6-Methoxyl Participation and Ion Pairs in Some Solvolysis Reactions[1]

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Abstract: The kinetics and products of solvolysis of 5-methoxy-1-pentyl *p*-bromobenzenesulfonate have been investigated to provide information regarding the mechanistic details of the MeO-6 solvolytic process. Good first-order kinetic and theoretical infinity values are observed with ethanol and formic acid. With acetic acid only about 50% of the theoretical amount of *p*-bromobenzenesulfonic acid is produced after eight half-lives. Inclusion of lithium perchlorate in acetolysis increases *p*-bromobenzenesulfonic acid formation to 100%. For acetolysis, substantial yields of tetrahydropyran, methyl *p*-bromobenzenesulfonate, methyl acetate, and 5-methoxy-1-pentyl acetate are obtained. In the case of ethanolysis, tetrahydropyran and 1-methoxy-5-ethoxypentane account quantitatively for product formation. Methyl *p*-bromobenzenesulfonate is not formed in either ethanolysis or formolysis. The results taken collectively are evidence for formation of the O-methyltetrahydropyranium ion. The appearance of methyl *p*-bromobenzenesulfonate in acetolysis is a clear case of ion pair chemistry and probably the result of external ion pair return. On this basis, acetolysis is interpreted with the aid of a solvent-separated and two intimate O-methyltetrahydropyranium ion pair intermediates. The same reaction scheme may be used to account for ethanolysis and formolysis. The reasons for the mechanistic differences between MeO-6 and MeO-5 participation are discussed.

In a communication summarizing our observations regarding methoxyl participation in solvolysis reactions,[2] preliminary kinetic and product studies were reported for 5-methoxy-1-pentyl *p*-bromobenzenesulfonate (I). These results illustrated that MeO-6 participation is substantial in acetic acid and formic acid, and significant in ethanol. Also, with acetic acid I was found to give only 50% of the theoretical amount of *p*-bromobenzenesulfonic acid after an estimated eight reaction half-lives. Such behavior clearly indicated that MeO-6 assisted acetolysis with I must differ mechanistically from related cases of MeO-5 participation.[3,4] This led us to investigate further the MeO-6 solvolytic process. The present paper describes the experimental details and discusses the mechanistic implications.

Results

Solvolysis Kinetics. The 5-methoxy-1-pentanol was prepared by reaction of the monosodium salt of 1,5-pentanediol with methyl iodide. Preparation of *p*-bromobenzenesulfonate I was accomplished by treating the alcohol with *p*-bromobenzenesulfonyl chloride in pyridine under the usual low-temperature conditions. The isolated crude *p*-bromobenzenesulfonate reaction product was used without further purification for all kinetic and product studies. This material was found to be 96% pure on the basis of 96.1 and 96.0% infinity titers for ethanol and acetic acid solutions of lithium perchlorate, respectively. After the kinetic and product studies were completed, we managed to purify a sample of *p*-bromobenzenesulfonate I by low-temperature recrystallization from ether–pentane solvent. This material had the correct elemental analyses. Pertinent kinetic data for solvolysis of 5-methoxy-1-pentyl *p*-bromobenzenesulfonate (I) are summarized in Table I. For ethanol and formic acid the rate constants were nicely first order, and the infinity titers were the theoretical values.

In acetic acid solvent, the solvolysis reaction appeared to proceed to *ca.* 50% completion and then form *p*-bromobenzenesulfonic acid at a very much reduced rate. This behavior is suggestive of a reaction which produces, in addition to *p*-bromobenzenesulfonic acid, another *p*-bromobenzenesulfonate which solvolyzes at a slower rate. An attempt to measure the rate constant of this second compound was thwarted by the solution turning yellow and finally darker brown until accurate titration became impossible. The logical cause of the low infinity value appeared to involve formation of methyl *p*-bromobenzenesulfonate. This substance acetolyzes at about $^1/_{50}$ of the rate estimated for the I bromobenzenesulfonate.[5] If this is the case, and if *p*-bromobenzenesulfonic acid and methyl *p*-bromobenzenesulfonate are formed in a constant ratio, it should be possible to calculate the rate constant of I with the aid of eq 1 and an estimated infinity value near 50% of theoretical. A consideration of the difference in acetolysis rates of the two *p*-bromobenzenesulfonates indicates that even if the solvolyzing material was initially 50% methyl compound, the latter would produce less than 2% of the total *p*-bromobenzenesulfonic acid when I has reacted 80%. On this basis, the acetolysis of I was followed titrimetrically until *ca.* 40% of the theoretical amount of *p*-bromobenzenesulfonic acid had been produced. The rate constant was evaluated with eq 1 by using the best estimated infinity titer obtained by a successive approximation treat-

$$k = \frac{2.303}{t} \log \left[\frac{(\mathrm{HOBs})_\infty - (\mathrm{HOBs})_0}{(\mathrm{HOBs})_\infty - (\mathrm{HOBs})_t} \right] \qquad (1)$$

(1) (a) This research supported by the National Science Foundation. (b) Paper XXX in the series, "The Role of Neighboring Groups in Replacement Reactions"; paper XXXIII in the series, "Salt Effects and Ion Pairs in Solvolysis and Related Reactions."

(2) S. Winstein, E. Allred, R. Heck, and R. Glick, *Tetrahedron*, 3, 1 (1958).

(3) E. L. Allred and S. Winstein, *J. Am. Chem. Soc.*, 89, 3991 (1967).

(4) E. L. Allred and S. Winstein, *ibid.*, 89, 3998 (1967).

(5) S. Winstein and H. Marshall, *ibid.*, 74, 1120 (1952), extrapolated from the data for methyl *p*-toluenesulfonate by multiplying by a factor of 3.

Table I. Solvolysis Rates of 5-Methoxy-1-pentyl *p*-Bromobenzenesulfonate (I)

Solvt	Concn of ROBs,[a] 10^2M	Temp, °C	Added salt	% infinity	k, sec^{-1}
EtOH	3.35	75.0	...	96.1[b]	$(1.60 \pm 0.01) \times 10^{-4}$
AcOH	3.45	75.1	...	46.2[c]	$(1.09 \pm 0.03) \times 10^{-4}$
AcOH	3.38	50.0	...	43.6[c]	$(9.02 \pm 0.08) \times 10^{-6}$
AcOH	3.33	50.0	0.030 M $LiClO_4$	100[d]	$(9.35 \pm 0.78) \times 10^{-6}$
AcOH	3.32	50.0	0.050 M $LiClO_4$	100[c]	$(1.18 \pm 0.03) \times 10^{-5}$
AcOH	3.31	50.0	0.060 M $LiClO_4$	100[c]	$(1.15 \pm 0.02) \times 10^{-5}$
AcOH	3.28	50.0	0.080 M $LiClO_4$	98.4[c]	$(1.28 \pm 0.04) \times 10^{-5}$
HCOOH	3.05	75.0	0.029 M NaOCHO	97.8[c]	$(1.16 \pm 0.02) \times 10^{-3}$

[a] Concentration is based on the weight of sample used. [b] Actual infinity titer based on the weight of sample used. [c] The infinity titer for ethanol is used as a measure of the purity of I for the reasons discussed in connection with the kinetic and product results. The reported values are corrected on the basis of 96.1% purity. [d] The solution with 0.030 M $LiClO_4$ became colored and could not be titrated beyond *ca.* 24% solvolysis. The reported rate constant was estimated on the basis of I being 96.1% pure.

Table II. Acetolysis Rate Calculations for 0.0345 M 5-Methoxy-1-pentyl *p*-Bromobenzenesulfonate at 75.1°

Time, sec	Amount of reaction— % of theory[a]	% of est infinity[b]	0.0368 M NaOAc,[c] ml	10^4k, sec^{-1}
0	3.51	7.60	0.163	...
1,514	10.61	22.95	0.492	1.20
2,408	13.84	29.94	0.642	1.15
3,375	16.77	36.29	0.778	1.10
4,697	20.33	43.98	0.943	1.07
5,525	22.47	48.60	1.042	1.06
7,973	27.73	59.98	1.286	1.05
10,395	32.56	70.43	1.510	1.10
14,354	37.58	81.30	1.743	1.10
47,568	52.07	...	2.415	...
∞ (est)	46.23	...	2.144[b]	...
∞	100	...	4.638[a]	...
				Av (1.10 ± 0.03)

[a] Calculated based on the assumption that the per cent infinity of 96.1% in ethanol represents the purity of I. [b] The best value obtained by a successive approximation treatment. [c] Per 5.14-ml aliquot.

Table III. Acetolysis Rate of 0.0331 M 5-Methoxy-1-pentyl *p*-Bromobenzenesulfonate (I) with Added 0.060 M Lithium Perchlorate at 50.0°

Time, sec	% reaction	0.0368 M NaOAc,[a] ml	10^5k, sec^{-1}
0	1.35	0.060	...
10,213	11.82	0.525	1.10
22,620	23.87	1.060	1.14
42,913	39.41	1.750	1.14
77,713	60.36	2.680	1.17
112,965	74.10	3.290	1.18
116,247	86.71	3.850	1.18
∞ (exptl)	96.04[b]	4.440	...
∞ (calcd)	...	4.623[c]	...
			Av (1.15 ± 0.02)

[a] Per 5.14-ml aliquot. [b] Based on the calculated infinity titer. All of the other values for per cent reaction are based on the experimental infinity titer. [c] Calculated based on the actual weight of I used to make up the acetolysis solution.

ment. The result is illustrated by the data shown in Table II. The best estimated infinity titers are 43.6 and 46.2% at 50 and 75°, respectively. For both temperatures good first-order rate constants were obtained.

The addition of lithium perchlorate to the acetolysis solution was found to have a profound effect on the infinity titer. Inclusion of only a 0.03 M concentration of this salt increased the value from 43.6 to near 100% at 50°. The rate constants with added lithium perchlorate all show good first-order behavior. Table III illustrates the results for a typical rate determination.

The effects of lithium perchlorate on the acetolysis of I are shown in Figure 1 by a plot of titrimetric rate constant k_t *vs.* molar lithium perchlorate concentration.

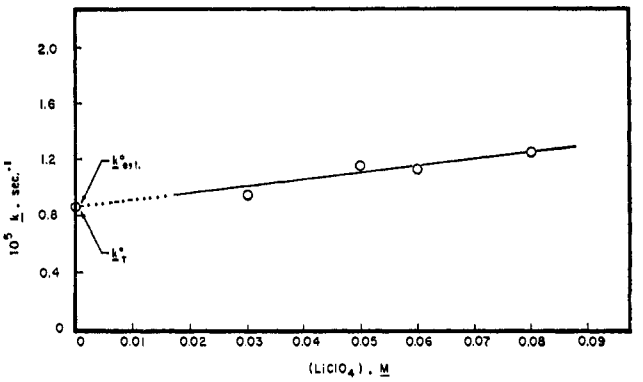


Figure 1. Effects of lithium perchlorate in acetolysis of 5-methoxy-1-pentyl *p*-bromobenzenesulfonate at 50.0°.

It is clear that an extrapolation of the linear plot to zero ($LiClO_4$) yields a k^0_{ext} value equal to k_t^0, within experimental error. The linear plot may be expressed analytically by eq 2, b being the slope. At 50° b is 5.8.

$$k_t = k_t^0[1 + b(LiClO_4)] \quad (2)$$

This compares to a b value of 8.4 for 4-methoxy-1-butyl *p*-bromobenzenesulfonate, a comparable system which shows MeO-5 participation.[6]

Products of Solvolysis. In order to substantiate the kinetic conclusions and to further illuminate the solvolysis mechanism, the products of total acetolysis and ethanolysis were examined. All reported yields are corrected based on a sample purity of 96%.

From acetolysis at 75°, methyl *p*-bromobenzenesulfonate and 5-methoxy-1-pentyl acetate were recovered after *ca.* eight reaction half-lives of I in 29 and 17% yields, respectively. While some methyl *p*-bromobenzenesulfonate was lost due to partial solvolysis and to recrystallization, enough was isolated to indicate that the kinetic treatment is essentially correct. In

(6) R. E. Glick, Ph.D. Dissertation, University of California, Los Angeles, Calif., 1954.

addition, tetrahydropyran and methyl acetate were detected by gas chromatography. Because of unfavorable tailing of the acetic acid chromatograms, accurate measurement of the yields of these products was not possible with our gas chromatographic columns. In an effort to estimate these total yields quantitatively, a sample of I was acetolyzed at 75° for *ca.* 47 half-lives and the fractions boiling below 117.5° (boiling point of AcOH) were carefully collected. These consisted of a fraction of nearly pure methyl acetate and intermediate fractions which were binary mixtures of methyl acetate and tetrahydropyran, and tetrahydropyran and acetic acid. The compositions of the mixtures were determined by comparison of refractive index with experimentally determined plots of refractive index *vs.* wt % obtained from known mixtures (see the Experimental Section). On this basis, the estimated yields are 77% tetrahydropyran and 67% methyl acetate. The latter value is probably low since indications are that methyl *p*-bromobenzenesulfonate was not solvolyzed completely under the conditions of the experiment.

In the case of ethanolysis of I, a high boiling ether product was recovered after 12 half-lives in 58.8% yield. Examination of this product by gas chromatography indicated the presence of only one component with a retention time identical with that of an authentic sample of 1-methoxy-5-ethoxypentane. This identification was confirmed by comparison of infrared spectra. The spectra of the authentic and isolated materials were superimposable. Gas chromatographic analysis of the total ethanol distillate from a completely solvolyzed sample of I revealed that tetrahydropyran was formed in a 40.8% yield. The accuracy of this determination was checked by analysis of a known solution made up to the same concentration.

It is clear that no significant amount of methyl *p*-bromobenzenesulfonate is formed in ethanolysis since the rate constant for this compound is 1.5 times that observed for the 5-methoxy-1-pentyl ester.[7] An upward drifting rate would have been observed; instead, the average deviation of the integrated rate constant values was only ±0.6%. Table IV summarizes the pertinent yields of solvolysis products.

Table IV. Summary of Solvolysis Products of 5-Methoxy-1-pentyl *p*-Bromobenzenesulfonate (I) at 75.0°[a]

Acetic acid				
% MeOBs	% MeOAc	% tetrahydropyran	% 5-MeO-1-pentyl OAc	% total yield accounted for
53.8[b]	67[c]	77	17	94
Ethanol				
% MeOBs	% tetrahydropyran	% 1-MeO-5-EtO-pentane	% total yield accounted for	
Ca. 0	40.8	58.8	99.6	

[a] All reported yields are corrected based on a sample purity of 96%. [b] Based on an estimated infinity value of 46.2% *p*-bromobenzenesulfonic acid. [c] Probably a somewhat low value since indications are that, under the experimental conditions, methyl *p*-bromobenzenesulfonate was not completely solvolyzed.

(7) Estimated from the data of R. E. Robertson, *Can. J. Chem.*, 31, 589 (1953).

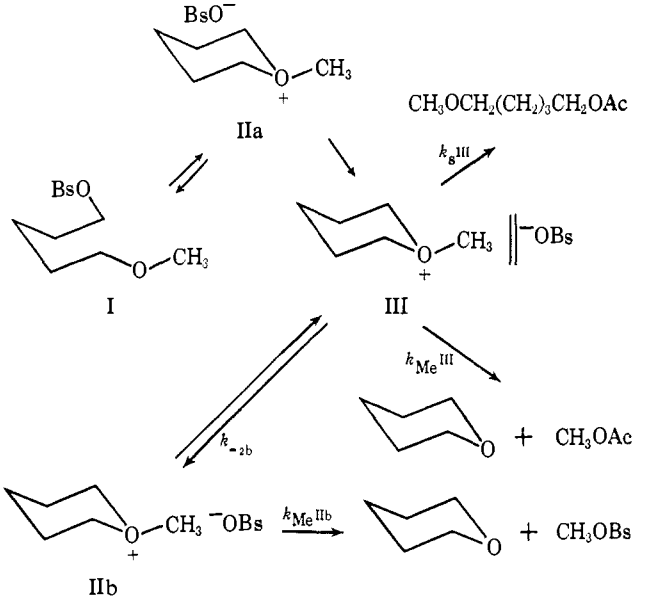
While formolysis products were not examined, it is evident that there was no appreciable formation of methyl *p*-bromobenzenesulfonate. If methyl *p*-bromobenzenesulfonate had been produced, a low infinity titer and a drifting rate constant would have resulted since the methyl ester solvolyzes *ca.* 40 times slower than I.[5] A 98% infinity titer and a good first-order rate constant were observed.

Discussion

From the product data summarized in Table IV, it is readily apparent that methoxyl-assisted solvolysis of 5-methoxy-1-pentyl *p*-bromobenzenesulfonate (I) results in the formation of the O-methyltetrahydropyranium ion. In the case of ethanolysis, the two recovered products, tetrahydropyran and 1-methoxy-5-ethoxypentane, account for 99.6% of the reaction of I. Tetrahydropyran is clearly a product of the cyclic tertiary oxonium ion, while 1-methoxy-5-ethoxypentane may have arisen either from a solvent-assisted k_s route, or from methylene C–O cleavage of the cyclic oxonium ion by solvent. Similarly, for acetic acid the sum of the recovered yields of tetrahydropyran and 5-methoxy-1-pentyl acetate accounts for a minimum 94% material balance. The formation of methyl *p*-bromobenzenesulfonate during acetolysis is ascribable to Me–O cleavage of the O-methyltetrahydropyranium ion by the bromobenzenesulfonate anion.

While many of the mechanistic details are still unclear, we can employ the oversimplified acetolysis Scheme I for discussion.[4,8-12] Two intimate ion pairs

Scheme I



are included, one of them being IIa formed directly by anchimerically assisted ionization *via* transition state[13]

(8) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *J. Am. Chem. Soc.*, **76**, 2597 (1954); *Chem. Ind.* (London), 664 (1954).

(9) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *J. Am. Chem. Soc.*, 78, 328 (1956).

(10) (a) S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958); (b) S. Winstein and A. H. Fainberg, *ibid.*, **80**, 459 (1958).

(11) (a) S. Winstein, P. E. Klinedinst, and G. C. Robinson, *ibid.*, **83**, 885 (1961); (b) S. Winstein, P. E. Klinedinst, and E. Clippinger, *ibid.*, **83**, 4986 (1961).

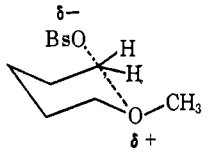
(12) S. Winstein, B. Appel, R. Baker, and A. Diaz, Special Publication No. 19, The Chemical Society, London, 1965, p 109.

Table V. Assignment of Reaction Paths for Some Methoxyalkyl *p*-Bromobenzenesulfonates Which Show MeO Participation

Compound, ROBs	Solvt	Temp, °C	Mode of reaction % by k_s	% by k_Δ	Methylene C–O cleavage % by SOH	% ion pair return by OBs	Me–O cleavage % by SOH	% by OBs	Total %
$CH_3OCH_2(CH_2)_3CH_2OBs$[a]	EtOH	75.0	41	59	18	*Ca.* 0	41	*Ca.* 0	41
	AcOH	75.0	2	98	16	?	28	54	82
$CH_3OCH(CH_3)(CH_2)_2CH_2OBs$[b]	EtOH	25.2	1	99	97	*Ca.* 0	2	*Ca.* 0	2
	AcOH	25.2	*Ca.* 0	100	98	70	*Ca.* 0	<2	<2
$CH_3OCH_2(CH_2)_2CH(CH_3)OBs$[b]	EtOH	25.2	5	95	94	*Ca.* 0	1	*Ca.* 0	1
	AcOH	25.2	1	99	97	70	*Ca.* 0	<2	<2

[a] Based on k/k_s data from ref 2. [b] Calculations based on product and relative rate data from ref 3.

V. This has the anion near C_α and not in proper position for nucleophilic attack on the methyl group. The other intimate ion pair is IIb with the anion in the vicinity of the methyl carbon atom. Ion pair return from IIb accounts for formation of methyl bromobenzenesulfonate. The scheme shows solvolysis products arising from solvent-separated ion pair III, but it seems most probable that at least some of it arises from a dissociated cation.[14] Other possible mechanistic variations may be involvement of one or more k_s^{II} paths as a result of solvent attack on intimate ion pairs.[4]



V

It is interesting that inclusion of lithium perchlorate eliminates essentially all of the formation of methyl bromobenzenesulfonate.[8-12] Thus, the intermediates involved in methyl bromobenzenesulfonate production must reach a stage of ionization–dissociation which is efficiently scavenged by lithium perchlorate.[8-12] Also interesting is the fact that the k^0_{ext} intercept of Figure 1 is equal to k_t^0 within experimental error. Thus, there is no ion pair return to the C_α or C_δ carbon atoms;[4] this is eliminated by lithium perchlorate in a special salt effect. This means that ion pair return to C_α or C_δ competes very poorly with ion pair return to the methyl group, or else that there is ion pair return to C_α or C_δ but this involves intermediates not scavenged by lithium perchlorate. While the former alternative seems somewhat more plausible, a definite answer would be obtained from solvolysis of labeled starting substrate. This would disclose whether rearrangement of the OBs group from C_α to C_δ by internal return accompanies acetolysis.

The observations in ethanol and formic acid may also be interpreted on the basis of acetolysis Scheme I. The lack of methyl *p*-bromobenzenesulfonate formation in ethanolysis is explained plausibly by the more nucleophilic solvent ethanol diverting the solvent-separated ion pair III to product by k_s^{III} and k_{Me}^{III} rather than allowing ion pair return. In the case of the strongly dissociating formic acid solvent, ion pair III probably dissociates to free O-methyltetrahydropyranium ion and reacts with solvent.[4,8-12,15]

On the basis of the formulation in Scheme I, it is a simple matter to divide the solvolysis of 5-methoxy-1-pentyl *p*-bromobenzenesulfonate (I) into k_s and k_Δ^{OMe} routes and further subdivide k_Δ^{OMe} into Me–O and methylene C–O cleavage paths. This is accomplished with the aid of the k/k_s data reported earlier,[2] and the product results are listed in Table IV. These estimates are given in Table V along with similar results for the cases of MeO-5 participation.[3]

From the data in Table V, it is apparent that solvent attack on the O-methyltetrahydropyranium ion results in considerably more Me–O than methylene C–O cleavage, the total over-all ratios being 2.3 and 1.7 for ethanol and acetic acid, respectively. These results contrast sharply with the observations for the five-membered O-methyl-2-methyltetrahydrofuranium ion where the ratio is probably <0.01 for both solvents.[16] On the other hand, these results are similar to the solvolytic cleavage of the open-chain tertiary oxonium salts. For example, trimethyloxonium fluoroborate is hydrolyzed *ca.* ten times faster than the triethyl analog.[17]

While the present data give no information concerning the relative rates of Me–O and methylene C–O cleavage of the five- and six-membered cyclic intermediates, it seems reasonable to attribute the differences in product formation to differences in ring strain and steric hindrance at the O-methylene carbon atoms. It is obvious that the O-methyltetrahydrofuranium ion cannot adopt a conformation entirely free from some H–H interaction and consequently torsional strain.[18] However, in the case of the six-membered ring, the cyclic ion can readily assume a strain-free chair form[13] where the adjacent $-CH_2-$ groups are rotated 60° with

(13) The favored conformation for the O-methyltetrahydropyranium ion is undoubtedly the chair form. In this connection several lines of evidence favor the chair form for tetrahydropyran and *p*-dioxane. See S. C. Burket and R. M. Badger, *J. Am. Chem. Soc.*, 72, 4397 (1950); F. M. Maherbe and H. J. Bernstein, *ibid.*, 74, 4408 (1952); and R. S. Armstrong, R. J. W. LeFevre, and J. Yates, *Australian J. Chem.*, 11, 147 (1958). It is likely that the equatorial position is preferred by the methyl group by analogy to N-methylpiperidine: N. L. Allinger, J. G. D. Carpenter, and F. M. Karkowski, *J. Am. Chem. Soc.*, 87, 1232 (1965).

(14) The successive approximation treatment used to calculate k_t^0 would obscure such subtle mechanistic features as common ion rate depression[4,9] since any small amount of rate drift will be removed through an overcorrection of the infinity value.

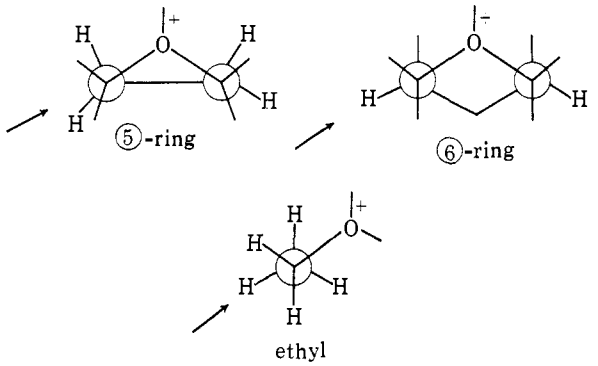
(15) S. Winstein, R. Baker, and S. Smith, *J. Am. Chem. Soc.*, 86, 2072 (1964).

(16) This ratio is estimated from the kinetic and product data for the 4-methoxy-1-pentyl and 5-methoxy-2-pentyl systems.[3]

(17) H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, and G. Willfang, *J. Prakt. Chem.*, 154, 83 (1939).

(18) The puckering of the cyclopentane ring is well known: K. S. Pitzer and W. E. Donath, *J. Am. Chem. Soc.*, 81, 3213 (1959). R. J. W. LeFevre and C. G. LeFevre, *Chem. Ind.* (London), 54 (1956), have assigned a puckered conformation to tetrahydrofuran on the basis of a comparison of experimental and calculated molar Kerr constants. However, even a nonplanar orientation leaves considerable H–H interaction.

respect to each other. This latter orientation is similar to the most favored conformation for ethyl and other straight-chain alkyl groups. Inspection of molecular models reveals that the O-methylene carbons of the five-membered ring are unhindered and quite open to nucleophilic attack while the corresponding carbon atoms of the six ring have equatorial hydrogen atoms on adjacent $-CH_2-$ groups which are partially in the line of nucleophile approach as shown by the following Newman projections.



In view of these considerations it is not surprising that the O-methyltetrahydropyranium ion resembles the open-chain tertiary oxonium salts more than the five-membered cyclic counterpart in Me–O and methylene C–O cleavage by solvent.

These same steric factors also serve to explain the differences in ion-pair return; the six-membered ring gives at least very predominantly Me–O cleavage by return of the *p*-bromobenzenesulfonate ion and the five-membered ring gives almost exclusively methylene C–O cleavage.

The other major difference between the 4-methoxy-1-butyl and 5-methoxy-1-pentyl systems is concerned with the rate of ring closure, the five-membered ring being closed about 14 times faster than the six-membered ring in acetic acid.[2] It is clear that this difference is due almost entirely to an entropy effect since the $\Delta H^{\pm}$ values are the same within experimental error but $\Delta S^{\pm}$ is 4.7 eu more negative for the six-ring formation.[2] This is in line with expectations since formation of the six-membered ring requires the restriction of more atomic motions.

Experimental Section

5-Methoxy-1-pentanol. The monosodium salt of 1,5-pentanediol was prepared by treating a stirred mixture of 227 g (2.18 moles) of freshly distilled diol in 250 ml of *p*-xylene at 115–120° with 17.0 g (0.73 g-atom) of sodium which was added in pea-size pieces. After the sodium had reacted the alkoxide mixture was cooled to 70° and 120 g (0.84 mole) of methyl iodide was added at such a rate that reflux could be controlled. Following addition, the reaction was stirred at 80–90° for 1 hr and then allowed to stand overnight at room temperature. Fractionation through an efficient column gave 67 g (77%) of 5-methoxy-1-pentanol, bp 85.5–86.5° (9 mm), $n^{25}D$ 1.4258, $n^{20}D$ 1.4279 [lit.[19] bp 83–84° (9 mm), $n^{20}D$ 1.4281].

5-Methoxy-1-pentyl *p*-Bromobenzenesulfonate (I). 5-Methoxy-1-pentanol was converted to the *p*-bromobenzenesulfonate by the low-temperature method described previously.[20] A 53.4-g (83%) yield of crude product was obtained from 22.5 g (0.19 mole) of alcohol in 70 ml of pyridine and 48.6 g (0.19 mole) of *p*-bromobenzenesulfonyl chloride in 70 ml of pyridine. The crude material had a 96.1% infinity titer for ethanolysis. A small sample recrystallized from ether–pentane solvent at low temperature had mp 28.0–28.5°.

Anal. Calcd for $C_{12}H_{17}O_4SBr$: C, 42.73; H, 5.08. Found: C, 42.46; H, 4.96.

1-Methoxy-5-ethoxypentane. The sodium salt of 5-methoxy-1-pentanol was made by treating 8.50 g (0.072 mole) of the alcohol with a stirring slurry of 2.5 g (0.11 mole) of sodium hydride in 75 ml of ether. After the mixture had refluxed overnight, most of the ether was evaporated and 30.0 g (0.19 mole) of ethyl iodide was added along with 25 ml of benzene. This mixture was heated under reflux for 48 hr. The excess hydride was decomposed with 20 ml of water. The upper organic layer was collected and combined with two ether washings of the aqueous layer. After drying with magnesium sulfate, the solvents were distilled off and the concentrate fractionally distilled to afford 4.3 g (41%) of 1-methoxy-5-ethoxypentane, bp 102–103° (82 mm), $n^{25}D$ 1.4090. This material and the ethanolysis product of I have identical infrared spectra and gas chromatography retention times (*vide infra*).

Methyl *p*-Bromobenzenesulfonate. This compound was obtained in the usual way from absolute methanol and *p*-bromobenzenesulfonyl chloride in pyridine, mp 60–61° (lit.[7] mp 60.5°).

Tetrahydropyran. A sample of Eastman Kodak Co. practical grade product was purified for use in identification by fractionation through an 8.0 mm × 80 cm concentric tube column, bp 88.0–88.3°, $n^{25}D$ 1.4182.

Methyl Acetate. A sample of Eastman Kodak Co. White Label grade methyl acetate was purified for identification purposes by fractional distillation, bp 57.1°, $n^{25}D$ 1.3585.

Kinetic Measurements. Absolute ethanol was dried further using sodium and ethyl phthalate according to the method outlined by Fieser.[21] Anhydrous acetic acid designed to contain 0.01 *M* acetic anhydride was prepared in the usual way.[11] Anhydrous formic acid was prepared from 98% formic acid according to a previously described method.[5] Lithium perchlorate was prepared and handled in anhydrous acetic acid as described previously.[22] Sodium formate in anhydrous formic acid was prepared as described previously.[20] All rate measurements were conducted by the usual sealed-ampoule technique.[23] The general titration methods have been described adequately.[20,22,23] In the cases where acetolysis solutions became yellowish brown, a fairly satisfactory end point reproducibility was achieved by titrating to the point where an additional drop of titrant did not impart any color change to the solution. For these titrations seven drops of a saturated acetic acid solution of brom phenol blue were used as indicator.

Total Acetolysis of 5-Methoxy-1-pentyl *p*-Bromobenzenesulfonate (I). A 20.44-g (0.061 mole) sample of I was dissolved in 500 ml of anhydrous acetic acid, and the solution was kept at 75.0° for 13 hr (*ca.* eight half-lives of I). The solution was cooled to 25° and the *p*-bromobenzenesulfonic acid was neutralized with 1.50 g of anhydrous sodium carbonate. Most of the acetic acid solvent was removed by vacuum distillation through a 45 × 1.1 cm column packed with 3-mm glass helices at 25.5° (15 mm). The black kettle residue was treated with 150 ml of water and extracted with ether. The ether extract was treated twice with decolorizing carbon and methyl *p*-bromobenzenesulfonate was induced to crystallize by cooling and addition of *n*-pentane. Total recovered yield after recrystallization was 4.2 g (29%), mp 60–61°, mmp 60–61° with authentic sample.

The water layer was continuously extracted overnight with ether, and this extract was combined with the filtrate from the methyl *p*-bromobenzenesulfonate crystallization. From this were recovered 1.6 g (17%) of 5-methoxy-1-pentyl acetate, bp 92–92.5° (19 mm), $n^{25}D$ 1.4151.

Anal. Calcd for $C_8H_{16}O_3$: C, 59.98; H, 10.07. Found: C, 59.72; H, 9.88.

A sample of low-boiling product was recovered from the Dry Ice traps used in the acetic acid distillation. Comparison of gas chromatography retention times with authentic samples indicated the presence of tetrahydropyran and methyl acetate. Poorly shaped chromatograms with especially unfavorable tailing were obtained for the acetic acid component on all columns tested. This made accurate quantitative analysis impossible by gas chromatography.

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Table VI. Distillation Results for Low Boiling Products from Acetolysis of 5-Methoxy-1-pentyl *p*-Bromobenzenesulfonate (I) at 75.0°

Fraction	Bp, °C	$n^{35}D$	Wt, g	Components	THP,[a,b] %
		(a) Products from Acetolysis of I			
1	57–59	1.3625	1.06	MeOAc–THP	4
2	59–88.5	1.3706	0.49	MeOAc–THP	18
3	88.5–107	1.4031	0.54	THP–AcOH	67
4	107–116	1.3985	1.20	THP–AcOH	57
5	116–117.5	1.3730	1.20	THP–AcOH	3
	Recovered yield of THP, 1.21 g (57%)				
	Recovered yield of MeOAc, 1.42 g (67%)				
		(b) Control Experiment[c]			
1	88–90	1.4174	1.00	THP–AcOH	99
2	90–106	1.4125	0.50	THP–AcOH	87
3	106–117.5	1.3861	0.80	THP–AcOH	30
4	117.5	1.3725	0.50	THP–AcOH	
	Recovered yield of THP, 1.7 g (62%)				

[a] Abbreviation for tetrahydropyran. [b] Estimated from the refractive indices of the fractions. [c] In the control experiment, *p*-toluenesulfonic acid was used in place of *p*-bromobenzenesulfonic acid.

In an effort to estimate the total acetolysis yield of these low boiling products, a 10.22-g (0.03 mole) quantity of bromobenzenesulfonate I in 100 ml of acetic acid was solvolyzed at 75.0° for 75 hr. After this the cooled solution was neutralized with 1.65 g of sodium carbonate and 2.5 g of acetic anhydride was added to ensure anhydrous conditions. The fraction boiling below 117.5° was collected by slow distillation of the refluxing acetic acid solution through the 45-cm, helices-packed column. Total refluxing time at a kettle temperature of 118.5° was 6 hr. This fraction was carefully refractionated through a highly efficient 8.0 mm × 80 cm concentric tube column. Five fractions which proved to be binary mixtures of methyl acetate and tetrahydropyran, and tetrahydropyran and acetic acid were collected. The compositions of these mixtures were estimated from their refractive indices since it was shown experimentally with known mixtures that plots of refractive index *vs.* wt % composition were linear for both MeOAc–THP and AcOH–THP binary systems. The results including the estimated yields are listed in Table VI.

In order to get a better estimate of the actual yield of tetrahydropyran a control run was carried out under the acetolysis conditions. This consisted of dissolving 2.69 g (0.03 mole) of freshly distilled tetrahydropyran in 100 ml of an acetic acid solution 0.028 *M* in *p*-toluenesulfonic acid and keeping the mixture at 75.0° for 48 hr. During this time the solution became yellowish brown. Following this the solution was worked up exactly as described for the acetolysis solution of I. The distillation fractions with compositions are listed in Table VI. As indicated, the recovered yield of tetrahydropyran was 62%.

Using the control experiment as a correction factor, an over-all yield of 77% tetrahydropyran is estimated for the acetolysis of I.

Total Ethanolysis of 5-Methoxy-1-pentyl *p*-Bromobenzenesulfonate (I). A solution of 8.43 g (0.025 mole) of I in 250 ml of anhydrous ethanol was kept at 75.0° for 15 hr (12 half-lives). Following this the solution was cooled to room temperature and the *p*-bromobenzenesulfonic acid was neutralized with the calculated amount (0.58 g) of sodium. After standing for a few hours the solid was removed by filtration, and the ethanol was removed by distillation through a 45-cm, glass-helices-packed column. The residue was taken up in ether and filtered to remove the remaining sodium *p*-bromobenzenesulfonate. After evaporating off the ether, the concentrate was distilled through a 15-cm Vigreux column to afford 2.15 g (58.8%) of high boiling product, bp 101–102° (81 mm), $n^{25}D$ 1.4088.

Anal. Calcd for $C_8H_{18}O_2$: C, 65.71; H, 12.41. Found: C, 65.41; H, 12.36.

This material had an infrared spectrum identical with the spectrum for authentic 1-methoxy-5-ethoxypentane. Only one component was found according to gas chromatography.

A 5-ml quantity of a 0.1 *M* solution of I in ethanol was solvolyzed at 75.0° for 13 half-lives. After cooling to 25°, the calculated amount of sodium was added. The neutralized solution was distilled to dryness and the ethanol distillate analyzed for tetrahydropyran by gas chromatography. A 2 m × 0.6 mm stainless steel column packed with 30% by weight Carbowax 1500 on sieved 40–60 mesh Firebrick was used. The yield of tetrahydropyran was 40.8% of theoretical. The accuracy of this was checked by analysis of a known solution made up to the same concentration.

The Influence of the R Group on the Brominative Formation of 4-Bromo-4-R-2,6-di-*t*-butylcyclohexadienones from the Corresponding Phenols[1]

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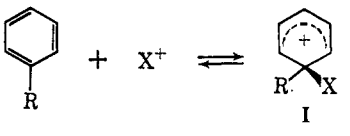
Abstract: The rate constants for the reaction of some 4-substituted 2,6-di-*t*-butylphenols with bromine in acetic acid solution to give *p*-cyclohexadienones derivatives have been determined at 25°. The data provide information on the scarcely known substituent effects at the point of attack where a geminal position is developed and are discussed in relation to the mechanism of both aromatic substitutions and nonconventional aromatic reactions.

A widely accepted mechanism for a great number of electrophilic aromatic substitutions involves the formation of a benzenonium ion (I) as a reactive intermediate (eq 1). On decomposition of I, normal substitution products are formed if R is a good leaving group.[2] However, the scope of eq 1 includes more



(1)

reactions than usually classified as aromatic substitutions

(1) Part V in the series: Nonconventional Paths in Electrophilic Aromatic Reactions.

(2) See, for example, R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier Publishing Co., Amsterdam, 1965, Chapters 9 and 10.