

THE SOLVOLYSIS OF ARENESULFINATES, SULFUR-OXYGEN VERSUS CARBON-OXYGEN BOND FISSION^{1,2}

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Dedicated to Professor R. B. Sandin on the Occasion of his Sixty-Eighth Birthday

ABSTRACT

The base-catalyzed solvolysis of *p*-methoxyneophyl benzenesulfinate and the corresponding 2,6-dimethyl-, 2-methyl-, 4-methyl-, and 2-chloro-benzenesulfinates has been studied in ethanol and aqueous ethanol. The reactions involve sulfur-oxygen bond fission. The rate of sulfur-oxygen bond fission is decreased by the introduction of two methyl groups ortho to the sulfur. The rate decrease may be partly due to steric hindrance to nucleophilic attack on the sulfinate sulfur, but this effect is very small compared to the effect in carboxylate ester hydrolysis. The reactions are catalyzed by ethoxide, acetate, and pyridine. Reaction is very slow in the presence of 2,6-lutidine. With certain arenesulfinate esters one can control the reaction to give sulfur-oxygen or carbon-oxygen bond fission by choice of an appropriate base.

INTRODUCTION

The solvolysis of arenesulfinates can involve either sulfur-oxygen or carbon-oxygen bond fission. Kenyon and co-workers (1, 2) have shown that (-)- α -phenylethyl dl-ptoluenesulfinate yields α -phenylethyl alcohol of retained configuration on hydrolysis and ethanolysis, indicating that sulfur-oxygen bond cleavage has taken place. The ethoxide ion catalyzed ethanolysis of the diasterioisomeric (-)-menthyl (+)-p-iodobenzenesulfinate and (-)-menthyl (-)-p-iodobenzenesulfinate both yield (-)-menthol in a concentration equivalent to the amount of ester originally present, indicating essentially exclusive sulfur-oxygen bond cleavage (3). Methyl p-toluenesulfinate undergoes a slow neutral hydrolysis as well as a rapid reaction in alkaline solution and an acid-catalyzed hydrolysis in dioxane-water mixtures. The base- and acid-catalyzed reactions have been shown (4) by the use of ¹⁸O tracers to involve sulfur-oxygen bond fission. Similarly, the sulfur-oxygen bond is broken on alkaline hydrolysis of diphenylmethyl p-toluenesulfinate (5). The formation of sulfones and substitution products on solvolysis of arenesulfinates (6, 7, 8) indicates that under certain conditions carbonoxygen bond fission must occur.

Our interest in the reaction of arenesulfinates centered mainly on reactions involving carbon-oxygen bond fission (8, 9). However, it was necessary to investigate the sulfur-oxygen bond cleavage reactions to choose conditions under which sulfur-oxygen bond fission would not take place as an undesirable side reaction. Two general approaches were followed. First, an examination of the effect of substituents upon the rate of sulfur-oxygen bond fission was made. Secondly, the effect of various nucleophiles upon the rate of reaction was investigated.

Different products are obtained from alcoholysis of arenesulfinates involving sulfuroxygen and carbon-oxygen bond fission. Sulfur-oxygen bond fission gives rise to ester interchange and yields a new arenesulfinate ester as shown in eq. [1]. Carbon-oxygen

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$$\begin{array}{c} O & O \\ \uparrow \\ R - O - S - Ar + R'OH \rightarrow R' - O - S - Ar + ROH \\ O \\ R - O - S - Ar + R'OH \rightarrow ArSO_2H + ROR' (+ olefin) \end{array}$$

bond fission gives rise to an arenesulfinic acid and solvolysis products as shown in eq. [2]. Thus, product analysis provides information on the type of bond cleavage. If water is the substituting agent, a sulfinic acid and an alcohol are produced by both sulfur-oxygen and carbon-oxygen bond fission. One must then use other criteria to determine the type of bond fission which has occurred.

The systems chosen for this study were arenesulfnate esters of p-methoxyneophyl alcohol. Since these esters have a neophyl type of structure, one can rule out direct nucleophilic displacement on the primary carbon as a major route for carbon-oxygen bond fission. If carbon-oxygen bond fission were to occur, the reaction should involve neighboring p-anisyl participation (10), giving rise to products from the rearranged carbonium ion as shown in eq. [3]. Sulfur-oxygen bond fission would yield the unrearranged alcohol, p-methoxyneophyl alcohol. Therefore, with this system one can distinguish between carbon-oxygen and sulfur-oxygen bond fission by product analysis, even with water as the nucleophile.

[3]

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 $\begin{array}{cccc} & & & An & & O \\ & & & \uparrow & & \uparrow \\ H_3C--C-CH_2-O-S-Ar & \rightarrow CH_3-C-CH_2-Au & + ArSO_2^- & \rightarrow \text{ products} \\ & & & & \downarrow \\ CH_3 & & & CH_3 \\ & & & CH_3 \end{array}$ RESULTS

Preparation of Esters

The 2,6-dimethyl-, *o*-chloro-, and *o*-methyl-benzenesulfinic acids were prepared by a method described by Hanke (11) which involved diazotization of the corresponding substituted aniline and treatment of the solution with sulfur dioxide in the presence of copper powder. Benzene- and *p*-toluene-sulfinic acids were prepared by reduction of the corresponding sulfonyl chlorides with zinc powder.

The arenesulfinic acids were treated with thionyl chloride in pentane to obtain the corresponding acid chlorides. The acid chlorides were dissolved in pyridine and treated with the appropriate alcohol to yield the arenesulfinate esters after work-up.

Rate Measurements

A summary of the rate constants for the reaction of a number of p-methoxyneophyl are nesulfinates is presented in Table I. In most cases the reactions were followed by measuring the increase in absorption of the band at ca. 11.35 μ where the corresponding ethyl are nesulfinates have an intense absorption band. These reactions were therefore studied by measuring the rate of formation of the product of sulfur-oxygen bond fission. In the cases where the solvent was an ethanol-water mixture the disappearance of absorption at ca. 10.4 μ , associated with the p-methoxyneophyl are nesulfinate, was measured.

In every case first-order rate constants were calculated within any run. Good first-order rate constants were obtained with ethoxide or acetate as the added base, except for the reactions of *p*-methoxyneophyl 2,6-dimethylbenzenesulfinate in the presence of acetate ion. These rate constants showed a marked upward drift as the reaction progressed. The initial rate constants reported for these reactions are obtained from the slope of the curve obtained by plotting log (a - x) versus time. When 2,6-lutidine and pyridine were

[1]

[2]

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p-Methoxyneophyl arenesulfinate	Solvent	Temp. (°C)	Ester $(10^2 M)$	Added base	Base $(10^2 M)$	${10^5 k_1 \over ({ m s}^{-1})}$	$\frac{10^3 k_1}{\text{mole}^{-1} \text{s}^{-1}}$
Benzenesulfinate	EtOH	90.0	2.56	KOAc	1.59	10.7	6.7
	EtOH	90.0	2.53	KOAc	3.18	19.6	6.2
	EtOH	90.0	2.50	KOAc	4.78	27.8	5.8
	EtOH	90.0	2.50	KOAc	7.96	48.1	6.0
	EtOH	90.0	2.42	2,6-Lutidine	5.04	0.008	
	EtOH	90.0	2.46	Pyridine	5.42	0.12	
2-Chlorobenzene-				-			
sulfinate	EtOH	90.0	2.50	KOAc	1.95	18.9	9.7
	EtOH	90.0	2.50	KOAc	3.89	32.5	8.4
	EtOH	90.0	2.49	KOAc	4.78	40.5	8.5
	EtOH	90.0	2.49	KOAc	7.96	65.5	8.2
2-Methylbenzene-							
sulfinate	EtOH	90.0	2.57	KOAc	4.78	11.9	2.5
	EtOH	90.0	2.41 \cdot	KOAc	7.79	16.8	2.2
4-Methylbenzene-							
sulfinate	EtOH	90.0	2.46	KOAc	4.78	16.0	3.4
	EtOH	90.0	2.51	KOAc	7.79	31.3	4.0
2,6-Dimethylbenzene-							
sulfinate	EtOH	25.0	2.54	NaOEt	2.60	32.4	12.5
	EtOH	25.0	2.42	NaOEt	4.86	60.9	12.5
	80% EtOH	25.0	2.42	NaOEt	1.37	6.7	4.9
	80% EtOH	25.0	2.42	NaOEt	2.81	16.2	5.7
	80% EtOH	25.0	2.42	NaOEt	5.12	24.8	5.5
	80% EtOH	25.0	2.42	NaOEt	9.73	55.1	5.7
	ÉtOH	90.0	2.41	KOAc	3.18	0.60	0.19
	EtOH	90.0	2.42	KOAc	4.78	0.75	0.16
	EtOH	90.0	2.47	KOAc	7.76	0.87	0.15
	EtOH	90.0	2.41	Pyridine	5.12	0.013	
	EtOH	90.0	2.47	2,6-Lutidine	5.05	0.0006	
	60% EtOH	90.0	2.53	KOAc	5.73	0.047	
	60% EtOH	90.0	2.49	2.6-Lutidine	6.04	0.007	

 TABLE I

 Summary of solvolysis rate constants of *p*-methoxyneophyl arenesulfinates

the added bases the reactions were very slow, and again only initial rate constants were estimated. The rate constants estimated for the reaction of the 2,6-dimethylbenzenesulfinate in the presence of added acetate ion and for all the reactions with added pyridine and 2,6-lutidine are very crude. These rate constants may be in error by as much as a factor of two. As shown in Table I the reactions were second order: first order in ester and first order in added ethoxide or acetate. The order of the reaction with respect to added pyridine and lutidine was not determined.

Titrations for acid were also carried out at each point in the rate determinations when ethoxide or acetate was the base. In the reactions involving anhydrous ethanol as solvent, acid production would indicate reaction via carbon-oxygen bond fission. No change in acid titer was detected in the course of the reactions in solvent ethanol. Therefore, only sulfur-oxygen bond fission occurred.

Reaction Products

In solvent ethanol the reaction product was the corresponding ethyl arenesulfinate as shown by the kinetic studies. A product run was carried out on the reaction of methoxyneophyl 2,6-dimethylbenzenesulfinate in 60% ethanol-water with 2,6-lutidine as added base. The reaction mixture was heated for 46 days at 90.0°, corresponding to ca. 20%reaction. The reaction mixture was separated into ester and alcohol fractions by chromatography. The ester was unreacted *p*-methoxyneophyl 2,6-dimethylbenzenesulfinate and the alcohol was *p*-methoxyneophyl alcohol as shown by infrared spectroscopy. Can. J. Chem. Downloaded from www.nrcresearchpress.com by 120.117.138.77 on 11/20/14 For personal use only.

DISCUSSION

The displacement reaction must involve sulfur-oxygen bond fission as shown by the reaction products.

The reaction is second order: first order with respect to the ester and first order with respect to the base when ethoxide or acetate is the added base. The order of the reactions with respect to pyridine and 2,6-lutidine has not been determined.

There are four types of mechanisms which are consistent with the data. These four mechanisms can be divided into two categories. (i) Catalysis, which involves a nucleophilic displacement on sulfur by the base to yield a substitution product. In the case of ethoxide ion the substitution product would be the product ethyl arenesulfinate. In the case of acetate ion a mixed anhydride would be formed. The mixed anhydride would be converted rapidly to the ethyl arenesulfinate by reaction with the solvent. (ii) General base catalysis, which involves attack by the solvent on the ester concerted with transfer of a proton to the added base. The ethyl arenesulfinate would be produced directly regardless of the nature of the base.

Within each of the mechanistic schemes described above a further subdivision can be made. Substitution could involve concerted bond-making and bond-breaking to yield the substitution product in a manner analogous to that for a nucleophilic displacement on saturated carbon. Alternatively, displacement could occur in a stepwise fashion involving, first, addition of the nucleophile to sulfur followed, in a second step, by loss of the leaving group. In the hydrolysis of cyclic sulfite esters Bunton *et al.* (12) have reported that ¹⁸O exchange with the solvent does not occur in significant competition with hydrolysis. Davis (14) suggested that the small amount of exchange observed by Bunton (12) indicated that there was evidence for an intermediate. However, de la Mare *et al.* (13) have indicated that the exchange may represent experimental error.

The data here reported cannot distinguish between these four alternative mechanisms. For the amines, one can exclude mechanisms in which the lyate ion of the solvent is formed in a rapid preequilibrium step by reaction with the added base followed by a slow reaction of the lyate ion with the substrate as shown in eqs. [4] and [5].

 $B: + C_2H_4OH \stackrel{K}{\rightleftharpoons} C_2H_4O\Theta + BH^{\oplus}$

 $C_2H_5O\Theta$ + $RO_2SAr \xrightarrow{k} C_2H_5O_2SAr$ + $RO\Theta$

The latter alternative is ruled out as follows. 2,6-Lutidine is a stronger base than pyridine. If reaction occurred by the above scheme, then the reaction should be faster in the presence of 2,6-lutidine than in the presence of pyridine. The opposite result is observed and, therefore, this alternative can be excluded.

Within the framework of the four mechanisms the effects of substituents, solvents, and bases are consistent and are discussed below.

Substituent Effects

[4]

[5]

A summary of the relative rates of ethanolysis of a number of arenesulfinates is presented in Table II. It is instructive to compare these relative rates with the relative rates of base-catalyzed hydrolysis of the correspondingly substituted ethyl benzoates in 85%aqueous ethanol (25). One ortho substituent has a small and roughly equivalent effect on both reactions. Two ortho methyl groups have a much smaller effect on the rate of reaction of the arenesulfinate ester than on the rate of hydrolysis of the benzoate ester.

CANADIAN JOURNAL OF CHEMISTRY, VOL. 43, 1965 TABLE II

Benzenesulfinate	Ester (M)	Base (M)	$10^{4} k$ (s ⁻¹)	Relative rates		
2-Chloro	0.02486	0.0478	4.05	1.45		
4-Methyl	0.02465	0.0478	1.60	0.58		
2-Methyl	0.02510	0.0478	1.15	0.41		
Unsubstituted	0.02502	0.0478	2.78	1.0		
2,6-Dimethyl	0.02422	0.0478	0.075	0.028		

Relative rates of reaction of various p-methoxyneophyl arenesulfinates at

If the decrease in rate on changing from the benzenesulfinate to the 2-methybenzenesulfinate is ascribed entirely to an electronic effect and if it is assumed that the electronic effect of a second ortho methyl group would reduce the rate by a similar amount, then the 2.6-dimethylbenzenesulfinate reacts at a rate which is ca. 1/6 of the anticipated value. This extra rate decrease may be associated with steric hindrance to attack on the sulfinate sulfur. Even if all of the rate reduction observed in comparing the benzenesulfinate and 2,6-dimethylbenzenesulfinate is ascribed to a steric effect, the difference in rates is less than a factor of 40. In contrast, the hydrolysis of ethyl benzoate is nearly five powers of 10 faster than the hydrolysis of ethyl 2,6-dimethylbenzoate.

Any increase in non-bonded interactions at the transition state relative to the ground state must be very small for the arenesulfinate esters as compared to the large effect for the carboxylate esters. The carbon-sulfur bond in the arenesulfinates is longer (ca. 1.8 Å) than the carbon-carbon bond of the Ar-C=O system (1.5 Å). Therefore, the region of greatest size of the transition state may effectively be removed further from the ortho methyl groups in the arenesulfinate than in the benzoate ester reactions and may account for much of the difference in behavior of the two systems.

The arenesulfinate esters appear to be more nearly analogous in behavior to the sulfonate esters than to the benzoate esters. Thus, Bunnett and Bassett (15) have observed that there is no detectable steric hindrance on the rate of sulfur-oxygen bond fission of a number of arenesulfonate esters.

Solvent Effects

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The change of solvent from anhydrous ethanol to 80% ethanol and 60% ethanol reduced the rate constant for 2,6-dimethylbenzenesulfinate ester disappearance with ethoxide and acetate ion, respectively, as added bases. The reaction in the presence of 2,6-lutidine was faster in 60% ethanol-water than in anhydrous ethanol. These observations are consistent with all four mechanisms. The reaction of the negatively charged bases with the ester must involve charge dispersal at the transition state and, hence, increasing the polarity of the medium should hinder reaction (16). The reaction of neutral bases with the ester must involve charge formation at the transition state and will be facilitated by increasing the polarity of the solvent.

The above discussion of solvent effects must be qualified, since it considers only changes in charge distribution and solvent polarity. Other factors, such as the extent of ion pairing of the salts, and the change from ethoxide to hydroxide ion as the water content of the solvent is increased, may also be of importance. Bunton and co-workers (5) have reported that the hydroxide ion catalyzed hydrolysis of methyl p-toluenesulfinate is 40 times faster in 40% dioxane-water than in 60% dioxane-water. This reaction would

be expected to be faster in 60% dioxane-water than 40% dioxane-water, if only the effect of solvent polarity on changes in charge distribution were important.

Effect of the Base

The rate of sulfur-oxygen bond fission varies enormously with the nature of the added base. The esters are particularly susceptible to attack by the strongly basic ethoxide ion; the nitrogen bases 2,6-lutidine and pyridine are much less effective than acetate ion at facilitating the reaction. Edwards and Pearson (17) have suggested that basicity is of prime importance for nucleophilic character towards tetrahedral sulfur. On this basis, if the reactions of the arenesulfinates involved nucleophilic attack on sulfur by the added base, then one would predict the observed reactivity order. Similarly, if the reactions of the esters involved general base catalysis, the observed order of reactivity would be anticipated. The fact that pyridine is a more effective catalyst than 2,6-lutidine would, in the first case, reflect the steric hindrance of the methyl groups to attack on sulfur by the nitrogen base. In the latter, it would be required that steric hindrance to general base catalysis be invoked to explain the greater effectiveness of pyridine than 2,6-lutidine. Westheimer and co-workers (18, 19) have reported a number of examples of reactions which exhibit steric hindrance in general base catalysis.

The difference in rates for ethanolysis of the arenesulfinates with pyridine and 2,6lutidine as added bases may be larger than it appears from an examination of the data in Table I. The 2,6-lutidine used in these experiments contained a small amount of a methylpyridine. The observed reaction may have involved catalysis by the impurity and not by the 2,6-lutidine. If the reaction in the presence of pure 2,6-lutidine were significantly slower than the value reported, it would tend to suggest that the reactions of the other bases involve a nucleophilic substitution on sulfur by the added base.

The most important result of these experiments is the demonstration that one can greatly reduce the rate of sulfur-oxygen bond fission in arenesulfinate esters by the use of weak bases. In systems which can undergo facile carbon-oxygen as well as sulfur-oxygen bond fission, it is possible to control the type of bond cleavage by choosing the appropriate base. A remarkable illustration of this behavior is found in the ethanolysis of allyl 2,6-dimethylbenzenesulfinate (20). In anhydrous ethanol at 90.0° with acetate ion as the added base, allyl 2,6-dimethylbenzenesulfinate yielded ethyl 2,6-dimethylbenzenesulfinate plus a trace of allyl 2,6-dimethylphenylsulfone. Under the same conditions but with 2,6-lutidine as the added base, the reaction was slower and allyl 2,6-dimethylphenyl sulfone was the only detectable reaction product.

EXPERIMENTAL

 α, α -Dimethyl-p-methoxybenzyl Cyanide

This compound was prepared by the method of Heyningen (21, 10) from *p*-methoxybenzyl cyanide (22). The yield of product, b.p. 110–113° at 2 mm pressure, η_D^{25} 1.5142 (reported (10), b.p. 110° at 3 mm pressure, η_D^{25} 1.5143), was 50%.

p-Anisyldimethylacetic Acid

 α, α -Dimethyl-*p*-methoxybenzyl cyanide was hydrolyzed by the method described by Heyningen (21). The acid, recrystallized from aqueous methanol, melted at 88–89.5° (reported (10), 88–89.5°).

p-Methoxyneophyl Alcohol

Lithium aluminium hydride reduction of the above acid produced p-methoxyneophyl alcohol, m.p. 46.5–48.5° (reported (10), m.p. 45–46.5°) after recrystallization from Skellysolve B.

Arenesulfinic Acids

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Benzene- and p-toluene-sulfinic acids were prepared by reduction of the corresponding sulforyl chlorides with zinc dust by the method described by Vogel (23).

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					Ester	2,6-(CH ₃) ₂ C ₆ H ₅ SO ₃ R [*] 2-CH ₃ C ₆ H ₄ SO ₂ R 4-CH ₅ C ₆ H ₄ SO ₂ R C ₆ H ₅ SO ₂ R 2-CIC ₆ H ₄ SO ₂ R 2-CIC ₆ H ₅ SO ₂ C ₂ H ₅ 2-CH ₃ C ₆ H ₅ SO ₂ C ₂ H ₅ 4-CH ₃ C ₆ H ₅ SO ₂ C ₂ H ₅ 2-CIC ₆ H ₅ SO ₂ C ₂ H ₅ 2-CIC ₆ H ₅ SO ₂ C ₂ H ₅	*R represents p-methoxyneopt #Melting point (°C). ## C1. Ec
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1% Cl: found, 17.24; calcd. 17.32. The bands at lower frequency, where recorded, were used in the rate determinations.

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The 2,6-dimethyl-, 2-chloro-, and 2-methyl-benzenesulfinic acids were prepared by the method described by Hanke (11) from the correspondingly substituted anilines. In a typical experiment 31 g of 2,6-dimethyl-aniline yielded 32.6 g of 2,6-dimethylbenzenesulfinic acid, m.p. 95–98°.

Arenesulfinates

All the arensulfinates were prepared by the same general procedure. In a typical preparation 4.6 g of 2,6-dimethylbenzenesulfinic acid was treated with 15 ml of thionyl chloride in 50 ml of pentane. After vigorous reaction had subsided, the solution was filtered through a glass wool filter. The solution was warmed on a steam bath to remove the pentane. The thionyl chloride was removed by pumping under vacuum overnight. The residual 2,6-dimethylbenzenesulfinyl chloride, an oil, was dissolved in 15 ml of anhydrous pyridine and cooled in a dry ice – acetone bath. A solution of 5 g of p-methoxyneophyl alcohol in 25 ml of pyridine was added. The reaction mixture was then allowed to warm up to room temperature. The mixture was poured into a mixture of ice and 35 ml of concentrated hydrochloric acid and extracted with ether. The ether extract was washed 3 times with water, then with dilute hydrochloric acid, again with water, and then 6-8 times with 10% sodium carbonate solution or until no yellow color appeared in the aqueous layer. After the extract was dried over magnesium sulfate, the ether was removed by warming the solution on a steam bath. The residue was recrystallized from 10% ether-pentane to yield 4.5 g of p-methoxyneophyl 2,6-dimethylbenzenesulfinate, m.p. 57–58.5°.

Analyses and physical properties of the arenesulfinates are summarized in Table III. The nuclear magnetic resonance spectra of these and other arenesulfinates are of interest and will be described in a subsequent paper.

Solvents

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Ethanol was dried by treatment with magnesium ethoxide as described by Fieser (24).

Ethanol-water (80% by volume) was prepared by mixing 8 volumes of anhydrous ethanol to which the appropriate amount of base had been added and 2 volumes of boiled distilled water which had previously been equilibrated at 25°.

Ethanol-water (60% by volume) was prepared by mixing 6 volumes of ethanol to which the appropriate amount of base had been added and 4 volumes of boiled distilled water which had previously been equilibrated at 25° .

Kinetic Measurements

A sample of ester was accurately weighed into a 100-ml volumetric flask. A stock solution of the solvent containing the appropriate base was added and the solution was made up to the mark with the solvent. For rates at 90° the sealed ampoule technique was employed. Ampoules were removed from the constant temperature bath controlled to $\pm 0.03^{\circ}$ and quenched in ice water. The ampoules were equilibrated to 25° and a 5-ml aliquot was removed by means of a calibrated 5-ml automatic pipette. The 5-ml aliquots were delivered into a 60-ml separatory funnel containing 25 ml of pentane and 10 ml of water. The pentane layer was washed 4 times with 10 ml of water. The pentane layer was dried over anhydrous granular potassium carbonate. The combined water washings were titrated with standard hydrochloric acid (for reactions in which ethoxide was the base) or standard sodium methoxide in methanol using phenolphtholein as the indicator. The residual oil, obtained by removal of the pentane from the dried pentane solution, was diluted with two 1-ml aliquots of carbon disulfide using a 1-ml automatic pipette. The infrared spectrum of the

TABLE IV

Rate of ethanolysis of *p*-methoxyneophyl 2-methylbenzenesulfinate (0.02571 M) in anhydrous ethanol with potassium acetate (0.04776 M) as base

(T)			
(s)	Base*	Absorbance	$\frac{10^4 k_1}{(s^{-1})}$
$\begin{array}{c} 0\\ 960\\ 2\ 700\\ 3\ 600\\ 4\ 500\\ 5\ 460\\ 7\ 200\\ 10\ 800\\ 12\ 720\\ 18\ 840\\ 25.5\ h\\ \mathrm{Average}\end{array}$	$\begin{array}{c} 0.055\\ 0.053\\ 0.052\\ 0.056\\ 0.051\\ 0.057\\ 0.060\\ 0.051\\ 0.051\\ 0.051\\ 0.055\\ 0.045\\ \end{array}$	$\begin{array}{c} 0.0792 \\ 0.198 \\ 0.250 \\ 0.318 \\ 0.332 \\ 0.332 \\ 0.509 \\ 0.572 \\ 0.641 \\ 0.717 \end{array}$	$\begin{array}{c} 1.22\\ 1.20\\ 1.19\\ (1.31)\\ 1.14\\ (0.86)\\ 1.14\\ 1.25\\ 1.19\\ 1.19\pm 0.03\end{array}$

*Milliliters of 0.0347 M so dium methoxide in methanol required to neutralize the aqueous extracts.

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solution was recorded in the region from 10 to 12μ with the 20 cm per micron scale using a Perkin-Elmer model 21 infrared spectrophotomer. The reference cell containing carbon disulfide was of the variable spacer type. The values of log (I_0/I) were measured using the base line technique. For rates at 25° the volumetric flask was immersed in the constant temperature bath. Aliquots were removed using a 5-ml automatic pipette and quenched by transferring to a 60-ml separatory funnel containing 25 ml of pentane and 10 ml of water. The rest of the procedure was as described for reactions at 90°.

Controls were run on all the esters to ensure that a linear relationship between absorbance and concentration was obeyed after the extraction procedure had been carried out. A sample rate run is presented in Table IV.

Product Run

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A 0.844-g quantity of p-methoxyneophyl 2,6-dimethylbenzenesulfinate and 0.447 g of 2,6-lutidine were dissolved in 100 ml of ethanol (60% by volume) and transferred to a 250-ml flask having a constricted neck. The flask was sealed and placed in the 90° constant temperature bath for 46 days. The cooled reaction mixture was poured onto ice containing 1 ml of 6 N hydrochloric acid. The mixture was extracted twice with ether. The combined ether extracts were washed twice with saturated aqueous sodium bicarbonate and dried over magnesium sulfate. The ether was removed by careful distillation through a Vigreux column. The residue was separated into ester and alcohol fractions by chromatography on 30 g of alumina. The infrared spectrum of the ester fraction (0.72 g, 85%) showed it to be the starting material, p-methoxyneophyl 2,6-dimethylbenzenesulfinate. The infrared spectrum of the alcohol (25 mg, 6%) corresponded to the spectrum of authentic *p*-methoxyneophyl alcohol. The presence of less than 5% of ethyl 2,6-dimethylbenzenesulfinate or 1-p-anisyl-2-methyl-2-propanol in the ester and alcohol fractions respectively would not have been detected.

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