action of benzoin with ammonium nitrate where only 40% was converted to benzil, while in the presence of cupric acetate a quantitative yield was obtained.[1] Experimentally, we have verified these ideas and have been able to prepare piperil in 89% yield.

### Experimental

In a 250-cc. flask fitted with a reflux condenser are placed 4.5 g. of piperonyloin, 1.5 g. of cupric acetate, 1.5 g. of ammonium nitrate and 100 cc. of an 80% by volume acetic acid–water solution. The flask is heated gently, over an asbestos-covered wire gauze, agitating to prevent a local concentration of ammonium nitrate. Reflux gently for one hour. Toward the end of the reaction, a variable amount of cupric oxalate precipitates (*ca.* 20 mg.). The solution is filtered hot, with suction, before allowing the piperil to crystallize. When cool, 50 cc. of water is added to precipitate the remaining piperil. The piperil is collected on a Buechner funnel and washed well with water. The yield is 4.0 g. or 89%, m. p. 173–174° cor.; Fehling test negative.

The piperil was checked by cleaving it with sodium cyanide in aqueous alcohol. The piperonylic acid formed showed no melting point depression when mixed with piperonylic acid obtained by the oxidation of piperonal.

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## Mercaptans from Aldehydes

BY FRANK KIPNIS, ISIDORE LEVY AND JOHN ORNFELT

The method for the preparation of mercaptans by the interaction of aldehydes with hydrogen sulfide, followed by reduction of the disulfide, has been reported by several workers,[1,2] though details were not complete. During the present study, it was found possible to prepare previously unreported mercaptans by the above procedure, and indications are that the method is rather versatile for the preparation of difficulty available aromatic and heterocyclic mercaptans.

Aluminum amalgam seems to be the reducing agent of choice, though zinc in acetic acid has been used in the reduction of the disulfide[2] from piperonal.

### Experimental

**5-Methylfurfurylmercaptan.**—In a 1000-ml. three-neck flask fitted with a sealed stirrer, reflux condenser and drying tube, was placed 24 g. (0.22 mole) of 5-methylfurfural[3] and 500 ml. of an ethanolic solution of ammonium hydrogen sulfide.[4] The mixture was stirred at room temperature for five hours, heated on a water-bath for one hour and allowed to stand overnight. The volatiles were removed by distillation from the steam-bath at reduced pressure, leaving a brown residue.

Without further purification, the presumed disulfide was transferred to a 1000-ml. three-neck flask containing a sealed stirrer, reflux condenser and dropping funnel. Five hundred milliliters of solvent ether was added, together with aluminum amalgam[5] prepared from 30 g. of aluminum turnings. The stirrer was started and 30 ml. of water was added to the suspension during ten minutes. The reduction commenced almost immediately and continued steadily, the mixture being heated from time to time with a warm water-bath when the reaction showed signs of slackening. After standing overnight, the aluminum sludge was separated by filtration, washed with 100 ml. of ether, the filtrate and washings combined, dried with calcium sulfate, filtered and the solvent stripped, finally under reduced pressure. The residue was fractionated at 70° (3 mm.) to give 8 g. (28.4% yield) of a colorless liquid, $n^{20}\text{D}$ 1.5258.

*Anal.*[6] Calcd. for $C_6H_8OS$: C, 56.22; H, 6.28. Found: C, 56.71; H, 6.43.

**3-Methoxy-5-hydroxybenzyl Mercaptan.**—bis-(3-Methoxy-4-hydroxybenzyl) disulfide, m. p. 129–130°, was prepared from vanillin according to the method of Manchot,[2] and reduced with aluminum amalgam as above to give a 59% yield of a colorless oil distilling at 75–80° (0.03 mm.), $n^{20}\text{D}$ 1.5940.

*Anal.* Calcd. for $C_8H_{10}O_2S$: C, 56.44; H, 5.92; S, 18.84. Found: C, 56.57; H, 6.21; S, 18.95.

It was reported that the disulfide was not reduced with zinc and acetic acid.[2]

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(1) Staudinger and Reichstein, U. S. Patent 1,715,795 (1929); 1,748,527 (1930).

(2) Manchot and Zahn, *Ann.*, **345**, 315 (1906).

(3) Rinkes, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 393.

(4) Prepared as follows: 500 ml. of absolute ethanol was saturated with anhydrous ammonia at 15°. The solution was divided into two equal portions and dry hydrogen sulfide was passed into one portion until crystallization began, after which the two solutions were mixed and used immediately.

(5) Hartman and Phillips, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 233.

(6) Analyses by Oakwold Laboratories, Alexandria, Va.

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# NEW COMPOUNDS

### D-Glucose-thiophene-2′-methyl Mercaptal

The procedure used was based on the methods devised by Levene[1] and Wolfrom.[2] In a 300-ml. pressure bottle, 18 g. (0.1 mole) of D-glucose was dissolved in 27 ml. of concentrated hydrochloric acid. To this was added 27 g. (0.207 mole) of thiophene-2-methyl mercaptan. The bottle was stoppered and shaken at 35° for thirty minutes, after which time the contents were poured into 500 ml. of ice-water, causing the precipitation of a semicrystalline product. The precipitate was removed by filtration, washed with much cold water and then recrystallized successively from hot water, aqueous methanol and much isopropyl ether to give 20 g. (47.4% yield) of a product melting at 130–131°.

*Anal.*[3] Calcd. for $C_{16}H_{22}O_5S_4$: C, 45.47; H, 5.25; S, 30.35. Found: C, 45.66; H, 5.50; S, 30.38.

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(1) Levene and Meyers, *J. Biol. Chem.*, **74**, 695 (1927).

(2) Wolfrom, THIS JOURNAL, **52**, 2466 (1930).

(3) Analyses by Oakwold Laboratories, Alexandria, Va.

(4) Present address: Oxford Products, Inc., Cleveland 3, Ohio.

### 5-Mercaptomethylfuroic Acid

A solution of 12.6 g. (0.05 mole) of 2-carbomethoxyfuran-5-methylisothiouronium chloride,[1] 5 g. (0.125 mole) of sodium hydroxide, 50 ml. of ethanol and 20 ml. of water

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(1) British Patent 588,377, May 21, 1947.