TABLE II

HYDRAZIDES OF THIODIACETIC ACID AND HOMOLOGS

Compound	M.P.	Formula	C Calcd.	C Found	H Calcd.	H Found
		$S(CH_2CONHNHR)_2$				
R = H	117–119[a]	$C_4H_{10}N_4O_2S$	26.9	27.2	5.6	5.6
C_6H_5	212–215	$C_{16}H_{18}N_4O_2S$	58.2	58.2	5.5	5.4
		$S(CH_2CH_2CONHNHR)_2$				
R = H	152–153	$C_6H_{14}N_4O_2S$	34.9	35.0	6.8	6.9
C_6H_5	204–206[b]	$C_{18}H_{22}N_4O_2S$	60.3	59.6	6.2	6.3
		$S(CH_2CH_2CH_2CONHNR)_2$				
R = H	128–131[c]	$C_8H_{18}N_4O_2S$	41.0	41.0	7.7	7.7
C_6H_5	151–153	$C_{20}H_{26}N_4O_2S$	62.1	60.6[d,e]	6.8	6.6
		$S[CH(CH_3)CONHNR]_2$				
R = H	174–175[b]	$C_6H_{14}N_4O_2S$	34.9	35.8	6.8	7.1
C_6H_5	169–170	$C_{18}H_{22}N_4O_2S$	60.3	62.5[e]	6.2	6.2

[a] Recrystallized from methanol. [b] Recrystallized from methanol/dimethylformanide. [c] W. Reppe, *Ann.*, **596**, 158 (1955), m.p. 130°. [d] Recrystallized from ethanol/dimethylformanide. [e] The analysis could not be improved by further recrystallization.

ters were treated with sodium sulfide in aqueous ethanol. The thiodiacid esters were isolated and, on reaction with excess hydrazine, furnished the corresponding hydrazides. The latter were converted into the aralkylidene hydrazides by the method of Zimmer and George.[3] The hydrazides are characterized by an extremely low solubility in most of the common solvents. They are, however, soluble in *N*,*N*-dimethylformamide and can be recrystallized from this solvent. They all have rather unsharp melting points and melt with considerable decomposition. Therefore, these derivatives are not well suited for possible identification of carbonyl compounds. In the preparation of the phenylhydrazides,[4] it was found advantageous to use the acids rather than the esters as starting materials.

EXPERIMENTAL

Melting points are uncorrected. Microanalyses are by A. Bernhardt, Microanalytisches Laboratorium im Max-Planck-Institut, Mulheim/Ruhr, Germany.

Materials. Generally, Eastman White Label products or comparable grades were employed without further purification. Ethyl 4-bromobutyrate was obtained from Fluka, A.G., Buchs, Switzerland.

The preparations of the hydrazides were generally performed as follows: To a solution of the corresponding thiodiacid diester (0.05 mole) in 25 ml. absolute methanol, a 30% excess of hydrazine hydrate (85%) was added. After 3 drops of glacial acetic acid had been added as a catalyst, the mixture was refluxed for about 3 hr. After the mixture was cooled, an additional 25 ml. of absolute methanol was added, and the mixture was left overnight for crystallization. An additional crop of compound could be obtained by keeping the mother liquor for a short period in the refrigerator. The compounds were recrystallized from a minimum amount of *N*,*N*-dimethylformamide (Table II).

3,3'-Thiodipropionic acid, bis(p-dimethylaminobenzylidenehydrazide). To a solution of 2.67 g. (0.015 mole) of 3,3'-thiodipropionic acid dihydrazide in 40 ml. of water, a solution of 5.97 g. (0.04 mole) of *p*-dimethylaminobenzaldehyde in 70 ml. of ethanol was added. After a brief period, crystals began depositing and were collected after about 1 hr. They were washed with ethanol and air-dried. Yield, 5.69 g. (81%), m.p. 247–250°. The analytical sample was recrystallized from *N*,*N*-dimethylformamide, m.p. 247–250° (dec.). The remaining aralkylidene hydrazides were prepared similarly (Table I).

3,3'-Thiodipropionic acid, bis(phenylhydrazide). To a solution of 6.5 g. phenylhydrazine in 25 ml. tetrahydrofuran, 3.56 g. (0.02 mole) of 3,3'-thiodipropionic acid was added. After being refluxed for 7 hr., the mixture was cooled and the deposited phenylhydrazide was filtered and washed with ether. Yield, 5.02 g. (70%), m.p. 197–200°. The analytical sample was recrystallized from a minimum amount of *N*,*N*-dimethylformamide, m.p. 204–206°. The remaining phenylhydrazides were prepared similarly (Table II).

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[2] G. M. Bennett and L. V. D. Scorah, *J. Chem. Soc.*, **194** (1927); J. M. Loven, *Ber.*, **29**, 1136 (1896).

[3] H. Zimmer and D. K. George, *Chem. Ber.*, **89**, 2285 (1956).

[4] R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, 3rd ed., John Wiley & Sons, Inc., New York, p. 158 (1948).

A Procedure for Converting Aryl Halides to High Molecular Weight Phenols

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Authentic specimens of phenols were desired for part of an extensive program on characterizing

TABLE I

PREPARATION OF SOME HIGH MOLECULAR WEIGHT PHENOLS

Compound	Yield, %	M.p.	$\lambda_{max}^{cyclohexane}$, m$\mu$	Log ϵ
2-Fluorenol	23	169–170[a]	315.2, 308.3, 304.0, 282.3, 276.5, 271.0, 267.0, 262.0	3.76, 3.72, 3.74, 4.18, 4.25, 4.33, 4.30, 4.22[b]
5-Acenaphthenol	15	121.5–123[c]	331, 323.5, 316.0, 301.2, 290.5	3.69, 3.55, 3.70, 3.82, 3.78[d]
2-Methyl-1-naphthol	51	61–63[e]	330.0, 324.2, 316.3, 310.0, 303.2, 296.5, 292.5, 285.0	2.97, 3.35, 3.29, 3.45, 3.52, 3.64, 3.65, 3.63
4-Methyl-1-naphthol	33	83–85[f]	326.6, 318.8, 312.2, 305.0, 299.6, 290.0	3.50, 3.51, 3.63, 3.68, 3.75, 3.67
3-Phenylphenol	61	72–74[g]	290.0, 281.0, 249.0	3.50, 3.60, 4.21[h]

[a] M.p. 171°, I. Heilbron and H. M. Bunbury. *Dictionary of Organic Compounds*, Oxford University Press, New York, 1953. [b] $\lambda_{max}^{cyclohexane}$ 315.2, 308.3, 304.0, 282.3, 276.5, 271.0, 267.0, 262.0 mμ (log ϵ 3.75, 3.70, 3.74, 4.17, 4.24, 4.32, 4.31, 4.26), R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley & Sons, New York, 1951. [c] M.p. 125–126°, H. Rapoport, T. P. King, and J. B. Lavigne, *J. Am. Chem. Soc.*, **73,** 2718 (1951). [d] Log ϵ values reliable only with respect to relative size since precise concentration of saturated solution used was not known. [e] M.p. 62.4°, P. P. T. Sah, *Rec. trav. chim.*, **60,** 373 (1941). [f] M.p. 84–85° (Heilbron). [g] M.p. 72–76°, G. F. Woods, F. T. Reed, T. E. Arthur, and H. Ezekial, *J. Am. Chem. Soc.*, **73,** 3854 (1951). [h] λ_{max}^{EtOH} 290, 287, 249 mμ (log ϵ 3.52, 3.58, 4.20), V. Prelog, O. Metzler, and O. Jeger, *Helv. chim. acta*, **30,** 675 (1947).

components isolated from low temperature coal tars. Hawthorne has presented a procedure for converting aryl halides to the corresponding phenols, in which he demonstrated good yields for phenol, 1-naphthol, and 4-methylphenol.[2] Since a relatively large number of aryl halides has been made available for purchase in recent years, this apparently general method of synthesizing phenols seemed to offer an appealingly ready route for preparing authentic specimens. However, it was soon discovered that most of the higher molecular weight aryl halides gave little or no phenol according to the procedure described by Hawthorne.

The difficulty was readily shown to lie in lack of oxidation of the arylboronic acid with 10% hydrogen peroxide. Good yields of the arylboronic acid could be obtained from the reaction of methyl borate with the arylmagnesium halide, but the subsequent oxidation to the phenol failed to take place. Kuivila[3] has demonstrated that the reaction of hydrogen peroxide with benzeneboronic acid proceeds by way of the hydroperoxide ion, HOO^-, which attacks the boron atom. The rate of the reaction depends on concentration of hydroperoxide ion, as shown by Kuivila; it is also logical to assume that an increase in reaction temperature will increase the reaction rate. Therefore 30% hydrogen peroxide was used in place of 10% hydrogen peroxide and, possibly of more importance, the original refluxing ether solution employed by Hawthorne during the oxidation step was replaced by a refluxing benzene solution. This meant an increase of about 45° in the reaction temperature. Under these conditions most of the high molecular weight arylboronic acids were readily oxidized to the corresponding phenols.

EXPERIMENTAL

Synthesis of high molecular weight phenols. A brief description of the synthesis of a few of the less common high molecular weight phenols follows.

Preparation of the Grignard reagents was straightforward, although some of the aryl halides, such as 2-bromofluorene and 5-bromoacenaphthene, were insufficiently reactive and required introduction of ethyl bromide to keep the magnesium active.[4] After the Grignard reagent was added to the ether solution of the trimethyl borate, as described by Hawthorne, the reaction mixture was refluxed 15 min. as recommended by Seaman and Johnson for increased yields of arylboronic acid.[5] Nearly all of the ether was removed by evaporation over a water bath, and an equivalent volume of benzene was added. This benzene solution was heated to reflux and 30% hydrogen peroxide was added slowly in a nitrogen atmosphere and the reaction mixture refluxed for 45 min. The remainder of the procedure was essentially that described by Hawthorne. Yields given in Table I are based on the aryl halides.

Infrared spectra of high molecular weight phenols. The infrared spectra were determined with a Perkin-Elmer Model 21 instrument, using about 1.1 to 1.5% in potassium bromide pellets for all of the phenols except 5-acenaphthenol, for which a 0.70% cyclohexane solution was used in a 0.5 mm. sodium chloride cell. The absorption bands of analytical significance are presented in Table II. These have not been reported previously in the literature.

TABLE II

ANALYTICAL INFRARED ABSORPTION BANDS[a]

2-Fluorenol	5-Acenaphthenol	2-Methyl-1-naphthol	4-Methyl-1-naphthol	3-Phenylphenol
1266 s	1178 s	909 s	816 s	882 m
930 m	1129 s	799 vs	775 m	861 m
896 m	920 m	773 m	763 vs	853 m
853 m	826 m	742 m	739 m	754 vs
824 s	808 s	738 m		694 s
762 vs	771 vs	733 m		
728 vs		648 s		

[a] Values are frequencies in cm.$^{-1}$; vs = very strong, s = strong, m = medium.

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(2) M. F. Hawthorne, *J. Org. Chem.*, **22,** 1001 (1957).

(3) H. G. Kuivila, *J. Am. Chem. Soc.*, **76,** 870 (1954).

(4) L. F. Fieser, *Experiments in Organic Chemistry*, 3rd Ed., D. C. Heath and Co., Boston, 1955, p. 268.

(5) W. Seaman and J. R. Johnson, *J. Am. Chem. Soc.*, **53,** 711 (1931).

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Reactions of Long-Chain Acids with Thiolacetates

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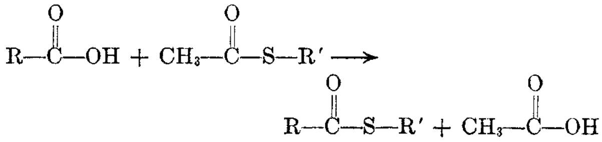
Vinyl esters of long-chain acids have been prepared by acidolysis of vinyl acetate in the presence of mercuric acetate and sulfuric acid.[1,2] This note describes the preparation of *n*-decyl and *n*-dodecyl thiol esters of myristic, palmitic, and stearic acids as well as *n*-dodecyl thiollaurate, *n*-butyl thiolstearate, phenyl thiolpalmitate and diphenyl dithiolsebacate by acidolysis of thiolacetates with long-chain acids in 46–61% yield. The results of these reactions are summarized in Table I. We believe that this is the first reported instance of the acidolysis of thiol esters. Traces of unreacted acids were removed from the crude thiol esters by chromatography with Florisil.



$$R{-}\overset{O}{\overset{\|}{C}}{-}OH + CH_3{-}\overset{O}{\overset{\|}{C}}{-}S{-}R' \longrightarrow R{-}\overset{O}{\overset{\|}{C}}{-}S{-}R' + CH_3{-}\overset{O}{\overset{\|}{C}}{-}OH$$

TABLE I

THIOL ESTERS PREPARED BY ACIDOLYSIS

	M.P.	Yield, %
n-Dodecyl thiollaurate	37–38	48
n-Decyl thiolmyristate	38–38.5	61
n-Dodecyl thiolmyristate	43.5–44	46
n-Decyl thiolpalmitate	43–44	48
n-Dodecyl thiolpalmitate	48–49	51
n-Decyl thiolstearate	50–50.5	51
n-Dodecyl thiolstearate	54–55	47
Phenyl thiolpalmitate	28–28.5	60
Diphenyl dithiolsebacate	60–61	52
n-Butyl thiolstearate	31–32	49

Attempts to prepare the monophenyl thiol ester of sebacic acid by the reaction of sebacic acid and phenyl thiolacetate were unsuccessful. Heating of equimolar ratios of sebacic acid and phenyl thiolacetate in the presence of 100% sulfuric acid and mercuric acetate for 6 hr. on a steam bath resulted in the formation of diphenyl dithiolsebacate. A similar experiment with two molar ratio of sebacic acid to phenyl thiolacetate yielded diphenyl dithiolsebacate and not monophenyl thiolsebacate.

EXPERIMENTAL

Starting materials. Lauric, myristic, palmitic and stearic acids, *n*-decanethiol, *n*-dodecanethiol, *n*-butanethiol, thiophenol, and acetyl chloride were the best available commercial materials and were used as received.

n-Decyl thiolacetate. A mixture of 17.4 g. (0.1 mole) of *n*-decanethiol and 11.8 g. (0.15 mole) of acetyl chloride was allowed to stand overnight at room temperature. The reaction mixture then was heated on a steam bath for 4 hr., dissolved in 100 ml. of ether, washed with water until the washings were neutral to litmus, and the ether solution was dried over anhydrous sodium sulfate. The ether was removed by distillation and the product was distilled under diminished pressure. Yield, 16.1 g. (74.5%), b.p. 91–92° at 0.3 mm., n_D^{30} 1.4595, d_4^{30} 0.8956.

Anal. Calcd. for $C_{12}H_{24}OS$: S, 14.8. Found: S, 14.4. Molecular Refraction Calcd. 66.03. Found: 66.11.[3] *n*-Butyl thiolacetate[4] b.p. 160–163°, *n*-dodecyl thiolacetate[5] b.p. 164–166° at 10 mm. and phenyl thiolacetate[6] b.p. 110° at 12 mm. were prepared in an analogous manner.

General acidolysis reaction. To 0.05 mole of thiolacetate and 0.025 mole of the appropriate fatty acid in a 200 ml. round bottomed flask, fitted with a reflux condenser, was added 0.1 g. of mercuric acetate and one drop of 100% sulfuric acid and the reaction mixture was heated on a steam bath for 4 hr. After cooling to room temperature, 0.3 g. of sodium acetate dihydrate was added and the product was crystallized from acetone or acetone-alcohol mixture. To remove traces of unreacted acids, the thiol esters were chromatographed, using 12 g. of Florisil per gram of thiol ester. The column was eluted with a total of 400 ml. of petroleum ether and after the solvent was removed by distillation, the product was crystallized once from acetone or acetone-alcohol mixture. The thiol esters showed no depression of melting point when mixed with an authentic sample. These compounds were prepared by methods described in previous papers.[7-9]

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(1) W. J. Toussaint and L. G. MacDowell, Jr., U.S. Patent 2,299,862 (1942).

(2) D. Swern and E. F. Jordan, Jr., *J. Am. Chem. Soc.*, 70, 2334 (1948).

(3) Molecular refractions were calculated using the values reported by A. J. Vogel, *J. Chem. Soc.*, 1842 (1948).

(4) F. W. Wenzel, Jr. and E. E. Reid, *J. Am. Chem. Soc.*, 59, 1089 (1937).

(5) R. L. Frank, S. S. Drake, P. V. Smith, Jr., and C. Stevens, *J. Polymer Sci.*, **3**, 50 (1948).

(6) H. Boehme and H. Schran, *Chem. Ber.*, **82**, 453 (1949).

(7) G. S. Sasin, R. Sasin and N. Capron, *J. Org. Chem.*, 21, 852 (1956).

(8) R. Sasin, W. F. Ashley, J. W. Manning, Jr., A. Paolini, Jr., and G. S. Sasin, *J. Am. Oil Chem. Soc.*, **35**, 192 (1958).

(9) R. Sasin, G. S. Weiss, A. E. Wilfond, and G. S. Sasin, *J. Org. Chem.*, 21, 1304 (1956).