

## The Synthesis of 3-Methyl-3*H*-4,1-benzoxathiepin-5-one 1,1-Dioxide, a New Ring System

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As a part of a synthetic program involving the synthesis of  $\alpha,\beta$ -acetylenic sulfones, an attempt was made to prepare *o*-(1-propynylsulfonyl)benzoic acid (II) by the oxidation of the corresponding sulfide (I). The product which was obtained was not the expected acetylenic sulfone, but was 3-methyl-5*H*-4,1-benzoxathiepin-5-one 1,1-dioxide (III). To the author's knowledge, this is the first reported example of the 5*H*-4,1-benzoxathiepin-5-one 1,1-dioxide ring system.

The reaction between *o*-mercaptobenzoic acid and propargyl bromide under basic conditions afforded *o*-(1-propynylthio)benzoic acid (I) in good yield. Oxidation of I with 30% hydrogen peroxide in acetic acid afforded 3-methyl-5*H*-4,1-benzoxathiepin-5-one 1,1-dioxide (III) presumably *via* the intermediacy of the acetylenic sulfone (II).

The structural assignment of III is partially based on the following analytical information. The elemental analysis corresponds to the empirical formula  $C_{10}H_8O_4S$ . The infrared spectrum possesses absorptions at 1765 (C=O); 1630, 1595, 1570 (C=C); and 1325, 1300, 1270, 1175  $cm^{-1}$  ( $SO_2$ , other). The nmr spectrum (deuteriochloroform) consists of absorptions at  $\delta$  2.14 (3H, doublet,  $J=1Hz$ ),  $\delta$  7.12 (1H, quartet,  $J=1Hz$ ) and  $\delta$  7.97 (4H,

broad singlet). These absorptions correspond to the methyl, vinyl, and aromatic protons, respectively. The molecular weight as determined by mass spectroscopy is 224 which is the calculated value.

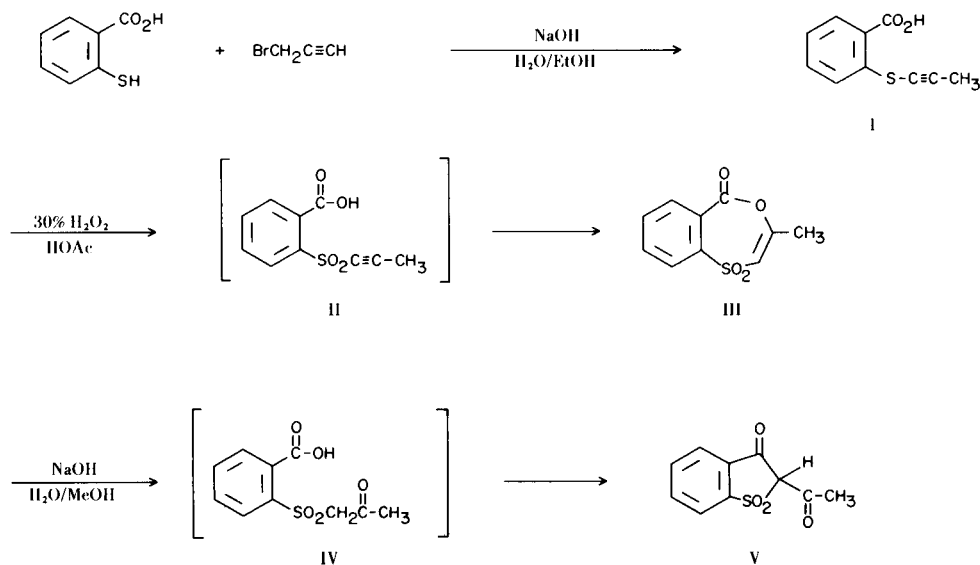
Chemical support for the proposed structure was obtained by treatment of III with sodium hydroxide in methanol-water to afford the known 2-acetylbenzo[*b*]-thiophen-3(2*H*)-one 1,1-dioxide (V) (1). This compound presumably arises by ring opening to the intermediate IV which then cyclizes to V.

### EXPERIMENTAL

All melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were obtained on a Parkin-Elmer Model 421 recording spectrophotometer in Nujol mulls. The nmr spectra were recorded on a Varian A-60A spectrometer with chemical shifts measured in ppm downfield from tetramethylsilane. The mass spectra were determined on an Atlas  $CH_4$  spectrometer.

*o*-(1-Propynylthio)benzoic Acid (I).

*o*-Mercaptobenzoic acid (77 g., 0.50 mole) was added portionwise to a solution of sodium hydroxide (40 g., 1.0 mole) in a mixture of water (400 ml.) and ethanol (250 ml.) maintained at 20°. The mixture was stirred until the solid had dissolved and



propargyl bromide (59.5 g., 0.50 mole) was added over a one-hour period. The solution was maintained at 20-30° throughout the addition and then stirred at room temperature for four days. The solution was diluted with water (1.5 l.), acidified with dilute hydrochloric acid, and cooled at 5° for several hours. The precipitate was removed by filtration and recrystallized from absolute methanol to afford 51 g. (54% yield) of product, m.p., 196-197°; infrared:  $\lambda$  max 3050, 2670, 2570, 2530, 1670, 1590, 1570, 1320, 1290, 1265, 895 and 745  $\text{cm}^{-1}$ ; nmr (deuteriochloroform-DMSO- $d_6$ ):  $\delta$  2.18 (3H, singlet) and  $\delta$  7.1-8.2 (4H, series of complex multiplets).

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_8\text{O}_2\text{S}$ : C, 62.50; H, 4.20; S, 16.67; eq. wt., 192; mol. wt., 192. Found: C, 62.50; H, 4.54; S, 16.82; eq. wt., 196; mol. wt., 192 (mass spectroscopy).

### 3-Methyl-5H-4,1-benzoxathiepin-5-one 1,1-Dioxide (III).

*o*-(1-Propynylthio)benzoic acid (I) (19.2 g., 0.10 mole) was dissolved in warm (70°) acetic acid (600 ml.) and 30% hydrogen peroxide (60 ml.) was added over a one-half hour period. After the initial exothermic reaction had subsided, the solution was maintained at 80-90° by external heat for an additional two hours. The solution was placed in a large evaporating dish and the acetic acid was removed by a current of air. The semi-solid residue was warmed on a steam bath with water (200 ml.), cooled and filtered. The precipitate was recrystallized from absolute methanol to afford 10.15 g. (45% yield) of product, m.p., 157.5-158.5°; infrared:  $\lambda$  max 1765, 1630, 1595, 1570, 1325, 1300, 1270, 1220, 1175, 1125, 1050, 1010 and 755  $\text{cm}^{-1}$ ; nmr (deuteriochloroform):  $\delta$  2.14 (3H, doublet,  $J = 1\text{Hz}$ ),  $\delta$  7.12 (1H, quartet,  $J = 1\text{Hz}$ ) and  $\delta$  7.97 (4H, broad singlet).

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_8\text{O}_4\text{S}$ : C, 53.57; H, 3.57; S, 14.31; mol. wt., 224. Found: C, 53.77; H, 3.76; S, 14.48; mol. wt., 224 (mass spectroscopy).

### 2-Acetylbenzo[*b*]thiophen-3(2H)-one 1,1-Dioxide (V).

3-Methyl-5H-4,1-benzoxathiepin-5-one 1,1-dioxide (III) (2.24 g., 0.010 mole) was added to a stirred, cooled (ice-bath) solution of sodium hydroxide (0.40 g., 0.010 mole) in a mixture of water (10 ml.) and methanol (10 ml.). The solid dissolved within 10 minutes to form a clear solution which then deposited a white precipitate in an additional 15-20 minutes. The solid was dissolved by the addition of water (30 ml.) and the solution was stirred for an additional hour at room temperature. The solution was acidified with dilute hydrochloric acid and the precipitate was removed by filtration. The precipitate was recrystallized from absolute methanol to afford 1.4 g. (67% yield) of product, m.p., 163-164° [lit. (1), m.p., 164°]; infrared:  $\lambda$  max 3090, 1665, 1595, 1580, 1330, 1290, 1235, 1160, 1125 and 755  $\text{cm}^{-1}$ ; nmr (deuteriochloroform):  $\delta$  2.53 (3H, singlet),  $\delta$  7.6-8.1 (4H, complex multiplet), and  $\delta$  12.8 (1H, broad singlet). The infrared and nmr spectra were identical to those of an authentic sample prepared according to the procedure of Cohen and Smiles (1). The mixed melting point with the authentic sample was 163-164°.

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_8\text{O}_4\text{S}$ : C, 53.57; H, 3.57; S, 14.31; eq. wt., 224; mol. wt. 224. Found: C, 53.61; H, 3.73; S, 14.30; eq. wt., 230; mol. wt., 224 (mass spectroscopy).

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### REFERENCES

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