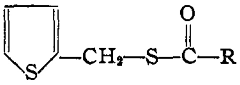
TABLE I

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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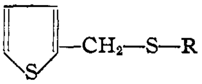
2-Thenyl Sulfides

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