fine sintered glass funnel. The precipitate was dried in the open air, powdered, and then dried in a vacuum over phosphorus pentoxide at 100° for ten hours. A yield of 99% was obtained.

Anal. Calc'd for $Ag(C_{25}H_{21}N_4O_2)$: C, 58.04; H, 4.09; N, 10.83. Found: C, 57.50; H, 4.20; N, 10.70.

Visible spectra. Visible spectral data were obtained using the Cary automatic recording spectrophotometer and the Beckman Model DU spectrophotometer with 1-cm. quartz cells. Stock solutions of zolon blue, zolon red, and silver nitrate in 50 per cent methanol-water were made up containing 0.0005 mole per liter. Solutions suitable for visible spectra were made up by diluting one-milliliter samples of zolon blue and zolon red solutions to 25 ml. with 50 per cent methanol-water. A solution of the silver-zolon red complex was made up from one-milliliter samples of zolon red and silver nitrate stock solutions diluted to 25 ml. Spectra were run from 400 to 800 millimicrons using quartz cells in the Cary spectrophotometer.

Infrared spectra. Infrared spectra of zolon red, zolon blue, and the silver-zolon red complex were determined by means of the potassium bromide disk technique[9,10] on a Perkin-Elmer Model 21 infrared spectrophotometer.

Continuous variation study. The combining ratio of the silver-zolon red complex was determined by the method of continuous variations described by Job.[11] To one-milliliter samples of the 0.0005 *molar* silver nitrate stock solution 0.1- to 3-ml. samples of the 0.0005 *molar* zolon red stock solution were added and the resulting solutions were diluted to 25 ml. with 50 per cent methanol-water. The absorbance of each of these samples then was determined on the Beckman Model DU spectrophotometer at 620 millimicrons. The combining ratio was obtained from a plot of the absorbance against the molar ratio of zolon red to silver ion (Fig. 1).

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[9] M. M. Stimson and M. J. O'Donnell, *J. Am. Chem. Soc.*, **74**, 1805 (1952).

[10] U. Schiedt and H. Reinwein, *Z. Naturforsch.*, **7b**, 270 (1952).

[11] P. Job, *Ann. chim.*, [10] **9**, 113 (1928).

The Preparation of Bis-(ethyl 3,5-dimethylphenoxyacetate)-4,4'-disulfide[1]

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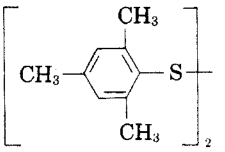
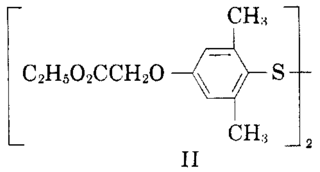
In a recent publication[2] it was shown that dimesityldisulfide (I) was an effective bis-type modifier in the emulsion polymerization of butadiene. This modifier lacks the reactive group needed to test thoroughly the usefulness of such modifiers in making synthetic rubber vulcanizates of improved resilience. This paper describes the preparation of bis-(ethyl 3,5-dimethylphenoxyacetate)-4,4'-disulfide (II) which does have an ester group as the active group needed in the modified polymer.

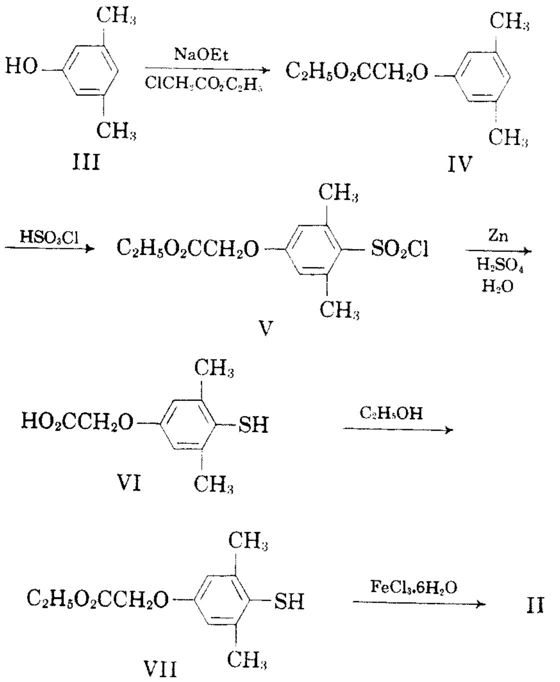


I



II

The following five step synthesis has been accomplished in an over-all yield of about 30%:



The chlorosulfonation reaction (step 2) might produce isomeric materials but it appears to give a single material which is assumed to be the isomer with the sulfonyl chloride group *para* to the ether oxygen. In the reduction step some of the chlorosulfonyl group is removed by hydrolysis and the ester group is hydrolyzed. Thus a re-esterification is needed.

The disulfide has a modifier effectiveness (in bulk styrene) which is very similar on a molar basis to that of other 2,6-dimethylphenyldisulfides.[3]

The chlorosulfonation of 3,5-dimethylphenoxyacetic acid and the oxidation of 4-mercapto-3,5-dimethylphenoxyacetic acid to the disulfide are also reported.

EXPERIMENTAL

Preparation of ethyl 3,5-dimethylphenoxyacetate. To a 3000-ml. three-necked flask fitted with a stirrer and reflux condenser was added 500 ml. of ethanol and 24 g. (1.0 mole) of sodium. After the sodium had dissolved, a solution of 112 g. of 3,5-dimethylphenol in 200 ml. of ethanol was added, and the solution was stirred for 15 minutes. A solution of 122 g. (1.0 mole) of ethyl chloroacetate then was added, and the mixture was heated under reflux for 4–6 hours and allowed to stand overnight. A solution of 6 g. of sodium in 100 ml. of ethanol was added, followed by 30 g.

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[1] The work discussed herein was performed as a part of the synthetic rubber research project sponsored by the National Science Foundation.

[2] A. J. Costanza, R. J. Coleman, R. M. Pierson, C. S. Marvel, and Charles King, *J. Polymer Sci.*, **17**, 319 (1955).

[3] Private communication from Mr. R. M. Pierson.

of ethyl chloroacetate. The mixture was refluxed an additional hour. Approximately 200 ml. of benzene was added to precipitate the sodium chloride which then was removed by filtration. The filtrate was washed three times with water, and the solvent was stripped under reduced pressure. The residue was fractionated yielding 160 g. (78%) of ethyl 3,5-dimethylphenoxyacetate, b.p. 110–115° (1 mm.), $n_D^{25.0}$ 1.499.

Anal. Calc'd for $C_{12}H_{16}O_3$: C, 69.3; H, 7.67. Found: C, 69.23; H, 7.78.

This synthesis has also been carried out using two mole quantities, when the reflux time was extended to 48 hours. The excess reagents were added after 24 hours of reflux time. The yield was 60%.

Chlorosulfonation of ethyl 3,5-dimethylphenoxyacetate. A solution of 208 g. (1.0 mole) of the above ester in 500 ml. of chloroform was placed in a 2000-ml. three-necked flask fitted with a stirrer and dropping funnel. The solution was cooled in ice to 0° and 260 g. (2.3 moles) of chlorosulfonic acid was added over a period of 1.5 hours, while the reaction mixture was kept at 0°. The reaction mixture was stirred an additional 20 minutes at 0°, and then was poured with stirring into 2000 ml. of ice-water. The chloroform layer was washed twice with ice-water, and 200 ml. of benzene was added. The solvent was stripped under a vacuum to yield 230 g. (75%) of a white crystalline material. This material decomposed upon standing in air but may easily be stored at −10°. A sample was recrystallized from petroleum ether; m.p. 64.5–65°.

Anal. Calc'd for $C_{12}H_{15}ClO_5S$: C, 46.8; H, 4.88; Cl, 11.3. Found: C, 47.03; H, 5.11; Cl, 11.05.

Chlorosulfonation of 3,5-dimethylphenoxyacetic acid. In a 500-ml. three-necked flask equipped with a stirrer, a condenser, and a dropping-funnel were placed 36 g. of 3,5-dimethylphenoxyacetic acid[4] and 200 ml. of chloroform. The solution was cooled in an ice-bath, and then 75 g. of redistilled chlorosulfonic acid was added quickly to the rapidly stirred solution. The addition took 18 minutes and the mixture was stirred for another 20 minutes at 0°. The mixture was poured onto ice-water and the aqueous layer was decanted. After three more washings with ice-water, the product was filtered and dried to yield 40 g. (69.5%) of crude material. Recrystallization from benzene gave material with m.p. 120–125° (decomp.).

Anal. Calc'd for $C_{10}H_{11}ClO_5S$: C, 43.09; H, 3.95. Found: C, 43.28; H, 3.74.

Reduction of ethyl [3,5-dimethyl-4-chlorosulfonylphenoxy]-acetate. In a 1000-ml. three-necked flask equipped with a reflux condenser, gas outlet tube, and high-speed stirrer was placed a cooled solution of 160 ml. of sulfuric acid in 300 ml. of water. To this solution was added 200 g. of zinc amalgam,* followed by 100 g. (0.33 mole) of sulfonyl chloride. The mixture then was heated with vigorous stirring until the sulfonyl chloride began to melt (*ca.* 60°) and a vigorous reaction set in. [THE HEATING MANTLE SHOULD BE IMMEDIATELY REMOVED SINCE A VIGOROUS REFLUXING OCCURS.] When the reaction had subsided, the mantle was replaced, and the mixture was refluxed an additional hour.

The reaction mixture then was cooled and extracted with about 300 ml. of ether. The ether extract was washed with water, then dried over magnesium sulfate. The drying agent was removed by filtration, and the solvent was stripped *in vacuo;* yield, 68 g. (85%) of a white crystalline solid; m.p. 125–130°. This is a mixture of a small amount of 3,5-dimethylphenoxyacetic acid and the desired mercapto acid. Reversal of the chlorosulfonation reaction during this step accounts for the large m.p. range. Repeated recrystallizations of the crude product from cyclohexane-ether mixtures yielded the mercapto acid, m.p. 146–148°.

Anal. Calc'd for $C_{10}H_{12}O_3S$: C, 56.50; H, 5.66; S, 15.09. Found: C, 56.92; H, 5.94; S, 14.67.

Esterification of 3,5-dimethyl-4-mercaptophenoxyacetic acid. A two-liter one-necked flask was equipped with a fractionating column fitted with a Dean-Stark reflux trap and reflux condenser. A solution of 200 g. of the mercaptan in 600 ml. of benzene and 400 ml. of ethanol was placed in the flask. About 5 g. of *p*-toluenesulfonic acid was added and the solution was refluxed until the ternary azeotrope ceased to separate (about 48 hours). The solution was washed with dilute base, then water, and the solvent was stripped off under reduced pressure. The crude white crystalline residue was placed in a flask fitted with a Claisen head and fractionated at 0.5 mm. pressure. The forerun consisted of about 35 g. of material distilling at 100–120° at 0.5 mm. ($n_D^{25°}$ forerun = 1.5051; $n_D^{25°}$ ethyl 3,5-dimethylphenoxyacetate = 1.4991. This indicated that the forerun was ethyl 3,5-dimethylphenoxyacetate contaminated with mercaptan.) The presence of a small amount of this impurity in the phenoxy ester would raise its refractive index to a considerable extent.

The fraction distilling above 135°/0.5 mm. was collected as product; 165 g. (72%) of a white crystalline material was obtained, m.p. 65°.

Anal. Calc'd for $C_{12}H_{16}SO_3$: C, 60.0; H, 6.67. Found: C, 59.65; H, 6.92.

Oxidation of ethyl 3,5-dimethyl-4-mercaptophenoxyacetate. An ether solution of 20 g. of the above mercaptan was placed in a 1000-ml. Erlenmeyer flask. An ethereal solution of ferric chloride hexahydrate was added until no more ferrous chloride precipitated. A very dark color was produced when this addition was begun. The reaction mixture was washed thoroughly with water, and the ethereal solution was dried over magnesium sulfate. The ether was evaporated on a steam-bath after removal of the drying agent, and the dark yellow viscous residue was allowed to stand until it crystallized. The crude bis-ethyl (3,5-dimethylphenoxyacetate)-4,4′-disulfide was recrystallized from an ether-cyclohexane solution. Yield, 15 g. (73%) of bright yellow crystals; m.p. 80–81°.

Anal. Calc'd for $C_{24}H_{30}O_6S_2$: C, 60.23; H, 6.27; S, 13.38. Found: C, 59.98; H, 6.18; S, 13.22.

Difficulties in obtaining the product were encountered when batches larger than 40 g. were oxidized. It was found that the oxidation of smaller amounts gave more satisfactory results.

Bis-(3,5-dimethylphenoxyacetic acid)-4,4′-disulfide. To a solution of 2 g. of 4-mercapto-3,5-dimethylphenoxyacetic acid in 10 ml. of ether was added a saturated solution of ferric chloride hexahydrate in ether. An intermediate dark color was observed and ferrous chloride precipitated. The ferric chloride hexahydrate solution was added until no mercaptan odor could be observed and no more ferrous chloride formed. The mixture was washed with water to remove the ferrous chloride precipitate and any excess ferric chloride hexahydrate. The solution then was washed with a saturated solution of sodium chloride. The last traces of water were removed by adding benzene and distilling off the azeotrope. A pale yellow solid crystallized from the benzene solution and recrystallization from an acetone-cyclohexane solution gave 1.2 g. (57.4%) of the disulfide, m.p. 199–201°.

Anal. Calc'd for $C_{20}H_{22}O_6S_2$: C, 56.89; H, 5.21; S, 15.15; Neut. eq., 211. Found: C, 56.95; H, 5.53; S, 15.01; Neut. eq., 207.

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(4) A. R. Albright, *J. Am. Chem. Soc.*, **55**, 1736 (1933).

* Preparation of zinc amalgam: Powdered zinc (400 g.) was washed with dilute (2%) hydrochloric acid. The acid solution was decanted and the zinc powder was added with stirring to a solution of 80 g. of mercuric chloride and 100 ml. of concentrated hydrochloric acid in 2000 ml. of water. The mixture was stirred vigorously for 15 minutes and the powdered zinc amalgam was removed by filtration. It was washed with ethanol, then ether, and allowed to dry.