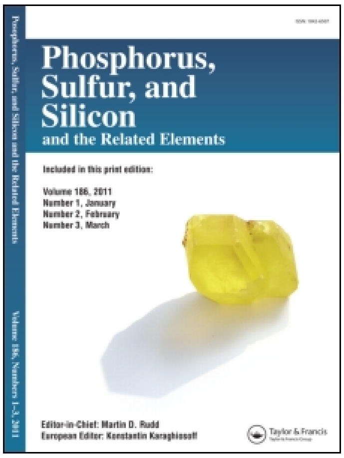


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Highly Reactive Sulfinates. II[1]. The Solvolysis and Rearrangement of Benzyl Trifluoromethanesulfinates

To cite this Article (1976) 'Highly Reactive Sulfinates. II[1]. The Solvolysis and Rearrangement of Benzyl Trifluoromethanesulfinates', Phosphorus, Sulfur, and Silicon and the Related Elements, 2: 1, 213 — 215

To link to this Article: DOI: 10.1080/03086647608078952

URL: http://dx.doi.org/10.1080/03086647608078952

Phosphorus and Sulfur
1976, Vol. 2, pp. 213-217

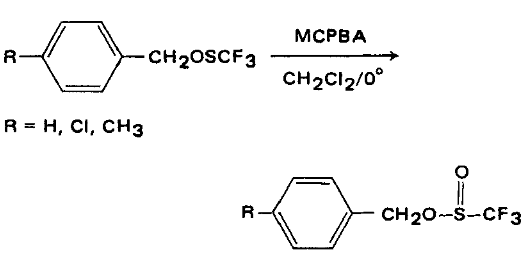
Communications to the Editor

Highly Reactive Sulfinates. II[1]. The Solvolysis and Rearrangement of Benzyl Trifluoromethanesulfinates

Sir:

In recent years considerable attention has been focused on the high reactivity of trifluoromethanesulfonates (triflates) in various substitution reactions. It is well known[2] that under solvolytic conditions these esters are more reactive than the corresponding tosylates or halides by a factor of 10^5-10^7. The triflate anion has therefore been considered as the most effective leaving group[3]. In accord with this observation, alkyl triflates have been reported as the most powerful alkylating agents of their type,[4] while vinyl triflates have been of immense value in the generation and study of the unstable vinylic cations[5] and more recently also in the generation of vinylidene carbenes.[6]

In view of the significant role played by triflates in mechanistic studies, and as a consequence of our interest in the chemistry of sulfinates in general[7] and trihalomethanesulfinates in particular,[1] we have undertaken an investigation on the reactivity of trifluoromethanesulfinates (triflinates).[8] Although the preparation of several simple alkyl triflinates has recently been described in the literature,[9] and although the ability of the triflinate anion as an effective leaving group has been suggested by the study of Hendrickson and coworkers on triflamides,[10] the chemical behavior of such esters has apparently never been reported. We have synthesized benzyl, *p*-chloro, and *p*-methybenzyl triflinates by a very convenient method, oxidation of the appropriate sulfenate ester[11] with *m*-chloroperbenzoic acid in methylene chloride, at 0° (eq 1).



(1)

All the esters prepared[12] were obtained in almost quantitative yield. It is interesting to note that further oxidation to the sulfonate does not take place even in the presence of an excess of oxidizing agent at room 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,[13] as well as with reports that benzyl trifluoro-[14] and trichloromethyl[15] sulfides can be oxidized to the corresponding sulfones. It is also of interest that the *p*-methoxybenzyl (*p*-anisyl) triflinate could not be obtained by this method. Rearrangement to the corresponding sulfone took place under the normal reaction conditions. These observations are analogous to those reported for the trichloromethanesulfinates.[1]

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[1] For part I see S. Braverman and Y. Duar, *Tetrahedron Lett.*, 343 (1975).

[2] R. L. Hansen, *J. Org. Chem.*, **29**, 4322 (1965); A. Streitwieser, Jr., C. L. Wilkins, and E. Kiehlmann, *J. Am. 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); P. J. Stang and R. H. Summerville, *ibid.*, **91**, 4600 (1969).

[3] Recently, the "nonaflate" anion was reported as a better leaving group than the triflate anion by a factor of about 2: L. R. Subramanian and M. Hanack, *Chem. Ber.*, **105**, 1465 (1972).

[4] J. Burdon and V. C. R. McLoughlin, *Tetrahedron*, **21**, 1 (1965).

[5] 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); see also, R. H. Summerville and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **96**, 1110 (1974).

[6] P. J. Stang, M. G. Mangum, D. P. Fox, and P. Haak, *J. Am. Chem. Soc.*, **96**, 4562 (1974).

[7] e.g. (*a*) S. Braverman and S. Steiner, *Israel J. Chem.*, **5**, 267 (1967), (*b*) S. Braverman, *Int. J. Sulfur Chem. Part C*, **6**, 149 (1971), (*c*) S. Braverman and T. Globerman, *Tetrahedron*, **30**, 3873 (1974), (*d*) S. Braverman and H. Mechoulam, *ibid.*, **30**, 3883 (1974).

[8] This term mentioned in ref. 10*a* for the CF_3SO_2 anion is here adopted for the ester.

[9] D. T. Sauer and J. M. Shreeve, *Inorg. Chem.*, **10**, 358 (1971).

[10] (*a*) J. B. Hendrickson, R. Bergeron, A. Giga, and D. Sternbach, *J. Am. Chem. Soc.*, **95**, 3412 (1973), (*b*) J. B. Hendrickson and R. Bergeron, *Tetrahedron Lett.*, 4607 (1973).

[11] S. Braverman and H. Manor, following communication.

[12] Satisfactory ir, ^{1}H-nmr, ms spectra and elemental analyses were obtained for all new compounds.

[13] R. M. Coates and J. P. Chen, *Tetrahedron Lett.*, 2705 (1969).

[14] V. V. Orda, L. M. Yagupol'skii, V. F. Bystrov, and A. U. Stepanyants, *Zh. Obshch. Khim.*, **35**, 1628 (1965); *C.A.*, **63**, 17861e (1965).

[15] L. A. Paquette and L. S. Wittenbrook, *J. Am. Chem. Soc.*, **90**, 6790 (1968).

In order to test the reactivity of triflinates we have investigated their behavior under solvolytic conditions. We have found that all the benzyl esters prepared undergo facile ethanolysis with exclusive C–O bond fission as evidenced by formation of the corresponding ethyl ether and sulfinic acid (eq 2).

$$ArCH_2OS(O)CF_3 + EtOH \rightarrow ArCH_2OEt + CF_3SO_2H \qquad (2)$$

In sharp contrast with these results, benzyl 2,6-dimethylbenzenesulfinate has been reported[7a] to undergo ethanolysis by complete S–O bond cleavage and at a much slower rate even at 90° ($k = 2 \times 10^{-7}$ sec^{-1}). A comparison between the rate of ethanolysis of this ester with that of the corresponding triflinate (see Table), taking into account the differences in bond cleavage and temperature, indicates that the reactivity of the triflinate is higher by some six powers of ten. This factor is similar to that found for the triflate/tosylate ratio.[2] Furthermore, the reactivity of benzyl triflinates, somewhat surpassed by the analogous trichloromethanesulfinates is of the same order of magnitude as that of the corresponding tosylates,[16] as can be seen from the data shown in the Table.

TABLE I

Rate Constants for the Solvolysis[a] of Benzyl Trihalomethanesulfinates at 32°

		10^5k, sec^{-1}		
Benzyl Ester	Solvent	*p*-Cl	*p*-H	*p*-Me
Triflinate	EtOH	0.92	1.04	6.56
	MeOH	1.84	3.21	23.71
	80% EtOH	2.67	4.34	88.19
Trichlinate[b]	EtOH	1.27	3.05	12.53
	MeOH	–	7.14	42.50
	80% EtOH	–	9.25	121.30
Tosylate[c]	EtOH		5.33	
	MeOH		16.70	
	80% EtOH		32.40	

[a] In the presence of 2,6-lutidine, acting as buffer.

[b] Trichloromethanesulfinate. Data taken from ref. 1.

[c] At 25°. Data taken from ref. 16.

The unusual high reactivity of the triflinates may be attributed to the high acid strength of CF_3SO_2H, and the consequent high leaving group ability of its anion. On the other hand, the lack of rearrangement to sulfone during solvolysis as normally observed with arenesulfinates[7a,c] may reflect the reduced nucleophilicity of the sulfur atom in this case. The same explanation may also be advanced for the lack of triflinate to triflate oxidation.

Further evidence for the mechanism of solvolysis was obtained from a kinetic study of the reaction. A summary of first-order rate constants for the solvolysis of benzyl triflinates in various solvents is presented in the Table. In order to analyze the kinetic results with respect to the substituent and solvent effects, we have examined the Hammett and Winstein correlations. The rates of solvolysis in methanol and 80% ethanol-water correlate quite well with σ. Although the size of $\rho = -2.69$ for the first solvent is smaller than usually observed with ionizing systems, it compares favorably with the value recorded for the solvolysis of other benzylic systems, such as chlorides and sulfonates.[17] On the other hand, the size of $\rho = -3.76$, obtained for 80% ethanol is suggestive of an ionization mechanism.

Good linear correlations were found when log *k* for solvolysis of *p*-chloro- and *p*-methylbenzyl triflinates, using the solvents mentioned in the Table at 32°, were plotted against log *k* for ionization of *p*-methoxyneophyl tosylate[18] in the same solvents at 25°. The slope (*a* value) of the straight line of 0.52 for the *p*-chlorobenzyl ester indicates a relatively low sensitivity to variation in solvent ionizing power. It is therefore suggested that this ester, as well as the unsubstituted one react by both S_N1 and S_N2 mechanisms. On the other hand a slope of 1.2 was obtained for the *p*-methylbenzyl triflinate, similar to the values reported for other ionizing systems.[1,7a,c,19] Consequently it is suggested that in this case, capable of developing a more stable carbonium ion, complete ionization takes place.

Inspection of the data shown in the Table indicates a close resemblance between the reactivity of the trifluoro- and trichloromethanesulfinates. Although it has been stated[20] that trifluoroacetic acid is a stronger acid than trichloroacetic acid, the given pK_a values, 0.3 and 0.08 respectively[20] point to the

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[16] S. Winstein, E. Grunwald, and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951).

[17] R. W. Alder, R. Baker, and J. M. Brown in "Mechanism in Organic Chemistry", Wiley, London, 1971, p. 36; G. S. Hammond, C. E. Reeder, F. T. Fang, and J. M. Kochi, *J. Am. Chem. Soc.*, **80**, 568 (1958).

[18] S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Am. Chem. Soc.*, **83**, 618 (1961).

[19] S. Braverman and B. Sredni, *Tetrahedron*, **30**, 2379 (1974); S. Braverman and D. Reisman, *ibid.*, **30**, 3891 (1974).

[20] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Wiley, New York, N.Y., 1967, pp. 1194, 1219.

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.

Acknowledgment

One of us (H.M.) thanks the National Council for Research and Development for the award of a scholarship.

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Received June 16, 1975

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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).

[4] S. Braverman and B. Sredni, *Tetrahedron*, **30**, 2379 (1974).

[5] D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *J. Amer. Chem. Soc.*, **88**, 3138 (1966); E. G. Miller, D. R. Rayner, H. J. Thomas, and K. Mislow, *Ibid.*, **90**, 4861 (1968).

[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).

[7] J. Burdon and V. C. R. McLoughlin, *Tetrahedron*, **21**, 1 (1965).