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Citation

CHEMICAL & PHARMACEUTICAL BULLETIN, 54(11), 1622-1623

https://doi.org/10.1248/cpb.54.1622

Issue Date

2006-11

Doc URL

http://hdl.handle.net/2115/17095

Type

article

File Information

C&PB54-11.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP
Dirhodium(II) Tetrakis(perfluorobutyrate)-Catalyzed 1,4-Hydrosilylation of α,β-Unsaturated Carbonyl Compounds

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Received August 28, 2006; accepted September 6, 2006; published online September 19, 2006

The use of dirhodium(II) catalysts in the 1,4-hydrosilylation of α,β-unsaturated ketones and aldehydes was explored. Dirhodium(II) tetrakis(perfluorobutyrate), Rh₂(pfb)₄ (Ia), proved to be the catalyst of choice for this process, providing the corresponding silyl enol ethers in high yields.

Key words dirhodium(II) complex; 1,4-hydrosilylation; silyl enol ether; α,β-enone

Silyl enol ethers are useful and versatile synthetic intermediates available to the organic chemist. The catalytic 1,4-hydrosilylation of α,β-unsaturated carbonyl compounds is generally recognized as a powerful method for the direct and regioselective synthesis of silyl enol ethers. Consequently, a number of transition metal complexes based on rhodium, platinum, and copper as well as Lewis acids such as B(C₆F₅)₃ have been developed for that purpose.

Aside from their effectiveness in diazo decomposition, dirhodium(II) complexes are also recognized as Lewis acid catalysts as well as catalysts for hydrosilylation of terminal alkyynes, and enaminoids, silylformylation of terminal alkyynes, and silane alcoholysis. However, to the best of our knowledge, no examples of the dirhodium(II) complex-catalyzed 1,4-hydrosilylation of α,β-unsaturated carbonyl compounds have been reported. As part of a program to explore dirhodium(II) complex-catalyzed transformations, we wish to report herein that dirhodium(II) tetrakis(perfluorobutyrate), Rh₂(pfb)₄ (Ia), is an exceptionally effective catalyst for the 1,4-hydrosilylation of α,β-unsaturated ketones and aldehydes.

At the outset of this work, the 1,4-hydrosilylation of 2-cyclohexen-1-one (2a) with triethylsilane (3a) in the presence of 0.01 mol% of Rh₂(pfb)₄ (Ia) was examined. The reaction in dichloromethane as the solvent, without compromising product yield (entry 10). In addition to triethylsilane, a variety of monohydrosilanes such as diethylmethylsilane (3b), dimethylphenylsilane (3e), and triethoxysilane (3d) could be used in the Rh₂(pfb)₄-catalyzed 1,4-hydrosilylation of 2a (entries 11-13). On the other hand, the reaction of 2a with diphenylsilane (3e) led to the exclusive formation of the 1,2-hydrosilylation product 5, as observed in the (Ph₂P)₂RhCl-catalyzed hydrosilylation with dihydrosilanes (Chart 2).

The applicability of this catalytic system to a range of α,β-unsaturated carbonyl compounds was then investigated.

![Chart 1](image1)

![Chart 2](image2)

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Table 2. 1,4-Hydrosilylation of α,β-Unsaturated Carbonyl Compounds Catalyzed by Dirhodium(II) Carboxylates

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Rh(II) (mol%)</th>
<th>Time (h)</th>
<th>Product Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Scheme 2b</td>
<td>la (0.05)</td>
<td>0.3</td>
<td>4e (91.5%)</td>
</tr>
<tr>
<td>2</td>
<td>Scheme 2b</td>
<td>la (0.01)</td>
<td>0.5</td>
<td>4f (95%)</td>
</tr>
<tr>
<td>3</td>
<td>Scheme 2d</td>
<td>la (0.01)</td>
<td>0.5</td>
<td>4g (95%)</td>
</tr>
<tr>
<td>4</td>
<td>Scheme 2f</td>
<td>la (0.01)</td>
<td>0.5</td>
<td>4h (95%)</td>
</tr>
<tr>
<td>5</td>
<td>Scheme 1a</td>
<td>la (0.01)</td>
<td>0.3</td>
<td>4i (97%, (E^1 = 92.8))</td>
</tr>
<tr>
<td>6</td>
<td>Scheme 2g</td>
<td>la (0.01)</td>
<td>1</td>
<td>4j (94%, (E^1 = 78.2))</td>
</tr>
<tr>
<td>7</td>
<td>Scheme 2h</td>
<td>la (0.01)</td>
<td>1</td>
<td>4k (94%, (E^1 = 80.7))</td>
</tr>
<tr>
<td>8</td>
<td>Scheme 2i</td>
<td>la (0.01)</td>
<td>2</td>
<td>4l (94%, (E^1 = 81.1))</td>
</tr>
<tr>
<td>9</td>
<td>Scheme 2j</td>
<td>lb (0.1)</td>
<td>3</td>
<td>4m (95%)</td>
</tr>
<tr>
<td>10</td>
<td>Scheme 2k</td>
<td>la (0.01)</td>
<td>1</td>
<td>4n (94%, (E^1 = 94.2))</td>
</tr>
<tr>
<td>11</td>
<td>Scheme 2l</td>
<td>lb (0.1)</td>
<td>2</td>
<td>4o (95%)</td>
</tr>
</tbody>
</table>

a) All reactions were performed on a 5 mmol scale with 1.2 eq of 3a in CH₂Cl₂ under reflux. b) Isolated yield. c) Determined by \(^1\)H-NMR. d) Combined yield of 1,4-adduct and 1,2-adduct.

and the results are summarized in Table 2. The use of cyclic α,β-enones, including 2-cyclopenten-1-one (2b), 2-cyclohepten-1-one (2c), and 4,4-dimethyl-2-cyclohexen-1-one (2d), afforded the corresponding silyl enol ethers 4e—g in high yields (entries 1—3). \(^{20}\) (E)-2-Ethylidene cyclohexanone (2e) was converted to silyl enol ether 4h in high yield (entry 4). The 1,4-hydrosilylation also proceeded smoothly with mesityl oxide (2f), 3-heptene-2-one (2g), and crotonaldehyde (2h), although the products were a mixture of stereoisomers (entries 5—7). However, in the cases of benzalacetone (2i) and (E)-cinnamaldehyde (2j), containing a phenyl group at the \(\beta\)-position, reactions with 3a gave predominantly silyl enol ethers 4i, m, along with very small amounts of 1,2-hydrosilylation products 6a, b (entries 8, 10). Gratifyingly, this problem could be overcome by changing the catalyst from \(\text{Rh}_2(\text{pfb})_4\) to \(\text{Rh}_2(\text{OAc})_4\). The reactions in the presence of 0.1 mol% of \(\text{Rh}_2(\text{OAc})_4\) afforded exclusively silyl enol ethers 4l, m in high yields with no evidence of (2-hydrosilylation (entries 9, 11).

In summary, we have reported the first example of the 1,4-hydrosilylation of \(\alpha,\beta\)-unsaturated ketones and aldehydes catalyzed by dirhodium(II) complexes and have shown that \(\text{Rh}_2(\text{pfb})_4\) is an exceptionally effective catalyst for this process. The effective use of \(\text{Rh}_2(\text{OAc})_4\) as a backup catalyst for \(\text{Rh}_2(\text{pfb})_4\) was also demonstrated, in cases where \(\beta\)-phenyl substituted substrates are used. The dirhodium(II) carboxylate catalysts are air-stable, and easily handled. Further studies of the scope of the reaction as well as mechanistic studies are currently under investigation.

Acknowledgements This research was supported, in part, by a Grant-in-Aid for Scientific Research on Priority Areas "Advanced Molecular Transformations of Carbon Resources" from the Ministry of Education, Culture, Sports, Science and Technology, Japan. We thank S. Oka, M. Kiuchi, A. Maeda, H. Matsumoto and T. Hirose of the Center for Instrumental Analysis at Hokkaido University for mass measurements.

References and Notes
3) Ojima I., Kogure T., Organometallics, 1, 1390—1399 (1982).
19) Typical procedure (Table 1, entry 1): Et₃SiH (3a) (1.9 ml, 12 mmol) was added to a solution of 2-cyclohexen-1-one (2a) (960 mg, 10 mmol) and \(\text{Rh}_2(\text{pfb})_4\) (1.1 mg, 0.001 mmol, 0.001 mol%) in CH₂Cl₂ (3 ml) and the mixture was refluxed for 1 h. Evaporation in vacuo gave the crude product (2.2 g), which was purified by short-path column chromatography (5 g of WAKO-gel C-200, 94.3 : 4.7 : 1. hexane/ether/Et₃N) followed by Kugelrohr distillation (5 mmHg, 100°C) to provide 4a (2.05 g, 96%) as a colorless oil.
20) The present method was found to be somewhat sensitive to the structure of the substrate; 3-methyl-2-cyclohexen-1-one and 2-methyl-2-cyclohexen-1-one were recovered unchanged.