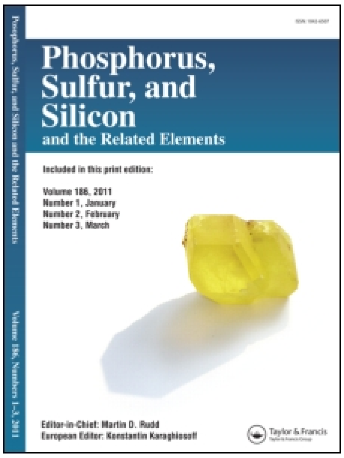

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Highly Reactive Sulfinates.II

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reverse. However, other available data[21] show that CF_3CO_2H is indeed several times stronger than CCl_3CO_2H, while the substituent constants of CF_3 and CCl_3 and their acid strengthening effects are almost identical. Assuming that this relation applies also for trihalomethanesulfinic acids, the observed resemblance between triflinates and trichlinates seems reasonable. In view of these findings one would predict that the practically unknown trichloromethanesulfonates may serve as good substitutes for the triflates. On the other hand, as judged by the results of a comparison between trifluoro- and trichloromethanesulfenates,[11] this prediction may not be exactly correct.

Finally, it has been reported[22] 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 homogeneous state. 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.[7a] In contrast, we have found that benzyl triflinate rearranged to benzyl trifluoromethyl sulfone[12,14] on heating in acetonitrile at 100° in the presence of 2,6-lutidine ($t_{\frac{1}{2}} \sim 3.5$ hr). The *p*-chloro- and *p*-methylbenzyl triflinates also rearranged to the corresponding sulfones under similar condition. The rearrangement to sulfone which clearly involves C–O bond cleavage is further evidence for the high reactivity of the triflinates. The rearrangement of the *p*-anisyl ester at 0° in CH_2Cl_2 may be indicative of an ionization mechanism for the reaction.

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[21] G. Kortüm, W. Vogel, and K. Andrusson, "Dissociation Constants of Organic Acids in Aqueous Solutions", IUPAC, Butterworths, London, 1961, p. 295; G. B. Barlin and D. D. Perrin in "Elucidation of Organic Structures by Physical Methods" Part I, 2nd Edition, Eds. K. W. Bentley and G. W. Kirby, Ch. IX. Wiley-Interscience, New York, N.Y., 1972, pp. 615, 638, 653.

[22] A. H. Wragg, J. S. McFadyen, and T. S. Stevens, *J. Chem. Soc.*, 3603 (1958).

The Reactivity of Trifluoro- *versus* Trichloromethanesulfenates

Sir:

Recently, we have reported that benzyl trichloromethanesulfenates show unique reactivity with respect to both solvolysis and rearrangement. For example, while *p*-anisyl trichloromethanesulfenate readily undergoes ethanolysis at room temperature with complete C–O bond cleavage by an ionization mechanism, the ethanolysis of the corresponding 2-nitrobenzenesulfenate proceeds at a similar rate only at 100°, involves exclusive S–O bond fission and may be explained by an S_N2-type mechanism.[1] Similarly, while the rearrangement of allyl[2a] and propargyl[2b] trichloromethanesulfenates to sulfoxides generally parallels that of the corresponding arenesulfenates,[3] and proceeds by a concerted [2,3]-sigmatropic mechanism, the rearrangement of benzyl trichloromethanesulfenates,[4] unlike that of benzyl arenesulfenates,[5] proceeds by an ionization mechanism.

It is well known[6] that under solvolytic conditions trifluoromethanesulfonates (triflates) are more reactive than the corresponding tosylates or halides by a factor of 10^5-10^7. The extremely high reactivity of these esters has found important synthetic[7] and mechanistic applications, especially in the generation and

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[1] S. Braverman and D. Reisman, *Tetrahedron Lett.*, 3563, (1973); *Tetrahedron*, **30**, 3891 (1974).

[2] (*a*) S. Braverman and Y. Stabinsky, *Chem. Comm.*, 270 (1967); *Israel J. Chem.*, **5**, 71 (1967); (*b*) *Ibid*, **5**, 125 (1967).

[3] R. Tang and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 2100 (1970) and previous references cited therein; G. Smith and C. J. M. Stirling, *J. Chem. Soc.* (C) 1530 (1971).

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[6] R. L. Hansen, *J. Org. Chem.*, **29**, 4322 (1965); A. Streitwiser Jr., C. L. Wilkins, and E. Kiehlmann, *J. Amer. Chem. Soc.*, **90**, 1598 (1968); T. M. Su, W. F. Sliwinsky, and P. v. R. Schleyer, *ibid*, **91**, 5386 (1969); S. A. Sherrod, R. G. Bergman, G. L. Gleicher, and D. G. Moris, *Ibid.*, **94**, 4615 (1972).

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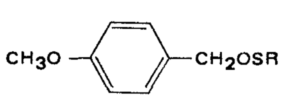
study of the unstable vinylic cations,[8] and more recently also in the generation of vinylidene carbenes.[9] In view of the significant role played by these esters, as well as the unusual results recorded with benzyl trichloromethanesulfenates we have decided to investigate the behavior of the corresponding trifluoromethanesulfenates (triflenates).

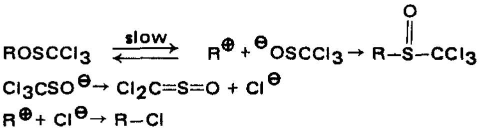
Although several alkyl triflenates have been prepared by Andreades[10] their chemical behavior has not been described in the literature as yet. We have synthesized *p*-anisyl triflenate (**1**)[11] as well as other triflenates, by reaction of the appropriate alcohol with CF_3SCl[12] in ether at 0° in the presence of triethylamine. In contrast to *p*-anisyl trichloromethanesulfenate (**2**) which rearranged quantitatively to the corresponding sulfoxide[4] on heating in hexane for 3 hours at 80°, ester **1** remained completely unchanged after heating in the same solvent for seven days at the reflux temperature or even after three days at 100°. Similarly, while ester **2** was converted almost completely to *p*-anisyl chloride and dichlorosulfine[4] on heating in acetonitrile for 2 hours at 80°, ester **1** remained unchanged after seven days of heating in the same solvent at the reflux temperature or after three days at 100°. Heating of **1** in other solvents such as chloroform or carbon tetrachloride under similar conditions had also no effect.



1 = R = CF_3
2 = R = CCl_3
3 = R = $2\text{-}NO_2C_6H_4\text{-}$

These results appeared quite surprising, especially because of our initial intention to use the trichloromethanesulfenate → chloride transformation as a model for a general and most convenient synthesis of organofluorides *via* the parallel transformation of triflenates. Assuming the ionization mechanism suggested for the rearrangement of benzyl trichloromethanesulfenates to sulfoxides and chlorides[4] is correct (Scheme I), and assuming that the published data[13] on the practical identity between the inductive effects of the trifluoro- and trichloromethyl groups, as reflected by their substituent constants and acid strengthening effects, are also correct, it is then difficult to explain the lack of rearrangement of **1**, since one would expect the leaving group ability of the trifluoromethanesulfenate anion to be quite comparable to its chloro analog. In support of the last statement one finds that the reactivity of trifluoromethanesulfinates[14] is quite similar to that of the corresponding trichloroesters,[15] with regard to both rearrangement to sulfone and solvolysis.

SCHEME I



$$ROSCCl_3 \underset{}{\overset{\text{slow}}{\rightleftarrows}} R^{\oplus} + {}^{\ominus}OSCCl_3 \rightarrow R{-}\overset{\overset{\large O}{\|}}{S}{-}CCl_3$$

$$Cl_3CSO^{\ominus} \rightarrow Cl_2C{=}S{=}O + Cl^{\ominus}$$

$$R^{\oplus} + Cl^{\ominus} \rightarrow R{-}Cl$$

However, one should point out that the lack of formation of *p*-anisyl fluoride when considered separately, does not by itself exclude an ionization mechanism, since the decomposition of the trifluoromethanesulfenate anion to difluorosulfine and fluorid anion may be more difficult than the analogous decomposition of the trichloromethanesulfenate anion, because of the much stronger carbon-fluoride bond. Furthermore, if the cyclic intramolecular mechanism suggested tentatively[16] for the rearrangement of *t*-but trichloromethanesulfenate to the corresponding chloride, or the mechanism suggested[17] for the solvolysis of aryl trichloromethanesulfenates involving initial ionization of the C–Cl bond, would also apply for the benzyl esters, the lack of rearrangement of the triflenates to fluorides would also appear reasonable. Although the evidence presented[1,4] seems to exclude these mechanisms, one cannot rule out completely a concerted heterolytic cleavage of C–O and C–Cl bonds, with accompanying formation of dichlorosulfine. Such a mechanism may again explain the lack of rearrangement of triflenates to fluorides but since it cannot apply to the sulfenate → sulfoxide rearrangement, which must involve only C–O bond cleavage, the original problem of explaining the un-

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[8] For reviews see M. Hanack, *Accounts Chem. Res.*, **3**, 209 (1972); G. Modena and U. Tonellato, *Adv. Phys. Org. Chem.*, **9**, 185 (1971); P. J. Stang, *Prog. Phys. Org. Chem.*, **10**, 205 (1973).

[9] P. J. Stang, M. G. Mangum, D. P. Fox, and P. Haak, *J. Amer. Chem. Soc.*, **96**, 4562 (1974); P. J. Stang, J. Davis, and D. P. Fox, *J. Chem. Soc., Chem. Comm.*, 17 (1975); P. J. Stang and M. G. Mangum, *J. Amer. Chem. Soc.*, **97**, 1459 (1975).

[10] S. Andreades, *C.A.*, **59**, 5024^b (1963).

[11] The compound gave satisfactory elemental analysis as well as nmr, ir and mass spectral data in accord with the assigned structure.

[13] G. B. Barlin and D. D. Perrin in "Elucidation of Organic Structures by Physical Methods", Part I, 2nd Edition, Eds. K. W. Bentley and G. W. Kirby, Ch. IX., Wiley-Interscience, New York, N.Y., 1972, pp. 615, 638, 653.

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expected low leaving group ability of $CF_3SO^{\ominus}$ remains unsolved.

In view of the surprising results on the attempted rearrangement of **1**, we decided to investigate the solvolysis of this ester under conditions similar to those of **2**. In contrast to the last compound, which undergoes facile ethanolysis with complete C–O bond cleavage,[1] the ethanolysis of ester **1** at 0°, involves complete S–O bond fission as evidenced by formation of ethyl triflenate and *p*-anisyl alcohol.

$$1 + EtOH \xrightarrow[0^\circ]{KOA_c} p\text{-}CH_3OC_6H_4CH_2OH + EtOSCF_3$$

Inspection of the kinetic data presented in the Table indicates that the reaction of **1** was second-order, first-order with respect to each, ester and added base.

TABLE I

Summary of Solvolysis Rate Constants[a] of *p*-Anisyl Sulfenates

Sulfenate	Solvent	Temp °C	[KOAc], M	10^4k_1 sec^{-1}	10^3k_1/[Base] $l\ mol^{-1}\ sec^{-1}$
1[b]	EtOH	0	0.0400	2.3	5.85
	EtOH	0	0.0606	3.7	6.00
	EtOH	0	0.0830	5.4	6.40
2[c]	MeOH	0	0.1998	0.23	–
3[d]	EtOH	100	0.0499	0.67	1.34

[a] Determined by nmr.
[b] [Ester] = 0.040M.
[c] [Ester] = 0.05M (ref. 1).
[d] [Ester] = 0.0275M.
Data taken from ref. 1.

These results are consistent with an S_N2-type mechanism involving nucleophilic displacement on sulfur by the acetate or lyate ion to yield a reactive intermediate or final product, respectively. This interpretation parallels that suggested for the solvolysis of *p*-anisyl 2-nitrobenzenesulfenate[1] (**3**) and of related systems.[18]

The contrast between the solvolytic behavior of esters **1** and **2** is consistent with the observation on the lack of rearrangement of **1** to sulfoxide and fluoride, and provides further support of the conclusion that the $CF_3SO^{\ominus}$ is a poorer leaving group than $CCl_3SO^{\ominus}$. Because of the absence or extreme sluggishness of the ionization of **1**, the alternative displacement at sulfur can take place. This process is expected to proceed much faster with ester **1** than with **2**, due to the greater steric hindrance caused by the CCl_3 group to attack at sulfur.

Finally, a comparison between the rates of the acetate-catalyzed ethanolysis of esters **1** and **3**, which proceed by the same mechanism, indicates that the first ester reacts several times faster at 0° than the second ester at 100°. This great rate enhancement, which is of similar magnitude to that observed in the triflate/arenesulfonate[6] and triflinate/arenesulfinate[14] series may be used as evidence for the inductive effect of the trifluoromethyl group, which for some unknown reason is able to influence sulfur-oxygen but not carbon-oxygen bond fission in sulfenate esters.

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[18] e.g. D. Darwish and J. Noreyko, *Can. J. Chem.*, **43**, 1366 (1965); D. R. Hogg and J. Stewart, *J. Chem. Soc., Perkin II*, 43 (1974).