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Neighboring Carbon and Hydrogen. XXVIII. Ar_2-6 Participation in Solvolysis of Some ω-Aryl-1-alkyl Bromobenzenesulfonates[1,2]

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In searching for Ar_2-participation in solvolysis, acetolysis and formolysis of suitably substituted ω-aryl-1-alkyl *p*-bromobenzenesulfonates have been studied. In the case of 4-aryl-1-butyl bromobenzenesulfonates, substantial rate enhancements result from introduction of one or two *m*-methoxyl groups into the benzene ring. These enhancements are ascribed to increased importance of Ar_2- assisted ionization in solvolysis. The product of formolysis of 4-(3,5-dimethoxyphenyl)-1-butyl *p*-bromobenzenesulfonate contains mainly 5,7-dimethoxytetralin, formate ester being a minor product. The product composition agrees within experimental error with that predicted from the k_Δ and k_s values obtained by dissection of the solvolysis rate constant by the method outlined in the previous paper. For Ar_2-*n* participation, the rate sequence is $5 \ll 6 \gg 7$, only Ar_2-6 being important in the present work. The observed sequence contrasts with that observed for Ar_1-*n*, for which $5 \gg 6$. This contrast may be understood by considering the respective transition states for the rate-determining steps. The comparison of rates of Ar_1- and Ar_2-assisted ionizations discloses that Ar_1-5 and Ar_2-6-assisted ionizations have nearly equal rates for equivalent degrees of activation of the benzene ring.

In this paper are presented more data bearing on anchimeric effects of aryl groups more distant than *beta*. In contrast with the ω-aryl-1-alkyl bromobenzenesulfonates stressed in the previous paper,[3] the compounds treated in the present manuscript were substituted so as to favor Ar_2- rather than Ar_1-participation in the rate-determining ionization step. The results obtained in the study of these compounds supply considerable orientation on the scope of Ar_2-participation and the comparison of such participation with the Ar_1-variety.

ω-Aryl-1-alkyl Systems.—The list of *p*-bromobenzenesulfonates examined in the present study is shown in Table I, which also summarizes their solvolysis rate constants.

The alcohols which were required for preparation of the bromobenzenesulfonates were obtained by a variety of methods. Of the propanols, 3-*m*-anisyl-1-propanol was prepared in fair yield by the reduction of *m*-methoxycinnamic acid with lithium aluminum hydride. 3-(3,5-Dimethoxyphenyl)-1-propanol was obtained by a lithium aluminum hydride reduction of 3-(3,5-dimethoxyphenyl)-propanoic acid, the latter being derived from the malonic ester synthesis on 3,5-dimethoxybenzyl chloride.

Of the butanols, 4-*m*-anisyl-1-butanol was prepared in poor yield from γ-*m*-anisylpropylmagnesium chloride and formaldehyde. 4-(3,4-Dimethoxyphenyl)-1-butanol was prepared by a lithium aluminum hydride reduction of 4-(3,4-dimethoxyphenyl)-butanoic acid, the latter being obtained by Clemmensen reduction of the Friedel–Crafts succinoylation product from veratrole.[4] The 4-(3,5-dimethoxyphenyl)-1-butanol was prepared by the reaction of β-3,5-dimethoxyphenylethylmagnesium bromide with ethylene oxide. The required bromide was obtained from a displacement reaction on the *p*-bromobenzenesulfonate of β-3,5-dimethoxyphenylethanol. The preparation of this material by way of 3,5-dimethoxyphenylacetic acid has been described previously.[5]

The pentanol, 5-(3,4-dimethoxyphenyl)-1-pentanol, was prepared by a Friedel–Crafts reaction between veratrole and glutaric anhydride,[6] followed by Clemmensen and lithium aluminum hydride reductions.

Kinetic Search for Ar_2-Participation.—All the substances investigated displayed good first-order behavior in acetolysis and formolysis. As regards enhancement of solvolysis rate by methoxyl substitution in the benzene ring, no substantial rate enchancement is observed with the ω-aryl-1-propyl esters, as was pointed out already in the previous paper.[3] This is true even for 3,5-dimethoxyl substitution.

In the 4-phenyl-1-butyl series, substantial rate enhancements are observed[2] on addition of *m*-methoxyl groups to the benzene ring. Thus, 4-*m*-anisyl-1-butyl *p*-bromobenzenesulfonate is 1.86 times as reactive, and the 4-(3,5-dimethoxyphenyl)-1-butyl ester I, 6.24 times as reactive, as the 4-phenyl-1-butyl derivative in formic acid at 75°. The rate comparisons are summarized in Table II. In line with the previous arguments,[3] the observed rate enhancements are ascribed to increased importance of Ar_2-participation in the case of solvolysis of the *m*-methoxyl-substituted derivatives.

The procedure for dissecting the solvolysis rate constant into k_Δ, the rate constant of anchimerically assisted ionization, and k_s, the rate constant of anchimerically unassisted solvolysis, which was applied previously,[3] may be employed on the present data. Using a k_s equal to that for 4-phenyl-1-butyl *p*-bromobenzenesulfonate,[3] one obtains the k_Δ and k_Δ/k_s values summarized in Table II. As in the case of Ar_1-participation,[2,3] two methoxyl groups suffice to make Ar_2-participation dominate formolysis of a 4-aryl-1-butyl ester. Just as for Ar_1-participation,[3] the importance of Ar_2-participation is greater in formic acid than in acetic acid solvent.

Since k_Δ is responsible for most of the formolysis rate constant of the 4-(3,5-dimethoxyphenyl)-1-butyl derivative I, the value for $\Delta S^{\ddagger}$ listed in Table I, namely, -15.8 e.u., is the value for Ar_2-6-assisted ionization. This is lower than the value[3] for Ar_1-5-assisted ionization, and not very different from the value for anchimerically unassisted formolysis.

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[1] 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] R. Heck and S. Winstein, THIS JOURNAL, **79**, 3105 (1957).

[4] M. Haq, M. Kapur and J. N. Ray, *J. Chem. Soc.*, 1087 (1933).

[5] S. Winstein and R. Heck, THIS JOURNAL, **78**, 4801 (1956).

[6] R. D. Haworth and J. R. Atkinson, *J. Chem. Soc.*, 797 (1938).

TABLE I

SUMMARY OF SOLVOLYSIS RATE CONSTANTS

Compound	Solvent	Temp., °C.	[ROBs] $10^2 M$	k (sec.$^{-1}$)	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, e.u.
m-$CH_3OC_6H_4(CH_2)_3OBs$	HOAc	75.00	2.43	$(1.11 \pm 0.02) \times 10^{-6}$		
3,5-$(CH_3O)_2C_6H_3(CH_2)_3OBs$	HOAc	75.00	3.42	$(1.10 \pm .04) \times 10^{-6}$		
	HCOOH[a]	50.00	2.94	$(1.70 \pm .09) \times 10^{-6}$	22.0	−17.0
	HCOOH[a]	75.00	2.94	$(2.15 \pm .04) \times 10^{-5}$		
m-$CH_3OC_6H_4(CH_2)_4OBs$	HOAc	75.00	2.94	$(2.02 \pm .02) \times 10^{-6}$	24.5	−14.6
	HOAc	100.00	2.75	$(2.31 \pm .01) \times 10^{-5}$		
	HCOOH[a]	75.00	2.53	$(6.24 \pm .06) \times 10^{-5}$	22.4	−13.9
	HCOOH[a]	100.20	2.53	$(5.92 \pm .10) \times 10^{-4}$		
3,4-$(CH_3O)_2C_6H_3(CH_2)_4OBs$	HOAc	75.00	2.74	$(3.30 \pm .02) \times 10^{-6}$		
	HOAc	100.05	2.74	$(3.59 \pm .13) \times 10^{-5}$	23.9	−15.3
	HCOOH[b]	75.00	2.62	$(1.08 \pm .02) \times 10^{-4}$		
3,5-$(CH_3O)_2C_6H_3(CH_2)_4OBs$	HCOOH[a]	50.00	2.83	$(1.88 \pm .04) \times 10^{-5}$		
	HCOOH[a]	75.00	2.84	$(2.09 \pm .09) \times 10^{-4}$	20.9	−15.8
3,4-$(CH_3O)_2C_6H_3(CH_2)_5OBs$	HCOOH[a]	75.00	2.72	$(3.50 \pm .06) \times 10^{-5}$		

[a] 0.0315 M sodium formate. [b] 0.0302 M sodium formate. [c] 0.0291 M sodium formate.

TABLE II

ANALYSIS OF SOLVOLYSIS RATES OF SOME 4-ARYL-1-BUTYL p-BROMOBENZENESULFONATES AT 75.00°

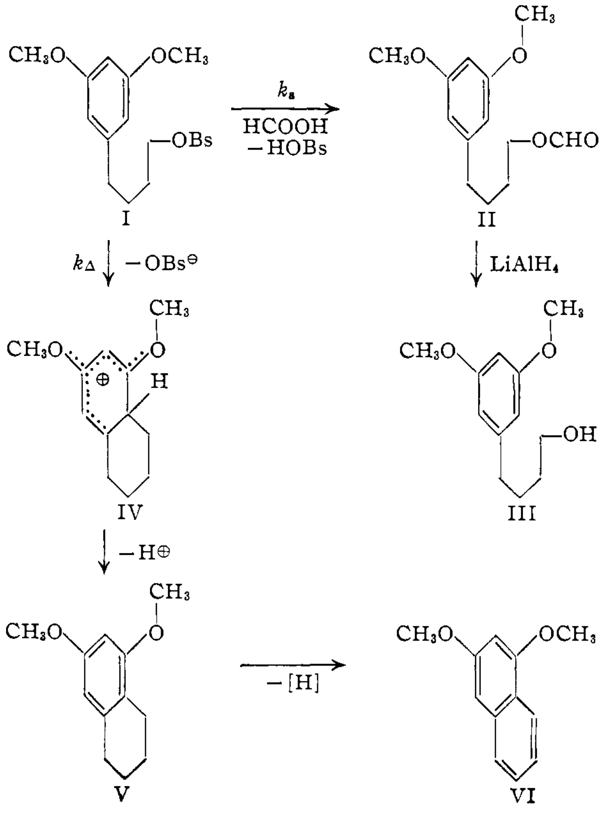
Compound	Rel. rates		AcOH			HCOOH			Rel. k_Δ
	AcOH	HCOOH	$10^6 k_s$	$10^6 k_\Delta$	k_Δ/k_s	$10^5 k_s$	$10^5 k_\Delta$	k_Δ/k_s	HCOOH
$C_6H_5(CH_2)_4OBs$	1.00	1.00	1.37	0.08[a]	0.06	2.78	0.65[a]	0.23	1.00[a]
m-$CH_3OC_6H_4(CH_2)_4OBs$	1.39	1.86	1.37	0.65	0.47	2.78	3.46	1.24	5.32
3,4-$(CH_3O)_2C_6H_3(CH_2)_4OBs$	2.28	3.15	1.37	1.93	1.41	2.78	8.02	2.88	12.3
3,5-$(CH_3O)_2C_6H_3(CH_2)_4OBs$		6.24				2.78	18.1	6.51	27.9

[a] Not apportioned between Ar_1-5 and Ar_2-6.

Formation of Tetralin.—The products of formolysis of 4-(3,5-dimethoxyphenyl)-1-butyl p-bromobenzenesulfonate (I) were examined in the usual way.[3] Reduction of the crude formolysis products with lithium aluminum hydride and chromatography on alumina yielded a minor alcohol fraction and a major more easily eluted fraction. The alcohol yielded a p-nitrobenzoate which was shown by mixed melting point to be the p-nitrobenzoate of the parent alcohol, 4-(3,5-dimethoxyphenyl)-1-butanol (III).

The major fraction was a colorless liquid, inert to potassium permanganate in acetone. Dehydrogenation of this material with chloranil[7] produced 1,3-dimethoxynaphthalene (VI) which was characterized by mixed melting point of its picrate with the authentic material described previously.[3] Thus, the major solvolysis product was 5,7-dimethoxytetralin (V), the same substance obtained in formolysis of 4-(2,4-dimethoxyphenyl)-1-butyl p-bromobenzenesulfonate,[3] the isomer of I substituted so as to favor Ar_1-5 participation.

The products observed in formolysis of the 4-(3,5-dimethoxyphenyl)-1-butyl derivative I agree closely with those predicted on the basis of the k_s and k_Δ values in Table II, assuming k_s is associated with formation of formate II and k_Δ associated with formation of tetralin V. As is clear from Table III, the observed per cent. tetralin in the product agrees within experimental error with the value, $100\ k_\Delta/(k_\Delta + k_s)$, just as in the previous cases favoring Ar_1-participation.[3] The available facts, therefore, suggest that the formolysis of the 4-(3,5-dimethoxyphenyl)-1-butyl derivative I proceeds to the extent of 12% by the anchimerically unassisted process leading to formate II, and to the extent of 88% by anchimerically assisted ionization. Anchimerically assisted ionization must be very predominantly



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[7] R. T. Arnold and C. J. Collins, THIS JOURNAL, 61, 1407 (1939).

Ar$_2$-6 in type, probably leading to an intermediate IV. Loss of a proton by IV leads to tetralin V.

TABLE III

PRODUCTS OF FORMOLYSIS OF 4-(3,5-DIMETHOXYPHENYL)-1-BUTYL *p*-BROMOBENZENESULFONATE AT 75°[a]

Total yield, %	% ROH	% Tetralin	$\frac{100\ k_\Delta}{k_\Delta + k_s}$
87.5	12.0	88.0	86.6

[a] 0.0454 *M* ROBs; 0.0515 *M* NaOCHO; 12 hours at 75.0°.

Ar$_2$-Participation and Ring Size. Comparison with Ar$_1$.—The tendency for Ar$_2$-7 participation in formolysis was assessed roughly by measuring relative rates of formolysis of 5-phenyl-1-pentyl and 5-(3,4-dimethoxyphenyl)-1-pentyl *p*-bromobenzenesulfonates. While the latter substance is substituted to favor both Ar$_2$-7 and Ar$_1$-6 participations, it was easily available, and its rate could be used to set an upper limit on the rate enhancement due to Ar$_2$-7-participation. As is brought out in Table IV, any increase in rate due to 3,4-dimethoxyl substitution in the 5-phenyl-1-pentyl system is small. Consequently, the k_Δ calculated on the assumption that k_s is equal to the rate constant of the 5-phenyl-1-pentyl ester is also small.

TABLE IV

ANALYSIS OF RATES OF FORMOLYSIS OF 5-ARYL-1-PENTYL *p*-BROMOBENZENESULFONATES AT 75°

Compound	Rel. rate	$10^5 k_s$	$10^5 k_\Delta$	k_Δ/k_s
$C_6H_5(CH_2)_5OBs$	1.00	3.39		
$3,4\text{-}(CH_3O)_2C_6H_3(CH_2)_5\text{-}OBs$	1.03	3.39	0.11	0.03

As is brought out in Table V, the available data on relative rates of Ar$_2$-assisted solvolysis suggest the sequence of ring sizes, 5 << 6 >> 7. With the ω-aryl-1-alkyl bromobenzenesulfonates of the type reported in the present article, only Ar$_2$-6 participation, not Ar$_2$-5 or Ar$_2$-7, has proved important.[8]

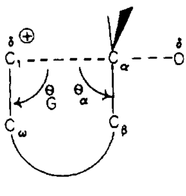
TABLE V

RELATIVE RATES OF Ar$_2$-*n* RING CLOSURES

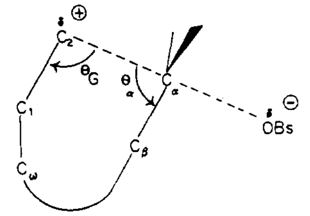
Ar group	Solvent	Size of ring being formed 5	6	7
ω-(3-Methoxyphenyl)	HOAc	0.06[a]	1.00	
	HCOOH	..	1.00	<0.04[b]
ω-(3,5-Dimethoxyphenyl)	HCOOH	0.01[a]	1.00	

[a] Values calculated using the rate of 3-phenyl-1-propyl *p*-bromobenzenesulfonate as k_s. [b] The value obtained from 5-(3,4-dimethoxyphenyl)-1-pentyl *p*-bromobenzenesulfonate.

It is interesting that a maximum in rate is observed for $n = 6$ in the case of Ar$_2$-participation, whereas the rate sequence observed[3] for Ar$_1$ was 5 >> 6. This contrast is relatively easy to understand by considering the transition states for the Ar$_1$- and Ar$_2$-assisted ionizations. These may be represented by VII and VIII, respectively, C_1 and C_2 denoting the respective carbon atoms of the neighboring phenyl group. The partial bonds between C_α and the leaving group, and between C_1 or C_2 and C_α in the transition state for the rate-determining step are symbolized by dotted lines. Also shown are the angles, θ_α and θ_G.



VII



VIII

In the transition states, the angle θ_α would have the value of 90° if the usual hybridization at C_α is assumed. In order to estimate θ_G, we should take into account the fact that the degree of involvement of the aryl group with C_α is quite small. For Ar$_1$, the low degree of involvement of aryl was clear from the relatively small effect of methoxyl substitution.[3] As is clear from Table II, methoxyl substitution has only a relatively small effect on rate in the case of Ar$_2$ also. This low degree of involvement of phenyl in the transition state suggests a value of θ_G close to 90°, the approach of C_α to C_1 or C_2 of the benzene ring being from a direction perpendicular to the plane of the benzene ring. Examination of models which employ a value of 90° for both θ_α and θ_G shows the transition state to be relatively strainless for Ar$_1$-5. However, it is quite strained in Ar$_2$-5, and becomes relatively comfortable when ring size is increased to Ar$_2$-6.

Comparing rates of Ar$_1$- and Ar$_2$-assisted solvolysis, the available data show that rates are comparable for Ar$_1$-5 and Ar$_2$-6 for equal degrees of activation of the benzene ring with methoxyl groups. This comparison is shown explicitly in Table VI.

TABLE VI

COMPARISON OF Ar$_1$-5 AND Ar$_2$-6 RING CLOSURES AT 75°

Compound	Main participation type	$10^6 k_\Delta$ (sec.$^{-1}$) AcOH	HCOOH
m-$(CH_3O)C_6H_4(CH_2)_4OBs$	Ar$_2$-6	0.65	34.6
p-$CH_3OC_6H_4(CH_2)_4OBs$	Ar$_1$-5	0.53	33.0
$3,5\text{-}(CH_3O)_2C_6H_3(CH_2)_4\text{-}OBs$	Ar$_2$-6	..	181
$2,4\text{-}(CH_3O)_2C_6H_3(CH_2)_4\text{-}OBs$	Ar$_1$-5	4.89	312

From this table it is evident that Ar$_1$-5 is slightly slower than Ar$_2$-6 in the case of mono-methoxyl-substituted neighboring phenyl. On the other hand, Ar$_1$-5 is faster than Ar$_2$-6 for di-methoxyl-substituted neighboring phenyl. An amusing consequence of this is that the rate of formation of the tetralin V is smaller by the more direct Ar$_2$-6 route from I than it is by the less direct Ar$_1$-5 route from

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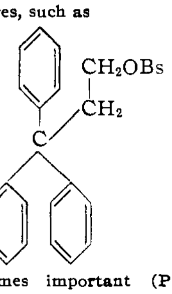
[8] For certain structures, such as



Ar$_2$-5 participation becomes important (P. Magee, unpublished work).

4-(2,4-dimethoxyphenyl)-1-butyl *p*-bromobenzenesulfonate.[3]

Since a maximum in rate occurs at the 5-ring for Ar_1- and the 6-ring for Ar_2-participation, and since Ar_1-5-assisted ionization results in final formation of a six-membered ring, the present results help one understand the pronounced tendency toward closure of 6- rather than 5-membered rings in cyclodehydrations and related reactions.[9] For neighboring vinyl rather than aryl, closure of 6-rings is similarly favored.[10]

An interesting compound, not yet commented on, whose solvolysis rate was investigated, is 4-(3,4-dimethoxyphenyl)-1-butyl *p*-bromobenzenesulfonate. This material is substituted so as to favor both Ar_1-5 and Ar_2-6 participation. If both Ar_1-5 and Ar_2-6 participations were completely independent of each other, and if a second methoxyl (*meta* to the substitution spot) had no significant effect on rate, one could expect k_Δ for the 3,4-dimethoxyl case to equal approximately the sum of the k_Δ values for the 4-methoxyl and 3-methoxyl cases. Actually, k_Δ for the 3,4-dimethoxyl case exceeds the calculated value. For example, in formic acid, k_Δ is 8.02×10^{-5} sec.$^{-1}$, as shown in Table II, while the calculated sum of the separate k_Δ values is 6.76×10^{-5} sec.$^{-1}$. The lack of agreement could conceivably be due to a rate-enhancing effect of a *meta* methoxyl group on either Ar_1-5 or Ar_2-6 or both. Such an effect is observed in bromination of the benzene ring.[11] However, it is doubtful that the Ar_1-5 and Ar_2-6 participation reactions in hand are sufficiently electron-demanding to bring forth a rate-enhancing response from a *meta* methoxyl group. For example, in Ar_1-3 participation, which is even more electron-demanding than the present examples of Ar_1-5 and Ar_2-6, a *meta* methoxyl is rate-retarding.[5]

It seems possible that Ar_1-5 and Ar_2-6 participations are not completely distinct in cases such as the 4-(3,4-dimethoxyphenyl)-1-butyl derivative. Whether C_α is lodging onto C_1 or C_2 of the benzene ring, it seems likely that, in the transition state, there is some bonding interaction between C_α and C_2 in the case of Ar_1-5 and between C_α and C_1 in the case of Ar_2-6.

Experimental Part

3-*m*-Anisyl-1-propanol.—The reduction of *m*-methoxycinnamic acid[12] with lithium aluminum hydride by the usual method gave 3-*m*-anisyl-1-propanol, b.p. 135–140° (3.5 mm.), $n^{25}D$ 1.5339, in 57.5% yield.

3-(3,5-Dimethoxyphenyl)-propanoic Acid.—To a solution of 3.6 g. of sodium metal in 200 ml. of anhydrous ethanol was added 39 g. of ethyl malonate, followed by 20 g. of 3,5-dimethoxybenzyl chloride.[13] After the mixture was refluxed overnight, most of the alcohol was distilled off, and the residue was mixed with cold dil. hydrochloric acid. The product was extracted with ether. The extract was washed with water, and the solvent was evaporated. The residue was refluxed for 4 hours with 25 g. of sodium hydroxide in 100 ml. of water and 50 ml. of ethanol. About 100 cc. of the solvent was distilled, and water was added to the residue. A trace of oil was extracted with ether and the aqueous solution was acidified. The crude malonic acid was heated to 150° until carbon dioxide evolution ceased, and then the product was distilled *in vacuo*. The acid, b.p. 177–178° (3 mm.), crystallized on standing. Recrystallization from a mixture of ether and petroleum ether gave 15.5 g. of material, m.p. 59–61° (reported[14] 61–62°).

3-(3,5-Dimethoxyphenyl)-1-propanol.—The reduction of 3-(3,5-dimethoxyphenyl)-propanoic acid with lithium aluminum hydride gave the desired alcohol, b.p. 145–150° (3 mm.), $n^{25}D$ 1.5332, in 63% yield; the remainder of the unreacted acid was recovered.

Anal. Calcd. for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 66.83; H, 8.18.

The *p*-bromobenzenesulfonate of this alcohol was obtained as a viscous liquid, $n^{25}D$ 1.5689, 93.3% pure as determined by equivalent weight measurements in acetic and formic acid, by the low temperature procedure previously described.[5]

4-*m*-Anisyl-1-butanol.—This alcohol, b.p. 112° (0.5 mm.), $n^{25}D$ 1.5260, was prepared in poor yield by the action of the Grignard reagent from 3-*m*-anisylpropyl chloride, $n^{25}D$ 1.5287, on formaldehyde.

4-(3,4-Dimethoxyphenyl)-butanoic Acid.—The Clemmensen reduction of 3-(3,4-dimethoxybenzoyl)-propanoic acid[4] gave 4-(3,4-dimethoxyphenyl)-butanoic acid, m.p. 56–58° after crystallization from a mixture of ether and pentane.

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.15; H, 6.99.

4-(3,4-Dimethoxyphenyl)-1-butanol.—The reduction of the above acid with lithium aluminum hydride gave impure 4-(3,4-dimethoxyphenyl)-1-butanol, b.p. 155–157° (3 mm.), $n^{25}D$ 1.5343, in 30% yield. The remainder of the material was unreacted acid.

2-(3,5-Dimethoxyphenyl)-ethyl Bromide.—A solution of 50 g. of lithium bromide and 35 g. of 2-(3,5-dimethoxyphenyl)-ethyl *p*-bromobenzenesulfonate[5] in 500 cc. of pure acetone was refluxed for one hour. The acetone was distilled off, the residue was dissolved in water, and the bromide was extracted with ether. The extracts were washed with water, dried and distilled. The bromide, b.p. 125–128° (1.5 mm.), $n^{25}D$ 1.5573, m.p. 24–26°, weighed 20.5 g.

Anal. Calcd. for $C_{10}H_{13}O_2Br$: C, 49.00; H, 5.34. Found: C, 49.03; H, 5.39.

4-(3,5-Dimethoxyphenyl)-1-butanol.—To a Grignard reagent prepared from 20 g. of 2-(3,5-dimethoxyphenyl)-ethyl bromide under dry nitrogen, an excess of ethylene oxide was added. The solution was refluxed for three hours and worked up with an ammonium chloride solution. Distillation gave 8 g. of forerun and 7 g. of still impure alcohol, b.p. 162–168° (2 mm.), $n^{25}D$ 1.5297, $n^{25}D$ 1.5290 after another distillation.

The residue from the above distillation could be distilled at high temperatures. Two recrystallizations from absolute ethanol yielded 2 g. of a substance, m.p. 100.5–101.5°, probably 1,4-di-(3,5-dimethoxyphenyl)-butane.

Anal. Calcd. for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93. Found: C, 72.43; H, 7.63.

The *p*-nitrobenzoate of the above alcohol was prepared by the conventional pyridine method and chromatographed on alumina with 50% ether–pentane. Two recrystallizations from methanol gave the compound, m.p. 65–66°, in the form of small yellow needles. The mixed m.p. with 4-(2,4-dimethoxyphenyl)-1-butyl *p*-nitrobenzoate was 44–51°.

Anal. Calcd. for $C_{19}H_{21}O_6N$: C, 63.50; H, 5.89. Found: C, 63.65; H, 5.57.

5-(3,4-Dimethoxyphenyl)-pentanoic Acid.—The Clemmensen reduction of 4-(3,4-dimethoxybenzoyl)-butanoic acid[6] afforded a 50% yield of 5-(3,4-dimethoxyphenyl)-pentanoic acid. The substance, recrystallized twice from petroleum ether (b.p. 60–80°), formed colorless crystals, m.p. 75–76°.

Anal. Calcd. for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.79; H, 7.75.

5-(3,4-Dimethoxyphenyl)-1-pentanol.—A solution of 8 g. of the above acid in 400 ml. of ether was refluxed with 3 g. of

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[9] *E.g.*, (a) R. O. Roblin, Jr., D. Davidson and M. T. Bogert, THIS JOURNAL, **57**, 151 (1935); (b) M. T. Bogert, Jr. and D. Davidson, *ibid.*, **56**, 185 (1934); (c) J. v. Braun and K. Weissbach, *Ber.*, **64**, 1785 (1931).

[10] *E.g.*, (a) R. P. Linstead, A. B. Wang, J. H. Williams and K. P. Errington, *J. Chem. Soc.*, 1136 (1937); (b) R. P. Linstead, A. H. Millidge and A. L. Walpole, *ibid.*, 1140 (1937).

[11] P. B. D. de la Mare and C. A. Vernon, *ibid.*, 1764 (1951).

[12] S. N. Chakravarti, R. D. Haworth and W. H. Perkin, *ibid.*, 2269 (1927).

[13] R. Adams, S. MacKenzie, Jr., and S. Loewe, THIS JOURNAL, **70**, 666 (1948).

[14] A. H. Salaway, *J. Chem. Soc.*, **97**, 2412 (1910).

TABLE VII

PROPERTIES AND ANALYSES OF SOME *p*-BROMOBENZENESULFONATES

Compound	M.p., °C.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
m-$CH_3OC_6H_4(CH_2)_3OBs$	36–38	$C_{16}H_{17}O_4SBr$	49.88	49.72	4.44	4.27
m-$CH_3OC_6H_4(CH_2)_4OBs$	36–38	$C_{17}H_{19}O_4SBr$	51.13	51.08	4.80	4.75
3,4-$(CH_3O)_2C_6H_3(CH_2)_4OBs$	68–71	$C_{18}H_{21}O_5SBr$	50.35	50.65	4.93	4.80
3,5-$(CH_3O)_2C_6H_3(CH_2)_4OBs$	56–57	$C_{18}H_{21}O_5SBr$	50.35	50.20	4.93	4.83
3,4-$(CH_3O)_2C_6H_3(CH_2)_5OBs$	73–73.5	$C_{19}H_{23}O_5SBr$	51.47	51.19	5.23	4.99

lithium aluminum hydride for 12 hours. The alcohol, b.p. 160–163° (2 mm.), $n^{25}D$ 1.5278, was a viscous colorless liquid weighing 5 g. A small sample was redistilled for analysis; $n^{25}D$ 1.5272.

Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.87; H, 8.78.

2-(3,4-Dimethoxyphenyl)-ethanol.—The reduction of 3,4-dimethoxyphenylacetic acid with lithium aluminum hydride by the usual method afforded a 37% yield of alcohol, b.p. 140–143° (3 mm.), m.p. 43–45°.

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.91; H, 7.75. Found: C, 65.86; H, 7.75.

Preparation of Bromobenzenesulfonates and Kinetic Measurements.—The *p*-bromobenzenesulfonates of the various alcohols were prepared by the low temperature method described previously.[5] Physical properties and analyses of these derivatives are summarized in Table VII.

Kinetic measurements were carried out as described previously.[5]

Formolysis Products of 4-(3,5-Dimethoxyphenyl)-1-butyl *p*-Bromobenzenesulfonate.—A solution of 1.95 g. of the *p*-bromobenzenesulfonate was solvolyzed for ten hours at 75° in a solution of 0.35 g. of sodium formate in 100 ml. of anhydrous formic acid. The resulting solution was diluted with 700 ml. of water and extracted with 500 ml. of petroleum ether in three portions. The extracts were washed with water and a sodium bicarbonate solution. The solvent was carefully distilled off, and the residue was reduced with 2 g. of lithium aluminum hydride.

The reduced product was chromatographed on 50 g. of alumina. The first fraction was eluted with 500 ml. of pentane. This solution contained 0.67 g. of 5,7-dimethoxytetralin, b.p. 100° (1.55 mm.), $n^{25}D$ 1.5452. This material was dehydrogenated with 2 g. of chloranil in boiling xylene as described previously.[3,7] The 1,3-dimethoxynaphthalene formed gave 0.35 g. of pure picrate, m.p. 140–141°, mixed m.p. with the picrate obtained from the corresponding solvolysis product from 4-(2,4-dimethoxyphenyl)-1-butyl *p*-bromobenzenesulfonate,[3] 140–141°.

A second fraction from the chromatography was eluted with 700 ml. of ether. There was obtained from this fraction 0.10 g. of alcohol, $n^{25}D$ 1.5310, which formed 0.11 g. of a nitrobenzoate, m.p. 64.5–66°, mixed m.p. with 4-(3,5-dimethoxyphenyl)-1-butyl nitrobenzoate, 65–66°.

LOS ANGELES 24, CALIFORNIA

[CONTRIBUTION FROM THE INSTITUTE OF SCIENTIFIC AND INDUSTRIAL RESEARCH, OSAKA UNIVERSITY]

Reactivities of Several ω-Substituted Primary Alkyl Bromides with Tertiary Amines[1,2]

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Rate constants, heats of activation and entropies of activation have been determined for a series of reactions between ω-substituted primary alkyl bromides and tertiary amines in two different solvents, *i.e.*, nitrobenzene and 50% ethanol. Alternation of reactivities was observed when nitrobenzene was used as a solvent, but no such phenomenon was observed when the solvent was 50% ethanol. The phenyl group showed little polar influence on the reactivities.

Our previous investigations[5] have been extended to the quaternization reactions of ω-substituted primary alkyl bromides with tertiary amines in two different solvents, *i.e.*, nitrobenzene and 50% ethanol, with the thought that these quaternization reactions might give a different trend from those of the reactions of the same bromides with thiosulfate ion, since it has been suggested[6] that the polar characteristic of the quaternization reaction is quite different.

Many studies of the quaternization reaction of alkyl halides with tertiary amines have been reported and our present experiments were carried out following the typical procedure used by Laidler and Hinshelwood[7] and later by Brown and Eldred.[8]

Experimental

The methods of preparations and purifications of all the organic halides have been described elsewhere.[5] The nitrobenzene was purified by partially freezing the fractionated material, which melted around 5.0–5.7°. The portions which melted from 5.5–5.7° were collected for use. Ethanol 50%, was made as reported in the previous paper.[5]

Investigation of Products.—It is known that primary alkyl halides gives quaternary ammonium salts in quantitative yield[9] and also that β-haloalkyl alcohols give quaternary ammonium chlorides in the reaction with trimethylamine.[10] No report has indicated any formation of olefin in the reaction of primary halide with tertiary amine.

In this study, the reaction products were investigated only in the case of β-bromoethyl ether in both 50% ethanol and in nitrobenzene, because among those studied kinetically this compound would be the most likely to give elimination products. The mixture of 1.53 g. of β-bromoethyl ethyl ether and 1.01 g. of triethylamine was placed in a 25-ml.

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(2) Presented at the 9th General Meeting of the Japanese Chemical Society, Kyoto, April, 1956.

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