phous series. This was further substantiated by the preparation of mixed sodium copper zinc salts by addition of sodium chromate solution to an equimolar mixture of zinc and copper trichromate solution until all zinc and copper were precipitated. The first crystals formed were a brownish maroon, indicating a predominance of the copper salt. As precipitation progressed, a continuous graduation in color to reddish-yellow was noted with no change in crystal form, a zinc-rich salt precipitating directly on the copper-rich crystals first formed. A typical product was uniform, brownish-red in color, composed mostly of aggregates of well-defined crystals of the general shape previously described. Single crystals showed a crystal angle of 62–63°. The crystals were identified as belonging to the general family of compounds by analysis for sodium and chromium: Found: Na_2O, 7.49; CrO_3, 47.52; molecular ratio, CrO_3: Na_2O = 3.94. Calculated (Cu salt): Na_2O, 7.43; CrO_3, 47.94; (Zn salt) Na_2O, 7.37; CrO_3, 47.55. Isomorphism evidently exists, but there is a considerable discrepancy in solubility of the two salts, the copper salt being the more insoluble at the lower *p*H.

An interesting development in the case of the ammonium double salts is the existence of a new series of compounds of the general formula $3NH_3 \cdot 4M^{ii}O \cdot 4CrO_3 \cdot 3H_2O$. The exact structure of these compounds is unknown, but a simple concept of their formation is the replacement of a water molecule in $(NH_4)_2O \cdot 4M^{ii}O \cdot 4CrO_3 \cdot 3H_2O$ by NH_3. They appear to crystallize in hexagonal plates in those cases where discrete crystals have been observed.

Conclusion

1. The following new compounds have been prepared and described, members of the isomorphous series $M^{i}_2O \cdot 4M^{ii}O \cdot 4CrO_3 \cdot 3H_2O$: $Na_2O \cdot 4CuO \cdot 4CrO_3 \cdot 3H_2O$, $Na_2O \cdot 4CoO \cdot 4CrO_3 \cdot 3H_2O$. They form characteristic tabular diamond-shaped crystals over a range of *p*H and concentration.

2. A new series of compounds, of the general formula $(NH_4)_2O \cdot 4M^{ii}O \cdot 4CrO_3 \cdot NH_3 \cdot 2H_2O$, or $3NH_3 \cdot 4M^{ii}O \cdot 4CrO_3 \cdot 3H_2O$, crystallizing in six-sided plates or aggregates, has been noted. The zinc and cobalt salts have been prepared and described.

3. Precipitates have been obtained approximating the above formulas in the case of ammonium copper chromate, ammonium nickel chromate, sodium nickel chromate, and potassium nickel chromate. These materials exhibit substantial variation in appearance and composition with varying precipitation conditions. They appear to be solid-solution type compounds with the property of forming definite crystals with an excess or deficiency of certain components of the lattice.

4. The series of compounds falls within a logical pattern, as determined by ionic ratios. The non-existence of the sodium cadmium chromate is in accord with this pattern, as are the non-stoichiometric compounds formed.

5. Preliminary data have been presented which may be helpful in the eventual determination of the structure of these compounds.

RESEARCH LABORATORIES
MUTUAL CHEMICAL COMPANY OF AMERICA
BALTIMORE, MARYLAND
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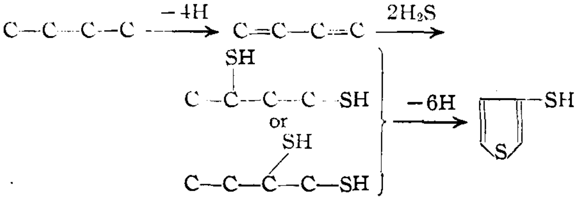
Derivatives of 3-Thiophenethiol

BY J. W. BROOKS, E. G. HOWARD[1] AND J. J. WEHRLE

The preparation of thiophene by the reaction of sulfur with *n*-butane at elevated temperatures has been reported by Rasmussen, Hansford and Sachanen.[2] These investigators obtained approximately one pound of so-called "tar" for every pound of thiophene produced. The tar has been investigated and found to contain 20–30% of 3-thiophenethiol. A possible mechanism for the formation of this compound is given.



In order to identify the thiol obtained from the tar as 3-thiophenethiol, the 2,4-dinitrophenyl sulfide derivative was prepared (m. p. 132.5–133°). The melting point corresponds to that of the 2,4-dinitrophenyl sulfide made from a sample of 3-thiophenethiol synthesized by Caesar and Branton.[3] Their synthesis involved the reaction of sulfur with the Grignard reagent prepared from 3-iodothiophene. The corresponding derivative of 2-thiophenethiol melts at 119°.[4]

3-Thiophenethiol is a colorless liquid possessing an offensive stench similar to that of benzenethiol.

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[1] Present address: Experimental Station, du Pont, Wilmington, Delaware.

[2] Rasmussen, Hansford and Sachanen, *Ind. Eng. Chem.*, **38**, 376 (1946).

[3] Unpublished work of P. D. Caesar and P. D. Branton of this Laboratory.

[4] Bost, Turner and Norton, THIS JOURNAL, **54**, 1985 (1932).

TABLE I

3-THIENYL SULFIDES, $C_4H_3S_2R$[a]

Reaction of 3-thiophenethiol with	3-Thienyl sulfide	Method	Yield, %	M. p. or b. p. °C.	Mm.	$n^{25}D$	d^{20}_4	Molecular formula	Sulfur, % Calcd.	Sulfur, % Found
Isopropyl chloride	Isopropyl	A	79	65–66	3	1.5532	1.0742	$C_7H_{10}S_2$	40.51	39.8
Isobutylene	*t*-Butyl	B	..	65–67	1	1.5440	....	$C_8H_{12}S_2$	37.21	36.84
Octene-1	1-Octyl	C	..	108–111	1	....	....	$C_{12}H_{20}S_2$	28.07	27.5
Diisobutylene	1,1,3,3-Tetramethylbutyl	B	76	102–113	1	1.5356	1.0140	$C_{12}H_{20}S_2$	28.07	28.32
Triisobutylene	*t*-Dodecyl	B	60	174–176	8	1.5343	....	$C_{16}H_{28}S_2$	22.54	23.04
1-Tetradecyl chloride	1-Tetradecyl	A	80	M.[b] 44–45		....	....	$C_{18}H_{32}S_2$	20.51	20.8
Allyl chloride	Allyl	A	86	50–54	0.5	1.5964	1.1541	$C_7H_8S_2$	41.04	41.20
α-Pinene	Pinyl	B	55	118–122	1	1.5720	1.0923	$C_{14}H_{20}S_2$	25.40	25.6
Benzyl chloride	Benzyl	A	81	M. 37–38		....	....	$C_{11}H_{10}S_2$	31.08	31.1
Styrene	2-Phenylethyl	D	67	120–122	0.5	1.6168	1.1591	$C_{12}H_{12}S_2$	29.10	28.9
2,4-Dinitrochlorobenzene	2,4-Dinitrophenyl	A	..	M. 132.5–133		....	....	$C_{10}H_6N_2O_4S_2$	22.71	22.4
1,4-Dichlorobutane	1,4-Butylene di-	A	87	M. 62–63		....	....	$C_{12}H_{14}S_4$	44.77	44.05
1,2-Dichloroethane	1,2-Ethylene di-	A	97	M. 54–55		....	....	$C_{10}H_{10}S_4$	49.63	49.41

[a] The addition of 3-thiophenethiol to olefins is assumed to proceed in accordance with Markownikoff's rule when BF_3-ether catalyst is employed, and contrary to Markownikoff's rule in the absence of an acid catalyst, as has been reported by Ipatieff, Pines and Friedman[5] for the alkylation of benzenethiol with olefin in the presence of sulfuric acid and in the absence of acid catalysts, respectively. The BF_3·ether catalyst was shown to catalyze the alkylation of benzenethiol with isobutylene in the same manner as sulfuric acid, since the sulfone prepared from the BF_3·ether catalyzed *t*-butyl phenyl sulfide melted at 97.5–98°. Ipatieff reported a melting point of 98–99° for the sulfone of the sulfuric acid catalyzed product. [b] M means melting point.

It is soluble in aqueous potassium hydroxide solution and in most organic solvents. It is unstable and changes in composition on standing at room temperature, as is indicated by an increase in its refractive index. Some of its physical properties are: b. p. 171°, d^{25}_{25} 1.251 and $n^{20}D$ 1.6157.

TABLE II

DI-3-THIENYL MERCAPTALS AND MERCAPTOLES, $(C_4H_3S_2)_2CHR$ AND $(C_4H_3S_2)_2CRR'$

Di-3-thienyl mercaptal or mercaptole	Yield, %	M. p., °C.	Molecular formula	Sulfur, % Calcd.	Sulfur, % Found
Butyraldehyde[a,c]	58	....	$C_{12}H_{14}S_4$	44.72	44.47
Acetone[b,d]	84	....	$C_{11}H_{12}S_4$	47.07	46.9
2-Acetothienone[b]	79	85–86	$C_{14}H_{12}S_5$	47.09	47.05
Benzophenone[b]	80	152	$C_{21}H_{16}S_4$	32.34	32.16

[a] Mercaptal. [b] Mercaptole. [c] B. p. 173–176° (2 mm.) [d] B. p. 148–153° (1 mm.)

TABLE III

ESTERS OF 3-THIOPHENETHIOL, $C_4H_3S_2COR$

Compound	Yield, %	M. p., °C.	Molecular formula	Sulfur, % Calcd.	Sulfur, % Found
3-Thienyl thiolacetate[a]	76	41.5–43	$C_6H_6OS_2$	40.52	40.50
3-Thienyl thiolbenzoate	..	69–70	$C_{11}H_8OS_2$	29.11	28.98
3-Thienyl thiolfuroate	81	51–52	$C_9H_6O_2S_2$	30.50	30.46

[a] B. p. 84–86° (1 mm.).

3-Thiophenethiol from thiophene "tar" reacts with various compounds to yield several different types of derivatives, all of which involve the SH group. Attempts to alkylate the ring without interfering with the SH group failed and mixtures of 3-thienyl sulfides and alkylated 3-thienyl sulfides resulted. The preparation and properties of the 3-thiophenethiol derivatives are described under the following headings: (1) 3-thienyl sulfides (Table I), (2) 3-thienyl mercaptals and mercaptoles (Table II), (3) 3-thiophenethiol esters (Table III) and (4) miscellaneous 3-thiophenethiol derivatives (Table IV).

I. 3-Thienyl Sulfides

Method A.—Three and one-half moles of 3-thiophenethiol and 3.5 moles of potassium hydroxide were dissolved in 450 ml. of ethyl alcohol and 250 ml. of water. To this mixture was added 1.5 moles of ethylene chloride at such a rate that the temperature stayed around 45-50°. The reaction mixture was then stirred for five hours at 75°. Water was added to precipitate the 1,2-di-(3-thienylthio)-ethane, which was recrystallized from cyclohexane.

Method B.—To a flask containing one mole of 3-thiophenethiol and 20 g. of BF_3·ether complex was added 2 moles of diisobutylene at such a rate as to maintain the temperature at 40-50°. After the addition of olefin was complete the reaction mixture was washed with aqueous potassium hydroxide, with water, dried over anhydrous magnesium sulfate and distilled under reduced pressure to yield 1,1,3,3-tetramethylbutyl 3-thienyl sulfide.

For the reaction of isobutylene, the gas was bubbled through a solution of thiophenethiol in cyclohexane at such a rate as to keep the temperature at 30-40°. The

TABLE IV

MISCELLANEOUS 3-THIOPHENETHIOL DERIVATIVES

Compound	Yield, %	M. p., °C.	Molecular formula	Sulfur, % Calcd.	Sulfur, % Found	Phosphorus, % Calcd.	Phosphorus, % Found
β-(3-Thienylthio)-ethanol[a]	72	....	$C_6H_8OS_2$	40.01	39.97		
3-Thienylthioacetic acid	61	51.5–52.5	$C_6H_6O_2S_2$	36.80	36.78		
3-Thienylthiosuccinic acid	96	130–131	$C_8H_8O_4S_2$	27.61	27.38		
Tri-3-thienyl trithiophosphite	51	71.5–73	$C_{12}H_9S_6P$	51.09	49.6	8.23	7.9
Tri-3-thienyl trithiophosphate	51	....	$C_{12}H_9S_6OP$	49.01	49.3	7.89	8.14
Tri-3-thienyl tetrathiophosphate	61	76.5–78	$C_{12}H_9S_7P$	54.94	54.1	7.58	7.50

[a] B. p. 125° (1 mm.).

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(5) Ipatieff, Pines and Friedman, THIS JOURNAL, 60, 2731 (1938).

amount of BF_3·ether catalyst employed varied from 5 to 20 wt. % of the 3-thiophenethiol.

Method C.—Two moles of 3-thiophenethiol, 3 moles of octene-1, 200 g. of petroleum ether and 75 g. of a silica-alumina cracking catalyst reacted in a bomb at 400°F. for two hours. The reaction mixture was filtered and distilled.

Method D.—One mole of styrene was added to one mole of 3-thiophenethiol. The reaction mixture developed much heat about five minutes after being mixed and was placed in an ice-bath. After being stored at room temperature for one month it was extracted with aqueous potassium hydroxide and vacuum distilled to give 2-phenylethyl 3-thienyl sulfide.

II. Di-3-thienyl Mercaptals and Mercaptoles.—Several ketones and one aldehyde were converted to the corresponding mercaptoles and mercaptal by bubbling anhydrous hydrogen chloride through a cooled mixture of the thiol and carbonyl compound. The details of the experiment with benzophenone are typical.

Di-3-thienyl Mercaptole of Benzophenone.—To 2 moles of benzophenone in 400 ml. of xylene was added 4 moles of 3-thiophenethiol. The mixture was cooled to 10°, anhydrous hydrogen chloride was bubbled through for two hours keeping the temperature at 10–15°, and the mixture was placed in a refrigerator overnight. The reaction mixture was filtered and the filtrate was washed with cold water, dried over anhydrous magnesium sulfate and topped to 100° at 2-mm. pressure. The solid remaining in the flask combined with the solid removed by filtration weighed 630 g. It was recrystallized several times from cyclohexane.

Since the products prepared from butyraldehyde and acetone were liquids they were distilled after washing the xylene solution with water to remove the hydrogen chloride.

III. 3-Thiophenethiol Esters.—Several acid chlorides were treated with 3-thiophenethiol to form the corresponding thiol esters. The details of the preparation of 3-thienyl thiolfuroate are typical.

3-Thienyl Thiolfuroate.—One and one-half moles of furoyl chloride was added to a mixture of 2 moles of 3-thiophenethiol, 500 ml. of benzene and 1.5 moles of pyridine over a period of two hours so as to keep the temperature around 40–50°. After the addition was complete the reaction mixture was stirred for two hours at 70°, then cooled and filtered to remove the pyridine hydrochloride. The filtrate was washed with cold sodium hydroxide solution, then with water and was finally topped under vacuum. The resulting solid weighed 255 g. and appeared as white crystals after several recrystallizations from cyclohexane.

3-Thienyl thiolacetate was prepared in a similar manner. This product remained as a water-white liquid for one year and it was then crystallized by seeding. The crystals used for seeding were obtained from a similar preparation, which crystallized the day it was made.

IV. Miscellaneous 3-Thiophenethiol Derivatives. (a) **β-(3-Thienylthio)-ethanol.**—This product was formed by the reaction of β-chloroethanol under conditions similar to those employed for the formation of 3-thienyl sulfides under method A.

(b) **3-Thienylthioacetic Acid.**—To 3 moles of monochloroacetic acid in 300 g. of water was slowly added 1.5 moles of sodium carbonate in 500 g. of water. This mixture was added to a flask containing 3 moles of 3-thiophenethiol and 3 moles of sodium hydroxide in 200 g. of water at such a rate that the reaction temperature stayed around 40°. Approximately four hours were required for the addition. The reaction mixture was then heated for two hours at 55°, cooled and acidified with hydrochloric acid. The product was separated from the water layer, the water layer extracted with ether, and the combined product and extract topped to a pot temperature of 130° at 2-mm. pressure, yielding 318 g. (61%) of solid product. After several recrystallizations from ASTM Precipitation Naphtha (50–130°) it was obtained as a white crystalline solid, m. p. 51.5–52.5°. Challenger, *et al.*,[6] reported a m. p. of 50.5–51°.

(c) **3-Thienylthiosuccinic Acid.**—One and one-half moles of 3-thiophenethiol was added to 1 mole of maleic anhydride in 700 ml. of water at such a rate that the temperature stayed around 45°. Approximately two hours were required for complete addition. The reaction mixture was stirred for ten hours at 80°, cooled to room temperature and the water layer separated from the product. A yield of 222 g. of white solid crystallized from the product layer. This was recrystallized from cyclohexane.

(d) **Tri-3-thienyl Trithiophosphite, Trithiophosphate and Tetrathiophosphate.**—All three of these products were prepared under essentially the same conditions using phosphorus trichloride, phosphorus oxychloride and phosphorus thiochloride, respectively. The example cited below for tri-3-thienyl trithiophosphite is typical.

Tri-3-thienyl Trithiophosphite.—A mixture of 2.1 moles of 3-thiophenethiol, 200 ml. of toluene and 2.1 moles of pyridine was cooled to 10° and 0.7 mole of phosphorus trichloride was slowly added, keeping the temperature at 10–12°. The temperature was then raised to 120° over a period of four hours. The reaction product was cooled, filtered to remove pyridine hydrochloride, and the filtrate was washed with cold water and dried over anhydrous magnesium sulfate. The toluene was distilled off and the product recrystallized from toluene. There resulted 137 g. of white crystals.

Acknowledgment.—The authors are indebted to Mrs. L. Fagundus for the preparation of some of the derivatives.

Summary

Twenty-five new derivatives of 3-thiophenethiol have been synthesized and their properties, with those of 3-thiophenethiol, are reported.

PAULSBORO, N. J. RECEIVED JULY 22, 1949

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[6] Challenger, Miller and Gibson, *J. Chem. Soc.*, 769 (1948).