[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF ROCHESTER]

Rates of Solvolysis of Deuterated 2-(*p*-Methoxyphenyl)-ethyl and 2,2-Diphenylethyl *p*-Toluenesulfonates[1]

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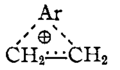
Rates of acetolysis and formolysis of 2-(*p*-methoxyphenyl)-ethyl and 2,2-diphenylethyl *p*-toluenesulfonates and their α- and β-deuterated analogs were determined. The pattern of results was the same as that previously observed with the deuterated 2-phenylethyl *p*-toluenesulfonates: the α-deuterated compounds reacted about 20% slower than, and the β-deuterated compounds at the same rate as, the undeuterated compounds. The bearing of these results on the nature of the transition state in aryl-participation reactions is discussed.

A recent study revealed that 2-phenylethyl-1,1-d_2 *p*-toluenesulfonate undergoes formolysis 17% slower than the undeuterated compound, but the 2-phenylethyl-2,2-d_2 isomer shows no isotope effect in this reaction.[2] The effect of α-deuterium probably arises mainly out of the change in hybridization from sp^3 to sp^2 at the α-carbon during ionization.[3] Evidently no similar change has occurred at the β-carbon and the transition state for ionization therefore cannot resemble the symmetrically-bridged ion I. We undertook the present investigation to determine whether structural and environmental changes leading to more effective aryl participation would affect this situation.


I

The first system chosen was 2-(*p*-methoxyphenyl)-ethyl. The 2-(*p*-methoxyphenyl)-ethanol-1,1-d_2 was obtained by reduction of *p*-methoxyphenylacetic acid with lithium aluminum deuteride. Efforts to prepare *p*-methoxyphenylacetic-α,α-d_2 acid *via* hydrolysis and decarboxylation of *p*-methoxyphenylmalonic ester in deuterium oxide (by analogy to the successful preparation of phenylacetic-α,α-d_2 acid[2]) gave poor and irreproducible yields. Consequently an exchange reaction of sodium *p*-methoxyphenylacetate with deuterium oxide was tried. Two exchanges gave material of 85–90% isotopic purity. Reduction with lithium aluminum hydride afforded 2-(*p*-methoxyphenyl)-ethanol-2,2-d_2. The *p*-toluenesulfonates were prepared in the usual manner.

The second system chosen was 2,2-diphenylethyl The α- and β-deuterated *p*-toluenesulfonates were prepared by reaction sequences completely analogous to those used in the 2-(*p*-methoxyphenyl)-ethyl system.

Rates of acetolysis and formolysis for each of the three 2-(*p*-methoxyphenyl)-ethyl *p*-toluenesulfonates are recorded in Table I. The inclusion of lithium perchlorate in the acetolysis was to minimize ion-pair return, which can be important in this system.[4] Return to arylethyl tosylate from a phenonium–tosylate ion pair would lead to "scrambling" of the deuterium label and hence to drifting rate constants. At the lithium perchlorate concentration used, only about 2% scrambling should occur in one half-life.[4] The steadiness of the rate constants confirms that return was satisfactorily suppressed. Return was found to be unimportant in the formolysis of 2-(*p*-methoxyphenyl)-ethyl *p*-toluenesulfonate.[4] Rates of acetolysis and formolysis of the 2,2-diphenylethyl *p*-toluenesulfonates were measured without complications and are recorded in Table II.

TABLE I

RATES OF SOLVOLYSIS OF DEUTERATED 2-(*p*-METHOXYPHENYL)-ETHYL *p*-TOLUENESULFONATES

Position of D	Solvent	Temp., °C.	$k^a \times 10^5$ sec.$^{-1}$	k_H/k_D
..	HOAc[b]	75.0	4.01 ± 0.01[d]	..
α	HOAc[b]	75.0	3.40 ± .01	1.18
β	HOAc[b]	75.0	4.00 ± .02	1.00
..	HCOOH[c]	50.0	15.3 ± .2[e]	..
α	HCOOH[c]	50.0	12.7 ± .2	1.20
β	HCOOH[c]	50.0	15.8 ± .2	0.97

[a] Each constant is the average of two or (usually) three runs with average deviation. [b] Solution was 0.05 *M* in the *p*-toluenesulfonate and 0.06 *M* in lithium perchlorate. [c] Solution was 0.04–0.05 *M* in the *p*-toluenesulfonate and 0.055 *M* in sodium formate. [d] Ref. 4 reports 4.14 × 10^{-5} sec.$^{-1}$ at 75.00°. [e] Ref. 7 reports 1.46 × 10^{-4} sec.$^{-1}$ at 50.01°.

TABLE II

RATES OF SOLVOLYSIS OF DEUTERATED 2,2-DIPHENYLETHYL *p*-TOLUENESULFONATES AT 75.0°

Position of D	Solvent	$k^a \times 10^5$ sec.$^{-1}$	k_H/k_D
..	HOAc[b]	0.264 ± 0.005[d]	..
α	HOAc[b]	.219 ± .002	1.21
β	HOAc[b]	.259 ± .006	1.02
..	HCOOH[c]	39.1 ± .3	..
α	HCOOH[c]	32.4 ± .3	1.21
β	HCOOH[c]	38.6 ± .5	1.01

[a] [b],[c] See corresponding footnotes of Table I. [d] Ref. 8 reports 2.61 × 10^{-6} sec.$^{-1}$ at 74.71°.

An immediately obvious conclusion from Tables I and II is that the results follow the pattern previously observed in the formolysis of 2-phenylethyl *p*-toluenesulfonate.[2] The α-deuterium effects are all within experimental error of each other, but do tend to be slightly higher in the 2,2-diphenylethyl series.[5] Probably all of these solvolyses belong in the limiting[6] category. Our results thus suggest

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(1) This work was supported by the Office of Ordnance Research, U. S. Army.

(2) W. H. Saunders, Jr., S. Ašperger and D. H. Edison, THIS JOURNAL, **80**, 2421 (1958).

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

(4) E. F. Jenny and S. Winstein, *Helv. Chim. Acta*, **41**, 807 (1958).

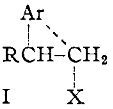
(5) $\Delta\Delta F^{\ddagger}$ per D is 57 cal./mole in the acetolysis and 58 cal./mole in the formolysis of 2-(*p*-methoxyphenyl)-ethyl *p*-toluenesulfonate; $\Delta\Delta F^{\ddagger}$ for 2,2-diphenylethyl *p*-toluenesulfonate is 66 cal./mole in both acetolysis and formolysis.

(6) S. Winstein, E. Grunwald and H. W. Jones, THIS JOURNAL, **73**, 2700 (1951).

that constancy of the α-deuterium isotope effect with solvents of differing ionizing powers may be a useful criterion for assigning solvolyses to the limiting category.

On the basis of products and rates, Winstein concluded that the solvolyses used in this study occur with predominating aryl participation.[4,7,8] The absence of β-deuterium isotope effects is consistent with his conclusions and provides further examples of the conformational requirements of such effects.[2,9]

Judging from rate enhancement, aryl participation is more effective in both the 2-(*p*-methoxyphenyl)-ethyl and 2,2-diphenylethyl systems than in the 2-phenylethyl system. We felt that the transition state might be far enough along the reaction coördinate in one or both of these cases to give an appreciable change in hybridization at the β-carbon and hence a β-deuterium isotope effect.[2,3] Obviously this has not happened. The transition state for ionization in all of the reactions we have studied so far appears to be best represented by II, where the C_α–X bond is largely ionic and the C_α–Ar bond very weak relative to the C_β–Ar bond. The range of systems showing the same behavior makes it likely that a transition state similar to II is general for carbon-participation reactions.[10,11]



II

$$\overset{\text{Ar}}{\text{RCH}}\text{–}\underset{\text{X}}{\text{CH}_2}$$

Whether the conclusions drawn here can be extended to participation by neighboring functional groups is uncertain. We hope to explore this problem in a future investigation.

Experimental[12]

***p*-Methoxyphenylacetic-α,α-d_2 Acid.**—Equal weights of the sodium salt of *p*-methoxyphenylacetic acid and deuterium oxide were refluxed overnight.[13] The deuterium oxide was removed in high vacuum and the procedure was repeated once more. Acidification of an aqueous solution of the sodium salt yielded *p*-methoxyphenylacetic-α,α-*d*, acid. This procedure gave 85–90% isotopic purity.

2-(*p*-Methoxyphenyl)-ethanols.—The reduction of ethyl *p*-methoxyphenylacetate with lithium aluminum hydride in ether was performed in the usual fashion and the reaction mixture worked up as described by Amundsen and Nelson.[14] There was obtained 88% of 2-(*p*-methoxyphenyl)-ethanol, b.p. 110–112° (1 mm.) (lit.[7] b.p. 139–141° (10 mm.)).

The reduction of ethyl *p*-methoxyphenylacetate with lithium aluminum deuteride gave 91% of 2-(*p*-methoxyphenyl)-ethanol-1,1-d_2.

The reduction of *p*-methoxyphenylacetic-α,α-d_2 acid with lithium aluminum hydride gave 59% of 2-(*p*-methoxyphenyl)-ethanol-2,2-d_2.

α,α-Diphenylacetic-α-d_2 Acid.—Sodium diphenylacetate was treated twice with deuterium oxide by the procedure described above for *p*-methoxyphenylacetic acid. The product had 98% of the calculated deuterium content.

2,2-Diphenylethanols.—Reduction with lithium aluminum hydride of either diphenylacetic acid or ethyl diphenylacetate in the manner described for ethyl *p*-methoxyphenylacetate gave 86–89% of 2,2-diphenylethanol.

Reduction with lithium aluminum deuteride of ethyl diphenylacetate gave 91% of 2,2-diphenylethanol-1,1-d_2.

Reduction with lithium aluminum hydride of α,α-diphenylacetic-α-*d* acid gave 87% of 2,2-diphenylethanol-2-*d*.

***p*-Toluenesulfonates** of the alcohols were prepared by the procedure of Tipson.[15]

2-(*p*-Methoxyphenyl)-ethyl *p*-toluenesulfonate was recrystallized from petroleum ether to give 85% of material of m.p. 58–58.5° (lit.[7] 57–58°).

2-(*p*-Methoxyphenyl)-ethyl-1,1-d_2 *p*-toluenesulfonate was obtained in 76% yield, m.p. 58.5°; 2.02, 2.00 atoms D/molecule.

2-(*p*-Methoxyphenyl)-ethyl-2,2-d_2 *p*-toluenesulfonate was obtained in 81% yield, m.p. 56.5–57°; 1.76, 1.77 atoms D/molecule.

2,2-Diphenylethyl *p*-toluenesulfonate was recrystallized from *n*-hexane to yield 96% of material of m.p. 116–117° (lit.[8] m.p. 116°).

2,2-Diphenylethyl-1,1-d_2 *p*-toluenesulfonate was obtained in 93% yield, m.p. 116–117°; 2.00 atoms D/molecule.

2,2-Diphenylethyl-2-*d* *p*-toluenesulfonate was obtained in 94% yield, m.p. 116–116.5°; 0.98, 1.01 atoms D/molecule.

Deuterium analyses were performed by the "falling drop" method. The procedure and apparatus were essentially as described by previous workers.[16]

Kinetic Methods.—Procedures for purifying solvents and reagents and for following the reactions were closely similar to those previously reported.[2,17] In the acetolyses, solutions were initially 0.05 *M* in *p*-toluenesulfonate. The solutions of the 2-(*p*-methoxyphenyl)-ethyl *p*-toluenesulfonates were also 0.06 *M* in lithium perchlorate (to minimize ion-pair return[4]). Aliquots were quenched in cold acetic acid and titrated potentiometrically with 0.04 *M* sodium acetate in acetic acid (sodium carbonate plus glacial acetic acid). In the formolyses, solutions were initially 0.04 or 0.05 *M* in *p*-toluenesulfonate and 0.055 *M* in sodium formate. Aliquots were quenched in cold acetic acid and titrated potentiometrically with 0.05 *M* perchloric acid in acetic acid.

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[7] S. Winstein, C. R. Lindegren, H. Marshall and L. L. Ingraham, THIS JOURNAL, **75**, 147 (1953).

[8] S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, *ibid.*, **74**, 1113 (1952).

[9] V. J. Shiner, Jr., *ibid.*, **78**, 2653 (1956).

[10] Professor S. Winstein has pointed out (private communication) that the effect on rate of a *p*-methoxyl group in aryl-participation reactions is much less than in aromatic substitution. This fact offers independent evidence that the interaction between the aryl group and C_α is weak in the transition state.

[11] A referee has pointed out that unequal α- and β-isotope effects would be observed even with a symmetrical transition state if the frequencies of the α- and β-C–H vibrations in the ground state differed significantly. We consider unlikely differences sufficient to account for any appreciable fraction of the observed effects. Examination of the infrared spectra of the 2-phenylethyl alcohols (we did not have spectra of the *p*-toluenesulfonates or of the substances used in the present investigation) supports this belief. A peak in the stretching region (2900 cm.$^{-1}$) differs by 20–30 cm.$^{-1}$ and a peak in the bending region (1450 cm.$^{-1}$) differs by *ca.* 5 cm.$^{-1}$ between α- and β-deuterated alcohols, being at higher frequencies for the latter. These facts suggest that the effect would not only be small (1–2%) but would tend to reinforce rather than cancel a β-isotope effect.

[12] Melting points and boiling points are uncorrected.

[13] The procedure is similar to that used by D. J. G. Ives, *J. Chem. Soc.*, 81 (1938), on phenylacetic acid.

[14] L. H. Amundsen and L. S. Nelson, THIS JOURNAL, **73**, 242 (1951).

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

[16] W. von E. Doering and A. K. Hoffman, THIS JOURNAL, **77**, 521 (1955); A. S. Keston, D. Rittenberg and R. Schoenheimer, *J. Biol. Chem.*, **122**, 227 (1937).

[17] S. Winstein and H. Marshall, THIS JOURNAL, **74**, 1120 (1952).