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OF *α*-CHLOROALKYL ALKANETHIOSULFONATE ESTERS¹

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Abstract: Sulfines react with sulfinyl chlorides giving α -chloroalkyl alkanethiosulfonate esters and with thionyl chloride giving α -chloroalkanesulfenyl chlorides, both in good yields.

A standard method for the synthesis of sulfines involves the reaction of alkanesulfinyl chlorides with triethylamine (eq 1).³ We find that the reaction of *two equivalents* of alkanesulfinyl chlorides with *one equivalent* of triethylamine leads instead, cleanly and in good yield, to α -chloroalkyl alkanethiosulfonates, RCHClSSO₂CH₂R (eq 2). Illustrative of the procedure is the preparation of α -chloroethyl ethanethiosulfonate, CH₃CHClSSO₂CH₂CH₃ (1). Thus, a solution of

$$\operatorname{RCH}_2 S(0)C1 + \operatorname{Et}_3 N \longrightarrow \operatorname{RCH}^+ S^- 0 + \operatorname{Et}_3 N H^+ C1$$
(1)

$$2RCH_2 S(0)C1 + Et_3 N \longrightarrow RCHC1SSO_2 CH_2 R + Et_3 NH^{T} C1^{T}$$
(2)

0.165 mol of ethanesulfinyl chloride and 0.1 mol of triethylamine⁴ in 575 mL of CFCl₃ at -20° C was allowed to warm to 25° C overnight and the solution was filtered, concentrated in vacuo and the residue distilled affording 1 in 82% isolated yield.⁵ Additional examples of this new reaction are given in the Table.

We propose that these reactions involve as a key step nucleophilic attack by a sulfine on a sulfinyl chloride followed by intramolecular rearrangement as shown in eq 3. Precedence for this proposal includes thiosulfinate formation on reaction of certain sulfines with arenesulfenyl chlorides (eq 4)⁷ and thiosulfonate formation on reaction of thiirane S-oxide with ethanesulfinyl chloride (eq 5).⁸ In order to test the mechanism in eq 3 a freshly distilled sample of propanethial S-oxide (the onion lachrymatory factor⁹) was treated with methanesulfinyl chloride diluted with twice its volume of benzene. An immediate exothermic reaction occurred affording α -chloropropyl methanethiosulfonate ($\frac{5}{0}$) in 64% yield (eq 6), a result in accord with the mechanism proposed in eq 3. At this time it is not possible to choose between paths A or B, eq 3. The reaction noted in eq 6 significantly extends the scope of the chloroalkyl alkanethiosulfonate

synthesis permitting the inclusion of products derived in a selective manner from pairs of different sulfinyl chlorides. It should be noted that chlorinated thiosulfonates are of interest as bactericides and fungicides.¹⁰



$$Me_{3}SiCH_{2}C1 \xrightarrow{Li_{2}S_{2}} (Me_{3}SiCH_{2}S)_{2} \xrightarrow{Cl_{2}, Ac_{2}O} Me_{3}SiCH_{2}S(0)C1$$
(7)
THF, 78% (Me_{3}SiCH_{2}S)_{2} \xrightarrow{-35^{\circ}, 67\%} 6

In connection with our interest in silicon-containing organosulfur compounds,¹¹ we have prepared the previously unknown trimethylsilylmethanesulfinyl chloride (6) according to eq 7. Treatment of two equivalents of 6 with one equivalent of triethylamine gives the interesting functionalized thiosulfonate 4 (see Table).¹²,¹³ We have also examined the reaction of a sulfine with thionyl chloride. Ethanethial S-oxide reacts with one-half an equivalent of thionyl chloride in CFCl₂ solution affording in 52% isolated yield di- α -chloroethyldisulfide, presumably via the intermediacy of l-chloroethanesulfenyl chloride (eq 8). When cyclohexene was employed as the solvent in the reaction of ethanethial S-oxide with thionyl chloride there was isolated in 75% yield a substance identical to the addition product of authentic l-chloroethanesulfenyl chloride¹⁴ with cyclohexene (eq 8).

Apart from the transformation of eq 4 and an example of an O-alkylation of a sulfine by triethyloxonium fluoroborate, ¹⁵ little is known about the reactions of sulfines with electro-

philes. Our present work suggests that a variety of unusual structures may become available through interaction of sulfines with electrophilic partners.



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Entry	Starting Material	Product ^a	Isolated Yield
1	EtS(0)Cl	MeCHClSSO ₂ Et (1)	823 ^b
2	n-PrS(0)C1	EtCHC1SSO ₂ Pr (2)	79% ^b
3	$n-C_{12}H_{25}S(0)C1$	$n-C_{11}H_{23}CHCISSO_{2}-n-C_{12}H_{25}$ (3)	78% ^C
4	Me₃SiCH₂S(0)C1 (6) ∿	$Me_3 SiCHC1SSO_2 CH_2 SiMe_3$ (4)	62% ^C
5	EtCHSO/MeS(0)C1	EtCHC1SSO ₂ Me (5) \sim	64 % ^b
6	MeCHSO/SOC l ₂	MeCHClSSCHClMe ^d	52% ^b
7	MeCHSO/SOCl ₂ /cyclohexene	SCHC 1Me	75 <i>%</i> ^b

Table: Reaction of Sulfines with Sulfinyl Chlorides and Thionyl Chloride

a Spectroscopic data on new compounds 1-5 are given in Ref. 5. b Yield after distillation. c Heat sensitive material; could not be distilled. d Ref. 13.

References and Footnotes

- a) Presented at the 9th International Symposium on Organosulfur Chemistry, Riga, USSR, June, 1980. b) Part 8 of this series: E. Block, R.E. Penn, A.A. Bazzi, and D. Cremer, *Tetrahedron Lett.*, <u>22</u>, 29 (1981).
- 2. Address correspondence to this author at the State University of New York at Albany.
- a) W.A. Sheppard and J. Diekmann, J. Am. Chem. Soc., <u>86</u>, 1891 (1964).
 b) J. Strating, L. Thijs, and B. Zwanenburg, Rec. Trav. Chim. Pays-Bas, <u>83</u>, 631 (1964).
- 4. A 1.65:1 ratio of sulfinyl chloride to amine was found to give superior yields compared to a 2:1 ratio of reagents.
- 5. 1, bp 56°C/0.03 mm, IR (neat) 1325 (vs) and 1133 (vs) cm⁻¹ (SO₂), ¹H NMR (CDCl₃) δ 5.70 (q, J=6.8 Hz, 1H, CHCl), 3.52 (apparent d of q, 2H, CH₂SO₂), 1.96 (d, J=6.8 Hz, 3H, CH₃CHCl), 1.47 (t, J=7.3 Hz, 3H, CH₃CH₂), ¹³C NMR (CDCl₃) δ 64.28 (CHCl), 57.70 (CH₂SO₂), 26.17 (CH₃CHCl), 8.14 (CH₃CH₂SO₂), and MS m/e 188/190 ($\xi_{\rm H}$ H₃S₂O₂Cl, M⁺), 153 (M⁺-Cl).⁶ 2, bp 60°C/0.02 mm, IR (neat) 1320 (vs) and 1128 (vs) cm⁻¹ (SO₂), ¹H NMR (CDCl₃) δ 5.60 (t, CHCl), 3.48 (d of t, CH₂SO₂), 2.07 (m, 2CH₂), 1.12 (q, 2CH₃), ¹³C NMR (CDCl₃) $\delta_{\rm C}$ 70.71 (CHCl), 65.06 (CH₂SO₂), 32.60 (CH₂CHCl), 17.25 (CH₂CH₂SO₂), 12.52 (CH₃CH₂CHCl), 11.06 (CH₃CH₂SO₂), and MS m/e 188/190 (s, 2H₃, $\xi_{\rm SO}$, 1.25 (CH₃CH₂CHCl), 11.06 (CH₃CH₂SO₂), 1.25 (br, (CH₂)₁₉), 0.98 (br, 2CH₃), ¹³C NMR (CDCl₃) $\delta_{\rm C}$ 69.6 (CHCl), 63.60 (CH₂SO₂), 1.25 (br, (CH₂)₁₉), 0.98 (br, 2CH₃), ¹³C NMR (CDCl₃) $\delta_{\rm C}$ 69.6 (CHCl), 63.60 (CH₂SO₂), 31.97 (CH₂CHCl), 29.70, 29.39 (remaining CH₂), 14.13 (CH₃). 4, IR (neat) 1320 and 1125 cm⁻¹ (SO₂), ¹H NMR (CDCl₃) δ 5.17 (s, 1H, CHCl), 3.40 (s, 2H, CH₂SO₂), 0.30 (s, 27H), ¹³C NMR (CDCl₃) $\delta_{\rm C}$ 64.80 (CHCl), 59.0 (CH₂SO₂), -0.88 (Si(CH₃)₃), MS m/e 304/306 (C₈H₂₁Si₂So₂Cl, M⁺). 5, bp 35°C/0.001, IR (neat) 1345 and 1150 cm⁻¹ (SO₂), ¹H NMR (CDCl₃) $\delta_{\rm C}$ 70.86 (CHCl), 3.49 (s, CH₃SO₂), 2.16 (Q, CH₃CH₂), 1.16 (t, CH₃CH₂), ¹³C NMR (CDCl₃) $\delta_{\rm C}$ 70.86 (CHCl), 51.71 (CH₃SO₂), 2.21 (CH₂), 11.06 (CH₃CH₂), MS m/e 188/190 (C₄H₉So₂O₂Cl, M⁺).
- 6. A curious feature of the ¹H NMR spectrum of $CH_3 CHClSSO_2 CH_2 CH_3$ (1), namely the complexity of the CH_2 multiplet at $\delta 3.52$ despite the presence of a simple triplet at $\delta 1.47$ for the adjacent CH_3 group was clarified through LAOCON analysis. The observed spectrum could be simulated using calculated shifts of $\delta 3.52$ and 3.49 for the diastereotopic CH_2 protons, functioning as the AB part of an ABX₃ system, with J $_{AB}$ = 0.103 Hz, coupling with the CH_2 protons at $\delta 1.47$ with J $_{AX}$ = 7.331 Hz and J = 7.162 Hz.
- F. Klivenyi, G. Stajer, A.E. Szabo, and J. Pintye, Acta Chim. Acad. Sci. Hung., <u>75</u>, 177 (1973).
- 8. K. Kondo, A. Negishi, and G. Tsuchihashi, Tetrahedron Lett., 2743 (1969).
- 9. E. Block, R.E. Penn, and L.K. Revelle, J. Am. Chem. Soc., <u>101</u>, 2200 (1979); E. Block, L.K. Revelle, and A.A. Bazzi, *Tetrahedron Lett.*, <u>21</u>, 1277 (1980).
- S.S. Block, J.P. Weidner, and A. Walsh, Chem. Spec. Mfr. Ass., Proc. Annu. Meet., 1969 (Pub. 1970), 56, 117; Chem. Abstr. <u>73</u>, 65315h (1970).
- 11. See, for example E. Block and M. Aslam, Tetrahedron Lett., in press.
- 12. a) Previous preparation of (Me₃SiCH₂S)₂, Q.W. Decker and H.W. Post, J. Org. Chem., <u>25</u>, 249 (1960). b) Preparation of Li₂S₂/THF, J.A. Gladysz, V.K. Wong, and B.S. Jick, Tetrahedron, <u>35</u>, 2329 (1975).
- 13. Separate experiments established the intermediacy of (E,Z)-trimethylsilylmethanethial S-oxide in this reaction. Details of the chemistry and properties of this novel sulfine will be reported separately.
- 14. S.B. Tjan, J.C. Haakman, C.J. Teunis, and H.G. Peer, Tetrahedron, 28, 3489 (1972).
- 15. L. Carlsen and A. Holm, Acta Chem. Scand., <u>B30</u>, 277 (1976). (Received in USA 26 July 1982)