

Tetrahedron Letters 39 (1998) 9697-9698

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

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Received 1 September 1998; revised 2 October 1998; accepted 16 October 1998

## Abstract

Double silylation of 1,3-butadienes with chlorosilanes was found to proceed by using titanocene dichloride as the catalyst in the presence of "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 silulation reactions is the double silulation of unsaturated hydrocarbons, which enables concomitant introduction of two silul 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 silulating reagents.<sup>[1]</sup> We report herein the first example of a metal-catalyzed double silulation of dienes and alkenes with chlorosilanes,<sup>[2]</sup> which proceeds under mild conditions by the use of  $Cp_2TiCl_2$  in the presence of "BuMgCl.<sup>[3]</sup>

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 "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)<sup>[4]</sup> (eq 1). Under similar conditions, 1,3-butadiene afforded **1b** in 68% yield,<sup>[5]</sup> whereas 2,3-dimethylbutadiene failed to give the corresponding disilylated product. When chlorodimethylphenylsilane (3 equiv) and "BuMgCl (3 equiv) were used, **1c** was obtained in 78% yield (eq 2).

0040-4039/98/\$ - see front matter © 1998 Elsevier Science Ltd. All rights reserved. *PII:* S0040-4039(98)02227-8 We then applied this procedure to the double silvlation 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<sub>2</sub>PhSi<sup>n</sup>Bu. This result suggests that silvlation of *p*-chlorostyrene is slow and competes with the direct reaction of Me<sub>2</sub>PhSiCl with <sup>n</sup>BuMgCl.<sup>(6)</sup> 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 <sup>n</sup>BuMgCl (3.0 equiv) in THF (6.7 mL) was added a THF solution (10 mL) containing Me<sub>2</sub>PhSiCl (3.0 equiv) and Cp<sub>2</sub>TiCl<sub>2</sub> (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).<sup>[7]</sup> In a similar manner **2b** was formed in 64% yield from styrene, whereas double silvlation did not proceed with alkenes having no aromatic substituent such as 1-octene.

Ar + PhMe<sub>2</sub>SiCl  $\xrightarrow{\text{cat. Cp}_2\text{TiCl}_2}$   $\xrightarrow{\text{Ar}}$  SiPhMe<sub>2</sub> (3) SiPhMe<sub>2</sub> 2a, 72%, Ar = p-ClC<sub>6</sub>H<sub>4</sub> 2b, 64%, Ar = Ph

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

Acknowledgment. This work was supported, in part, by a Grant-in-Aid from the Ministry of Education, Science, Sports and Culture, Japan. Thanks are due to the Instrumental Analysis Center, Faculty of Engineering, Osaka University. J.T. is grateful to JSPS for the Research Fellowship Program for Young Scientists.

## **References and Notes**

- 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<sub>2</sub>ZrCl<sub>2</sub> to give monosilylated products (alkenyl and/or allylsilanes): Angew. Chem., Int. Ed. Engl. in press. For a unique reaction of Cl(SiMe<sub>2</sub>)<sub>2</sub>Cl 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 1,2dialkylated products: J. Am. Chem. Soc., in press.
- [4] The products la-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 <sup>1</sup>H and <sup>13</sup>C NMR spectra with those of a related compound Me<sub>3</sub>SiCH<sub>2</sub>CH=CHCH<sub>2</sub>SiMe<sub>3</sub> (Marciniec B, Pietraszuk C, Foltynowicz Z. J. Organomet. Chem. 1994;474:83-87), since sufficient spectral data are not available for 1b. The products la-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<sub>2</sub>TiCl<sub>2</sub> into a THF solution of Et<sub>3</sub>SiCl, "BuMgCl, 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 "BuMgCl 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<sup>-1</sup>; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  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; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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, %, <sup>35</sup>Cl) 408 (M<sup>+</sup>, 1), 238 (24), 223 (65), 135 (100), 107 (16), 105 (14). HRMS calcd for C<sub>24</sub>H<sub>29</sub>Si<sub>2</sub>Cl 408.1496, found 408.1506; Anal. Calcd for C<sub>24</sub>H<sub>29</sub>Si<sub>2</sub>Cl; C, 70.46; H, 7.15. Found: C, 70.41; H, 7.22.