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SYNTHETIC APPLICATION OF THIOSILANES TO THIOESTERS

Wataru ANDO*, Toshiya FURUHATA, Hidetoshi TSUMAKI, and Akira SEKIGUCHI
Department of Chemistry, The University of Tsukuba,
Niiharigun, Ibaraki 305

Thiosilanes such as ethylthiotrimethylsilane, hexamethyldisilthiane, and t-butylthiotrimethylsilane, react readily with acyl chlorides at room temperature in the presence of potassium fluoride to give the corresponding thioesters in excellent yields.

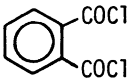
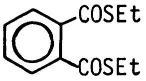
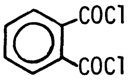
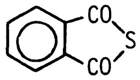
In recent years, interest in thioesters for organic synthesis has been increasing, and a number of new methods for preparation of these compounds have been developed.[1)] Here, we wish to report that thiosilanes including the sterically hindered one such as t-butylthiotrimethylsilane react cleanly with acyl chlorides in the presence of fluoride ion to afford thioesters in nearly quantitative yields.

The reactions of thiosilanes with acyl chlorides were carried out under a nitrogen atmosphere. A typical reaction is as follows. Dry potassium fluoride (116 mg, 2.0 mmol), benzoyl chloride (281 mg, 2.0 mmol), dicyclohexyl-18-crown-6 ether (6 mg), and anhydrous methylene chloride (3 ml) were placed in a 10 ml flask. To the mixture, ethylthiotrimethylsilane (266 mg, 2.0 mmol) was added by a syringe with stirring. After 6h, the reaction mixture was concentrated, and the residue was chromatographed on silica gel with hexane/benzene (1:1) to give S-ethyl thiobenzoate (319 mg) in 96% yield. In a similar manner, various thioesters were obtained in high yields. These results are summarized in Table. For comparative purpose, we have also investigated the reaction of ethylthiotrimethylsilane with acyl chlorides without potassium fluoride. The reactions are more sluggish, and the yields of thioesters are low (Table).[2)]

The reaction of the sterically hindered t-butylthiotrimethylsilane with acyl chlorides also afforded S-t-butylthioesters in the presence of potassium fluoride. As well, hexamethyldisilthiane reacted with two equivalents of acyl chlorides to give thioanhydrides.

The reaction proceeds through the initial attack of fluoride ion on silicon atom to produce mercaptide ions which react with acyl chlorides, giving the thioesters.

Table. Preparation of Thioesters from Thiosilanes and Acyl Halides.[a]

Thiosilane	Acyl Halide	Crown Ether(mol%)[b]	Time(h)	Product[c]	Yield(%)[d]
Me$_3$SiSEt	PhCOCl	1.6	6(72h reflux)	PhCOSEt	96(65)[e]
"	Me$_2$CHCH$_2$COCl	6	2(18)	Me$_2$CHCH$_2$COSEt	98(44)[e]
"	Me(CH$_2$)$_6$COCl	6	3(35h reflux)	Me(CH$_2$)$_6$COSEt	85(0)[e]
"	MeCH=CHCOCl	6	2(35)	MeCH=CHCOSEt	85(20)[e]
"		6	6		80
"	PhCOF[f]	0	24h reflux	PhCOSEt	trace
Me$_3$SiS^{t}Bu	PhCOCl	5	10	PhCOS^{t}Bu	85
"	Me(CH$_2$)$_6$COCl	5	15	Me(CH$_2$)$_6$COS^{t}Bu	93
Me$_3$SiSSiMe$_3$	PhCOCl[g]	10	3	(PhCO)$_2$S	75
"	Me(CH$_2$)$_6$COCl[g]	10	5	[Me(CH$_2$)$_6$CO]S	73
"		10	6		70

a; The reactions were carried out at room temperature in methylene chloride, using equivalents of thiosilanes, acyl chlorides, and potassium fluoride. b; Dicyclohexyl-18-crown-6 ether, mol% based on thiosilanes. c; All products were fully characterized by the usual spectroscopic properties. d; Isolated yields by column chromatography. e; Yields without potassium fluoride and crown ether. f; The reaction without potassium fluoride. g; Two equivalents of acyl chlorides and potassium fluoride to hexamethyldisilthiane were used.

References

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2) Very recently, Tally reported the reaction of octyl and phenylthiotrimethylsilanes with acyl chlorides to obtain thioesters. However, t-butylthiotrimethylsilane did not produce any thioesters even under forcing conditions, J.J.Tally, Synthesis, 1981, 549.

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