NUCLEOPHILIC ADDITION TO BENZO[b]THIENO[2,3-b]BENZO[b]THIOPHENE S,S,S',S'-TETROXIDE

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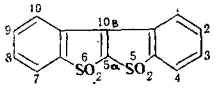
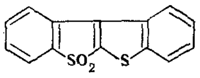
The reaction of benzo[b]thieno[2,3-b]benzo[b]thiophene S,S,S',S'-tetroxide with primary and secondary amines and with alcohols gave 10 b-amino- and 10 b-alkoxy-5a, 10b-dihydrobenzo[b]thieno[2,3-b]benzo[b]thiophene S,S,S',S'-tetroxides. These nucleophilic reagents do not add to benzo[b]thieno[2,3-b]benzo[b]thiophene S,S-dioxide.

Within our plan for research on nucleophilic addition to heterocyclic sulfones [1] we investigated the properties of the central $C_{5a}-C_{10b}$ bond in benzo[b]thieno[2,3-b]benzo[b]thiophene S,S,S',S'-tetroxide (I) and S,S-dioxide (II).



I



II

According to x-ray diffraction data [2, 3], the oxygen atoms of the sulfone groups of I are in the plane of the heteroring, and this creates a steric barrier to the addition of a reagent to the 5a position. In conformity with this, attempts to add reagents of the Michael and Grignard type to disulfone I were unsuccessful [2].

However, we have established that the $C_{5a}-C_{10b}$ bond in disulfone I is nevertheless capable of adding a number of nucleophilic reagents. 10b-Amino-5a,10b-dihydrobenzo[b]thieno[2,3-b]benzo[b]thiophene

TABLE 1. 10b-Amino- and 10b-Alkoxy-5a, 10b-dihydrobenzothienc [2,3-b]benzothiophene S,S,S',S'-Tetroxides III and IV

Compound	R	mp, °C (from dioxane)	Empirical formula	Found, %			Calc., %			PMR spectrum: δ, ppm		Yield, %
				C	H	N	C	H	N	aromatic protons	H_{5a}	
IIIa	C_4H_9NH	188—189[a]	$C_{18}H_{19}NO_4S_2$	57,3	5,2	3,6	57,3	5,1	3,7	7,67—7,90	5,12	80
IIIb	Piperidino	235—240[b]	$C_{19}H_{19}NO_4S_2$	58,6	4,9	3,6	58,6	4,9	3,6	7,60—8,00	5,00	79
IIIc	Morpholino	254—255	$C_{18}H_{17}NO_5S_2$	55,5	4,4	3,4	55,2	4,4	3,6	7,60—7,90	5,04	78
IIId	Piperazino	268—270[b]	$C_{18}H_{18}N_2O_4S_2$	55,1	4,6	7,0	55,3	4,6	7,1	—	—	78
IIIe	N-Methyl-piperazino	217—218	$C_{19}H_{20}N_2O_4S_2$	56,7	4,9	6,6	56,4	5,0	6,9	7,60—7,90	5.01	81
IIIf	$NHCH_2CH_2OH$	176—177[c]	$C_{16}H_{15}NO_5S_2$	52,5	4,1	3,7	52,6	4,1	3,8	7,70—7,90	5,25	79
IVa	CH_3	310—312[d]	$C_{15}H_{12}O_5S_2$	53,9	3,6	—	53,6	3,6	—	7,75—7,90	5,07	65
IVb	C_2H_5	310—312[d]	$C_{16}H_{14}O_5S_2$	54,4	3,8	—	54,8	4,0	—	—	—	66

[a] From hexane–benzene. [b] With decomposition. [c] From ethanol. [d] Converted to disulfone I at 240°.

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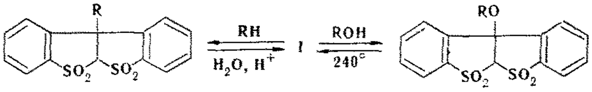
S,S,S',S'-tetroxides (III) are formed in ~80% yields when it is heated with primary aliphatic and secondary cyclic amines and amino alcohols in benzene (Table 1).

In acidic media III are readily hydrolyzed, possibly through a step involving the formation of the corresponding hydroxy derivative, which, however, cannot be isolated. The addition of amines to the $C_{5a}-C_{10b}$ bond is confirmed by the PMR spectra.

In addition to multiplets of aromatic protons at δ 5.00-5.25ppm, the spectra of IIIa-f contain singlet signals corresponding to the resonance of aliphatic protons in the 5a position [2], which are absent in the spectrum of disulfone I (Table 1).



III a-f   IV a, b

IIIa $R=NHC_4H_9$; b R=piperidino; c R=morpholino; d R=piperazino; e R=N-methylpiperazino; f $R=NHCH_2CH_2OH$; IV a $R=CH_3$; b $R=C_2H_5$

The IR spectra of amines IIIa-f contain strong absorption bands of stretching vibrations of the SO_2 group at 1330 and 1145-1160 cm^{-1}. The absorption maxima at 3360 cm^{-1} in the spectra of amines IIIa-f correspond to the stretching vibrations of NH groups. The strong absorption band of a hydroxyl group at 3600 cm^{-1} in the spectrum of IIIf constitutes evidence for the addition of the amino alcohol to disulfone I through the amino groups.

Aliphatic alcohols also add to disulfone I in the presence of catalytic amounts of alkali. In this case, 10b-alkoxy-5a, 10b-dihydrobenzo[b]thieno[2,3-b]benzo[b]thiophene S,S,S',S'-tetroxides (IV) are formed in ~65% yields (Table 1); IV undergo dealkoxylation at 230-240°. The IR spectra of IV contain absorption maxima of stretching vibrations of SO_2 groups at 1330 and 1140 cm^{-1} and of a C−O−C group at 1050 cm^{-1}. Three groups of signals are observed in the PMR spectra: signals of aromatic protons at δ 7.7-7.9, of an aliphatic H_{5a} proton at 5.1, and of protons of the OR substituent at 3.10 ppm.

The $C_{5a}-C_{10b}$ bond in sulfone II proved to be incapable of adding nucleophilic reagents – amines and alcohols. No reaction whatsoever was observed when II was heated with butylamine and piperidine in benzene or with aliphatic alcohols in the presence of alkali for 5 h.

EXPERIMENTAL

The PMR spectra of $CDCl_3$ solutions of the compounds were recorded with an R-12A spectrometer (60 MHz) with hexamethyldisiloxane or tetramethylsilane as the internal standard.

10b-Amino-5a, 10b-Dihydrobenzo[b]thieno[2,3-b]benzo[b]thiophene S,S,S',S'-Tetroxides (IIIa-f). A mixture of 1 mmole of disulfone I [2] and 2 mmole of the appropriate amine in 20 ml of benzene was refluxed for 2 h. The resulting precipitate was removed by filtration (in the case of IIIa the solvent was removed by distillation), washed with water, and recrystallized.

5a-Hydro-10b-alkoxy-5a, 10b-Dihydrobenzo[b]thieno[2,3-b]benzo[b]thiophene S,S,S',S'-Tetroxides (IVa, b). A 0.2-mmole sample of KOH was dissolved in 15 ml of the appropriate alcohol, 1 mmole of disulfone I was added, and the mixture was refluxed for 1 h. The solution was filtered, and the filtrate was neutralized with dilute hydrochloric acid. The resulting precipitate was removed by filtration, washed with water, and recrystallized from dioxane.

Hydrolysis of Amino Derivatives III. A solution of 5 mmole of amino derivative IIIa-f in 5 ml of 6 N H_2SO_4 was heated on a boiling-water bath for 40 min. The resulting precipitate was washed with water and recrystallized from dioxane. The yield of disulfone I with mp 310-312° was 75-80%.

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