

Bisoxathiolane Sulfides from a Dioxoene Fatty Acid

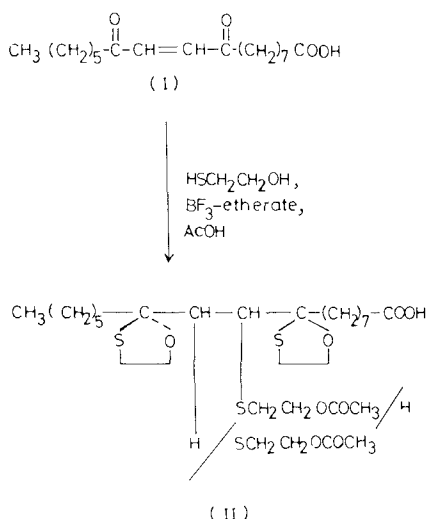
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A quantitative preparation of bisoxathiolane from 9,12-dioxo-*trans*-10-octadecenoic acid is discussed. The reagents used are β -mercaptoethanol and BF_3 -etherate in acetic acid. The structure of the product was established with the help of elemental analysis, infrared, nuclear magnetic resonance and mass spectroscopy data.

KEY WORDS: BF_3 -etherate, bisoxathiolane, condensation reaction, dioxoene fatty acid, β -mercaptoethanol.

The importance of the synthesis of oxathiolanes has been emphasized in recent times by the widespread use of these compounds in pharmaceuticals (1) and in neoplastic therapy (2). These also have been identified as radio protectants (3) and fungicides (4). As a part of our project to prepare new fatty heterocycles of possible industrial utilization, we have treated 9,12-dioxo-*trans*-10-octadecenoic acid (I) with β -mercaptoethanol and freshly distilled BF_3 -etherate with a view to achieve long chain bisoxathiolane (Scheme 1). In a previous paper (5) we have described the formation of a long chain mono-oxathiolane.



SCHEME 1

EXPERIMENTAL PROCEDURES

Methods. Methods were as in previous publications (5,6). Compound (I) was obtained from the method of Abbot *et al.* (7).

Reaction of 9,12-dioxo-*trans*-10-octadecenoic acid (I) with β -mercaptoethanol and BF_3 -etherate. A solution of I (1M), β -mercaptoethanol (10M) and freshly distilled BF_3 -etherate (3M) in acetic acid was first stirred at room

temperature for 15 hr. The reaction mixture was then heated at 60°C for 10 hr to complete the reaction. Progress of the reaction was monitored by thin-layer chromatography (TLC), which indicated the formation of isomeric product. Column chromatographic purification (benzene/ether, 96:4, v/v) of the dense reaction mixture gave II (yield 98%) as an oil. Analysis: (Found: C, 56.66; H, 8.40; S, 17.39%; requires for $\text{C}_{26}\text{H}_{46}\text{O}_6\text{S}_3$: C, 56.69; H, 8.41; S, 17.46%). IR (nujol): 3430 (COOH), 1740 (OCOCH_3), 1710 (COOH), 1440 (S-CH_2 deformation), 1265 (acetate), 1240 (S-CH_2 wagging), 1180 (C-O), 1025 cm^{-1} (oxathiolane ring). NMR (CCl_4): δ 4.39 - 3.90 br, m (6H, 4H α to oxygen in both rings and $\text{S-CH}_2\text{-CH}_2\text{-OCOCH}_3$), 3.0-2.50 br, m (7H, 4H α to sulfur in both rings, $-\text{CH-S-CH}_2-$), 2.7 m (2H, $\text{CH}_2\text{-COOH}$), 2.0 s (3H, $-\text{OCOCH}_3$), 1.78 m (6H, protons α to both rings) and 8.50 br, s (1H, $-\text{COOH}$, D_2O exchangeable). Mass: M: 550.

RESULTS AND DISCUSSION

We have reported previously the preparation of fatty acids possessing oxathiolane and thioether functionalities (5,8). Now we report a condensation reaction of 9,12-dioxo-*trans*-10-octadecenoic acid (I) with β -mercaptoethanol and freshly distilled BF_3 -etherate in 1:10:3 ratio. The dense reaction mass afforded a single product on column chromatographic purification.

The compound (II) was analyzed for $\text{C}_{26}\text{H}_{46}\text{O}_6\text{S}_3$. The infrared (IR) spectrum had not shown a band for isolated ketone in the region of 1720 cm^{-1} , which indicated the formation of oxathiolane ring at both C_9 and C_{12} carbonyls. Two other significant bands in the carbonyl region were observed at 1740 (OCOCH_3) and 1710 (COOH). Bands associated with oxathiolanes were illustrated at 1440 (S-CH_2 deformation), 1180 (C-O) and 1025 (oxathiolane ring). Two structure-revealing broad multiplets in the nuclear magnetic resonance (NMR) spectrum at δ 4.39 - 3.9 (6H) and 3.0 - 2.5 (7H), were assigned to the protons α to oxygen and sulfur in the molecule. An equally important multiplet was displayed at δ 1.78 (6H, protons α to both rings). A multiplet at δ 2.7 was assigned to two protons α to acid carbonyl. A singlet at δ 2.0 was observed for three acetate protons. These values supported the formula as 9,12-bisoxathiolane-10(11)-(S- β -mercaptoethylacetate)octadecanoic acid (II). Mass spectrum was more informative to confirm the *bis* nature of this structure by showing a molecular ion at m/z 550 (Fig. 1). α -Cleavage produced mass ions at 173, 465 and 231, 407, which confirmed the location of two oxathiolane rings, one each at C_9 and C_{12} . Mass ions at 303 and 245 confirmed the presence of thioether on both of the olefinic carbons (Scheme 2).

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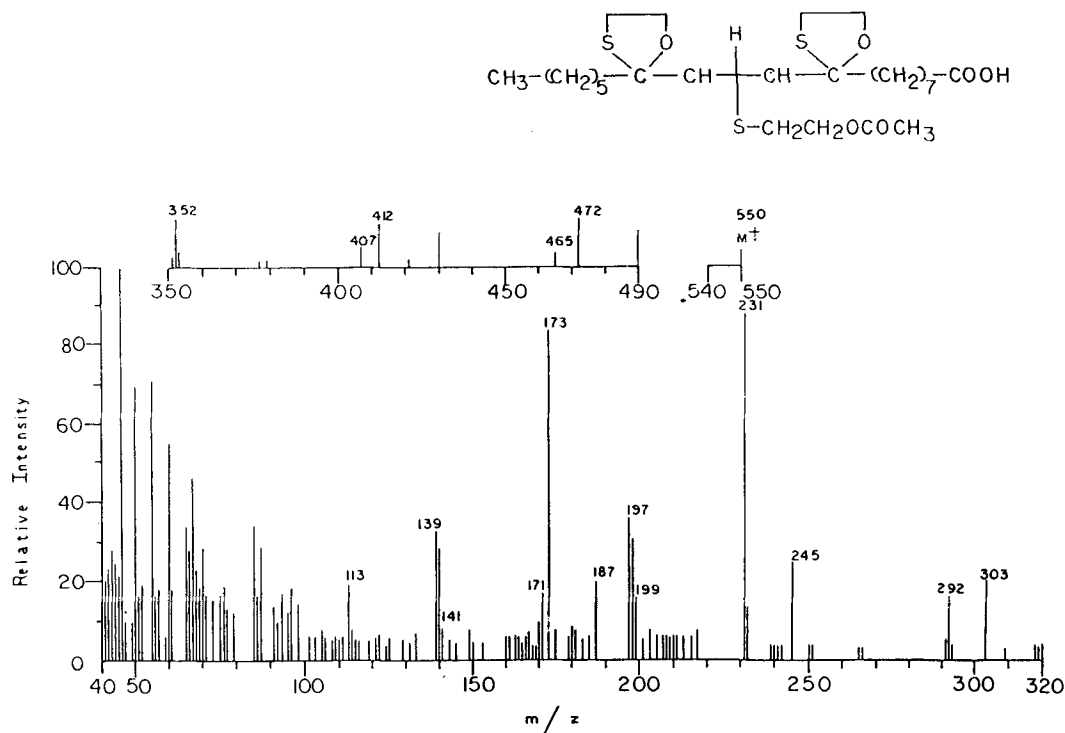
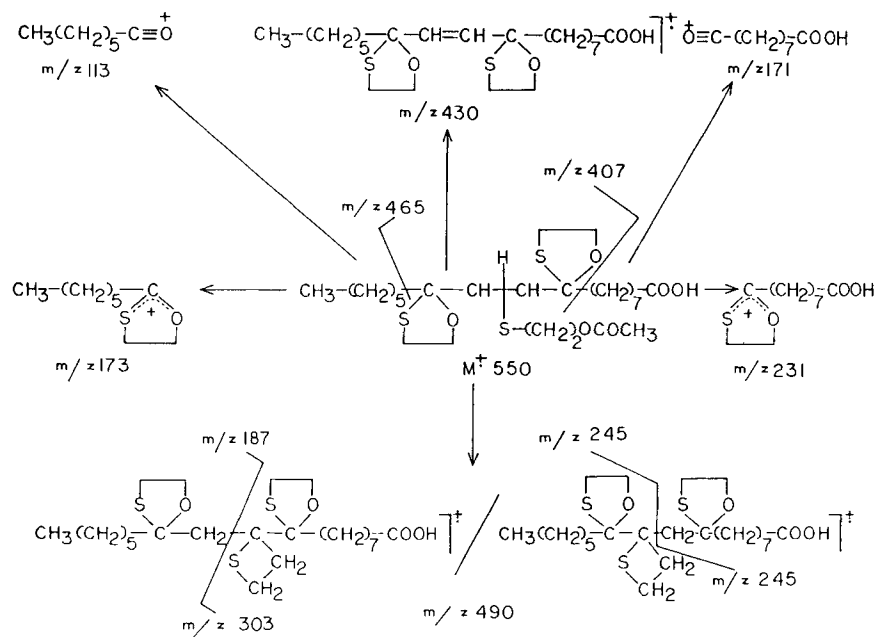


FIG 1. Mass spectrum of II.



SCHEME 2

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