Acknowledgment. Special thanks are due Miss Patricia A. Estep for determining the infrared spectra.

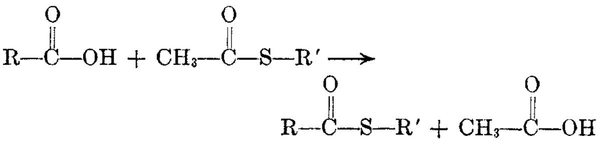
THE LOW-TEMPERATURE TAR LABORATORY
BRANCH OF BITUMINOUS COAL
BUREAU OF MINES
MORGANTOWN, W. VA.

Reactions of Long-Chain Acids with Thiolacetates

RICHARD SASIN, GORDON S. BINNS, ROBERT M. HAFF, AND GEORGE S. SASIN

Received February 5, 1959

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]

DEPARTMENT OF CHEMISTRY
DREXEL INSTITUTE OF TECHNOLOGY
PHILADELPHIA 4, PA.

---

(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).