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THE REACTION OF TRIMETHYLSILYL SULFIDES WITH CARBOXYLIC ESTERS. A CONVENIENT METHOD FOR THE PREPARATION OF THIOLESTERS

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In the presence of $AlCl_3$, trimethylsilyl sulfides react with carboxylic esters to give the corresponding thiolesters in high yields.

In general, thiolesters are prepared by the reaction of acyl chlorides with excess amounts of thiols in pyridine[1] or with lead mercaptides.[2] In the present experiment, it was established that the thiolesters are obtained directly from carboxylic esters by treating with trimethylsilyl sulfides. When carboxylic esters are allowed to react with trimethylsilyl sulfides in the presence of an equimolar amount of $AlCl_3$, the corresponding thiolesters are produced in high yields. It was also found that, in the case of α,β-unsaturated ester such as ethyl cinnamate, only α,β-unsaturated thiolester was obtained and any by-product as the addition product of thiol and α,β-unsaturated thiolester was not isolated.

$$R^1\text{-}\overset{O}{\overset{\|}{C}}\text{-}OR^2 + (CH_3)_3Si\text{-}SR^3 \xrightarrow{AlCl_3} R^1\text{-}\overset{O}{\overset{\|}{C}}\text{-}SR^3$$

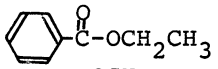
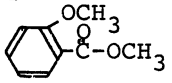
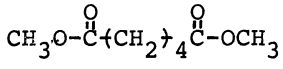
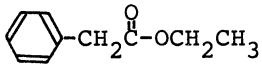
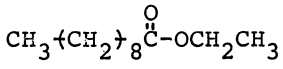
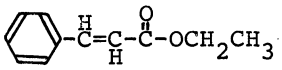
$R^3 = CH_3CH_2-$

The typical reaction procedure is described for the reaction of ethyl trimethylsilyl sulfide with ethyl cinnamate; To a THF (3 ml) solution of $AlCl_3$ (1.1 mmol) and ethyl cinnamate (1.0 mmol) was added ethyl trimethylsilyl sulfide (2.0 mmol)[3] under an argon atmosphere. After refluxing for 1 hr, the reaction mixture was poured into a phosphate buffer solution (pH 7.0) and an organic layer was extracted with ether. The extract was condensed under reduced pressure. The residue was chromatographed on silica gel and ethyl thiolcinnamate was isolated in 97% yield.

In a similar manner, various ethyl or phenyl thiolesters were obtained in high yields from ethyl or methyl esters of carboxylic acids as shown in the following table.

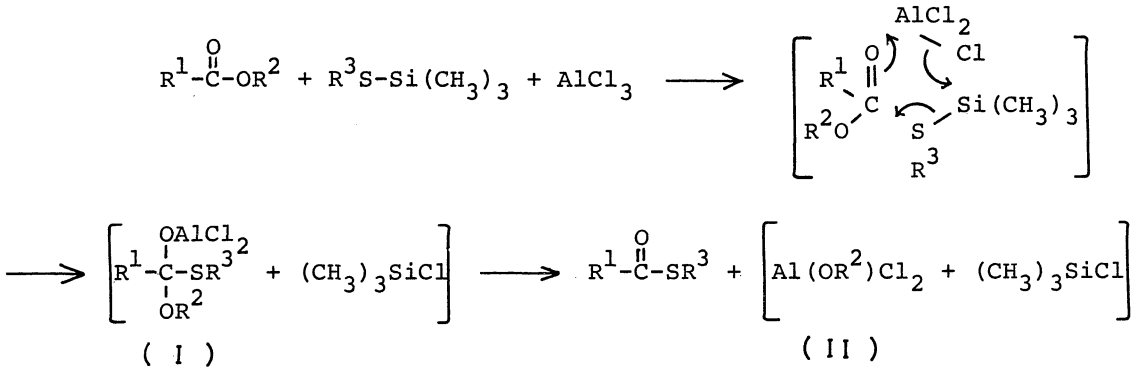
It is noted that the yields of thiolesters by the present reactions depend on the amount of $AlCl_3$ used. For example, when a catalytic amount of $AlCl_3$ is used in the above experimental procedure, only a trace amount of thiolester was isolated.

Table. The reaction of trimethylsilyl sulfides with carboxylic esters

Carboxylic ester	$(CH_3)_3SiSCH_2CH_3$ Time(hr)	Yield(%)	$(CH_3)_3Si$-S-Ph Time(hr)	Yield(%)
	1.5	90	4.0	72
	1.0	91	1.5	85
	1.5	94	2.0	82 *
	1.0	86	1.0	89
	2.0	94	1.0	87
	1.0	97	2.0	85

* The mono thiolester was obtained in 11% yield.

Based on these facts, it is reasonable to assume that the reaction may proceed through an initial formation of intermediate (I) from $AlCl_3$, trimethylsilyl sulfide and ester. The intermediate affords thiolester by the immediate elimination of aluminum alkoxide (II) as shown in the following scheme.



(I) (II)

REFERENCES

1) O. Jeger, J. Norymberski, S. Szpilfogel, and V. Prelog, Helv. Chim. Acta., 29, 684 (1946).
2) R. H. Levin, A. V. Mcintosh, Jr., G. B. Spero, D. E. Rayman, and E. M. Meinzer, J. Amer. Chem. Soc., 70, 511 (1948).
3) With 1.2 molar amounts of trimethylsilyl sulfide, 88% of thiolester was obtained and unreacted ester was recovered.

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