SOME REACTIONS OF 3-HYDROXYTHIETANE

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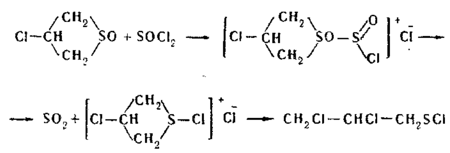
3-Hydroxythietane is readily oxidized by hydrogen peroxide in acetone or acetic acid solution at 0° C to give 3-hydroxythietane-1-oxide. 3-Thietyl acetate is oxidized similarly. 3-Hydroxythietane-1-oxide reacts vigorously with $SOCl_2$ in benzene, with the formation of bis-2, 3-dichloropropyl disulfide. 3-Hydroxythietane-1, 1-dioxide reacts with phosgene to give 3-thietyl-1, 1-dioxide chloroformate, which gives with diethylamine 3-thietyl-1, 1-dioxide N, N-dimethylcarbamate. Sodium peroxide and barium perbenzoate with the chloroformate give the corresponding di-(3-thietyl-1, 1-dioxide) peroxydicarbonate and 3-thietyl-1, 1-dioxide perbenzoate.

3-Hydroxythietane is readily oxidized by hydrogen peroxide to 3-hydroxythietane-1,1-dioxide (I) [1]. We have modified somewhat the conditions of the oxidation, using an equimolecular amount of hydrogen peroxide and carrying out the reaction at 0° C in acetic acid or acetone, to give 3-hydroxythietane-1-oxide (II). Using similar conditions, we have succeeded in obtaining 3-acetoxythietane-1-oxide (III) by the oxidation of 3-thietyl acetate.

The sulfoxides thus obtained, and also 3-hydroxythietane-1, 1-dioxide, were the subject of further investigation.

In dry benzene, II reacted vigorously with $SOCl_2$ with evolution of SO_2 and HCl and the formation of bis-2, 3-dichloropropyl disulfide (IV). It may be supposed that the hydroxyl group is first replaced by chlorine.

According to [2], acyclic sulfoxides react with HCl to give the corresponding sulfide and Cl_2. Also, the intermediate 3-chlorothietane-1-oxide can react with $SOCl_2$ as in [3]:

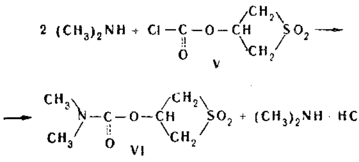


The sulfenyl chloride obtained reacts with 3-chlorothietane with opening of the four-membered ring and formation of IV. The reaction mixture was observed to contain sulfuryl chloride, detected by the presence of sulfuric acid (reaction with barium chloride) in the hydrolysis products of the reaction mixture. In a control experiment in which the sulfoxide was omitted, SO_2Cl_2 was not observed.

The structure IV was confirmed by comparison with the disulfide obtained by the $FeCl_3$ oxidation of 2, 3-dichloropropane-1-thiol, prepared by treatment of thioepichlorohydrin with HCl [4].

The methods of preparing 3-thietyl acetate [5] and of 3-hydroxythietane [1] were modified to give substantially improved yields of I.

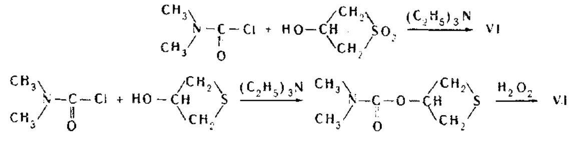
Compound I reacted smoothly with phosgene in benzene in the presence of triethylamine to yield 3-thietyl-1,1-dioxide chloroformate (V), which reacted with a twofold excess of dimethylamine in ethyl acetate to give 3-thietyl-1,1-dioxide N,N-dimethylcarbamate (VI).



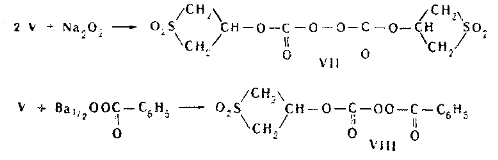
The physical and chemical properties of VI are identical with those of the compound prepared previously [6] from 4-chloromethyl-5-oxa-2-thiolan-1-one and dimethylamine, to which we incorrectly assigned the structure 4-dimethylaminomethyl-5-oxa-2-thiolan-2,2-dioxide-1-one from its breakdown to 3-hydroxythietane-1,1-dioxide, erroneously assumed to be hydroxymethyl ethylene sulfone [7]. This structure is also confirmed by the results reported in a recent paper [8].

Nevertheless, comparison of the methods described above for the synthesis of VI with that described previously [6, 7] shows that the latter is more convenient, gives higher yields, and has greater possibilities for the preparation of a wider range of carbamates.

We have also synthesized VI by the following route:



Treatment of V with sodium peroxide in aqueous solution or with barium perbenzoate affords the following percarbonates:



These peroxides are stable compounds, which decompose on melting, and liberate iodine from acidified KI solution. At temperatures of about 70° C, VIII accelerates the polymerization of styrene, while VII is inactive.

EXPERIMENTAL

3-Thietyl acetate. A mixture of 100 g (0.93 mole) of thioepichlorohydrin, 120 g (1.22 mole) of potassium acetate and 500 ml of water was heated for 3 hr on a boiling water bath with vigorous stirring. The organic layer was separated, and the aqueous layer extracted with ether. The ethereal extract was combined with the separated acetate layer, and dried over $CaCl_2$. The ether was removed and the residue distilled in vacuo, giving 110 g (90%) of 3-thietyl acetate, bp 72–73° C (9 mm); n_D^{20} 1.4880; d_4^{20} 1.1784 [(lit. [5] bp 82° C (20 mm)], n_D^{20} 1.4898).

3-Hydroxythietane was obtained by hydrolysis of the acetate [7].

3-Hydroxythietane-1,1-dioxide (I). A 110 g (0.83 mole) quantity of 3-thietyl acetate was added dropwise to 250 ml (2.06 mole) of 28% hydrogen peroxide which had previously been heated to 40° C. When the addition was complete, the mixture was heated for a further 1 hr on a boiling water bath, then evaporated on the water bath in the presence of Pt wire to decompose any remaining hydrogen peroxide, until a sample placed on a watch glass and cooled did not crystallize. The mixture was cooled, and the sulfone recrystallized from methanol to give 88 g (88%) of I, mp 99–100° C (lit. [1], mp 101–102° C). Found, %: C 29.20, 29.23; H 4.99, 4.65; S 26.63, 26.82; M 125 (Rast). Calculated for $C_3H_6O_3S$, %: C 29.60; H 4.92; S 26.62; mol. wt. 122.

3-Hydroxythietane-1-oxide (II). To a solution of 33 g (0.37 mole) of 3-hydroxthietane in 40 ml of acetic acid was added dropwise 46.2 ml (0.38 mole) of 28% H_2O_2 with vigorous stirring and external cooling such that the temperature did not exceed +5° C. The mixture was kept at room temperature for 1.5–2 hr. The solvent was then removed under reduced pressure, followed with gentle heating (40–45° C) by unreacted 3-hydroxythietane. The sulfoxide crystallized on cooling, giving 35.3 g of II, mp 67–68° C (from acetone). Found, %: C 33.91, 33.56; H 5.66, 5.60; S 30.01, 29.91; OH 15.50, 15.40; M 103; 105. Calculated for $C_3H_6O_2S$, %: C 35.96; H 5.66; S 30.18; OH 16.00; mol. wt. 106.

3-Thietyl-1-oxide acetate (III). To a solution of 20 g (0.135 mole) of 3-thietyl acetate in 30 ml of acetic acid (or in acetone) was added dropwise 18.5 ml (0.152 mole) of 28% H_2O_2. The temperature was kept below +5° C by external cooling. After the hydrogen peroxide had been added, the mixture was kept for 1.5–2 hr at room temperature and the solvent removed in vacuo. The residue crystallized, and was recrystallized from benzene to give 11.5 g of III, mp 53–54° C. Found, %: C 40.20, 40.66; H 5.41, 5.48; S 21.44, 21.41; M 150; 152. Calculated for $C_5H_8O_3S$, %: C 40.54; H 5.40; S 21.62; mol. wt. 148.

Reaction of II with $SOCl_2$. A 7.07 g (0.067 mole) quantity of II was added in small portions with strong cooling to a solution of 20 ml of $SOCl_2$ in 50 ml of benzene. The benzene solution was poured onto ice, the organic layer separated, dried over $MgSO_4$, and the benzene distilled off. Recrystallization of the residue from ethanol gave 2.8 g (29.2%) of product mp 70–71° C (lit. [9] mp 67–69° C). A mixed melting point with bis(2,3-dichloropropyl) disulfide obtained by oxidation of 2,3-dichloro-1-propanethiol with $FeCl_3$ gave no depression. Found, %: C 26.02, 25.03; H 3.47, 3.39; Cl 49.52, 49.32; S 21.91, 21.71; mol. wt. 285, 287. Calculated for $C_6H_{10}Cl_4S_2$, %: C 25.00; H 3.47; Cl 49.25; S 22.90; mol. wt. 288. The residue from the mother liquors was a viscous, undistillable material which was not further investigated. A 1 g (0.01 mole) quantity of II was treated with 3 ml of $SOCl_2$, and the mixture was poured into water. The aqueous layer was extracted with ether, and a solution of $BaCl_2$ added giving 0.3105 g (28.6%) and 0.3427 g (31.0%) of $BaSO_4$ in two experiments. A solution of II in water, acidified with acetic acid or sulfuric acid, did not liberate iodine from KI. Iodine was only liberated on acidification with hydrochloric acid, in support of the suggested liberation of free chlorine [2].

3-Thietyl-1,1-dioxide chloroformate (V). To 24.4 g (0.2 mole) was added with cooling 40 ml of phosgene. After stirring for 30 min, 50 ml of cold benzene was added, and with external cooling and stirring such that the temperature did not exceed +5° C, a solution of 20.2 g of triethylamine in 30 ml of benzene was added from a dropping funnel. The mixture was slowly warmed to room temperature, and kept overnight. On the following day, the precipitate was filtered off, and the benzene solution evaporated to dryness in vacuo. The solids were combined and extracted with ethyl acetate (5 portions of 30–40 ml), the ethyl acetate extracts evaporated under reduced pressure, and V recrystallized from ethyl acetate, or from a mixture of dioxan and CCl_4. In the latter case, V was dissolved in dioxan, CCl_4 added until turbid, and cooled. Yield 32 g of V, mp 119° C (from dioxan and CCl_4). Found, %: C 26.02, 26.41; H 3.11, 3.16; Cl 17.89, 18.03; S 17.18, 16.80. Calculated for $C_4H_5ClO_4S$, %: C 26.00; H 2.71; Cl 18.01; S 17.40.

3-Thietyl-1,1-dioxide N,N-dimethylcarbamate (VI). To a solution of 5 g of dimethylamine in 30 ml of ethyl acetate was added in small portions 5 g of V, with cooling (at 0–5° C). The temperature was gradually raised, and stirring continued at room temperature for 3 hr. The precipitate was filtered off and washed with water to remove dimethylamine hydrochloride. The residue was recrystallized from hot water to give 2.5 g of VI, mp 148–149° C. A mixed mp with **VI** obtained as described in [6] gave no depression. Found, %: C 36.98, 36.72; H 5.48, 5.20; N 7.80, 7.20; S 16.60, 16.75; mol. wt. 198 (Rast). Calculated for $C_6H_{11}NO_4S$, %: C 37.30; H 5.70; N 7.26; S 16.55; mol. wt. 193.

b) To a mixture of 12.2 g (0.1 mole) of triethylamine and 50 ml of acetone was added dropwise 10.7 g (0.1 mole) of N,N-dimethylcarbamoyl chloride. The mixture was boiled for 2 hr, the acetone distilled off and the residue recrystallized from water giving 3 g of VI, mp 148–149° C. A mixed mp with material obtained by method A gave no depression.

c) To a mixture of 18 g (0.2 mole) of 3-hydroxythietane, 21 g (0.21 mole) of triethylamine and 50 ml of benzene was added dropwise with stirring 21.5 g (0.2 mole) of N,N-dimethylcarbamoyl chloride in 30 ml of benzene. The mixture was stirred for 6 hr a day for 10 days at room temperature. The precipitated triethylamine hydrochloride was filtered off, the benzene removed and the residue distilled in vacuo, giving 5 g of material, bp 86–87° C (1 mm), which was redistilled repeatedly and the fractions collected, bp 87° C (1 mm); n_D^{20} 1.5033; d_4^{20} 1.1500. Chromatography showed that the liquid contained substantial amounts of 3-hydroxythietane and 3-thietyl dimethylacarbamate. A portion of the liquid was oxidized with H_2O_2 to give VI, mp 143–149° C. A mixed mp with VI obtained by methods a) or b) gave no depression.

Di-(3-thietyl-1,1-dioxide)peroxydicarbonate (VII). To a solution of 5.5 g (0.03 mole) of V in 20 ml of ethyl acetate was added dropwise a cold solution of sodium peroxide (prepared from 1.2 g (0.03 mole) of NaOH in 10 ml of water and 2.5 g (0.03 mole) of 28% hydrogen peroxide), with external cooling, so that the temperature did not exceed 0° C. Stirring was continued for 2 hr, the precipitate filtered off, washed with water and dried in the vacuum desiccator, giving 4 g of **VII**, mp 122–123° C. Found, %: C 29.17, 29.19; H 2.92, 3.33; S 19.70, 19.59; O_{act} 4.84; 4.92. Calculated for $C_8H_{10}O_{10}S_2$, %: C 29.10; H 3.10; S 19.30; O_{act} 4.85.

3-Thietyl-1,1-dioxide perbenzoate (VIII). To a suspension of 8 g (0.0136 mole) of freshly-prepared barium perbenzoate (70%) [10] in 50 ml of ethyl acetate was added 5 g (0.03 mole) of V in small portions with cooling, at −2 to −5° C. When half the V had been added, 4 ml of water was introduced, and the addition of **V** continued. Stirring was continued for 4 hr at +1° C, and the mixture was kept overnight in the refrigerator at +2° C. On the following day, the pre-

The Polymerization of Styrene

Amount of initiator, moles	Weight of polymer							
	without initiator		benzoyl peroxide		VII		VIII	
	69.2 ± 0.1^{0}	79.5 ± 0.1^{0}	69.2 ± 0.1^{0}	79.5 ± 0.1^{0}	69.2 ± 0.1^{0}	79.5 ± 0.1^{0}	69.2 ± 0.1^{0}	79.5 ± 0.1^{0}
$1 \cdot 10^{-4}$	0.09	0.6	0.9	Solid	0.4	0.54	1.24	2.4
$2 \cdot 10^{-3}$			Solid*	Solid	0.47	0.60	1.65	Solid

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*Completely polymerized.

cipitate was filtered off, and the ethyl acetate evaporated to dryness in vacuo. The peroxide obtained was dissolved in acetone, water added until turbid, and cooled to give 3.5 g of **VIII**, mp 108° C. Found, %: C 46.33, 46.20; H 3.45, 3.47; S 11.19, 11.30; O_{act} 5.70; 5.60. Calculated for $C_{11}H_{10}O_7S$, %: C 46.00; H 3.50; S 11.05; O_{act} 5.60.

Polymerization of styrene. A known amount of the peroxide and 5 ml of freshly-distilled styrene were sealed in an ampul after displacement of the air by pure nitrogen. The ampuls were placed in a thermostatic bath and kept for 6 hr with occasional shaking. The contents were then poured into methanol, the polymer washed with methanol and dried in vacuo. The results of the experiments are given in the table.

It will be seen from the table that **VII** did not behave as an initiator at the temperatures employed. Compound **VIII** was the more active peroxide.

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