Anti-Hydrosilylation Reactions of Alkynes Catalyzed by Palladium Nitrate

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Hydrosilylation of alkynes catalyzed by transition metal complexes is the most effective method for the preparation of vinylsilanes that might be the excellent precursors to silicon polymers.1 Although thermodynamically stable syn-hydrosilylation products are generally observed in this type of reactions,2 changing catalyst and reaction conditions can lead to an unusually high degree of anti-hydrosilylation.3,4 We performed the hydrosilylation reactions of RC≡CH (R = Ph, C_{10}H_{21}) with R'_{3}SiH (R'={Et, t-BuMe_{2}, Me}_{3}Ph) in the presence of 2 mol % palladium nitrate at room temperature. Initially, Pd(NO_{3})_{2}-phosphine was used as the catalyst in order to expand our previous works since it had been found to be an effective catalyst for the activation of both aromatic and aliphatic carbon-hydrogen bonds in our laboratory.5 However, palladium (II) was reduced to palladium (0) in the presence of phosphine in this work and the reaction did not proceed further. Here we report the unusual anti-hydrosilylation reactions of alkynes with R'_{3}SiH using Pd(NO_{3})_{2} as the catalyst without phosphine, which has rarely been reported in this kind of reactions previously.

The cis and trans products (1 and 2, respectively) were obtained along with dialkynylated silanes (3) as described in Scheme 1 and the results are summarized in Table 1. As shown in Table 1, it is unusual that thermodynamically less stable cis isomers 1 derived from anti-hydrosilylation were obtained almost exclusively over trans isomers 2 for the entries 1, 2, 4 and 5 with selectivity of 96-99%. More surprisingly, only anti-hydrosilylation product 1 was observed at the beginning of the reaction in GC analysis and it was slowly converted to 2, of which ratios reached 1 to 4% at most and the ratios were unchanged since then. Usually, the reaction mechanism has been reported to proceed through the initial syn-addition of the hydrosilanes to alkynes giving the trans product, followed by isomerization to the cis product, even in the case of the other predominant anti-hydrosilylation reactions.3,7,8 In fact, the isomerization of cis product to trans product was first observed by Watanabe et al., but the selectivity was not high enough.4 The investigation of the reaction mechanism in this work is in progress and will be published later.

It is noteworthy that the above results were observed only for the aliphatic silanes. In the case of aromatic silane, Me_{2}PhSiH, the reactions with PhC≡CH and C_{10}H_{21}C≡CH gave 62:38 and 49:51, respectively, in the ratios of the

![Scheme 1](image)

Table 1. Hydrosilylation of alkynes with tertiary silanes in the presence of Pd(NO_{3})_{2}.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reactants</th>
<th>Reaction time (h)</th>
<th>Products ratio (%)</th>
<th>Conversion yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R R'_{3} V inyl silanes (1:2) Dialkynylated silanes (3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Phenyl Et</td>
<td>3</td>
<td>70 (96:4)</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>Phenyl t-BuMe_{2}</td>
<td>12</td>
<td>53 (99:1)</td>
<td>47</td>
</tr>
<tr>
<td>3</td>
<td>Phenyl Me_{3}Ph</td>
<td>24</td>
<td>92 (62:38)</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>C_{10}H_{21} Et</td>
<td>3</td>
<td>75 (98:2)</td>
<td>24</td>
</tr>
<tr>
<td>5</td>
<td>C_{10}H_{21} t-BuMe_{2}</td>
<td>12</td>
<td>80 (98:2)</td>
<td>19</td>
</tr>
<tr>
<td>6</td>
<td>C_{10}H_{21} Me_{3}Ph</td>
<td>24</td>
<td>91 (49:51)</td>
<td>9</td>
</tr>
</tbody>
</table>

*The reactions were carried out at room temperature in toluene. The ratio of RC≡CH/R'_{3}SiH/Pd was 1/1/0.02. *Ratios and yields (based on alkynes reacted) of vinyl silanes and dialkynylated silanes were determined by GC using n-hexadecane as an internal standard.
anti- to the syn-hydrosilylation products (entries 3 and 6). Nile and his coworkers also found the similar results that good electron-donor ligands gave the cis product while good electron-acceptor ligands gave the trans product as the major species. These facts clearly indicate that the reactions of the aliphatic silanes in this work involve stereoselective anti-hydrosilylation to give the cis products.

For the entries 4 and 5, obtained were very small amounts of byproducts (1% yield) which were not listed in Table 1. They are assumed to be dehydrogenative silylation products from their GC-MS data, and the similar reactions were reported to arise from the initial insertion of the unsaturated substrate into the M-Si bond, followed by β-hydride elimination. Although a number of bis-silylation reactions of unsaturated substrates have been reported, dialkynylated silyl products of have rarely been reported before.

In summary, we found a very simple palladium(II) compound which catalyzed hydrosilylation of alkynes with the exclusive selectivity on the anti-hydrosilylation, and the cis products derived from anti-hydrosilylation were obtained unusually at the initial stage of the reactions. Obtained were the rarely reported dialkynylated silyl products along with dehydrogenated silylation products in a small amount.

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References and Notes
6. The 'H NMR (20 MHz) spectra of vinylsilanes (1 and 2) or dialkynylated silyl compounds (3) were taken as the isomeric mixtures, and the isomers of the dialkynylated products were described as A and B, since the stereochemistry could not be determined from the NMR spectral data. (2,4-Diphenylbuta-1,3-dienyl)trimethylsilane (3a). Isomer A (62%). 'H NMR: δ 7.28(7.25, m, 10H), 7.12(δ, J = 15.8 Hz, 1H), 6.67(δ, J = 15.8 Hz, 1H), 5.98(δ, 1H, 0.88(δ, J = 7.9 Hz, 9H), 0.34(δ, J = 7.9 Hz, 6H); GC-MS: m/z 320 (M+), 291, 189, 161. Isomer B (38%). 'H NMR: δ 7.28-7.25 (m, 11H), 6.43 (δ, J = 15.8 Hz, 1H), 5.75(δ, 1H), 1.08(δ, J = 7.9 Hz, 9H), 0.82(δ, J = 7.9 Hz, 6H); GC-MS: m/z 218 (M+), 161. 2-Butyldiphenylsilane (3b). Isomer A (89%). 'H NMR: δ 7.55 (δ, J = 15.4 Hz, 1H), 7.58-7.31 (m, 5H), 5.94 (δ, J = 15.4 Hz, 1H), 0.98 (δ, 9H), 0.00 (δ, 6H); GC-MS: m/z 218 (M+), 161. 1-Butoxy-2,4-diphenylbuta-1,3-dienylmethysilane (3c). Isomer A (97%). 'H NMR: δ 6.00 (δ, J = 15.7 Hz, 1H), 5.67 (δ, J = 15.7, 6.8 Hz, 1H), 5.28 (δ, 1H), 2.27-2.15 (m, 2H), 2.13-2.05 (m, J = 6.7 Hz, 2H), 1.20-1.50 (m, 32H) 0.95 (δ, J = 7.9 Hz, 9H), 0.88 (δ, J = 6.8 Hz, 6H), 0.61 (δ, J = 7.9 Hz, 6H); GC-MS: m/z 448 (M+), 419, 391, 307, 181, 85. Isomer B (3%). 'H NMR: m/z 448 (M+), 419, 391, 307, 181, 85. (2,4-Dodecenyldiethylsilane (1f). 'H NMR: δ 6.37 (δ, J = 14.2, 7.4 Hz, 1H), 5.47 (δ, J = 14.2, 1.3 Hz, 1H), 2.11 (q, J = 7.0 Hz, 2H), 1.4-1.2 (m, 16H), 0.95-0.85 (m, 12H), 0.09 (s, 6H); GC-MS: m/z 282 (M+), 225, 99, 85. (2,4-Dodecenyldiethylsilane (1e). 'H NMR: δ 6.60 (δ, J = 15.7 Hz, 1H), 5.67 (δ, J = 15.7, 6.8 Hz, 1H), 5.36 (s, 1H), 1.4-1.2 (m, 32H), 0.95-0.85 (m, 15H), 0.09 (s, 6H); GC-MS: m/z 448 (M+), 391. Isomer B (7%). 'H NMR: m/z 448 (M+), 391. (Z)-Dodec-1-enylidemethylphenylsilane (1d). 'H NMR: δ 6.76-6.75 (m, 5H), 6.44 (dt, J = 14.0, 7.4 Hz, 1H), 5.63 (dt, J = 14.0, 1.1 Hz, 1H), 2.19 (q, J = 7.0 Hz, 2H), 1.4-1.2 (m, 16H), 0.87 (q, J = 6.9 Hz, 3H), 0.39 (s, 6H); GC-MS: m/z 302 (M+), 287, 161, 135. (E)-Dodec-1-enylidemethylphenylsilane (2f). 'H NMR: δ 7.47-7.3 (m, 5H), 6.14 (dt, J = 18.5, 6.2 Hz, 1H), 5.74 (dt, J = 18.6, 1.4 Hz, 1H), 2.19 (q, J = 7.0 Hz, 2H), 1.4-1.2 (m, 16H), 0.87 (q, J = 6.9 Hz, 3H), 0.34 (s, 6H); GC-MS: m/z 302 (M+), 287, 161, 135.