CHEMISTRY LETTERS, pp. 133-134, 1981.

A FACILE PREPARATION OF THIOL ESTERS FROM CARBOXYLIC ACIDS AND THIOLS

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Thiol esters can be conveniently prepared by the reaction of carboxylic acids with thiols and 1-fluoro-2,4,6-trinitrobenzene in the presence of 4-dimethylaminopyridine. The thiol ester formation is found to be very effective for simple carboxylic acids.

Thiol esters have attracted a great deal of recent attention as active acylating agents, especially in the synthesis of macrocyclic lactones.[1]

We wish to report a new convenient method for the preparation of thiol esters which proceeds under mild conditions. During the course of examining the synthetic utility of 1-fluoro-2,4,6-trinitrobenzene (FTNB),[2-4] we observed that treatment of carboxylic acids with FTNB and thiols in the presence of 4-dimethylaminopyridine (DMAP)[5] in acetonitrile results in the direct conversion of carboxylic acids into thiol esters.

Clear conclusions regarding the reaction mechanism await furthur study. Presumably, the reaction proceeds via the intermediacy of trinitrophenyl ester by initial formation of trinitrophenyl-4-dimethylaminopyridinium salt from which the trinitrophenyl group is transferred to the carboxylic acid.

The following procedure is representative for the preparation of thiol esters. To a mixed solution of benzoic acid (123 mg, 1.0 mmol), FTNB (235 mg, 1.0 mmol), and DMAP (249 mg, 2.0 mmol) in acetonitrile (4 ml) at room temperature was added 1-butanethiol (98 mg, 1.1 mmol). After stirring at room temperature for 4 hr, the precipitated salts were filtered off, the solution was evaporated, and the residue was purified by filtration through a short column of silica gel employing methylene chloride as an eluant. The desired thiol ester (184 mg, 95%) was the only compound observed on solvent removal.

The preparation of thiol esters has been performed on both arene- and alkanecarboxylic acids utilizing primary, secondary, tertiary, and aryl thiols. Table I summarizes some of the typical experimental results. Generally, arene- and simple alkanecarboxylic acids give the corresponding thiol esters in high yields. However, hindered carboxylic acids like pivalic acid or diphenylacetic acid do not work well with thiols.

TABLE I. PREPARATION OF THIOL ESTERS

RCOOH	R'SH	TIME[a]	YIELD (RCOSR')[b]
benzoic	n-BuSH	4 hr	95%
benzoic	t-BuSH	15	95
benzoic	PhSH	3	98
trans-cinnamic	n-BuSH	1	92
trans-cinnamic	s-BuSH	12	87
trans-cinnamic	t-BuSH	24	94
trans-cinnamic	PhSH	12	97
stearic	n-BuSH	12	84
stearic	s-BuSH	24	80
diphenylacetic	n-BuSH	24	36
diphenylacetic	PhSH	24	46
pivalic	n-BuSH	24	44

[a] Not optimized. [b] Isolated yields. Each thiol ester was homogeneous on the tlc. In addition, spectral data (nmr, ir) were consistent with the indicated structure.

Even though the yields are not good for the hindered carboxylic acids, the present method offers the advantages of direct synthesis, the mildness of reaction condition, and simple work-up for the isolation of the product. Although there are several methods to bring about such conversions,[6] we consider the present method as useful addition to them.

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(Received November 10, 1980)