THIIRANO-3,4-THIOLANE 1,1-DIOXIDE AND A METHOD FOR ITS PREPARATION

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Thiirano-3,4-thiolane 1,1-dioxide was obtained by the action of triphenylphosphine sulfide on oxirano-3,4-thiolane 1,1-dioxide in the presence of an excess of trifluoroacetic acid.

The present communication is devoted to the synthesis of thiirano-3,4-thiolane 1,1-dioxide (I), which is of interest in connection with the possibility of obtaining pesticides from it and also for comparison of its characteristics with the characteristics of known thiiranes [2] and of the oxygen analog [3]. Attempts to obtain thiirane (I) by a method similar to that in [4] by the action of triphenylphosphine sulfide on oxirano-3,4-thiolane 1,1-dioxide (II) at room temperature in the presence of catalytic or equimolar amounts of trifluoroacetic acid were unsuccessful. We were able to realize the reaction at 80°C in the presence of an excess of trifluoroacetic acid:

II I

Thiirano-3,4-thiolane 1,1-dioxide is a white crystalline substance melting at 157-159°C and readily soluble in alcohol, dioxane, and acetone. Its structure was confirmed by IR and NMR spectroscopy. The IR spectrum of (I) contains characteristic frequencies for the absorption of the CH and CH_2 groups at 3000-3100, the C—S—C group at 645, and the sulfone S—O bond at 1130-1320 cm^{-1}. The presence of the three-membered and five-membered rings is confirmed by the proton and ^{13}C NMR spectra. In the PMR spectra of solutions of the thiirane (I) in acetone or trifluoroacetic acid the signals for the α- and β-protons are not resolved. It was possible to separate the signals by using the upfield shift of the proton signals by benzene characteristic of three-membered heterocycles [5, 6]. Owing to the limited solubility of the thiirane (I) in benzene we used a 3:1 mixture of benzene and trifluoroacetic acid. The PMR spectrum obtained in this solvent consists of two broad multiplets centered at 2.5 and 2.7 ppm, which we assigned to the α- and β-protons respectively of the five-membered ring.

In the ^{13}C NMR spectra of (I) there are two signals at 54.9 and 32.9 ppm with an integral intensity ratio of 1:1. We assigned the first signal to the carbon atoms at positions 2 and 5 and the second to the carbon atoms at positions 3 and 4 of the 1,1-dioxothiolane ring. The signals were assigned by comparison of the spectra recorded with and without proton decoupling.

During comparison of the spectra of compounds (I) and (II) with the spectra of thiolane 1,1-dioxide (III) [7], thiirane (IV) [8], and oxirane (V) [8] (Table 1) a small difference is observed in the chemical shift of the signals for the α-carbon atoms in the thio (I) and oxo (II) analogs and in compound (III), and this is probably due to the β-effect of the sulfide function of the thiirane ring and the oxygen function of the oxirane ring. This effect is similar in sign to the β effect of the sulfide function in linear and cyclic sulfides [7] and is greater in value than the β effect of the oxygen function in the oxirane ring (Table 1). The substantial difference in the chemical shifts of the signals for the β-carbon atoms ($C_{(3)}$ and $C_{(4)}$) in compounds (I) and (II) is due to the nature of the

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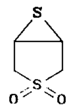
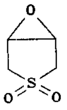
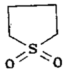
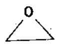
TABLE 1. The ^{13}C Chemical Shifts of Compounds (I-V)*

Compound	 I	 II	[7]  III	[8]  IV	[8]  V
Solvent	$(CD_3)_2CO$	$(CD_3)_2CO$	$CDCl_3$	Without solvent	$(CH_3)_2CO$
δ_{TMS}, ppm	54,9 (2-C, 5-C) 32,9 (3-C, 4-C)	53,9 (2-C, 5-C) 52,3 (3-C, 4-C)	51,1 (2-C, 5-C) 22,7 (3-C, 4-C)	18,9	39,7

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*The spectral data for (III) were taken from [7], and those for (IV) and (V) were taken from [8]. In [8] the chemical shifts were given with reference to benzene.

heteroatom entering into the three-membered ring and is consistent with the α effect of the sulfur and oxygen functions in three-membered rings [8]. Thus, in the thiirane ring in (IV) compared with the oxirane ring in (V) the signal of the ^{13}C nuclei is shifted downfield by 20.8 ppm. A similar difference in the sign and magnitude (19.4 ppm) of the chemical shift is observed in the spectra of compounds (I) and (II) (Table 1).

EXPERIMENTAL

The IR spectra were recorded in tablets with potassium bromide on a UR-20 spectrophotometer. The PMR spectra of (I) in deuteroacetone, trifluoroacetic acid, and a 3:1 mixture of benzene and trifluoroacetic acid with HMDS as internal standard were recorded on a Tesla BS-467 instrument at 60 MHz at room temperature. The ^{13}C NMR spectra of compounds (I) and (II) in deuteroacetone were obtained on a Bruker WP-80 spectrometer at 20 MHz with $^{13}C-^{1}H$ decoupling by a pulsed technique with Fourier transformation. Acetone-d_6 was used as internal standard. The resonance conditions were stabilized against ^{2}H nuclei in the solvent. The accuracy of the ^{13}C chemical shift measurement was ±0.1 ppm.

Thiirano-3,4-thiolane 1,1-Dioxide (I). To a solution of 2.7 g (0.02 mole) of oxirano-3,4-thiolane 1,1-dioxide in a mixture of 30 ml of benzene and 4.5 ml of trifluoroacetic acid we added a solution of 5.9 g (0.02 mole) of triphenylphosphine sulfide in 50 ml of benzene. The reagents were stirred at 70-80°C for 60 h. a. The thiirano-3,4-thiolane 1,1-dioxide was isolated by preparative column chromatography with Skh-2 silica gel as sorbent and diethyl ether as eluant. We obtained 1.8 g (60%) of the thiirane (I); mp 157-159°C (from acetone). Found, %: C 32.3; H 4.1; S 42.3. $C_4H_6O_2S_2$. Calculated, %: C 32.0; H 4.0; S 42.5. b. The solvents and trifluoroacetic acid were removed under vacuum, and the residue was crystallized from acetone. The yield was 1.5 g (50%); mp 157-159°C.

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