[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DREXEL INSTITUTE OF TECHNOLOGY]

Ester Interchange Reactions of Long Chain Thiol Esters[1]

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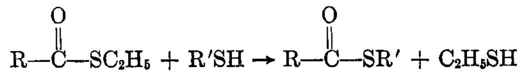
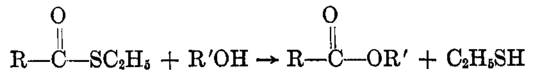
Ethanethiol esters of lauric, myristic, palmitic, and stearic acids undergo ester interchange reactions with alkanethiols, arylthiols, alcohols, and phenol in the presence of sodium methoxide or β-naphthalenesulfonic acid. Eight previously unreported thiol esters were prepared by ester interchange.

This paper presents ester interchange of thiol esters with alkanethiols, arylthiols, alcohols, and phenol. The authors believe that these reactions are being reported for the first time.



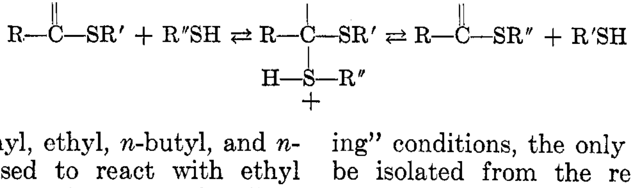
$$R{-}\overset{\overset{O}{\|}}{C}{-}SC_2H_5 + R'SH \rightarrow R{-}\overset{\overset{O}{\|}}{C}{-}SR' + C_2H_5SH$$



$$R{-}\overset{\overset{O}{\|}}{C}{-}SC_2H_5 + R'OH \rightarrow R{-}\overset{\overset{O}{\|}}{C}{-}OR' + C_2H_5SH$$

The ester interchange reactions involving thiols were effected by treating ethanethiol esters of lauric, myristic, palmitic, and stearic acids with *n*-heptanethiol, *n*-octanethiol, β-naphthalenethiol and benzyl mercaptan as well as isobutyl thiostearate with β-naphthalenethiol. In each instance a less volatile thiol displaced more volatile ethanethiol or 2-propanethiol. The reactions were first attempted by heating the thiol esters with a slight excess of thiol on a steam bath in the presence of a trace of sodium ethoxide or sodium methoxide. This procedure resulted in low yields. When the reactions were repeated in pyridine, they proceeded very smoothly and were essentially complete at the end of a 1-hr. heating period. Yields of about 60% were obtained. The reaction appears to be general; the results are summarized in Table I. Altogether seventeen interchange reactions with thiols were attempted. All of these were successful. The reactions involving *n*-heptanethiol and *n*-octanethiol resulted in the formation of eight new thiol esters.

The course of the reaction is probably the same as that of alcoholysis of esters, and may be illustrated by the following equations.[2]



$$R{-}\overset{\overset{O}{\|}}{C}{-}SR' + R''SH \rightleftarrows R{-}\underset{\underset{H-\underset{+}{S}-R''}{|}}{\overset{\overset{O-}{|}}{C}}{-}SR' \rightleftarrows R{-}\overset{\overset{O}{\|}}{C}{-}SR'' + R'SH$$

Large excesses of methyl, ethyl, *n*-butyl, and *n*-octyl alcohols were caused to react with ethyl thiostearate in the presence of a trace of sodium methoxide. A slight excess of phenol in pyridine and in the presence of sodium methoxide also reacted with ethyl thiostearate. The reaction rates in this case were considerably slower than the reaction rates with thiols. Phenyl and methyl stearates were formed after about 3 hr. heating on a steam bath, ethyl stearate was formed in 24 hr., while a 48-hr. heating period was required for the formation of a *n*-butyl and *n*-octyl stearates.

Attempts to effect ester interchange between ethyl thiostearate and alcohols in the presence of an acid catalyst were unsuccessful. When 0.005 mole of ethyl thiostearate was heated with large excesses of methyl, ethyl, *n*-butyl, and *n*-octyl alcohols in the presence of 0.1 g. of β-naphthalene sulfonic acid, the only solid material isolated from the reaction mixture was unchanged ethyl thiostearate even after the reaction mixture had been heated on a steam bath for 48 hr.

Similarly, all attempts to effect an ester interchange reaction between methyl stearate and thiols were unsuccessful. Heating methyl stearate with a slight excess of benzenethiol, *p*-toluenethiol, and dodecanethiol in pyridine and in the presence of sodium methoxide on a steam bath for 48 hr. resulted in the isolation of unchanged methyl stearate. Similar results were obtained when methyl stearate was heated with large excesses of benzenethiol in the presence of sodium methoxide or β-naphthalene sulfonic acid.

In our last attempt to effect an ester interchange reaction between methyl stearate and a thiol, the former compound was heated together with dodecanethiol in the presence of sodium methoxide under nitrogen at 250° for 24 hr. Even under these "forcing" conditions, the only solid material that could be isolated from the reaction mixture was unchanged methyl stearate.

EXPERIMENTAL

Materials. Lauroyl, myristoyl, and palmitoyl chlorides, alkanethiols and benzenethiols were obtained from Distillation Products Industries. Humko's commercial stearic acid was crystallized once from methanol and once from

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(1) From a thesis submitted by Paul R. Schaeffer to the Department of Chemistry of the Drexel Institute of Technology in partial fulfillment of the requirements for the degree of Master of Science.

(2) A. A. Frost and R. G. Pearson, *Kinetics and Mechanism*, John Wiley & Sons, Inc., New York, 1953, p. 209.

acetone and melted at 69°. All melting points are uncorrected.

Ethanethiol Esters. Ethyl thiolaurate, b.p. 116–118° at 1 mm., ethyl thiomyristate, b.p. 134–137° at 1 mm., and ethyl thiopalmitate, b.p. 173–176° at 1 mm. were prepared by the method of Ralston, *et al.*[3]

Ethyl Thiostearate. To 0.1 mole of molten stearic acid in a 125 ml. separatory funnel, protected by a calcium chloride drying tube, was added 5.5 g. of phosphorus trichloride. The mixture was heated with a steam-cone for 1 hr. and then allowed to stand overnight. The stearoyl chloride was separated from the phosphorous acid formed in the reaction and was added to 0.2 mole of ethanethiol in a 200 ml. round bottomed flask, fitted with a reflux condenser and cooled in an ice bath. The mixture was allowed to stand overnight and then was heated on a water bath for 6 hr. The resulting solid which contained some free fatty acid, was dissolved in 100 ml. of acetone and 6*N* sodium hydroxide solution in a 5% excess over that necessary to neutralize the free fatty acid was added with stirring. The insoluble sodium stearate was separated by filtration and washed with 20 ml. of acetone. The solution was cooled to 0° and the resulting solid was separated by filtration. The product was crystallized from acetone–alcohol and melted at 38°.[3] The yield was 20.3 g. or 61% of the theoretical amount.

Isobutyl Thiostearate. This compound was prepared by the method described in a previous paper.[4]

Reactions of Ethanethiol Esters and Isobutyl Thiostearate With Alkane Thiols, Benzene Thiols and Phenol. To 0.01 mole of thiol ester in a 200 ml. round bottomed flask, fitted with a reflux condenser, was added a mixture of 0.011 mole of alkane or benzenethiol, 0.05 g. of sodium methoxide, and 20 ml. of pyridine. After heating for 2 hr. on a steam bath, the pyridine was removed by distillation under diminished pressure. The product was then dissolved in 100 ml. of ether and washed with two 50 ml. portions of water. The ether solution was dried over anhydrous sodium sulfate and after removal of the solvent by distillation the products were crystallized from acetone or alcohol-acetone mixtures. The results of the interchange reactions are summarized in Table 1.

Reactions of Ethyl Thiostearate With Methyl, Ethyl, n-Butyl, and n-Octyl Alcohols. To 0.01 mole of ethyl thiostearate in a 200 ml. round bottomed flask, fitted with a reflux condenser, was added a mixture of 0.05 g. of sodium methoxide and 50 ml. of the appropriate alcohol. In the case of methyl alcohol, a 3-hr. heating period on the steam bath was required. Ethyl alcohol was heated for 24 hr. and *n*-butyl and *n*-octyl alcohols required 48 hr. At the end of the heating period, the excess alcohol was removed by distillation under reduced pressure and the product was dissolved in 100 ml. of ether and washed with two 50 ml. portions of water. After drying the ethereal solution over anhydrous sodium sulfate and removal of the solvent by distillation, the esters were crystallized from alcohol. The individual esters were identified by melting points and by admixture with an authentic sample of the appropriate ester. In each case there was no depression of melting point. A negative qualitative sulfur test was obtained after sodium fusion. The results of these reactions are summarized in Table 1.

TABLE I

ESTER INTERCHANGE REACTIONS OF ETHANETHIOL ESTERS

Product	Yield %	M.P. °C	Analyses Sulfur Calcd.	Found
β-Naphthyl thiolaurate	53	29.5–30	—	—
n-Heptyl thiolaurate	61	24	10.3	10.5
n-Octyl thiolaurate	63	21.5	9.8	10.0
Benzyl thiolaurate	51	35–36	—	—
β-Naphthyl thiomyristate	52	38.5–39	—	—
n-Heptyl thiomyristate	64	32	9.4	9.3
n-Octyl thiomyristate	62	31	9.0	9.0
Benzyl thiomyristate	67	45–46	—	—
β-Naphthyl thiopalmitate	60	47–47.5	—	—
n-Heptyl thiopalmitate	63	39–39.5	8.6	8.6
n-Octyl thiopalmitate	70	37.5	8.3	8.1
Benzyl thiopalmitate	55	52	—	—
β-Naphthyl thiostearate	60	56	—	—
n-Heptyl thiostearate	70	44–44.5	8.0	7.8
n-Octyl thiostearate	65	43.5–44	7.8	7.8
Benzyl thiostearate	63	59.5–60	—	—
Methyl stearate	70	39	—	—
Ethyl stearate	76	34	—	—
n-Butyl stearate	67	27.5	—	—
n-Octyl stearate	58	34	—	—
Phenyl stearate	68	52	—	—

Attempted Reaction Between Methyl Stearate and 1-Dodecanethiol. To 9.0 g. (0.03 mole) of methyl stearate in a 100 ml. round bottomed flask was added 24 g. (0.12 mole) of 1-dodecanethiol and 0.1 g. of sodium methoxide. The reaction mixture was heated on an oil bath at 250° for 24 hr. During the entire heating period nitrogen was bubbled through the reaction mixture. The reaction mixture was cooled and dissolved in 200 ml. of ether and washed with two 50-ml. portions of water, dried over anhydrous sodium sulfate, and the ether was removed by distillation. Three crystallizations from alcohol yielded 6.0 g. of unchanged methyl stearate. The melting point and mixed melting point with an authentic sample of methyl stearate was 39°. A qualitative test for sulfur was negative.

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(3) A. W. Ralston, E. W. Segebrecht, and S. T. Bauer, *J. Org. Chem.*, 4, 502 (1939).

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