[Contribution from the Chemistry Department, Drexel Institute of Technology]

Synthesis of Some Thiol Esters of Long-Chain Fatty Acids

GEORGE S. SASIN, RICHARD SASIN, and NICHOLAS CAPRON

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Thirty-one previously unreported aliphatic and aromatic thiol esters of lauric, myristic, palmitic and stearic acids were synthesized by the action of mercaptans or thiophenols on acid chlorides by a simplified procedure.

This paper presents a simplified procedure for the synthesis of aliphatic and aromatic thiol esters of long-chain fatty acids. This work was undertaken to evaluate the thiol esters as potential plasticizers for vinyl polymers and lubricating oil additives.

TABLE I

Thiol Esters

								Analyses			
								ArS-%		Sulfur %	
Compound	B.p., °C.	Mm.	M.p., °C.	d_4^{20}	n_D^{20}	Yield, %	Formula	Calc'd	Found	Calc'd	Found
Isobutyl thiolaurate	171–172	9		0.889	1.4640	52	$C_{16}H_{32}OS$			11.8	12.1
tert-Butyl thiolaurate	149–150	5		.885	1.4574	50	$C_{16}H_{32}OS$			11.8	11.9
n-Amyl thiolaurate	182–183	1		.890	1.4692	55	$C_{17}H_{34}OS$			11.2	11.4
n-Hexyl thiolaurate	178–179	5		.884	1.4661	47	$C_{18}H_{36}OS$			10.7	10.8
Benzyl thiolaurate			36			58	$C_{19}H_{30}OS$			10.4	10.7
Phenyl thiolaurate	180–181	1		.965	1.5096	73	$C_{18}H_{28}OS$	37.3	37.4		
p-Tolyl thiolaurate	191–192	1		.960	1.5119	70	$C_{19}H_{30}OS$	40.2	40.0		
β-Naphthyl thiolaurate			29.5–30			53	$C_{22}H_{30}OS$	46.5	46.7		
Isobutyl thiomyristate	148–149	3		.887	1.4604	64	$C_{18}H_{36}OS$			10.6	10.6
tert-Butyl thiomyristate	166–167	4		.883	1.4601	53	$C_{18}H_{36}OS$			10.6	10.3
n-Amyl thiomyristate	180–181	1	22			56	$C_{19}H_{38}OS$			10.2	10.0
n-Hexyl thiomyristate	183–184	3	21			45	$C_{20}H_{40}OS$			9.8	9.9
Benzyl thiomyristate			46			54	$C_{21}H_{34}OS$			9.6	9.8
Phenyl thiomyristate	203–204	1		952	1.5032	68	$C_{20}H_{32}OS$	34.1	34.3		
p-Tolyl thiomyristate			30			65	$C_{21}H_{34}OS$	36.8	36.6		
β-Naphthyl thiomyristate			38.5–39			57	$C_{24}H_{34}OS$	43.0	43.1		
Isobutyl thiopalmitate	174–176	4		0.886	1.4629	61	$C_{20}H_{40}OS$			9.8	9.9
tert-Butyl thiopalmitate	175–176	1	21			58	$C_{20}H_{40}OS$			9.8	10.1
n-Amyl thiopalmitate			31			60	$C_{21}H_{42}OS$			9.4	9.7
n-Hexyl thiopalmitate			29			55	$C_{22}H_{44}OS$			9.0	9.0
Phenyl thiopalmitate			28.5			64	$C_{22}H_{36}OS$	31.3	31.6		
p-Tolyl thiopalmitate			41			66	$C_{23}H_{38}OS$	34.0	34.2		
β-Naphthyl thiopalmitate			47–47.5			65	$C_{26}H_{38}OS$	40.0	40.1		
Isobutyl thiostearate	198–199	1	23			48	$C_{22}H_{44}OS$			9.0	9.3
tert-Butyl thiostearate			31			49	$C_{22}H_{44}OS$			9.0	9.3
n-Amyl thiostearate			38			58	$C_{23}H_{46}OS$			8.6	8.8
n-Hexyl thiostearate			40–41			52	$C_{24}H_{48}OS$			8.3	8.1
Benzyl thiostearate			60			58	$C_{25}H_{42}OS$			8.2	8.1
Phenyl thiostearate			39–40			55	$C_{24}H_{40}OS$	28.9	28.6		
p-Tolyl thiostearate			46.5			48	$C_{25}H_{42}OS$	31.6	31.6		
β-Naphthyl thiostearate			56–56.5			66	$C_{28}H_{42}OS$	37.4	37.4		

Previous to this study, Ralston and co-workers[1] prepared methyl, ethyl, *n*-propyl, and *n*-butyl thiol esters of lauric, myristic, palmitic, and stearic acids as well as *n*-propyl thiooleate by the action of the appropriate mercaptan on the acid chlorides. In like manner, Jeger and co-workers[2] prepared benzyl thiopalmitate.

In this research, Ralston's procedure for the preparation of thiol esters was modified in that the acid chlorides, prepared by Bauer's method,[3] were not isolated and purified. The crude acid chloride was treated with the appropriate mercaptan, and the unreacted acid then was removed from the reaction mixture by one of two general procedures, depending on whether the product was a liquid or a solid. Liquid thiol esters were dissolved in ether and washed with sodium bicarbonate solution. After the removal of the solvent by distillation, the thiol esters were distilled under diminished pressure. Solid thiol esters were dissolved in acetone and the unreacted long-chain fatty acids were removed by the method of Swern and co-workers.[4]

The physical properties and the analytical data for the thiol esters are summarized in Table I.

EXPERIMENTAL

General method for the preparation of acid chlorides. To 0.1 mole of the molten fatty 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 the steam-cone for one hour and then was allowed to stand overnight. The acid chloride was separated from the phosphorous acid formed in the reaction and was used without further purification.

Preparation of thiolesters. Method A. Isobutyl, *tert*-butyl, *n*-amyl, *n*-hexyl, phenyl, and *p*-tolyl thiolaurate; isobutyl, *tert*-butyl, *n*-amyl, *n*-hexyl, and phenyl thiomyristate; isobutyl and *tert*-butyl thiopalmitate; isobutyl thiostearate.

To 0.1 mole of the acid chloride in a 200-ml., round bottomed flask fitted with a reflux condenser was added 0.11 mole of the appropriate mercaptan and the mixture was allowed to stand overnight. The mixture then was heated on a water-bath for 6 hours. The resulting liquid was dissolved in 200 ml. of ether and was washed first with two 50-ml. portions of 5% sodium bicarbonate solution and then with two 50-ml. portions of water. After the ethereal solution was dried over sodium sulfate, the solvent was removed by distillation and the product was distilled under reduced pressure. *n*-Amyl and *n*-hexyl thiomyristate, *tert*-butyl thiopalmitate, and isobutyl thiostearate solidified after distillation and were crystallized from acetone-alcohol.

Method B. Benzyl and β-naphthyl thiolaurate; benzyl, *p*-tolyl, and β-naphthyl thiomyristate; *n*-amyl, *n*-hexyl, phenyl, *p*-tolyl, and β-naphthyl thiopalmitate; *tert*-butyl, *n*-amyl, *n*-hexyl, benzyl, phenyl, *p*-tolyl, and β-naphthyl thiostearate.

To 0.1 mole of the acid chloride in a 200-ml., round bottomed flask fitted with a reflux condenser was added 0.11 mole of the appropriate mercaptan and the mixture was allowed to stand overnight. The mixture then was heated on a water-bath for 6 hours. 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 soap was separated by filtration and washed with 20 ml. of acetone. The solution then was cooled to 0° and the resulting solid was separated by filtration. The product was crystallized from acetone-alcohol.

Analyses. The aromatic thiolesters were hydrolyzed by alcoholic potassium hydroxide solution, acidified with hydrochloric acid solution, and titrated with standard iodine. The results are reported as percentage of aryl mercaptide. The alkyl thiolesters could not be analyzed by the above procedure. The latter compounds were analyzed by semi-micro Parr bomb method.

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(3) Bauer, *Oil and Soap*, **23**, 1 (1946).

(4) Port, Hansen, Jordan, Dietz, and Swern, *J. Polymer Science*, **7**, 207 (1951).