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SILYLCUPRATION OF ACETYLENES

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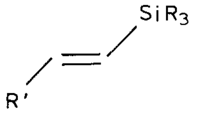
Summary

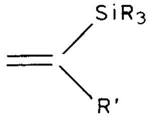
Several organosilylcuprates have been prepared and their reactions with acetylenes examined. It has been shown that $LiCu[Si(SiMe_3)_3]_2$ adds to acetylenes in only one manner, i.e., with *cis* addition and the $Si(SiMe_3)_3$ group in the least hindered cite as shown in the equation below. Similarly the sterically hindered $LiCu(SiMePh_2)_2$

$$LiCu[Si(SiMe_3)_2]_2 \cdot LiI + RC{\equiv}CH \rightarrow H^+,H_2O \rightarrow trans\text{-}RHC{=}CHSi(SiMe_3)_3$$

adds only in this fashion. If the less sterically hindered lithium compound, $LiSiMe_2Ph$, is used to prepare the copper reagent, then, when the Li/Cu ratio is reduced to 1/1 a mixture of products, **A** and **B** ($SiR_3 = SiMe_2Ph$; $R' =$ n-Bu) is obtained in a ratio of 2/1, but only one product, **A** ($SiR_3 = SiMe_2Ph$; $R' =$ n-Bu, t-Bu, Ph), is obtained when the ratio of Li/Cu is 2/1. Only **A** is obtained when either diphenylmethylsilyllithium or tris(trimethylsilyl)silyllithium ($SiR_3 = SiMePh_2$, $Si(SiMe_3)_3$; $R' =$ n-Bu, t-Bu, Ph) is used regardless of the Li to Cu ratio.



(A)



(B)

Introduction

Organocopper reagents have been extensively used in organic syntheses because of their usefulness in formation of specific products [1]. Silylcopper reagents on the other hand have been little used with only a few reports principally by Fleming [2,3], who initially reported this reagent and its usefulness in the preparation of 2,2-disubstituted vinylsilanes. They found that lithium bis(dimethylphenylsilyl)cuprate $\{(Me_2PhSi)_2CuLi \cdot LiCN\}$ can react with various substituted acetylenes to give products of *syn* addition of the dimethylphenylsilyl group and the copper. The resultant vinylcopper reagents react with a variety of electrophiles such as the proton, iodine, acyl, and alkyl halides, enones and epoxides to give vinylsilanes. This group subsequently has explored the utilization, principally of the LiCu(SiMe$_2$Ph)$_2$ reagent, in a number of other reactions but has only provided limited information on the effect of altering the SiR$_3$ group [4].

We now wish to report on the use of these reagents in addition reactions and specifically to explore the effect of sterically bulky groups on the reaction path. In order to began these studies on the effect of the substituents on the reactivity of the silylcuprates, we have prepared a series of substituted silylcuprates and reacted them with simple organic substrates.

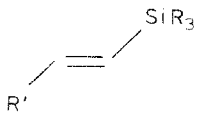
Results and discussion

The nature of the silylcopper reagent, LiCu(SiR$_3$)$_2$, has not been established, but presumably is similar to that of the organocuprates which are known to have complex structures [1]. Generally, etheral solutions of the silylcuprate reagents are prepared under an inert atmosphere at low temperature from silyllithium compounds and cuprous iodide or bromide in a 2/1 molar ratio as indicated in eq. 1. As the second equivalent of silyllithium is added, the reaction mixture becomes

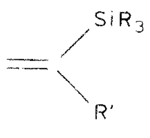
$$2\ \mathrm{LiSiR_3} + \mathrm{CuX} \rightarrow \mathrm{LiCu(SiR_3)_2} + \mathrm{LiX} \tag{1}$$

essentially homogeneous. Frequently color development accompanies formation of the silylcuprate owing to undesirable reactions or impurities, but this coloration appears to have little effect on the reactivity of the silylcuprate.

The reaction of the silylcuprate with most organic substrates is fast. For the sake of convenience our studies were carried out at 0°C, but these conditions are certainly more vigorous than necessary. In all nine reactions we observed that only one stereoisomer occurred in the products as long as the silylcopper reagent was prepared by mixing two equivalents of silyllithium compound with one equivalent of cuprous iodide. The vinylcopper species, as reported by Fleming et al. [2,3], is evidently regiostable and stereoselective in its reactions. The *syn*-stereoselectivity in these reactions is clear shown by exclusive formation of the *trans*-olefin as evidenced by the NMR spectrum which shows only a single coupling constant for the protons in the vinyl region characteristic of the *trans*-olefinic signals of the vinylsilanes. The regioselectivity of the silylcupration reaction is opposite to that which might have been expected by analogy with the corresponding carbocupration reaction [1]. The regioselectivity could be changed by altering the equivalents ratio of silyllithium with cuprous iodide. A reagent produced by mixing the dimethylphenylsilyllithium with cuprous iodide in a 1/1 ratio gave mixtures of A and **B** (SiR$_3$ = SiMe$_2$Ph; R′ = n-Bu) in a ratio of ca. 2/1, respectively, when reacted with



(A)



(B)

1-hexyne. However for the more crowded compounds, diphenylmethylsilyllithium and tris(trimethylsilyl)silyllithium, only a single *trans* isomer, A, (SiR$_3$ = SiMePh$_2$,

$Si(SiMe_3)_3$; R′ = n-Bu, t-Bu, Ph) was observed even upon changing the molar ratio in preparing the silylcopper reagent.

Steric hindrance around the silicon atom for the latter two compounds which prevents the silylcuprate reagents from adding to the more crowded carbon is likely to explain why only one *trans* isomer was isolated even when the reactions were performed under different conditions.

Experimental

The preparations of all of the silyllithium and copper reagents were carried out using standard Schlenk techniques under an argon atmosphere. All reagents and solvents were purified and dried by appropriate means just prior to use. The ^1H and ^{13}C NMR spectra were obtained on a G.E. QE-300 NMR spectrometer operating at 300.15 and 75.48 MHz, respectively. The ^{29}Si spectra were obtained on a GN-300 with a center band frequency of 59.62 MHz. All chemical shifts are referenced to TMS. The infrared spectra were obtained on a Nicolet 20-DXFTIR. Mass spectra were obtained either on a Krados MS 80 or on an AEI 902.

Preparation of silyllithium reagents

(a) Diphenylmethylsilyllithium. Finely cut lithium (5.0 g, 0.72 mol) was placed in a 1 l three-necked flask containing 300 ml of dry THF which was equipped with mechanical stirrer, reflux condenser, and dropping funnel (the latter two fitted with gas inlets for argon). Diphenylmethylsilyl chloride (48 g, 0.21 mol) dissolved in 250 ml of THF was added dropwise to the stirred suspension of lithium. The reaction mixture was stirred overnight and filtered through a glass wool plug under argon into another flask. This solution was used directly for the subsequent silylcupration reaction without isolation of the product.

(b) Dimethylphenylsilyllithium. Dimethylphenylsilyl chloride (3.4 g, 20 mmol) was stirred with lithium (42 mg, 60 mmol) in THF under argon for 24 h. After the reaction was complete, the red solution was decanted via a U-tube to another flask. The red solution is stable for several weeks when kept under argon in a freezer at $-25\,^\circ C$. This solution was used directly for the subsequent silylcupration reaction without isolation of the product.

(c) Tris(trimethylsilyl)silyllithium. $(Me_3Si)_3SiLi \cdot 3THF$ was prepared as described by Gutekunst and Brook [5] from $(Me_3Si)_4Si$ prepared by the procedure of Gilman and Smith [6]. A solution of $MeLi \cdot LiBr$ complex in ether (102 ml of 1.8 *M* soln.) was added dropwise over a period of 3 h to a stirred solution of 59.1 g (0.18 mol) of $(Me_3Si)_4Si$ in 800 ml of THF at room temperature. The solvent was removed immediately and the crude product purified by extraction with 1.5 l of pentane and recrystallization in a refrigerator. Yield 80 g (92%). NMR (C_6D_6): ^1H, 0.7; $^{13}C\{^1H\}$, 7.0; $^{29}Si\{^1H\}$, -4.86 (Si-β), -187.72(Si-α).

Preparation of the silylcuprate reagents

In general, silylcuprate reagents were obtained by direct reaction of 2 equiv. of silyllithium derivative in THF with a suspension of 1 equiv. of cuprous iodide in THF at -25 to $0\,^\circ C$ under a dry argon flow and the reaction mixtures were stirred for 30 min. They were used immediately.

Cuprous iodide was purified by dissolving 13.15 g (0.069 mol) of cuprous iodide in a solution of 130 g of potassium iodide in 100 ml of water. The solution was shaken for several min with 1 g of decolorizing charcoal and filtered. Upon dilution of the filtered solution with water, pure white cuprous iodide precipitated [7]. It was dried at 120°C for at least 12 h before use.

(a) $(Me_2PhSi)_2CuLi \cdot LiI$. Dimethylphenylsilyllithium (0.20 mol) in dry THF (200 ml) was added to cuprous iodide (19 g, 0.1 mol) at 0°C under argon and the mixture was stirred for 30 min yielding reagent **1**.

(b) $(MePh_2Si)_2CuLi \cdot LiI$. Diphenylmethylsilyllithium (0.20 mol) in 150 ml of THF was added dropwise to a stirred suspension of cuprous iodide, 19 g (0.10 mol) in THF (100 ml) over 30 min yielding reagent **2**.

(c) $[(Me_3Si)_3Si]CuLi \cdot LiI$. Tris(trimethylsilyl)silyllithium (4.9 g, 10 mmol) dissolved in 25 ml of THF was added dropwise to a stirred suspension of cuprous iodide (0.95 g, 5 mmol) and stirred for an additional 30 min yielding reagent **3**.

Reaction of silylcuprates with acetylenes

(a) Me_2PhSi-trans(CH=CHn-Bu). 1-Hexyne (8.2 g, 0.1 mol) dissolved in 10 ml of THF was added slowly to **1** and the mixture was stirred for 30 min at 0°C. It was then added to a cold saturated ammonium chloride solution and extracted with ether. The organic layer was washed with water and dried over anhydrous $MgSO_4$. After removal of the solvent and distillation under reduced pressure, 17.8 g (92% yield) of Me_2PhSi-*trans*-(CH=CH-n-Bu) was recovered as a clear colorless liquid. High resolution mass spectroscopy gave a molecular ion of 218.14880, calcd. 218.1490_6. IR: (film) 1617 (C=C), 1248 ($Si-CH_3$), 1113 (Si–Ph), 991 (*trans*-CH=CH); NMR ($CDCl_3$): ^1H, 7.53–7.31 (5H, m, Ph), 6.12 (1H, dt, *J* 18.6, *trans* and 6.2 Hz, CH=CHSi), 5.75 (1H, dt, *J* 18.6 and 1.3 Hz CH=CHSi), 2.17–2.08 (2H, m, CH_2=CH), 1.42–1.20 (4H, m, CH_2CH_2), 0.89 (3H, t, *J* 7.0 Hz, CH_2Me), 0.36 (6H, s, $SiMe_2$); $^{13}C\{^1H\}$, 149.44 (C(2)), 139.37 (*i*-C), 133.85 (*m*-C), 128.81 (*p*-C), 127.73 (*o*-C), 127.26 (C(1)), 36.55(C(3)), 30.87(C(4)), 22.31(C(5)), 13.99(C(6)), −2.40(C(1′)); $^{29}Si\{^1H\}$, −12.05.

(b) Me_2PhSi-trans-(CH=CH-t-Bu). 3,3-Dimethyl-1-butyne (8.2 g, 0.1 mol) dissolved in 10 ml of THF was added slowly to **1** and the mixture was stirred for 30 min at 0°C. After the usual work-up, 15.5 g (80% yield) of $MePh_2Si$-*trans*-(CH=CH-t-Bu) (b.p. 72–73°C/1 mmHg) was recovered as a clear colorless liquid. High resolution mass spectroscopy gave a molecular ion of 218.1490_7, calcd. 218.1490_6. IR (film): 1611 (C=C), 1248 ($Si-CH_3$), 1113 (Si–Ph), 995 (*trans*-CH=CH). NMR ($CDCl_3$): ^1H, 7.54–7.29 (5H, m, Ph), 6.13 (1H, d, *J* 19.0 Hz, CH=CHSi), 5.65 (1H, d, *J* 19.0 Hz, CH=CHSi), 1.01 (9H, s, t-Bu), 0.31 (6H, s, $SiMe_2$); $^{13}C\{^1H\}$, 159.61 (C(2)), 139.66 (*i*-C), 133.88 (*m*-C), 128.77 (*p*-C), 127.7 (*o*-C), 120.38 (C(1)), 35.22 (C(3)), 29.10 (C(4)), −2.34 (C(1′)); $^{29}Si\{^1H\}$, −11.19.

(c) Me_2PhSi-trans-(CH=CHPh). Phenylacetylene (10.2 g, 0.1 mol) in 10 ml of THF was added to **1** at 0°C. The reaction mixture was stirred for 30 min and then hydrolyzed with cold, saturated NH_4Cl. The organic layer was extracted with ether, washed with water and dried over anhydrous $MgSO_4$. Removing the solvent on the vacuum line, followed by distillation under reduced pressure yielded 15.1 g (72%) of Me_2PhSi-*trans*-(CH=CHPh) (b.p. 133–135°C/1 mmHg) as a colorless liquid. High resolution mass spectroscopy gave a molecular ion of 238.1175, calcd. 238.1177. IR (film): 1605 (C=C), 1249 ($Si-CH_3$), 1113 (Si–Ph), 990 (*trans*-CH=CH); NMR ($CDCl_3$): ^1H 7.58–7.27 (10H, m, Ph), 6.94 (1H, d, *J* 19.1 Hz, CH=CHSi), 6.58 (1H,

d, *J* 19.1 Hz, CH=CHSi), 0.43 (6H, s, $SiMe_2$); $^{13}C\{^1H\}$, 145.35 (C(2)), 138.48, 138.19, 133.91 126.52, 129.04, 128.49, 128.13, 127.83 (phenyl region), 127.03 (C(1)), −2.52 (C(1′)); $^{29}Si\{^1H\}$, −10.34.

(d) $MePh_2Si$-trans-(CH=CH-n-Bu). 1-Hexyne (4.1 g, 0.05 mol) in 10 ml of THF was added slowly to **2** and then the mixture was stirred for 30 min at 0°C. After work-up, 11 g (78% yield) of $MePh_2Si$-*trans*-(CH=CH-n-Bu) was recovered as a light yellow liquid. (b.p. 115–117°C/1 mmHg). High resolution mass spectroscopy gave a molecular ion of 280.1640, calcd. 280.1647. IR (film): 1616 (C=C), 1250 ($Si{-}CH_3$), 1112 (Si–Ph), 994 (*trans*-CH=CH).; NMR ($CDCl_3$): ^1H, 7.54–7.29 (10H, m, Ph), 6.17 (1H, dt, *J* 18.6 and 6.1 Hz, CH=CHSi), 5.95 (1H, dt, *J* 18.6 and 1.3 Hz, CH=CHSi), 2.22–2.15 (2H, m, $CH_2CH{=}CH$), 1.43–1.26 (4H, m, CH_2CH_2), 0.89 (3H, t, *J* 7.1 Hz, CH_2Me), 0.59 (3H, s, SiMe); $^{13}C\{^1H\}$, 151.66 (C(2)), 137.21 (*i*-C), 134.88 (*m*-C), 129.12 (*p*-C), 127.82 (*o*-C), 125.14 (C(1)), 36.66 (C(3)), 30.79 (C(4)), 22.32 (C(5)), 13.94 (C(6)), −3.67 (C(1)′)); $^{29}Si\{^1H\}$, −15.42.

(e) $MePh_2Si$-trans-(CH=CH-t-Bu). 3,3-Dimethyl-1-butyne (4.1 g, 0.05 mol) in 10 ml of THF was added to **2** dropwise and the reaction mixture stirred for 30 min at 0°C. Typical work-up and distillation under reduced pressure yielded 9.8 g (70%) of $MePh_2Si$-*trans*-(CH=CH-t-Bu) (b.p. 100–101°C/1 mmHg) as a colorless liquid. High resolution mass spectroscopy gave a molecular ion of 280.1647_5, calcd. 280.1647. IR (film): 1606 (C=C), 1251 ($Si{-}CH_3$), 1112 (Si–Ph), 998 (*trans*-CH=CH); NMR ($CDCl_3$): ^1H, 7.54–7.28 (10H, m, Ph), 6.21 (1H, d, *J* 19.0 Hz, CH=CHSi), 5.86 (1H, d, *J* 19.0 Hz, CH=CHSi), 1.03 (9H, s, t-Bu), 0.60 (3H, s, SiMe); $^{13}C\ \{^1H\}$, 161.62 (C(2)), 137.31 (*i*-C), 134.84 (*m*-C), 129.07 (*p*-C), 127.75 (*o*-C), 118.45 (C(1)), 35.42 (C(3)), 29.05 (C(4)), −3.56 (C(1′)); $^{29}Si\{^1H\}$, −14.69.

(f) $MePh_2Si$-trans-(CH=CHPh). Phenylacetylene (5.1 g, 0.05 mol) dissolved in 10 ml of THF was added to **2** and the mixture stirred for 30 min at 0°C. Aqueous work-up as before and distillation under reduced pressure gave 9.1 g (61% yield) of $MePh_2Si$-*trans*-(CH=CHPh) as a viscous light yellow liquid (b.p. 181–183°C/1 mmHg). High resolution mass spectroscopy gave an observed molecular ion of 300.1342_0, calculated 300.1334. IR (film): 1604 (C=C), 1251 ($Si{-}CH_3$), 1113 (Si–Ph), 991 (*trans*-CH=CH); NMR ($CDCl_3$): ^1H, 7.58–7.29 (15H, m, Ph), 6.97 (1H, d, *J* 19.1 Hz, CH=CHSi), 6.74 (1H, d, *J* 19.1 Hz, CH=CHSi), 0.69 (3H, s, SiMe); $^{13}C\{^1H\}$, 147.30 (C(2)), 138.05, 136.43, 134.91, 129.34, 128.44, 128.33, 127.88, 126.63 (phenyl region), 124.90 (C(1)), −3.63 (C(1′)); $^{29}Si\{^1H\}$, −13.85.

(g) $(Me_3Si)_3Si$-trans-(CH=CH-n-Bu). 1-Hexyne (0.41 g, 0.005 mol) dissolved in 10 ml of THF was added slowly to **3** at 0°C, hydrolyzed with cold, saturated ammonium chloride solution, extracted with ether, washed with water and then dried over anhydrous $MgSO_4$. The solvent was removed on a rotary evaporator and the residue chromatographed on silica gel eluting with light petroleum/ether (15/1, v/v) to yield 1.3 g (80%) of $(Me_3Si)_3Si$-*trans*-(CH=CH-n-Bu). Attempts to obtain high resolution mass spectra were unsuccessful due to the ease of fragmentation of compounds containing the tris(trimethylsilyl) group. The fragmentation pattern obtained did show peaks characteristic for the material. IR (CCl_4): 1600 (C=C), 1240 ($SiCH_3$), 970 (*trans*-CH=CH). NMR ($CDCl_3$): ^1H, 5.99 (1H, dt, *J* 18.1 and 6.5 Hz, CH=Si), 5.49 (1H, dt, *J* 18.1 and 1.4 Hz, CH=CHSi), 2.16–2.08 (2H, m, $CH_2CH{=}$), 1.41–1.29 (4H, m, CH_2CH_2), 0.90 (3H, t, *J* 7.1 Hz, CH_2CH_3), 0.16 (27H, s, $SiMe_3$); $^{13}C\{^1H\}$, 149.5 (C(2)), 120.47 (C(1)), 37.38 (C(3)), 31.44 (C(4)), 22.10 (C(5)), 13.91 (C(6)), 0.81 (C(1′)); $^{29}Si\{^1H\}$, −12.9 (Si-β), −86.04 (Si-α).

(h) $(Me_3Si)_3Si$-trans-(CH=CH-t-Bu). 3,3-Dimethyl-1-butyne (0.41 g, 0.005 mol) dissolved in 10 ml of THF was added to **3** at 0°C and stirred for 30 min. Work-up of the reaction as above gave 1.2 g (72% yield) of $(Me_3Si)_3Si$-*trans*-(CH=CH-t-Bu). Attempts to obtain high resolution mass spectra were unsuccessful due to the ease of fragmentation of compounds containing the tris(trimethylsilyl) group. The fragmentation pattern obtained did show peaks characteristic for the material. IR (CCl_4): 1600 (C=C), 1230 ($SiCH_3$), 970 (*trans*-CH=CH). NMR ($CDCl_3$): ^1H, 6.03 (1H, d, J 18.7 Hz, CH=CHSi), 0.98 (9H, s, CMe_3), 0.16 (27H, s, $SiMe_3$); $^{13}C\{^1H\}$, 160.06 (C(2)), 113.16 (C(1)), 35.79 (C(3)) 29.19 (C(4)), 0.77 (C(1′)); $^{29}Si\{^1H\}$, -12.90 (Si-β), -85.14 (Si-α).

(i) $(Me_3Si)_3Si$-trans-(CH=CHPh). Phenylacetylene (0.51 g, 0.005 mol) dissolved in 10 ml of THF was added to **3** at 0°C with stirring. The reaction was worked up as above yielding 1.1 g (63%) of $(Me_3Si)_3Si$-*trans*-(CH=CHPh). Attempts to obtain high resolution mass spectra were unsuccessful due to the ease of fragmentation of compounds containing the tris(trimethylsilyl) group. The fragmentation pattern obtained did show peaks characteristic for the material. IR (CCl_4): 1600 (C=C), 1240 ($SiCH_3$), 980 (*trans*-CH=CH). NMR ($CDCl_3$): ^1H, 7.44–7.18 (5H, m, Ph), 6.90 (1H, d, J 18.2 Hz, CH=CHSi), 6.44 (1H, d J 18.2 Hz, CH=CHSi), 0.22 (27H, s, $SiCH_3$); $^{13}C\{^1H\}$, 145.53 (C(2)), 139.11 (*i*-C), 128.51 (*o*-C) 127.43 (*p*-C) 125.99 (*m*-C), 122.79 (C(1)), 0.91 (C(1′)); $^{29}Si\ \{^1H\}$ -12.44 (Si-β), -83.41 (Si-α).

Acknowledgments

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