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SYNTHESIS AND STRUCTURE OF NOVEL HALOSULFURANES, 5-CHLORO- AND 5-BROMO-5,11-EPOXY-6,11-DIHYDRODIBENZO[*b,e*]THIEPINS

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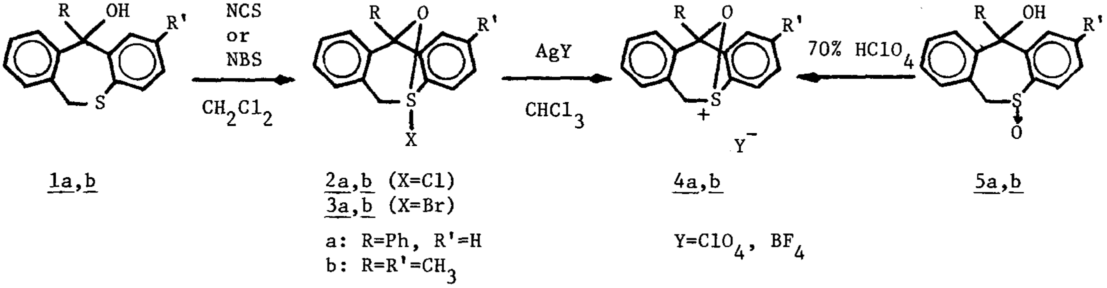
Summary: Novel halosulfuranes, 5-chloro- and 5-bromo-5,11-epoxy-6,11-dihydrodibenzo[b,e]-thiepins were synthesized. The covalency of the sulfur-halogen bond was established by ^{1}*H-NMR and MS(field desorption) data and by an X-ray crystal structure determination.*

Halosulfuranes have been studied for the last ten years.[1-3] However, there are so far few examples that confirmed the covalent nature of the sulfur-halogen bond.[2] In the course of our intensive studies on thiepin chemistry we have succeeded in synthesizing novel halosulfuranes, 5-chloro- and 5-bromo-5,11-epoxy-6,11-dihydrodibenzo[*b,e*]thiepins (2a,b and 3a,b). We wish to report here the synthesis of 2a,b and 3a,b and the covalency of the sulfur-halogen bond established by the ^{1}H-NMR and MS(field desorption) spectra, and an X-ray structure determination.



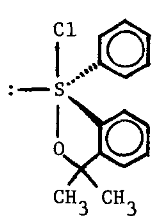
On the treatment of 6,11-dihydrodibenzo[*b,e*]thiepin-11-ols (1a,b)[4] with 1 eq. of N-chlorosuccinimide or N-bromosuccinimide at room temperature in CH_2Cl_2 for 1-3 hrs, the corresponding halosulfuranes (2a,b and 3a,b) were isolated as stable crystals. Chlorosulfuranes 2a,b were more stable thermally and hydrolytically than bromosulfuranes 3a,b during the process of recrystallization. In order to investigate the covalency of 2 and 3, we synthesized the corresponding thiepinium salts and compared their physico-chemical data with those of the halosulfuranes. On treatment with $AgClO_4$ or $AgBF_4$ for 24 hrs at room temperature, 2a,b

Table. Yields , Melting points , ^{1}H-NMR (200 MHz) data , and MS (field desorption) data for 2a,b - 4a,b

				^{1}H-NMR (200 MHz) Spectral data$^{b)}$					MS Spectral data$^{e)}$
Compd.	Yield (%)	mp$^{a)}$ (°C)	solvent	C$_4$-H	other aromatic absorption	CH$_2$ at C$_6$$^{d)}$	2-Me	11-Me	(field desorption)
2a	85.0	134-135	CDCl$_3$	9.24-9.11	7.71-7.02(12H)	5.46, 5.20(18.2Hz)			340*,338*,303**,302***
			CD$_3$OD	8.34-8.25	7.90-7.14(12H)	5.55, 4.39(17.6Hz)			320*****,302***
2b	98.2	158-159	CDCl$_3$	8.88(8.3Hz)$^{c)}$	7.43-7.30(4H) 7.09-6.98(2H)	5.28, 5.10(18.4Hz)	2.42	2.19	547****,545**** 292*,290*,255**
			CD$_3$OD	8.03(9.0Hz)$^{c)}$	7.65-7.35(5H) 7.22-7.12(1H)	5.35, 4.31(17.7Hz)	2.45	2.34	272*****
3a	76.0	129-130	CDCl$_3$	9.33-9.22	7.73-7.04(12H)	5.44, 5.33(18.2Hz)			688****,686**** 385*,383*,303**
			CD$_3$OD	8.38-8.30	7.94-7.14(12H)	5.55, 4.41(18.1Hz)			320*****,302***
3b	62.7	135-138	CDCl$_3$	8.98(8.3Hz)$^{c)}$	7.44-7.25(4H) 7.10-7.00(2H)	5.28, 5.21(18.2Hz)	2.42	2.20	
			CD$_3$OD	8.07(8.8Hz)$^{c)}$	7.65-7.35(5H) 7.23-7.10(1H)	5.36, 4.36(17.8Hz)	2.45	2.34	
4a Y=BF$_4$ (Y=ClO$_4$	85.6 87.8	212-214 222-225)	CDCl$_3$	8.63-8.53	7.84-7.07(12H)	5.31, 4.63(18.0Hz)			303**,302***
			CD$_3$OD	8.24-8.17	7.91-7.14(12H)	5.54, 4.30(18.1Hz)			320*****,303**
4b Y=ClO$_4$ (Y=BF$_4$	89.4 92.7	187-189 203-204)	CDCl$_3$	8.34(8.1Hz)$^{c)}$	7.50-7.36(4H) 7.16-7.06(2H)	5.20, 4.62(18.8Hz)	2.46	2.32	255**
			CD$_3$OD	7.95(8.8Hz)$^{c)}$	7.64-7.37(5H) 7.22-7.11(1H)	5.35, 4.25(17.5Hz)	2.45	2.35	255**

a) Melting point with decomposition. b) Chemical shifts(δ) are reported in parts per million downfield from Me$_4$Si. c) doublet. d) doublets of doublet. e) EC=14-16 mA , * =M$^+$, ** =M$^+$-X or M$^+$-Y , *** =M$^+$-HX or M$^+$-HY , **** =2M$^+$-X , ***** =M$^+$-X+OH or M$^+$-Y+OH.

afforded 5,11-epoxy-6,11-dihydrodibenzo[*b,e*]thiepinium salts (4a,b Y=BF_4, ClO_4) in high yields. 4a,b (Y=ClO_4) were also obtained by the treatment of 6,11-dihydrodibenzo[*b,e*]-thiepin-11-ol 5-oxide derivatives (5a,b) with 70% $HClO_4$ in good yields.5) The ^{1}H-NMR data of these sulfonium salts (4a,b) were compared with those of halosulfuranes (2a,b and 3a,b). Their yields, melting points, ^{1}H-NMR data, and MS(field desorption) data for compounds 2a,b-4a,b are shown in the Table.6)



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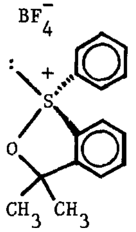

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Martin et al. have determined that compound 6 is a chlorosulfurane on the basis of ^{1}H-NMR and MS(field desorption) data.3) The evidence for the covalent nature of the S-Cl bond is a large downfield shift for the proton *ortho* to sulfur in the fused phenyl ring of 6 (δ=9.33 ppm in $CDCl_3$) relative to that in the analogous oxosulfonium salt 7 (δ=8.10 ppm in $CDCl_3$) in the ^{1}H-NMR absorption and the presence of a molecular ion in the MS(field desorption) spectrum. A similar downfield shift has been observed for 2a,b and 3a,b in $CDCl_3$. The chemical shift of C_4-H (proton *ortho* to sulfur in the fused ring) for 2a,b and 3a,b is distinctly δ=0.6-0.7 ppm downfield from that for 4a,b (see Table). In addition, molecular ions of 2a,b and 3a are also observed in their MS(field desorption in $CDCl_3$) spectra as weak peaks. These results clearly suggest that the covalency of the sulfur-halogen bond for 2a,b and 3a,b is closely parallel to that for 6. However, neither the large downfield shift for C_4-H nor the presence of the molecular ion peaks are observed, when they are measured in CD_3OD. These spectra resemble very closely those of 4a,b in CD_3OD. This result means that the sulfur-halogen bond is almost completely dissociated in CD_3OD and is the similar bond like 4a,b.

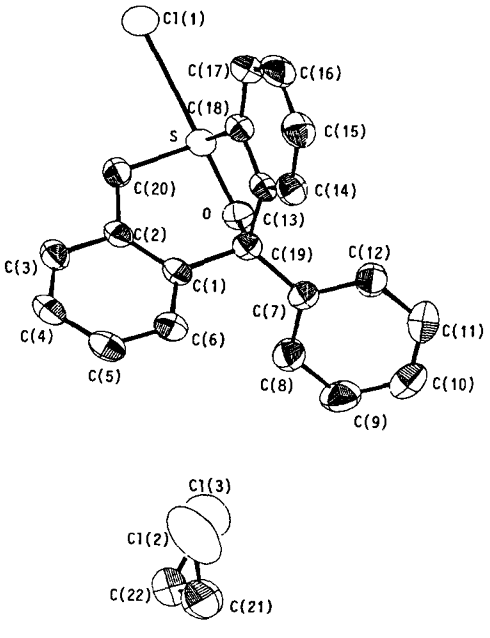

Figure. ORTEP Drawing of $2a\cdot ClCH_2CH_2Cl$ Adduct

In order to obtain further information regarding the structure and covalency in the halosulfuranes, the X-ray crystal structure analysis of 2a7) was carried out. Crystal data: $C_{20}H_{15}ClOS\cdot ClCH_2CH_2Cl$, triclinic, space group P$\bar{1}$, a=9.401(3), b=10.317(4), c=11.506(3)Å, α=100.97(3), β=109.24(2), γ=82.19(3)°, Dx=1.41 g/cm^3 and μ(MoKα)=5.5 cm^{-1}. The cell dimensions and intensities were measured on a Syntex R_3 four-circle diffractometer with a graphite-monochromated MoKα radiation with ω-scan mode for 2θ less than 50°. A total of 3634 independent reflections were collected, among which 3262 [I>1.96σ (I)] were stored as observed. The structure was solved by the direct method using MULTAN in Synthex XTL program.[8] Block-diagonal least-squares method was applied to the refinement, the final R-value being 4.6%. The ORTEP diagram of 2a[7] is shown in the Figure. The bond angles about sulfur are Cl(1)-S-O= 174.8° (bent away from the lone pair of electrons on sulfur), Cl(1)-S-C(20)=85.4°, Cl(1)-S-C (18)=92.7°, O-S-C(18)=91.7°, O-S-C(20)=96.5°, C(18)-S-C(20)=100.4°. This result reveals approximate trigonal-bipyramidal around sulfur. The bond lengths around sulfur are Cl(1)-S= 2.749(1)Å, S-O=1.639(2)Å, S-C(18)=1.797(3)Å, S-C(20)=1.817(3)Å. The apical S-Cl bond length (2.749Å) is ca. 0.72Å longer than the sum of the covalent radii (2.03Å)[9] and the apical S-O bond length (1.639Å) is ca. 0.06Å shorter than the sum of the covalent radii (1.70Å).[9] The 37% elongation in the apical S-Cl bond revealed in the X-ray structure of 2a clearly indicates the high degree of polarization of the three-center four-electrons hypervalent bond. This polarization is also reflected on studies of ^{1}H-NMR and MS(field desorption) data in CD_3OD.

The present investigation confirms the approximate trigonal-bipyramidal geometry around sulfur of halosulfuranes (2a,b and 3a,b) but the covalent sulfur-halogen bond is rather weak, so it shows completely ionic bond character in CD_3OD.

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6) All compounds gave satisfactory elemental analysis.

7) In order to get a fine crystal of 2a suitable for the X-ray analysis, we attempted so many times to recrystallize 2a from several solvents, and finally we succeeded in obtaining a very fine crystal as a 1:1-adduct of 2a and $ClCH_2CH_2Cl$. We therefore performed the X-ray analysis of the 1:1-adduct.

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