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Titanocene-Catalyzed Double Silylation of Dienes and Aryl Alkenes with Chlorosilanes

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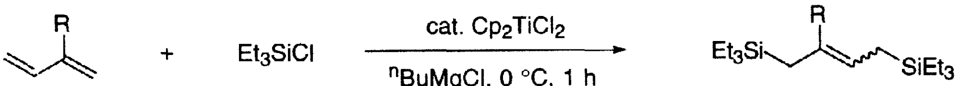
Abstract

Double silylation of 1,3-butadienes with chlorosilanes was found to proceed by using titanocene dichloride as the catalyst in the presence of ^{n}BuMgCl, giving rise to 1,4-disilylated 2-butenes in good yields. Aryl substituted alkenes also afforded 1,2-disilylated products under similar conditions. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Alkenes; Dienes; Chlorosilanes; Double Silylation; Grignard reagents; Titanium and compounds

Of particular importance among various silylation reactions is the double silylation of unsaturated hydrocarbons, which enables concomitant introduction of two silyl groups onto carbon centers. This reaction has been studied extensively using late transition metal catalysts, such as palladium and platinum complexes, and employing disilanes or hydrosilanes as the silylating reagents.[1] We report herein the first example of a metal-catalyzed double silylation of dienes and alkenes with chlorosilanes,[2] which proceeds under mild conditions by the use of Cp_2TiCl_2 in the presence of ^{n}BuMgCl.[3]

For example, into a mixture of isoprene (3.12 mmol), chlorotriethylsilane (2.2 equiv, 6.86 mmol) and titanocene dichloride (0.05 equiv) was added a THF solution of ^{n}BuMgCl (2.2 equiv, 0.9 M, 7.6 mL) at 0 °C. The solution was stirred for 1 h and the product was extracted with ether. The NMR analysis of the crude product indicated the formation of 1,4-bis(triethylsilyl)-2-butene **1a** in 91% yield (*E*/*Z* = 91/9)[4] (eq 1). Under similar conditions, 1,3-butadiene afforded **1b** in 68% yield,[5] whereas 2,3-dimethylbutadiene failed to give the corresponding disilylated product. When chlorodimethylphenylsilane (3 equiv) and ^{n}BuMgCl (3 equiv) were used, **1c** was obtained in 78% yield (eq 2).



(1)

1a, 91% [*E*/*Z* = 91/9], R = Me
1b, 68% [*E*/*Z* = 60/40], R = H

(2)

1c, 78% [*E*/*Z* = 69/31]

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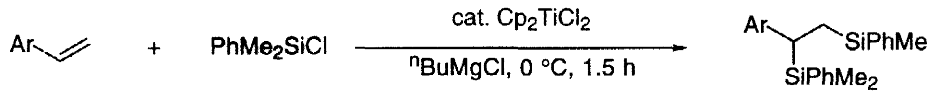
We then applied this procedure to the double silylation of alkenes. Under the same conditions as those of eq 2, *p*-chlorostyrene afforded **2a** in only 29% yield along with a substantial amount of Me_2PhSi^nBu. This result suggests that silylation of *p*-chlorostyrene is slow and competes with the direct reaction of $Me_2PhSiCl$ with ^nBuMgCl.[6] This problem was practically overcome by using a large amount of the catalyst and by adopting a dropwise addition procedure as follows. Into a mixture of *p*-chlorostyrene (2.02 mmol) and ^nBuMgCl (3.0 equiv) in THF (6.7 mL) was added a THF solution (10 mL) containing $Me_2PhSiCl$ (3.0 equiv) and Cp_2TiCl_2 (0.15 equiv) over a period of 30 min at 0 °C. After stirring the solution for another 1 h, **2a** was formed in 72% yield (eq 3).[7] In a similar manner **2b** was formed in 64% yield from styrene, whereas double silylation did not proceed with alkenes having no aromatic substituent such as 1-octene.



(3)

2a, 72%, Ar = *p*-ClC$_6$H$_4$
2b, 64%, Ar = Ph

The present titanocene-catalyzed reaction provides a new and synthetically useful method for double silylation of dienes and aryl alkenes with chlorosilanes. Studies on the mechanism of this reaction are currently in progress.

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References and Notes

[1] For a review, see: Horn KA. Chem. Rev. 1995;95:1317-1350. See also: Sakaki S, Ogawa M, Musashi Y. J. Organomet. Chem. 1997;535:25-28 and references therein.

[2] As the catalytic silylation of alkenes with chlorosilanes, we have revealed that terminal alkenes react with chlorosilanes in the presence of a Grignard reagent employing a catalytic amount of Cp_2ZrCl_2 to give monosilylated products (alkenyl and/or allylsilanes): Angew. Chem., Int. Ed. Engl. in press. For a unique reaction of $Cl(SiMe_2)_2Cl$ with acetylenes catalyzed by Pd complexes, see: Tanaka Y, Yamashita H, Tanaka M. Organometallics 1995;14:530-541.

[3] We have also found that double alkylation of aryl alkenes with alkyl halides proceeds under similar conditions to give 1,2-dialkylated products: J. Am. Chem. Soc., in press.

[4] The products **1a-c** and **2b** are known compounds and their yields and *E/Z* ratios were determined by NMR except the case of **1b**. The stereochemistry of **1b** was deduced by comparison of its ^{1}H and ^{13}C NMR spectra with those of a related compound $Me_3SiCH_2CH{=}CHCH_2SiMe_3$ (Marciniec B, Pietraszuk C, Foltynowicz Z. J. Organomet. Chem. 1994;474:83-87), since sufficient spectral data are not available for **1b**. The products **1a-c** (as a mixture of stereoisomers) and **2a**, **b** were obtained in pure form by HPLC in 86%, 62%, 76%, 66%, 54% yields, respectively.

[5] The reaction was performed by adding Cp_2TiCl_2 into a THF solution of Et_3SiCl, ^nBuMgCl, and butadiene, which was condensed at 0 °C under slightly reduced pressure, in a glass vessel equipped with a dry ice condenser.

[6] The direct reaction of Et_3SiCl with ^nBuMgCl is negligibly slow under the conditions employed; however, Et_3SiCl afforded only poor yields of the desired products (<10%) when styrenes were used as the substrates.

[7] **2a**: IR (neat) 3068, 2955, 1489, 1427, 1114, 1096, 863, 836, 811, 775, 729, 700 cm^{-1}; ^{13}C NMR (100 MHz, CDCl$_3$) δ 142.3, 138.8, 136.7, 133.9, 133.2, 129.7, 129.0, 128.8, 128.5, 127.6, 127.4, 127.3, 30.7, 15.4, -1.9, -2.9, -4.2, -5.7; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.38-7.30 (m, 10H), 7.11 (d, J = 8.5 Hz, 2H), 6.81 (d, J = 8.5 Hz, 2H), 2.30 (dd, J = 3.4, 11.8 Hz, 1H), 1.23 (dd, J = 11.8, 15.1 Hz, 1H), 1.17 (dd, J = 3.4, 15.1 Hz, 1H), 0.26 (s, 3 H), 0.17 (s, 3 H), 0.03 (s, 3 H), 0.02 (s, 3 H); MS (EI) *m/z* (relative intensity, %, ^{35}Cl) 408 (M$^+$, 1), 238 (24), 223 (65), 135 (100), 107 (16), 105 (14). HRMS calcd for $C_{24}H_{29}Si_2Cl$ 408.1496, found 408.1506; Anal. Calcd for $C_{24}H_{29}Si_2Cl$: C, 70.46; H, 7.15. Found: C, 70.41; H, 7.22.