

The Preparation of 3-Chloroalkenyltrimethylsilanes

Robert F. Cunico* and Cui-ping Zhang

Department of Chemistry, Northern Illinois University, DeKalb, IL 60115

Summary: 3,3-Dichloropropenyltrimethylsilane undergoes monosubstitution with organocuprates $\text{RCu}(\text{CN})\text{Li}$ to afford *E*-3-chloroalkenyltrimethylsilanes.

The preparation and synthetic applications of α,β -unsaturated acylsilanes are topics of some current interest.^{1,2} We now wish to report on a new approach to the construction of conjugated alkenylsilanes which is based on the elaboration of template molecule **1**. The preparation of **1** entailed the photolytic addition of bromotrichloromethane to (1-ethoxyethenyl)trimethylsilane to give a 1:1 adduct which readily underwent solvolysis and elimination to give **1** (eq. 1).³ Our intent was to develop a procedure which would allow the monosubstitution of **1** so as to afford entry to 3-chloro-3-alkyl derivatives, substrates which were expected to serve as valuable synthetic intermediates to other functionalized acylsilanes.



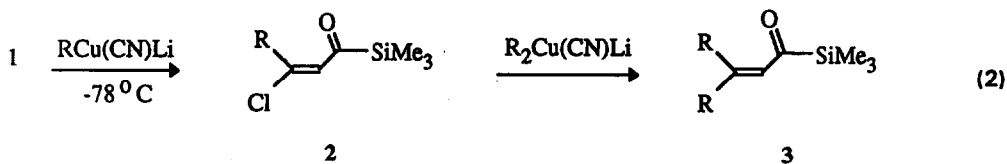
Although organocuprate species appeared to be the reagents of choice for this purpose,⁴ we were unaware of any report detailing the useful monosubstitution of a 3,3-dihaloenone by this approach. We have now developed conditions which allow for the preparation of monosubstituted

products **2**, while avoiding the formation of disubstituted enones **3** (eq. 2 and Table 1). The method of choice entailed the addition of the cold (-78°C) organocuprate [RCu(CN)Li] to a cold (-78°C) dilute THF solution of **1**. Optimization of the organocuprate:1 ratio was necessary on a case-by-case basis in order to achieve maximum consumption of **1** without generating dialkylated product.⁵ In contentious cases (**2b**, **2e**), it was advantageous to err in favor of incomplete conversion, as **1**, but not the diadducts **3**, could be separated from **2** upon chromatography. These substitutions appear to exhibit considerable stereoselectivity,⁶ in that each of the products **2a-e** consisted of a sole stereoisomer as obtained from a rapid workup of the reaction mixture.⁷ The configuration of **2a** was established as *E* by its oxidation⁸ to the known *E*-3-chlorobutenoic acid,⁹ and the configurations of the other **2** prepared are shown as *E* on this basis only.

Table 1. 3-Chloroalkenoyltrimethylsilanes from Organocuprates and 1.

<u>RCu(CN)Li</u>	<u>Ratio^a</u>	<u>Product^b</u>	<u>Yield(%)^c</u>
Me	1.2	2a	57
nBu	1.2	2b	64 ^d
sBu	1.5	2c	74
tBu	1.5	2d	75
Ph	1.8	2e	65 ^e

^aOrganocuprate:1. ^bAll products afforded appropriate spectral and analytical data. For **2c**, combustion data were obtained on the rearranged (β,γ) isomer only. ^cChromatographically pure product. ^dBased on 90% conversion. ^eBased on 55% conversion.



2,3 a, R = Me; b, R = nBu; c, R = sBu; d, R = tBu; e, R = Ph

Preliminary experiments indicate that symmetrically disubstituted alkenoylsilanes (**3a, b, e**) may be made the sole products from **1** by employing equivalent amounts of the appropriate $\text{R}_2\text{Cu(CN)Li}$ reagent. In addition, sequential in situ treatment of **1** with sBuCu(CN)Li and $\text{Me}_2\text{Cu(CN)Li}$ provided the mixed disubstitution product with high stereoselectivity, suggesting that both *E* and *Z* isomers may be individually accessed by alternating the sequence of organocuprate additions.

3,3-Dichloropropenoyltrimethylsilane (1). A mixture of (1-ethoxyethenyl)-trimethylsilane (1.4 g, 10 mmol), bromotrichloromethane (4.0 g, 20 mmol), pyridine (0.80 g, 10 mmol) and 5 mL of CCl_4 was placed in an argon-flushed flask topped by a reflux condenser and irradiated with a 150W spotlight for 20 min. Methanol (5 mL) and water (1 mL) were added and the mixture stirred for 1 h. After a water-pentane workup, the dried (MgSO_4) organic phase was distilled to afford 0.95 g (48%) of **1**, bp 60-65°C (1 mm). IR: 1624 cm^{-1} . $^1\text{H NMR}$: δ 0.20 (s, 9H), 6.90 (s, 1H). $^{13}\text{C NMR}$: δ -3.4, 128.7 (CH), 130.7, 222.1. UV: λ_{max} (hexane) = 252 nm ($\epsilon = 1.0 \times 10^4$), 436 nm ($\epsilon = 90$). Anal. Calcd for $\text{C}_6\text{H}_{10}\text{Cl}_2\text{OSi}$: C, 36.56; H, 5.11; Cl, 35.97. Found: C, 36.34; H, 5.05; Cl, 35.87.

3-Chloro-1-(trimethylsilyl)-2-heptenone (2b). This procedure is representative of all preparations of **2**. Copper (II) cyanide (0.22 g, 2.4 mmol) was dried by air-gun heating under vacuum (1 mm), and

20 mL of THF was added to the powder at 25°C under argon. The mixture was cooled to -78°C and 1.1 mL of 2.2M nBuLi in hexane was added. After allowing the temperature to rise to -20°C and recooling to -78°C, the clear solution was transferred to a jacketed addition funnel held at -78°C. Slow dropwise addition to a stirred solution of 1 (0.4 g, 2.0 mmol) in 100 mL of THF (50 mL for other 2) at -78°C was carried out, followed after 1 h by addition of dilute HOAc-THF at -78°C. After a water-pentane workup, the dried (MgSO₄) organic phase was filtered through Florisil and subjected to flash chromatography on silica gel (hexane elution) to give 0.04 g of recovered 1 followed by 0.25 g (64%) of isomerically and analytically pure 2b. ¹H NMR: δ 0.19 (s, 9H), 0.89 (t, 3H), 1.2 - 1.65 (m, 4H), 2.81 (m, 2H). Anal. Calcd for C₁₀H₁₉ClOSi: C, 54.93; H, 8.70. Found: C, 55.01; H, 8.86.

REFERENCES AND NOTES

1. See Nowick, J.S.; Danheiser, R.L. J. Org. Chem. **1989**, *54*, 2798 and references therein.
2. Acylsilane reviews: (a) Ricci, A.; Degl'Innocenti, A. Synthesis **1989**, 647. (b) Page, P.C.B.; Klair, S.S.; Rosenthal, S. Chem. Soc. Rev. **1990**, *19*, 147.
3. Similar chemistry has been reported for asilyl systems: Tarrant, P.; Stump, Jr., E.C. J. Org. Chem. **1964**, *29*, 1198.
4. Scattered reports exist concerning the substitution of (mono)-β-haloenones with organocuprate reagents. See, for example, (a) Posner, G.H. An Introduction to Synthesis Using Organocopper Reagents; John Wiley and Sons, New York, 1980. (b) Piers, E.; Nagakura, I. J. Org. Chem. **1975**, *40*, 2694.
5. The situation is complicated by the partial dimerization of the organocuprate.
6. The actual stereoselectivity must be viewed as unknown, as the lesser stereoisomer may be selectively destroyed under the reaction conditions.
7. Upon standing, 2b and 2c each rearranged to a mixture of the corresponding β,γ-geometric isomers. Asilyl ketones show parallel behavior: Suama, M.; Nakajima, A.; Sugita, T.; Ichikawa, K. Chemistry Lett. **1981**, 1459.
8. Method of Miller, J.A., Zweifel, G. J. Am. Chem. Soc. **1981**, *103*, 6217.
9. Allan, R.D., Johnston, G.A.R., Twitchin, G. Aust. J. Chem. **1980**, *33*, 1115.