Acknowledgment. This work was supported by the National Institutes of Health (Grant No. DA 01552-2).

Registry No.—1, 609-15-4; **2**, 60110-21-6; **3b**, 66552-43-0; **4b**, 66552-44-1; **7a**, 66552-45-2; **7b**, 66552-09-8; **7c**, 66552-10-1; **7d**, 66552-11-2; **7e**, 66552-12-3; **7f**, 66552-13-4; **7g**, 66552-14-5; **7h**, 66552-15-6; **7i**, 66552-16-7; **7j**, 66552-17-8; **7k**, 66552-18-9; **7l**, 66552-19-0; **8c** 6-methoxy deriv., 2400-35-3; **8c** 4-methoxy deriv., 66552-20-3; **8f** 6-carbomethoxy deriv., 66552-21-4; **8f** 4-carbomethoxy deriv., 66552-22-5; **8j** 6-bromo deriv., 66552-23-6; **8j** 4-bromo deriv., 66552-24-7; **8k** 6-benzyloxy deriv., 66552-25-8; **8k** 4-benzyloxy deriv., 66552-26-9; methylhydrazine carboxylate, 6294-89-9.

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(6) W. R. Boehme, *Org. Synth.*, **33**, 43 (1953).

(7) Aldrich Chemical Co., Inc.

(8) Only a small portion of azoene **4** was distilled successfully; an attempted large-scale distillation resulted in violent and rapid decomposition. The crude product is of excellent purity but polymerizes to a clear red solid after about a month even when stored at low temperatures.

(9) J. E. McMurray and J. Melton, *J. Org. Chem.*, **38**, 4367 (1973).

(10) A. G. Schultz and M. B. DeTar, *J. Am. Chem. Soc.*, **98**, 3564 (1976); see Experimental Section.

(11) Compounds **3b**, **6a**, **7a**, **8b**, **8h**, and **8l** gave satisfactory C, H elemental analyses (Spang Microanalytical Laboratory, Eagle Harbor, Mich.).

Mixed Carboxylic–Sulfinic Anhydrides? Concerning the Synthesis of 1,2-Oxathiolan-5-one 2-Oxide

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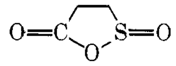
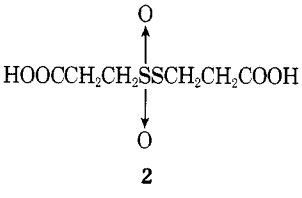
In 1969 Chiang, Luloff, and Schippes[1] reported the synthesis of 1,2-oxathiolan-5-one 2-oxide (**1**) by the chlorination of 3,3′-dithiodipropionic acid in methylene chloride. The reported analytical data for C, H, and S, as well as the molecular weight (Rast), were in good agreement with structure **1**, and the infrared and NMR spectra could also be assigned to **1**. To our knowledge this is the only reported example of a stable mixed carboxylic–sulfinic anhydride, though a mixed anhydride of this type was postulated as an intermediate in the reaction of sodium *p*-toluenesulfinate with acyl chlorides.[2]



1



$$\mathrm{HOOCCH_2CH_2}\underset{\substack{\downarrow\\ \mathrm{O}}}{\overset{\substack{\mathrm{O}\\ \uparrow}}{\mathrm{S}}}\mathrm{SCH_2CH_2COOH}$$

2

In our hands, the chlorination of 3,3′-dithiodipropionic acid as directed[1] did not give **1**. The only precipitate found in the reaction was unreacted 3,3′-dithiodipropionic acid which is quite insoluble in methylene chloride. We suggest that the product obtained by Chiang et al.[1] was not the carboxylic–sulfinic anhydride **1** but the thiosulfonate, *S*-(2-carboxyethyl)-3-thiosulfopropionic acid (**2**), which was formed by exposing the reaction mixture to moist air. That **2** should be found is not surprising as the chlorination of disulfides in the presence of carboxylic acids followed by the addition of water leads to thiosulfonates.[3] Indeed the addition of 2 mol of chlorine per mol of 3,3′-dithiodipropionic acid produced no precipitate until the mixture came into contact with moist air. The product that precipitates was shown to be **2** by comparison of its melting point, mixture melting point, and infrared and NMR spectra with an authentic sample prepared by the peracetic acid oxidation of 3,3′-dithiodipropionic acid.[4]

The following evidence suggesting that the compound prepared by Chiang et al.[1] is **2** and not **1** is put forth. First, the reported melting point of **2** (146–147 °C)[4] is virtually the same as that reported for **1** (148–150 °C). Second, the infrared spectrum of **2** has all the major absorptions (±10 cm^{-1}) reported for **1** though of course the assignments are different. Note particularly that assignment of the 1700-cm^{-1} absorption to a carboxylic acid carbonyl is more reasonable than assigning it to a cyclic anhydride.[5] Third, the NMR spectrum of **2** is similar to that reported[1] for **1**; however, we propose that the reported split doublet at δ 3.0 is really two overlapping triplets which we observed at δ 2.73 and 2.76 and that the multiplets at δ 3.4 and 3.9 are the triplets we observed at δ 3.29 and 3.79. Fourth, attempts to determine a Rast molecular weight of **2** gave widely varying results due to decomposition. Fifth, **2** was soluble in hot water and insoluble in cold water as reported for **1**. The report[1] that **1** dissolves in aqueous basic solution and is recovered unchanged upon neutralization can be rationalized since the action of hydroxide ion on thiosulfonates produces disulfides and sulfinic acids.[6] In this case, the 3,3′-dithiodipropionic acid which precipitates on neutralization could easily be mistaken for starting material since it is similar in appearance and melting point (157–159 °C).[7] Sixth, when **2** is heated with *o*-chloroaniline, 3,3′-sulfonyldipropio-*o*-chloroanilide is produced as reported[1] for **1**. Although we cannot explain the fact that the reported percentage hydrogen for **1** is 0.59% too low for **2**, we are satisfied that the compound described by Chiang et al.[1] is the thiosulfonate **2** and the existence of a stable mixed carboxylic–sulfinic anhydride has yet to be demonstrated.

Experimental Section[8]

Preparation of *S*-(2-Carboxyethyl)-3-thiosulfopropionic Acid (2). (a) To a stirred slurry of 0.2 mol of 3,3′-dithiodipropionic acid (Aldrich) in 100 mL of dichloromethane in a 500-mL, three-necked flask equipped with a thermometer, chlorine addition tube, and condenser with a calcium chloride drying tube was added 0.4 mol of chlorine gas over a period of 90 min. The temperature was kept at −30 ± 10 °C during the addition. The flask was allowed to warm to room temperature after addition had been completed. The reaction mixture was filtered to remove unreacted 3,3′-dithiodipropionic acid and the yellow filtrate, upon standing for 2 h, yielded compound **2** upon filtration. Compound **2** was recrystallized several times from water yielding 8.95 g: mp 149–150 °C dec; ^1H NMR (Me_2SO-d_6, 100 MHz) δ 3.79 (t, J = 6 Hz, 2 H), 3.29 (t, J = 6 Hz, 2 H), 2.76 (t, J = 6 Hz, 2 H), 2.73 (t, J = 6 Hz, 2 H); IR (KBr) 3200–2400 (broad, OH), 1690 (acid C=O), 1310 and 1110 (SO_2), and 1240 and 1160 (C–O stretch).

(b) Compound **2** was also prepared by the peracetic acid oxidation of 3,3′-dithiodipropionic acid in a manner similar to Dickinson,[4] mp 149–150 °C dec [lit.[4] mp 146–147 °C dec].

Preparation of 3,3′-Sulfonylydipropio-2-chloroanilide. Prepared according to the directions of Chiang et al.[1] from compound **2** and 2-chloroaniline, mp 233–235 °C [lit.[1] mp 234–235 °C].

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this work. In addition, we thank Dr. R. Volkmann and Dr. S. Georgian of Pfizer, Inc. for NMR and combustion analysis.

Registry No.—1, 19955-28-3; **2**, 18365-80-5; 3,3′-dithiodipropionic acid, 1119-62-6; peracetic acid, 79-21-0; 3,3′-sulfenyldipropio-2-chloroanilide, 19955-50-1; 2-chloroaniline, 95-51-2.

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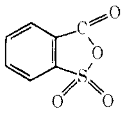
(5) For example, the carbonyl absorptions in succinic anhydride are reported at 1786 and 1850 and we found the carbonyl absorption of



to be at 1820 while the carbonyl absorption of 3,3′-dithiodipropionic acid is reported at 1690. Reported spectra are found in "Aldrich Library of Infrared Spectra", 2nd ed, 1974.

(6) W. E. Savige and M. A. Maclaren in "The Chemistry of Organic Sulfur Compounds", Vol 2, N. Karasch and C. Y. Meyers, Ed., Pargammon Press, Oxford, 1966, p 374, Chapter 15.

(7) "Aldrich Catalog/Handbook of Organic and Biochemicals", No. 18, Aldrich Chemical Co., Milwaukee, Wis., 1977, p 343.

(8) Melting points are uncorrected and no attempt was made to maximize yields. Infrared spectra were obtained using a Perkin-Elmer 727B spectrophotometer and nuclear magnetic resonance spectra were obtained using a Varian XL-100 spectrometer.

Reaction of Phenylglyoxal with Aniline under Acidic Conditions

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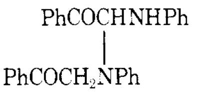
The reaction of phenylglyoxal with aniline in an acid medium has been investigated previously by two different groups.[1,2] Yates reported the isolation of only one product which he thought was phenylglyoxal anil (1). Proctor and co-workers made a more detailed investigation of this reaction in which they proposed structure 2 for Yates' product and isolated two new compounds: the major product (32%), which was not assigned a structure, and a minor product (10.5%). The minor product was reported to be the trans isomer of 1.

PhCOCH═NPh

1



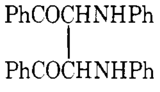
$$\begin{array}{l}\text{PhCOCHNHPh}\\ \quad\;| \\ \text{PhCOCH}_2\text{NPh}\end{array}$$

2

In this work, Proctor also described the synthesis of the two stereoisomers of 1 by a different reaction. Treatment of *N*-(*p*-toluenesulfonyl)phenacylaniline with base resulted in the formation of *cis*-1 and this, in turn, was isomerized to the trans isomer by reaction with a palladium catalyst.

It was of interest to us to repeat some of the above work to confirm the reported structures and to identify Proctor's major product of undetermined structure. We have reinvestigated the reaction of phenylglyoxal with aniline and have isolated compounds **3**, **4**, and **5** in pure form. Despite several attempts, we have failed to recover 1 from the reaction mixture or to detect its presence; however, *cis*- and *trans*-1 were prepared from *N*-(*p*-toluenesulfonyl)phenacylaniline and these structures were confirmed by reduction to **6**.

Compound **3** (0.3% yield)[3] is the product originally found by Yates. In support of its structure, it can be synthesized by the alkaline oxidation of phenacylaniline; presumably via initial oxidation to 1 followed by an aldol type condensation of phenacylaniline with **1**. Compound **3** also undergoes a retro-aldol reaction with concentrated HCl to give phenacylaniline back again.

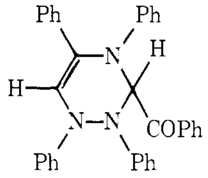


$$\begin{array}{l}\text{PhCOCHNHPh}\\ \quad\;| \\ \text{PhCOCHNHPh}\end{array}$$

3

PhCOCH(NHPh)$_2$

4

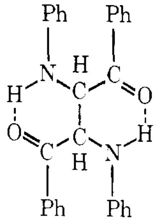


5

PhCHOHCH$_2$NHPh

6

The IR and NMR spectra of **3** provide conclusive evidence for its structure and show, furthermore, that it exists as the intramolecularly hydrogen bonded configuration **7**.



7

The ^{1}H NMR spectrum in anhydrous dimethyl-d_6 sulfoxide shows broad peaks at δ 5.65, 5.74 (2 H), and 6.11. The combined areas of the peaks at δ 5.65 and 6.11 correspond to 2 H but their area ratio is 1.8 to 1. Addition of D_2O to the sample showed that the δ 5.65 and 6.11 peaks were due to NH.

The signal at δ 5.65 is very nearly the same as the corresponding NH absorption of phenacylaniline (δ 5.70) in the same solvent. Therefore, the δ 5.65 peak is due undoubtedly to hydrogen bonding of **3** to solvent while the δ 6.11 peak represents the intramolecular hydrogen bonds in **7**.

The IR spectrum can be explained similarly. Compound **3** has absorption at 1665 cm^{-1} in the solid state. It is insoluble in most solvents but partially soluble in a few such as pyridine. An IR spectrum taken in pyridine has a shoulder at approximately 1695 cm^{-1} on one of the pyridine absorption bands. This is an indication that some of the intramolecular hydrogen bonding in **7** is broken and the normal carbonyl frequency is observed.

The mechanism by which **3** is formed from phenylglyoxal and aniline is purely a matter of speculation due to its low yield. No analogy appears to exist for what amounts to a reductive coupling of 1 under acidic conditions. A low yield of **3** was obtained when *cis*-1 was treated with acid but little can be inferred from this experiment.

Compound **4** (9% yield) proved to be a very unstable material as its structure would indicate. On standing or heating, it liberated aniline to give a mixture of products containing predominantly **5**. A good analysis could not be obtained for this substance due to its instability and difficulty in drying but its structure could be deduced from the following information.

The IR and NMR spectra indicate the presence of two NH groups, an aromatic ketone, and a one-proton singlet (>CH). The UV spectrum was similar to that of phenacylaniline but did have an increased intensity of absorption. The mass spectrum of **4** was unusual but particularly informative.

High resolution mass measurements show an apparent molecular ion at *m/e* 197 with an elemental composition of $C_{13}H_{13}N_2$. This cannot be a true molecular ion because of the inconsistency of the even number of nitrogens with an odd number molecular weight. If one infers the presence of a benzoyl group from the IR then a likely molecular formula would be $C_{20}H_{18}N_2O$. Thus there would have to exist in the

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