Tetrahedron Letters,Vol.28,No.28,pp 3261-3262,1987 0040-4039/87 \$3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

CONVENIENT PREPARATION OF ACYLTRIMETHYLSILANES FROM CARBOXYLIC ACID DERIVATIVES

Jahyo Kang*, Jae Hyoung Lee, Koan Seong Kim, Jae Uk Jeong and Chongsuh Pyun
Department of Chemistry, Sogang University
Mapoku, Seoul 121, KOREA

Summary : Acylsilanes are prepared in good yields by the reaction of acid chlorides (or anhydrides) with $LiAl(SiMe_3)_4$ or $LiMeAl(SiMe_3)_3$ in the presence of a catalytic amount of CuCN.

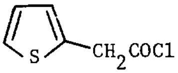
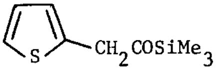
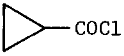
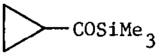
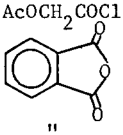
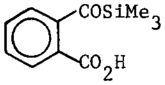
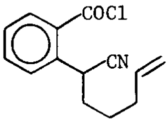
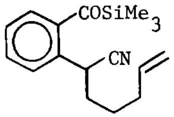
Acylsilanes are interesting class of compounds which undergo a variety of reactions.[1-3] For some applications of this functionality, a facile method for acylsilanes directly from carboxylic acids was needed in our laboratories even though there are available in literature a number of preparatively useful methods, most of which utilize acyl anion equivalents[4], due to the difficulty associated with generation of silyl anions under mild conditions.[5,6]

Since trimethylsilyl anion is usually generated under strongly basic conditions[7], it was thought to be inappropriate especially for carboxylic acid derivatives. In this regard, the readily available Al-Si reagents, $Al(SiMe_3)_3$ and $LiAl(SiMe_3)_4$[7], seemed to be attractive because of the low ionic character of the Al-Si bond. Consequently, acid chlorides were treated independently with the above reagents under various conditions: Generally, the tricoordinated $Al(SiMe_3)_3$ gave incomplete reactions with formation of only a minute quantity of the corresponding acylsilane, whereas the ate complex, $LiAl(SiMe_3)_4$ proved to be more satisfactory, especially in the presence of CuCN (10 mole %). The optimal mole ratio of acid chloride to $LiAl(SiMe_3)_4$ was close to 2.5, implying that only part of the four available trimethylsilyl groups in $LiAl(SiMe_3)_4$ was transferred to acid chloride at a synthetically useful rate (Table 1). Anhydrides could also be silylated; benzoic and phthalic anhydrides were individually converted to the corresponding acylsilanes in satisfactory yields (Entries 4 and 10). That the present system was inert to ketones, acylsilane itself, carbamoyl chlorides, esters, nitriles etc. suggests that even functionalized acid chlorides can be utilized (Entry 12).

Furthermore, addition of an equivalent amount of methyllithium to the hitherto useless $Al(SiMe_3)_3$ presumably provided the corresponding ate complex, which was also effective for the silylation reactions conducted in a similar fashion except that, due to the smaller number of the available trimethylsilyl groups, more $LiMeAl(SiMe_3)_3$ reagent ($RCOCl/Al(SiMe_3)_3 \cdot LiMe = 2$) was needed. Notably, methyl transfer to methyl ketones was not observed in any significant amounts. The following procedure for hexanoyltrimethylsilane is representative. To CuCN (0.036 g, 0.40 mmol) in 33 mL THF at -78°C was added dropwise 27.6 mL of 0.145 M solution of $LiAl(SiMe_3)_4$ in ether (4.0 mmol). The mixture was warmed up to 0°C, where it was stirred for 0.5 h. Hexanoyl chloride (1.35 g, 10.0 mmol) was added dropwise with stirring to the black solution at -78°C. After 2 h, the mixture was warmed to 0°C, and quenched by dropwise addition of aqueous sulfuric acid. The usual work-up followed by SiO_2 chromatography gave 1.63 g (95 %) of hexanoyltrimethylsilane.[8] For those reactions with $Al(SiMe_3)_3$, an equimolar ether solution of methyllithium was added at 0°C to a stirred solution of $Al(SiMe_3)_3$ in pentane-THF

(The pentane was a solvent for the aluminum reagent.). After stirring at 0°C for 0.5 h, solid CuCN (0.1 molar equiv. to the acid chloride to be added) was added under nitrogen blanket. Stirring at 0°C for 0.5 h furnished the active silylating agent.[9]

Table 1. Preparation of Acyltrimethylsilanes[a]

Entry	Starting Material	Reagent[b]	Mole Ratio[c]	Reaction Time[d]	Yield[e]	Product
1	n-$C_5H_{11}COCl$	A	2.5	2 h	95 %	n-$C_5H_{11}COSiMe_3$
2	$PhCOCl$	A	2.5	1.5	93	$PhCOSiMe_3$
3	"	B	2.0	2	73	"
4	$(PhCO)_2O$	A	2.5	1.5	88	"
5	$PhCH_2COCl$	A	2.5	1.5	89	$PhCH_2COSiMe_3$
6		A	2.5	1.5	90	
7	t-$BuCOCl$	A	2.5	1.75	89	t-$BuCOSiMe_3$
8		A	2.5	1.75	89	
9	$AcOCH_2COCl$	A	2.5	2.5	86	$AcOCH_2COSiMe_3$
10		A	2.5	1.5	81	
11	"	B	2.0	2	90	"
12		B	2.0	2	52	

[a] See text for reaction condition. [b] A, $LiAl(SiMe_3)_4$; B, $LiMeAl(SiMe_3)_3$. [c] Mole ratio of acid derivative to the reagent. [d] At -78°C. [e] Based on the amount of acid derivative used.

References

1. A.G. Brook, Adv. Organomet. Chem., 7, 96(1968); Acc. Chem. Res., 7, 77(1974).
2. a) D. Schinzer and C.H. Heathcock, Tetrahedron Lett., 22, 1881(1981). b) H.J. Reich, M.J. Kelly, R.E. Olson and R.C. Holtan, Tetrahedron, 39, 949(1983). c) J. Enda and I. Kuwajima, J. Am. Chem. Soc., 107, 5495(1985). d) H.J. Reich and E.K. Eisenhart, J. Org. Chem., 49, 5282(1984).
3. a) M.E. Scheller and B. Frei, Helv. Chim. Acta, 67, 1734(1984). b) C. Shih and J.S. Swenton, J. Org. Chem., 47, 2668(1982).
4. For most recent one; T. Mandai, H. Yamaguchi, Y. Nakayama, J. Otera and M. Kawada, Tetrahedron Lett., 26, 2675(1985); T. Aoyama and T. Shioiri, ibid, 27, 2005(1986).
5. a) D.C. Davis, Organomet. Chem. Rev. A, 6, 283(1970). b) W.C. Still, J. Org. Chem., 41, 3063(1976). c) T. Hiyama, M. Obayashi, I. Mori and H. Nozaki, J. Org. Chem., 48, 912 (1983).
6. Acysilanes from silyl anions, a) with Ph_3SiLi, see N. Duffaut, J. Dunogues, C. Biran and R. Calas, J. Organomet. Chem., 161, C23(1978) b) with $(Me_3Si)_2$, see A. Ricci, A. Degl'Innocenti, S. Chimichi, M. Fiorenza and G. Rossini, J. Org. Chem., 50, 130(1985).
7. L. Roesch and G. Altnau, J. Organomet. Chem., 195, 47(1980); Chem. Ber., 112, 3934(1979).
8. J.A. Miller and G. Zweifel, Synthesis, 288(1981).
9. This research was supported by the Korea Research Foundation.

(Received in Japan 3 March 1987)