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EFFICIENT METHOD FOR THE PREPARATION OF α-TRIMETHYLSILYLCARBOXYLIC ACID ESTERS

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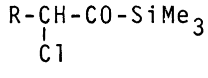
α-Chloroacyltrimethylsilanes are shown to behave as equivalents of α-trimethylsilylacyl derivatives in the reaction with lithium alkoxides to afford the corresponding α-trimethylsilylcarboxylic acid esters in good yield.

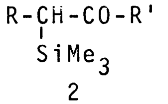
Trimethylsilylacetic acid esters have recently been employed as versatile synthetic reagents.[1] This type of compound has usually been prepared efficiently by treating α-bromoacetate with zinc and chlorotrimethylsilane.[2] However, preparation of its homolog, α-trimethylsilylcarboxylic acid esters, is reported to be quite difficult, since silylation of the corresponding ester enolates with the chlorosilane usually affords the O-silylated products, ketene alkyltrimethylsilyl acetals, exclusively.[3]

Recently, we have reported that, on treating with Grignard reagents, α-chloroacyltrimethylsilanes <u>1</u> afford the corresponding β-ketoalkyltrimethylsilanes <u>2</u> or β-hydroxyalkyltrimethylsilanes <u>3</u>, depending on the Grignard reagent used, in high yield.[4] Formation of these products can be explained by assuming a facile removal of chloride ion from the resulting magnesium alkoxide followed by rearrangement of silyl group to the neighboring carbon originally attached to chlorine atom. These features have strongly suggested that α-chloroacyltrimethylsilanes <u>1</u> might be employable as equivalents of α-trimethylsilylacyl derivatives in the reactions with nucleophiles.



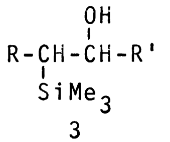
$R\text{-}\underset{\displaystyle Cl}{CH}\text{-}CO\text{-}SiMe_3$

1



$R\text{-}\underset{\displaystyle SiMe_3}{CH}\text{-}CO\text{-}R'$

2

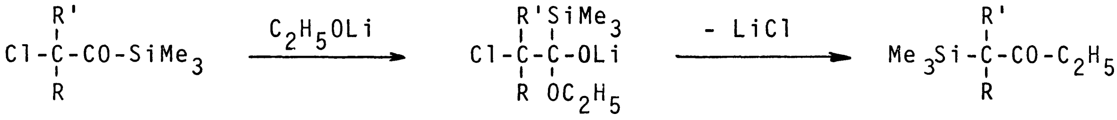


$R\text{-}\underset{\displaystyle SiMe_3}{CH}\text{-}\overset{\displaystyle OH}{CH}\text{-}R'$

3

In order to examine such a possibility and to establish an efficient method for α-trimethylsilylcarboxylic acid esters <u>4</u>, we have attempted the reaction of <u>1</u> with lithium alkoxide.[5] Typical example is as follows. To a THF solution (1 ml) of lithium ethoxide (1.2 mmol) was added a THF solution (2 ml) of 1-chloro-2-phenylpropionyltrimethylsilane <u>1</u> ($R = C_6H_5CH_2$; $R' = H$) (239 mg, 1 mmol) during 10 min at 0°C. After the mixture was left stirring for 30 min at 0°C, it was diluted with hexane (20 ml) pre-cooled to -78°C and was washed with aq NH_4Cl solution. From the aqueous layer, organic materials were extracted twice with ether (10 ml) and the organic layer was washed with saturated aq NaCl solution.

After drying and removal of the solvent, the residual oil was purified by thin layer chromatography, giving ethyl 2-trimethylsilyl-3-phenylpropionate 4 (R = $C_6H_5CH_2$; R' = H)(199 mg, 80%). The product exhibited the following spectral data: nmr(CCl_4; CH_2Cl_2 as internal standard); δ 0.11 (s, 9H), 1.10 (t, J = 7 Hz, 3H), 2.10∿2.42 (d.d, J = 4 and 11 Hz, 1H), 2.45∿2.80 (d.d, J = 4 and 14 Hz, 1H), 2.87∿3.17 (d.d, J = 11 and 14 Hz, 1H), 3.95 (q, J = 7 Hz, 2H), and 7.10 (s, 5H), ir(neat); 1715, 1255, and 850 cm^{-1}.



$$\underset{\mathbf{1}}{Cl\text{-}\overset{R'}{\underset{R}{C}}\text{-}CO\text{-}SiMe_3} \xrightarrow{C_2H_5OLi} Cl\text{-}\overset{R'}{\underset{R}{C}}\text{-}\overset{SiMe_3}{\underset{OC_2H_5}{C}}\text{-}OLi \xrightarrow{-\,LiCl} \underset{\mathbf{4}}{Me_3Si\text{-}\overset{R'}{\underset{R}{C}}\text{-}CO\text{-}C_2H_5}$$

By a similar procedure, various α-trimethylsilylcarboxylic acid esters were prepared in good yields as shown in the Table.

Table. Preparation of α-Trimethylsilylcarboxylic Acid Esters 4.

R	R'	Yield(%) of 4	Bp(°C/Torr)
C_4H_9	H	84	74-77/6
C_6H_{13}	H	87	92-100/6
$C_6H_5CH_2$	H	80	80-85/0.15
$CH_2=CH(CH_2)_7$	H	83	100-105/0.25
$-(CH_2)_5-$		81*	80-88/6

* About 7% of desilylated ester was included.

References and Notes

1) H. Taguchi, K. Shimoji, H. Yamamoto, and H. Nozaki, Bull. Chem. Soc. Jpn., 47, 2529 (1974); S. L. Hartzell, D. F. Sullivan, and M. W. Rathke, Tetrahedron Lett., 1403 (1974); E. Nakamura, T. Murofushi, M. Shimizu, and I. Kuwajima, J. Am. Chem. Soc., 98, 2346 (1976); E. Nakamura, M. Shimizu, and I. Kuwajima, Tetrahedron Lett., 1699 (1976).
2) R. J. Fessenden and J. S. Fessenden, J. Org. Chem., 32, 3535 (1967); M. W. Rathke and D. F. Sullivan, Syn. Commun., 3, 67 (1973).
3) C. Ainsworth, F. Chen, and Y.-N. Kuo, J. Organometal. Chem., 46, 59 (1972).
4) T. Sato, T. Abe, and I. Kuwajima, Tetrahedron Lett., 259 (1978).
5) Sodium alkoxides usually afforded much less satisfactory results.

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