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THE CERIUM MEDIATED CONVERSION OF ESTERS TO ALLYLSILANES

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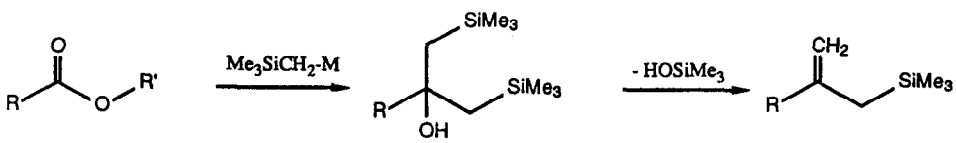
Abstract: Reaction of esters with the reagent prepared from $CeCl_3$ and $TMSCH_2MgCl$ in THF, followed by deoxysilylation on silica gel, effects efficient conversion to allylsilanes. Methyl 1-adamantane carboxylate, a sterically hindered ester, does not react under these conditions.

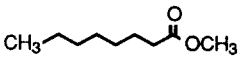
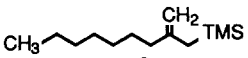
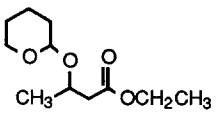
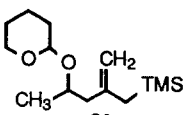
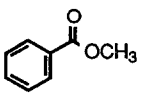
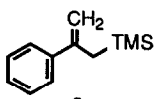
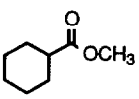
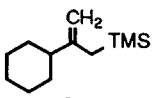
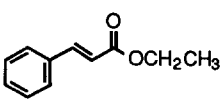
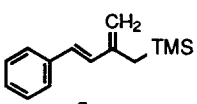
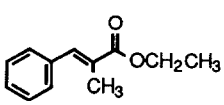
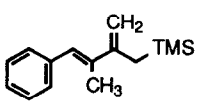
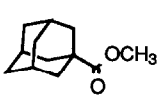
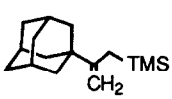
Allylsilanes are exceptionally versatile compounds with well-established utility in organic synthesis.[1] Thus, general methods for the development of the allylsilane functionality, particularly those applicable to complex molecules, are quite valuable. Consequently, there has been much recent interest in carboxylic acid derivatives as functional precursors for allylsilanes.[2,3] The transformation is conceptually staightforward: twofold addition of a trimethylsilymethyl-metal species to the ester 1 would give the bis(β-silyl) alcohol 2, which on deoxysilylation should lead to the allylsilane 3 (Eq. 1). Indeed esters of unbranched carboxylic acids have been converted to the corresponding allylsilanes with trimethylsilymethylmagnesium chloride.[2] The yields for this process, however, are generally low (∿50%), and the reaction fails completely for esters of α-branched carboxylic acids, such as methyl cyclohexanecarboxylate.[2b] In this case, the α-silyl-ketone intermediate apparently resists further addition of the Grignard reagent, suffering instead a kinetically-preferred enolization. This phenomenon was exploited by Demuth[4] in a general synthesis of α-silyl ketones.



1 2 3 Eq. 1

Imamoto has recently demonstrated that organocerium reagents are especially suited for additions to readily enolized carbonyl systems.[5] We reasoned that the trimethylsilylmethylcerium reagent would be effective in the conversion of esters to allylsilanes. While this manuscript was in preparation, Anderson and Fuchs[3] reported an excellent procedure for the conversion of acyl chlorides to allylsilanes based on the use of cerium reagent derived from $CeCl_3$ and $TMSCH_2Li$. Unfortunately, the results with esters were much less satisfactory. Our own work has focussed on

Table

ester	allylsilane	yield
 **1a**	 **3a**	>95%
 **1b**	 **3b**	90%[a]
 **1c**	 **3c**	95%
 **1d**	 **3d**	77%
 **1e**	 **3e**	93%
 **1f**	 **3f**	92%
 **1g**	 **3g**	0%[b]

a) Starting material and product each a 1:1 mixture of diastereomers.
b) Starting material recovered quantitatively.

a reagent prepared from $CeCl_3$ and $TMSCH_2MgCl$. Interestingly we have found that the Grignard-based species are quite effective for the conversion of esters to allylsilanes. Since we feel that elaboration of esters offers certain advantages over acid chlorides, we report here the results of our study.

The cerium reagent generated from $CeCl_3$ and trimethylsilylmethyl magnesium chloride reacts with the esters 1a-f to give bis(silymethyl) carbinols 2a-f. These were not isolated. Instead, treatment with silica gel caused smooth deoxysilylation to give allylsilanes 3a-f[6] in excellent yields (see Table). Particularly striking are the excellent results with esters 1e and 1f, where the allylsilanes were obtained in >90% yield. This is in sharp contrast to the findings for the $CeCl_3/TMSCH_2Li$ reagent,[3] where 1e gave only a 47% yield of allylsilane (50% ester unreacted) and 1f failed to react at all. This comparison demonstrates quite clearly a dramatic difference in the cerium reagents prepared from $TMSCH_2Li$ and $TMSCH_2MgCl$. Although the nature of our "organocerium" reagent is open to question, it is clear that the presence of $CeCl_3$ is essential. Control experiments establish that the Grignard reagent alone reacts very sluggishly under the low temperature conditions of our experiments; starting ester along with small amounts of α-silylketone is obtained. With the cerium reagent, we observed complete consumption of the ester under comparable conditions. It is worth noting the absence of detectable quantities of α-silyl ketones in the NMR spectra of the crude bis(silylmethyl) carbinols-enolization does not compete with addition. Presumably due to steric factors, the ester 1g fails to react at all, and only starting material is recovered.

The precise reaction conditions are crucial to the success of this method. The trimethylsilylmethylmagnesium chloride must be of good quality. Commercially available solutions in ether (Aldrich) are satisfactory, but we have found reliable results only with a freshly-opened bottle.[7] As has been indicated for other cerium reagents,[3,8] shortcuts in the preparation of the trimethylsilylmethyl cerium can lead to unsatisfactory results. A typical procedure follows:

Procedure:

Powdered $CeCl_3 \cdot 7H_2O$ (1.86g, 5.0 mmol) is dried at 150°C/0.1 torr for 2 hrs. The flask is cooled to room temperature, and vented to a dry-nitrogen atmosphere. Dry THF (10 ml, distilled from sodium-benzophenone) is added, and the suspension stirred at ambient temperature under N_2 for 2 hrs. The slurry is then cooled to -70°C, and trimethylsilylmethylmagnesium chloride (1M in ether, 5 ml) was run in via syringe. The cream-colored suspension is stirred at -70°C for 1 hr, at which time the ester (1.0 mmol) is added over 2-3 minutes. Stirring is continued for 2 hrs at -70°C, then the reaction is allowed to warm to room temperature overnight. After quenching with 1M HCl (50 ml), the crude bis(silylmethyl) carbinol is isolated by extraction with CH_2Cl_2, drying over $MgSO_4$, and removal of solvent under vacuum. Dehydroxysilylation is accomplished by stirring the product with 1g of silica gel (column chromatography grade) and 10 ml of CH_2Cl_2 for 2-3 hr. Filtration, followed by flash chromatography, provides the allylsilanes.[6]

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6. The allylsilanes were obtained in chromatographically homogeneous form (TLC, GC). Spectral data: (Selected IR bands are presented for neat liquid films. ^{1}H NMR spectra were recorded at 90 MHz on solutions in $CDCl_3$; ^{13}C NMR spectra were taken at 22.5 MHz in the same solvent. Chemical shifts are reported in ppm downfield of TMS). 3a: IR: ν 3070, 1630, 850 cm^{-1}; ^{1}HNMR: δ 4.57(1H,m), 4.51(1H,m), 1.95(2H,m), 1.52(2H,s), 1.29(10H,m), 0.89(3H,brt), 0.02ppm(9H,s); ^{13}CNMR: δ 147.9, 106.7, 38.3, 31.9, 29.5, 29.3, 28.0, 26.9, 22.7, 14.1, -1.2 ppm. 3b (fast-eluting diastereomer): IR: ν 3076, 1632, 1022, 851 cm^{-1}; ^{1}H NMR: δ 4.74(1H,m), 4.63(1H,m), 4.58(1H,m), 3.91(2H,m), 3.47(1H,m), 2.35(1H,dd, J=14,6Hz), 2.05(1H,dd,J=14,8Hz), 1.57(11H,m), 1.09(3H,d,J=7Hz), 0.02ppm (9H,s); ^{13}C NMR: δ 144.5, 109.7, 95.6, 70.0, 61.9, 46.3, 31.1, 26.9, 25.6, 19.4, 18.8, -1.4ppm. 3b(slow-eluting diastereomer): IR: ν 3076, 1632, 1022, 854 cm^{-1}; ^{1}H NMR: δ 4.62 (2H,m), 4.57(1H,m), 3.90(2H,m), 3.46(1H,m), 2.25(1H,dd,J=14,6 Hz), 1.94(1H,dd, J=14, 8Hz), 1.54(11H,m), 1.20(3H,d,J=7Hz), 0.02 ppm(9H,s); ^{13}C NMR: δ 144.4, 109.6, 98.1, 71.9, 62.6, 45.3, 31.0, 26.9, 25.4, 21.5, 19.8, -1.5 ppm. 3c: IR: ν 3082, 1616, 1159, 877, 839 cm^{-1}; HNMR: δ 7.40(5H,m), 5.22(1H, brs), 4.96(1H, brs), 2.12(2H,s), 0.00(9H,s); ^{13}C NMR: δ 146.6, 142.8, 128.0, 127.1, 126.3, 110.0, 26.1, -1.4 ppm. 3d: IR: ν 3078, 1620, 857 cm^{-1}; ^{1}H NMR: δ 4.48(1H,m), 4.42(1H,m)$_3$ 1.66(5H,m), 1.45(2H,brs), 1.07(6H,m), -0.08(9H,s); ^{13}C NMR: δ 153.2, 104.8, 45.9, 32.6, 27.0, 26.5, 26.3, -1.1 ppm. 3e[3]: IR: ν 3068, 1593, 872, 853, 838 cm^{-1}; ^{1}H NMR: δ 7.4 -7.1 (5H,m), 6.77(1H,d,J=16Hz), 6.45(1H,d,J=16Hz), 5.00(1H,d,J=1Hz), 4.83(1H,brs), 1.80(2H,brs), 0.01ppm(9H,s); ^{13}C NMR: δ 143.8, 137.4, 132.0, 128.7, 128.6, 127.3, 126.4, 114.8, 22.2, -1.2 ppm. 3f[3]: IR: ν 3081, 1599, 854 cm^{-1}; ^{1}H NMR: δ 7.3-7.2(5H,m), 6.58(1H,brs), 5.07(1H,d,J=1Hz), 4.81(1H,brs), 1.98(3H,d,J=1Hz), 1.90(2H,brs), 0.03ppm(9H,s); ^{13}C NMR: δ 147.4, 138.6, 137.5, 129.2, 128.0, 127.3, 126.3 , 110.2, 24.3, 15.7, -1.1 ppm.

7. Use of older Grignard reagent leads to a different set of products. These will be reported in due course.

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