Acknowledgment. The author is grateful to R. N. Rogers and Mary Fowler of Los Alamos Scientific Laboratory for preliminary information regarding their procedure for the preparation of 3,5-dinitrotriazole.

Registry No.—**1**, 66652-93-5; **2**, 66652-94-6; **3**, 66652-95-7; **4**, 66652-96-8; **5**, 66652-97-9; 3,5-dinitro-1,2,4-triazole, 26621-32-9; 3,5-dinitro-1,2,4-triazolepotassium salt, 50738-33-5; 3,5-dinitro-1,2,4-triazolelithium salt, 66652-98-0; picryl chloride, 88-88-0; ammonium chloronitrotriazole, 66652-99-1; 1-methyl-3-nitro-5-chloro-1,2,4-triazole, 31123-18-9.

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(4) The only instance in the literature where N_4-alkylation of 3,5-dinitro-1,2,4-triazole has been suggested is for its reaction with nitroalkenes: D. V. Sickman, U.S. Patent 2 987 520 (June 6, 1961). Thus the reaction of 3,5-dinitrotriazole with nitroethylene was reported to give 4-(2-nitroethyl)-3,5-dinitro-1,2,4-triazole, mp 146–147 °C. However, this is open to dispute as later authors (ref 6) report this reaction to give 1-(β-nitroethyl)-3,5-dinitro-1,2,4-triazole, mp 146 °C. In general, N_4 substitution of 1,2,4-triazoles is extremely rare. The only other reported case of N_4 substitution is for alkylation of 5-furyl-3-amino-1,2,4-triazoles with methyl iodide in neutral media: E. Akerblom, *Acta Chem. Scand.*, **19**, 1142 (1965).
(5) L. I. Bagal, M. S.Pevzner, and V. Ya. Samarenko, *Khim. Geterotsikl. Soedin.*, **6**, 269 (1970).
(6) L. I. Bagal, M. S. Pevzner, V. Ya. Samarenko, and A. P. Egorov, *Khim. Geterotsikl. Soedin.*, **12**, 1701 (1970).
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(9) Lithium dinitrotriazole gave a 20% yield of product, mp 161–163 °C. Potassium dinitrotriazole with 1 equiv of lithium chloride gave a 28% yield of product, mp 162–164 °C.
(10) The 30% sulfuric acid extract removes mainly 3,5-dinitrotriazole after which the warm water extract removes mainly picric acid. Addition of concentrated hydrochloric acid to the warm water extract gave 0.5 g of picric acid.
(11) The crystals were shown to be 2,4,6-trinitroaniline by comparison (mp, UV, TLC) with an authentic sample.

Synthesis of Indole-2-carboxylic Esters

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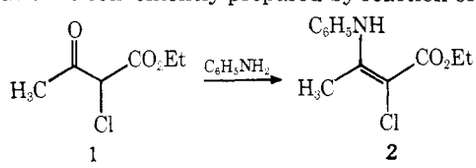
Recently, we reported that *N*-methyl-3-hydroxyindolines can be prepared in excellent yield by photocyclization–rearrangement of 2-(*N*-methylanilino)acetoacetates.[1] In acetic acid, the 3-hydroxyindolines undergo rapid dehydration to give *N*-methylindoles; alternatively, irradiation of the 2-(*N*-methylanilino)acetoacetate in acetic acid solution produces indoles directly. Experiments designed to probe the mechanism of 3-hydroxyindoline formation indicate that cyclization is completely stereoselective and occurs from the enol tautomer of the 2-anilinoacetoacetate.

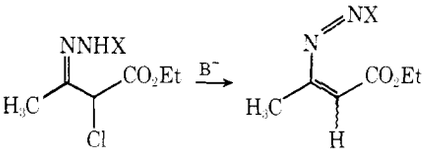
The 2-(*N*-methylanilino)acetoacetate required for indole preparation is conveniently prepared by reaction of the appropriate *N*-methylaniline with 2-chloro- or 2-bromoacetoacetate. However, reaction of aniline with ethyl 2-chloroacetoacetate (**1**) results in enamine formation to give **2** instead of the desired substitution product. Herein, we describe a useful, high yield preparation of *N*-unsubstituted-2-anilinoacetoacetates as well as their photoconversion to *N*-unsubstituted indoles.



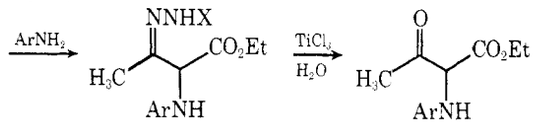
1 2

In 1960, Beyer and Badicke reported that the semicarbazone of ethyl 2-chloroacetoacetate **3a** undergoes base-catalyzed 1,4-elimination of hydrogen chloride to give azoene **4a** and that **4a** reacts in Michael fashion at C(2) with aniline to give the semicarbazone of ethyl 2-anilinoacetoacetate **5** in 65% yield.[2] We find the *N*-carbomethoxyhydrozone **3b** to be a superior intermediate;[3] azoene **4b** is produced by treatment of **3b** with mild base, and **4b** reacts with a variety of aniline derivatives to give addition products **6** in excellent yield (Table I).

Regeneration of the ketone carbonyl group in **6** is best accomplished by reaction with aqueous titanium trichloride,[4] from which the 2-anilinoacetoacetates **7** can be obtained

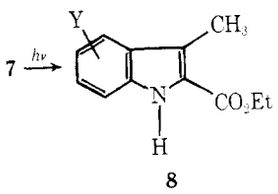


3a, X = $CONH_2$
b, X = CO_2CH_3 **4**



5, X = $CONH_2$; Ar = C_6H_5
6, X = CO_2CH_3 **7**

without the need for further purification. Pyrex-filtered irradiation of **7** in degassed benzene–methanol–acetic acid solution gives indoles **8** in excellent yield (Table I). We note that, except for example **7e**, alkoxy, halogen, and carbomethoxy



8

substituents on the benzene ring are compatible with photocyclization. On the other hand, the *p*-nitro derivative **7i** failed to give an indole on extended irradiation. With meta-substituted anilines, cyclization results in both 6- and 4-substituted indoles; however, with *m*-bromo-2-anilinoacetate **7j**, cyclization occurs mainly away from the bromine atom to give a 6-bromoindole as the major reaction product by a factor of 10:1. A halogen atom can serve as a blocking group as illustrated with example **7n**, in which cyclization gives only the 4-methoxy-7-chloroindole. Eventual removal of halogen by hydrogenolysis or lithium aluminum hydride reduction would give the 4-methoxyindole with complete overall regioselectivity.

The methodology presented here represents the first report of N-unsubstituted indole preparation by photochemical means. We consider photocyclization of 2-anilinoacetoacetates to be a useful alternative to the traditional Bischler indole synthesis. Carbon–carbon bond formation occurs in the absence of strong acids, and, in contrast to the Bischler synthesis, electron deficient aniline derivatives give indoles in high yield. It should be noted that indole-2-carboxylic esters may be hydrolyzed and decarboxylated on treatment with copper chromite in quinoline.[5]

Table I. Preparation of *N*-Carbomethoxyhydrozones 6 and Their Conversion to 2-Carboethoxy-3-methylindoles 8

	Ar	registry no.	6 (% yield)	registry no.	mp, °C	8 (% yield)[a]	registry no.	mp, °C[b]
a	C_6H_5	62-53-3	92	66552-27-0	155–156	96	26304-51-8	134–135 (lit. 133.5–134)[h]
b	2-$CH_3OC_6H_4$	90-04-0	98	66552-28-1	162–163	94	66552-39-4	116–117
c	3-$CH_3OC_6H_4$	536-90-3	95	66552-29-2	115–116	93		*c*
d	4-$CH_3OC_6H_4$	104-94-9	95	66552-30-5	118–119	89	16381-42-3	151–152 (lit. 150)[i]
e	2-$CH_3O_2CC_6H_4$	134-20-3	95	66552-31-6	165–166	0[d]		
f	3-$CH_3O_2CC_6H_4$	4518-10-9	97	66552-32-7	127–128	84		*e*
g	4-$CH_3O_2CC_6H_4$	619-45-4	90	66552-33-8	116–117	90	66552-40-7	164–165
h	2-Cl-5-$CH_3OC_6H_3$	2401-24-3	79	66552-34-9	135–137	95	66552-41-8	120–121
i	4-$NO_2C_6H_4$	100-01-6	43	66552-35-0	191–192	0		
j	3-BrC_6H_4	591-19-5	67	66552-36-1	143–144	50		*f*
k	3-$PhCH_2OC_6H_4$	1484-26-0	88	66552-37-2	111–113	95		*g*
l	C_6H_5[j]	103-32-2	87	66552-38-3	119–120	93	66552-42-9	61–62

[a] Yield based on starting hydrazone **6**. [b] Recrystallized from 95% ethanol. [c] A mixture of 6-methoxy (mp 123–124 °C, lit. 122 °C, T. Wieland and D. Grimm, *Chem. Ber.*, **98**, 1727 (1965)) and 4-methoxy (mp 152–153 °C) isomers (1:1) were produced which were separated by thick layer chromatography (silica gel, methylene chloride solvent). [d] Irradiation of **7e** gave a complex mixture of uncharacterized products. [e] A mixture of 6-carbomethoxy (mp 154–155 °C) and 4-carbomethoxy (mp 131–132 °C) isomers (56:44) were produced which were separated by thick layer chromatography (silica gel, methylene chloride solvent). [f] A mixture of 6-bromo and 4-bromo isomers (10:1) which were not separated. [g] A mixture of 6-benzyloxy and 4-benzyloxy isomers (1:1) which were not separated. [h] T. Lesiak, *Prsemysl. Chem.*, **41**, 140 (1962). [i] M. Julia and J. Lallemand, *Bull. Soc. Chim. Fr.*, 2046 (1973). [j] In this case, *N*-benzylaniline was employed; thus, secondary amines will add to C(2) of azoene **4**.

Experimental Section

General. ^1H NMR spectra were obtained on a Varian A-60A or EM-390 NMR spectrometer (tetramethylsilane internal standard, deuteriochloroform solvent). Infrared spectra were recorded on a Perkin-Elmer Model 137B infrared spectrometer, and melting points were measured on a calibrated Thomas-Hoover capillary melting point apparatus and are uncorrected. Photochemical reactions were performed in sealed test tubes degassed by four cycles of a freeze–pump–thaw routine. The light source for irradiation was a 450-W Ace-Hanovia medium pressure, mercury vapor lamp. Mass spectra were obtained on a Finnigan 3300 gas chromatograph–mass spectrometer.

Ethyl 2-Chloro-3-anilino-2-butenoate (2). A stirred solution of ethyl 2-chloroacetoacetate[6] (1) (4.74 g, 29 mmol), pyridine (2.4 mL), and aniline (4 mL, 44 mmol) in ethanol (7 mL) was refluxed for 12 h. After rotoevaporation of solvent, the residue was dissolved in chloroform (50 mL) and washed successively with 1 N hydrochloric acid (3 × 15 mL) and water (3 × 20 mL) and dried over anhydrous magnesium sulfate. Rotoevaporation of solvent and distillation gave **2** [4.11 g, 64%, bp 106–108 °C (0.03 mm)]: ^1H NMR δ 1.33 (3 H, triplet, J = 7.5 Hz), 2.20 (3 H, singlet), 4.26 (2 H, quartet, J = 7.5 Hz), 6.93–7.55 (5 H, multiplet), 11.75 (1 H, broad singlet); IR (neat) 6.08, 6.26, 6.32, 8.00 μm; electron impact mass spectrum *m/e* 241 (16%), 239 (45%), 203 (20%), 160 (22%), 158 (43%), 132 (100%).

Ethyl 2-Chloroacetoacetate Carbomethoxyhydrazone (3b). To a stirred solution of **1** (16.21 g, 0.10 mol) in anhydrous ether (100 mL) was added methylhydrazine carboxylate[7] (8.90 g, 0.10 mol). After the suspension was stirred at room temperature for 24 h, the solid was filtered and washed with petroleum ether (75 mL) to give **3b** (21.40 g, 92%, mp 103–103.5 °C): ^1H NMR δ 1.29 (3 H, triplet, J = 7.0 Hz), 1.96 (3 H, singlet), 3.83 (3 H, singlet), 4.25 (2 H, quartet, J = 7.0 Hz), 5.13 (1 H, singlet), 7.93 (1 H, broad singlet); IR (Nujol) 3.13, 5.71, 5.78 μm.

Ethyl 3-Carbomethoxyazocrotonate (4b). To a suspension of hydrazone **3b** (21.40 g, 90 mmol) in ether (200 mL) was added a 1 N sodium bicarbonate solution (150 mL). After stirring at room temperature for 45 min, the red ether solution was separated and dried over anhydrous magnesium sulfate. Rotoevaporation of solvent gave **4** as a bright red liquid [16.89 g, 93%, bp 68–70 °C (0.05 mm)][8] ^1H NMR δ 1.35 (3 H, triplet, J = 7.0 Hz), 2.25 (3 H, singlet), 4.05 (3 H, singlet), 4.31 (2 H, quartet, J = 7.0 Hz), 6.97 (1 H, quartet, J = 1.0 Hz); IR (neat) 5.66, 5.79, 6.06 μm.

Ethyl 2-Anilinoacetoacetate Carbomethoxyhydrazone (6a). General Procedure. To a stirred solution of **4** (408 mg, 2.04 mmol) in tetrahydrofuran (THF) or anhydrous ether (1 mL) was added a solution of aniline (190 mg, 2.04 mmol) in THF or ether (2.5 mL). After solidification and standing at room temperature for 7 h, *n*-pentane (3.5 mL) was added and the solid filtered and dried to give **6a** (547 mg, 92%, mp 155–156 °C): ^1H NMR δ 1.25 (3 H, triplet, J = 7.0 Hz), 1.76 (3 H, singlet), 3.86 (3 H, singlet), 4.25 (2 H, quartet, J = 7.0 Hz), 4.86 (2 H, sharp singlet and broad singlet superimposed), 6.76 (3 H, multiplet), 7.20 (2 H, multiplet), 7.78 (1 H, singlet); IR (Nujol) 2.95, 3.13, 5.74, 5.81 μm.

Using the appropriately substituted aniline ($ArNH_2$), hydrazones **6b–l** were prepared on the same scale (~2 mmol) by the same procedure with the following exceptions noted.

6d. The ether solution of **4** was cooled to 0 °C during the addition of the *p*-anisidine solution.

6e. The THF solution of **4** and methyl anthranilate was heated at 70 °C for 15 h and then cooled to 0 °C before the addition of pentane (8 mL).

6f. The THF solution of **4** and methyl *m*-aminobenzoate was heated at 70 °C for 1 h, the solvent removed by a stream of nitrogen gas, and the residue triturated with *n*-pentane.

6g. The THF solution of **4** and methyl *p*-aminobenzoate was heated at 70 °C for 5 h, the solvent rotoevaporated, and the residue triturated with ether.

6i. The THF solution of **4** and *p*-nitroaniline was heated at 70 °C for 24 h.

6l. The ether solution of **4** and *N*-benzylaniline was stirred at room temperature for 24 h.

Ethyl 2-Anilinoacetoacetate (7a). General Procedure. To a stirred solution of hydrazone **6a** (150 mg, 0.51 mmol) in acetone (2 mL) was added a 20% aqueous solution of titanium trichloride (0.6 mL, 0.78 mmol). After stirring at room temperature for 1.5 h, ether (30 mL) and water (10 mL) were added. The organic layer was separated, washed with water (3 × 10 mL), and dried over anhydrous magnesium sulfate. Rotoevaporation of solvent gave **7a:** ^1H NMR δ [keto ester tautomer, 62%] 1.23 (1.86 H, triplet, J = 7.0 Hz), 2.28 (1.86 H, singlet), 4.25 (1.24 H, quartet, J = 7.0 Hz), 5.08 (0.62 H, singlet), [enol ester tautomer, 38%], 1.13 (1.14 H, triplet, J = 7.0 Hz), 2.03 (1.14 H, singlet), 4.20 (0.76 H, J = 7.0 Hz), 12.36 (0.38 H, singlet), ~5.03 (1 H, broad singlet), 6.47–6.90 (3 H, multiplet), 7.04–7.34 (2 H, multiplet); IR (neat) 2.94, 5.71, 5.79, 6.06, 6.21 μm.

2-Anilinoacetoacetates (**7b–l**) were prepared on the same scale (~0.5 mmol) by the same procedure and were used without further purification in the subsequent photoreaction. It is interesting to note that **7i** was prepared without reduction of the NO_2 group by $TiCl_3$.[9]

Irradiation of Ethyl 2-Anilinoacetoacetate (7a). A solution of **7a** (as obtained from the reduction–hydrolysis of hydrazone **6a**) in benzene–methanol–acetic acid (15:15:1, 3.5 mL) in a sealed, degassed test tube[10] was irradiated through Pyrex for 20 h. Rotoevaporation of solvent and trituration with pentane gave ethyl 3-methylindole-2-carboxylate **8a** (100 mg, 96% from hydrazone **6a**, mp (EtOH) 134–135 °C): ^1H NMR δ 1.43 (3 H, triplet, J = 7.0 Hz), 2.61 (3 H, singlet), 4.41 (2 H, quartet, J = 7.0 Hz), 7.16–7.76 (4 H, multiplet); IR (Nujol) 3.03, 5.97 μm.[11]

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.

References and Notes

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(2) H. Beyer and G. Badicke, *Chem. Ber.*, **93**, 826 (1960). For other recent work with azoenes, see C. E. Sacks and P. L. Fuchs, *J. Am. Chem. Soc.*, **97**, 7372 (1975).
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(4) J. E. McMurry and M. Silvestri, *J. Org. Chem.*, **40**, 1502 (1975), and B. P. Chandrasekhar, S. V. Sunthankar, and S. G. Telang, *Chem. Ind.*, **18**, 87 (1975).
(5) B. Heath-Brown and P. G. Philpott, *J. Chem. Soc.*, 7185 (1965).
(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 polymerizies 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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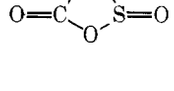
Received March 15, 1978

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]



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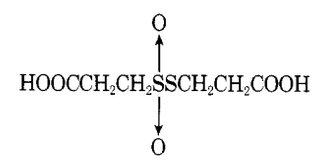

2

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′-Sulfonyldipropio-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].

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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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