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CHLORINATION OF α-SULFONYL CARBANIONS WITH HEXACHLOROETHANE[a]

A NOVEL PREPARATION OF α-HALOSULFONES

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Abstract—The cyclic sulfones **1**, **2**, and **3** are lithiated in benzene with n-butyllithium. Lithiation is demonstrated to lead to α-mono, α,α′-di and/or α,α-di and α,α,α′ trimetallation. The lithiated sulfones are chlorinated with hexachloroethane (HCE). Some mechanistic aspects of the reaction of the lithiosulfones with vicinal dihalides are discussed.

α-Chlorosulfones are mostly prepared by chlorination of sulfides with chlorine[1], sulfuryl chloride[2,3] or N-chlorosuccinimide[4] in an inert solvent and subsequent oxidation of the resulting chlorosulfides with *m*-chloroperbenzoic acid[5]. In recent years direct chlorination of sulfones has received increasing attention. α-Sulfonyl carbanions, prepared from the corresponding sulfones by metallation with n-butyllithium, have been chlorinated with sulfuryl chloride[6], N-chlorosuccinimide[7] and trichloromethanesulfonyl chloride[8] in moderate yield. Recently, chlorination has also been effected by generation of the anions with powdered potassium hydroxide in the presence of carbon tetrachloride as a halogen source.[9] However, the latter reaction can not be applied to sulfones possessing α and α′ hydrogens, since the initial reaction products enter *in situ* into the Ramberg-Bäcklund reaction.[10] As part of a broader investigation into improved methods for α-halogenation of sulfones we wish to report our results on the halogenation of α-lithiosulfones **1b**, **2b** and **3b** (Scheme 1) using hexachloroethane (HCE) as a chlorinating agent.

RESULTS AND DISCUSSION

The lithiated sulfones **1b**, **2b** and **3b**† were easily prepared at room temperature by treatment of the corresponding sulfones in THF or benzene with a hexane solution of *n*-butyllithium. The lithiosulfolane mixture formed from sulfolane (**1a**) was hydrolyzed with excess D_2O/D_2SO_4. Mass spectrometric analysis of the resulting partially deuterated sulfolane showed incorporation of deuterium at the positions α to the sulfone group as indicated in Table 1.

The data in Table 1 are in agreement with the average value of 0·98 D/molecule as calculated from the NMR. We presume that these exchange data reflect the distribution of lithium over the four available α-positions in the lithiated mixture, since treatment of sulfolane with D_2O/D_2SO_4, Li_2SO_4 or D_2O/LiOD under the same circumstances did not result in any H/D-exchange. The occurrence of polylithiated compounds has been demonstrated in the literature by the isolation of products derived from α,α′-dilithiosulfolane[11] and the observed stability of certain *gem*-α-dilithiosulfones[12] at room temperature.

The lithiated sulfone **2b** was assumed to have roughly the same metal distribution as observed for **1b**. Sulfone **3a** upon treatment with 1·1 mole of n-butyllithium and subsequent hydrolysis with D_2O/D_2SO_4 gave a mixture of sulfones deuterated only at the allylic α-positions, with the average content of 1·16 D/molecule. Since **3a** did not exhibit

Table 1. α-Deuterium incorporation on treatment of a suspension of **1b** in benzene with D_2O/D_2SO_4

	m/e	%*
D_0	120	21·5
D_1	121	67·8
D_2	122	8·5
D_3	123	2·2
D_4	124	—

*The percentages were calculated as an average of five scans, and corrected for ^{13}C, ^{33}S and ^{34}S.

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[a] Taken in part from the forthcoming Ph.D. Thesis of J. Kattenberg, University of Amsterdam.

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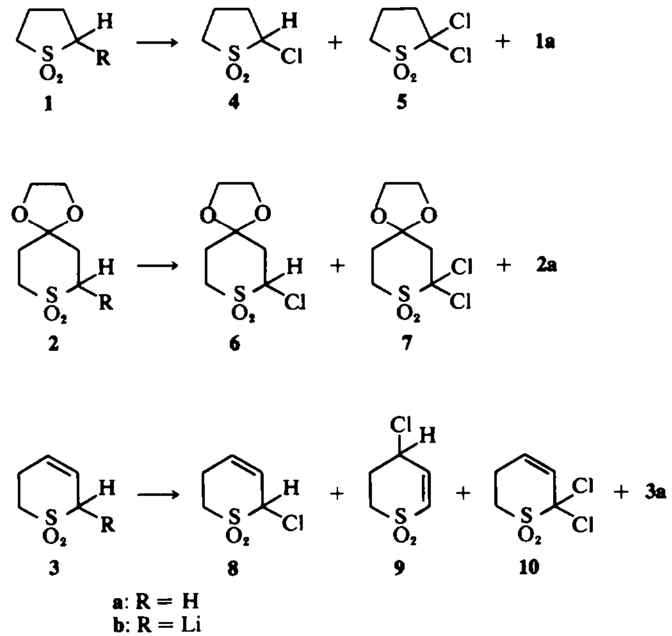
†For ease of representation the lithiosulfones are represented by one monomeric covalent structure, though lithiation is shown to lead to a mixture of mono- and polylithiated products and most organolithium compounds studies thus far are polymeric. The degree of polymerization varies with both structure and solvent.

H/D-exchange on treatment with D_2O/D_2SO_4, Li_2SO_4 (reaction with D_2O/LiOD gave exchange of the allylic α-hydrogens as expected) the distribution of lithium was likewise assumed to correspond to the observed deuteration of 15% α,α-D_2 and 85% α-D_1 plus D_0[*].

The HCE chlorination of **1b**, **2b** and **3b** in benzene resulted in a clean mixture. The isolated products are given in Scheme 1, the yields in Table 2. Although free halogen as a halogenating agent is experimentally often inconvenient[†] and less suited for molecules containing centers of insaturation we also performed the bromination of **1b** with bromine in THF for sake of comparison. The use of CCl_4 for halogenation of **1b** gave no reaction in THF and led to very impure reaction mixtures in benzene. We ascribe the observed tar formation to side reactions induced by the generated dichlorocarbene. Halogenation of anions with vicinal dihalides as a halogen source have been shown in the literature to proceed with excellent results in some reactions[13–16]. Disregarding their polymeric state, organolithium compounds may react as an anion in a S_NX-substitution on halogen (path A, Scheme 2) or in an electron transfer reaction (path B, Scheme 2) leading to alkylhalide radicalanions. It is not clear to us which mechanism is active. The fact that no sulfone dimers are detected can be interpreted in favour of a S_NX-substitution.

The main processes responsible for the product



SCHEME 1

Table 2. Reaction circumstances and yields of halogenation of **1b**, **2b** and **3b**

Compound	Solvent	Temp	Halogenating agent	Isolated products		
				monohalo	dihalo	recovered sulfone
1b	THF	r.t.	CCl_4	—	—	**1a** (99%)
	THF	−50°C	Br_2	23%	10%	**1a** (50%)
	ØH	50°C	CCl_4[a]	**4** (10%)	—	**1a** (49%)
	ØH	r.t.	HCE	**4** (25%)	**5** (16%)	**1a** (40%)
2b	ØH	r.t.	HCE	**6** (47%)	—	**2a** (32%)
3b	ØH	r.t.	HCE	**8** (32%) **9** (5%)[b]	**10** (12%)	**3a** (31%)

[a] This run was accompanied by considerable tar formation.
[b] **9** was isolated as a chromatographic fraction mixed with **8**.

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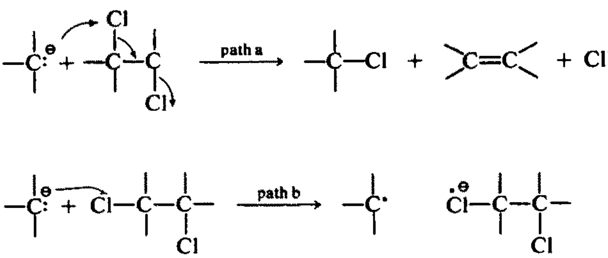
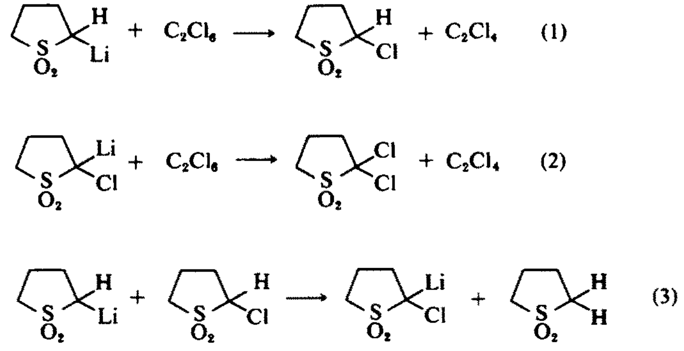
[*] The ratio D_1/D_0 could not be calculated from the NMR with sufficient accuracy.

[†] An attempted chlorination of α-lithiosulfolane with chlorine at −50°C led to an explosive reaction in our hands.



SCHEME 2

formation are given in Scheme 3. If the reactions 1 and 2 would go to completion, the ratio of isolated products would correspond directly to the initial lithium distribution. However, it is conceivable that acid-base reaction 3, leading to carbenoid α-lithio-α-chlorosulfones could increase the amount of recovered sulfone and dichlorosulfone at the cost of monochlorinated products.* This tendency indeed shows up in the isolated yields for chlorination of **1b**.



SCHEME 3

The stereochemical course of the HCE halogenation of conformationally rigid sulfones is presently under investigation. The results will be reported in a following paper, together with experiments on lithioenolates[18] and lithiated nitriles[19].

EXPERIMENTAL

All manipulations with organolithium compounds were carried out under N_2. The n-BuLi (Merck, Darmstadt) was a 20% hexane soln (*d* 0·70). HCE was purchased from Fluka. Benzene was dried over molecular sieves 4A and THF freshly distilled from LAH prior to use. Satisfactory elemental analyses, performed by Mr. H. Pieters of the Microanalytical Department of this Laboratory were obtained for all new compounds described. Mps are uncorrected. IR, NMR (TMS, $\delta = 0$) and mass spectra were recorded on a Unicam SP-200 spectrometer, Varian associates model HA-100 and Varian MAT-711 instrument, respectively.

4,4-Ethylenedioxytetrahydrothiapyran-1,1-dioxide (**2a**). Tetrahydrothiapyran-4-one (10·1 g)[20], prepared as described, was oxidized following an improved procedure. The sulfide was dissolved in ether (1 L) and the soln cooled to − 15°. *m*-Chloroperbenzoic acid (36 g, 85%) was added portionwise to the stirred mixture. The sulfone **2a** precipitated gradually during a period of 12 hr. The crude product (12 g, 92%, mp 164–174°) was filtered off and recrystallized (m.p. 175–177°, chloroform/ether) (lit.[21] 170°); IR (KBr): 1710 cm^{-1} (C=O), 1335 and 1125 cm^{-1} (sulfone); NMR (d_6-DMSO): 3·60 (SO_2—CH_2, m), 2·80 (CH_2—C=O, m). Tetrahydrothiapyran-4-one-1,1-dioxide (6·8 g), ethanediol (86 g), benzene (600 ml) and a trace of *p*-TsOH were boiled under reflux for 3 hr in a water separator filled with molecular sieves 4A. The mixture was cooled to r.t., the benzene layer separated and combined with a benzene extract of the glycol layer. The residual ethanediol was removed by addition of dehydrated K_2CO_3 and filtration. Evaporation of the solvent and recrystallization from chloroform/ether gave 7·1 g (81%) of pure **2a** (m.p. 192–193·5°); IR ($CHCl_3$): 1330 and 1125 cm^{-1} (sulfone), 1295 and 1105 cm^{-1} (acetal); NMR ($CDCl_3$): 4·00 (acetal, s), 3·15 (C(2)H and C(6)H, m) 2·20 (C(3)H and C(5)H, m).

Δ^3-Dihydrothiapyran-1,1-dioxide (**3a**). Dihydrothiapyran[22] was oxidized with *m*-chloroperbenzoic acid as described for **2a**. The sulfone **3a** was obtained in 64% yield (mp 68–70°). (Lit.[23] 67–69°.)

α-Lithiosulfones **1b**, **2b** *and* **3b** (*general procedure*). A hexane soln of n-BuLi (11 mmole) was diluted with benzene (10 ml) and added drop by drop at r.t. to a well-stirred soln of the sulfone (10 mmole) in benzene (60–80 ml). The so formed suspension of lithiated sulfones was stirred for 15 min. after completion of the addition, and used for halogenation or deuteration.

HCE-Chlorination of **1b**, **2b** *and* **3b** (*general procedure*). A suspension of α-lithiosulfone (10 mmole) in ben-

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*α-Chloro-α-lithiosulfones have been shown[17] to be stable in THF up to −55°.

zene was added dropwise to a stirred soln of HCE (50 mmole) in benzene (60 ml). After addition the mixture was stirred for 1 hr at r.t. and refluxed for 30 min. The precipitated LiCl was filtered off. The solvents were evaporated *in vacuo* and the excess of HCE removed in a rotary evaporator at 50°/1·5 mm to give a colourless residue of the crude halogenated sulfones. The crude mixture was chromatographed on silica with CH_2Cl_2-EtOAc as an eluant. The fractions collected consisted invariably in the order of decreasing R_f value of: residual HCE, dichloro, monochloro and unconverted sulfone.

HCE-Chlorination of **1b**. 2-Chlorosulfolane (**4**) was obtained as a colourless oil; IR ($CHCl_3$): 1320, 1155, 1130 and 1105 cm^{-1}; NMR ($CDCl_3$): 4·88 (C(2)H, t, J_{23} 5Hz), 3·25 (C(5)H, m), 2·9–2·2 (C(3)H and C(4)H, unresolved m).

2,2-Dichlorosulfolane (**5**) (m.p. 108–110°); IR (KBr): 1320 and 1130 cm^{-1}; NMR ($CDCl_3$): 3·35 (C(5)H, m), 2·90 (C(3)H, t, J_{34} 7Hz), 2·65 (C(4)H, broad m).

HCE-Chlorination of **2b**. Compound **6** was obtained in a colourless crystalline form (m.p. 201–203°); IR ($CHCl_3$): 1340, 1300, 1130 and 1100 cm^{-1}; NMR ($CDCl_3$): 4·85 (C(2)H, X-part of ABX-pattern, $J_{AX}+J_{BX}$ 16Hz), 4·0 (acetal, s), 3·25 (C(6)H, m), 2·65–1·80 (C(3)H and C(5)H, unresolved, m).

HCE-Chlorination of **3b**. Compound **8** was obtained as a colourless crystalline product (mp 85–87°); IR ($CHCl_3$): 1660 (weak), 1340, 1295 and 1125 cm^{-1}; NMR ($CDCl_3$): 5·85 (C(3)H and C(4)H, m), 4·95 (C(2)H, m), 3·7 and 2·7 (C(6)H and C(5)H, respectively, m).

Compound **9** was obtained in a fraction mixed with **8** in a ratio of 1:2; NMR ($CDCl_3$): in the mixture the following signals could be recognized: 6·40 (C(2)H and C(3)H, s), 4·68 (C(4)H, m).

Compound **10** crystallized in a colourless form (mp 113–116°); IR ($CHCl_3$): 1640 (weak), 1340, 1160 and 1125 cm^{-1}; NMR ($CDCl_3$): 6·1 (C(3)H, d, J_{34} 11 Hz), 5·75 (C(4)H, two t, J_{45} 3·5 Hz), 3·52 (C(6)H, t, J_{56} 6·2 Hz), 2·85 (C(5)H, m).

Bromination of **1b** *with bromine*. A hexane soln of n-BuLi (13 mmole) was introduced dropwise to a well-stirred soln of sulfolane (10 mmole) in THF (60 ml) at −70°. After completion of the addition the mixture was stirred for 2 hr at −50°, and the cooled suspension was added drop by drop to a freshly prepared soln of Br_2 (12 mmole) in THF (30 ml), cooled to −50°. After 10 min stirring the mixture was allowed to warm to r.t. The solvents were evaporated *in vacuo* and replaced by chloroform. The bulk of LiBr precipitated and was filtered off. Evaporation of the solvent furnished the crude product. Chromatographic separation yielded the products in the order mentioned above.

2-Bromosulfolane was obtained as a colourless liquid: IR ($CHCl_3$): 1320, 1150, 1120 and 1105 cm^{-1}; NMR ($CDCl_3$) 4·80 (C(2)H, t, J_{23} 4Hz), 3·18 (C(5)H, m), 3·0–2·1 (C(3)H and C(4)H, broad m).

2,2-Dibromosulfolane was obtained in a colourless crystalline form (m.p. 122–124°); IR ($CHCl_3$): 1335, 1150 and 1125 cm^{-1}; NMR ($CDCl_3$): 3·3 (C(5)H, m), 2·98 (C(3)H, t, J_{34} 6·5 Hz), 2·30 (C(4)H, m).

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