Table I

Fraction	[α]D, deg	Specific activity, μcuries/mole
1	−10.4	13.68
2	−10.4	16.08
3	−17.8	16.73
4	+9.4	8.51
5	+17.4	6.25
6	+27.2	1.99

solved in 10 ml of absolute ethanol, heated until the solution became clear, and then allowed to crystallize in a refrigerator. The resolution of the two cinchonidine salts was achieved using absolute ethanol to crystallize the levorotatory acid and 95% ethanol to obtain the dextrorotatory acid.[24] The cinchonidine salts were then converted to the free acids by treatment with 1 *N* hydrochloric acid and extraction with chloroform. The crude acids so obtained were purified by filtration of an ether solution through silicic acid followed by distillation or crystallization from acetonitrile. Six fractions of different optical purity were isolated (see Table I). The results show that the enantiomer XVIIa with [α]D −30.6°[24] is labeled with carbon-14 at the carboxyl position.

Mechanisms of Elimination Reactions. VII. Rates of Elimination of Some Deuterated Cyclohexyl Tosylates[1]

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Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627. Received September 26, 1966

Abstract: *trans*-Cyclohexanol-2-*d* was prepared by opening epoxycyclohexane with lithium aluminum deuteride, and *cis*-cyclohexanol-2-*d* resulted from deuterioboration of cyclohexene. Exchange of cyclohexanone with deuterium oxide followed by reduction yielded cyclohexanol-2,2,6,6-d_4. Cyclohexanol-1-*d* was obtained by treating cyclohexanone with lithium aluminum deuteride. These alcohols, along with undeuterated cyclohexanol, were converted to the tosylates. Rates of reaction of the tosylates with ethoxide in ethanol and *t*-butoxide in *t*-butyl alcohol at 50° were determined. The over-all reaction is at least 98% elimination. The rate data provide primary isotope effects for β deuteration, and secondary isotope effects for both α and β deuteration. The β-deuterium primary effect (4.5 in ethanol and 7.5 in *t*-butyl alcohol) resembles that previously noted for 2-phenylethyl-2,2-d_2 tosylate, and the α-deuterium secondary effect is of normal size (1.14 in ethanol and 1.15 in *t*-butyl alcohol). The β-deuterium secondary effect is considerably larger than expected (1.33 in ethanol and 1.52 in *t*-butyl alcohol). The nature of the transition state for elimination is discussed in the light of these findings.

Our interest in the structure of the transition state in E2 reactions[2,3] has led us to study deuterium isotope effects in elimination reactions of specifically deuterated cyclohexyl tosylates. This system provides an unusual opportunity to observe the primary β-deuterium effect and both α- and β-deuterium secondary effects. Previous studies had revealed that β-deuterium primary isotope effects in the 2-phenylethyl-2,2-d_2 series[4] vary considerably as the leaving group and base are changed. The correlation of these results with other evidence on transition-state structure has been discussed in a recent reinterpretation.[3]

Syntheses of the desired deuterated cyclohexanols were readily accomplished. Cyclohexanol-1-*d* resulted from reduction of cyclohexanone with lithium aluminum deuteride by the procedure of Streitwieser, *et al.*, for cyclopentanone.[5] Exchange of cyclohexanone with deuterium oxide[6] followed by reduction with lithium aluminum hydride gave cyclohexanol-2,2,6,6-d_4.

trans-Cyclohexanol-2-*d* was obtained by the action of lithium aluminum deuteride on cyclohexene epoxide. Although there seemed no reason to question the stereochemistry of this process,[5] subsequent work[7] demonstrated a small irregularity. Another sample of *trans*-cyclohexyl-2-*d* tosylate was converted to the *cis*-cyclohexyl-2-*d*-trimethylammonium salt by treatment with trimethylamine in nitromethane. To check the stereochemistry of the substitution, a Hofmann degradation was performed on the quaternary ammonium salt. Examination of the resulting cyclohexene in a mass spectrometer revealed *ca.* 4–5% of *dideuterated* material in addition to the monodeuterated material predicted for substitution with inversion.

A precedent for this result is to be found in the reduction of 4-*t*-butylcyclohexene epoxide with lithium aluminum deuteride,[8] which gives 11% of dideuterated product. The authors explain the result by invoking hydride abstraction by aluminum deuteride on the alkoxide intermediate, followed by reduction of the resulting ketone with more lithium aluminum deuteride. Evidently this side reaction is less important with our unsubstituted cyclohexene oxide, and the few per cent of dideuterated material having the hydroxyl *cis* to the 2-deuterium would not significantly change the measured isotope effect. There is, however, an evident need for caution in using epoxide opening as a route to stereospecifically deuterated products.

cis-Cyclohexanol-2-*d* was obtained by the deuterioboration method.[9–11] Although there is ample evi-

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(1) This work was supported by the National Science Foundation.

(2) W. H. Saunders, Jr., and R. A. Williams, *J. Am. Chem. Soc.*, **79**, 3712 (1957), and subsequent papers.

(3) W. H. Saunders, Jr., in "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, Inc., London, 1964, Chapter 2.

(4) W. H. Saunders, Jr., and D. H. Edison, *J. Am. Chem. Soc.*, **82**, 138 (1960).

(5) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *ibid.*, 80, 2326 (1958).

(6) C. H. DePuy, R. W. King, and D. H. Froemsdorf, *Tetrahedron*, 7, 123 (1959).

(7) Unpublished results of Dr. T. A. Ashe in these laboratories.

(8) B. Rickborn and J. Quartucci, *J. Org. Chem.*, **29**, 3185 (1964).

dence that this reaction gives stereospecifically *cis* product,[11] we took the precaution of isolating the cyclohexene from the action of ethoxide ion in ethanol on the tosylate. The cyclohexene contained 0.94 atom of deuterium per molecule, compared to 1.00 atom in the original tosylate. The result, unfortunately, is inconclusive. The most pessimistic interpretation of these facts would allow as much as 20–25% of *trans*-2-*d* tosylate (remember that elimination into the undeuterated branch is preferred), but the difference in deuterium content is barely outside of the combined experimental errors and, if real, is more likely the consequence of difficulty in purifying and analyzing the rather volatile cyclohexene.

The reactions of cyclohexyl tosylate with ethoxide in ethanol and with *t*-butoxide in *t*-butyl alcohol were shown to be essentially entirely eliminations. No cyclohexyl alkyl ether was found, and a control on a simulated reaction mixture showed that 2.5% was clearly observable by the gas-chromatographic analysis used. At the concentrations employed (0.1 *M* tosylate, 0.3 *M* base) solvolysis was negligible. In a parallel experiment without base, for example, only 4% ethanolysis was noted during the first half-life of the base-promoted reaction. Rate constants are recorded in Table I.

Table I. Rates of Elimination of Deuterated Cyclohexyl Tosylates at 49.90°[a]

Compound	Solvent[b]	10^5k_2,[c] l. mole^{-1} sec^{-1}
H	EtOH	14.8 ± 0.0[d]
1-*d*	EtOH	13.0 ± 0.1[d]
H	EtOH	13.7 ± 0.1
cis-2-*d*	EtOH	11.9 ± 0.4
H	EtOH	13.4 ± 0.1
trans-2-*d*	EtOH	8.2 ± 0.2
H	EtOH	13.4 ± 0.1
2,2,6,6-d_4	EtOH	3.2 ± 0.2
H	*t*-BuOH	8.71 ± 0.01
1-*d*	*t*-BuOH	7.55 ± 0.05
H	*t*-BuOH	8.73 ± 0.03
cis-2-*d*	*t*-BuOH	7.24 ± 0.05
H	*t*-BuOH	8.74 ± 0.05
trans-2-*d*	*t*-BuOH	4.95 ± 0.05
H	*t*-BuOH	8.72 ± 0.02
2,2,6,6-d_4	*t*-BuOH	1.39 ± 0.01

[a] Temperature control good to ±0.02°. [b] Bases (0.3 *M*) were sodium ethoxide and potassium *t*-butoxide in the respective alcohols as solvents. Tosylate concentration was 0.1 *M*. Aliquots were quenched in standard aqueous hydrochloric acids and back titrated with standard aqueous sodium hydroxide. [c] Average of duplicate or triplicate determinations with average deviations. [d] Temperature was 50.00°.

Ratios of these rate constants yield meaningful isotope effects only with 1-*d* and 2,2,6,6-d_4 compounds. For the 2-*d* compounds, one must consider only elimination into the deuterated branch to obtain a result having simple significance. If one assumes that elimination into the undeuterated branch of the 2-*d* compounds occurs at the same rate as in the undeuterated compound, one can calculate the isotope effect as $(R_D - 0.5R_H)/0.5R_H$, where R_D is the total rate for the deuterated, and R_H the total rate for the undeuterated compound. The isotope effects obtained in this fashion are recorded in Table II.

Table II. Isotope Effects in Elimination Reactions of Deuterated Cyclohexyl Tosylates at 49.90°[a]

Compound	Solvent[b]	k_H/k_D
1-*d*	EtOH	1.14
cis-2-*d*	EtOH	1.36[c]
trans-2-*d*	EtOH	4.47[c]
2,2,6,6-d_4	EtOH	4.19
1-*d*	*t*-BuOH	1.15
cis-2-*d*	*t*-BuOH	1.51[c]
trans-2-*d*	*t*-BuOH	7.53[c]
2,2,6,6-d_4	*t*-BuOH	6.27

[a,b] See corresponding footnotes in Table I. [c] Isotope for elimination into the deuterated branch, calculated on the assumption that there is no isotope effect on elimination into the undeuterated branch. Thus, $k_H/k_D = (R_D - 0.5R_H)/0.5R_H$, where R_D and R_H are the measured total rates for the deuterated and undeuterated compounds, respectively.

Brief comment on the precision of these derived effects is called for. The differences used in these calculations tend to magnify experimental error, so that uncertainties in k_H/k_D for the *trans*-2-*d* compound may run five to ten times the 1–2% error in the measured rate constants. The differences are larger with the *cis*-2-*d* compound, and the error consequently less, perhaps two to three times the error in the measured rates. Another possible error is our assumption of no isotope effect for elimination into the undeuterated branch, though it seems intuitively unlikely that the effect is more than 2–3%. The tetradeuterated compound should give a larger isotope effect than the *trans*-2-*d* compound, because it should exhibit both primary and secondary effects. The lack of complete deuteration will have its most serious effect here, however. The assumption that the 3.8 atoms of deuterium per molecule represents 80% of d_4 material and 20% of d_3 material (the most unfavorable assumption possible) reduces k_H/k_D substantially, but not quite enough to account for the difference in the d_4 and *trans*-2-*d* isotope effects. In view of the possible errors, it is not wise to attach too much significance to this observation.

Discussion

The primary isotope effects found with the *trans*-2-*d* and 2,2,6,6-d_4 compounds are of a reasonable magnitude for proton-transfer reactions. In fact, they are closely similar to those observed for 2-phenylethyl-2,2-d_2 tosylate[4] when allowance is made for the difference in temperature. This fact is somewhat surprising, for one might expect considerably greater carbanion character, and therefore a greater extent of proton transfer in the transition state, for the 2-phenylethyl system than for the cyclohexyl system. Possibly the difference in carbanion character does exist, but is caused primarily by a change in the extent of C–OTs stretching in the transition state.

The results on 2-phenylethyl tosylate[4] have been interpreted[3] as indicating that the proton was more than half transferred in the transition state of the re-

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(9) S. Wolfe, M. Nussium, Y. Mazur, and F. Sondheimer, *J. Org. Chem.*, **24**, 1034 (1959).

(10) H. C. Brown and B. C. Subba Rao, *ibid.*, **22**, 1135 (1957).

(11) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **81**, 247 (1959); **83**, 2544 (1961).

action with ethoxide ion in ethanol. One can then say, in accord with the Swain–Thornton rule,[12] that the stronger base, *t*-butoxide in *t*-butyl alcohol, gives a large isotope effect because the proton is less completely transferred and so nearer the midpoint[13] in the transition state. That almost the same change in isotope effect between ethoxide in ethanol and *t*-butoxide in *t*-butyl alcohol should result in the cyclohexyl as in the 2-phenylethyl system suggests that the extent of proton transfer in the transition state is governed primarily by the leaving group rather than the extent or nature of α or β substitution.

This conclusion is not certain, for it is possible that the similarities in the two systems are fortuitous. It is also possible that changes in the bending frequencies of the transition state[14] are responsible for the changes in isotope effect, so that there would be no necessary correlation of isotope effect with carbanion character. Such an explanation could more conveniently account for the apparent *increase* in carbanion character of the transition state, as measured by the Hammett ρ value, between ethoxide in ethanol and *t*-butoxide in *t*-butyl alcohol for 2-arylethyl tosylates.[15] The arguments given in the preceding paragraph predict a *decrease* unless one assumes that the extent of C–OTs cleavage decreases more than the extent of C–H cleavage when the change from ethoxide in ethanol to *t*-butoxide in *t*-butyl alcohol is made.

We now turn to the secondary isotope effects. The effect of α deuterium is the same within experimental error in both solvent–base systems. The magnitude of the effect is similar to that observed in solvolyses[5,16,17] and in an E2 reaction of 2-phenylethyl-1,1-d_2 bromide.[18] The α-deuterium effects in solvolyses are believed to arise from the change in hybridization from sp^3 to sp^2 as the carbonium ion forms,[5] and a change in hybridization also occurs during the E2 reaction. It is somewhat surprising that the results reveal no difference in hybridization (and hence in double-bond character) between the transition states in the two solvent–base systems. The effects are small enough, however, that significant differences are not easy to detect. Even with the solvolytic α-deuterium isotope effects there is little variation, with only SN2 reactions giving markedly different values.[19]

The most likely source of the secondary β-deuterium isotope effects would also seem to be hybridization changes.[5] If so, one must explain why the effects are distinctly larger than the α-deuterium effects usually attributed to changes in hybridization.[20] A trivial cause could be a lack of stereospecificity in the synthesis of *cis*-cyclohexanol-2-*d* and a consequent admixture of a primary isotope effect, but the evidence points to high stereospecificity in deuterioboration.[11] A more likely explanation lies in the apparent electron-repelling character of deuterium relative to hydrogen, which is attributed to anharmonicity of the carbon–hydrogen stretching motion.[20,21] In the solvolytic α-deuterium effects this factor would tend to reduce k_H/k_D by favoring the reaction of the deuterated compound in opposition to the hybridization effect. In the present case, electron density at the β carbon *increases* during the reaction so that both the hybridization change and the inductive effect would favor hydrogen over deuterium. A larger effect for *t*-butoxide than for ethoxide could arise from greater carbanion character, which would mean greater electron density and lesser sp^2 character. As noted above, however, attempts to reconcile greater carbanion character for the transition state in the *t*-butoxide reaction with the primary β-deuterium isotope effects are not without difficulties.

Experimental Section[22]

Cyclohexanone-2,2,6,6-d_4 was obtained by exchanging 0.5 mole of cyclohexanone six times with 99.5% deuterium oxide, using a potassium carbonate catalyst.[23] Fractionation gave 63% of product having bp 153–150°, 3.90 atoms of D/molecule.

Cyclohexanol-2,2,6,6-d_4 was obtained by reducing cyclohexanone-2,2,6,6-d_4 with lithium aluminum hydride, following a procedure[5] used for cyclopentanone-2,2,5,5-d_4.

Cyclohexanol-1-*d* was obtained by reducing cyclohexanone with lithium aluminum deuteride by the same procedure used on cyclohexanone-2,2,6,6-d_4. There was obtained 91% of cyclohexanol-1-*d*, bp 159°.

trans*-Cyclohexanol-2-*d was obtained by reducing cyclohexene oxide with lithium aluminum deuteride by the usual procedure in refluxing ether.[24] There was obtained 70% of product, bp 157–160°.

cis*-Cyclohexanol-2-*d resulted from deuterioboration of cyclohexene by a modification[9] of the Brown[10,11] method in which diborane-d_6 is generated *in situ* from boron trifluoride and lithium aluminum deuteride. To 12.3 g of cyclohexene and 11.4 g of boron trifluoride etherate in dry ether was added slowly a suspension of 2.1 g of lithium aluminum deuteride in dry ether. A few pieces of ice were added to destroy excess diborane-d_6. and the mixture was then treated with 40 ml of 3 *M* sodium hydroxide and 20 ml of 30% hydrogen peroxide. The aqueous layer was extracted three times with ether and the extracts were dried (magnesium sulfate) and fraction ated to yield 46% of product, bp 156–158°.

Cyclohexyl *p*-toluenesulfonate was prepared by the general procedure of Tipson,[25,26] except that the reaction mixture was treated with cold dilute sulfuric acid and extracted with ether. The ether extract was washed with dilute sulfuric acid, dilute sodium bicarbonate, and water, and then dried over magnesium sulfate. Removal of the ether and recrystallization from ether–pentane gave 86% of (undeuterated) cyclohexyl *p*-toluenesulfonate, mp 45–46° (lit.[26] 45–46°).

The same procedure was applied to the deuterated cyclohexanols to give cyclohexyl-1-*d* *p*-toluenesulfonate, mp 46–46.5°, 0.97 atom of D/molecule; *trans*-cyclohexyl-2-*d* *p*-toluenesulfonate, mp 42.5–43°, 0.94 atom of D/molecule; *cis*-cyclohexyl-2-*d* *p*-toluenesulfonate, mp 42–43°, 1.00 atom of D/molecule; and cyclohexyl-2,2,6,6-d_4 *p*-toluenesulfonate, mp 42.5–43°, 3.80 atoms of D/molecule. The low melting point of the last three are not unprecedented, the recent literature reporting values 43.5–44°[27] and 43.3–

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[12] C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, **84**, 817 (1962).

[13] F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).

[14] W. H. Saunders, Jr., *Chem. Ind.* (London), 663 (1966).

[15] C. H. DePuy and C. A. Bishop, *J. Am. Chem. Soc.*, **82**, 2532 (1960).

[16] W. H. Saunders, Jr., and K. T. Finley, *ibid.*, **87**, 1384 (1965).

[17] K. Mislow, S. Borčić, and V. Prelog, *Helv. Chim. Acta*, **40**, 2477 (1957).

[18] S. Ašperger, N. Ilakovac, and D. Pavlović, *J. Am. Chem. Soc.*, **83**, 5032 (1961).

[19] R. R. Johnson and E. S. Lewis, *Proc. Chem. Soc.*, 52 (1958).

[20] E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963).

[21] E. A. Halevi, M. Nussim, and A. Ron, *J. Chem. Soc.*, 866 (1963).

[22] Melting points and boiling points are uncorrected. Deuterium analyses were performed by Mr. J. Nemeth, University of Illinois, Urbana, Ill. Gas-chromatographic analyses were done on a Wilkins Aerograph, Model A-90-C.

[23] C. H. DePuy, R. W. King, and D. H. Froemsdorf, *Tetrahedron*, **7**, 123 (1959).

[24] L. W. Trevoy and W. G. Brown, *J. Am. Chem. Soc.*, **71**, 1675 (1949).

[25] R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

[26] R. S. Tipson, M. A. Clapp, and L. H. Cretcher, *ibid.*, **12**, 133 (1947).

[27] S. Winstein, E. Grunwald, R. E. Buckles, and C. Hanson, *J. Am. Chem. Soc.*, 70, 816 (1948).

43.8°.[28] The sharpness of the melting point and the near-theoretical deuterium analyses argue against significant contamination.

Cyclohexyl ethyl ether was obtained by treatment of an ether suspension of the sodium salt of cyclohexanol (prepared from cyclohexanol and sodium hydride in dry ether) with ethyl bromide. Filtration and distillation, followed by treatment with sodium metal and fractionation, gave a product of bp 148–149.5° (lit.[29] 148.5–149°).

Cyclohexyl *t*-butyl ether was prepared in the same manner as cyclohexyl ethyl ether, using *t*-butyl bromide instead of ethyl bromide. The product had bp 60–62° (12 mm) (lit.[30] 55–57° (10 mm)).

Kinetics of the Base-Promoted Elimination Reactions of the Cyclohexyl *p*-Toluenesulfonates. Anhydrous ethanol was prepared by the method of Lund and Bjerrum.[31–33] Anhydrous *t*-butyl alcohol was obtained by distilling Eastman Kodak White Label grade material twice from sodium. Gas chromatograms (15-ft Carbowax column) of both alcohols showed less than 0.05% of water. Standard solutions of alkoxides were obtained by dissolving the clean metal in the alcohol and were stored in polyethylene bottles. Standardization was performed just before each use. Standard aqueous sodium hydroxide and hydrochloric acid were prepared from carbonate-free water and standardized in the usual manner.

Reactions were run in a modified 50-ml volumetric flask with side arm as previously described.[2] Temperature control was good to ±0.02°, and the thermometer was calibrated against one calibrated by the National Bureau of Standards. In about 25 ml of the alcohol, 0.005 mole of the cyclohexyl *p*-toluenesulfonate was dissolved, the solution equilibrated for 1 hr or more, 25 ml of 0.6 *M* alkoxide (also equilibrated) added, and the volume adjusted to the mark. Aliquots of 3.89 ml were withdrawn with a calibrated syringe, quenched in 10 ml of standard aqueous hydrochloric acid, and back titrated with standard sodium hydroxide. Deuterated and undeuterated materials were run at the same time. Rate constants were calculated from the integrated second-order rate equation.

Attempted Detection of Substitution Products. The reaction mixture (10–12 ml) was diluted with an equal volume of water and extracted with three 20-ml portions of ligroin. The solution was dried over sodium sulfate, reduced to about 5 ml by fractionation through a 6-in. Vigreux column, and analyzed by gas chromatography on a 5-ft Carbowax column (flow rate *ca.* 50 cc/min and oven temperature *ca.* 100° for the products in ethanol–ethoxide and *ca.* 155° for the products in *t*-butyl alcohol–*t*-butoxide). Simulated reaction mixtures containing 97.5% of cyclohexene and 2.5% of the cyclohexyl alkyl ether in the appropriate alcohol were subjected to the same treatment and gave peaks corresponding in retention times to the cyclohexyl alkyl ethers. The actual reaction mixtures gave no peaks corresponding to the cyclohexyl alkyl ethers.

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[28] W. F. Edgell and L. Parts, *J. Am. Chem. Soc.*, 77, 4899 (1955).

[29] A. I. Vogel, *J. Chem. Soc.*, 1809 (1948).

[30] S. Lawesson and N. C. Yang, *J. Am. Chem. Soc.*, **81**, 4230 (1959).

[31] H. Lund, *Ber.*, 37, 936 (1934).

[32] H. Lund and J. Bjerrum, *ibid.*, **64**, 210 (1931).

[33] H. Lund, *J. Am. Chem. Soc.*, 74, 3188 (1952).

Mechanisms of Elimination Reactions. VIII. The Effect of Added Dimethyl Sulfoxide on Rates, Isotope Effects, and Substituent Effects in the Reaction of 2-Arylethyl Bromides with Potassium *t*-Butoxide in *t*-Butyl Alcohol[1]

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Abstract: Rates of elimination have been determined for the reactions of 2-arylethyl bromides with potassium *t*-butoxide in *t*-butyl alcohol containing varying concentrations of dimethyl sulfoxide. Kinetic deuterium isotope effects were determined using 2-phenylethyl and 2-phenylethyl-2,2-d_2 bromides. Hammett reaction constants were determined with the *para* substituents methoxyl, methyl, hydrogen, and bromine. The temperature range was 30–50°, and the dimethyl sulfoxide concentration was varied between 0 and 2.23 *M*, most measurements being made in the 0–0.965 *M* region. The rate of reaction increases markedly as dimethyl sulfoxide is added—about 120-fold from 0 to 2.23 *M*. In fact, the rate increases much faster than the basicity of the medium as measured by an H– function. In contrast to the effect on rate, neither k_H/k_D nor ρ is changed appreciably by added dimethyl sulfoxide. Possible explanations of these results are discussed. It is suggested that usual definitions of equilibrium or kinetic basicity are not suitable when discussing the effect of "basicity" upon transition-state structure in these elimination reactions.

Hammett reaction constants[2–4] and kinetic deuterium isotope effects[5] have been used to study transition-state structure in elimination reactions of 2-arylethyl bromides. The only solvents used so far have been ethanol and *t*-butyl alcohol. No significant change in ρ is observed,[4] but k_H/k_D is larger with *t*-butoxide in *t*-butyl alcohol than with ethoxide in ethanol. Interpretation of these results is rendered difficult by the fact that both solvent and base are varied simultaneously.

We felt that the use of potassium *t*-butoxide in *t*-butyl alcohol–dimethyl sulfoxide mixtures might enable us to dissect better the factors influencing rate and transition-state structure in these reactions. While dimethyl sulfoxide has a substantially greater dielectric constant than *t*-butyl alcohol, the E_T and Z values are nearly identical for the two solvents.[6] Consequently,

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[1] This work was supported by the National Science Foundation.

[2] W. H. Saunders, Jr., and R. A. Williams, *J. Am. Chem. Soc.*, **79**, 3712 (1957).

[3] C. H. DePuy and D. H. Froemsdorf, *ibid.*, **79**, 3705 (1957).

[4] C. H. DePuy and C. A. Bishop, *ibid.*, **82**, 2532 (1960).

[5] W. H. Saunders, Jr., and D. H. Edison, *ibid.*, **82**, 138 (1960).

[6] C. Reichardt, *Angew. Chem. Intern. Ed. Engl.*, **4**, 29 (1965).