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ION PAIRS IN THE REARRANGEMENT OF TRITYL 2-METHYLBENZENESULFINATE

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The rearrangement of several arenesulfinate esters to the corresponding sulfones has been interpreted (1) to proceed via ionic pathways. We now wish to report the synthesis of trityl 2-methylbenzenesulfinate and a study of its rearrangement to trityl 2-methylphenyl sulfone.

Trityl 2-methylbenzenesulfinate (RX) was prepared by treatment of triphenylcarbinol with 2-methylbenzenesulfinyl chloride in pyridine at -20° C. for four hours. The crude ester obtained after isolation was contaminated with pyridine. If all the pyridine was removed in the isolation procedure then triphenylcarbinol was the only product recovered. Low temperature crystallization of the ester from ether yielded trityl 2-methylbenzenesulfinate, m.p. 135-139°C. (with decomposition), equivalent weight on hydrolysis, 411.4, calcd. equivalent weight, 398.5. The nuclear magnetic resonance spectrum showed four bands, a quartet (one hydrogen) at τ 2.1, a complex multiplet at τ 2.5-3.0, and singlets at τ 7.8 and τ 8.1. The singlet at τ 8.1 indicates that trityl 2-methylphenyl sulfone is present as an impurity. The τ 2.1 band can be assigned to the hydrogen ortho to the sulfur in the arenesulfinate group. The ratio of the integrated intensities of the aromatic to methyl protons is 6.3:1; calculated, 6.3:1 for both the ester and the sulfone. The compound showed strong absorbtion in the infrared at 1135 cm.$^{-1}$ in carbon disulfide. A weak band appeared at 1310 cm.$^{-1}$ (sulfone). If all the absorbtion at 1310 cm.$^{-1}$ is ascribed to the sulfone then the compound contains 7.5% sulfone.

Trityl 2-methylphenyl sulfone (RX') is conveniently synthesized by refluxing a solution of trityl 2-methylbenzenesulfinate in chloroform for one-half hour. The sulfone showed strong absorbtion in the infrared at 1125, 1145 and 1310 cm.$^{-1}$ in carbon disulfide. The nuclear magnetic resonance spectrum displayed a complex multiplet at τ 2.7-3.3 and a singlet at τ 8.1, with relative areas of 6.4:1.

Trityl 2-methylbenzenesulfinate rearranges to trityl 2-methylphenyl sulfone at room temperature in carbon tetrachloride, chloroform, nitrobenzene, acetonitrile and dimethylsulfoxide. The first-order rate constants for rearrangement of the ester to sulfone in the first three solvents, containing 0.03 m 2,6-lutidine, at room temperature ate 3×10^{-6} sec.$^{-1}$, 5×10^{-4} sec.$^{-1}$ and 1.3×10^{-3} sec.$^{-1}$ respectively.

In acetonitrile solutions the addition of tetra-n-butylammonium azide diverts a portion of the product sulfone to trityl azide, but has little effect on the rate of disappearance of the ester. A summary of the first-order rate constants for disappearance of the ester and the mole fraction of trityl azide produced at several salt concentrations is presented in Table I.

Table I

Rate Constants and Trityl Azide Yields from Trityl 2-Methylbenzenesulfinate in Acetonitrile at Room Temperature.

[Ester]	$[Bu_4NN_3]$	10^3k sec.$^{-1}$	F_{azide}^{a}
0.0260	0.010	1.1 ± .1	0.33
.0260	.026	1.1 ± .1	.36
.0260	.051	.91 ± .05	.42
.0264	.230	*ca*. 1.0	*ca*. .45

(a) Based on 92.5% purity of ester

The solvent effects on the rates of rearrangement suggest that at least in the more ionizing solvents an ionic reaction is taking place. The exchange experiments involving the azide salt indicate that some, but not all, of the rearrangement in acetonitrile occurs via a readily trappable carbonium ion species. Suitable candidates for the capturable carbonium ion species would be a solvent-separated ion pair(2) or dissociated ions, or both.

The incomplete conversion of trityl 2-methylbenzenesulfinate to trityl azide is reminiscent of the behavior of systems such as *threo*-3-anisyl-2-butyl *p*-toluenesulfonate which exhibit a "special salt effect" and which rearrange (racemize) faster than they solvolyze in acetic acid even in the presence of large amounts of salts such as lithium perchlorate, lithium acetate and lithium bromide. (2,3) The results are in contrast to those observed (4) in the O^{18} scrambling of trityl benzoate-carbonyl-O^{18} in acetone where lithium azide completely inhibited the rearrangement reaction.

A competition experiment was carried out by adding trityl perchlorate (5) (0.027 M) to acetonitrile containing 0.071 M tetra-n-butylammonium azide and 0.071 M tetra-n-butylammonium 2-methylbenzenesulfinate, m.p. 105-107° C., (Anal. Calcd. for $C_{23}H_{43}O_2NS$: C, 69.5; H, 10.89; N, 3.52; S, 8.06. Found: C, 69.37, 69.41; H, 10.49, 10.61; N, 3.36; S, 8.24). Infrared spectral analysis indicated that a ca. 45% yield of trityl azide had been produced three minutes after mixing. The amount of trityl azide increased with time reaching a value of ca. 55% after one hour. Qualitative infrared measurements indicated that the yield of trityl 2-methylphenyl sulfone also increased with time. These observations are consistent with the formation of trityl azide, trityl 2-methylphenyl sulfone and trityl 2-methylbenzenesulfinate as initial reaction products.

To the extent that trityl perchlorate serves as a model for the capturable intermediate observed in the rearrangement of trityl 2-methylbenzenesulfinate the results indicate that there is approximately equal opportunity for equivalent concentrations of the azide and 2-methylbenzenesulfinate salts to react with the trityl cation species to give covalent products. The majority of the sulfone produced on rearrangement of the corresponding ester in the presence of a large excess of azide salt must arise by a route such that any intermediates which are produced cannot be efficiently captured by the azide salt.

We feel that the data are best interpreted by scheme I in which ($R^{\oplus}$ + $X^{\ominus}$) represents the capturable intermediate and may be equated with either dissociated ions or solvent-separated ion pairs or both,* and $R^{\oplus}X^{\ominus}$ represents an intimate ion pair. The intimate ion pair is not capable of facile

$$R\text{-}X \rightleftharpoons R^{\oplus}X^{\ominus} \rightleftharpoons (R^{\oplus} + X^{\ominus}) \xrightarrow{M^{\oplus}N_3^{\ominus}} RN_3 \qquad R^{\oplus}X^{\ominus} \rightarrow RX' \leftarrow (R^{\oplus} + X^{\ominus})$$

(I)

diversion to trityl azide by added azide salt. The maximum of ca. 45% conversion of ester to azide allows one to estimate that the relative rates of collapse of the intimate ion pair to sulfone compared to further separation to more dissociated ions are 1:0.8 in acetonitrile solution.

The results of the competition reaction using trityl perchlorate indicate that in acetonitrile ion pair return can occur with either carbon-oxygen or carbon-sulfur bond formation. On this basis rearrangement rate in acetonitrile would represent a lower limit to the ionization rate of the system.

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* Preliminary kinetic studies using trityl 2,6-dimethylbenzenesulfinate, which does not rearrange to a sulfone but does undergo exchange with added salts in acetonitrile, suggest that if dissociated ions are involved in the exchange reaction they cannot be regarded as the exclusive capturable intermediate.

REFERENCES

(1) D. Darwish and R. A. McLaren, Tetrahedron Letters, 26, 1231 (1962); A.H. Wragg, J. S. McFadyen and T. S. Stevens, J. Chem. Soc., 3608 (1958).

(2) S. Winstein, E. Clippinger, A.H. Fainberg and G. C. Robinson, Chemistry and Industry, 664 (1954).

(3) S. Winstein, P.E. Klinedinst, Jr., and G.C. Robinson, J. Am. Chem. Soc., 83, 885 (1961); S. Winstein, P.E. Klinedinst, Jr., and E. Clippinger, ibid., 83, 4986 (1961).

(4) C. G. Swain and G. Tsuchihashi, ibid., 84, 2021 (1962).

(5) H. J. Dauben, Jr., L. R. Honnen and K. M. Harmon, J. Org. Chem., 25, 1442 (1960).