## Synthesis and Thermolysis of 2H-1,2,3-Benzothiadiazine 1,1-Dioxide and 2,1-Benzoxathiin-3-one 1,1-Dioxide<sup>1,2</sup>

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2H-1,2,3-Benzothiadiazine 1,1-dioxide (6) and 2,1-benzoxathiin-3-one 1,1-dioxide (5), representatives of little-known heterocyclic systems, have been synthesized from sodium o-formylbenzenesulfonate (7). Thermolysis of 5 and 6 was investigated in the hope of finding evidence for the formation of a sulfene. No characterized product was obtained from 5, but 6 gave the sultine 3H-2,1-benzoxathiole 1-oxide (21), the compound expected from the sulfene 20.

La 2H-benzothiadiazine-1,2,3 dioxyde-1,1 (6) et la benzoxathiin-2,1 one-3 dioxyde-1,1 (5), des représentants de systèmes hétérocycliques peu connus, ont été synthétisés à partir de l'o-formylbenzènesulfonate de sodium (7). La thermolyse de 5 et 6 a été examinée dans l'espoir de trouver des indications concernant la formation d'un sulfène. Aucun produit caractérisé ne fut obtenu à partir de 5, mais 6 a donné la sultine 3H-benzoxathiole-2,1 oxyde-1 (21), le composé prévu du sulfène 20.

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#### Introduction

Sulfenes (RR'C=SO<sub>2</sub>) may now be regarded as established and respectable intermediates,<sup>3</sup> in certain reactions at least, even though they have thus far eluded all of the numerous attempts at their isolation and characterization. As a possible route leading to new information on sulfenes, and possibly even their isolation, we contemplated the synthesis of compounds which by the action of heat or light might fragment to give sulfenes. One tested recipe for the frangibility required to form high energy species requires the construction of a molecule so arranged that the other fragment of the reaction is a particularly stable species, e.g. molecular nitrogen, carbon dioxide, sulfur dioxide, and so on.<sup>4</sup> Among the possible ways of applying this notion to the formation of sulfenes is the synthesis of species of the general formula 1 which could undergo cycloreversion of the reverse Diels-Alder type to give vinylsulfene (2) and a stable fragment 3. For reasons of synthetic convenience we focussed our attention on benz-

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fused analogues of 1, the specific objectives in the work reported herein being 4H-1,2,3-benzothiadiazine 1,1-dioxide (4) and 2,1-benzoxathiin-3one 1,1-dioxide (5), alias "o-sulfophenylacetic anhydride".



The cyclic anhydride 5 was synthesized without difficulty but gave none of the hoped for fragmentation. The cyclic azo compound 4 was not obtained but its isomer 6 was prepared and found to extrude nitrogen on thermolysis with formation of a sultine (cyclic sulfinic ester); 6 is the parent of a heterocyclic system previously known only in the form of some 4-hydrazino-derivatives (3 and references cited) and the very recently reported 4-phenyl compounds (4). In the course of this work it was found that reaction of 6 with chlorine led to an interesting transformation possibly involving a sulfene; this is described in detail in the accompanying paper. Part of the substance of these two papers has already been reported in preliminary form (5).

<sup>&</sup>lt;sup>1</sup>Organic Sulfur Mechanisms. Part 8, For part 7 see ref. 1. <sup>2</sup>Some of the work recorded in this and the following

paper is taken from the following theses (University of Western Ontario): D. M. Deaken (Honors B.Sc., 1964), A. Hawson (M.Sc. 1968), J. Komery (M.Sc. 1969). <sup>3</sup>For a summary of the chemistry of sulfenes up to 1967 see Opitz' review (2); access to more recent work may be obtained from ref. 1 and papers cited therein

obtained from ref. 1 and papers cited therein. <sup>4</sup>Thermolysis of four-membered rings, with and without fragmentation, has also been explored and appears to lead to sulfenes (1).



#### **Results and Discussion**

## Synthesis of 2H-1,2,3-Benzothiadiazine 1,1-Dioxide (6)

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The starting material for all of the syntheses described in this paper is sodium *o*-formylbenzenesulfonate (7), a material which is commercially available in a "practical" grade apparently as the monohydrate (*cf.* ref. 6). Reaction of 7 with hydrazine hydrate gave the hydrazone **8**, which when treated without purification with a mixture of phosphorus oxychloride and phosphorus pentachloride, gave **6** in about 5–10% yield (see Scheme 1). Attempts to improve the yield led to the observation that recrystallization of the hydrazone led to an even poorer yield of **6**. Acting on the inference that residual hydrazine was responsible for the difference, hydrazine was added to the reaction of 8 with POCl<sub>3</sub>-PCl<sub>5</sub>. The yields of 6 were much improved, though erratic; the best yield in a number of such experiments was 80% (based on 8) but repetition of the procedure as recorded gave only low yields. Further study led to a procedure which incorporated minor changes in conditions and which gave yields of 30-50% with some consistency (see Experimental).

The structure **6** for the material thus obtained follows from elemental analysis and the following spectroscopic features: (a) bands at 3.1 (1H, NH), 7.9 (m, four aromatic hydrogens), and 8.2 p.p.m. (s, 1H, -CH=N-) in the n.m.r. spectrum, (b) i.r. peaks at 3280 (NH), 1657 (w, C=N-), 1345 (vs) and 1165 cm<sup>-1</sup> (vs) ( $-SO_2-$ ). Final confirmation of the structure (**6**) is provided by its synthesis from *o*-formylbenzenesulfonyl chloride (**9**) as described below.

Because of the erratic yields of 6 from 7 on treatment with the phosphorus chloride – hydrazine mixture, the *p*-toluidine anil 10 and the tosylhydrazone 13 (prepared from 7 via 12) were investigated as possible precursors of 6 (see Scheme 2). The anil 10 apparently gave 11, whereas the tosylhydrazone 13 gave a 3% yield of 6. No attempt was made to improve the tosylhydrazone route because of the discovery of another, and evidently better, way of making 6.

An obvious precursor of 6 is *o*-formylbenzenesulfonyl chloride (9), a compound which, prior



to this study, was unknown. The reaction of 7 with  $PCl_5-POCl_3$  has been known for many years (6, 7) to lead, not to 9, but to its cyclic isomer 14, which does not give 6 on reaction with hydrazine hydrate. As is described in detail in the following paper we have found that chlorination of 6 in the presence of water gives 9. As a route for the synthesis of 6, this procedure is, of course, valueless, but it did lead to the characterization of 9 so that it could be readily recognized when made in other ways, even when mixed with other materials. In addition, by treating a sample of 9 prepared from 6 with hydrazine, it was possible to get 6 back in very good yield; this, as has been mentioned above, confirmed the structure of 6.

Treatment of 7 with thionyl chloride gave no reaction, and conversion of 7 to o-formylbenzenesulfonic acid followed by reaction with thionyl chloride gave the cyclic chloride 14. When 7 was allowed to react with thionyl chloride in the presence of a catalytic amount of dimethylformamide, however, the product was evidently mainly o-formylbenzenesulfonyl chloride (9) mixed with a little of the cyclic isomer (14) (Scheme 3). Reaction of this mixture with hydrazine hydrate led to the isolation of 6 in an overall yield of about 50% from 7. The crude product also contains 14, but this is readily separated by taking advantage of the acidity of 6. This procedure is simple and gives reasonably consistent yields, and became our method of choice for the synthesis of 6. It was found that only a short reaction time was required to convert 7 to 9, longer times (or treatment of 9 with thionyl chloride) led to the benzal chloride 15, which did



not yield 6 under the conditions used to convert 9 to 6.

## Synthesis of 2,1-Benzoxathiin-3-one 1,1-Dioxide (5) ("o-Sulfophenylacetic Anhydride")

The synthesis of 5 is straightforward and is summarized in Scheme 4. The starting material (16) was obtained from 7 via 14, following the method of List and Stein (7) as described in detail by Helberger *et al.* (8). The structure of 5 follows from its mode of synthesis and is confirmed by elemental analysis and spectra; a conspicuous feature in the i.r. is a strong band at 1818 cm<sup>-1</sup>. As would be expected of a mixed carboxylic – sulfonic anhydride, 5 is very easily hydrolyzed, for example, by atmospheric moisture, to *o*-sulfophenylacetic acid (18), and reacts very readily with aniline to give 19.



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#### Thermolysis of 5 and 6

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All attempts at thermal fragmentation of 5 to give 20 or materials evidently derived from 20 were without avail. On the basis of the results (1, 9) with thermolysis of thiete 1,1-dioxide (23), which appears to rearrange via vinylsulfene (CH<sub>2</sub>=CH-CH=SO<sub>2</sub>), we might have expected that 20 below 700-800° would have given the "sultine" (cyclic sulfinic ester) 21, and at higher temperatures the "desulfinylation" (1) product, o-quinone methide (22). An authentic specimen of 21 was available from work connected with the chlorinolysis of 6 (see the following paper), and 22 and its trimerization product have been described (10) and should have been readily recognizable, if present. In either the simple quartz tube at 380–550° and pressures of 5–7  $\mu$ , or the flash thermolysis apparatus (1) at 600°, 5 was recovered substantially unchanged. In the flash apparatus at 1000°, only general decomposition was observed.

Thermolysis of the thiadiazine (6) at  $600-620^{\circ}$ in the flash apparatus gave back starting material and at 750° yielded only an uncharacterized gum. In a quartz tube at 500° and about 1 mm, 6 gave a roughly 25% yield of the sultine 21; the yields appeared to be improved by the presence of a plug of glass wool in the tube. It has also been noted by Dr. L. J. Danks in these laboratories (private communication) that 21 is formed (in addition to black tar) in an estimated 10% yield on heating 6 in the melt at 180°. The sultine (21) is the product expected at these temperatures from 20 if, in fact, it were formed. When taken with our evidence (1) for the intermediacy of vinylsulfene in the rearrangement of 23 to 24, and also the formation of the 4-chloro analogue of 21 on chlorinolysis of 6 as described in the following paper, this result would suggest that the simplest route to 21 from 6 is via 20, though the present evidence does not exclude other pathways. Formation of 20 from 6 formally requires migration of a hydrogen from nitrogen to carbon; this could perhaps take place via 4, followed by fragmentation as originally visualized, or conceivably by cleavage of one of the ring bonds in 6, with formation of the diazene (diimide), followed by hydrogen migration accompanying loss of nitrogen. With either of these processes it is not surprising that the quartz tube apparatus and the melt, with their much greater likelihood of collisions with the walls and other molecules, would be more favorable conditions for a two (or more) step process than the flash apparatus.

#### Experimental

Sodium o-formylbenzenesulfonate (7) was obtained from Koch-Light Laboratories Limited, Colnbrook, England, under the designation "o-sulfobenzaldehyde Na salt" and indicated as "75-89%" or "practical" grade. No attempt was made either to assay or to purify the 7 before use; the yields given are based on the assumption that it is the pure mono-hydrate and would presumably be somewhat higher if pure 7 were used. All other reagents and solvents were of commercial reagent grade unless otherwise indicated.

Unless otherwise specified melting points were determined on a Kofler hot stage and are uncorrected. The i.r. spectra were obtained with Beckman IR-7 or IR-10 instruments using sodium chloride cells. The n.m.r. values given were determined on a Varian A60 instrument using tetramethylsilane as internal standard; a Varian T60 spectrometer was used in some instances to ascertain product composition. The t.l.c. was carried out using Camag Kieselgel DF5 or "GF-254 (acc. to Stahl)" silica gel supplied by E. Merck, Darmstadt, Germany. Petroleum ether refers to the fraction of boiling range 35-60°. Unless otherwise stated magnesium sulfate was used to dry the organic phase following extraction in a separatory funnel.

#### Preparation of 2H-1,2,3-Benzothiadiazine 1,1-Dioxide (6) from Sodium o-Formylbenzenesulfonate (7) via the Hydrazone (8)

Sodium o-formylbenzenesulfonate (7) (40.0 g) and hydrazine hydrate (99%) (50 ml) were refluxed together for 2 h. The hydrazine hydrate was then evaporated off under reduced pressure and the crude product was dissolved in methanol. The methanol insoluble material was removed by filtration and the methanol soluble material recrystallized from methanol-ether giving 24.0 g (56%) of white crystals.

The crude hydrazone 8 (10 g) obtained as above, was placed in a three-necked round-bottomed flask fitted with a condenser, mechanical stirrer, and dropping funnel. Hydrazine hydrate (99%, 5 ml) was added and the mixture stirred and cooled to  $0^{\circ}$  in an ice bath. Phosphorus oxychloride (50 ml) was added dropwise over a period of 45 min, followed by phosphorus pentachloride (10 g), and the mixture warmed to  $60^{\circ}$  and stirred until the mixture became smooth (about 4.5 h). The mixture

was poured onto crushed ice and allowed to stand until the phosphorus oxychloride appeared to have hydrolyzed completely, and extracted with chloroform. The extracts were washed with water, dried with anhydrous sodium sulfate, and the solvent evaporated leaving a pale yellow solid 2.4 g (30%). Recrystallization from chloroform gave crystals of 3 (1.35 g, 17%) melting at 142–143°.

A number of repetitions of this procedure with varying quantities of **8** gave erratic results with crude yields sometimes as low as 5–10% and on one occasion as high as 80%. The use of benzene or dimethylformamide as solvent led to little or no **6**. In one experiment with this general method, starting with a smaller quantity (3.9 g) of **8** and appropriately reduced amounts of the other reagents, further hydrazine hydrate (5 ml) was added after the addition of the phosphorus oxychloride was complete; this led to a 50% yield of crude product (25% after recrystal-lization).

The i.r. spectrum of 6 (Nujol mull) showed the following bands: 3280, 1657 (w), 1598 (w), 1565 (m), 1479 (w), 1448 (m), 1360 (sh), 1345 (vs), 1268 (m), 1225 (m), a very strong band with peaks at 1183, 1165, and 1145, 1080 (m), 993 (s), 970 (m), 915 (s), 883 (m), 858 (m), 780 (w), 785 (s), 735 (m), 690 (w), 640 (s). The n.m.r. spectrum (in acetone- $d_6$ ) showed a broad hump at 3.1 which disappeared on addition of D<sub>2</sub>O<sub>4</sub> a singlet at 8.1, and a complex band from 7.8-8.0 p.p.m.

Anal. Calcd. for  $C_7H_6SO_2N_2$ : C, 46.14; H, 3.32; N, 15.38; S, 17.59. Found: C, 46.19; H, 3.29; N, 15.24; S, 17.42.

The  $pK_a$  of 6 was determined in 50% ethanol-water (by weight) by titration with 0.1 N sodium hydroxide measuring the pH with a Radiometer 25 pH meter with glass and calomel electrodes standardized with aqueous buffer solution, pH 7.00; to obtain the hydrogen ion activity in the aqueous alcohol medium 0.18 was subtracted from meter readings of the pH (cf. Bates et al. (11)). By this technique the following  $pK_a$  values were obtained: 6, 7.2; benzaldehyde tosylhydrazone, 8.6; benzenesulfon-p-toluidide, 10.1. Dauphin et al. (12) report a  $pK_a$  value of 10.17 for benzenesulfon-p-toluidide in the same medium.

#### Preparation of 2H-1,2,3-Benzothiadiazine 1,1-Dioxide (6) via o-Formylbenzenesulfonyl Chloride (9)

Sodium *o*-formylbenzenesulfonate (7) (5 g, 0.24 mol) was suspended in thionyl chloride (20 ml) and dimethylformamide (12 drops) added. The mixture was refluxed for 1 h and then evaporated to dryness. The residue was extracted with methylene chloride and filtered. The filtrate was concentrated to about 25 ml and hydrazine hydrate (99%) (3 ml) cautiously added dropwise with stirring. The mixture was stirred at room temperature for 10 min, then diluted with water, cooled in an ice bath and acidified with concentrated HCl. The aqueous mixture was extracted with chloroform, the chloroform extract was extracted with 5% NaOH. The chloroform layer was dried, and the solvent evaporated, leaving a pale yellow solid (0.59 g) which melted at 113-115° and had the same i.r. spectrum as a sample of the "pseudo acid chloride" (14) prepared by the method of Helberger et al. (10). The sodium hydroxide extracts were acidified and extracted with chloroform; the chloroform extracts were dried and the solvent removed to give a crude

2H-1,2,3-benzothiadiazine 1,1-dioxide (6) (2.08 g, 50%), which after one recrystallization from chloroform melted at  $141-142^{\circ}$ .

It was found that best conversion of 4 to *o*-formylbenzenesulfonyl chloride (9) was obtained using only a very brief reaction time with thionyl chloride (*e.g.* 3 min reflux). Under such conditions using 7 (5 g), thionyl chloride (20 ml) and dimethylformamide (25 drops) and taking the product up in pentane and washing with water, 9 was obtained as a pale yellow oil (3.7 g, 76%), identified by i.r. and n.m.r. spectra. With longer reaction times 9 was further transformed to 15 (see below).

#### Attempted Synthesis of 2H-1,2,3-Benzothiadiazine 1,1-Dioxide (6) via the Anil 10. Formation of the Carbinolamine Ether 11

Sodium o-formylbenzenesulfonate (7) (10.4 g, 0.05 mol) and p-toluidine (5.4 g, 0.05 mol) were partially dissolved in absolute ethanol (50 ml) and gently refluxed for 20 min. The hot solution was filtered and the filtrate evaporated to dryness. Ether was added to the oily residue and the colorless crystals, presumed to be 10 (11 g 74%), collected by filtration. The i.r. spectrum (Nujol) showed bands at 1620 (w), 1565 (w), 1500 (w), 1190 (vs), 1140 (m), 1090 (m), 1045 (w), 1025 (s), 970 (w), 880 (w), 820 (m), 760 (m), 716 (s).

The anil (10) (5 g) was mixed with phosphorus pentachloride (5 g) and ground in a mortar for 5 min, and then left at room temperature for 0.5 h. The mixture was poured into ice-water and extracted with methylene chloride. The extracts were dried over anhydrous sodium sulfate and the solvent evaporated to give a yellow solid (4.3 g). Extensive recrystallization from methylene chloride – petroleum ether and methanol gave crystals melting at 129–130°, for which structure 11 is assigned. The i.r. spectrum showed peaks at 3000 (w), 1510 (m), 1450 (w), 1310 (s), 1270 (m), 1170 (s), 1130 (m), 1090 (m), 1040 (s), 970 (m), 600 (m), 580 (m) and the n.m.r. spectrum showed complex aromatic absorption from 7.1–8.0 (8H), and singlets at 6.40 (1H), 3.12 (3H) and 2.37 p.p.m.

Anal. Calcd. for  $C_{15}H_{15}NO_3S$ : C, 62.27; H, 5.23; N, 4.84; S, 11.06. Found: C, 62.46; H, 5.34; N, 4.91; S, 11.06.

# Synthesis of 2H-1,2,3-Benzothiadiazine 1,1-Dioxide (6) via the Tosylhydrazones 12 and 13

*p*-Toluenesulfonylhydrazine (tosylhydrazine) (4.7 g) and sodium *o*-formylbenzenesulfonate (7) were partially dissolved in methanol (25 ml) and refluxed for 1 h. The hot solution was filtered and the filtrate treated with ether to give a white, crystalline solid (12) (6.1 g) which showed the following peaks in the i.r. (Nujol); 3350 (m), 1600 (w), 1320 (m), 1205 and 1170 (vs), 1140 (sh), 1090 (m), 1065 and 1045 (m), 1025 (m), 965 (m), 835 (m), 810 (m), 787 and 780 (w), 760 (w), 730 and 720 (m), and 700 (w).

The tosylhydrazone 12 was mixed with phosphorus pentachloride (2 g) and ground in a mortar. The resultant yellow paste was left at room temperature for 10 min whereupon it was mixed with water (50 ml) and the mixture extracted with ether. The extracts were dried over anhydrous sodium sulfate and the solvent removed leaving a colorless oil (1.2 g, 61 %) which solidified on standing. The i.r. spectrum showed characteristic bands at

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1375 and 1325 and 1174 ascribable to the  $SO_2CI$  and  $-SO_2N$  functions. Recrystallization from methylene chloride – petroleum ether gave colorless crystals (presumed to be 13) (768 mg), m.p. 136–140° (dec) which were not further characterized.

The sulfonyl chloride – hydrazone (13) (3 g) was mixed with hydrazine hydrate (99%, 10 ml) and warmed at 60° for 1.5 h. The pale yellow solution was cooled, diluted with water, and acidified with concentrated hydrochloric acid. The mixture was extracted with chloroform and the extracts dried over anhydrous sodium sulfate. Removal of the solvent gave an orange oil (1.25 g), which on trituration with chloroform gave a small amount (105 mg) of colorless crystals, m.p. 137–410°, which gave no depression of m.p. on admixture with authentic 6. The remaining products were not investigated further.

#### Preparation of o-Dichloromethylbenzenesulfonyl Chloride (15)

Sodium o-formylbenzenesulfonate (7) (5 g, 0.024 mol) was suspended in thionyl chloride (20 ml) and dimethylformamide (25 drops) added. The mixture was refluxed for 0.5 h. The excess thionyl chloride was then removed under reduced pressure, the residue was taken up in methylene chloride and the mixture filtered. Removal of the methylene chloride gave an oily residue which partially dissolved in pentane. The pentane solution was washed with water and dried; removal of the solvent gave a yellow oil (4.2 g) which crystallized on cooling in a Dry Ice acetone mixture. Recrystallization from carbon tetrachloride – pentane at  $-60^{\circ}$  gave colorless crystals (3.4 g, 55%) melting at 50-52°; recrystallization gave the analy-tical specimen, m.p. 54-55°. The i.r. spectrum showed bands at 3000 (w), 1570 (w), 1470 (w), 1445 (m), 1380 (vs), 1320 (w), 1285 (w), 1180 (vs), 1120 (m), 1060 (w), 980 (w), 840 (s), and 680  $\text{cm}^{-1}$  (m). The n.m.r. spectrum showed only complex absorption from 7.4-8.4 with a prominent peak at 7.86 p.p.m.; the mass spectrum indicated a molecular weight of 258 with another peak at 260 of the same intensity.

Anal. Calcd. for  $C_7H_5Cl_3O_2S$ : C, 32.39; H, 1.94; Cl, 40.98; S, 12.35. Found: C, 32.58; H, 1.95; Cl, 41.18; S, 12.45.

o-Formylbenzenesulfonyi chloride (9) (1.01 g), thionyl chloride (5 ml), and dimethylformamide (5 drops) were refluxed for 0.5 h. The excess thionyl chloride was removed under reduced pressure and water and pentane added to the residue. The pentane extract was dried and the solvent evaporated leaving colorless crystals; the i.r. spectrum was virtually identical with that of 15 prepared as above except for a rather small peak at 1700 cm<sup>-1</sup>, presumably due to a small amount of 9. Recrystallization from carbon tetrachloride – pentane gave crystals melting at 49–52°.

#### Reaction of 3H-2,1-Benzoxathiole 1,1-Dioxide (16) with Sodium Cyanide

3H-2,1-Benzoxathiole 1,1-dioxide (16) (10) (5 g, 0.029 mol) was dissolved in absolute alcohol (150 ml) and was added slowly with stirring over a period of 30 min to a solution of sodium cyanide (1.48 g, 0.03 mol) in water (15 ml). The reaction mixture was refluxed for 4 h. Evaporation of solvent yielded sodium *o*-cyanomethylbenzene-sulfonate (17) (6.4 g, 100%). The product was recrystallized three times from methanol, m.p. 298-301°.

Anal. Calcd. for  $C_8H_6NaNO_3S$ : C, 43.84; H, 2.76; N, 6.39; S, 14.63. Found: C, 43.95; H, 2.70; N, 6.41; S, 14.32.

The i.r. spectrum (Nujol) showed absorption bands at 3060 (w), 2240 (w), 1408 (w), 1235 (s), 1215 (s), 1195 (s), 1180 (s), 1145 (m), 1095 (m), 1050 (w), 1030 (m), 955 (w), 755 (m), 725 (m), 705 (m), 625 cm<sup>-1</sup> (m). The n.m.r. spectrum (dimethyl sulfoxide- $d_6$ ) showed absorption bands at 4.43 (s, 2H) and 7.25-8.0 p.p.m. (aromatic hydrogen absorption, 4H).

## Hydrolysis of Sodium o-Cyanomethylbenzenesulfonate (17)

Sodium *o*-cyanomethylbenzenesulfonate (**17**) (2 g, 9.1 mmol) was dissolved in water (20 ml). Concentrated hydrochloric acid (20 ml) was added dropwise with stirring. The reaction mixture was refluxed for 45 min and then evaporated to dryness. The material (2.2 g) obtained was not characterized but was dissolved in water and passed through a column of Dowex 50W-X8 ion exchange resin in the acid form. The aqueous solution was immediately evaporated under reduced pressure (0.1 mm) without heating, to yield *o*-sulfophenylacetic acid (**18**) (2.2 g, 94%, assuming one molecule of water of crystallization). The product was recrystallized three times from methanol, m.p. 215–219°.

Anal. Calcd. for  $C_8H_8O_5S \cdot CH_3OH: C, 43.51; H, 4.87;$ S, 12.91. Found: C, 43.55; H, 5.17; S, 12.95.

The i.r. spectrum (Nujol) showed bands at 3200 (s), 1705 (s), 1680 (s), 1315 (w), 1285 (m), 1270 (s), 1210 (s), 1195 (s), 1145 (m), 1085 (m), 1020 (s), 970 (w), 925 (w), 880 (w), 830 (w), 780 (m), 755 (m), 715 (m), 670 (w), 625 (m), 605 (m), 585 (m), and 575 cm<sup>-1</sup> (m). The n.m.r. (dimethyl sulfoxide- $d_6$ ) bands were at 3.57 (s, 3H), 4.13 (s, 2H) 6.30 (s, 1H) 7.06-7.45 (complex aromatic hydrogen absorption and a hydroxyl group, 4H), 7.7-7.95 (complex aromatic absorption, 1H), and 8.01 p.p.m. (s, 1H); on addition of D<sub>2</sub>O, peaks at 6.30, 7.15, and 8.01 p.p.m. disappeared.

#### Reaction of o-Sulfophenylacetic Acid (18) with Thionyl Chloride

Freshly distilled thionyl chloride (15 ml) was added to o-sulfophenylacetic acid (18) (0.3 g, 1.39 mmol). The reaction mixture was heated under reflux for 1 h under anhydrous conditions. The thionyl chloride was decanted from a sludge of 50 mg and was evaporated under reduced pressure without heating. The yield of crude solid material was 250 mg. Recrystallization from dried methylene chloride and pentane in a water-free atmosphere, yielded 2,1-benzoxathiin-3-one 1,1-dioxide ("o-sulfophenylacetic anhydride") (5) (160 mg, 60%), m.p. 107.5-108.5° (vacuum capillary). The product (5) had to be dried and stored over phosphorus pentoxide to prevent hydrolysis. Anal. Calcd. for C<sub>8</sub>H<sub>6</sub>O<sub>4</sub>S: C, 48.48; H, 3.05; S, 16.17.

Found: C, 48.15; H, 3.24; S, 16.04.

The i.r. spectrum (CH<sub>2</sub>Cl<sub>2</sub>) showed absorption bands at 2900 (w), 1818 (s), 1600 (w), 1585 (w), 1480 (m), 1455 (w), 1385 (w), 1205 (s), 1195 (s), 1150 (w), 1085 (m), 1070 (m), 1015 (w), 965 (w), 940 (w), 845 (s), 790 (m), and 655 cm<sup>-1</sup> (w). The n.m.r. spectrum (CDCl<sub>3</sub>) showed bands at 4.28 (s, 2H) and 7.25-8.15 p.p.m. (aromatic absorption, 4H).

A similar yield of 2,1-benzoxathiin-3-one 1,1-dioxide (5) was obtained when the reaction was carried out at room temperature.

Reaction of 2,1-Benzoxathiin-3-one 1,1-Dioxide (5) with Aniline in Methylene Chloride

In a water-free atmosphere, 2,1-benzoxathiin-3-one 1,1-dioxide (5) (0.1 g, 0.51 mmol) was dissolved in dried methylene chloride (1 ml). Distilled aniline (0.096 g, 1.03 mmol) was added. The reaction mixture was left for 30 min at 5°, after which the methylene chloride was evaporated. The product was recrystallized from methanol to yield the anilinium derivative (19) (153 mg, 78%), m.p. 229-231°

Anal. Calcd. for C20H20N2O4S: C, 62.48; H, 5.25; N, 7.29; S, 8.34. Found: C, 62.48; H, 4.99; N, 7.38; S, 8.42.

The i.r. spectrum (Nujol) showed absorption bands at 3270 (m), 2600 (w), 1650 (s), 1600 (s), 1560 (s), 1520 (m), 1500 (s), 1355 (m), 1320 (w), 1290 (w), 1260 (w), 1220 (s), 1185 (s), 1160 (s), 1140 (s), 1080 (m), 1050 (w), 1030 (w), 1020 (s), 970 (w), 910 (w), 855 (w), 845 (w), 820 (w), 800 (w), 780 (w), 760 (s), 745 (m), 720 (m), 710 (m), 700 (m), 660 (m), and 620 cm<sup>-1</sup> (s). The n.m.r. spectrum (dimethyl sulfoxide- $d_6$ ) showed bands at 4.6 (s, 2H), 6.8-8.9 (aromatic absorption plus ammonium protons, 17H), 10.53-10.71 p.p.m. (broad band, 1H).

## Quartz Tube Thermolysis of 2H-1,2,3-Benzothiadiazine 1,1-Dioxide (6)

The thermolyses were carried out in a tubulated quartz tube essentially as previously described (1) except that a 1-2 in. plug of glass wool was placed roughly in the center of the heated zone of the tube. The tube was heated for 12" of its length by a Lindberg/Hevi-Duty oven (made by Hevi-Duty Heating Equipment Co., Watertown, Wisconsin). A sample of 6 was placed in one end of the tube and sublimed into the hot zone of the apparatus using a microburner and an i.r. heating lamp. In one run 106 mg of 6 gave 69 mg of crude product which on t.l.c. gave a fraction

(22 mg, 25%) which appeared spectroscopically to be almost entirely the sultine 21. A second run with 103 mg of 6 gave 60 mg of crude product which afforded 24 mg (27%) of the t.l.c. fraction. Combination of these two t.l.c.-purified specimens of **21**, followed by treatment with decolorizing charcoal and crystallization, gave 21 (21 mg) melting at 39-40°; mixed m.p. with an authentic specimen of 21 prepared as described in the following paper 39-42°. The i.r. and n.m.r. spectra were identical with those of the authentic material.

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