[Contribution from the Department of Chemistry, University of California, Los Angeles]

Neighboring Carbon and Hydrogen. XXVII. Ar_1-5 Aryl Participation and Tetralin Formation in Solvolysis[1,2]

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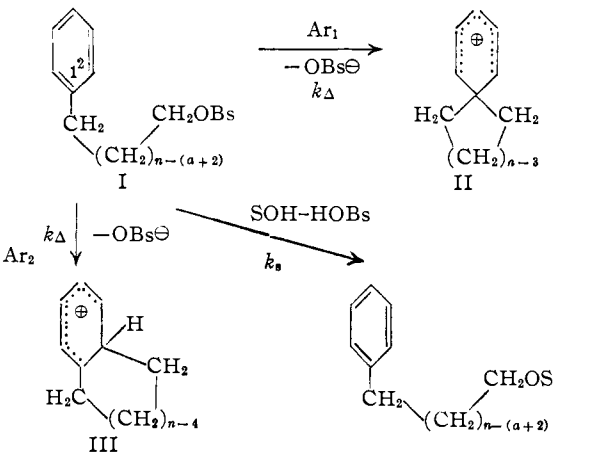
It is possible, by suitable choice of structure and solvent, to arrange for participation of δ-aryl groups in solvolysis of 4-aryl-1-butyl *p*-bromobenzenesulfonates. When the aryl group is activated by one *p*- or two *o,p*-methoxyl groups, the participation is Ar_1-5 in type; a spiro-carbonium ion is produced by anchimerically assisted ionization of the 4-aryl-1-butyl bromobenzenesulfonate. Rearrangement of the spiro-carbonium ion intermediate and proton loss give rise to a tetralin product. On the assumption that k_s, the rate constant of anchimerically unassisted solvolysis, is associated with formation of ester, and that k_Δ, the rate constant of anchimerically assisted ionization, is associated with formation of tetralin, it is possible to dissect the acetolysis and formolysis rate constants for 4-phenyl-1-butyl bromobenzenesulfonate into the appropriate k_s and k_Δ values. Assuming k_s is insensitive to methoxyl substitution, one can assign k_s and k_Δ values in solvolysis of the substituted 4-aryl-1-butyl bromobenzenesulfonates. These values of k_s and k_Δ predict product compositions within experimental error, assuming k_s and k_Δ are associated with formation of ester and tetralin, respectively. As regards variation of k_Δ in Ar_1-*n* participation with the size of the ring being formed in the intermediate spiro-carbonium ion, the observed rate sequence is $3 \gg 4 \ll 5 \gg 6$. Both the 3:5 and 5:6 ratios are of the order of 10^2. Of the *n* values, 4, 5 and 6, only in the case of 5 were substantial values of k_Δ and k_Δ/k_s observed.

Many cases of ionization of a β-arylethyl *p*-bromobenzenesulfonate, with the degree of methyl or phenyl substitution sufficiently large[3] on C_β and not too large[3] on C_α, are anchimerically[4] assisted,[3,5] leading to a bridged intermediate[6,7] or a rearranged carbonium ion. It is convenient to employ the symbol k_Δ for the rate constant of such anchimerically assisted ionization. Still other cases of ionization, rate constant k_s, are anchimerically unassisted. Such ionization may lead to an unrearranged carbonium ion intermediate which may rearrange subsequently. With a properly substituted structure, which is not too favorable[8] for one of the classical open forms of the carbonium ion, the bridged form of the carbonium ion is preferred.

It is convenient to adopt a notation[2] in which participation of a β-phenyl group is symbolized Ar_1-3. The general notation is Ar_a-*n*, where Ar denotes aryl and the subscript *a* refers to the position in the participating aryl group involved in the creation of the ring in the transition state for anchimerically assisted ionization. The size of the ring being made is indicated by the number *n*.

As has already been reported in preliminary communications,[2] it is possible, by suitable choice of structure and solvent, to arrange for participation of aryl groups more distant than β in solvolysis of arylalkyl benzenesulfonates I. Examples of such participation are Ar_1-5 and Ar_2-6, illustrated schematically by the conversion of I to II ($n = 5$) or III ($n = 6$), respectively.



In seeking information on Ar-4, 5 and 6 participation, a large number of arylsulfonates has been studied. Some of the results bearing principally on the Ar_1-variety are reported in the present paper, while Ar_2 is treated in the following one.

In searching for anchimeric effects of aryl groups, the procedure employed was first to explore the rates of solvolysis of various phenylalkyl bromobenzenesulfonates and the corresponding methoxyphenylalkyl esters. We expected[9] anchimerically unassisted solvolysis, with rate constant k_s, to be quite insensitive to methoxyl substitution, but anchimerically assisted solvolysis, with rate constant k_Δ, quite sensitive to suitably oriented methoxyl groups. On this basis, an anchimerically assisted process was not contributing seriously to the solvolysis of a methoxyphenylalkyl bromobenzenesulfonate unless the introduction of the methoxyl group was accompanied by an increase in solvolysis rate. Using kinetics as a guide, cases were selected for examination of the products of solvolysis for further elucidation of the nature of the solvolysis in question.

Arylalkyl Systems.—The various arylsulfonates employed in this work appear in Table I, which

(1) (a) Paper XXV, S. Winstein and E. T. Stafford, This Journal, **79**, 505 (1957); paper XXVI, S. Winstein and R. Baird, *ibid.*, **79**, 756 (1957); (b) Research supported by the Office of Naval Research.

(2) Most of the material of this paper has been reported in summary: (a) Paper by S. Winstein at the Symposium on Dynamic Stereochemistry of the Chemical Society, Manchester, England, March 31, 1954 (see *Chemistry & Industry*, 562 (1954); (b) S. Winstein, R. Heck, S. Lapporte and R. Baird, *Experientia*, **12**, 138 (1956).

(3) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, This Journal, **74**, 1113 (1952).

(4) S. Winstein, C. R. Lindegren, H. Marshall and L. L. Ingraham, *ibid.*, **75**, 147 (1953).

(5) *E.g.*, S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2171 (1952).

(6) D. J. Cram, *ibid.*, **71**, 3863 (1949); **74**, 2129 (1952).

(7) S. Winstein, M. Brown, K. C. Schreiber and A. H. Schlesinger, *ibid.*, **74**, 1140 (1952).

(8) (a) D. J. Cram and J. D. Knight, *ibid.*, **74**, 5839 (1952); (b) F. A. Abd Elhafez and D. J. Cram, *ibid.*, **75**, 339 (1953); (c) C. J. Collins and W. A. Bonner, *ibid.*, **77**, 92 (1955); (d) W. A. Bonner and C. J. Collins, *ibid.*, **77**, 99 (1955).

(9) S. Winstein and R. Heck, *ibid.*, **78**, 4801 (1956).

TABLE I

SUMMARY OF SOLVOLYSIS RATE CONSTANTS

Compound	Solvent	Temp., °C.	Concn. $\times 10^2$, M	k (sec.$^{-1}$)	$\Delta H^{\pm}$, kcal./mole	$\Delta S^{\pm}$, e.u.
$C_6H_5(CH_2)_3OBs$	HOAc	75.00	3.18	$(1.07 \pm 0.00) \times 10^{-6}$	24.0	−17.5
	HOAc	100.05	2.71	$(1.17 \pm .01) \times 10^{-5}$		
	HCOOH[a]	50.00	2.75	$(1.54 \pm .08) \times 10^{-6}$		
	HCOOH[a]	75.00	2.75	$(1.99 \pm .03) \times 10^{-5}$	22.2	−16.6
p-$CH_3OC_6H_4(CH_2)_3OBs$	HOAc	75.00	3.04	$(1.15 \pm .03) \times 10^{-6}$		
2,4-$(CH_3O)_2C_6H_3(CH_2)_3OBs$	HOAc	75.00	2.57	3.95×10^{-6}[b]		
$C_6H_5(CH_2)_4OBs$	HOAc	75.00	3.09	$(1.45 \pm 0.03) \times 10^{-6}$		
	HOAc	75.00	3.02	$(1.49 \pm .05) \times 10^{-6}$	23.9	−16.8
	HOAc	100.05	3.68	$(1.62 \pm .01) \times 10^{-5}$		
	HCOOH	75.00	2.70	$(3.35 \pm .01) \times 10^{-5}$		
	HCOOH[a]	25.00		1.41×10^{-7}[d]		
	HCOOH[a]	75.00	2.68	$(3.43 \pm 0.03) \times 10^{-5}$	22.0	−16.2
	HCOOH[a]	100.20	2.68	$(3.13 \pm .07) \times 10^{-4}$		
p-$CH_3OC_6H_4(CH_2)_4OBs$	HOAc	75.00	2.66	$(1.90 \pm .01) \times 10^{-6}$	24.4	−15.0
	HOAc	100.05	2.15	$(2.16 \pm .01) \times 10^{-5}$		
	HCOOH[a]	50.00	2.70	$(5.03 \pm .18) \times 10^{-6}$		
	HCOOH[a]	75.00	2.70	$(6.08 \pm .11) \times 10^{-5}$	21.6	−16.1
2,4-$(CH_3O)_2C_6H_3(CH_2)_4OBs$	HOAc	75.00	2.66	$(6.26 \pm .06) \times 10^{-6}$	25.0	−10.7
	HOAc	100.00	1.94	$(7.56 \pm .05) \times 10^{-5}$		
	HOAc[c]	75.00	2.89	$(7.2 \pm .1) \times 10^{-6}$		
	HCOOH[a]	25.00		1.27×10^{-6}[d]		
	HCOOH[a]	50.00	2.24	$(2.58 \pm 0.02) \times 10^{-5}$		
	HCOOH[a]	75.00	2.24	$(3.40 \pm .06) \times 10^{-4}$	22.4	−10.4
$C_6H_5(CH_2)_3CH(OTs)CH_3$	HCOOH[a]	25.00	3.13	$(5.43 \pm .10) \times 10^{-5}$		
2,4-$(CH_3O)_2C_6H_3(CH_2)_3CH(OTs)CH_3$	HCOOH[a]	25.00	3.63	$(1.36 \pm .13) \times 10^{-4}$		
$C_6H_5(CH_2)_5OBs$	HOAc	75.00	2.77	$(1.54 \pm .03) \times 10^{-6}$	23.8	−17.1
	HOAc	100.00	2.64	$(1.65 \pm .01) \times 10^{-5}$		
	HCOOH[a]	50.00	2.70	$(2.90 \pm .08) \times 10^{-6}$		
	HCOOH[a]	75.00	2.70	$(3.39 \pm .02) \times 10^{-5}$	21.3	−18.2
2,4-$(CH_3O)_2C_6H_3(CH_2)_5OBs$	HOAc	75.00	2.40	$(1.61 \pm .03) \times 10^{-6}$	23.9	−16.7
	HOAc	100.10	2.40	$(1.76 \pm .01) \times 10^{-5}$		
	HCOOH[a]	75.00	2.69	$(3.63 \pm .11) \times 10^{-5}$		

[a] Formic acid, 0.03151 M in NaOCHO. [b] Extrapolated initial constant from a plot of ln $[(ROBs)_0/(ROBs)]$ *versus* time. [c] Acetic acid, 0.0300 M in $LiClO_4$. [d] Extrapolated from data at another temperature.

summarizes also the kinetic data obtained with them.

Of the required primary alcohols, 3-phenyl-1-propanol was available commercially. 3-*p*-Anisyl-1-propanol and 3-(2,4-dimethoxyphenyl)-1-propanol were prepared from the corresponding cinnamic acids by reduction with lithium aluminum hydride, the cinnamic acids being obtained from anisaldehyde[10] and 2,4-dimethoxybenzaldehyde[10] by the Knoevenagel reaction. The several butyl alcohols, 4-phenyl-, 4-*p*-anisyl-, and 4-(2,4-dimethoxyphenyl)-1-butanols were all prepared by Friedel–Crafts succinoylation of the proper benzene derivatives, followed by Clemmensen and lithium aluminum hydride reduction.

Of the two primary pentanols which were studied, the 5-phenyl-1-pentanol was prepared from γ-phenylpropylmagnesium chloride and ethylene oxide, while the 5-(2,4-dimethoxyphenyl)-1-pentanol was prepared from the corresponding acid by reduction with lithium aluminum hydride. The 5-(2,4-dimethoxyphenyl)-pentanoic acid was prepared by Clemmensen reduction of γ-(2,4-dimethoxybenzoyl)-butyric acid, prepared by a Friedel–Crafts reaction between *m*-dimethoxybenzene and glutaric anhydride.

One of the two secondary alcohols which were studied, 1-phenyl-4-pentanol, was prepared from γ-phenylpropylmagnesium chloride and acetaldehyde.[11] The 1-(2,4-dimethoxyphenyl)-4-pentanol was prepared from the corresponding ketone by reduction with lithium aluminum hydride. This ketone was obtained from the reaction of 4-(2,4-dimethoxyphenyl)-butyric acid with methyllithium.

Kinetic Search for Ar_1.—As summarized in Table I, all the arylsulfonates displayed good first-order kinetics of acetolysis and formolysis, except 3-(2,4-dimethoxyphenyl)-1-propyl *p*-bromobenzenesulfonate. This substance displayed a downward drifting first-order rate constant in acetolysis, an extrapolated initial value being given in Table I.

In the kinetic search for neighboring aryl participation, the ω-phenylalkyl arylsulfonates are reference compounds, and the relative rates of acetolysis and formolysis of these reference compounds are summarized in Table II. For this comparison, rate

(10) K. H. Slotta and H. Heller, *Ber.*, **63**, 3029 (1930).

(11) R. O. Roblin, Jr., D. Davidson and M. T. Bogert, THIS JOURNAL, **57**, 151 (1935).

Table II

Relative Solvolysis Rates of Phenylalkyl *p*-Bromobenzenesulfonates

Compound	AcOH, 75.00° Rel. rate	AcOH, 75.00° $\Delta S^{\ddagger}$, e.u.	HCOOH, 75.00° Rel. rate	HCOOH, 75.00° $\Delta S^{\ddagger}$, e.u.
$C_6H_5(CH_2)_2OBs$	0.79	−15.2	5.08	− 8.6
$C_6H_5(CH_2)_3OBs$	1.00	−17.5	1.00	−16.6
$C_6H_5(CH_2)_4OBs$	1.36	−16.8	1.72	−16.2
$C_6H_5(CH_2)_5OBs$	1.44	−17.1	1.70	−18.2
$CH_3(CH_2)_3OBs$	1.39[a]	−17.0	1.79[a]	−19.9
$CH_3(CH_2)_2OBs$	1.53[b]			

[a] Data of R. Glick. [b] Data of P. Magee.

constants for 3-phenyl-1-propyl *p*-bromobenzenesulfonate are taken as unity. Using the entropy of activation as a guide to mechanism,[9] the indications are that substantially the whole of the solvolysis is anchimerically unassisted in acetolysis of the 3-, 4- and 5-phenyl-1-alkyl esters. In formic acid, the ω-phenyl-1-alkyl esters except 2-phenylethyl again have the low $\Delta S^{\ddagger}$ characteristic of anchimerically unassisted solvolysis. The relatively high $\Delta S^{\ddagger}$ for the phenylethyl ester was ascribed previously[9] to the importance of anchimerically assisted ionization in formic acid.

The relative rates themselves support the conclusions derived on the basis of the $\Delta S^{\ddagger}$ values in Table II. The relatively smooth small increase in acetolysis rate, by less than a factor of two, in the series from phenylethyl to phenylpentyl is in line with the decreasing rate-retarding polar (and steric) effect of the phenyl group. The rate constants for the 4-phenyl-1-butyl and 5-phenyl-1-pentyl esters are essentially equal to the value for the *n*-butyl ester, giving no indication of substantial contribution from anchimerically assisted solvolysis. The situation is similar in formic acid, except that the rate-retarding effect of the phenyl group in phenylethyl *p*-bromobenzenesulfonate is more than compensated by the incursion of anchimerically assisted ionization.[4,9]

Methoxy substitution in the phenyl group of the ω-phenylalkyl esters will, of course, tend to favor aryl participation in solvolysis. In scrutinizing the effect of such substitution on solvolysis rate, it is convenient to consider first the series of 3-phenyl-1-propyl derivatives. In Table III are summarized the relative solvolysis rates of 3-phenyl-1-propyl *p*-bromobenzenesulfonate, together with those of the 4- and 2,4-methoxy derivatives, substituted so as to favor Ar_1-4 aryl participation. Included also in the comparison are the 3- and 3,5-methoxy derivatives, reported in detail in the next article. Examination of Table III reveals that all the 3-aryl-1-propyl *p*-bromobenzenesulfonates display nearly identical solvolysis rates, except the 2,4-dimethoxy derivative which displays a higher initial acetolysis rate constant than the others. However, there is no reason to ascribe the observed rate enhancement to Ar_1-4 participation. Instead, the rate enhancement is to be ascribed to participation of the *ortho* methoxyl group with formation of the intermediate IV. Such participation is common with ω-*o*-anisylalkyl arylsulfonates,[12,13] and the 3-*o*-anisyl-1-propyl *p*-bromobenzenesulfonate displays even a slightly higher rate constant[12] than the one observed with the 3-(2,4-dimethoxyphenyl)-1-propyl ester. Thus, the comparison in Table III shows that no appreciable incursion of Ar_1-4 (or Ar_2-5) aryl participation is indicated for the methoxyphenylpropyl esters examined.

With the 4-phenyl-1-butyl *p*-bromobenzenesul-

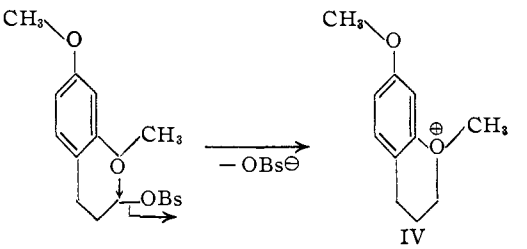
Table III

Relative Solvolysis Rates of Substituted γ-Phenylpropyl *p*-Bromobenzenesulfonates at 75.00°

	$C_6H_5(CH_2)_3OBs$	*p*-$CH_3OC_6H_4(CH_2)_3OBs$	2,4-$(CH_3O)_2C_6H_3(CH_2)_3OBs$	*m*-$CH_3OC_6H_4(CH_2)_3OBs$	3,5-$(CH_3O)_2C_6H_3(CH_2)_3OBs$
AcOH	1.00	1.07[a]	3.69	1.04[b]	1.03[b]
HCOOH	1.00				1.08[b]

[a] k_Δ is below 8×10^{-8} sec.$^{-1}$. [b] From data reported in the following article.

fonates, substantial rate enhancements are observed when methoxyl groups are substituted in the benzene ring. As is summarized in Table IV, the 4-*p*-anisyl- and 4-(2,4-dimethoxyphenyl)-1-butyl esters exceed the unsubstituted 4-phenyl-1-butyl *p*-bromobenzenesulfonate in solvolysis rate by factors of 1.3 and 4.3, respectively, in acetic acid and 1.77 and 9.91, respectively, in formic acid. The rate enhancements must be ascribed to the incursion of anchimerically assisted solvolysis in the case of the methoxyl-substituted 4-phenyl-1-butyl esters. Otherwise, methoxyl substitution would be expected to be without appreciable effect on solvolysis rate, just as in the case of the 3-phenyl-1-propyl esters.



IV

Additional support for the idea that Ar_1-5 participation grows more important with methoxyl substitution in 4-phenyl-1-butyl bromobenzenesulfonate is provided by the $\Delta S^{\ddagger}$ values recorded in Table I. These change from the level of *ca.* −17 e.u. associated with anchimerically unassisted solvolysis (rate constant k_s) to a level of *ca.* −10 e.u. for 4-(2,4-dimethoxyphenyl)-1-butyl bromobenzenesulfonate. The latter substance, with the most enhanced formolysis rate, must undergo very largely anchimerically assisted solvolysis, so $\Delta S^{\ddagger}$ for Ar_1-5-assisted ionization in formic acid must be close to −10 e.u.

Products.—Further insight into the nature of the solvolytic reactions of the 4-aryl-1-butyl bromobenzenesulfonates is provided by the results of an examination of the derived products. In this examination, the crude product from formolysis or acetolysis was reduced with lithium aluminum hydride to reduce ester to alcohol. Then hydro-

(12) R. Heck, unpublished work.

(13) See, *e.g.*, S. Winstein, *Experientia Supplementum*, II, 137 (1955).

TABLE IV

ANALYSIS OF SOLVOLYSIS RATES OF SEVERAL 4-ARYLBUTYL *p*-BROMOBENZENESULFONATES AT 75.00°

Compound	Relative rates AcOH	Relative rates HCOOH	Assignments of k_Δ and k_s: AcOH 10^6k_s	AcOH 10^6k_Δ	HCOOH 10^6k_s	HCOOH 10^6k_Δ
$CH_3(CH_2)_3OBs$	1.03	1.04	1.49[a]		3.57[a]	
$C_6H_5(CH_2)_4OBs$	1.00	1.00	1.37[b]	(0.08)	2.78	(0.65)
p-$CH_3OC_6H_4(CH_2)_4OBs$	1.31	1.77	1.37	0.53	2.78	3.30
2,4-$(CH_3O)_2C_6H_3(CH_2)_4OBs$	4.32	9.91	1.37	4.89	2.78	31.22

[a] Data of R. Glick. [b] Assuming products are the same at 75° as at 100°. At 100°, k_s is 1.53×10^{-5} and k_Δ is 9×10^{-7} sec.$^{-1}$.

carbon and alcoholic products were separated by chromatography.

From formolysis of 4-(2,4-dimethoxyphenyl)-1-butyl bromobenzenesulfonate (V) was obtained an 8% yield of an alcohol which was converted into *p*-nitrobenzoate in *ca.* 70% yield. This was shown by mixed melting point to be the *p*-nitrobenzoate of 4-(2,4-dimethoxyphenyl)-1-butanol (VI). A second product, obtained in 76% yield, was a colorless liquid which later crystallized. It was inert to potassium permanganate in acetone, and it analyzed correctly for a tetralin. It yielded a monobromide on treatment with bromine in carbon tetrachloride. The substance was readily dehydrogenated in good yield with the aid of chloranil.[14] From the dehydrogenated product was obtained a picrate which was shown by mixed melting point to be identical with the picrate of 1,3-dimethoxynaphthalene (X) prepared by decarboxylating 1,3-dimethoxy-2-naphthoic acid (XI). This naphthoic acid was prepared from ethyl 1,3-dihydroxy-2-naphthoate, which had been previously prepared by Metzner.[15] This establishes the structure of the major solvolysis product as 5,7-dimethoxytetralin (IX).

Except for the proportions of tetralin and alcohol products, 4-*p*-anisyl-1-butyl bromobenzenesulfonate behaved analogously to the 4-(2,4-dimethoxyphenyl)-1-butyl derivative in formolysis. From the 4-*p*-anisyl-1-butyl ester was obtained a 43% yield of alcohol and a 51% yield of a material, inert to potassium permanganate in acetone, with physical properties in agreement with those reported for 7-methoxytetralin.[16,17]

The solvolysis of 4-phenyl-1-butyl *p*-bromobenzenesulfonate was also examined in both formic and acetic acids. In the former solvent, 4-phenyl-1-butyl bromobenzenesulfonate gave rise to a 16.7% yield of tetralin, identified by boiling point, refractive index, infrared spectrum and by its conversion in high yield to naphthalene by a dehydrogenation with tetrachloro-1,2-benzoquinone.[18] From the formolysis there was obtained also a 72% yield of 4-phenyl-1-butanol. In acetic acid, 4-phenyl-1-butyl bromobenzenesulfonate gave rise to an even smaller proportion of tetralin than in formic acid, the yield of tetralin being 4.9%.

For the solvolyses in which the products were examined, summarized in Table V, sufficient controls were run to establish that tetralin did not arise from the formate or acetate ester subsequent to its formation. Thus, 4-(2,4-dimethoxyphenyl)-1-butanol survived essentially quantitatively under the conditions for the formolysis. With 4-phenyl-1-butanol, no tetralin was observed after treatment in formic acid for the length of time involved in a solvolysis of the bromobenzenesulfonate, even when the formic acid solvent was acidified with toluenesulfonic acid. Similarly, no tetralin was observed to be formed from 4-phenyl-1-butyl acetate in acetic acid containing toluenesulfonic acid.

TABLE V

SUMMARY OF PRODUCTS OF FORMOLYSIS AT 75.00°

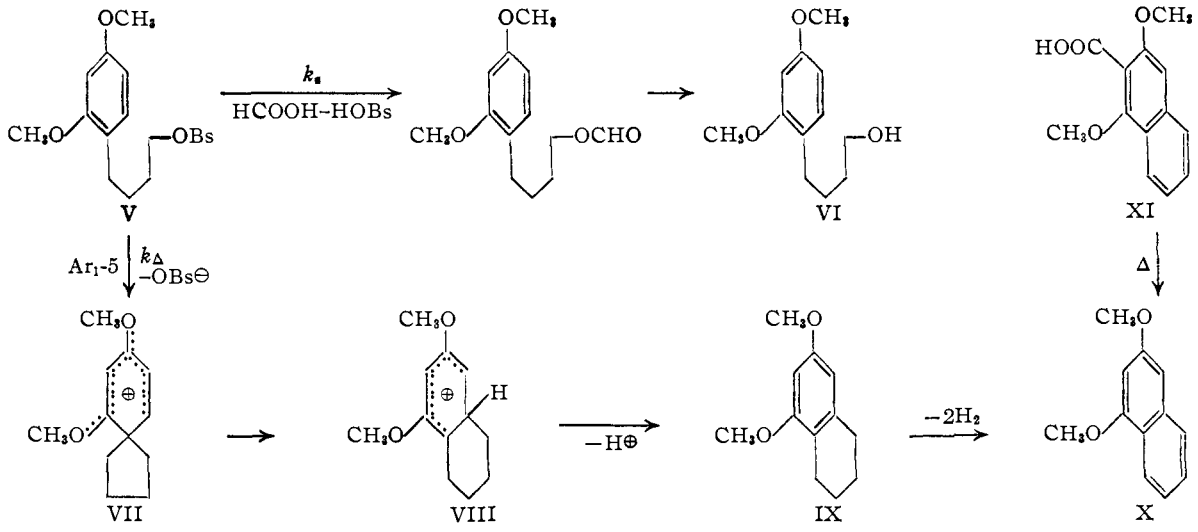
Compound	Total yield, %	% ROH	% Tetralin	$\frac{100\,k_\Delta}{(k_s + k_\Delta)}$
$C_6H_5(CH_2)_4OBs$	88.7[a]	81.0[a]	19.0[a]	..
	89.3[b]	94.5[b]	5.5[b]	..
p-$CH_3OC_6H_4(CH_2)_4OBs$[c]	93.8	45.8	54.2	54.3
2,4-$(CH_3O)_2C_6H_3(CH_2)_4$-OBs[d]	84.2	9.3	90.7	91.8

[a] 0.0500 *M* ROBs; 0.0500 *M* NaOCHO; 66 hours at 75°. [b] Acetolysis products at 100.0°, 0.0452 *M* ROBs; 127 hours at 100°. [c] 0.0286 *M* ROBs; 0.0302 *M* NaOCHO; 42 hours at 75°. [d] 0.0476 *M* ROBs; 0.0555 *M* NaOCHO; 6 hours at 75°.

Dissection of k into k_Δ and k_s and Mechanism of Tetralin Formation.—By dissecting the solvolysis rate constants for the 4-aryl-1-butyl *p*-bromobenzenesulfonates into k_Δ, the rate constant for anchimerically assisted solvolysis, and k_s, the rate constant for anchimerically unassisted solvolysis, composition of solvolysis products can be connected quantitatively with observed rates. The dissection of rate constants is based on the k_s assigned to 4-phenyl-1-butyl *p*-bromobenzenesulfonate on the assumption that anchimerically assisted solvolysis leads only to tetralin and anchimerically unassisted solvolysis gives no tetralin. This assumes that any intermediate[19,20] in the anchimerically unassisted solvolysis of a simple primary arylsulfonate, such as 4-phenyl-1-butyl, would be too unstable and short-lived to lead to serious amounts of electrophilic attack on the benzene ring instead of collapsing to acetate or formate. The values assigned to k_Δ and k_s on this basis are listed in Table IV.

For the methoxyphenylbutyl esters, k_s is assumed equal to k_s for the unsubstituted 4-phenyl-1-butyl derivative, by analogy with the 3-aryl-1-propyl esters, where k_s is insensitive to methoxyl substitution. Subtracting k_s from the observed solvolysis rate constants leads to the derived values of k_Δ

(14) R. T. Arnold and C. J. Collins, THIS JOURNAL, **61**, 1407 (1939).
(15) H. Metzner, *Ann.*, **298**, 388 (1898).
(16) R. B. Woodward and R. H. Eastman, THIS JOURNAL, **66**, 674 (1944).
(17) P. C. Mitter and S. De, *J. Indian Chem. Soc.*, **16**, 35 (1939).
(18) R. Linstead, *et al.*, *Chemistry & Industry*, 1174 (1954).
(19) S. Winstein, E. Grunwald and H. W. Jones, THIS JOURNAL, **73**, 2700 (1951).
(20) See: (a) A. Streitwieser, Jr., *ibid.*, **77**, 1117 (1955); (b) A. Streitwieser, Jr., and W. D. Schaeffer, Page 52-N of Abstracts, American Chemical Society, Dallas, Texas, April 8–13, 1956.



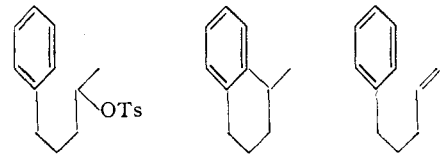
summarized in Table IV. These are, of course, much larger for the methoxyphenyl cases than for the unsubstituted phenyl derivative.

The assumption for the methoxy-substituted 4-phenyl-1-butyl esters, just as in the case of the 4-phenyl-1-butyl derivative, that k_Δ is connected with tetralin formation, allows one to calculate the expected product composition. The calculated values for per cent. tetralin in the product, namely, $100\ k_\Delta/(k_s + k_\Delta)$, are shown in Table V, along with the observed product compositions. It is apparent that the calculated and observed product compositions agree within experimental error, so that the underlying assumptions are at least semi-quantitatively valid.

The mode of formation of the observed tetralins from the methoxy-substituted 4-phenyl-1-butyl bromobenzenesulfonates is especially interesting, since the *ortho* and *para* methoxyl groups favor Ar_1-5 participation. It is reasonable to believe that k_Δ is predominantly connected with formation of a spiro-carbonium ion, VII in the case of solvolysis of the 4-(2,4-dimethoxy-phenyl)-1-butyl bromobenzenesulfonate. This must rearrange, as in the related dienone–phenol rearrangement,[21] probably to another intermediate VIII, finally leading to tetralin IX. In the present examples, no more direct evidence is available for the spiro-carbonium ion intermediate like VII, but such direct evidence is available in cases where, for example, C_δ of the original bromobenzenesulfonate is dimethylated.[2b]

Secondary Systems.—Two secondary arylsulfonates, 5-phenyl-2-pentyl (XII) and 5-(2,4-dimethoxyphenyl)-2-pentyl toluenesulfonates were examined for comparison with their primary analogs. As summarized in Table VI, the 2,4-methoxyl groups enhance formolysis rate in the 5-phenyl-2-pentyl system, but the factor is only 2.5 instead of *ca.* 10 observed in the primary case.

The products of formolysis of 5-phenyl-2-pentyl toluenesulfonate (XII), after lithium aluminum hydride reduction, were 46.6% 5-phenyl-2-pentanol and 47.8% hydrocarbon. The hydrocarbon contained 30% of olefin according to quantitative hydrogenation. Removal of olefin by reaction with osmium tetroxide left a hydrocarbon which was inert to potassium permanganate in acetone and analyzed correctly and possessed the correct physical properties for 1-methyltetralin (XIII). On this basis, the composition of solvolysis product may be restated as 35% tetralin, 50% alcohol and 15% olefin.



XII XIII XIV

That the formation of the 1-methyltetralin (XIII) obtained in formolysis of 5-phenyl-2-pentyl toluenesulfonate is associated with the solvolysis reaction and it is not formed from reaction of formate ester or olefin subsequent to their formation is clear from control experiments. Under conditions of formolysis of the toluenesulfonate XII, 5-phenyl-2-pentanol yields no tetralin XIII. Similarly, the olefin produced in solvolysis of toluenesulfonate is quite inert to the solvolysis conditions. Even a sample of 5-phenyl-1-pentene (XIV), the straight chain olefin expected to be most reactive in tetralin formation, reacts only very slowly with formic acid. Even in the absence of added sodium formate, the 5-phenyl-1-pentene (XIV) in formic acid solution is only about one third converted to tetralin and formate ester in a ratio of 0.6:1 after a reaction time *ca.* 15 times that employed in solvolysis of the toluenesulfonate XII.

When it comes to dissecting the rate constant of solvolysis of the secondary toluenesulfonates into

(21) (a) See ref. 2b for other references; (b) a very closely related dienonephenol rearrangement is the following example studied in these Laboratories (R. Baird, unpublished work)

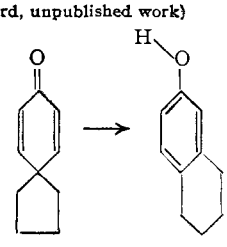


TABLE VI

ANALYSIS OF RATES OF FORMOLYSIS OF 4-ARYLBUTYL AND 5-ARYL-2-PENTYL *p*-TOLUENESULFONATES AT 25.00°

Compound	Relative rates		k_s (sec.$^{-1}$)	k_Δ (sec.$^{-1}$)	Rel. k_s	Rel. k_Δ	k_Δ/k_s
$C_6H_5(CH_2)_4OTs$		1.00[a,b]	3.80×10^{-8}[c]	9.00×10^{-9}[c]	1.00	1.00	0.24
$2,4\text{-}(CH_3O)_2C_6H_3(CH_2)_4OTs$		9.00[a,b]	3.80×10^{-8}	3.85×10^{-7}	1.00	42.8	10.1
$C_6H_5(CH_2)_3CHCH_3$ (OTs)	1.00	1155	5.43×10^{-5}	.....	1429	...	...
$2,4\text{-}(CH_3O)_2C_6H_3(CH_2)_3CHCH_3$ (OTs)	2.50	2894	5.43×10^{-5}	8.2×10^{-5}	1429	9111	1.51

[a] The value of the *p*-bromobenzenesulfonate divided by three. [b] Extrapolated from data at other temperatures. [c] Assuming products are the same at 25° as at 75°.

k_s and k_Δ, we cannot assume for the 5-phenyl-2-pentyl toluenesulfonate that tetralin formation is connected only with k_Δ, as we did for the 4-phenyl-1-butyl system. A carbonium ion intermediate[19] in the anchimerically unassisted formolysis of the secondary toluenesulfonate could well lead to substantial amounts of electrophilic attack on the benzene ring, resulting finally in tetralin formation. Thus, at least part of the tetralin formation could be connected with k_s. What has been done in writing down the values of k_s and k_Δ in Table VI for 5-(2,4-dimethoxyphenyl)-2-pentyl toluenesulfonate is to assume the rate constant of 5-phenyl-1-pentyl toluenesulfonate is entirely k_s, k_Δ being zero. On this basis, the k_s values are maximal, and k_Δ for 5-(2,4-dimethoxyphenyl)-2-pentyl toluenesulfonate is a minimum figure.

The k_Δ and k_s values for the secondary toluenesulfonates listed in Table VI are sufficiently clear to bring out the point that the α-methyl group which converts the primary to secondary arylsulfonates increases k_s more than k_Δ. This results in a lower k_Δ/k_s ratio for secondary arylsulfonate than for primary, aryl participation being considerably less dominant with secondary than primary arylsulfonate. Such an effect of α-methyl substitution is quite common in cases of participation of β-neighboring groups.[3,22]

Ar_1-*n* and Ring Size.—Contrasting with the substantial increase in rate produced by *o,p*-dimethoxy substitution in the 4-phenyl-1-butyl system, is the small increase produced in the case of 5-phenyl-1-pentyl bromobenzenesulfonate. In Table VII are compared the 5-phenyl-1-pentyl and 5-(2,4-dimethoxyphenyl)-1-pentyl bromobenzenesulfonates. By using the rate constant for the 5-phenyl-1-pentyl ester as k_s, one obtains an estimate for k_Δ only *ca.* 0.07 times k_s in the case of 5-(2,4-dimethoxyphenyl)-1-pentyl bromobenzenesulfonate. Thus, it is clear that rates associated with Ar_1-6 participation are much lower than those associated with Ar_1-5. Consequently, it will be more difficult to arrange conditions of structure and solvent so as to have Ar_1-6 participation dominate the rate-determining step of solvolysis of an arylsulfonate.[23]

In Table VIII are summarized relative k_Δ values for acetolysis and formolysis of ω-aryl-1-alkyl bromobenzenesulfonates for alkyl systems from ethyl to pentyl. In this comparison, k_Δ for 4-*p*-anisyl-1-butyl was taken as unity. Also summarized in Table VIII are the corresponding values of k_Δ/k_s. These orient one on the extent to which Ar_1-*n* participation dominates the solvolysis, while the relative k_Δ values are useful for outlining the variation of k_Δ with ring size or degree of methoxyl substitution.

TABLE VII

ANALYSIS OF SOLVOLYSIS RATES OF 5-ARYL-1-PENTYL BROMOBENZENESULFONATES AT 75°

Compound	Rel. rates HOAc	Rel. rates HCOOH	10^6k in AcOH- (sec.$^{-1}$) k_s	10^6k in AcOH- (sec.$^{-1}$) k_Δ	10^5k in HCOOH (sec.$^{-1}$) k_s	10^5k in HCOOH (sec.$^{-1}$) k_Δ
$C_6H_5(CH_2)_5OBs$	1.00	1.00	1.54	..	3.39	..
$2,4\text{-}(CH_3O)_2C_6H_3\text{-}(CH_2)_5OBs$	1.05	1.07	1.54	0.07	3.39	0.24

TABLE VIII

RELATIVE VALUES OF k_Δ AND VALUES OF k_Δ/k_s FOR SOLVOLYSIS OF ω-ARYL-1-ALKYL BROMOBENZENESULFONATES AT 75°

Aryl group	Alkyl system	Rel. k_Δ AcOH	Rel. k_Δ HCOOH	k_Δ/k_s AcOH	k_Δ/k_s HCOOH
C_6H_5	Ethyl	....	3[a]	.....	6[a,b]
C_6H_5	Butyl	0.15	0.20	0.06	0.23
$4\text{-}CH_3OC_6H_4$	Ethyl	147[c]	161[d]	92[e]	310[b]
$4\text{-}CH_3OC_6H_4$	Propyl	<0.2	.....	<0.1	.....
$4\text{-}CH_3OC_6H_4$	Butyl	1.00	1.00	0.39	1.19
$2,4\text{-}(CH_3O)_2C_6H_3$	Ethyl	2420[f]	2060	1510[e]	4000[b]
$2,4\text{-}(CH_3O)_2C_6H_3$	Butyl	9.22	9.45	3.6	11.7
$2,4\text{-}(CH_3O)_2C_6H_3$	Pentyl	0.13	0.07	0.05	0.07

[a] Rough values based on a k_Δ equal to the solvolysis rate constant.[9] [b] Based on a k_s equal to twenty times the rate constant for acetolysis of β-phenylethyl *p*-bromobenzenesulfonate.[9] [c] Based on a k_Δ three times k^0_{ext} for the *p*-toluenesulfonate.[24] [d] Based on rate constant three times the value for the toluenesulfonate.[4] [e] Based on a k_s equal to rate constant for acetolysis of β-phenylethyl *p*-bromobenzenesulfonate.[9] [f] Based on salt-enhanced rate constant.[9]

The values in Table VIII reveal that both Ar_1-4 and Ar_1-6 participations compete very poorly in solvolysis of ω-aryl-1-alkyl arylsulfonates in acetic or formic acid solvents. In fact, the measured solvolysis rate constants of the corresponding bromobenzenesulfonates were so little greater than the k_s values, that the k_Δ values in Table VIII are very rough.

It is clear from the comparison in Table VIII that anchimerically assisted solvolysis is much more dominant with β-arylethyl than 4-aryl-1-butyl systems, rate of ionization with Ar_1-3 being much higher than the one with Ar_1-5 participation. The

(22) S. Winstein and E. Grunwald, THIS JOURNAL, **70**, 828 (1948).

(23) See R. L. Letsinger and P. T. Lansbury [*ibid.*, **78**, 2648 (1956), Page 40-O of Abstracts, American Chemical Society, Atlantic City, N. J., Sept. 16–21, 1956] for a case of 1,5-phenyl migration during treatment of 8-benzhydryl-1-naphthoic acid under Friedel–Crafts acylation conditions. The relative timing of the steps which involve ionization of a group away from the acyl carbon atom and phenyl shift to the acyl carbon atom is not clear.

(24) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2767 (1956).

sequence of rates of ionization with Ar_1-*n* participation as *n* varies is explicitly given in Table IX. From this it is clear that the sequence is $3 > 4 < 5 > 6$, both the 3:5 and the 5:6 ratios being of the order of 10^2.

Table IX

Relative Rates of Ar_1-*n* Ring Closures in Solvolysis of ω-Aryl-1-alkyl Bromobenzenesulfonates at 75°

Ar group	Solvent	Ring size, *n* 3	4	5	6
4-$CH_3OC_6H_4$	AcOH	147	<0.2	1.00	
	HCOOH	161		1.00	
2,4-$(CH_3O)_2C_6H_3$	AcOH	262		1.00	0.014
	HCOOH	227		1.00	.007

Effect of Methoxy.—Reference to Tables IV and VIII reveals that the effects of methoxyl substitution in the benzene ring of 4-phenyl-1-butyl *p*-bromobenzenesulfonate on k_Δ tends to be less than with the 2-phenyl-1-ethyl system. The second methoxyl group (*ortho*) increases Ar_1-5 rate by a factor of 9 and Ar_1-3 by a factor of 13–16. The first methoxyl group (*para*) increases k_Δ in the 4-aryl-1-butyl system by a factor of only *ca.* 5–7, much smaller than in the case of Ar_1-3 rates. However, if the k_Δ for 4-phenyl-1-butyl *p*-bromobenzenesulfonate could be dissected into Ar_1-5 and Ar_2-6 components, the factor by which a *p*-methoxy group would be calculated to increase Ar_1-5 rate might be substantially larger than the value of *ca.* 5–7.

The factor by which a methoxyl group on the benzene ring facilitates electron-demanding reactions varies widely. In bromination,[25] for example, a *p*-methoxyl group increases rate by a factor of *ca.* 10^{10}. The relatively small effect of methoxyl in Ar_1-5 indicates a rather low degree of aryl involvement at the transition state configuration.

Experimental

3-*p*-Anisyl-1-propanol.—This alcohol was prepared in 44% yield by the reduction of *p*-methoxycinnamic acid[10] with lithium aluminum hydride, the acid being added to a stirred suspension of 1.5 moles of lithium aluminum hydride by means of a Soxhlet extractor.

3-(2,4-Dimethoxyphenyl)-1-propanol.—This material was prepared by addition of 46 g. of 2,4-dimethoxycinnamic acid[10] to an ether suspension of 12 g. of lithium aluminum hydride. The acid was added from a Soxhlet extractor, two days being required for the addition. The alcohol product, b.p. 144–145° (3.5 mm.), $n^{25}D$ 1.5320, m.p. 36–38°, was obtained in 39% yield.

Anal. Calcd. for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.16; H, 8.25.

4-Phenyl-1-butanol.—This material was prepared in high yield by lithium aluminum hydride reduction of γ-phenylbutyric acid.

Treatment of the alcohol with acetic anhydride and a few drops of pyridine for 1 hour on the steam-bath gave rise to 4-phenyl-1-butyl acetate, b.p. 120° (8.5 mm.), $n^{25}D$ 1.4948.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 74.73; H, 8.10.

4-*p*-Anisyl-1-butanol.—The reduction of 4-*p*-anisylbutyric acid[26] with lithium aluminum hydride gave rise to 4-*p*-anisyl-1-butanol, b.p. 125–130° (1.5 mm.), $n^{25}D$ 1.5201, in 91.5% yield. A small sample, redistilled for analysis, had $n^{25}D$ 1.5200.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.43; H, 9.05.

(25) P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 1764 (1951).

(26) E. L. Martin, This Journal, **58**, 1438 (1936).

4-(2,4-Dimethoxyphenyl)-1-butanol.—The reduction of 4-(2,4-dimethoxyphenyl)-butyric acid[17] with lithium aluminum hydride afforded the alcohol, b.p. 157–161° (2.5 mm.), $n^{25}D$ 1.5296, in quantitative yield.

Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.68; H, 8.40.

The *p*-nitrobenzoate of the alcohol prepared in the usual fashion, had the m.p. 52–53° after two recrystallizations from methanol.

Anal. Calcd. for $C_{19}H_{21}O_6N$: C, 63.50; H, 5.89. Found: C, 63.73; H, 6.01.

5-Phenyl-1-pentanol.—This material, b.p. 110–113° (3 mm.), $n^{25}D$ 1.5149, was prepared from γ-phenylpropylmagnesium chloride and ethylene oxide. A b.p. of 151° (13 mm.) has been reported[11] for this alcohol.

ω-Aryl-1-alkyl *p*-Bromobenzenesulfonates.—The primary alcohols were converted to *p*-bromobenzenesulfonates by the low temperature method described previously,[9] the physical properties and analyses of the products being summarized in Table X.

γ-(2,4-Dimethoxybenzoyl)-butyric Acid.—To a mixture of 40 g. of glutaric anhydride and 50 g. of resorcinol dimethyl ether in 450 cc. of purified tetrachloroethane, cooled to 0°, was added 100 g. of anhydrous aluminum chloride in small portions with stirring. The mixture became purple and a viscous solid separated. After *ca.* 30 min. at 0°, ice and dilute hydrochloric acid were added. After working up the reaction mixture and recrystallizing the product from aqueous methanol, 18 g. of the desired acid was obtained. A small sample, recrystallized for analysis had a melting point of 106–107°.

Anal. Calcd. for $C_{13}H_{16}O_5$: C, 61.89; H, 6.39. Found: C, 61.61; H, 6.19.

5-(2,4-Dimethoxyphenyl)-valeric Acid.—The above keto acid (17 g.) was reduced by the Clemmensen method using 50 g. of zinc (amalgamated), 30 cc. of toluene, 30 cc. of water and 70 cc. of concd. hydrochloric acid. The mixture was refluxed for two days while 10 cc. of concd. hydrochloric acid was added every 6 hours. The product was extracted from the toluene phase with bicarbonate solution. Acidification of the bicarbonate extract gave the acid which was recrystallized from aqueous methanol to yield 5.5 g. of the acid, m.p. 95–98°. A small sample, recrystallized for analysis had m.p. 97–98.5°.

Anal. Calcd. for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.72; H, 7.63.

5-(2,4-Dimethoxyphenyl)-1-pentanol.—This alcohol, b.p. 144–145° (2 mm.), $n^{25}D$ 1.5247, was obtained in 96% yield by the lithium aluminum hydride reduction of 5-(2,4-dimethoxyphenyl)-valeric acid.

Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.55; H, 8.79.

The *p*-bromobenzenesulfonate of the alcohol was obtained as a liquid, 90% pure according to the equivalent weight in acetolysis and formolysis.

1-Phenyl-4-pentyl *p*-Toluenesulfonate.—To a solution of 15 g. of 5-phenyl-2-pentanol,[11] b.p. 80–84° (1 mm.), $n^{25}D$ 1.5108, in 75 ml. of dry pyridine was added 25 g. of *p*-toluenesulfonyl chloride. The mixture was kept below room temperature until the exothermic reaction was over, and then it was left at room temperature for another 2 hours. Working up the reaction mixture and evaporation of an ether solution of the product gave rise to an oil which was chromatographed on alumina. From the fraction eluted by benzene–pentane was obtained 9.5 g. of product, $n^{25}D$ 1.5382, 93% pure by equivalent weight in formolysis.

1-(2,4-Dimethoxyphenyl)-4-pentanol.—4-(2,4-Dimethoxyphenyl)-butyric acid (16 g.) in 50 ml. of ether was added dropwise with stirring to a solution of methyllithium prepared from 25 g. of methyl iodide and 2.5 g. of lithium ribbon in 200 ml. of ether. After 30 minutes stirring, cold dil. hydrochloric acid was added. The ether phase was separated and washed with water and a sodium bicarbonate solution. After being dried, the ether solution was distilled, the fraction, b.p. 120–150° (2 mm.), being then reduced with lithium aluminum hydride. A 3.5-g. quantity of the alcohol, b.p. 135–139° (2 mm.), $n^{26}D$ 1.5219, was obtained.

Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.88; H, 9.21.

TABLE X

PROPERTIES AND ANALYSES OF SOME *p*-BROMOBENZENESULFONATES

Compound	M.p., °C.	Formula	Analyses, % Calcd. Carbon	Found Carbon	Calcd. Hydrogen	Found Hydrogen
$C_6H_5(CH_2)_3OBs$	35.5–37.5	$C_{15}H_{15}O_3SBr$	50.71	50.72	4.26	3.98
p-$CH_3OC_6H_4(CH_2)_3OBs$	62–64	$C_{16}H_{17}O_4SBr$	49.88	50.03	4.44	4.36
2,4-$(CH_3O)_2C_6H_3(CH_2)_3OBs$	56–57	$C_{17}H_{19}O_5SBr$	49.16	49.08	4.61	4.76
$C_6H_5(CH_2)_4OBs$	21–23.5[a]	$C_{16}H_{17}O_3SBr$	52.04	52.09	4.64	4.56
p-$CH_3OC_6H_4(CH_2)_4OBs$	43–45	$C_{17}H_{19}O_4SBr$	51.13	51.33	4.80	4.63
2,4-$(CH_3O)_2C_6H_3(CH_2)_4OBs$	54.5–56.5	$C_{18}H_{21}O_5SBr$	50.35	50.63	4.93	4.99
$C_6H_5(CH_2)_5OBs$	34–35.5	$C_{17}H_{19}O_3SBr$	53.27	53.44	5.00	4.79

[a] $n^{25}D$ 1.5694.

The *p*-toluenesulfonate of the alcohol was obtained as an impure liquid, $n^{25}D$ 1.5250, 70% pure according to the equivalent weight in formolysis.

Kinetic Measurements.—The procedure for the kinetic measurements was identical to that employed previously.[9]

Only with 3-(2,4-dimethoxyphenyl)-1-propyl *p*-bromobenzenesulfonate did the acetolysis fail to obey first-order kinetics strictly. The rate constant drifted down in a run, as is illustrated in Table XI. The initial rate constant was obtained from a plot of log $[(ROBs)_0/(ROBs)]$ *vs.* time.

TABLE XI

ACETOLYSIS OF 0.0257 *M* 3-(2,4-DIMETHOXYPHENYL)-1-PROPYL *p*-BROMOBENZENESULFONATE AT 75.00°

Time, 10^{-2}, sec.	NaOAc, ml. per 5-ml. aliquot.	Integrated $10^5 k$, sec.$^{-1}$
0	0.015	..
289	.460	3.83
466	.685	3.68
892	1.180	3.60
1396	1.652	3.49
1812	1.970	3.41
3483	2.850	3.17
4722	3.260	3.06
∞	4.260	..
∞ (calcd.)	4.267	..

Products of Formolysis of 4-(2,4-Dimethoxyphenyl)-1-butyl *p*-Bromobenzenesulfonate.—A mixture of 18.4 g. of 4-(2,4-dimethoxyphenyl)-1-butyl *p*-bromobenzenesulfonate and 3.40 g. of sodium formate in 900 cc. of dry formic acid was heated at 75° for six hours. The resulting solution was diluted with water and extracted with four 500-ml. portions of ether. The combined extracts were washed with water and aqueous sodium bicarbonate. After the extract was dried, the solvent was removed and the residue was reduced with 2 g. of lithium aluminum hydride in ether. The reduction product was extracted with dilute sodium hydroxide. The basic extract became colored orange, but only a negligible amount of material appeared when this extract was acidified. The reduction product yielded three fractions when it was chromatographed on 500 g. of alumina.

The first fraction was eluted with 5 liters of pentane. The tetralin product, b.p. 102–105° (2 mm.), $n^{25}D$ 1.5454, weighed 5.5 g. This material was inert to potassium permanganate in acetone. A sample, b.p. 105° (2 mm.), was analyzed.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 75.14; H, 8.61.

This material crystallized after standing several months; m.p. 36.5–38°.

It formed a monobromide, m.p. 78–80°, when it was treated with bromine in carbon tetrachloride.

Anal. Calcd. for $C_{12}H_{15}O_2Br$: C, 53.15; H, 5.28. Found: C, 53.02; H, 5.51.

The dehydrogenation of 2 g. of the tetralin with 6 g. of chloranil in 20 ml. of xylene at reflux temperature for 15 hours as described by Arnold and Collins,[14] yielded 0.8 g. of the picrate of 1,3-dimethoxynaphthalene, m.p. 141–142°, undepressed by the synthetic material described below.

Anal. Calcd. for $C_{18}H_{15}O_9N_3$: C, 51.80; H, 3.62. Found: C, 51.84; H, 3.64.

A second fraction from the chromatography was eluted with four liters of ether. This material (0.8 g.) was also the tetralin mentioned above, b.p. 110° (3 mm.), $n^{25}D$ 1.5401, inert to potassium permanganate in acetone.

The third fraction was eluted with three liters of methanol. The product, 0.7 g., b.p. 130° (3 mm.), was converted into the *p*-nitrobenzoate. It was necessary to chromatograph the ester before it could be crystallized. Crystallization of the chromatographed product from methanol gave two fractions. The first fraction, m.p. 49–51°, mixed m.p. with authentic material 49–52°, weighed 0.8 g. The second fraction, m.p. 48–51°, mixed m.p. 48–51°, weighed 0.1 g.

In a control experiment, a solution of 2 g. of 4-(2,4-dimethoxyphenyl)-1-butanol in 150 ml. of 98–100% formic acid was heated at 75° for 15 hours. Working up in the manner described for the solvolysis reactions yielded 1.65 g. (82.5%) of recovered alcohol, b.p. 150–152° (2 mm.), $n^{25}D$ 1.5296.

In another control experiment, a solution of 0.5 g. of 4-(2,4-dimethoxyphenyl)-1-butanol in 30 cc. of 0.0315 *M* sodium formate in formic acid was heated at 75° for 10 hours. When the mixture was worked up as described for the solvolysis, 0.35 g. (70%) of the alcohol was recovered. This gave 0.40 g. (67%) of *p*-nitrobenzoate, m.p. 50–53°.

1,3-Dimethoxynaphthalene.—Ethyl 1,3-dihydroxy-2-naphthoate[15] (13 g.) was treated with a solution of diazomethane in 200 ml. of ether prepared from 15 g. of nitrosomethylurea. After the mixture was allowed to stand overnight, the ether was evaporated and the remaining oil was vacuum distilled. The fraction, b.p. 155–175° (2 mm.), weighing 11 g., was refluxed with 10 g. of sodium hydroxide in a mixture of 15 ml. of water and 15 ml. of ethanol overnight. The dark solution and solid was treated with water, and the product was extracted with ether. The product, b.p. 145–150° (3 mm.), was a dark colored oil weighing 2.8 g. The color was removed readily by chromatography on alumina, but the substance soon became colored again on standing. The purified product, $n^{25}D$ 1.6140, was analyzed.

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.79; H, 6.45.

The picrate of this substance crystallized from ether in the form of long orange-red needles, m.p. 140–141°.

Products of Formolysis of 4-*p*-Anisyl-1-butyl *p*-Bromobenzenesulfonate.—A solution of 8 g. of 4-*p*-anisyl-1-butyl *p*-bromobenzenesulfonate in 700 ml. of 0.03022 *M* sodium formate in dry formic acid, was heated at 75° for 42 hours. After dilution with water, the products were extracted with three portions of pentane. The oil remaining after the pentane was evaporated was reduced with 1 g. of lithium aluminum hydride. The product mixture was then chromatographed on 100 g. of alumina. The 7-methoxytetralin was eluted with 700 ml. of pentane. This substance, b.p. 76° (1.5 mm.), $n^{25}D$ 1.5414, weighed 1.65 g. and was inert to potassium permangante in acetone. The b.p. of this compound has been reported as 103–105° (5.5 mm.)[17] and 129–131° (11 mm.).[16] The 4-*p*-anisyl-1-butanol was eluted with 600 ml. of ether. This product, b.p. 118–119° (1.5 mm.), $n^{25}D$ 1.5239, weighed 1.55 g.

Products of Formolysis of 4-Phenyl-1-butyl *p*-Bromobenzenesulfonate.—To a solution of 3.4 g. of dry sodium formate in 1000 ml. of dry formic acid (containing 0.31% water by Karl Fischer titration) heated to 75.0° was added 18.5 g. of the purified bromobenzenesulfonate. The solution was mixed well and left at 75.0° for 66 hours. The resulting solution was cooled, poured into 3 liters of water, and ex-

tracted with 4 portions of pure pentane. The extracts were washed with water and aqueous sodium bicarbonate. After they were dried, the solvent was distilled off carefully through a Vigreux column, and the products were reduced with 2 g. of lithium aluminum hydride in ether. The reduced products were chromatographed on 500 g. of alumina. The pentane eluates yielded 1.10 g. (16.7%) of hydrocarbon, b.p. 101–103° (22 mm.), $n^{25}D$ 1.5388 (reported[27] for tetralin, b.p. 89° (12 mm.), $n^{25}D$ 1.5392). The infrared spectrum of the hydrocarbon was identical with that of pure tetralin. Also, an 80% yield of naphthalene, m.p. 75–77°, mixed m.p. 77–80°, was obtained from the hydrocarbon by dehydrogenation with tetrachloro-1,2-benzoquinone in benzene.[18]

Elution with methanol, concentration and distillation gave 5.4 g. (72.0%) of alcohol, b.p. 87–90° (1.5 mm.), $n^{25}D$ 1.5191 ($n^{25}D$ 1.5202 for pure 4-phenyl-1-butanol). The infrared spectrum of the alcohol was identical with that of 4-phenyl-1-butanol.

Treatment of 4-Phenyl-1-butanol with Acidic Formic Acid.—A solution of 2.0 g. of 4-phenyl-1-butanol and 0.6 g. of *p*-toluenesulfonic acid in 100 cc. of dry formic acid (0.31% water) was heated at 75.0° for 67 hours. Cooling and pouring into water gave rise to an oil which was extracted with three portions of pure pentane. The extracts were washed, concentrated and reduced with lithium aluminum hydride. Distillation of the product gave 1.7 g. (85%) of alcohol, $n^{25}D$ 1.5189, b.p. 124–127° (10 mm.), with no sign of any lower boiling tetralin.

Products of Acetolysis of 4-Phenyl-1-butyl *p*-Bromobenzenesulfonate.—A 20.0-g. quantity of pure 4-phenyl-1-butyl *p*-bromobenzenesulfonate was added to 1200 cc. of dry acetic acid already heated to 100.0°, and the solution was kept at this temperature for 101 hours. The cooled solution was poured into 3 liters of water and extracted with 5 portions of pure pentane. The extracts were washed, concentrated and reduced with lithium aluminum hydride. The reduced products were chromatographed on alumina. There was obtained 0.35 g. (4.9%) of tetralin, b.p. 75° (10 mm.), $n^{25}D$ 1.5370, and 6.85 g. (84.4%) of alcohol, b.p. *ca.* 100° (2 mm.), $n^{25}D$ 1.5205. The infrared spectrum of the tetralin product was essentially the same as that of pure tetralin except for the presence of 2 small additional bands at 960 and 680 $cm.^{-1}$. The alcohol product had an infrared spectrum identical with that of pure 4-phenyl-1-butanol.

In a control experiment, a solution of 11.0 g. of 4-phenyl-1-butyl acetate, 11.4 g. of *p*-toluenesulfonic acid and 1 cc. of acetic anhydride in 1200 cc. of dry acetic acid was kept at 100.0° for 140 hours. The solution was cooled, poured into water, and the products were extracted as before. The crude acetates were reduced with lithium aluminum hydride and the product distilled. The product, b.p. 120–123° (8.5 mm.), $n^{25}D$ 1.5202, weighed 8.2 g. (95%). There was no sign of any lower boiling tetralin.

Formolysis of 5-Phenyl-2-pentyl *p*-Toluenesulfonate.—A solution of 9.2 g. of the toluenesulfonate (93% pure) and 2.45 g. of dry sodium formate in 600 cc. of dry formic acid (0.31% water) was kept at 25.0° for 43.5 hours. The products were isolated in the usual way. Chromatography on 200 g. of alumina yielded two fractions, a hydrocarbon fraction, 2.05 g., b.p. 112–115° (25 mm.), $n^{25}D$ 1.5229, and an alcohol fraction, 2.20 g., b.p. 95–100° (1.5 mm.), $n^{25}D$ 1.5107. The alcohol had an infrared spectrum identical with that of 5-phenyl-2-pentanol.

The hydrocarbon fraction contained 30% olefin according to quantitative hydrogenation. The 1-methyltetralin was isolated from the hydrocarbon mixture by oxidizing the olefin with osmium tetroxide. For this purpose, 0.75 g. of the mixture was added to 1.0 g. of osmium tetroxide in 20 cc. of ether containing 2 drops of pyridine. After standing for 30 minutes, 150 cc. of pure methylene chloride and a solution of 2.5 g. of potassium hydroxide and 2. 5 g. of mannitol in 50 cc. of water was added. The two phase mixture was shaken in a shaking machine for two hours. The aqueous phase was separated and extracted again with methylene chloride. The combined extracts were washed with water, dried and concentrated under a Vigreux column. Vacuum distillation yielded 0.4 g. (53%) of 1-methyltetralin, b.p. 55° (1.5 mm.), $n^{25}D$ 1.5323 (reported[28] for 1-methyltetralin, b.p. 87–88° (7 mm.), $n^{25}D$ 1.5332). The material was inert to potassium permanganate in acetone. The infrared spectrum indicated a trace (*ca.* 1–2%) of alcoholic impurity.

Anal. Calcd. for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.30; H, 9.46.

In a control experiment, a solution of 5.0 g. of the alcohol and 0.35 g. of sodium formate in 500 cc. of dry formic acid (0.14% water) was kept at 25.0° for 41 hours. The products were isolated as usual. Reduction with 1.5 g. of lithium aluminum hydride in ether gave 5.0 g. of alcohol, b.p. 117–120° (8 mm.), $n^{25}D$ 1.5108. There was no sign of any lower boiling material. An analogous treatment of 4.4 g. of alcohol in 500 ml. of formic acid without sodium formate for 27 days at 25° gave only 0.06 g. of a hydrocarbon fraction and 4.0 g. (91%) of alcohol, b.p. 145–148° (30 mm.), $n^{25}D$ 1.5106.

In another control experiment, a solution of 1.0 g. of the olefin–tetralin mixture obtained from solvolysis of 5-phenyl-2-pentyl *p*-toluenesulfonate was kept at 25.0° with 0.050 g. of pure sodium formate in 150 cc. of 98–100% formic acid for 42.5 hours. The products were isolated as usual and distilled. There was obtained 0.95 g. of product, $n^{25}D$ 1.5231, 26% olefin by quantitative hydrogenation. The infrared spectrum was nearly like that of the starting mixture except for weak bands at 1720, 1180 and 1110 $cm.^{-1}$, probably indicating a few per cent. of a formate ester.

Reaction of 5-Phenyl-1-pentene with Formic Acid.—A solution of 4.4 g. of 5-phenyl-1-pentene,[29] b.p. 77–78°, $n^{25}D$ 1.5019, in 500 ml. of 98–100% formic acid was kept at 25.0° for 27 days. The resulting solution was poured into water and extracted with 5 portions of pure pentane. The extracts were washed, dried, concentrated and reduced with lithium aluminum hydride. Chromatography yielded 3.2 g. (73%) of hydrocarbon, b.p. 106–108° (*ca.* 30 mm.), $n^{25}D$ 1.5054, and 1.0 g. (20%) of alcohol, b.p. 95° (2 mm.), $n^{25}D$ 1.5099. The hydrocarbon fraction was determined to be 16% tetralin by quantitative hydrogenation over palladium-on-charcoal.

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(27) G. Egloff, "Physical Constants of Hydrocarbons," Vol. IV, Reinhold Publ. Corp., New York, N. Y., 1940, p. 29.

(28) Reference 27, page 33.

(29) J. v. Braun, H. Deutsch and A. Schmatlock, *Ber.*, **45**, 1255 (1912).