2-Amino-4-methyl-5-thioformamidomethylpyrimidine (XI).—To 1.8 g. (0.01 mole) of the hydrochloride of X dissolved in 5 cc. of water and cooled below 15° a solution of 1.2 g. of potassium carbonate in 4.0 cc. of water was added as rapidly as possible with cooling. A solution of 1.2 g. of potassium dithioformate in 3.5 cc. of water was added immediately and the mixture was stirred for four hours at room temperature. The solid material was isolated by filtration and washed with water. The washed product was dissolved in 8 cc. of 50% acetic acid and filtered from a small amount of insoluble material. The warm solution was neutralized with ammonium hydroxide (sp. gr. 0.89), cooled, and filtered. The dried solid, which had a slightly green cast, weighed 1.3 g. (71%), m. p. 192–198°. After two recrystallizations from water, XI melted at 212–213°.

Anal. Calcd. for $C_7H_{10}N_4S$: C, 46.13; H, 5.53; N, 30.74. Found: C, 46.04; H, 5.76; N, 30.31.

3-(2′-Amino-4′-methyl-5′-pyrimidylmethyl)-4-methyl-5-(2-hydroxyethyl)-thiazolium Bromide Hydrobromide (XII).—With stirring, 6.8 g. (0.037 mole) of XI was added to a solution of 8.62 g. (0.039 mole) of 3-bromo-3-acetopropyl acetate in 15 cc. of anhydrous formic acid warmed to 45°. The temperature was maintained at 45° for two and one-half hours and at 60° for one and one-half hours. The mixture was allowed to stand in a refrigerator overnight. Very little solid had appeared and the mixture was evaporated to dryness under a jet of air. The solid residue was taken up in 20 cc. of 10% aqueous hydrobromic acid and extracted twice with 20-cc. portions of methylene chloride. After stirring twice with Darco at 40° for one-half hour periods the solution was evaporated to a volume of about 7 cc. and 60 cc. of absolute ethanol was added to the warm solution. From the cold solution 1.9 g. of yellow needles, m. p. 190–192° (dec.), were obtained. Recrystallization from a water–ethanol mixture produced white needles which decomposed at 184–185° (dec.).

Anal. Calcd. for $C_{12}H_{16}N_4OS{\cdot}2HBr$: C, 33.82; H, 4.26. Found: C, 33.74; H, 4.55.

Summary

An isomer of thiamin, 3-(2′-amino-4′-methyl-5′-pyrimidylmethyl)-5-(2-hydroxyethyl)-4-methylthiazolium bromide hydrobromide, has been prepared and was found to be devoid of thiamin activity.

The sulfa derivative of 2-amino-4-methyl-5-carboxypyrimidine has been prepared. The acetyl derivative possessed no antimalarial activity.

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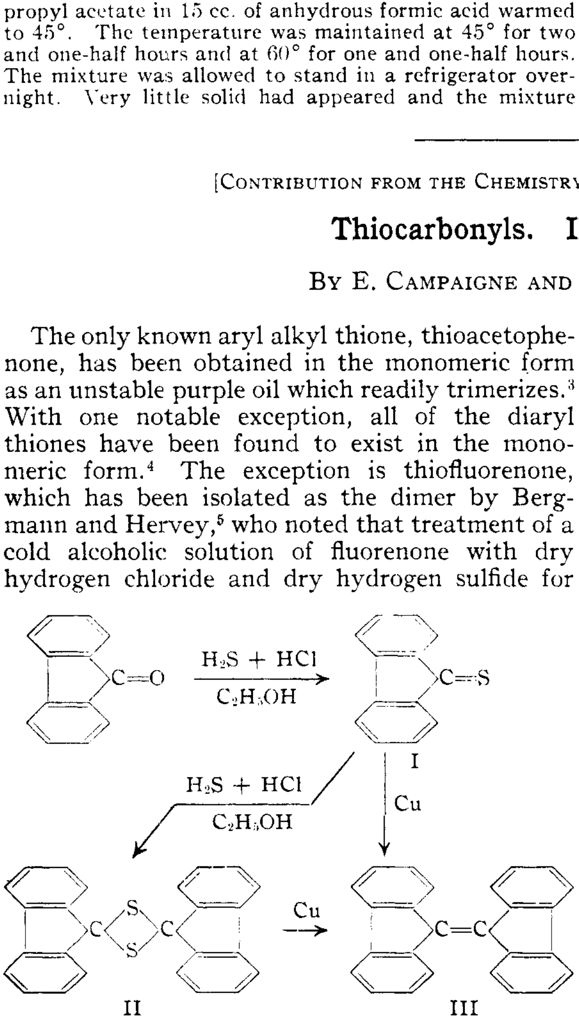
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF INDIANA UNIVERSITY]

Thiocarbonyls. II. Thiofluorenone[1]

BY E. CAMPAIGNE AND WM. BRADLEY REID, JR.[2]

The only known aryl alkyl thione, thioacetophenone, has been obtained in the monomeric form as an unstable purple oil which readily trimerizes.[3] With one notable exception, all of the diaryl thiones have been found to exist in the monomeric form.[4] The exception is thiofluorenone, which has been isolated as the dimer by Bergmann and Hervey,[5] who noted that treatment of a cold alcoholic solution of fluorenone with dry hydrogen chloride and dry hydrogen sulfide for twenty-four hours yielded a yellow precipitate of dithiofluorenone, II.



Smedley[6] attempted to prepare thiofluorenone in several ways, none of which were successful. The action of potassium bisulfide on 9,9-dichlorofluorene yielded a compound which was shown by Bergmann and Hervey[5] to be 9,9′-difluorenyl disulfide. Potassium sulfide and the keto-dichloride yielded bis-diphenylene-ethylene, III, and the action of phosphorus pentasulfide on the ketone gave no identifiable products.

In view of the fact that all other thiones having an aryl group adjacent to the thiocarbonyl group can be obtained in the monomeric form, it would seem probable that monomeric thiofluorenone could be isolated. In the preparation of trithioacetophenone by the action of dry hydrogen sulfide and dry hydrogen chloride on a cold alcoholic solution of acetophenone,[3] the monomeric thione is first deposited as a purple oil, which gradually trimerizes to a white crystalline solid. Dithiofluorenone has been found to be formed by a similar process; by stopping the reaction after three hours the monomeric thiofluorenone (I) has been isolated in green needles, melting at 75–76° on recrystallization from petroleum ether. If the addition of hydrogen sulfide and hydrogen chloride was allowed to continue for fifteen hours, the deep green color of the solution which developed during the first few hours gradually disappeared, and a golden yellow solid was deposited, which proved to be the dimer, II. In addition to analy-

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(1) For the first paper of this series, see THIS JOURNAL, **66**, 1136 (1944).

(2) Taken from part of a thesis to be submitted by Wm. Bradley Reid, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Indiana University.

(3) Baumann and Fromm, *Ber.*, **28**, 895 (1895).

(4) Campaigne, *Chem. Rev.*, in press.

(5) Bergmann and Hervey, *Ber.*, **62**, 911 (1929).

(6) Smedley, *J. Chem. Soc.*, **87**, 1253 (1905).

ses and molecular weight determinations, the structures of I and II were confirmed by conversion of these compounds to III when they were refluxed with freshly reduced copper powder in xylene. This is a characteristic reaction of thiocarbonyl compounds.[7]

Monomeric thiofluorenone resembles thiobenzophenone, in that it is unstable in air and must be isolated and stored in an inert atmosphere. Exposure to the air slowly converted the compound to a yellow trisulfide, $C_{26}H_{16}S_3$, of unknown structure, similar to the trisulfide obtained by exposure of thiobenzophenone to dry air.[8] Thiofluorenone forms an addition complex with mercuric chloride in ether solution, which is quite stable to heat, but is rapidly hydrolyzed in water solutions to form mercuric sulfide and fluorenone.

Experimental

Thiofluorenone.—Eighteen grams (0.1 mole) of fluorenone (m. p. 83–83.5°, prepared by the oxidation of fluorene[9]) was dissolved in 300 ml. of 95% ethyl alcohol, and cooled to $-12°$ with stirring. Some fluorenone crystallized from the solution at this point, but redissolved as the gases were added. Hydrogen sulfide and hydrogen chloride were passed into the stirred mixture at such a rate as to keep the temperature of the solution below 0° (about 1 mole/hour for each gas). After three hours a deep olive-green sludge of crystals had appeared in the reaction flask. At this point the addition of hydrogen chloride was stopped, but hydrogen sulfide addition was continued for another two hours. The green precipitate was filtered in an atmosphere of carbon dioxide, washed with 100 ml. of 50% alcohol, 100 ml. of cold 95% alcohol, and finally dried in vacuum over calcium chloride. The yield of thiofluorenone was 11.2 g. or 57%. A sample of this material, melting at 74–75°, was recrystallized by cooling a petroleum ether solution in a flask filled with carbon dioxide in a Dry Ice-acetone-bath. The compound crystallized in green needles, melting at 75–76°. A mixed melting point with fluorenone was from 60–68°.

Anal. Calcd. for $C_{13}H_8S$: S, 16.32; mol. wt., 196. Found: S, 16.54; mol. wt., 183 (cryoscopically in cyclohexane).

Dithiofluorenone.—Nine and three-tenths grams (0.05 mole) of fluorenone was dissolved in 300 ml. of 95% alcohol which was saturated with dry hydrogen chloride and hydrogen sulfide. This solution was poured into a tall cylinder and the gases passed into the solution at a rate of about 2 moles/hour for fifteen hours. The temperature of the reaction mixture was not controlled. After a few hours the solution became deep green but the color gradually lightened as a golden yellow precipitate settled out of the solution. At the end of fifteen hours the reaction was stopped and 4.68 g. of crude material, m. p. 197–205°, was recovered. Two recrystallizations from a benzene-alcohol mixture yielded 1.53 g. (15%) of cream colored crystals, m. p. 227° dec. This corresponded in analysis to the compound isolated by Bergmann and Hervey[6] which melted at 232° on recrystallization from propyl alcohol.

Anal. Calcd. for $C_{26}H_{16}S_2$: S, 16.32; mol. wt. 392. Found: S, 16.36; mol. wt. (cryoscopically in benzene), 389.

Bis-diphenylene-ethylene.—About 0.4 g. of thiofluorenone was refluxed in 25 ml. of dry xylene with 1.6 g. of freshly reduced copper powder for five hours. The mixture was then filtered, and the xylene removed by vacuum distillation. The red oil which remained was purified by formation of the picrate, decomposition with ammonium hydroxide, and recrystallization of the solid obtained in this way[10] from a chloroform-alcohol mixture. The bis-diphenylene-ethylene was obtained in low yield as red plates, m. p. 188° (cor.).

A similar experiment with dithiofluorenone also yielded bis-diphenylene-ethylene.

Difluoryl Trisulfide.—The crude thiofluorenone obtained from 36 g. (0.2 mole) of fluorenone as described above, was dissolved in 800 ml. of petroleum ether (b. p. 70–90°) and the green solution allowed to stand exposed to the air for six days. At the end of this time the solution was muddy yellow in color, and an orange solid had deposited on the walls of the flask. This material was collected, dissolved in 100 ml. of chloroform, and reprecipitated by the addition of 800 ml. of petroleum ether (b. p. 30–60°). In this way 2.8 g. of a trisulfide, melting at 137–138° with decomposition, was obtained.

Anal. Calcd. for $C_{26}H_{16}S_3$: S, 22.65; mol. wt., 424. Found: S, 22.91; mol. wt. (cryoscopically in benzene), 420.

Thiofluorenone—Mercuric Chloride Addition Compound.—Two-tenths gram of pure thiofluorenone was dissolved in 10 ml. of dry ether, and poured into 100 ml. of a saturated solution of mercuric chloride in dry ether. A white precipitate formed immediately. After stirring for a few minutes, the precipitate was filtered, washed with 50 ml. of dry ether, and dried in air. The yield of white crystalline solid was 0.46 g., or 98.5% of theoretical. The compound did not melt at 300°, but gradually darkened on exposure to sunlight. Treatment of this material with water or water solutions caused the precipitation of a mixture of black mercuric sulfide and yellow fluorenone.

Anal. Calcd. for $C_{13}H_8S \cdot HgCl_2$: S, 6.84; Hg, 42.78. Found: S, 6.89; Hg, 43.09.

Summary

Thiofluorenone has been isolated by treating fluorenone with hydrogen sulfide and hydrogen chloride in alcohol solution.

Thiofluorenone is an unstable green compound, easily oxidized in air to a trisulfide and converted by copper to bis-diphenylene-ethylene. It forms an addition compound with mercuric chloride.

BLOOMINGTON, INDIANA RECEIVED JANUARY 21, 1946

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[7] Schonberg, Schutz and Nickel, *Ber.*, **61B**, 1375 (1928).

[8] Schonberg, Schutz and Nickel, *ibid.*, **61B**, 2175 (1928).

[9] Huntress, Hershberg and Cliff, THIS JOURNAL, **53**, 2720 (1931).

[10] Arzruni, *Jahresber*, 383 (1887).