Synthesis of cross-conjugated trienes by rhodium-catalyzed dimerization of monosubstituted allenes

Tomoya Miura, Tsuneaki Biyajima, Takeharu Toyoshima and Masahiro Murakami*

Abstract
A rhodium(I)/dppe catalyst promoted dimerization of monosubstituted allenes in a stereoselective manner to give cross-conjugated trienes, which are different from those obtained by a palladium catalyst.

Introduction
Cross-conjugated trienes, known as [3]dendralenes [1], are attractive synthetic precursors used for consecutive double [4 + 2] cycloaddition reactions [2-4] to provide a rapid access to polycyclic carbon frameworks. Thus, a number of methods for the preparation of the parent 3-methylenepenta-1,4-diene [5] and its substituted derivatives [6-17] has been developed. Among these, transition-metal-catalyzed dimerization of allenes presents a unique entry to substituted cross-conjugated trienes. For example, a nickel(0)/triphenylphosphine complex catalyzes a dimerization reaction of 3-methylbuta-1,2-diene to afford 2,5-dimethyl-3,4-bismethylenehex-1-ene [18,19]. The nickel-catalyzed reaction, however, leads to a complex mixture of products when monosubstituted allenes such as penta-1,2-diene and 1-phenylpropa-1,2-diene are employed [20]. On the other hand, a palladium-catalyzed dimerization reaction of monosubstituted allenes produces substituted cross-conjugated trienes 2 in high yield (Scheme 1) [21]. We report here that dimerization of monosubstituted allenes is also catalyzed by a rhodium(I)/dppe complex to form cross-conjugated trienes 3, which are different from those obtained with the palladium catalyst.

Results and Discussion
We initiated our study using undeca-1,2-diene (1a) as the model substrate and a rhodium(I) complex as the catalyst (Table 1). When 1a was treated with a catalytic amount of [RhCl(cod)]2 (2.5 mol %, cod = cycloocta-1,5-diene) in toluene at 130 °C for 12 h, 2a was formed in 40% NMR yield along with another minor dimerized product (13% NMR yield) and unidentified...
compounds (Table 1, entry 1). The structure of the minor dimerized product was determined to be \((E)-10,11\text{-dimethyleneicos-8-ene} (3a)\) by \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy. Thus, the two isomeric dimers, one identical to the isomer obtained by the palladium-catalyzed reaction and the other a different isomer, were produced by the rhodium-catalyzed reaction. Next, several phosphine ligands were examined (Table 1, entries 2–5). To our delight, the use of the dppe ligand suppressed the formation of \(2a\) and the unidentified compounds, and increased the NMR yield of \(3a\) to 96% (86% isolated yield, Table 1, entry 4). A complex mixture of products was obtained when the reaction temperature was lowered from 130 °C to 90 °C (Table 1, entry 6). Moreover, the use of \(\text{[Rh(OH)(cod)]}_2\) and \(\text{Rh(acac)(cod)}\) as the precatalyst resulted in a decrease of the reaction rate (Table 1, entries 7 and 8).

Under the optimized reaction conditions using dppe as the ligand, various monosubstituted allenes \(1b\)–\(j\) were subjected to the catalytic dimerization reaction (Table 2). In most cases, essentially one isomer \(3\) was formed, and the other isomer \(2\) was barely detectable in the \(^1\text{H}\) NMR spectrum of the crude reaction mixture (<5%). Allenes \(1b\)–\(i\) possessing a primary alkyl group reacted well to afford the corresponding products \(3b\)–\(i\) in yields ranging from 63% to 90% (Table 2, entries 1–8). Functional groups such as benzyloxy, siloxy, hydroxy and cyano groups were tolerated in the alkyl chain under the reaction conditions. Cyclohexylpropa-1,2-diene (1\(j\)) possessing a secondary alkyl group also participated in the dimerization reaction (Table 2, entry 9). On the other hand, 1,1-disubstituted allenes such as 3-methylbuta-1,2-diene and 3-pentylolta-1,2-diene failed to undergo the dimerization reaction, in contrast to the nickel-catalyzed reaction [18,19].
Table 2: Synthesis of cross-conjugated trienes by the allene dimerization reaction.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>R'</th>
<th>3</th>
<th>Yield (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>1b</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;</td>
<td>H</td>
<td>3b</td>
</tr>
<tr>
<td>2</td>
<td>1c</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Ph</td>
<td>H</td>
<td>3c</td>
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<tr>
<td>3</td>
<td>1d</td>
<td>Cy</td>
<td>H</td>
<td>3d</td>
</tr>
<tr>
<td>4</td>
<td>1e</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;OBn</td>
<td>H</td>
<td>3e</td>
</tr>
<tr>
<td>5</td>
<td>1f</td>
<td>(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;OBn</td>
<td>H</td>
<td>3f</td>
</tr>
<tr>
<td>6</td>
<td>1g</td>
<td>(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;OSiMe&lt;sub&gt;2&lt;/sub&gt;-tBu</td>
<td>H</td>
<td>3g</td>
</tr>
<tr>
<td>7</td>
<td>1h</td>
<td>(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;OH</td>
<td>H</td>
<td>3h</td>
</tr>
<tr>
<td>8</td>
<td>1i</td>
<td>(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;CN</td>
<td>H</td>
<td>3i</td>
</tr>
<tr>
<td>9</td>
<td>1j</td>
<td>(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;5&lt;/sub&gt;</td>
<td>-</td>
<td>3j</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reactions conducted on a 0.4 mmol scale.
<sup>b</sup>Isolated yield unless otherwise noted.
<sup>c</sup>The product was accompanied by a small amount of an unidentified impurity.
<sup>d</sup>NMR yield using mesitylene as an internal standard.

Next, we examined the consecutive double [4 + 2] cycloaddition reaction of the cross-conjugated trienes obtained in the present study. Triene 3<sub>a</sub> was treated with 4-phenyl-1,2,4-triazoline-3,5-dione (4, PTAD), a highly reactive dienophile, in toluene at 0 °C (Scheme 3). The conversion of 3<sub>a</sub> was complete within 1 h, and after chromatographic isolation, bisadducts 5<sub>a</sub> and 5<sub>a'</sub> were obtained in 75% and 6% yields, respectively. The major bisadduct 5<sub>a</sub> resulted from initial addition to the more congested diene moiety of 3<sub>a</sub> (site β). When tetracyanoethylene (6, TCNE), which was a less reactive dienophile than 4, was used, [4 + 2] cycloaddition also occurred preferentially at site β, but only once on heating at 60 °C for 24 h.

**Conclusion**

In summary, we have developed a new dimerization reaction of monosubstituted allenes catalyzed by a rhodium(I)/dppe complex, allowing the stereoselective formation of substituted cross-conjugated trienes. It is interesting that the rhodium catalyst and the palladium catalyst gave different types of cross-conjugated trienes.

**Experimental**

**General procedure for rhodium-catalyzed dimerization of monosubstituted allenes**

To a side-arm tube equipped with a stirrer bar, was added [RhCl(cod)]<sub>2</sub> (4.9 mg, 2.5 mol %) and dppe (7.7 mg, 5 mol %). The tube was evacuated and refilled with argon three times. Then, toluene (4 mL) and substrate 1 (0.4 mmol) were added via syringe and the tube was closed. After heating at 130 °C for 6 h, the reaction mixture was cooled to room temperature, passed through a pad of Florisil® and eluted with ethyl acetate (≈ 90–100 mL). The filtrate was concentrated under reduced pressure and the residue purified by preparative thin-layer chromatography to give product 3. Although the isolated 3 was relatively labile, it could be kept at −30 °C for days without any detectable decomposition or polymerization.
Supporting Information

Supporting Information File 1
Experimental details and spectroscopic data for new compounds.
[http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-7-67-S1.pdf]

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References

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