Tetrahedron Letters No. 5, pp 343 - 346, 1975. Pergamon Press. Printed in Great Britain.

HIGHLY REACTIVE SULFINATES

THE SYNTHESIS AND SOLVOLYSIS OF BENZYL TRICHLOROMETHANESULFINATES[1]

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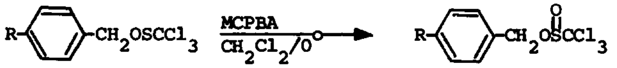
(Received in UK 26 November 1974; accepted for publication 23 December 1974)

Our interest in the behaviour of trichloromethanesulfinates is a consequence of some unique results previously obtained on the rearrangement and solvolysis of the corresponding sulfenates. For example, while the rearrangement of allyl trichloromethanesulfenates to sulfoxides[2] generally parallels that of the corresponding arenesulfenates[3], and proceeds by a concerted [2,3]-sigmatropic shift mechanism, the rearrangement of benzyl trichloromethanesulfenates[4], unlike that of benzyl arenesulfenates[5], proceeds by an ionization mechanism. Similarly, we have found[6] that p-anisyl trichloromethanesulfenate readily undergoes ethanolysis at room temperature with complete C-O bond cleavage, by an ionization mechanism. In sharp contrast, the ethanolysis of the corresponding 2-nitrobenzenesulfenate proceeds at a similar rate only at 100°, it involves exclusive S-O bond fission, and may be explained by an S_N2-type mechanism.

Although esters of trichloromethanesulfinic acid have long been considered of interest[7], they have received little attention in the past. Schöllkopf and Hilbert[8] have used methyl trichloromethanesulfinate as a source for the generation of dichlorocarbene. It appears to us that the lack of activity on these esters may be a result of the difficulties involved in their preparation. We have synthesized benzyl and variously p-substituted benzyl trichloromethanesulfinates by a very convenient method, oxidation of the appropriate sulfenate with m-chloroperbenzoic acid in methylene chloride, at 0° (eq.1).



(1)

R = H, CH_3, Cl, NO_2

All the esters prepared were obtained in almost quantitative yield as nice crystalline solids[9]. It is interesting to note that further oxidation to the sulfonate does not take place, even in the presence of a large excess of oxidizing agent in chloroform, at reflux temperature. This contrasts with the observation that arenesulfinates are easily oxidized to sulfonates at 0°, a reaction used for the preparation of highly active arenesulfonates[10]. It is also worthwhile to mention that the p-anisyl ester could not be obtained by this method. Rearrangement to sulfone, accompanied by decomposition took place under the normal reaction conditions.

As an extension of our studies on the solvolysis of benzylic arenesulfinates[11] and trichloromethanesulfenates[6], we have investigated the behaviour of the corresponding trichloromethanesulfinates under solvolytic conditions. We have found that all the benzyl esters prepared, including the p-nitrobenzyl one, underwent facile ethanolysis with exclusive C-O bond fission as evidenced by formation of the corresponding ethyl ether and sulfinic acid (eq.2).

$$ArCH_2OS(O)CCl_3 + EtOH \xrightarrow[32^\circ]{} ArCH_2OEt + Cl_3CSO_2H \qquad (2)$$

This result contrasts sharply with the observation that benzyl 2,6-dimethylbenzenesulfinate undergoes ethanolysis by complete S-O bond cleavage, and at a much slower rate even at 90° ($k = 2x10^{-7}$ sec^{-1})[11]. From a comparison between the rate of ethanolysis of this ester with that of the corresponding trichloromethanesulfinate (see Table), taking into account the differences in bond cleavage and temperature, one finds that the reactivity of trichloromethanesulfinate is higher by some 6 powers of ten. Perhaps it may be more instructive to indicate that the reactivity of benzyl trichloromethanesulfinate is quite similar to that of the corresponding tosylate[12] as can be seen from the data shown in the Table.

TABLE

Rate Constants for the Solvolysis[a] of

Benzyl Trichloromethanesulfinates at 32°

Sulfinate	Solvent	10^5k, sec^{-1}	Relative Rate
Benzyl	EtOH	3.05	1
	MeOH	7.14	1
	80% EtOH	9.25	1
	60% EtOH	19.00	1
p-Methylbenzyl	EtOH	12.53	4.1
	MeOH	42.50	5.9
	80% EtOH	121.30	13.1
p-Chlorobenzyl	EtOH	1.27	0.4
p-Nitrobenzyl	EtOH	0.130	0.043
	MeOH	0.261	0.037
	80% EtOH	0.439	0.047
Benzyl Tosylate[b]	EtOH	5.33	
	MeOH	16.70	
	80% EtOH	32.40	

a. In the presence of 2,6-Lutidine, acting as buffer.

b. At 25°. Data taken from ref. 12.

In order to find out whether the solvolysis takes place by an S_N1 or S_N2 mechanism, a kinetic study of the reaction of the four esters under various conditions was carried out and the results are presented in the Table. The reaction of all the esters showed first order kinetics. The data of the Table provide information on the effect of the solvent ionizing power and of the substituent on the rate of solvolysis. Inspection of these data indicates that an increase in the ionizing power of the solvent enhances the rate of solvolysis, consistent with an ionization mechanism. However from a comparison of the rates of solvolysis of the variously substituted esters in the same solvent it is obvious that at least some of the esters do not react by a purely S_N1 mechanism. For example, the relative rate factor for the *p*-nitro group of app. 25 is much too small for such a mechanism.

In order to analyze the results in a more quantitative manner, we have examined the Hammett and Winstein correlations. The rates of solvolysis in ethanol correlate fairly well ($r = 0.98$) with σ^+. However, the size of $\rho = -1.8$ is smaller than usually observed with ionizing systems, but compares favourably with the values obtained for the solvolysis of other benzylic systems such as chlorides and sulfonates[14]. Good linear correlations were found when log k for solvolysis of benzyl, *p*-nitrobenzyl and *p*-methylbenzyl trichloromethanesulfinates using the solvents mentioned in the Table, at 32°, were plotted against log k for ionization of *p*-methoxyneophyl tosylate[15] in the same solvents, at 25°. The slopes (*a* values[15]) of the straight lines of 0.57 and 0.58 for the benzyl and *p*-nitrobenzyl esters indicate a relatively low sensitivity to variation in solvent ionizing power, and speak against a purely S_N1 mechanism. It is suggested that these esters react by both S_N1 and S_N2 mechanisms. On the other hand, a slope of 1.1 is obtained for the *p*-methylbenzyl ester, similar to the values obtained for other ionizing systems[4,6,11,16]. It is therefore concluded that in this case, capable to develop a more stable carbonium ion, complete ionization takes place.

The unusual high reactivity reported above for the new sulfinates, may be attributed to the high acid strength of Cl_3CSO_2H, and the consequent high leaving group ability of its anion. On the other hand, the lack of rearrangement to sulfone which generally accompanies the solvolysis of arenesulfinates[11,16] may reflect the lower nucleophilicity of the sulfur atom in this case. The same explanation may also be advanced for the lack of sulfinate to sulfonate oxidation, mentioned above.

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