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

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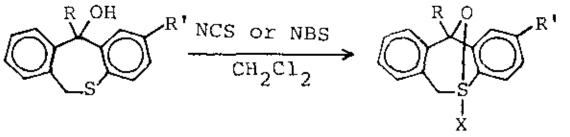
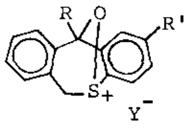
5-Chloro- (2a,b) or 5-bromo-5,11-epoxy-5,11-dihydrodibenzo[b,e]thiepins (3a,b) were synthesized by the reaction of dibenzothiepin-11-ols (1a,b) with N-chloro- (NCS) or N-bromosuccinimide (NBS), respectively. Chlorosulfuranes (2a,b) were more stable thermally and hydrolytically than bromosulfuranes (3a,b).

The covalency of the sulfur-halogen bond of the halosulfuranes (2a,b-3a,b) was established by the ^{1}H-NMR and MS (field desorption) spectra, and X-ray structure determination. The absorption of C_4-H at δ 9.11-9.24 for 2a was shifted to downfield relative to that of the corresponding sulfonium salt 4a in the ^{1}H-NMR spectra. Other halosulfuranes (2b,3a,b) showed this distinctive downfield shifts (0.6-0.7 ppm lower than those of 4a,b). The MS (field desorption) spectra of the sulfuranes showed the molecular ion peaks. The crystal structure of 2a reveals approximate trigonal bipyramidal geometry about sulfur. The apical S-Cl bond. length (2.749 A) is ca 0.72 A longer than the sum of the covalent radii (2.03 A) and the apical S-O bond length (1.639 A) is ca 0.06 A shorter than the sum of the covalent radii (1.70 A).



1a,b

2a: R=Ph; R'=H; X=Cl
2b: R=R'=Me; X=Cl
3a: R=Ph; R'=H; X=Br
3b: R=R'=Me, X=Br



4a: R=Ph; R'=H
4b: R=R'=Me
Y=BF_4, ClO_4