm{d}t = \frac{4k_{\mathrm{H}}}{(A + B)(k_\alpha - k_t)(t_2 - t_1)} \times \ln\left[\frac{(A + B) + (3A - B)e^{-(k_\alpha - k_t)t_2}}{(A + B) + (3A - B)e^{-(k_\alpha - k_t)t_1}}\right] + \frac{4k_{\mathrm{H}}}{(A + B)} \quad (4)$$

and Wong[2b] for 2-*d*-II), we have calculated the values of $\overline{(k_{\mathrm{H}}/k_{\mathrm{D}})}_t$ through one and three half-lives of solvolysis and at $t = \infty$ for 6-*endo*-*d*-I and for 6-*exo*-*d*-I, assuming that there is no isotope effect for D at C-1, C-6, and C-6′ (entries 1 and 5, Table II). Clearly, even at infinite time, $\overline{(k_{\mathrm{H}}/k_{\mathrm{D}})}_t$ does not attain the measured values of 1.09 and 1.11. If a more realistic extent of scrambling were used, the calculated isotope effects through one and three half-lives would be even lower.[8,9] If, in addition to $k_{\mathrm{H}}/k_{\mathrm{D}_2} = 1.20$, one takes an isotope effect at C-1 of 1.10,[11] $\overline{(k_{\mathrm{H}}/k_{\mathrm{D}})}_t$ still falls short of the measured values (entries 2 and 6, Table II). It is necessary to take $k_{\mathrm{H}}/k_{\mathrm{D}_2} = 1.20$ and *two* other isotope effects of 1.10 (or the equivalent of this combination) to achieve agreement with the acetolysis experiments (*e.g.*, entries 3 and 4). The aqueous ethanolysis data impose further restrictions. If one supposes that only one C–H bond at C-6 exhibits an isotope effect, then (*e.g.*, entries 7 and 8) the calculated average value through three half-lives is 1.10 for 6-*exo*-*d*-I, but it is at most 1.040 for 6-*endo*-*d*-I (entry 8).[12]

We conclude that an isotope effect of 1.10 ± 0.02 (within the limits of our present precision) must be operative for D at both sites, C-6 and C-6′, to account for the behavior of brosylates I in aqueous ethanol; and because solvent effects on secondary isotope effects are known to be small,[13] these same isotope effects must operate in acetolysis. Furthermore, the major contribution to the isotope effect must necessarily be on the *ionization* of the brosylate.[14] We plan to determine these isotope effects by precision conductance to measure any difference between the *exo* and *endo* positions at C-6.

Our observed γ-isotope effects for the *endo*-brosylates II are those expected of a transition state for ionization to a classical cation.[16] However, the extraordinarily large γ-isotope effects on the solvolysis of 6-*exo*-*d*-I and 6-*endo*-*d*-I are not expected on the basis of the "classical transition state" hypothesis, at least in its present form.[19,19a]

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[11] Note that, for a transition state to a classical ion, the isotope effect at the bridgehead, C-1, is expected to be small or inverse [V. J. Shiner and J. S. Humphrey, *J. Am. Chem. Soc.*, **85**, 2416 (1963)].

[12] The magnitude of the discrepancy may be seen by calculation of the value of $k_{\mathrm{H}}/k_{\mathrm{D}_2}$ necessary to attain the observed $\overline{(k_{\mathrm{H}}/k_{\mathrm{D}})}_t$ through three half-lives if there were no isotope effects at C-1, C-6, and C-6′. This requires (1) $(k_{\mathrm{H}}/k_{\mathrm{D}_2}) \geq 1.50$ for acetolysis; (2) $(k_{\mathrm{H}}/k_{\mathrm{D}_2}) > 4$ for aqueous ethanolysis; and (3) an upward drift of *ca.* 10% in $(k_{\mathrm{D}})_t$ through three half-lives. No drift was detected.

[13] G. J. Frisone and E. R. Thornton, *J. Am. Chem. Soc.*, **86**, 1900 (1964).

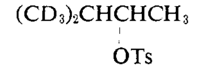
[14] The accepted scheme for solvolysis of *exo*-norbornyl brosylate is

$$\mathrm{R{-}X} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{R^+X^-} \xrightarrow{k_2} \mathrm{R^+||X^-} \xrightarrow{k_3} \text{product}$$

Product forms inevitably from solvent-separated ion pair.[6b] The fraction, F, of intimate ion pairs that suffers dissociation is $k_2/(k_2 + k_{-1})$. There can be no isotope effect on F if there is no isotope effect on k_1. Even with an isotope effect on k_1, isotope effects on F are expected to be negligible.[15]

[15] J. G. Evans and G. Y. S. Lo, *J. Am. Chem. Soc.*, **88**, 2118 (1966).

[16] For example, the reported γ-isotope effect on acetolysis of III is $(k_{\mathrm{H}}/k_{\mathrm{D}}) = 1.00$ for *six* deuterium atoms,[17] and other reported γ-isotope effects are slightly inverse.[18]



$$\underset{\displaystyle\mathrm{OTs}}{(\mathrm{CD_3})_2\mathrm{CHCHCH_3}}$$

III

[17] S. Winstein and J. Takahashi, *Tetrahedron*, **2**, 316 (1958).

[18] K. T. Leffek, J. A. Llewellyn, and R. E. Robertson, *J. Am. Chem. Soc.*, **82**, 6315 (1960); S. Borčić, M. Nikoletic and D. E. Sunko, *ibid.*, **84**, 1615 (1962).

[19] H. C. Brown, *Chem. Brit.*, **2**, 199 (1966).

[19a] NOTE ADDED IN PROOF. Torsional effects in the norbornyl system as recently discussed (P. von R. Schleyer, *J. Am. Chem. Soc.*, **89**, 699, 701 (1967)) would not account for our isotope effects at C-6.

[20] National Institutes of Health Predoctoral Fellow, 1962–1966.

[21] Du Pont Teaching Fellow, 1963–1965.

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Secondary Deuterium Kinetic Isotope Effects in Acetolysis of 2-Norbornyl-6-*d* Brosylates

Sir:

It has been proposed[1-4] that solvolyses of *exo*-2-norbornyl brosylate, in contrast to the *endo* epimer, proceed with anchimeric assistance leading to a nonclassical norbornonium ion (V) in the rate-determining step. This view has been challenged by Brown, *et al.*[5,6] According to these authors, the solvolysis rate of the *exo*-brosylate is *not* abnormally large, and the difference in rates between the two epimeric brosylates is to be sought in the slow reaction rate of the *endo*-brosylate. The cause of the latter deceleration is seen in the steric hindrance to ionization. The *endo*-6-hydrogen should, because of its vicinity, hinder the departure of the sulfonate ester group at C_2 from the same side of the molecule. On these grounds and owing to the smaller size of deuterium, it was predicted[7] that the solvolysis of compound II would proceed with an inverse ($k_{\mathrm{H}}/k_{\mathrm{D}}$ < 1.00) kinetic isotope effect.

We now wish to report the acetolysis rate constants for compounds I–IV, which were prepared according to the procedure of Nickon, *et al.*[8,9] The acetolysis rates were followed by continuous titration of the liberated acid by means of a pH-stat (Radiometer, Copenhagen, Model TTT1). Thus, complete rate curves with a very large number of points were obtained. Moreover, only a small amount of the sulfonate ester

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[1] S. Winstein and D. S. Trifan, *J. Am. Chem. Soc.*, 71, 2953 (1949).

[2] J. D. Roberts and C. C. Lee, *ibid.*, **73**, 5009 (1951).

[3] S. Winstein and D. S. Trifan, *ibid.*, **74**, 1147, 1154 (1952).

[4] J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *ibid.*, **76**, 4501 (1954).

[5] H. C. Brown, F. J. Chloupek, and M.-H. Rei, *ibid.*, **86**, 1248 (1964).

[6] H. C. Brown and G. L. Tritle, *ibid.*, **88**, 1320 (1966).

[7] H. C. Brown, Special Publication No, 16, The Chemical Society, London, 1962, p 140.

[8] A. Nickon, J. H. Hammons, J. L. Lambert, and R. O. Williams, *J. Am. Chem. Soc.*, **85**, 3713 (1963); A. Nickon, J. L. Lambert, R. O. Williams, and N. H. Werstiuk, *ibid.*, **88**, 3354 (1966).

[9] B. L. Murr, A. Nickon, T. D. Swartz, and N. H. Werstiuk, *ibid.*, **89**, 1730 (1967).