SOLVOLYSES OF 2-(2,4-DIMETHOXYPHENYL)-1,1-d_2-ETHYL AND 2-(3,5-DIMETHOXYPHENYL)-1,1-d_2-ETHYL *p*-BROMOBENZENESULFONATES; ION-PAIR RETURNS IN SOLVOLYSES OF 2-ARYLETHYL SYSTEMS

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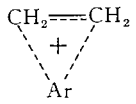
ABSTRACT

Acetolysis and formolysis of 2-(2,4-dimethoxyphenyl)-1,1-d_2-ethyl and 2-(3,5-dimethoxyphenyl)-1,1-d_2-ethyl *p*-bromobenzenesulfonates were allowed to proceed for about two half-lives, and the corresponding acetate and formate products as well as the unsolvolyzed sulfonate esters were recovered and analyzed by nuclear magnetic resonance. In the 2,4-dimethoxy substituted system, both acetolysis and formolysis gave products showing practically equal distributions of the deuterium in the C-1 and C-2 positions of the ethyl chain. For the 3,5-dimethoxy substituted system, deuterium isotope position rearrangements from C-1 to C-2 in the products were found to be 14 and 26%, respectively, for acetolysis and formolysis. These results provide more quantitative verifications of earlier conclusions, based on kinetic data, regarding the extents of involvement of bridged ions as reaction intermediates. The unsolvolyzed sulfonate ester recovered from the acetolysis of either the 2,4- or 3,5-dimethoxy substituted system showed a significant amount of deuterium rearrangement from C-1 to C-2, indicating the occurrence of ion-pair returns. On the other hand, such rearrangements were negligibly small in the sulfonates recovered after partial formolysis. By utilizing data on isotopic rearrangements in the recovered sulfonates obtained from the present work or from the literature, values of k_a/k_t, the ratio of the total reaction rate to the titrimetric rate, were calculated for a number of 2-arylethyl systems. Implications of the present results on a general mechanism for the solvolyses of 2-arylethyl arenesulfonates are also discussed.

INTRODUCTION

From considerations of relative rates and entropies of activation, Winstein and Heck (1) concluded that the chief contributor to the rate of both acetolysis and formolysis of 2-(2,4-dimethoxyphenyl)-ethyl *p*-bromobenzenesulfonate (I-OBs) is the anchimerically assisted rate constant (k_Δ), whereas for 2-(3,5-dimethoxyphenyl)-ethyl *p*-bromobenzenesulfonate (II-OBs), acetolysis is chiefly anchimerically unassisted (k_s) and both k_s and k_Δ contribute to the formolysis of II-OBs. The anchimerically assisted process involves a nonclassical, bridged ion, such as the ethylene-2,4-dimethoxyphenonium ion, as an intermediate (1). Such bridged ions may be generalized for 2-arylethyl systems, as shown by III, which may be termed an ethylenearonium ion. These qualitative conclusions



III

derived from kinetic data can be verified more quantitatively by isotope position rearrangement studies. In the present work, 2-(2,4-dimethoxyphenyl)-1,1-d_2-ethyl and 2-(3,5-dimethoxyphenyl)-1,1-d_2-ethyl *p*-bromobenzenesulfonates (I-OBs-1-d_2 and II-OBs-1-d_2, respectively) were subjected to acetolysis and formolysis, and the deuterium distributions in the ethyl chain of the resulting products were determined to ascertain the extents of involvement of III.

The solvolyses of I-OBs-1-d_2 and II-OBs-1-d_2 were interrupted before completion and

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the deuterium distributions in the recovered *p*-bromobenzenesulfonates gave indications of the extents of return from ion-pairs to covalent bonding. The return processes for optically active systems which proceed via symmetrical bridged ions, such as in the solvolyses of *threo*-3-phenyl-2-butyl and *threo*-3-anisyl-2-butyl arenesulfonates (2, 3), have been measured by a comparison of the polarimetric rate constant (k_α) and the titrimetric rate constant (k_t). Recently, Smith and Showalter (4) have utilized data on isotopic rearrangements to calculate an equivalent of k_α/k_t for the acetolysis of *erythro*-3-phenyl-2-butyl *p*-toluenesulfonate. In studies with 2-arylethyl systems, it is impossible to evaluate k_α because of the lack of optical activity. The method of Smith and Showalter (4), however, can be employed. This treatment is applied to the present results on returns as well as to other 2-arylethyl systems for which isotopic rearrangement data on returns are available from the literature.

RESULTS AND DISCUSSION

I-OBs-1-d_2 and II-OBs-1-d_2 were prepared from the corresponding deuterated alcohols, which were obtained, respectively, from the lithium aluminium deuteride reduction of 2,4-dimethoxyphenylacetic acid (IV) and 3,5-dimethoxyphenylacetic acid (V). As indicated by Winstein and Heck (1), IV was prepared from 2,4-dimethoxybenzaldehyde by the azlactone method (5) and V was obtained from 3,5-dimethoxybenzoic acid by way of the corresponding benzyl alcohol, benzyl chloride, and nitrile. Acetolysis and formolysis of I-OBs-1-d_2 and II-OBs-1-d_2 were interrupted after the reactions had proceeded for about two half-lives (see Experimental). The resulting acetates and formates (I-OAc-*x*-d_2, II-OAc-*x*-d_2, I-OCHO-*x*-d_2, and II-OCHO-*x*-d_2) as well as the recovered unsolvolyzed sulfonates (I-OBs-*x*-d_2 and II-OBs-*x*-d_2) were examined by nuclear magnetic resonance (n.m.r.). The pertinent parts of typical sets of spectra are shown in Figs. 1 and 2. Integration of a number of such sets of spectra gave the averaged deuterium distributions in the C-1 and C-2 positions of the ethyl chain of the various compounds analyzed. The results are given in Table I.

The reaction of III-d_2 from I-OBs-1-d_2 or II-OBs-1-d_2 could give rise to products with an equal amount of deuterium at the C-1 and C-2 positions (eq. [1]). This prediction is fully

[1] $$\underset{\text{III-}d_2}{\overset{CH_2{=}{=}{=}CD_2}{\underset{Ar}{+}}} \xrightarrow{OS^-} ArCH_2CD_2OS + ArCD_2CH_2OS$$

met in both the acetolysis and formolysis of I-OBs-1-d_2, confirming the earlier conclusion based on kinetic data (1). The small excess over 50% of deuterium at C-2 (Table I) for I-OAc-*x*-d_2 and I-OCHO-*x*-d_2 may be attributable to an isotope effect, the reaction with III-d_2 being slightly more favorable at the carbon position containing hydrogen than at the one containing deuterium.

The isotope position rearrangements of deuterium in the products from the acetolysis and formolysis of II-OBs-1-d_2 indicate the partial involvement of III, again confirming the conclusion (1) that k_s competes favorably with k_Δ in this system. Winstein and Heck (1) have pointed out that a *m*-methoxy group on a participating phenyl group may give rise to either a small retardation or a small acceleration of the rate, depending on the relative influence of the inductive and resonance effects. In the formolysis of II-OBs, it was noted that the two *m*-methoxy groups in the 2-phenylethyl system decreased the rate by a factor

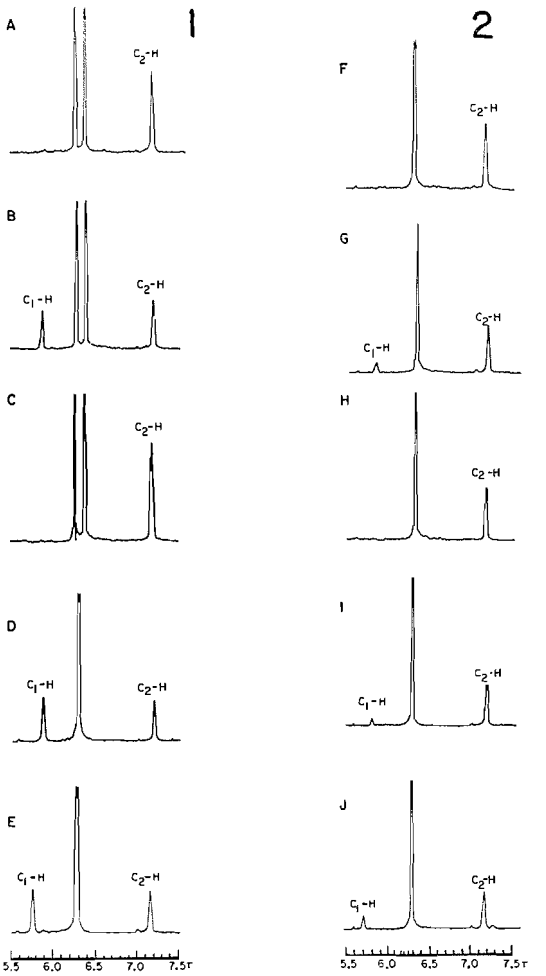


FIG. 1. Pertinent parts of the n.m.r. spectra obtained on the HA-100 spectrometer: A, 2-(2,4-dimethoxyphenyl)-1,1-d_2-ethyl *p*-bromobenzenesulfonate (I-OBs-1-d_2); B, I-OBs-x-d_2 recovered from acetolysis after 70.6% reaction; C, I-OBs-x-d_2 recovered from formolysis after 77.6% reaction; D, I-OAc-x-d_2 product from acetolysis; E, I-OCHO-x-d_2 product from formolysis. The undesignated peaks shown are caused by methoxyl hydrogens.

FIG. 2. Pertinent parts of the n.m.r. spectra obtained on the HA-100 spectrometer: F, 2-(3,5-dimethoxyphenyl)-1,1-d_2-ethyl *p*-bromobenzenesulfonate (II-OBs-1-d_2); G, II-OBs-x-d_2 recovered from acetolysis after 74.7% reaction; H, II-OBs-x-d_2 recovered from formolysis after 71.2% reaction; I, II-OAc-x-d_2 product from acetolysis; J, II-OCHO-x-d_2 product from formolysis. The undesignated peaks shown are caused by methoxyl hydrogens.

of 3 and that, when the $\Delta S^{\ddagger}$ values are considered, the formolysis rate for II-OBs "is not so predominantly composed of k_Δ as in the case of the parent $C_6H_5CH_2CH_2OBs$ system" (1). This statement is borne out more quantitatively by a comparison of the present results with known data from ^{14}C-labeled 2-phenylethyl *p*-toluenesulfonate (VI-OTs); the formolysis of II-OBs-1-d_2 gave 26% isotopically rearranged II-OCHO-2-d_2 (Table I) whereas the formolysis of VI-OTs-1-^{14}C resulted in 45% isotope position rearrangement to VI-OCHO-2-^{14}C (6).

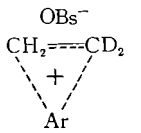
TABLE I

Rearrangements of deuterium from C-1 to C-2 in the products and recovered *p*-bromobenzenesulfonates from the solvolyses of 2-(2,4-dimethoxyphenyl)-1,1-d_2-ethyl and 2-(3,5-dimethoxyphenyl)-1,1-d_2-ethyl *p*-bromobenzenesulfonates (I-OBs-1-d_2 and II-OBs-1-d_2, respectively)

Reactant	Reaction	Compound analyzed	% deuterium at C-2*
I-OBs-1-d_2	Acetolysis	I-OAc-x-d_2	51
		I-OBs-x-d_2	40
I-OBs-1-d_2	Formolysis	I-OCHO-x-d_2	52
		I-OBs-x-d_2	<0.5
II-OBs-1-d_2	Acetolysis	II-OAc-x-d_2	14
		II-OBs-x-d_2	15
II-OBs-1-d_2	Formolysis	II-OCHO-x-d_2	26
		II-OBs-x-d_2	<0.5

*Corresponding to the proton content in the C-1 position, as measured by n.m.r.

Ion-pair returns involving III-d_2 and its counter ion will result in the location of some deuterium at the C-2 position of the recovered sulfonate (eq. [2]). The data in Table I

[2]  $\rightarrow$ $ArCH_2CD_2OBs + ArCD_2CH_2OBs$

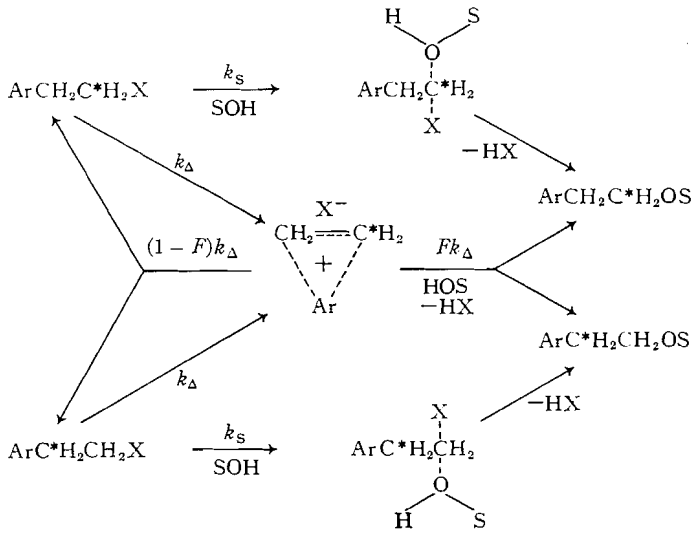
show that such returns are significant in the acetolyses of both I-OBs-1-d_2 and II-OBs-1-d_2, but are negligible in the formolyses. Similar studies on the solvolyses of other 2-arylethyl systems labeled with ^{14}C, including 2-(*p*-anisyl)-1-^{14}C-ethyl, 2-(α-naphthyl)-1-^{14}C-ethyl, and 2-(β-napthyl)-1-^{14}C-ethyl *p*-toluenesulfonates (VII-OTs-1-^{14}C, VIII-OTs-1-^{14}C, and IX-OTs-1-^{14}C, respectively) (7–9), also resulted in significant returns for acetolysis and negligible returns for formolysis. The fact that acetic acid is an optimum medium for ion-pair returns has been discussed in the early formulation of the theory on such processes (10). Returns from ionic intermediates to covalent starting material have also been studied in the solvolyses of 2-phenyl-1-^{14}C-ethyl *p*-toluenesulfonate (VI-OTs-1-^{14}C) (11, 12). In this case, significant returns were observed for formolysis. By investigating the formolysis of VI-OTs-1-^{14}C in the presence of added sodium ^{35}S-*p*-toluenesulfonate, it was shown that the major contributor to the return processes may be intermolecular external return involving exchangeable *p*-toluenesulfonate anion, rather than intramolecular internal return from intimate ion-pairs (12).

Following the mechanistic schemes given by Jenny and Winstein (7) and by Clayton and Lee (12), the processes occurring during the solvolyses of 2-arylethyl arenesulfonates are shown in Reaction Scheme 1, with the asterisk designating the isotopic label, either ^{14}C or D.

As pointed out earlier, the ionization rate constant (k_Δ) for optically active systems which proceed via symmetrical bridged ions can be followed polarimetrically as k_α. Because of the return processes, k_α is greater than the titrimetric rate constant (k_t) (2, 3). According to the scheme shown in Reaction Scheme 1, one can define k_α as the total reaction rate constant (eq. [3]) whereas the titrimetric rate constant is given by eq. [4]. Again, if returns occur ($F < 1$), k_α will be greater than k_t. Values for the k_α so defined can

[3] $$k_\alpha = k_\Delta + k_s$$

[4] $$k_t = Fk_\Delta + k_s$$



REACTION SCHEME 1.

be calculated according to the method of Smith and Showalter (4). For example, in the present studies, the acetolysis of I-OBs-1-d_2 was interrupted after 3 h at 60.6 °C when the reaction was 70.6% complete ($k_t = 1.13 \times 10^{-4}$ s^{-1}). The recovered sulfonate (I-OBs-x-d_2) showed 40% isotope position rearrangement of the deuterium label, which indicated that $2 \times 40 = 80\%$ of the recovered sulfonate has been involved in the return processes. Since the amount of sulfonate remaining was $100 - 70.6 = 29.4\%$, $(80/100) \times 29.4 = 23.5\%$ of the reactant would have been involved in returns. The total involved would be the sum of the percentage solvolyzed and the percentage return, namely, $70.6 + 23.4 = 94.0\%$. The total reaction rate constant would thus be $k_\alpha = (2.303/(3 \times 3\,600))(\log 100/(100 - 94.0)) = 2.5 \times 10^{-4}$ s^{-1}. These calculations can be summarized by eqs. [5]–[7].

[5] % return = 2(% rearrangement in recovered sulfonate/100) × (100 − % solvolyzed)

[6] % total involved = % solvolyzed + % return

[7] $k_\alpha = (2.303/\text{time})(\log 100/(100 - \%\text{ total involved}))$

In this way, k_α as well as k_α/k_t can be evaluated for the acetolysis of I-OBs-1-d_2, II-OBs-1-d_2, VII-OTs-1-^{14}C, VIII-OTs-1-^{14}C, and IX-OTs-1-^{14}C. These data are summarized in Table II.

It can be seen from Table II that, for the three acetolyses of VII-OTs-1-^{14}C which were interrupted at different stages of completion, the calculated values of k_α and k_α/k_t were quite constant. Also, as expected, k_α/k_t decreased markedly when the acetolyses of VII-OTs-1-^{14}C were carried out in the presence of lithium perchlorate. The latter salt is believed to prevent return from solvent-separated ion-pairs, but does not prevent returns from intimate ion-pairs (3, 7). According to eqs. [3] and [4], $k_\alpha/k_t = (k_\Delta + k_s)/(Fk_\Delta + k_s)$. In systems to which k_s does not contribute significantly, such as in the solvolyses of I-OBs-1-d_2 and VII-OTs-1-^{14}C, k_α/k_t would be equal to $1/F$. For the acetolysis of VII-OTs-1-^{14}C, the calculated k_α/k_t of about 3.9 is in reasonably good agreement with the value of 3.77 for $1/F$ reported by Jenny and Winstein (7).

TABLE II

Calculated k_α and k_α/k_t for the acetolyses of a number of labeled 2-arylethyl arenesulfonates

Reactant*	Reaction time (h)	Reaction temperature (°C)	% solvolyzed	$10^5 k_t$ (s^{-1})	% rearrangement†	% return	% total involved	$10^5 k_\alpha$ (s^{-1})	k_α/k_t
I-OBs-1-d_2	3	60.6	70.6	11.3	40	23.4	94.0	25	2.2
II-OBs-1-d_2	37	100.0	74.7	1.03	15	7.5	82.3	1.3	1.3
VII-OTs-1-^{14}C‡	3	75.00	7.3	0.70	10.0	18.5	25.8	2.8	4.0
VII-OTs-1-^{14}C‡	6.1	75.00	13.7	0.67	17.5	30.2	43.9	2.6	3.9
VII-OTs-1-^{14}C‡	19.3	75.00	38.0	0.69	38.0	47.1	85.1	2.7	3.9
VII-OTs-1-^{14}C‡,§	10	75.00	43	1.6	15.9	18.1	61.1	2.6	1.6
VII-OTs-1-^{14}C‡,‖	7.5	75.00	49	2.5	5.0	5.1	54.1	2.9	1.2
VII-OTs-1-^{14}C‡,¶	6	75.00	51	3.3	2.3	2.3	53.3	3.5	1.06
VII-OTs-1-^{14}C‡,**	6	75.00	58	4.0	2.0	1.7	59.7	4.2	1.05
VIII-OTs-1-^{14}C††	12.33‡‡	110.6	45.6	1.37	38	41.3	86.9	4.6	3.4
IX-OTs-1-^{14}C§§	18.5	110.6	50.0	1.04	31	31.0	81.0	2.5	2.4

*I-OBs-1-d_2 and II-OBs-1-d_2 are, respectively, 2-(2,4-dimethoxyphenyl)-1,1-d_2-ethyl and 2-(3,5-dimethoxyphenyl)-1,1-d_2-ethyl *p*-bromobenzenesulfonates; VII-OTs-1-^{14}C, VIII-OTs-1-^{14}C, and IX-OTs-1-^{14}C are, respectively, 2-(*p*-anisyl)-1-^{14}C-ethyl, 2-(α-naphthyl)-1-^{14}C-ethyl, and 2-(β-naphthyl)-1-^{14}C-ethyl *p*-toluenesulfonates.

†Isotope position rearrangement from C-1 to C-2 in the recovered arenesulfonate.

‡Data from ref. 7.

§In the presence of 0.002 *M* $LiClO_4$.

‖In the presence of 0.01 *M* $LiClO_4$.

¶In the presence of 0.03 *M* $LiClO_4$.

**In the presence of 0.06 *M* $LiClO_4$.

††Data from ref. 8.

‡‡In ref. 8, this reaction time was erroneously reported as one half-life based on the preliminary kinetic work carried out before the active runs. More accurate kinetic data show that the reaction was 45.6% complete.

§§Data from ref. 9.

For the 2-phenylethyl system, in the earlier work on ion-pair returns during the solvolyses of VI-OTs-1-^{14}C (11), kinetic measurements were not made in conjunction with isotopic rearrangement studies. From the later investigation on the formolysis of VI-OTs-1-^{14}C (12), both kinetic data and isotope position rearrangements in the recovered sulfonate are available. In this case, however, intermolecular external return involving exchangeable *p*-toluenesulfonate anion may be chiefly responsible for the rearrangements observed in the recovered sulfonate (12). In such an event, the rate for that portion of the reaction proceeding via the bridged ion should be dependent upon the *p*-toluenesulfonate anion concentration, as given in eq. [8] (13), where k_1, k_2, and k_3 are, respectively, the rate constants for ionization, for return from the carbonium ion to the starting material, and for product formation from the carbonium ion.

$$\text{Rate} = \frac{k_1[\text{ArOTs}]}{(k_2/k_3)[\text{OTs}^-] + 1} \qquad [8]$$

However, if $(k_2/k_3)[\text{OTs}^-]$ is small compared with 1, first-order kinetics would still be observed. Apparently, this condition may have been met in the formolysis of VI-OTs-1-^{14}C, because the extent of return was not large and no significant downward drift in the rate was detectable during a kinetic run (12). It is thus possible to apply the first-order kinetic treatments, as given by eqs. [5]–[7], to calculate k_α for the formolysis of VI-OTs-1-^{14}C.

Summarized in Table III are the results from the formolysis of 0.350 *M* VI-OTs-1-^{14}C at 74 °C carried out with no added salt (12). The k_α values calculated from the data obtained after the reaction was interrupted at various stages of completion may be regarded as satisfactorily constant, the average being 3.4×10^{-5} s^{-1}. Since k_t, under the same conditions, has been found to be 3.0×10^{-5} s^{-1} (12), k_α/k_t is about 1.1. This average value of k_α/k_t gave at least a correct indication of the order of magnitude for the return processes; the factor *F*, which is the fraction of the bridged ion proceeding to products, has been evaluated as 0.91 (12).

TABLE III

Calculated k_α for the formolysis of 0.350 *M* 2-phenyl-1-^{14}C-ethyl p-toluenesulfonate (VI-OTs-1-^{14}C) at 74 ± 0.2 °C with no added salt*

Reaction time (min)	% solvolyzed	% rearrangement†	% return	% total involved	$10^5 k_\alpha$ (s^{-1})
51	10.0	0.17	0.3	10.3	3.5
167	29.7	0.76	1.1	30.8	3.7
275	42.9	1.83	2.1	45.0	3.6
600	66.4	3.37	2.3	68.7	3.2
600	65.6	3.30	2.3	67.9	3.2
900	80.0	5.78	2.3	82.3	3.2
1 155	89.9	8.60	1.7	91.6	3.6
1 200	88.5	8.88	2.0	90.5	3.3
				Average	3.4

*Experimental data from ref. 12.
†Isotope position rearrangement from C-1 to C-2 in the recovered *p*-toluenesulfonate.

Recently, Brown and his co-workers (14) have emphatically questioned the existence of nonclassical, bridged phenonium ions as intermediates, and special attention was directed to the 3-phenyl-2-butyl and 2-phenylethyl systems. As an alternative to nonclassical ions, these workers have suggested rapidly equilibrating classical ions. On the other hand, Cram (15) has strongly stated the case for phenonium ions. The existence of bridged ions has not been questioned in systems in which anchimeric rate enhancements have definitely been

established, such as in the solvolyses of I-OBs and VII-OTs. Moreover, the recent direct observation of the n.m.r. spectrum of the carbonium ions derived from the 3-phenyl-2-butyl system under highly acidic conditions at low temperatures favored the bridged-ion formulation (16). The present results on deuterium scrambling in the products of the solvolyses of I-OBs-1-d_2 and II-OBs-1-d_2 also further strengthen the already known correlation that the extents of isotope position rearrangement generally are closely related to the extents of involvement of bridged ions predicted from structural, kinetic, or stereochemical considerations. The phenomena of returns from ionic intermediates to covalent starting materials are also adequately explained by bridged ions. Finally, for the 2-phenylethyl system, Jensen and Ouellette (17) have reported significant rate enhancements for the solvolyses of 2-phenylethylmercuric perchlorate in acetic acid and in formic acid. It is of interest to point out that preliminary work in this laboratory on the acetolysis and formolysis of 2-phenyl-1-^{14}C-ethylmercuric perchlorate gave products in which the ^{14}C-label was almost equally distributed in the C-1 and C-2 positions.[2] From all of these considerations, it appears quite reasonable to conclude that, for 2-arylethyl systems, the nonclassical ethylenearonium ion III may be utilized confidently to correlate the existing experimental data.

EXPERIMENTAL

2-(2,4-Dimethoxyphenyl)-1,1-d_2-ethyl and 2-(3,5-Dimethoxyphenyl)-1,1-d_2-ethyl p-Bromobenzenesulfonates (I-OBs-1-d_2 and II-OBs-1-d_2)

2,4-Dimethoxyphenylacetic acid or 3,5-dimethoxyphenylacetic acid was reduced to the corresponding alcohol as described by Winstein and Heck (1), except that lithium aluminium deuteride instead of lithium aluminium hydride was used as the reducing agent. These alcohols were treated with *p*-bromobenzenesulfonyl chloride in pyridine, again by the procedure of Winstein and Heck (1), to give the desired sulfonate esters. 2-(2,4-Dimethoxyphenyl)-1,1-d_2-ethyl *p*-bromobenzenesulfonate (I-OBs-1-d_2), m.p. 73° C (lit. (1) m.p. 72–73 °C), was obtained in a 48% yield, and the yield of 2-(3,5-dimethoxyphenyl)-1,1-d_2-ethyl *p*-bromobenzenesulfonate (II-OBs-1-d_2), m.p. 76 °C (lit. (1) m.p. 76.5–77.5 °C), was 43%. Deuterium analyses[3] showed the presence of 1.92 and 1.90 deuterium atoms per molecule in I-OBs-1-d_2 and II-OBs-1-d_2, respectively.

Acetolysis of I-OBs-1-d_2

A solution of 6.0 g (0.015 mole) of I-OBs-1-d_2 in 500 ml of reagent-grade glacial acetic acid was heated in a water bath at 60.6 °C for 3 h (70.6% solvolyzed). The mixture was poured into 2 l of ice water and then extracted with two 500 ml portions of ether. The extract was washed three times with cold water, twice with cold, diluted sodium carbonate solution, and finally once more with cold water. After the solution was dried over anhydrous magnesium sulfate, the ether was removed *in vacuo* at room temperature. The residue was triturated in 6 ml of a 1:2 solution of ether – petroleum ether (b.p. 40–60 °C) and then allowed to remain in the refrigerator for 2 days. The crystalline unsolvolyzed sulfonate ester was collected by filtration and recrystallized from ether – petroleum ether. The recovery was 1.4 g (79% based on 70.6% solvolyzed).

The filtrate obtained after the removal of the unsolvolyzed sulfonate was evaporated to an oil which, on vacuum distillation, gave 1.6 g (67% based on 70.6% solvolyzed) of 2-(2,4-dimethoxyphenyl)-*x*-d_2-ethyl acetate (I-OAc-*x*-d_2), b.p. 144° at 2 mm. The corresponding protio acetate isolated from a similar run boiled at 142 °C and 2 mm.

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.22; H, 7.21.

Acetolysis of II-OBs-1-d_2

A solution of 6.0 g (0.015 mole) of II-OBs-1-d_2 in 500 ml of reagent-grade glacial acetic acid was heated in a thermostated oil bath at 100.0 °C for 37 h (74.7% solvolyzed). The reaction mixture was worked up in the same manner as described for the acetolysis of I-OBs-1-d_2. The recovery of unsolvolyzed sulfonate ester was 1.2 g (79% based on 74.9% solvolyzed). The yield of acetate product (II-OAc-*x*-d_2), b.p. 148–150 °C at 2 mm, was 1.3 g (52% based on 74.7% solvolyzed). The corresponding protio acetate obtained from a similar run boiled at 146 °C and 1.5 mm.

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.20; H, 7.14.

[2]*Results of R. J. Tewari, to be published.*
[3]*By Josef Nemeth, Urbana, Illinois.*

Formolysis of I-OBs-1-d_2

A solution of 6.0 g (0.015 mole) of I-OBs-1-d_2 in 500 ml of reagent-grade 98–100% formic acid was kept at 25.0 °C in a water bath for 1 h (77.6% solvolyzed). The reaction mixture was worked up as described for the acetolyses. The recovery of unsolvolyzed sulfonate was nearly quantitative (1.3 g), and the yield of formate product (II-OCHO-x-d_2), b.p. 138 °C at 1.5 mm, was 1.5 g (60% based on 77.6% solvolyzed). The corresponding protio formate obtained in an analogous experiment boiled at 140° and 2 mm.

Anal. Calcd. for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71. Found: C, 62.58; H, 6.78.

Formolysis of II-OBs-1-d_2

A solution of 6.0 g (0.015 mole) of II-OBs-1-d_2 in 500 ml of reagent-grade 98–100% formic acid was heated in a water bath at 60.0 °C for 50 h (71.2% solvolyzed). The reaction mixture was worked up in the same way as described above. The recovery of unsolvolyzed sulfonate was again essentially quantitative (1.7 g). Some technical difficulty was experienced in the isolation of the formate product, and the yield of purified formate (II-OCHO-x-d_2), b.p. 150–152° at 3.5 mm, was only 0.5 g (22% based on 71.2% solvolyzed). The corresponding protio formate boiled at 152 °C and 3.5 mm.

Anal. Calcd. for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71. Found: C, 62.93; H, 6.85.

Nuclear Magnetic Resonance Analyses

The n.m.r. analyses of the various compounds were carried out in deuteriochloroform solution with Varian Associates HR-100 and HA-100 spectrometers by Mr. G. W. Bigam of the Department of Chemistry, University of Alberta, Edmonton, Alberta, and by Mr. M. Mazurek of the Prairie Regional Laboratory, National Research Council, Saskatoon, Saskatchewan.

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REFERENCES

1. S. WINSTEIN and R. HECK. J. Am. Chem. Soc. **78**, 4801 (1956).
2. S. WINSTEIN and K. C. SCHREIBER. J. Am. Chem. Soc. **74**, 2165 (1952).
3. S. WINSTEIN and G. C. ROBINSON. J. Am. Chem. Soc. **80**, 169 (1958).
4. W. B. SMITH and M. SHOWALTER. J. Am. Chem. Soc. **86**, 4136 (1964).
5. R. PSCHORR and G. KNÖFFLER. Ann. **382**, 50 (1911).
6. C. C. LEE, G. P. SLATER, and J. W. T. SPINKS. Can. J. Chem. **35**, 1417 (1957).
7. E. F. JENNY and S. WINSTEIN. Helv. Chim. Acta, **41**, 807 (1958).
8. C. C. LEE and A. G. FORMAN. Can. J. Chem. **43**, 3387 (1965).
9. C. C. LEE and A. G. FORMAN. Can. J. Chem. **44**, 841 (1966).
10. W. G. YOUNG, S. WINSTEIN, and H. L. GOERING. J. Am. Chem. Soc. **73**, 1958 (1951).
11. C. C. LEE, R. TKACHUK, and G. P. SLATER. Tetrahedron, **7**, 206 (1959).
12. J. W. CLAYTON and C. C. LEE. Can. J. Chem. **39**, 1510 (1961).
13. J. HINE. Physical organic chemistry. 2nd ed. McGraw-Hill Book Co., Inc., New York. 1962. pp. 132–134.
14. H. C. BROWN, K. J. MORGAN, and F. CHLOUPEK. J. Am. Chem. Soc. **87**, 2137 (1965).
15. D. J. CRAM. J. Am. Chem. Soc. **86**, 3767 (1964).
16. G. A. OLAH and C. U. PITTMAN, JR. J. Am. Chem. Soc. **87**, 3509 (1965).
17. F. R. JENSEN and R. J. OUELLETTE. J. Am. Chem. Soc. **85**, 367 (1963).