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THE SOLVOLYSIS AND REARRANGEMENT OF ARYLSULFINATE ESTERS

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The rearrangement of arylsulfinate esters to sulfones has been known for many years. The reported data do not, however, allow a clear decision as to the reaction mechanism. Optically active α-phenylethyl p-toluenesulfinate was reported by Kenyon and co-workers[2] to yield a small amount of optically active sulfone of retained configuration on formolysis in formic acid containing sodium formate. The result was interpreted as evidence for an intramolecular rearrangement. The rearrangement of allyl, crotyl and α-methylallyl benzenesulfinates to sulfones was studied by Cope, Morrison and Field.[3] In this case no final decision as to mechanism was made. It appeared probable that at least some of these observations could be interpreted as a recombination of ion pair species. Therefore, we have carried out an investigation of the solvolysis and rearrangement of arylsulfinate esters in an attempt to further elucidate the reaction mechanism.

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[1] National Research Council Studentship 1962-1963.

[2] C.L. Arcus, M.P. Balfe and J. Kenyon, J. Chem. Soc. 485 (1938).

[3] A.C. Cope, D.E. Morrison and L. Field, J. Amer. Chem. Soc. 72, 59 (1950).

The 2,6-dimethylbenzenesulfinate esters of t-butyl, α-phenylethyl, α-(p-methoxyphenyl) ethyl and benzhydryl alcohols were prepared by treatment of the appropriate alcohol with 2,6-dimethylbenzenesulfinyl chloride in pyridine in the cold. Some pertinent physical properties of the esters and corresponding sulfones are listed in Table I.

Table I

Properties of 2,6-Dimethylbenzenesulfinate Esters and Sulfones.[a]

2,6-Dimethylbenzenesulfinate			2,6-Dimethylphenyl Sulfone	
	m.p.°C.	I.R. abs. (microns)	m.p.°C.	I.R. abs. (microns)
t-Butyl	n_D^{25}1.5257	11.68	56.5-58.5	7.68
α-Phenylethyl	66-67	11.43	133.5-135.5	7.73
α-(p-Methoxyphenyl)ethyl	69-71	11.6	116-117	7.71
Benzhydryl	80-82	10.52	178-180	7.60

[a] All compounds have acceptable carbon, hydrogen and/or sulfur analysis.

In Table II some representative rate constants for the disappearance of the sulfinate esters, and the fraction sulfone produced, are summarized. It is apparent that all the esters listed yield some sulfone along with solvolysis products.

Sulfone formation could occur by three conceivable reaction paths. These are (i) an internal, cyclic, non-ionizing

Table II

Summary of Rate Constants and Sulfone Yields on Solvolysis of Some 2,6-Dimethylbenzenesulfinates at 90.0°C.

2,6-Dimethylbenzenesulfinate	Solvent	$10^5 k$ sec^{-1}	$F_{sulfone}$
t-Butyl	60% Ethanol[a]	2.07	0.01
Benzhydryl	90% Dioxane[a]	0.0912	.68
	90% Acetone[a]	.241	.50
	Ethanol[b]	2.38	.35
	80% Ethanol[a]	23.0	.37
	Acetic Acid[c]	79.4	.57
α-Phenylethyl	60% Ethanol[b]	1.14	.12
	Ethanol[a]	.027	ca.05
α-(p-Methoxyphenyl)ethyl	Ethanol[a]	307	.27

a. 2,6-Lutidine present b. Potassium acetate present

c. Sodium acetate present

rearrangement, (ii) ion pair recombination and (iii) recombination of dissociated ions.

The following observations aid in distinguishing between an ionic and non-ionic pathway for sulfone formation. First the rates of sulfone formation and solvolysis tend to reflect a similar sensitivity to ionizing power of the solvent.[4]

For the solvents listed in Table II plots of log k for solvolysis and rearrangement of benzhydryl 2,6-dimethylbenzenesulfinate versus log k for solvolysis of benzhydryl chloride

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[4] Preliminary results indicate a similar behavior for the solvolysis of cumyl 2,6-dimethylbenzenesulfinate. Unpublished results, R. Mermelstein.

at 25°C. yield lines with slopes of 0.87 and 0.73 respectively. Significantly the rate constants for both solvolysis and rearrangement in acetic acid appear to be too large by over two powers of ten as judged by the rate of acetolysis of benzhydryl chloride in comparison with other solvents. This apparently enhanced rate must be at least partly due to the fact that ion pair return is probably very extensive in the acetolysis of benzhydryl chloride and thus the titrimetric rate constant is much smaller than the ionization rate constant.[5] It is also conceivable that a portion of the rate enhancement in acetic acid may be due to a specificity in solvation[6] of the 2,6-dimethylbenzenesulfinate leaving group.

The second point to be noted is found in a comparison of the rates of reaction of α-phenylethyl and α-(*p*-methoxyphenyl)ethyl 2,6-dimethylbenzenesulfinates. In solvent ethanol introduction of the methoxy group into the aromatic ring enhances both solvolysis and sulfone formation rates by approximately four powers of ten. An effect of this magnitude is indicative of the formation of ionic species. Thus both substituent effects and solvent effects indicate that sulfone formation proceeds by way of an ionic intermediate rather than by an intramolecular, non-ionizing rearrangement.

That the sulfones cannot arise solely by dissociated ion recombination is shown by the following observations.

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[5] S. Winstein, J.S. Gall, M. Hojo and S. Smith, *J. Amer. Chem. Soc.* **82**, 1010 (1960).

[6] S. Winstein, A.H. Fainberg and E. Grunwald, *J. Amer. Chem. Soc.* **79**, 4146 (1957).

The fraction of sulfone formed appears to be constant throughout any run. Furthermore, as is illustrated in Table III, the addition of 2,6-dimethylbenzenesulfinate ion did not change the fraction sulfone formed in the solvolysis of the *t*-butyl, α-(*p*-methoxyphenyl)ethyl and benzhydryl 2,6-dimethylbenzenesulfinates in the solvents indicated. An increase in sulfone yield would have been expected if solvent and 2,6-dimethylbenzenesulfinate ion were competing for the carbonium ion to yield products. Finally, exchange to yield sulfone does not occur in the solvolysis of *t*-butyl chloride, α-phenylethyl bromide or benzhydryl chloride in the presence of lutidinium 2,6-dimethylbenzenesulfinate in the solvents listed in Table III. Although these data do not exclude a small portion of the sulfone arising by way of dissociated ion recombination, they do exclude this as the principal pathway for sulfone formation.[7]

We therefore feel that these data are best interpreted by the assumption that sulfone formation proceeds primarily via ionization and ion pair recombination as shown below.

$$\mathrm{ROSOAr} \rightarrow \mathrm{R}^{+}\ \mathrm{OSOAr}^{-} \quad \begin{matrix} \text{solvolysis products} \\ \mathrm{RSO_2Ar} \end{matrix}$$

The question of the existence of one or more than one type of ion pair[8] as precursor of the sulfone cannot as yet be answered.

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[7] A.H. Wragg, J.S. Fadyen and T.S. Stevens, *J. Chem. Soc.*, 3603 (1958) report exchange in acetolysis of benzhydryl *p*-toluenesulfinate in the presence of *p*-chlorobenzenesulfinic acid. The reaction was carried out in unbuffered acetic acid and therefore cannot be directly compared with our results.

[8] S. Winstein, E. Clippinger, A.H. Fainberg and G.C. Robinson, *Chemistry and Industry*, 664 (1954).

Table III

Summary of Sulfone Yields at 90.0°C.

2,6-Dimethylbenzenesulfinate	Solvent	[Base[a]] M	[ArSO$_2$H] M	F$_{sulfone}$
t-Butyl	60% Ethanol	0.06357	-	0.01
		0.06611	0.0291	0.01
Benzhydryl	80% Ethanol	0.08236	-	0.372
		0.07902	.0374	0.379
α-(*p*-Methoxyphenyl)ethyl[b]	Ethanol	0.09649	-	0.28
		0.09649	.0307	0.295
Alkyl Halide				
t-Butyl chloride	60% Ethanol	0.07768	.0356	0
α-Phenylethyl bromide	60% Ethanol	0.09057	.0273	<.004
Benzhydryl chloride	Ethanol	0.07563	.0339	ca.0

[a] 2,6-Lutidine [b] At 70.0°C.

Nor is the fraction of ion pairs trapped as sulfone known.[9]

The 2,6-dimethylbenzenesulfinate esters contain a leaving group which can react to yield a stable rearranged product as a result of recombination with a carbonium ion. The use of this leaving group yields results similar to those reported by Winstein[5,10], Pocker[11], Goering[12] and Smith[13] with

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[9] If a portion of the ion pair return regenerated the sulfinate ester, it would not have been detected as ion pair return.

[10] S. Winstein, M. Hojo and S. Smith, Tetrahedron Letters No. 22, 12 (1960).

[11] Y. Pocker, Proc. Chem. Soc. 140 (1961).

[12] H.L. Goering and J.F. Levy, Tetrahedron Letters No. 18, 644 (1960).

[13] S. Smith, private communication.

regard to ion pair formation on solvolysis of benzhydryl and substituted benzhydryl systems. In addition it appears that this method can be extended to the study of systems such as the _t_-butyl system, which yield relatively more reactive carbonium ion species than that formed in the benzhydryl system.