

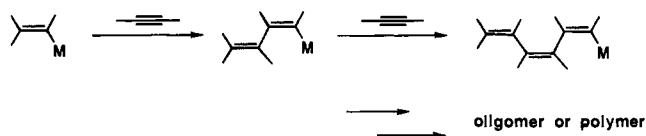
## A Vinylzirconation Reaction of Alkynes

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Carbometalation is a very attractive method for direct preparation of organometallic compounds.<sup>2</sup> However, some carbometalation products, such as alkenylmetalation products of alkynes, have a reactivity similar to that of the starting organometallic compounds. This type of carbometalation results in oligomerization or polymerization reactions. This is one of the major reasons for limiting the scope of alkenylmetalation of alkynes.<sup>2</sup>



Under controlled conditions, alkenylmetalation products of alkynes could be obtained in the case of aluminum<sup>3</sup> or copper.<sup>4</sup> However, in these reactions, two same alkynes were inserted into an alkyl–aluminum or –copper bond. Since the initiation of these reactions is the insertion of alkyne into an alkyl–metal bond, fundamentally, this method does not provide a vinylmetalation product. On the other hand, vinylcopper reagent does not react with alkynes. When an activated alkyne such as propargylic alcohol was used, vinylmagnesium chloride could react to give a vinylmetalation product.<sup>5</sup> However, unactivated alkynes do not react with vinylmagnesium chloride. Therefore, surprisingly, there is no procedure to provide vinylmetalation compounds of unactivated alkynes, to the best of our knowledge.

In this paper we report a novel method to provide vinylzirconation products of unactivated alkynes by a combination of Cp<sub>2</sub>ZrEt<sub>2</sub> and vinyl ethers. Vinylzirconation products produced by this method were not reactive toward second alkynes.

Recently we reported the reaction of Cp<sub>2</sub>ZrEt<sub>2</sub>, which is in situ converted into Cp<sub>2</sub>Zr(CH<sub>2</sub>=CH<sub>2</sub>),<sup>6</sup> with alkynes to give zirconacyclopentenes in excellent yields.<sup>7–9</sup> The ethylene moiety of zirconacyclopentene compounds could be easily replaced by unsaturated compounds.<sup>7,10</sup> We used vinyl ethers as unsaturated compounds. Abstraction of the X group from zirconacyclopentene was expected to afford vinylzirconation products of alkynes.

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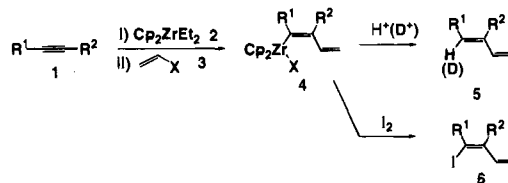
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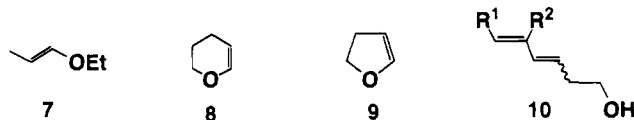
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Typical procedure is as follows. To a solution of Cp<sub>2</sub>ZrEt<sub>2</sub> (**2**), which was prepared from Cp<sub>2</sub>ZrCl<sub>2</sub> (1.25 mmol, 0.365 g) and 2 equiv of EtMgBr (2.5 mmol, 2.5 mL, 1.0 M THF solution) in 3.5 mL of THF at –78 °C, was added 5-decyne (1 mmol, 0.138 g) at –78 °C. The mixture was warmed to 0 °C and stirred for 2 h. A clean formation of zirconacyclopentene was observed (90% yield by NMR) as described previously.<sup>7</sup> To this was added 2.0 mmol of vinyl ethyl ether (0.144 g) at room temperature. After the mixture was stirred for 6 h at 50 °C, quenching with I<sub>2</sub> gave *cis*-4-iodo-3-butyl-1,3-octadiene (**6**, R<sup>1</sup> = R<sup>2</sup> = C<sub>4</sub>H<sub>9</sub>) in 85% yield.



Results are shown in Table 1. In the case of symmetrical internal alkynes such as 5-decyne and diphenylacetylene, vinylzirconation products were obtained in high yields. After hydrolysis, the desired product **5** was obtained in 82% yield (R<sup>1</sup> = R<sup>2</sup> = C<sub>4</sub>H<sub>9</sub>) with a high isomeric purity (>98%). This reaction proceeded in a syn fashion (>98%), as is usually observed for carbometalation of alkynes. Vinyl *n*-butyl ether could be used for this reaction. Unsymmetrical alkynes such as **1** (R<sup>1</sup> = Ph, R<sup>2</sup> = Me) gave a mixture of regioisomers. Vinyl *tert*-butyl ether did not improve the regioselectivity in the case of unsymmetrical alkynes. Substituted alkenyl ethers such as **7** and **8** did not give the corresponding products. Five-membered cyclic vinyl ether 2,3-dihydrofuran (**9**) reacted smoothly to give **10** in 66% yield (R<sup>1</sup> = R<sup>2</sup> = C<sub>3</sub>H<sub>7</sub>, *cis*/*trans* = 61:39) after hydrolysis.



The vinylzirconation product **4** (R<sup>1</sup> = R<sup>2</sup> = Ph) was clearly observed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, and those spectra were consistent with the formula.<sup>11</sup> Deuterolysis of the reaction mixture (R<sup>1</sup> = R<sup>2</sup> = Ph, X = OEt) gave *cis*-1,2-diphenyl-1-deuterio-1,3-butadiene in 78% yield with >98% deuterium

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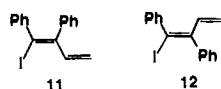
(11) **4** (R<sup>1</sup> = R<sup>2</sup> = Ph): <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, Me<sub>4</sub>Si) δ 5.01 (dd, *J* = 17.4, 1.9 Hz, 1H), 5.28 (dd, *J* = 10.6, 1.6 Hz, 1H), 5.99 (s, 10H), 6.30 (dd, *J* = 17.2, 10.6 Hz, 1H), 6.51 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.75–7.30 (m, 9H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, Me<sub>4</sub>Si) δ 110.42, 116.55, 126.05, 127.69, 128.82, 129.47, 129.59, 131.89, 141.85, 142.33, 147.24, 192.45.

**Table 1.** Vinylzirconation Reactions of Alkynes Using  $\text{Cp}_2\text{ZrEt}_2$  and Vinyl Ethers

run	alkyne	vinyl ether	temp/°C	time/h	quench	product	yield/% <sup>a</sup>	
							GC	isolated (purity/%)
1	$\text{C}_4\text{H}_9\text{—C}\equiv\text{C—C}_4\text{H}_9$	$\text{CH}_2=\text{CH—OEt}$	50	6	$\text{H}^+$		82	50 (98)
2	$\text{C}_4\text{H}_9\text{—C}\equiv\text{C—C}_4\text{H}_9$	$\text{CH}_2=\text{CH—OBu}$	50	6	$\text{H}^+$		80	52 (95)
3	$\text{C}_4\text{H}_9\text{—C}\equiv\text{C—C}_4\text{H}_9$	$\text{CH}_2=\text{CH—OEt}$	50	6	$\text{I}_2$		85	62 (95)
4	$\text{C}_6\text{H}_5\text{—C}\equiv\text{C—C}_6\text{H}_5$	$\text{CH}_2=\text{CH—OEt}$	50	3	$\text{H}^+$		85	72 (95)
5	$\text{C}_6\text{H}_5\text{—C}\equiv\text{C—C}_6\text{H}_5$	$\text{CH}_2=\text{CH—OEt}$	50	3	$\text{D}^+$		78	57 (95)
6	$\text{C}_6\text{H}_5\text{—C}\equiv\text{C—C}_6\text{H}_5$	$\text{CH}_2=\text{CH—OEt}$	50	3	$\text{I}_2$		78 <sup>b</sup>	63 (98)
7	$\text{C}_6\text{H}_5\text{—C}\equiv\text{C—CH}_3$	$\text{CH}_2=\text{CH—OEt}$	50	12	$\text{I}_2$		66 <sup>c</sup>	44 <sup>d</sup> (95)

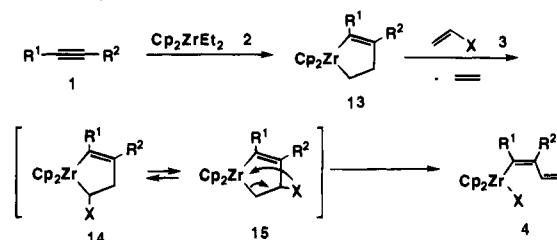
<sup>a</sup> Yields were determined by GC. Combined yields of isomers. <sup>b</sup> A 50:50 mixture of *E/Z* isomers. <sup>c</sup> Hydrolysis product gives a mixture of 81:19 regioisomers for  $\text{C}_6\text{H}_5$  and  $\text{CH}_3$  groups. Iodination induced an *E/Z* isomerization when Ph group was an  $\alpha$  substituent. <sup>d</sup> A 60:40 mixture of *E/Z* isomers. Column chromatography could separate its regioisomers.

incorporation. Iodination of the reaction mixture, however, gave a 1:1 mixture of **11** and **12** in 78% combined yield. Stereo-



somerization occurred during the iodination. In the case of alkyl-substituted alkynes such as 4-octyne, no stereoisomerization was observed during the iodination reaction. The zirconocene alkyne complex stabilized with  $\text{PMe}_3$ ,  $\text{Cp}_2\text{Zr}(\text{PhCCPh})(\text{PMe}_3)$ , did not react with vinyl ethers at 50 °C, even after 24 h. This is in contrast to the allylzirconation of alkynes using allylic ethers.<sup>12</sup>

A plausible reaction mechanism of this reaction is shown in Scheme 1. It is known that the reaction of alkynes with  $\text{Cp}_2\text{ZrEt}_2$  gives zirconacyclopentene compounds. Also, the ethylene part of the zirconacyclopentene can be replaced by unsaturated compounds. Although the intermediate compound could not be detected, alkoxy-substituted zirconacyclopentenes are the reasonable intermediate compounds. Two regioisomers, **14** and **15**, could be considered to be in equilibrium. Abstraction of the X group from the  $\beta$  position of zirconacyclopentene **15** gives

**Scheme 1**

the desired vinylzirconation products of alkynes. Actually a reaction of zirconacyclopentene **13** ( $\text{R}^1 = \text{R}^2 = \text{Ph}$ ) with ethyl vinyl ether gave **4** ( $\text{R}^1 = \text{R}^2 = \text{Ph}$ ) in 83% yield (yield determined by  $^1\text{H}$  NMR). Its hydrolysis product **5** ( $\text{R}^1 = \text{R}^2 = \text{Ph}$ ) was obtained in 85% yield.

Further investigations are in progress in this area.

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**Supplementary Material Available:** Experimental details and analytical data for all compounds described herein (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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