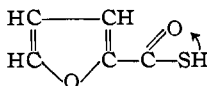


removed by distillation. Vacuum distillation of the residue yielded 10.4 g. of a yellow oil boiling 101–103° at 16 mm. *Anal.* Calcd. for  $C_9H_8O_2S$ : C, 46.9; H, 3.1; S, 25.4. Found: C, 46.5; H, 3.1; S, 23.9. This oil upon hydrolysis with dilute alkali yielded furoic acid and hydrogen sulfide.

Some of the physical and chemical characteristics of this compound are as follows: m. p.  $-9^\circ$ ;  $n_D^{25}$  1.589; it has a disagreeable sulfide-like odor; it is heavier than and insoluble in water, miscible with alcohol and ether; its sodium salt is yellow and water soluble; it gives a green-yellow precipitate with dilute copper sulfate solution and no color reaction with sodium nitroprusside. Earlier attempts to distil the compound at atmospheric pressure were unsuccessful. On standing, the thioacid gives rise to colorless needles m. p. 107–108° which have been identified as difuroyl disulfide (see below). The following structure seems indicated for thiofuroic acid.



A by-product was isolated from the distillation residue, as colorless needles, m. p. 107–108°, by recrystallization from an acetone-water mixture. Hydrolysis of this compound with dilute alkali yielded furoic acid and hydrogen sulfide. A mixed melting point with difuroyl disulfide prepared by Frank, *et al.*,<sup>1</sup> showed no depression (106–108°). *Anal.* Calcd. for  $C_{10}H_8O_4S_2$ : C, 47.2; H, 2.4; S, 25.2. Found: C, 47.1; H, 2.8; S, 25.6.

The disulfide has a disagreeable odor resembling that of biphenyl. It is insoluble in water and dilute alkali, soluble in alcohol and ether.

The reaction, used in these experiments to synthesize thiofuroic acid, appears to be virtually quantitative when the yield of disulfide is also considered.

The author is indebted to A. P. Dunlop of the Quaker Oats Co. for helpful suggestions concerning this research.

(1) R. L. Frank, J. R. Blegen and Deutschman, *J. Polymer Sci.*, **3** (1), 58–65 (1948).

DEPARTMENT OF DAIRY HUSBANDRY  
THE PENNSYLVANIA STATE COLLEGE  
STATE COLLEGE, PENNSYLVANIA

S. PATTON

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#### Alkyl Quinolyl Sulfides

The formation of the hydrochlorides of several aromatic quinolyl sulfides<sup>1</sup> took place readily when 4-chloroquinoline was refluxed with the mercaptan in a solvent such as chloroform. However, when certain aliphatic sulfides of quinoline were desired, reaction failed to take place even at a higher reflux temperature. Alkyl quinoline sulfides were prepared from 2- and 4-chloroquinolines by refluxing with the mercaptan in alcohol in the presence of sodium ethylate, as reported by Clinton and Suter,<sup>2</sup> and as described by Hannan, *et al.*<sup>3</sup>

**6-Methoxy-4-*n*-butylthio-2-methylquinoline.**—A 0.05-mole run was refluxed in 8 volumes of absolute ethanol for six hours. Sodium chloride separated in the theoretical yield and alcohol was removed under reduced pressure. A chloroform solution of the crude product was washed with normal sodium hydroxide. The oily solid recovered from chloroform was suspended in hexane, filtered, and crystallized from 1.5 volumes of ligroin (90–100°); yield,

about 50% of theory. Three crystallizations from ligroin gave a colorless solid melting at 67.3–68°. This sulfide was slightly soluble in pentane and readily soluble in benzene, acetone, methanol and ethanol. *Anal.* Calcd. for  $C_{18}H_{19}ONS$ : N, 5.36; S, 12.26. Found: N, 5.34; S, 12.33.

**6-Methoxy-4-*n*-tetradecylthio-2-methylquinoline.**—The alcoholic solution of sodium ethylate, tetradecylthiol<sup>4</sup> (myristyl mercaptan) and 6-methoxy-4-chloro-2-methylquinoline was refluxed for fifteen hours. After treatment with chloroform and alkali, the colorless sulfide was crystallized from 1.2 and from 6 volumes of acetone, m. p. 64–64.5°. Little loss occurred in recrystallizing this product from 10 volumes of methanol; the sulfide is fairly soluble in benzene. *Anal.* Calcd. for  $C_{25}H_{39}ONS$ : N, 3.49; S, 7.98. Found: N, 3.40; S, 8.16.

(4) We are indebted to Dr. B. J. Humphrey of the Connecticut Hard Rubber Company of New Haven Connecticut, for the tetradecylthiol.

DEPARTMENT OF RESEARCH IN  
PURE CHEMISTRY

ALICE G. RENFREW

MELLON INSTITUTE OF INDUSTRIAL RESEARCH

PITTSBURGH 13, PA.

PAULINE PIATT

RECEIVED JULY 5, 1949

#### 4-Chloro-4'-*t*-butylbenzophenone and 4-Chloro-4'-*t*-butyldiphenylmethane

**4-Chloro-4'-*t*-butyl-benzophenone.**—A mixture of 20.4 g. of *t*-butylbenzene, 29.1 g. of *p*-chlorobenzoyl chloride and 115 ml. of anhydrous nitrobenzene was cooled to about 5°. The mixture was stirred and 22.3 g. of powdered aluminum chloride was added slowly. After all the aluminum chloride had been added, the ice-bath was removed and the mixture was stirred overnight at room temperature. The mixture was now cooled to about 5° and small pieces of ice were dropped in. The decomposition was completed with concentrated sulfuric acid. The nitrobenzene was removed by steam distillation and the residue was taken up in ether, washed with water and dried over "Drierite." When the ether was distilled off, the residue crystallized. Recrystallization from 95% ethanol gave white crystals, m. p. 79–81°; yield 34 g. (82%).

*Anal.* Calcd. for  $C_{17}H_{17}OCl$ : C, 74.85; H, 6.28; Cl, 13.00. Found: C, 75.11; H, 6.40; Cl, 13.41.

**4-Chloro-4'-*t*-butyldiphenylmethane.**—A mixture of 50 g. of the above ketone, 50 g. of 47% hydriodic acid and 50 g. of red phosphorus was refluxed for forty hours with mechanical stirring. The mixture was cooled and made basic with 10% sodium hydroxide solution. The mixture was then extracted with ether, the red phosphorus was filtered off, and the ethereal solution was washed with 10% sodium hydroxide solution and then with water. Finally the ethereal solution was dried over "Drierite" and concentrated. The residue was fractionated under reduced pressure. The entire residue distilled at 176–177° (5 mm.), yield 39.5 g. (84%).

*Anal.* Calcd. for  $C_{17}H_{19}Cl$ : C, 78.90; H, 7.40. Found: C, 79.05; H, 7.45.

DEPARTMENT OF CHEMISTRY  
VIRGINIA POLYTECHNIC INSTITUTE  
BLACKSBURG, VIRGINIA

FRANK A. VINGIELLO

DEPARTMENT OF CHEMISTRY

DUKE UNIVERSITY

DURHAM, NORTH CAROLINA

CHARLES K. BRADSHAW

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(1) Renfrew, *THIS JOURNAL*, **68**, 1433 (1946).

(2) Clinton and Suter, *ibid.*, **70**, 491 (1948).

(3) Hannan, *et al.*, *ibid.*, **71**, Nov. (1949).