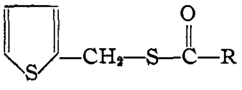
TABLE I

THIOPHENE-2-METHYL THIOL ESTERS


R	B. p.,[a] °C.	Mm.	Yield, %	Formula	Analyses,[b] % Calculated C	H	Found C	H
CH_3	56–60	2	80	$C_7H_8OS_2$	48.80	4.68	49.06	4.92
C_2H_5	79–83	2	53	$C_8H_{10}OS_2$	51.58	5.41	51.68	5.74
C_6H_5	155	2.5	81	$C_{12}H_{10}OS_2$	61.50	4.30	62.17	4.50
C_4H_3O (furyl)	[c]		78.5	$C_{10}H_8O_2S_2$	53.55	3.59	52.93	3.91

[a] Boiling points are uncorrected. [b] Analyses by Oakwold Laboratories, Alexandria, Virginia. [c] M. p. 55°, recrystallized from aqueous methanol.

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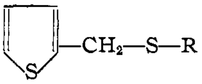
2-Thenyl Sulfides

During work on compounds containing the 2-thenyl grouping, it became desirable to prepare a series of sulfides bearing that loading. Certain of these compounds were obtained in good yields from the interaction of 2-thenyl chloride and the appropriate potassium mercaptide, while 2-(2′-thenylmercapto)-ethyl cyanide and the corresponding mercaptopropionic ester were synthesized by the addition of 2-thenyl mercaptan to the respective acylic compounds in the presence of a trace of alkaline catalyst.[1] The new compounds are listed in Table I.

TABLE I

2-THENYL SULFIDES


R	Yield, %	B. p., °C.[a]	Mm.	Formula	Analyses,[b] % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Sulfur Calcd.	Sulfur Found
C_2H_5–	76	66–69	3	$C_7H_{10}S_2$	53.12	53.35	6.37	6.71	40.52	39.75
i-C_4H_9–	70	89–91	3.5	$C_9H_{14}S_2$	58.01	57.43	7.57	7.59	34.41	34.92
n-C_6H_{13}–	65.5	106–109	2	$C_{11}H_{18}S_2$	61.62	61.09	8.46	8.17	29.91	30.19
$C_6H_5CH_2$–	79.5	120–121	1.5	$C_{12}H_{12}S_2$	65.41	65.34	5.49	5.70	29.10	29.21
$C_4H_3SCH_2$–[c]	78	129–131	1.5	$C_{10}H_{10}S_3$	53.06	52.91	4.45	4.49	42.49	42.98
C_2H_5OCO–$(CH_2)_2$–	40	126	1	$C_9H_{12}O_2S_2$					29.64	29.79
NC–$(CH_2)_2$–	47	127–130	2.5	$C_8H_9NS_2$					34.99	34.27

[a] Boiling points are uncorrected. [b] Analyses by Oakwold Laboratories, Alexandria, Virginia. [c] Thiophene-2-methyl.

***i*-Butyl-2-thenyl Sulfide.**—In a 250-ml. 3-neck flask fitted with a sealed Hershberg stirrer, reflux condenser, thermometer and dropping funnel, was dissolved 6.6 g. (0.1 mole) of 85% potassium hydroxide in 100 ml. of absolute ethanol with stirring and heating. After solution was complete, the temperature was allowed to drop to about 25° and 10 g. (0.11 mole) of *i*-butyl mercaptan was added from the dropping funnel during ten minutes, the temperature being maintained constant. At the end of this time, 13.2 g. (0.1 mole) of 2-thenyl chloride[2] was added dropwise at the same temperature (fifteen minutes). The precipitation of potassium chloride began almost immediately, and the mixture was stirred and refluxed for three hours, after which time further heating did not increase the yield. The cooled mixture was poured into 900 ml. of water, causing separation of an oil which was removed by extraction with a total of 400 ml. of ether. The solvent layer was dried with calcium sulfate, filtered from the desiccant, stripped (finally at reduced pressure) and then fractionated through a 30-cm. Vigreux column to give 13 g. (70% yield) of a colorless oil boiling at 89–91° (3.5 mm.).

2-(2′-Thenylmercapto)-ethyl Cyanide.—In a 250-ml. 3-neck flask fitted as above was placed 26 g. (0.2 mole) of 2-thenyl mercaptan,[3] 0.05 g. (0.0022 mole) of sodium and 100 ml. of anhydrous benzene. The mixture was stirred and refluxed until the sodium had reacted completely. The mixture was cooled to 5° and 11.1 g. (0.21 mole) of freshly distilled acrylonitrile in 50 ml. of benzene was added dropwise during five minutes, the temperature rising to 40°.[4] The solution was refluxed for one hour, cooled, acidified with glacial acetic acid and the volatiles removed from the steam-bath at reduced pressure. The residue was fractionated at 127–130° (2.5 mm.) to give 17.3 g. (47% yield) of a colorless oil.

The thenylmercaptopropionic ester was prepared in a similar manner using methyl acrylate instead of acrylonitrile.

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[1] Rapoport, Smith and Newman, THIS JOURNAL, 69, 693 (1947); Gershbein and Hurd, *ibid.*, 69, 241 (1947); Hurd and Gershbein, *ibid.*, 69, 2328 (1947).

[2] Blicke and Leonard, *ibid.*, 68, 1934 (1946).

[3] From 2-thenyl chloride and thiourea, followed by treatment of the isothiouronium salt with alkali.

[4] The reaction could be performed in the absence of solvent, but it proceeded with almost explosive violence.

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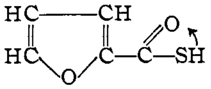
Thiofuroic Acid

Sixteen and four-tenths grams of furoyl chloride was added with agitation to 75 ml. of 10% aqueous sodium hydrosulfide. The reaction proceeded smoothly in the cold (4°). The reaction mixture was acidified to liberate the thioacid and then extracted with ether. The ether solution was dried with anhydrous sodium sulfate and the solvent 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 $C_5H_4O_2S$: 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°; $n^{24}\text{D}$ 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.*,[1] showed no depression (106–108°). *Anal.* Calcd. for $C_{10}H_6O_4S_2$: 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.

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

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Alkyl Quinolyl Sulfides

The formation of the hydrochlorides of several aromatic quinolyl sulfides[1] 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,[2] and as described by Hannan, *et al.*[3]

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 $C_{15}H_{19}ONS$: 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[4] (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.

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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).

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

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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.

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