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HIGHLY REACTIVE SULFINATES. THE SYNTHESIS, SOLVOLYSIS AND REARRANGEMENT OF BENZYL TRICHLOROMETHANESULFINATES

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Abstract: Benzyl trichloromethanesulfinates are easily obtained by oxidation of the corresponding sulfenates, in excellent yields. Examination of their reactivity revealed some unique features. In contrast to benzyl arenesulfinates which undergo solvolysis with complete S-O bond fission, these esters undergo solvolysis with exclusive C-O bond fission, and with a rate enhancement by a factor of 6 powers of ten, comparable to benzyl tosylates. Similarly, unlike benzyl arenesulfinates, these esters undergo a facile rearrangement to sulfones on heating in polar nonhydroxylic solvents. A kinetic study of these reactions under various conditions has been performed, and the sensitivity of solvolysis to substituent and solvent effects has been analyzed by examination of the Hammett and Winstein correlations. The mechanisms of both reactions are discussed.

INTRODUCTION

Since the introduction of the Tipson procedure for the preparation of tosylates,[1a] almost half a century ago, synthetic and especially physical organic chemistry has been well served by arenesulfonate leaving groups.[1b] The more recent introduction of trifluoromethanesulfonates (triflates)[2a] has further increased their utility.[2b] Although not as famous as sulfonates, esters of arenesulfinic acids[3] have also received considerable attention in the past. The rearrangement and solvolysis of such esters have been of particular mechanistic interest, and the former subject has been recently reviewed.[4] The solvolysis of arenesulfinates can involve either sulfur-oxygen or carbon-oxygen bond fission. An unequivocal indication for S-O bond cleavage in the alcoholysis of sulfinate esters is the production of the parent alcohol and a new sulfinate ester, the latter corresponding to the alcohol used as solvent. On the other hand, if C-O bond fission occurred under the same conditions the product would be sulfinic acid, ether and/or sulfone. For example, Kenyon and coworkers[5] have found that ethyl *p*-toluenesulfinate yields only *d*-2-octyl *p*-toluenesulfinate when heated with *d*-2-octanol, and that on refluxing a solution of (-)-α-phenylethyl *dl*-*p*-toluenesulfinate in ethanol with added potassium acetate or carbonate, α-phenylethanol of retained configuration is formed. These results are clear evidence for S-O bond fission. Subsequently, Herbrandson and Cusano[6] have also observed S-O bond fission in the ethoxide-ion catalyzed ethanolysis of epimeric (-)-menthyl *p*-iodobenzenesulfinates. Bunton and Hendy[7] determined the position of bond fission in the hydrolysis

of methyl and benzhydryl *p*-toluenesulfinates in aqueous dioxan by the use of H_2O^{18} enriched solvent. The base-catalyzed reaction of both esters, as well as the acid-catalyzed hydrolysis of the first ester, have thus been shown to involve S-O bond fission. The same type of cleavage has also been reported by Darwish and Noreyko[8] for the solvolysis of various *p*-methoxyneophyl arenesulfinates in aqueous and absolute ethanol in the presence of such bases as ethoxide ion, potassium acetate and 2,6-lutidine. On the other hand, exclusive carbon-oxygen bond fission by an ionization mechanism has been reported for the solvolyses of esters likely to develop stable carbenium ions such as *t*-butyl, α-phenylethyl, benzhydryl[9] and *p*-methoxybenzyl (*p*-anisyl)[10] arenesulfinates under conditions appropriate for the competing rearrangement to sulfone. The following example nicely illustrates the remarkable dependence of bond cleavage on carbenium ion stability. In contrast to benzyl arenesulfinate which undergoes ethanolysis by sulfur-oxygen bond fission (Eq 1), the ethanolysis of the *p*-methoxybenzyl ester involves only carbon-oxygen bond fission and is accompanied by sulfone formation (Eq 2).[10] A kinetic study of the solvolysis revealed that the rate enhancement due to the *p*-methoxy group is approximately ten to the power of 4.

$$ArS(=O)-OCH_2Ph + EtOH \xrightarrow{90^\circ} ArS(=O)-OEt + PhCH_2OH \qquad (1)$$

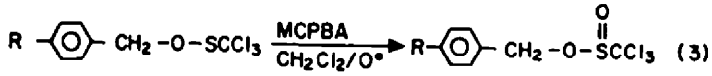
$$ArS(=O)-OCH_2An\text{-}p + EtOH \xrightarrow{75^\circ} ArSO_2H + p\text{-}AnCH_2OEt + ArS(=O)_2-CH_2An\text{-}p \qquad (2)$$

Interestingly, all the sulfinates considered so far were derived from arenesulfinic acids (pKa = 2.76).[3a] Although considerably stronger than carboxylic acids, the ionization ability of these is much poorer than that of corresponding sulfonates. For this reason, and in view of the dramatic rate enhancement by a factor of 10^8-10^7 displayed by the trifluoromethyl group on the reactivity of sulfonate esters under solvolytic conditions,[2,11] we have decided to investigate the behavior of trihalomethanesulfinates[12] in the expectation of a similar effect on the reactivity of sulfinates. Furthermore, our interest in the behavior 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[13,14] generally parallels that of the corresponding arenesulfenates,[15] and proceeds by a concerted [2,3]-sigmatropic shift mechanism, the rearrangement of benzyl trichloromethanesulfenates,[16] unlike that of benzyl arenesulfenates,[17] proceeds by an ionization mechanism. Similarly, we have found[18] 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. A detailed report of our results on the synthesis, solvolysis and rearrangement of benzyl trichloromethanesulfinates is presented below.

RESULTS AND DISCUSSION

Synthesis of benzyl trichloromethanesulfinates. Although esters of trichloromethanesulfinic acids have long been considered of interest,[19] they have received little attention in the past. Schöllkopf and Hilbert[20] have used methyl trichloromethanesulfinate as a source for the generation of dichlorocarbene. This ester was prepared by reaction of methanol with Cl_3CSOCl. The latter was obtained from the corresponding sulfinic acid by an old procedure[21] insufficiently detailed at the time. This method involves oxidation of Cl_3CSCl to the corresponding sulfonyl chloride, followed by H_2S reduction of the product to Cl_3CSO_2H. In continuation, the sulfinic acid is converted to Cl_3CSOCl by treatment with thionyl chloride, before esterification. Our attempts to prepare Cl_3CSO_2H by this method were unsuccessful, and we therefore decided to circumvent this problem.[22] We have synthesized benzyl and variously *p*-substituted benzyl trichloromethanesulfinates (trichlinates) by a general and very convenient method, oxidation of the appropriate sulfenate esters with *m*-chloroperbenzoic acid in methylene chloride at 0°. (Eq. 3)



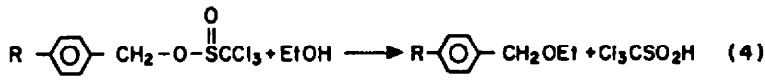
(3)

R = H, CH_3, Cl, NO_2

All the esters prepared were obtained in practically quantitative yield as nice crystalline solids. The sulfenate esters are also readily available[16,18] by reaction of the appropriate alcohol with commercially available and inexpensive Cl_3CSCl. 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 result contrasts with the observation that arenesulfinates are easily oxidized to sulfonates at 0°, a reaction used for the preparation of highly active arenesulfonates.[23] It is also worthwhile to mention that the *p*-anisyl ester could not be prepared by this method. Rearrangement to sulfone, accompanied by decomposition took place under the normal reaction conditions.

Solvolysis of benzyl trichloromethanesulfinates. This study was initiated by an examination of the solvolysis of the unsubstituted benzyl

ester in anhydrous ethanol, methanol and aqueous ethanol solutions. We have found that this ester undergoes facile ethanolysis at 32° with exclusive C-O bond cleavage as evidenced by formation of the corresponding ethyl ether and sulfinic acid (Eq. 4, R=H).



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 = 2 x 10^{-7} sec^{-1}).[10] From a comparison between the rate of ethanolysis of this ester with that of the corresponding trichloromethanesulfinate (see Table 1), taking into account the differences in bond cleavage and temperature, one finds that the reactivity of the trichloromethanesulfinate is higher by some 6 powers of ten. This dramatic rate effect displayed by the trichloromethyl group on the reactivity of sulfinate esters, is very similar to the rate effect displayed by the trifluoromethyl group on the reactivity of sulfonate esters,[2,11] as expected. Perhaps it may be more instructive to indicate that the reactivity of benzyl trichloromethanesulfinates is quite similar to that of the corresponding tosylates[24] as can be seen from the data shown in Table 1. This observation raises the possibility of using such esters as substitutes of sulfonates, which may have some interesting mechanistic or synthetic application or advantage.

The unusual high reactivity reported above for the new sulfinate ester 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[2,10,25] may reflect the reduced nucleophilicity of the sulfur atom in this case. The same rational may also be advanced for the lack of sulfinate to sulfonate oxidation, mentioned above.

In order to find out whether the alcoholysis takes place by an S_N1 or S_N2 mechanism. a kinetic study of the reaction was performed using the titrimetric method. A summary of first-order rate constants for the solvolysis of benzyl trichloromethanesulfinate under various conditions is presented in Table 1. Inspection of the data in this table indicates that the rate of solvolysis of this ester is enhanced by increasing the ionizing power of the solvent. For example. the rate increases by a factor of 3 on going from 100% to 80% ethanol. These results are consistent with a polar transition state and are suggestive of an S_N1 or S_N2 mechanism or a combination of these two. In order to analyze the results in a more quantitative manner. equation 5. suggested by Winstein and coworkers,[26] has

Table 1. Rate constants for the solvolysis of benzyl trichloromethanesulfinate[a] at 32°.

Benzyl ester	Solvent	Added Base	[Base],M	10^5k, sec^{-1}
Trichloromethanesulfinate	EtOH	–	–	2.70 ± 0.01
	EtOH	2,6-Lutidine	0.160	3.05 ± 0.04
	EtOH	2,6-Lutidine	0.320	3.32 ± 0.09
	MeOH	2,6-Lutidine	0.160	1.14 ± 0.07
	80%EtOH-H_2O[b]	2,6-Lutidine	0.160	9.26 ± 0.06
	60%EtOH-H_2O[c]	2,6-Lutidine	0.160	19.04 ± 0.80
	60%EtOH-H_2O	KOAC	0.168	22.03 ± 0.20
Tosylate[d]	EtOH	0.0200	–	5.33 ± 0.25
	MeOH	0.1200	–	16.70 ± 0.40
	80%EtOH-H_2O	0.0500	–	32.40 ± 3.0

a. [Ester] = 0.0366 M. b. In this solvent, the ratio $PhCH_2OEt/PhCH_2OH$ = 3.10. c. In this solvent, the ratio $PhCH_2OEt/PhCH_2OH$ = 1.47. d. At 25°. Data taken from ref. 24

been used:

$$\log k_{\text{reaction}} = a \log k_1 + b \qquad (5)$$

where k_{reaction} and k_1 are the rate constants for the reaction being examined and that of ionization of *p*-methoxyneophyl *p*-toluenesulfonate, respectively. The *a* value in the above equation was suggested by these authors as a measure of relative sensitivity of a reaction to the ionizing power of the solvent. A good linear correlation was found when log *k* for solvolysis of benzyl trichloromethanesulfinate, using the solvents mentioned in Table 1 at constant concentration of 2,6-lutidine at 32°, were plotted against log *k* for ionization of *p*-methoxyneophyl tosylate in the same solvents at 25°. The slope (*a* value) of the straight line of 0.57 indicates a relatively low sensitivity to variation in solvent ionizing power. For comparison, for the solvolysis of *p*-anisyl benzenesulfinate[10] at 75° and trichloromethanesulfenate[18] at 0°, *a* values of 1.5 and 1.3, respectively, were obtained, indicating the operation of a fully ionizing mechanism. It is therefore suggested that in the present case, benzyl trichloromethanesulfinate reacts by an S_N2 mechanism.

In view of this interpretation, one may expect some dependence of the rate of solvolysis on the identity and concentration of the base used as buffer. To test this hypothesis, the rates of solvolysis of the ester at different concentrations of 2,6-lutidine in 100% EtOH and with KOAc as buffer in 60% EtOH-H_2O were also measured and are shown in Table 1. Inspection of these data indicates a moderate enhancement of rate of solvolysis with increase in concentration of 2,6-lutidine, or its replacement by potassium acetate. Furthermore, the acetate anion was found

to participate in the reaction giving rise to benzyl acetate as an additional product. The ratio of benzyl alcohol, benzyl ethyl ether and benzyl acetate was 1.3:2.5:1.0, as determined by gas chromatography. A plot of the rate constants of solvolysis in anhydrous ethanol *vs.* concentration of 2,6-lutidine gave a good straight line with a slope of 1.959×10^{-5} (Fig. 1), thus indicating that the rate constants may be accommodated by the rate equation $k_{obs} = k_0 + k_1[B]$, where [B] is the concentration of added base, k_{obs} is the measured rate constant, and k_0 can be obtained graphically, i.e. $k_{obs} = 2.707 \times 10^{-5} + 1.959 \times 10^{-5}[B]$. One may conclude that the second term of this equation represents a general base catalyzed second order reaction or, alternatively, a mechanism in which the base attacks the substrate in the rate-determining step with the formation of an unstable intermediate, followed by its rapid interception by solvent to give the observed products. The first term of the equation (2.707×10^{-5}) may also arise from two different sources it may represent the rate constant of a monomolecular reaction (S_N1), or it may represent the rate constant of a second-order reaction in which the solvent acts as a basic autocatalyst.[27] A combination of the last two alternatives is yet another possibility.

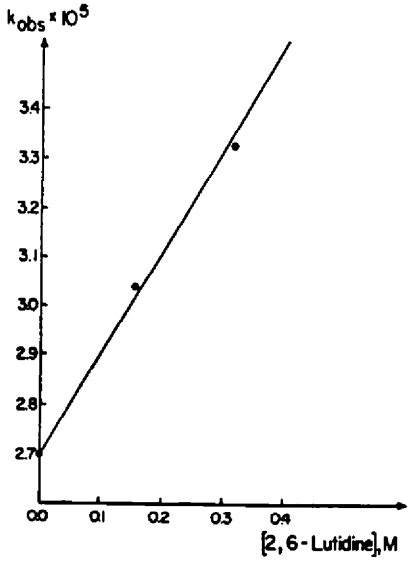


Fig. 1. Plot of rate constants for the solvolysis of benzyl trichlinate vs concentration of 2,6-lutidine at 32°. Slope $(1.959 \pm 0.09) \times 10^{-5}$. Intercept 2.70×10^{-5} ($r = 0.995$).

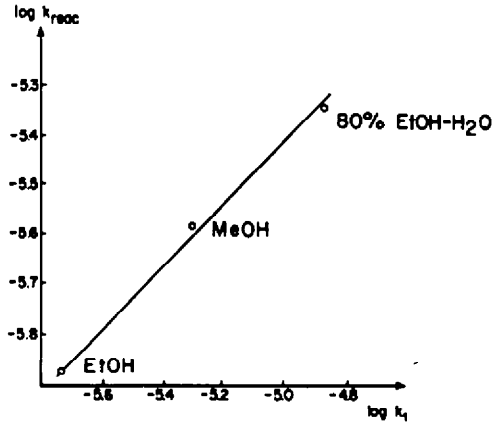


Fig. 2. Plot of log *k* for solvolysis of *p*-nitrobenzyl trichlinate at 32° vs log *k* for ionization of *p*-methoxyneophyl tosylate at 25°. Slope (*a* value) 0.589 ± 0.03 ($r = 0.994$).

In order to gain further insight into the reaction mechanism, we decided to examine the effect of substitution in the phenyl ring on the rate and nature of solvolysis of benzyl trichloromethanesulfinate. For this reason, we first attempted to prepare the *p*-anisyl ester, to compare its

reactivity with that of the corresponding benzenesulfinate[10] and trichloromethanesulfenate.[18] However, as mentioned above, this ester could not be isolated due to its high reactivity and spontaneous rearrangement to sulfone. On the other hand, the preparation of the *p*-methyl-, *p*-chloro- and *p*-nitrobenzyl trichlinates proceeded as usual, in practically quantitative yields, and afforded nice crystalline compounds. Similar to the unsubstituted esters, the solvolysis of these esters in anhydrous ethanol or methanol and 80% aqueous ethanol took place with complete C-O bond cleavage, and showed good first-order kinetics. A summary of the rate constants for the solvolysis of these esters, obtained by the titrimetric method is shown in Table 2.

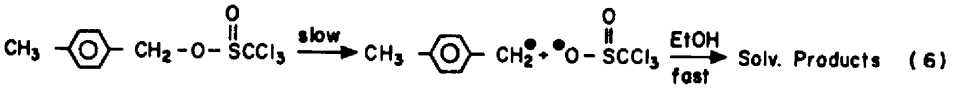
Table 2. Rate constants for the solvolysis of *p*-substituted benzyl trichloromethanesulfinates[a] at 32°.

Trichloromethane-sulfinate	Solvent	[Ester],M	[Base],[a]M	[$LiClO_4$].M	10^5k, sec^{-1}
p-Methylbenzyl	EtOH	0.0348	0.1420	-	12.53 ± 0.3
	EtOH	0.0344	0.1410[b]	-	12.61 ± 0.7
	EtOH	0.0104	0.0410	0.0104	14.35 ± 0.3
	EtOH	0.0104	0.0410	0.0208	16.47 ± 0.1
	EtOH	0.0104	0.0410	0.0313	18.11 ± 0.3
	EtOH	0.0104	0.041	0.0626	23.92 ± 1.9
	MeOH	0.0083	0.0332	-	42.50 ± 0.7
	80% EtOH	0.0083	0.0334	-	121.30 ± 9.0
	80% EtOH	0.00834	0.0332[b]	-	121.30 ± 7.0
p-Chlorobenzyl	EtOH	0.0324	0.1220	-	1.27 ± 0.03
p-Nitrobenzyl	EtOH	0.0314	0.1270	-	0.130 ± 0.005
	MeOH	0.0084	0.0354	-	0.261 ± 0.011
	80% EtOH	0.0084	0.0352	-	0.439 ± 0.003

a. 2,6-Lutidine, except otherwise indicated.
b. Pyridine.

The data of Table 2 provide information on the effect of the solvent ionizing power and of the substituent on the rate of solvolysis of benzyl trichlinates. As illustrated in Fig. 2, log *k* for solvolysis of *p*-nitrobenzyl trichlinate, using ethanol, methanol and 80% ethanol as solvents at 32°, correlated quite well with log *k* for ionization of *p*-methoxyneophyl tosylate in the same solvents at 25° The slope (*a* value) of the straight line, 0.569, indicates a relatively low sensitivity to variation in solvent ionizing power, very similar to the unsubstituted analogue. It is therefore suggested that this ester also undergoes solvolysis by an S_N2 mechanism. On the other hand, a slope of 1.1 is obtained for the *p*-methylbenzyl ester (Fig. 3), comparable to the values obtained for other ionizing systems.[10,16,19,25] It is consequently concluded that in this case, which is capable of developing a more stable

carbenium ion, complete ionization of the carbon-oxygen bond takes place during solvolysis. In order to test this conclusion. the effect of added base and salt on the rate of ethanolysis were examined. The data of Table 2 indicates that substitution of 2,6-lutidine by pyridine had no effect on the rate of reaction. This result is consistent with a rate determining unimolecular process involving complete ionization of the C-O bond (Eq. 6).



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Further support for this conclusion can be derived by inspection of the effect of added lithium perchlorate on the rate of ethanolysis of the *p*-methylbenzyl ester. The rates of ethanolysis in the presence of $LiClO_4$ with the ratio of salt to ester concentration of 1:1, 2:1, 3:1 and 6:1 were measured. As illustrated in Fig. 4, a plot of the rate constants for ethanolysis at 32° *vs.* the concentration of the added salt gives a nice straight line, which intercepts the *y* axis at a point corresponding exactly to the rate constant in the absence of perchlorate ion (12.51×10^{-5} sec^{-1}, Fig. 4). This result indicates a normal salt effect, and ionization of the ester in the rate determining step to dissociated ions. The *b* value calculated from the Winstein equation $k=k^{\circ}(1 + b[LiClO_4])$, is 14.3. This *b* value is similar to those obtained for the ionization of *p*-methoxyneophyl tosylate (*b* = 15.0) and of α,α-dimethyl-*p*-methoxybenzyl tosylate (*b* = 15.4). in acetic acid in the presence of the same added salt.[29]

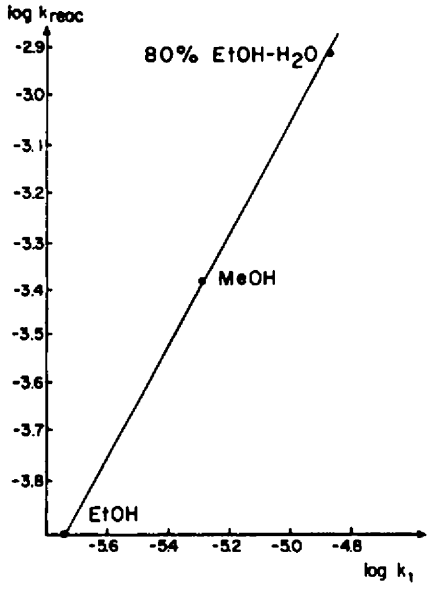


Fig. 3. Plot of log *k* for solvolysis of *p*-methylbenzyl trichlinate at 32° vs log *k* of ionization of *p*-methoxyneophyl tosylate at 25°. Slope 1.096 ± 0.029 (r = 0.998).

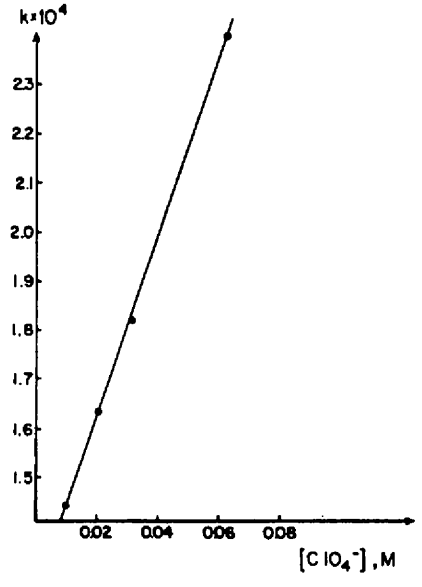


Fig. 4. Plot of rate constants of ethanolysis of *p*-methylbenzyl trichlinate vs concentration of added perchlorate. Slope (1.820 ± 0.029) × 10^{-3}. Intercept 1.251×10^{-4} (r = 0.999).

In order to analyze the kinetic results presented in Tables 1 and 2 with respect to the substituent effect we have examined the Hammett correlation. The rates of solvolysis of *p*-chloro-, *p*-nitro- and benzyl trichlinates in ethanol, which react by the same mechanism, correlate nicely with σ (Fig. 5). The sign and size of $\rho = -1.75$ indicate the development of a positive charge in the transition state, consistent with an ionization mechanism. This ρ value compares favorably with the values reported for the solvolysis of other benzylic systems such as benzyl chlorides ($\rho = -1.33$) and tosylates ($\rho = -2.2$).[29] This result is consistent with the observation mentioned above about the similar reactivity of benzyl trichlinates and tosylates. The high solvolytic reactivity of the trichlinate esters can be explained in terms of the unusual stability of the $Cl_3CSO_2^-$ anion, which is derived from a strong acid, responsible for its high leaving group ability. The occurrence of carbon-oxgyen bond fission, independent of substitution is unique for sulfinate esters. Of further interest is the observation that the reactivity of the trichlinate esters exceeds even the reactivity of the corresponding triflinate esters,[12b] by a factor of two to three, since the former esters are much easier to prepare. This observation is also surprising, since other available data show that CF_3CO_2H is several times stronger than CCl_3CO_2H. In view of these findings, one would predict that the practically unknown trichloromethanesulfonates may serve as good substitutes for the triflates.

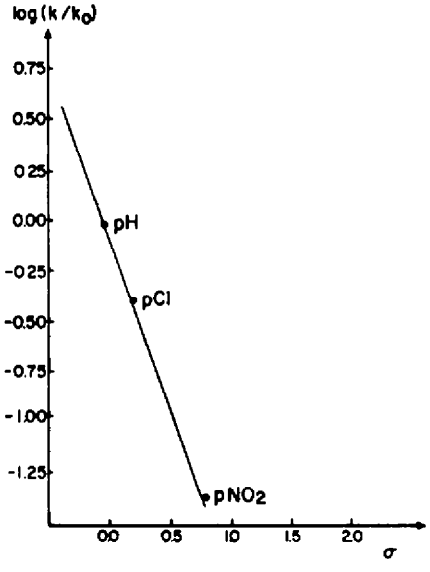
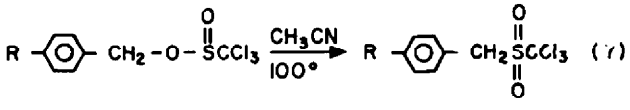


Fig. 5. Hammett correlation. Plot of log k/k_0 vs σ for solvolysis of benzyl trichlinates

Rearrangement of benzyl trichloromethanesulfinates. Prompted by the observation of the high reactivity of benzyl trichlinates involving C-O bond fission under solvolytic conditions, and in view of the lack of rearrangement to sulfone under such conditions, we decided to investigate the rearrangement of these esters to sulfone under nonhydroxylic conditions. Rearrangements of sulfinates to sulfones in general have

received considerable attention in the past.[4] With the exception of allylic and propargylic arenesulfinates which rearrange to sulfones *via* concerted [2,3]-sigmatropic shift mechanism,[13c,31] the rearrangement of practically all the other sulfinates proceeds by an ionic mechanism, as first suggested by Kenyon and coworkers.[32] More recently, however, the mechanistically detailed studies by Darwish and coworkers[9] have shown that the main route to sulfone formation in the rearrangement of *t*-butyl, benzhydryl, α-phenylethyl and trityl arenesulfinates under various conditions is ion pair recombination, and not recombination of free ions.

Previously, it has been reported that no rearrangement of benzyl *p*-toluenesulfinate to benzyl *p*-tolyl sulfone takes place on heating the ester in a mixture of acetic and hydrochloric acids or in a homogenous state.[33] Similarly, on heating a solution of benzyl benzenesulfinate in formamide (dielectric constant 109) during 70 hr on a steam bath, the ester rearranged to benzyl phenyl sulfone in low yield. In contrast, we have found that benzyl trichlinate rearranged to benzyl trichloromethyl sulfone on heating in dry acetonitrile at 100° in the presence of 2,6-lutidine acting as a buffer with a rate constant of $1.697 \pm 0.05 \times 10^{-4}$ sec^{-1} (Eq. 7). The first-order rate constant for the rearrangement was conveniently measured by the decrease in intensity of the methylene nmr double doublet signal of the benzyl ester, using *p*-dimethoxybenzene as internal standard. The *p*-methylbenzyl trichlinate also rearranged to the corresponding sulfone under similar conditions. In order to test the effect of solvent ionizing power, the rate of rearrangement in nitromethane was also measured, and was found to be 2.2 times faster than in acetonitrile ($k = 3.818 \pm 0.16 \times 10^{-4}$ sec-1) at the same temperature. In view of the evidence presented above in favour of an ionization mechanism for the solvolysis of benzyl trichlinates and since the ionization of *p*-methoxyneophyl tosylate is also enhanced by a factor of 2 on going from acetonitrile to nitromethane, we suggest that the rearrangement of the benzyl trichlinates which clearly involves C-O bond fission, also proceeds by an ionization mechanism. The high reactivity of the benzyl trichlinates, relative to benzyl arene-



(7)

sulfinates is again explained by the high leaving group ability of the $Cl_3CSO_2^-$ anion. Interestingly, and similar to the higher solvolytic reactivity, the benzyl trichlinates also rearrange to sulfones several times faster than the corresponding triflinates.[12b] This observation is of considerable significance since it offers the synthetic chemist a convenient route to the synthesis of trichloromethyl sulfones which may be

used as substitutes to the less accessible and more expensive trifluoro analogues (triflones). The latter are of special interest for the organic chemist in the variety of ways they facilitate carbon-carbon bond construction, a subject extensively investigated and reviewed by Hendrickson.[34]

Finally, the results described above are supported not only by our own results on the rearrangement of the benzyl triflinates, but also by the independent observations made by Hendrickson and Skipper[35] on the isomerization of a number of primary triflinates to the corresponding triflones. For example, heptyl triflinate rearranged to heptyl triflone on heating at 145° in HMPA for 4 hr in 87% yield. This result is in sharp contrast to the complete absence of rearrangement of simple primary arenesulfinates.

EXPERIMENTAL

M.ps and b.ps are uncorrected. IR spectra were recorded on Perkin Elmer Grating Infrared Spectrometer Model 457, NMR spectra were recorded on Varian HA 100 NMR Spectrometer, using TMS as internal standard, and mass spectra on Perkin Elmer Hitachi RMU6 Mass Spectrometer. Microanalyses were performed by the Mycroanalytical Laboratory, at the Weizmann Institute of Science, Rehovoth.

Solvents, reagents and materials. Ethanol was dried by the method of Lund and Bjerrum, as described by Fieser.[36a] X% ethanol-water means a soln prepared by mixing X volumes of ethanol with 100-X volumes of boiled and distilled water at 25°. The same pipette was used for measuring all volumes. Acetonitrile and nitromethane were purified by the method described by Smith, *et al.*[36c] 2,6-Lutidine was purified by refluxing with, and distillation from, barium oxide (b.p. 140-142°). Pyridine was purified by the same method (b.p. 115-116°). Benzyl *p*-chloro- and *p*-methylbenzyl trichloromethanesulfenates were prepared from the appropriate alcohol and Cl_3CSCl as previously described.[16,18] *p*-Nitrobenzyl trichloromethanesulfenate was prepared by reaction of the corresponding alcohol with Cl_3CSCl using the same method as for the other esters, except that the reaction was conducted at room temperature and stirring was continued for three days (yield 65%). IR (neat) 850, 945, 965, 1340 and 1515 cm^{-1}. ^1H NMR ($CDCl_3$) δ 8.24 (d, 2H), 7.54 (d, 2H), 5.4 (s, 2H).

Preparation of the sulfinates.

Benzyl trichloromethanesulfinate. To a soln of 10.0g (0.039 mole of benzyl trichloromethanesulfenate[18] in 50 ml of dry methylene chloride cooled in an ice-water bath, was gradually added a solution of 11.2 g (0.056 mole) of 80% MCPBA in 100 ml of dry CH_2Cl_2 during 1hr, and with continuous magnetic stirring. A white precipitate was observed during the addition. The cooling bath was removed and stirring of the reaction mixture was continued for another hour at room temp, followed by addition of 250 ml of ether and consecutive washings with several portions of 100 ml of 5% KI, saturated $Na_2S_2O_3$, 5% $NaHCO_3$ and water. The KI washings result in deep violet coloration of both organic and aqueous phases due to reduction of the excess peracid present. On removal of the solvents after drying ($MgSO_4$), the product was obtained as a white solid and crystallized from pentane as white needles (10.5g, 98% yield). Mp 45.5 - 46.0°, IR ($CHCl_3$) 901, 935 and 1180 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.32 (s, 5H), 5.14 (d, J=12Hz, 1H), 5.36 (d, J=12Hz, 1H). The two benzylic methylene protons of this ester are diastereotopic[37] due to the proximal asymmetric S atom, and are very useful

for identification of such sulfinates in general. Calcd. for $C_8H_7O_2SCl_3$; C, 35,12; H, 2.58; S, 11.72; Cl, 38.88. Found: C, 35, 22; H, 2.57; S, 11.86; Cl, 38.64.

p-Chlorobenzyl trichloromethanesulfinate was prepared by oxidation of the corresponding sulfenate[15] with MCPBA as described for the unsubstituted trichlinate ester, except that stirring of the reaction mixture was continued for 90 min at 0° and 30 min at room temp (yield 97%). Mp 56.0-56.5°, IR ($CHCl_3$) 900, 950 and 11.70 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.32 (s, 4H), 5.16 (d, J=12Hz, 1H), 5.40 (d, J=12Hz, 1H). Calcd. for $C_8H_6O_2SCl_4$; C, 31.19; H, 1.96; S, 10.41; Cl,46.04. Found: C, 31.20;H, 1.99; S, 10.50; Cl, 45.77

p-Methylbenzyl trichloromethanesulfinate was prepared by oxidation of *p*-methylbenzyl trichloromethanesulfenate[15] with MCPBA as described for the unsubstituted ester. The product was obtained as a white crystalline material in 97% yield. but should be stored in the cold. preferably in CH_2Cl_2 soln to avoid decompn. Mp 57.0-57.5°, characteristic IR absorption ($CHCl_3$) at 900, 950 and 1170 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.22 (m, 4H) 5.13 (d, J=12Hz, 1H), 5.37 (d, J=12Hz, 1H), 2.36 (s, 3H).

p-Nitrobenzyl trichloromethanesulfinate was prepared by oxidation of the *p*-nitrobenzyl trichloromethanesulfenate with MCPBA as described for the unsubstituted ester, with the exception that stirring was continued for 90 min at 0° and 120 min at 25°, and the product was purified several times with active charcoal. The product was then crystallized from pentane as light yellowish crystals in 90% yield. Mp 49.0-49.5°, characteristic IR absorption ($CHCl_3$) at 900, 950 and 1180 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.26 (d, 2H) 7.58 (d, 2H), 5.30 (d, J=12Hz, 1H), 5.54 (d, J=12Hz, 1H). Calcd. for $C_8H_6O_4Cl_3NS$: C, 30.16; H, 1.90; S, 10.06; Cl, 33.39; N, 4.40. Found: C, 30.30; H, 1.89; S, 10.18; Cl. 33.55; N. 4.42.

Rearrangement of Sulfinates to Sulfones.

(a) A soln of 1,000 mg (3.66 mmole) of benzyl trichlinate and 780 mg (7.3 mmole) of 2,6-lutidine in 50 ml of freshly dried and distilled acetonitrile was heated in a sealed tube in a constant temp. bath at 100° for 4.5 hr. After cooling to room temp, the product was extracted with 150 ml of ether and washed 3 times with 100 ml portions of 1% HCl and 3 times with 100 ml of water. After drying of the ether layer over anhydrous $MgSO_4$ and evaporation of the solvent. the product (750 mg. 75% yield) was obtained as a yellowish oil which was crystallized from petroleum ether (60°-80°) as white long needles. Mp 101-102°, and identified as benzyl trichloromethyl sulfone by its spectral data: IR ($CHCl_3$) 1350(s), 1125 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.42 (s, 5H), 4.57 (s, 2H). (b). A soln of 500 mg (1.73 mmole) of *p*-methylbenzyl trichlinate and 380 mg (3.56 mmole) of 2,6-lutidine in 30 ml of freshly dried and distilled acetonitrile was heated in a sealed ampoule in a constant temperature bath at 100° for 4 hr. Isolation of the product as described for the benzyl sulfone afforded 390 mg (78% yield) of a yellowish solid which was crystallized from petroleum ether and identified as *p*-methyl trichloromethyl sulfone by its spectral data: IR ($CHCl_3$) 1355 (s), 1160 (s) cm^{-1}; ^1H NMR ($CDCl_3$) 7.26 (m, 4H), 4.72 (s, 2H). 2.35 (s, 3H). Mp 139-140°.

Solvolysis of trichloromethanesulfinates.

Solutions of each one of the four esters benzyl, *p*-nitro-, *p*-chloro- and *p*-methylbenzyl trichlinates (~0.05M) in anhydrous ethanol or methanol. in the presence of 2,6-lutidine (~0.15M) were kept in a constant temperature bath at 32° for 3 days, except the first ester which was kept for 10 days. The alcoholysis product was extracted with pentane in each case. followed by several washings with 1% HCl. water. and drying of the

organic layer over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was weighed and identified by its NMR spectrum. In the case of the *p*-substituted benzyl ethyl ethers the NMR spectra could be compared with those published in the literature.[30] For the identification of ethyl benzyl ether, we prepared this compound by reaction of sodium ethoxide with benzyl chloride, and characterized it (yield 60%): Bp 186°. ^1H NMR (CCl_4) δ 7.2 (s, 5H), 4.4 (s, 2H), 3.44 (q, J=7Hz, 2H), 1.18 (t, J=7Hz, 3H).

The solvolysis of the trichlinate esters in aqueous ethanol solutions was performed in the same manner as described for their alcoholysis. Inspection of the NMR spectrum of the reaction products indicated the presence of both the appropriate benzyl alcohol and its ethyl ether. The ratio of benzyl alcohol to benzyl ethyl ether obtained in the solvolysis of benzyl trichlinate in 80% and 60% ethanol-water was determined by gas chromatography, using a flame detector Packard g.l.c. Model 873 gas chromatograph with an Autolab System IV integrator. A 2 m Carbowax 15% 20M on Chromosorb W Column at 150°, and a flow rate of helium of 20 ml/min were used, and the detector and inlet temperature were set at 180°. Under these conditions and injection of 5 μl samples the retention time of benzyl ethyl ether is 120 sec and of benzyl ethyl ether is 590 sec. The molar ratios of alcohol to ether are based on the averages of multiple injections from each reaction, using appropriate calibration measurements to determine the relation between the peak area ratios and molar ratios of known samples.

Kinetic measurements.

(a) *Solvolysis reaction.* Solutions of the appropriate ester (~0.04M) in the appropriate solvent, in the presence of 2,6-lutidine (~0.16M) acting as buffer, were prepared in a 50 ml volumetric flask and immersed in a 32° constant temperature bath. At different time intervals, 5 ml aliquots of the solution were removed by means of a pipette, diluted with 5 ml of distilled and boiled water, and titrated with a 0.02M solution of sodium ethoxide in ethanol at 0°, using phenolphthalein as indicator. The rate constants were calculated from the first order kinetic expression, $k=(2,303/t) \log (T_\infty-T_o/T_\infty-T_t)$. Errors were calculated by means of the least square method. All calculations and plots were obtained by means of an IBM 360/150 computer, using the APL language.

(b) *Rearrangement of benzyl trichlinate.* A typical procedure is described. A 500 mg quantity (1.83 mmole) of the ester, 391 mg (3.66 mmole) of 2,6-lutidine and 67.2 mg (0.437 mmole) of *p*-dimethoxybenzene. serving as standard, were weighed in a 50 ml volumetric flask, and dry acetonitrile was added to the mark. The solution was shaken and transferred to ampoules in 5 ml portions. After the ampoules were sealed and immersed in the constant temperature bath at 100°, they were removed at appropriate time intervals and quenched in an ice-water bath. Each sample was extracted with 50 ml of ether and after the usual washings, drying and removal of the solvent, the NMR spectrum of the residue in $CDCl_3$ using TMS as internal standard, was recorded. The rate constant was calculated from the first-order kinetic rate expression $k = (2.303/t) \log (a/a-x)$, where a represents the ratio of the signal area of the benzylic methylene protons of the ester (δ 5.26) to the peak area of the methyl protons of the *p*-dimethoxybenzene standard (δ 3.76), at t = o. while (a-x) is the same ratio after t seconds. The plot of log (a-x) *vs.* time gave a good straight line (r = 0.992). Errors were calculated by means of the least square method. All calculations and plots were obtained as described above.

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