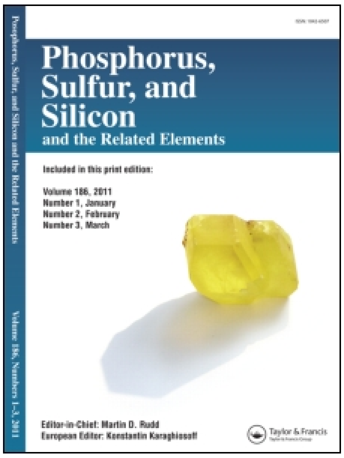

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Dan Grinstein[a]; Samuel Braverman[a]; Hugo E. Gottlieb[a]
[a] Department of Chemistry, Bar-Ilan University, Ramat Gan, Israel

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NMR IDENTIFICATION OF TRICHLOROMETHYL SULFOXIDES, SULFONES AND THEIR PRECURSORS

DAN GRINSTEIN, SAMUEL BRAVERMAN and HUGO E. GOTTLIEB*

Department of Chemistry, Bar-Ilan University, Ramat Gan 52900, Israel

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The unusual chemistry of trichloromethylsulfenates, sulfinates, sulfoxides and sulfones is briefly reviewed. ^{13}C NMR chemical shifts for both Cα (the carbon directly bound to the functional group) and the CCl_3 group are reported, as a useful diagnostic tool for determining the nature of the sulfur-containing moiety.

Keywords: sulfenates; sulfinates; sulfoxides; sulfones; Trichloromethyl group; NMR

Trichloromethanesulfenyl chloride was the first sulfenyl chloride to be prepared by Rathke,[1] as early as 1870, by reacting carbon disulfide with chlorine. This compound, also known as perchloromethyl mercaptan or PCMM, is the most stable sulfenyl chloride. For example, one can use even steam distillation for its purification. Hydrolysis takes place only in acidic or basic aqueous solutions.[2,3] Unlike other sulfenyl chlorides, this compound has a variety of synthetic applications of both academic and industrial interest especially in the area of pesticides.

Due to the powerful electronic withdrawing ability of the trichloromethyl group which is similar to the well-known trifluoromethyl group, the properties of Cl_3CSCl and its derivatives are rather unique. In our studies on the rearrangement and solvolysis of various organosulfur compounds during the past three decades, Cl_3CSCl and its derivatives have played a central role.[4] We have thus shown that allylic trichloromethanesulfenates exhibit enhanced thermal stability with regard to the [2,3]-sigmatropic rearrangement to allylic sulfoxides and that in certain cases such as the

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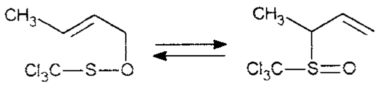
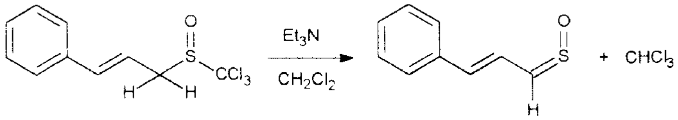
* *Corresponding author.*

cinnamyl ester the rearrangement occurs without allylic shift.[5] The study of the allylic trichloromethanesulfenates was thus essential in the discovery of the now famous reversible allylic sulfenate-sulfoxide interconversion, also known as the Mislow-Braverman-Evans rearrangement (eq.1).[6]

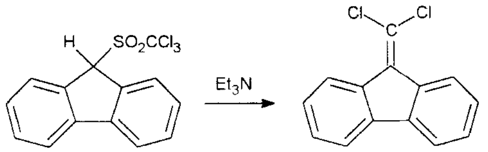


Our subsequent discovery of the propargylic trichloromethanesulfenate to allenylic trichloromethyl sulfoxide rearrangement was just an obvious extension.[7] Another example of the effect of the CCl_3 group was nicely demonstrated in the case of the benzylic sulfenates.[8] Thus, unlike benzylic arenesulfenates which undergo rearrangement to sulfoxide only under drastic conditions, the thermal rearrangement of benzylic trichloromethanesulfenates proceeds readily in highly nonpolar solvents such as hexane by an ionization mechanism. Undoubtedly, this may be attributed to the relative high acid strength of Cl_3CSOH, and the consequent high leaving group ability of its anion as compared to sulfenate anions in general. The use of more polar solvents such as acetonitrile or even CH_2Cl_2 lead to the formation of benzylic chlorides and dichlorosulfine due to dissociation of the Cl_3CSO anion and recombination of the generated chloride ion with the initial carbocation. The reactivity of benzyl trichloromethanesulfenates with regards to solvolysis is also unique. In sharp contrast to the benzyl arenesulfenates which undergo solvolysis by sulfur-oxygen bond scission, under drastic conditions, the corresponding trichloromethanesulfenates undergo solvolysis at room temperature with carbon-oxygen bond scission by an ionization mechanism.[9] More recently, we have shown that both allylic and benzylic trichloromethyl sulfoxides undergo a facile and unexpected β-elimination of chloroform and afford mono and disubstituted sulfines (eq. 2).[10]



(2)

Benzyl trichloromethanesulfinates are easily obtained by oxidation of the corresponding sulfenates[11] or by a modified Sharpless procedure.[12] Their behavior with regard to solvolysis and rearrangement parallels the behavior of the corresponding sulfenates, and represent the most reactive sulfinates reported to date with respect to both reactions. Their solvolytic reactivity is quite similar to the corresponding tosylates, and some 6 orders of magnitude faster than the equivalent benzyl arenesulfinates. The rearrangement of these esters affords the corresponding sulfones which can be used as excellent substrates to the well known but much more expensive trifluoromethyl sulfones.[13] An unusually facile Ramberg-Bäcklund rearrangement of these sulfones has recently been observed (eq. 3). [14]



(3)

The brief survey presented above demonstrates the effect and utility of the trichloromethyl group substitution in the various organosulfur functionalities described. The low price of the Cl_3CSCl on the one hand and the similar inductive effect of the trichloro and trifluoromethyl groups should provide a further incentive for the use of these compounds. In the course of this work, we have often been faced with the identification of the sulfur-containing moiety. We found that the chemical shift of the carbon directly connected to the substituent, and also that of the $^{13}CCl_3$ had the best diagnostic value for that purpose. In this paper, we provide a compilation of such data, which may be of use as future reference.

RESULTS AND DISCUSSION

We have obtained carbon spectra for a variety of trichloromethylsulfenates, sulfinates, sulfoxides and sulfones. In the Table we show, for a few representative compounds, the chemical shifts for C_α (the carbon directly bound to the functional group) and for the trichloromethyl carbon; we also provide averages for the chemical shifts of the CCl_3. We see that the latter are quite insensitive to the nature of the rest of the molecule; the shift ranges are narrow enough to provide unambiguous assignment of the oxidation state of the sulfur function. The deshielding of the CCl_3 group when the sulfenate is oxidized to a sulfinate is reminiscent of the deshielding of carbons α to a carbonyl group, as compared to the related hydrocarbon. We should point out, however, that this facile analogy does not hold for the sulfoxide/sulfone pair, in which the second oxygen causes shielding.

TABLE ^{13}C chemical shifts

R	alcohol	sulfenate		sulfinate		sulfoxide		sulfone	
	C_α	C_α	CCl_3	C_α	CCl_3	C_α	CCl_3	C_α	CCl_3
allyl	63.65			69.38	108.46	56.26	106.45	50.89	103.33
cinnamyl	63.50	82.28	100.47			56.59	106.67	51.59	103.60
p-methoxybenzyl	64.71	81.92	100.58			58.21	106.49	51.79	103.38
4,4′ dichlorobenzhydryl	74.78	91.00	100.21	83.87	108.61			68.48	104.32
9-fluorenyl	75.10	89.44	100.62	81.83	108.58	67.92	107.82	69.62	104.21
2-propenyl						126.29	107.22	120.52	103.73
allenyl						97.05	107.90	90.39	104.59
average± st.dev.			100.6±0.3		108.6±0.1		107.1±0.7		104.0±0.4
n[a]			13		6		27		14

[a] Number of compounds examined.

The chemical shifts of the α carbons also show definite patterns, if compared e.g. to the corresponding alcohols. Sulfenates and sulfinates are deshielded relative to the alcohol, with the former at considerably lower field. In contrasts in the sulfoxides and sulfones C_α is at higher field than the corresponding carbinol, as expected for a sulfur as opposed to an oxygen substituent. Again, the sulfones are surprisingly shielded relative to the corresponding sulfoxides (see previous paragraph), except for doubly benzylic methines such as fluorenyl or benzhydryl.

EXPERIMENTAL

^1H NMR and ^{13}C NMR spectra were recorded on Bruker AC-200, DPX-300 or DMX-600 spectrometers in either $CDCl_3$ or other deuterated solvents and using TMS as internal standard. Chemical shifts are reported in ppm units.

Acknowledgements

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References

[1] B. Rathke, *Chem. Ber.* **3,** 858 (1870).

[2] G. Sosnovski, *Chem. Rev.* **58,** 509 (1958).

[3] E. Kühle, *Synthesis,* 579 (1970); *id.,* 628 (1971); E. Kühle, *The Chemistry of the Sulfenic Acids* (Thieme, Stuttgart, 1973).

[4] (a) S. Braverman, *Rearrangements of Sulfones and Sulfoxides* in *The Chemistry of Sulfones and Sulfoxides* (S. Patai, Z. Rappoport and C. J. M. Stirling, eds., Wiley, New York, 1988), Chap. 13 and 14. (b) S. Braverman, *Rearrangements of Sulfenic Acids* in *The Chemistry of Sulfenic Acids* (S. Patai, ed., Wiley,Chichester, 1990), Chap. 8. (c) S. Braverman, *Rearraingements* in *The Chemistry of Sulfinic Acids* (S. Patai, ed., Wiley, Chichester, 1990), Chap. 11.

[5] S. Braverman and Y. Stabinsky, *J. Chem. Soc. Chem. Comm.* 270 (1967).

[6] A. Hassner and C. Stumer, *Organic Syntheses Based on Name Reactions and Unnamed Reactions* (Pergamon Press, Oxford, 1994), p. 266.

[7] S. Braverman and Y. Stabinsky, *Isr. J. Chem.* **5,** 125 (1967).

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

[9] S. Braverman and D. Reisman, *Tetrahedron* **30,** 3891 (1974).

[10] (a) S. Braverman, D. Grinstein and H.E. Gottlieb, *Tetrahedron Lett.* **35,** 953 (1994). (b) S. Braverman, D. Grinstein and H.E. Gottlieb, *Tetrahedron,* **53,** 13933 (1997).

[11] S. Braverman and Y. Duar, *Tetrahedron* **46,** 2975 (1990).

[12] (a) S. Braverman, D. Grinstein and Z. Lior, *Phosphorus, Sulfur and Silicon* **74,** 443 (1974). (b) J.M. Klunder and K.B. Sharpless, *J. Org. Chem.* **52,** 5298 (1987).

[13] J.B. Hendrickson, D.D. Sternbach and K.K. Bair, *Acc. Chem. Res.* **10,** 306 (1977).

[14] S. Braverman and Y. Zafrani, *ISOCS-16* (Merseburg, July 10–15, 1994), Abstracts p. 208.