Norbornadiene as an Efficient Hydrogen Scavenger for the Palladium-Catalyzed Conversion of Hydrosilanes to Alkoxy Silanes

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Abstract: A palladium-catalyzed mild and efficient method for the alcoholysis of hydrosilanes containing a C=C bond in the presence of norbornadiene (NBD) is reported. The highly strained NBD acts as a hydrogen scavenger, which abstracts the hydrogen produced during the process, protecting the C=C bond from being hydrogenated.

(Isopropoxy)vinylosilanes 1 have been shown to be useful precursors of synthetic interest.1 Vinlyc silyl hydrides 2 or siloxane-tethered cyclophanes 3 are readily obtained from the corresponding 1 that can be easily accessible from the nickel-catalyzed olefination of dithioacetals with (PrO)Me2SiCH2MgCl (Scheme 1).1,2 Recently, we were interested in incorporating these vinylsilane moieties into the inorganic–organic hybrid materials by the sol gel technique. Due to the poor reactivity of the isoproxy moiety under the reaction conditions, the process resulted in the formation of the corresponding cyclic dimer 3 in reasonably good yield.1e

A more viable alternative would be to convert the isoproxy group into a less bulky alkoxy group. However, conventional methods such as the acid-catalyzed isopropoxy group into a less bulky alkoxy group. How-

\[
R_3Si-H + ROH \rightarrow R_3Si-OR + H_2
\]

(1)

tion of the alkoxy silanes.3 PdCl2 has been recently reported to be an efficient catalyst for this purpose.4 Since hydrogen is formed as the byproduct from this reaction and palladium is an active catalyst for hydrogenation, substrates containing a double bond may also be reduced under these conditions. It is envisaged that a strained olefin would be able to trap the liberated hydrogen so that this side reaction can be avoided. We report here an efficient PdCl2-catalyzed conversion of vinylsilyl hydrides to the corresponding silyl ethers using norbornadiene (NBD) as a hydrogen scavenger.

This strategy was tested by treating β-styryldimethylosilane (4) with different types of alcohols in the presence

TABLE 1. PdCl2-Catalyzed Reaction of 4 and 2 with ROH in the Presence of NBD

<table>
<thead>
<tr>
<th>entry</th>
<th>reaction time (h)</th>
<th>product</th>
<th>% yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>5a (R = Me)</td>
<td>79</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>5b (R = Et)</td>
<td>76</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>5c (R = i-Pr)</td>
<td>70</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>5d (R = s-Bu)</td>
<td>72</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>5e (R = t-Bu)</td>
<td>65</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>5f (R = Bn)</td>
<td>72</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>5g (R = Ph)</td>
<td>a</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>5h (R = Ac)</td>
<td>b</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>6a</td>
<td>79</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>6b</td>
<td>78</td>
</tr>
<tr>
<td>11</td>
<td>2</td>
<td>6c</td>
<td>92c</td>
</tr>
</tbody>
</table>

a Starting material 4 was recovered. b Decomposition occurred leading to insoluble solid product, which was not characterized. c Reaction carried out in benzene.

of 1.5 equiv of NBD and a catalytic amount of PdCl₂ (Table 1). After the usual workup, alkoxy silyl siloxanes 5 were obtained in good yield. No hydrogen evolution was noticed from the reaction, which is in contrast to the conventional systems in which the completion of the reaction was monitored by the cessation of evolved hydrogen. As can be seen from Table 1, the reaction proceeded nicely with primary and secondary alcohols. Longer reaction time was required for tertiary alcohol. Phenol was unreactive under these conditions, starting material 4 being recovered. When acetic acid was employed, decomposition occurred, giving an insoluble solid mixture that was not characterized.

An extension of this procedure to the synthesis of bis-ethoxysilanes 6a–c proceeded smoothly. Three equivalents of NBD was used to trap the liberated hydrogen leading to 6 in satisfactory yield. In the absence of NBD, when 2a was treated with PdCl₂ in EtOH, a 1:1 mixture of 6a and 7 was obtained. The results are summarized in Table 1. Bis-ethoxysilanes 6a underwent rapid polymerization even at low temperature (−15 °C) in CDCl₃. Presumably, a trace amount of acid or water may catalyze decomposition of 6a.

A terminal vinyl group was also found to be stable under these conditions. Thus, reaction of 2c in the presence of an equal molar amount of styrene, under the same reaction conditions, afforded 6c in 92% yield along with the quantitative recovery of styrene (>98% by GC). This observation suggests that NBD could serve as an efficient hydrogen trapping agent and prevent the hydrogenation of a variety of alkenes.

In summary, we have demonstrated a convenient procedure for the synthesis of alkoxy silanes by means of PdCl₂-catalyzed alcoholysis of the corresponding silyl hydrides in the presence of NBD. NBD apparently has played a significant role in trapping the liberated hydrogen. No reduction product was obtained at all. A variety of alcohols can be used for this purpose. Further applications of this reaction in organic synthesis and in sol gel chemistry are in progress in our laboratory.

Experimental Section

General Procedure for the Preparation of 5. To a solution of 4 (1 equiv) and NBD (1.5 equiv) in absolute ethanol (15 equiv) under N₂ was added a catalytic amount of palladium(II) chloride (0.2 mol%). The mixture was stirred at room temperature for the desired time. The resulting liquid was removed from the insoluble palladium salts by filtering through a filter cartridge, followed by removal of the solvent, NBD, and its hydrogenated products in vacuo to yield the title compounds.

General Procedure for the Preparation of 6a–c. In a manner similar to that described in the general procedure for 5a–f, a mixture of bis[β-(dimethylsilyl)vinyl]arenes 2a–c (1 equiv), NBD (3.0 equiv), a catalytic amount of palladium(II) chloride (0.4 mol%), and absolute ethanol (15 equiv) in dry THF or benzene under N₂ was stirred at room temperature for 2 h. (Note: For the preparation of 6a, 30 equiv of ethanol was used and THF was added so as to be easily solvable in ethanol.) After the usual workup, 6a was obtained.

Control experiments with styrene were carried out in a similar manner.

Compounds 5a: ¹H NMR (400 MHz, CDCl₃) δ 0.26 (s, 6 H), 3.46 (s, 3 H), 6.41 (d, J = 19.3 Hz, 1 H), 6.99 (d, J = 19.3 Hz, 1 H), 7.25–7.29 (m, 1 H), 7.30–7.36 (m, 2 H), 7.42–7.48 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ −2.3, 50.5, 125.8, 126.6, 128.4, 128.6, 137.9, 145.8; IR (neat) 3064, 3029, 2963, 2908, 2834, 1605, 1254, 1194, 1089, 993, 846, 783, 734 cm⁻¹; HRMS m/z (EI) for C₁₂H₁₈O₄Si (M⁺) calculated 212.1072, found 212.1081.

Compounds 5b: ¹H NMR (400 MHz, CDCl₃) δ 0.26 (s, 6 H), 1.2 (t, J = 7.0 Hz, 3 H), 3.37 (q, J = 7.0 Hz, 2 H), 6.42 (d, J = 19.3 Hz, 1 H), 6.98 (d, J = 19.3 Hz, 1 H), 7.25–7.28 (m, 1 H), 7.29–7.36 (m, 2 H), 7.41–7.48 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ −17.1, 18.5, 58.5, 125.6, 126.5, 128.3, 128.5, 138.0, 145.5; IR (neat) 3065, 3029, 2971, 2901, 2878, 1608, 1254, 1174, 991, 946, 838, 782, 735 cm⁻¹; HRMS m/z (EI) for C₂₆H₃₈O₄Si (M⁺) calculated 406.2127, found 406.2132.

Compounds 5c: ¹H NMR (400 MHz, CDCl₃) δ 0.26 (s, 6 H), 1.16 (d, J = 6.1 Hz, 6 H), 4.06 (sept, J = 6.1 Hz, 1 H), 6.46 (d, J = 19.3 Hz, 1 H), 6.99 (d, J = 19.3 Hz, 1 H), 7.25–7.28 (m, 1 H), 7.29–7.36 (m, 2 H), 7.41–7.48 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ −0.9, 26.2, 65.7, 127.1, 127.9, 128.8, 129.1, 138.8, 145.6; IR (neat) 3065, 3029, 2974, 2935, 2878, 1608, 1253, 1174, 1128, 1093, 983, 849, 781, 736 cm⁻¹; HRMS m/z (EI) for C₂₆H₃₈O₄Si (M⁺) calculated 406.2127, found 406.2132.

Compounds 5d: ¹H NMR (400 MHz, CDCl₃) δ 0.26 (s, 6 H), 0.87 (d, J = 7.4 Hz, 3 H), 1.14 (d, J = 6.1 Hz, 3 H), 1.35–1.55 (m, 2 H), 3.70–3.80 (m, 1 H), 6.44 (d, J = 19.3 Hz, 1 H), 6.96 (d, J = 19.3 Hz, 1 H), 7.24–7.26 (m, 1 H), 7.29–7.36 (m, 2 H), 7.41–7.47 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ −11.1, −10.6, 10.3, 23.4, 32.3, 70.3, 126.6, 127.3, 128.3, 128.5, 138.1, 145.2; IR (neat) 3065, 3029, 2970, 2934, 2879, 1608, 1253, 1172, 1133, 1051, 1012, 993, 850, 782, 737 cm⁻¹; HRMS m/z (EI) for C₃₀H₄₄O₄Si (M⁺) calculated 440.2440, found 440.2431.

Compounds 5e: ¹H NMR (400 MHz, CDCl₃) δ 0.26 (s, 6 H), 1.27 (s, 9 H), 6.47 (d, J = 19.2 Hz, 1 H), 6.92 (d, J = 19.2 Hz, 1 H), 7.23–7.28 (m, 1 H), 7.29–7.36 (m, 2 H), 7.42–7.47 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 1.2, 32.1, 72.6, 126.5, 128.1, 128.5, 129.5, 138.3, 143.9; IR (neat) 3065, 3029, 2970, 2988, 1608, 1266, 1253, 1108, 1026, 993, 883, 781, 738 cm⁻¹; HRMS m/z (EI) for C₂₆H₃₈O₄Si (M⁺) calculated 424.2140, found 424.2141.
Compound 6c: $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 0.27 (s, 12 H), 1.21 (t, $J$ = 7.0 Hz, 6 H), 3.72 (q, $J$ = 7.0 Hz, 4 H), 6.46 (d, $J$ = 19.2 Hz, 2 H), 7.01 (d, $J$ = 19.2 Hz, 2 H), 7.40–7.65 (m, 8 H); IR (neat) 3023, 2964, 2897, 1604, 1495, 1394, 1251, 1107, 1077, 990, 945, 836, 791 cm$^{-1}$.

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Supporting Information Available: $^{13}$C NMR spectra for 5a–f and 6a,b. This material is available free of charge via the Internet at http://pubs.acs.org.

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