

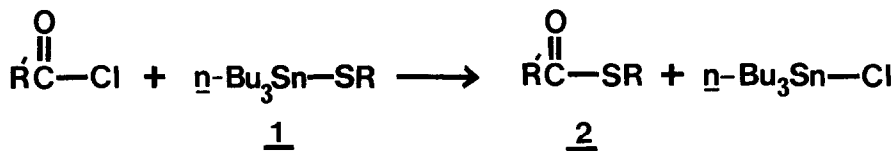
## FACILE PREPARATION OF THIOL ESTERS FROM ORGANOTIN MERCAPTIDES AND ACYL CHLORIDES<sup>1</sup>

David N. Harpp\*, T. Aida and T.H. Chan\*  
Department of Chemistry, McGill University,  
Montreal, Quebec, Canada H3A 2K6

*Organotin mercaptides condense with acyl chlorides to give thiol esters in excellent yield. Of note are efficient syntheses of t-butyl and phenyl thiol esters.*

Thiol esters are considered as the universal acylating agents in biochemical reactions. Recently, the use of thiol esters in organic synthesis, especially for the efficient formation of macrocyclic lactones,<sup>2-4</sup> has led to a search for new methods of preparation for this important class of compounds.<sup>5-8</sup>

We wish to report a facile synthesis of thiol esters from organotin mercaptides and acyl halides. The advantages of the present method are excellent yields under relatively



mild reaction conditions, simple work-up for the isolation of the product, and the presumed lack of toxicity and lower cost of the tin reagent.<sup>9</sup>

Tri-n-butyltin mercaptides are prepared by a slight modification of a known procedure.<sup>10</sup> The synthesis of tri-n-butyltin t-butylmercaptide (1a) is illustrative. To a solution of t-butylmercaptan (33 mmol) and triethylamine (39 mmol) in 200 ml carbon tetrachloride, tri-n-butyltin chloride (33 mmol) was added dropwise in 20 minutes at room temperature with vigorous stirring. The reaction mixture was stirred overnight at room temperature. The reaction mixture was filtered and the filtrate was washed with 5% aqueous acetic acid and with water. The organic layer was separated, dried ( $\text{Na}_2\text{SO}_4$ ), evaporated in vacuo and distilled to give 1a, bp 110 /0.1 mm in 94% yield.

The reactions of organotin mercaptides and acyl chlorides were carried out under nitrogen. A typical example is given as follows. To a solution of 1a (1.15 mmol) in 5.0 ml chloroform, sebacyl chloride (0.6 mmol) was added at room temperature. The reaction mixture was warmed at 60° for 30 minutes. After removal of solvent, the oily product was purified by column chromatography on silica gel.<sup>11</sup> Tri-n-butyltin chloride was first removed by elution with pentane. The product, thiol ester 2, was eluted with dichloromethane. The isolated yields of thiol esters in all cases examined (Table) were excellent.

For comparative purposes, we have also investigated the reaction of trimethylsilyl mercaptides with acyl chlorides. In general, the reaction to give thiol ester is more sluggish compared to the organotin system. When the mercaptide is sterically hindered (e.g., t-butylmercaptide), either there was no reaction or, under forcing conditions extensive decomposition took place.

The reaction of organotin mercaptides with acyl chlorides thus appears to be a highly useful method for the preparation of thiol esters.

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TABLE

## Preparation of Thiol Esters



R	R' <sup>a</sup>	T °C	Time (hr)	% yield <sup>b</sup> R'CSR
(CH <sub>3</sub> ) <sub>3</sub> C-	C <sub>6</sub> H <sub>5</sub> -	60	0.5	95
	CH <sub>3</sub> -	60	0.5	93
	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> -	60	0.5	93
	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> -	60	0.5	89
	-(CH <sub>2</sub> ) <sub>8</sub> -	60	0.5	90
C <sub>6</sub> H <sub>5</sub> -	C <sub>6</sub> H <sub>5</sub> -	rt	12	92
	CH <sub>3</sub> -	rt	12	95
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> -	C <sub>6</sub> H <sub>5</sub> -	rt	1	96
	CH <sub>3</sub> -	rt	0.5	93
	-(CH <sub>2</sub> ) <sub>8</sub> -	rt	0.5	87

<sup>a</sup> Each organotin derivative was prepared in ca. 90% yield; (R = <sup>t</sup>Bu) bp 110°/0.1 mm; (R = C<sub>6</sub>H<sub>5</sub>) bp 140°/0.2 mm; (R = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>) bp 165°/0.1

<sup>b</sup> Isolated yields. Each ester was homogeneous on the tlc and glpc. In addition, pmr spectra were consistent with the indicated structures.

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9. Relative to the thallium compounds used,<sup>5</sup> the organotin mercaptides may be considered as less toxic; cf. "Organotin Compounds: New Chemistry and Applications", pp. 167-176, Advances in Chemistry Series, American Chemical Society, J.J. Zuckerman, Ed. (1976). We must emphasize however that no toxicological data are available for these compounds and due caution should be exercised in their handling. It can be mentioned that thallium derivatives require special disposal procedures and, at present, cost over ten times their tin counterparts in the preparation of the title compounds.
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11. The silica gel used was activated by heating at 150° under 0.05 mm Hg for one hour.

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