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β-CHLOROALKYL SULFIDES FROM Me_2S/ SO_2Cl_2/Me_2SO AND ALKENES

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Abstract. A novel method to prepare β-chloroalkyl sulfides from alkenes and Me_2S-SO_2Cl_2-Me_2SO is described, methanesulfenyl chloride being suggested as intermediate.

Halosulfonium salts are versatile intermediates that give rise to a number of transformations involving the sulfur atom and the α- or β- carbon atom;[1] they also show oxidant properties, illustrated by the dimethylchlorosulfonium chloride, known as Swern's reagent, which selectively oxidises primary and secondary alcohols to carbonyl derivatives.[2] Dialkylchlorosulfonium salts are usually prepared following two different routes, the first from sulfides and Cl_2[3] or SO_2Cl_2,[4] the other from $SOCl_2$ and sulfoxides.[4]

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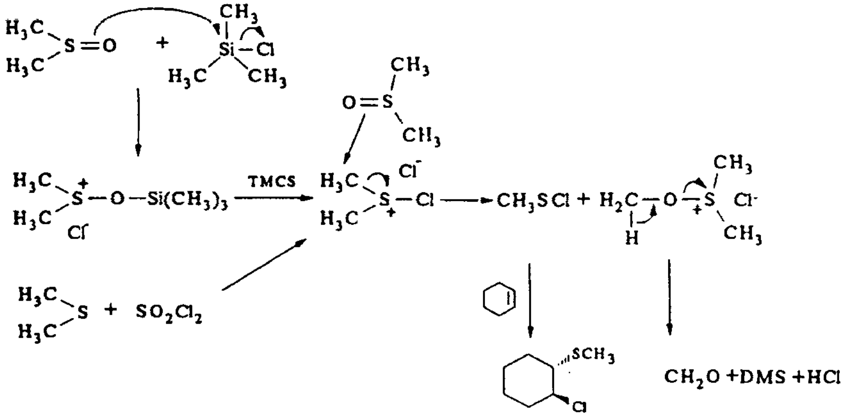
scheme 1

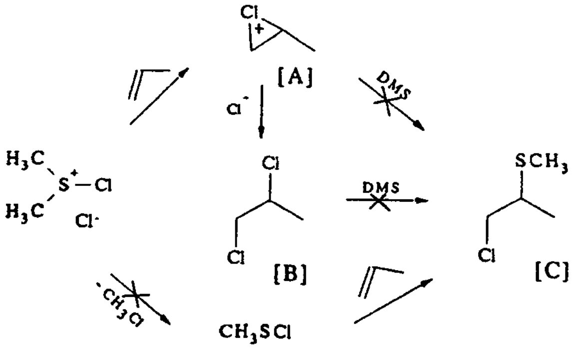


Previously, we reported that alkenes are easily transformed by dialkylsulfoxide-trimethylchlorosilane to β-chloroalkyl sulfides,[5] suggesting the intermediacy of sulfenyl chlorides produced by the dialkylsulfoxide attack upon a chlorosulfonium derivative (see scheme 1).

In a recent paper[6] on the preparation of β-chloroalkyl sulfides from alkenes and Me_2SO (DMSO) and $POCl_3$ or phenyl dichloro phosphate, the authors suggest the intermediacy of a β-chloroalkyl-dimethylsulfonium salt, but neglect the possible intervention of methanesulfenyl chloride.

Assuming that the pathway of scheme 1 is generally applicable for all the systems that give rise to a dialkylchlorosulfonium intermediate,[7] we coupled the Me_2S (DMS)-SO_2Cl_2 reagent with DMSO in the treatment of a series of alkenes.[8] As the table shows, very

scheme 2



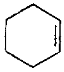
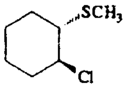
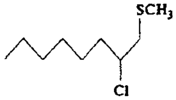
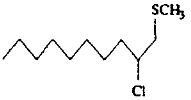
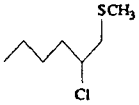
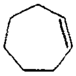
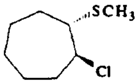
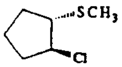
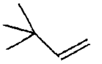
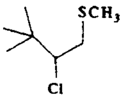
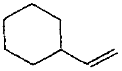
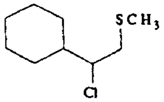
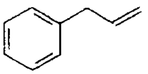
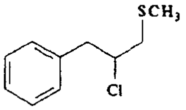
good yields of β-chloroalkyl sulfides, from a stereospecific trans addition are obtained.[9]

In the absence of DMSO, the main products are the dichlorides, with only traces (<1%) of sulfurated adducts. This observation excludes (see scheme 2) the possibility that the β-chloroalkyl sulfide [C] originates from a DMS attack on the halonium ion [A] or on the vicinal dichloride [B], and also from a regression of the dimethylchlorosulfonium salt.

The DMSO as a source of the thiomethylic moiety in the products is ruled out by the following experiments on 1-octene: on substituting diethylsulfide for DMS, the corresponding thioethyl adduct is obtained;[10] and, on employing DMSO-d_6, the isolated β-chloroalkyl sulfide is free of any deuteration.

All the observations may be accounted for by a methanesulfenyl chloride formation via DMSO attack on the halosulfonium intermediate (see scheme 1).

Table

Substrate	Product	Yield %	B.p./°C (mmHg)	δ($CDCl_3$)	(M^+)
		91	65-68^a (0.5)	1.20-2.50 (8H), 2.20 (3H,s), 2.75 (1H,m), 4.05 (1H,m).	164
		85^b	88-91 (1)	0.84 (3H,t), 1.10-1.90 (10H) 2.16 (3H,s), 2.85 (2H,m), 4.00 (1H,m).	194
		93	97-100 (0.3)	0.84 (3H,t), 1.10-1.90 (14H) 2.16 (3H,s), 2.85 (2H,m), 4.00 (1H,m).	222
		84^b	105-108 (2.5)	0.84 (3H,t), 1.10-1.90 (6H) 2.16 (3H,s), 2.85 (2H,m), 4.00 (1H,m).	166
		81	80-83 (0.5)	1.43-2.25 (10H), 2.14 (3H,s) 3.04 (1H,m), 4.31 (1H,m).	178
		86	51-54^c (0.5)	1.25-2.50 (6H), 2.14 (3H,s), 3.18 (1H,m), 4.23 (1H,m).	150
		94	100-103 (3)	1.01 (9H,s), 2.15 (3H,s), 2.77 (2H,m), 3.80 (1H,dd).	166
		93	121-124 (0.9)	1.00-2.00 (11H), 2.12 (3H,s), 2.80 (2H,m), 3.92 (1H,m).	192
		95	102-105 (0.6)	2.27 (3H,s), 2.90 (2H,m), 3.29 (2H,m), 4.30 (1H,m), 7.34 (5H,s).	200

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a) Lit. B.p. (15) 105°C, Beilstein 6, IV, 82; b) + 6-9 % of antiMarkovnikov adduct; c) Lit. B.p. (15.5) 80°C, Beilstein 6, IV, 18.

The exclusive trans-addition, and the preferred initial formation of anti-Markovnikov adducts, which gradually isomerize to the Markovnikov ones (data reported in the table refer to the equilibrium mixture),[11] agree with the expected behaviour of a sulfenyl chloride addition to olefins.[12]

DMSO intervention must occur as soon as the dialkylchlorosulfonium chloride is formed, since this intermediate tends to be transformed into chloromethyl methyl sulfide[13] through a Pummerer's rearrangement;[1,4] indeed, conversions are strongly decreased on delaying DMSO addition.

On submitting cyclopentene to the reported general procedure, a polymer is also produced in about 50% yield; this product, however, is not formed by starting from a more diluted reaction mixture. The polymer is a polysulfone and its formation is explained by a copolymerization of evolved SO_2 with the alkene, according to literature.[14]

The reaction of chlorodialkylsulfonium ion with sulfoxides to afford a sulfenyl chloride is therefore the key step of this type of transformation.[5] Other reagents systems can work through similar patterns: on treating, for example, 1-octene with DMSO-$SOCl_2$ (2:1) the corresponding β-chloroalkyl sulfide is obtained in 90% yield. DMSO and $POCl_3$ or phenyl dichlorophosphate,[6] therefore, very likely react through the same intermediates.

Experimental

General reaction procedure with DMSO-DMS-SO_2Cl_2. In a 25 ml three necked round bottom flask, fitted with a condenser and adapted with a $CaCl_2$ valve, CH_3CN (8 ml), DMSO (15 mmol) and DMS (15 mmol) are poured. The stirred mixture is cooled to -15°C and then SO_2Cl_2 (15 mmol), diluted with 2 ml of CH_3CN, is added in one minute from a dropping funnel. About two minutes later the olefin (10 mmol) is added, and the mixture heated to 70°C. The conversion and anti-Markovnikov to Markovnikov isomerization are monitored by GC. After about two hours, the mixture is poured in 10 ml of water and extracted with CH_2Cl_2 (2 x 10 ml). The organic phase is dried (Na_2SO_4) and then evaporated under vacuum (40 mmHg). The products are isolated and purified by distillation or chromatography on silica gel. They tend slowly to darken and to polymerize; these processes are retarded by cold storage (-25°C).

Preparative scale reaction. Starting from 1-octene (5.6 g, 50 mmol) and DMSO (5.85 g, 75 mmol)-DMS (4.65 g, 75 mmol)-SO_2Cl_2 (10.1 g, 75 mmol) in CH_3CN (50 ml), the corresponding β-chloroalkyl sulfides are obtained in 94% yield, the ratio between the Markovnikov and anti-Markovnikov product being 83:11.

Reaction procedure with DMSO-$SOCl_2$. In a round bottom flask, fitted with a condenser and a dropping funnel, CH_3CN (8 ml), DMSO (30 mmol) and 1-octene (10 mmol) are poured. The mixture is thermostatted at room temperature and $SOCl_2$ (15 mmol) is dropped in about 1 minute; the temperature is then increased to 70°C. Subsequent workup is as described above.

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Notes and References

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6) Liu, H. G. and Nyangulu, J. M., Tetrahedron Lett., 1988, 5467.

7) DMSO produces a chlorosulfonium intermediate from both $POCl_3$ and phenyl dichloro phosphate; Liu, H. G. and Nyangulu, J. M., Tetrahedron Lett., 1988, 3167; Liu, H. G. and Nyangulu, J. M., Tetrahedron Lett., 1989, 5097.

8) With DMSO-SO_2Cl_2 the β-chloroalkyl sulfide is also obtained, but in lower yields, for example 63% from 1-octene, and with a remarkable amount of vicinal dichloride (i. e. 17% from 1-octene) and other unidentified products.

9) Cis isomers from cyclic alkenes are virtually absent.

10) With DES, the β-chloroalkyl sulfide (80% yield) is accompanied by some 1,2-dichloro octane (8% yield).

11) Schmid, G. H., Strukely, M., Dalipi, S. and Ryan M. D., J. Org. Chem., 1987, 52, 2403.

12) Rasteikiene, L., Greiciute, D., Lin'kova, M. G., and Knunyants, I. L., Russ. Chem. Rev., 1972, 46, 548; Smit, W. A., Zefirov, N. S., and Bodrikov, I. V., in "Organic Sulfur Chemistry", eds. Freidlina, R. Kh., and Skorova, A. E., Pergamon, Oxford, 1981, p 159.

13) Since 1-octene is not attacked by chloromethyl methyl sulfide-DMSO, the possibility that the methanesulfenyl chloride could derive from the reaction of these compounds is also ruled out.

14) Leplyanin, G. V., Vorob'eva, A. I., Sysoeva, L. B. and Varsil'eva, E. V., Vysokomol. Soedin., 1988, 30, ser A, 2567; De Simone, J. M., McGrath, J. E. and Smith, S. D., Polym. Prepr. 1988, 29, 345.

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