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Synthesis and Reactions of 1-(Trimethylsilyl)allyl Chloride[1)]

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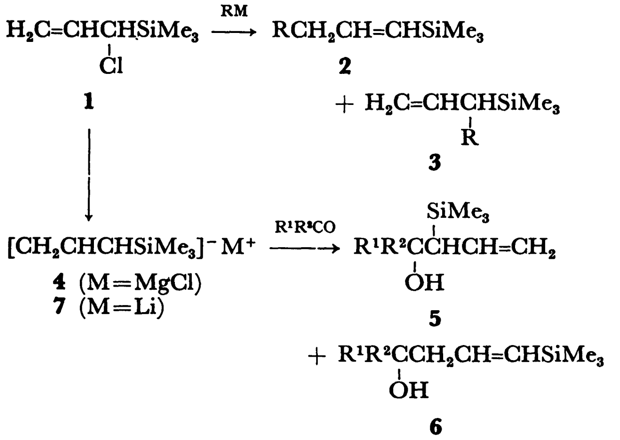
Synopsis. 1-(Trimethylsilyl)allyl chloride prepared conveniently from 1,3-dichloropropene reacted smoothly with organocopper compounds yielding terminal alkenylsilanes, while its Grignard reactions with carbonyl compounds gave the corresponding alcohols with the regioselection depending sensitively on substrates.

Silylated allyl halides are useful synthetic intermediates.[2)] 3-Silylallyl halides are obtainable from allylsilanes or 3-silylallyl alcohols[3,4)] but no practical method is so far available for 1-silylallyl halides, although 3-chloro-3-(trimethylsilyl)allyltriphenyllead was reported to yield 1-(trimethylsilyl)allyl chloride (**1**) as a minor product on treating with butyllithium followed by hydrolysis.[5,6)] We here describe a convenient route to **1** and several reactions of this material.

1,3-Dichloropropene reacted with chlorotrimethylsilane on mixing in the presence of magnesium at room temperature in a THF/ether (1:1) solution to give **1** in 40% yield.[7)] The product contained a small amount of 1-chloro-3-trimethylsilylpropene as an impurity which was difficult to be removed.[8)]



Treatment of **1** with organocopper compounds led to the regioselective γ-alkylation affording terminal alkenylsilanes **2** (**2**/**3**>97/3 in most cases) in good yields. The results are given in Table 1. Stereochemistry of the product **2** was dependent on the organometallic species involved. For example, lithium dibutylcuprate(I) reacted with **1** to give *trans*-1-trimethylsilylheptene predominantly, whereas butylcopper yielded the *cis*-isomer as the major product. In the alkylation with Grignard reagents (RMgX) in the presence of a catalytic amount of copper(I) iodide, *cis*-products significantly increased when RMgX was slowly added to a mixture of **1** and CuI instead of the addition of **1** to an admixture of RMgX and CuI. Probably, RCu is involved as a reactive species under the former conditions; a cuprate(I) may be operative under the latter conditions.

A Grignard reagent **4** prepared from **1** added regioselectively to aldehydes to give the corresponding α-alcohols **5** together with a small amount of regioisomeric γ-alcohols **6**. Low reaction temperature favored the formation of **5** and so did THF as compared to ether as solvent. In contrast, the reagent **4** reacted with ketones yielding **6** exclusively irrespective of the reaction conditions, as shown in Table 2. The silylated carbon terminus of the species **4** is probably more electronegative than is the unsubstituted CH_2-terminus; so electronically a carbonyl group would preferentially attack the former site, as is indeed observed for aldehydes. A marked change in the regioselectivity for ketones presumably arises from the steric hindrance around a carbonyl group. The regioselection also depends on a counter cation of the allyl anion. Thus, the present results contrast with the fact that a related species **7** reacts with both aldehydes and ketones to give **6** as the sole product.[9)] This is probably associated with the difference in the ionic character of a carbon-metal bond.

TABLE 1. REACTIONS OF **1** WITH ORGANOMETALLIC REAGENTS[a)]

Reagent	Yield/% of **4**[f)]	Isomer ratio (*Z*)/(*E*)
n-BuMgBr/CuI (10 mol%)	83	0.72[i)], 0.43[j)]
PhMgBr/CuI (10 mol%)	84[g)]	1.4[i)], 0.67[j)]
c-C_6H_{11}MgBr/CuI (10 mol%)	69	0.79[i)], 0.32[j)]
t-BuMgCl/CuI (10 mol%)	84	0.63[i)]
n-BuMgBr[b)]	36[h)]	0.49
n-Bu_2CuLi[c)]	68	0.67
n-BuCu[c)]	97	2.1
$NCCH_2Cu$[d)]	72	0.79
$PhCOCH_2CH_2CH_3$/NaH[e)]	21	k)

a) Reactions were carried out in THF at 0 °C for 30 min under nitrogen unless otherwise noted. b) At room temperature for 3 h. c) At −50 °C. d) At −25 °C. e) In 1, 2-dimethoxyethane under reflux. f) GLC yield. g) **2**/**3**=92/8. h) **2**/**3**=70/30. i) RMgX was added to a mixtue of **1** and CuI. j) **1** was added to a mixture of RMgX and CuI. k) Not determined.

TABLE 2. REACTIONS OF **4** WITH CARBONYL COMPOUNDS

Substrate	Conditions	Product ratio **5**:**6**	Yield/%[a)]
i-PrCHO	ether, 0 °C	76:24	76
	THF, 0 °C	84:16	67
	THF, −75 °C	94:6	b)
PhCHO	ether, 0 °C	66:34	81
	THF, 0 °C	79:21	73
	THF, −75 °C	82:18	b)
cyclohexanone	ether, 0 °C	~0:100	83
	THF, 0 °C	~0:100	88
	THF, −75 °C	~0:100	b)
$PhCOCH_3$	ether, 0 °C	~0:100	79

a) GLC yield. b) Not determined.

Experimental

NMR spectra were determined in carbon tetrachloride solutions with a Hitachi R-600 spectrometer and IR spectra were recorded on a Hitachi 260-10 spectrophotometer.

1-(Trimethylsilyl)allyl Chloride (1). A mixture of 1,3-dichloropropene (Tokyo Chemical Industry, 43 g, 0.39 mol), chlorotrimethylsilane (42 g, 0.39 mol), and 1,2-dibromoethane (0.1 cm^3) was added to a stirred mixture of magnesium (13 g) and chlorotrimethylsilane (20 g) in THF/ether (1:1) (400 cm^3) over a period of 4 h at room temperature. The mixture was stirred for further 4h at room temperature and quenched with a sodium hydrogencarbonate solution. Usual workup gave a colorless oil (23 g), bp 73—76 °C (100 Torr: 1 Torr=133.3 Pa), which was a mixture of **1** and 1-chloro-3-trimethylsilylpropene in the ratio 93:7. The spectral data for these two compounds were superimposable with those reported.[5,10)]

Reactions of 1 with Organometallic Reagents. The following example is representative.

Butylmagnesium bromide (16 mmol) in THF (20 cm^3) was added to a mixture of **1** (0.79 g, 5.3 mmol), copper(I) iodide (0.3 g, 1.5 mmol), and ethylbenzene (50 mg, as an internal standard) in THF (5 cm^3) over a period of 15 min at 0 °C. Aqueous workup of the mixture gave 1.01 g of 1-trimethylsilylheptene ($E/Z=1.08$) (37%; 84% based on GLC), bp 90—97 °C (47 Torr) (Found: C, 70.50; H, 13.06%). An analytical sample of each isomer was obtained by GLC. (*E*): IR 1620 (C=C) cm^{-1}; NMR δ=0.03 (9H, s), 0.7—1.6 (9H, m), 1.8—2.3 (2H, m), 5.48 (1H, d, J=17 Hz), 5.7—6.2 (1H, m). (*Z*): IR 1610 cm^{-1}; NMR δ=0.09 (9H, s), 0.7—1.6 (9H, m), 1.75—2.35 (2H, m), 5.35 (1H, d, J=13 Hz), 6.25 (1H, d of t, J=13 and 6 Hz).

Similarly, the following alkenylsilanes ($RCH_2CH=CHSiMe_3$) were prepared and characterized. R=*t*-Bu ($E/Z=1.6$), bp 100—107 °C (135 Torr) (Found: C, 70.84; H, 13.02%): NMR (Signals for the (*Z*)-isomer were shown in italics.) δ= 0.03 and *0.10* ($SiMe_3$), *5.46* (d, J=14 Hz) and 5.55 (d, J=18 Hz) (=$CHSiMe_3$). R=*c*-C_6H_{11} ($E/Z=1.3$), bp 102—107 °C (11 Torr): NMR δ=0.03 and *0.08* ($SiMe_3$), *5.37* (d, J=13 Hz) and 5.46 (d, J=18 Hz) (=$CHSiMe_3$). R=CH_2CN ($E/Z=1.3$), bp 134—136 °C (82 Torr) (Found: C, 62.50; H, 9.85; N, 9.01%): NMR δ=0.08 and *0.15* ($SiMe_3$), *5.66* (d, J=14 Hz) and 5.4—6.1 (complicated due to coalescence of the two olefinic protons) (=$CHSiMe_3$). R=Ph ($E/Z=0.7$), bp 95—99 °C (25 Torr): NMR δ=0.05 and *0.17* ($SiMe_3$), *5.55* (d, J=13 Hz) and 5.60 (d, J= 16 Hz) (=$CHSiMe_3$). These alkenylsilanes showed an IR band (C=C) near 1605 (for *Z*-isomer) or near 1620 cm^{-1} (for *E*-isomer). R=PhCOCHEt: IR 1680 and 1620 cm^{-1}; NMR δ=−0.04 (9H, s), 0.87 (3H, t), 1.7 (2H, m), 2.4 (2H, m), 3.37 (1H, m), 5.4—6.1 (2H, m), 7.3—8.0 (5H, m)

Reactions of 1-(Trimethylsilyl)allylmagnesium Chloride (4) with Carbonyl Compounds. The Grignard reagent **4** prepared from **1** (0.4 g, 2.7 mmol) in ether (20 cm^3) was added to a solution of isobutyraldehyde (240 mg) and decane (54 mg, internal standard) in ether (10 cm^3) at 0 °C. Usual workup gave 127 mg of two isomeric alcohols **5** and **6** (R^1=*i*-Pr, R^2=H) (76:24), bp 95—96 °C (41 Torr). Each alcohol was isolated by GLC. **5**: IR 3500, 1635 cm^{-1}; NMR δ=0.02 (9H, s), 0.7—1.0 (6H, m), 3.1—3.5 (1H, m), 4.6—5.1 (2H, m), 5.5—6.2 (1H, m) (Found: C, 64.04; H, 11.87%). **6**: IR 3410, 1625 cm^{-1}; NMR δ=0.05 (9H, s), 0.88 (6H, d, J=6 Hz), 2.20 (2H, m), 3.30 (1H, m), 5.64 (1H, d, J=18 Hz), 5.6—6.4 (1H, m).

The following alcohols were also characterized. **5** (R^1=Ph, R^2=H): IR 3400, 1620 cm^{-1}; NMR δ=−0.02 (9H, s), 1.7 (1H, broad s), 1.88 (1H, d of d, J=9 and 6 Hz), 4.2—6.2 (3H, m), 7.2 (5H, s). **6** (R^1=Ph, R^2=Me): IR 3450, 1620 cm^{-1}; NMR δ=0.09 (9H, s), 1.7 (1H, s), 2.55 (2H, m), 5.6—5.9 (2H, m), 7.1—7.5 (5H, m) (Found: C, 71.49; H, 9.47%).

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6) Another route to 1-silylallyl halides has been reported recently: M. Ando, A. Hosomi, and H. Sakurai, 49th National Meeting of the Chemical Society of Japan, Tokyo, March 1984, Abstr. No. 1229.

7) The coupling reaction in THF in place of THF/ether gave 1,3-bis(trimethylsilyl)propene as the major product.

8) The impurity was inert to organometallic reagents as well as metallic magnesium.

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