

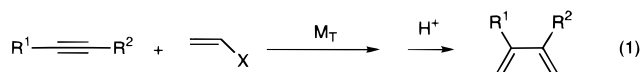
Intermolecular Coupling Reaction of Alkynes with Vinyl Bromide with Selective Skeletal Rearrangement

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Received January 7, 1997

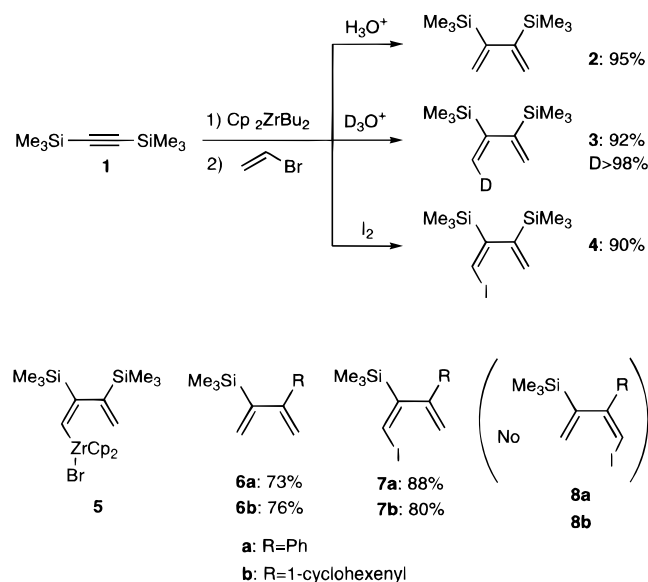
Intermolecular coupling reaction of two molecules with skeletal rearrangement is a very attractive area which remains to be studied in organic synthesis.^{2,3} In this paper, we report a novel type of zirconium-mediated coupling reaction of alkynes with vinyl bromide to give 2,3-disubstituted diene derivatives and a structure of a zirconium-containing intermediate. This reaction involves a selective carbon–carbon bond cleavage of vinyl derivatives as shown in eq 1.



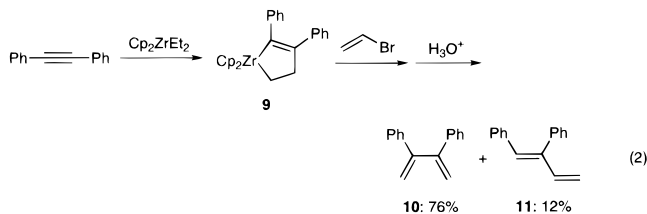
Treatment of bis(trimethylsilyl)acetylene (**1**) with Cp_2ZrBu_2 (Negishi reagent)⁴ in THF at room temperature and then with vinyl bromide at 50 °C for 3 h selectively gave 2,3-bis(trimethylsilyl)-1,3-butadiene (**2**)⁵ in 95% yield after hydrolysis. This reaction product indicated that the carbon–carbon bond of vinyl bromide was selectively cleaved during the reaction. Deuterolysis and iodolysis of the same reaction mixture afforded the monodeuterated compound **3** in 92% with >98% deuterium incorporation and the monoiodinated product **4** in 90% yield, respectively. The deuterium and iodine on **3** and **4** are all in a *trans* position to one of the two trimethylsilyl groups as shown in Scheme 1. The formation of **3** and **4** indicated that the zirconium containing complex **5** was formed in the reaction mixture as a product.

Not only symmetrical alkynes but also unsymmetrical alkynes such as (trimethylsilyl)phenylacetylene and (trimethylsilyl)-cyclohexenylacetylene showed similar reactions. Treatment of a mixture of the alkyne, Cp_2ZrBu_2 , and PMe_3 with vinyl bromide at 50 °C for 15 h afforded **6a** and **6b** in 73% and 76% yields, respectively. Iodinolysis of the reaction mixture led to the monoiodinated compounds **7a** and **7b** in 88% and 80% yields, respectively. The carbon of diene close to the trimethylsilyl group was iodinated. No formation of **8a** or **8b** was observed.

Scheme 1

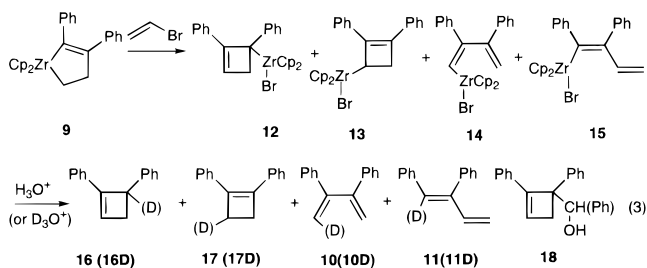


Similar type of diene formation was observed for diphenylacetylene and vinyl bromide using Cp_2ZrEt_2 instead of Cp_2ZrBu_2 (eq 2). It is known that zirconacyclopentene **9** is formed in the reaction of diphenylacetylene with Cp_2ZrEt_2 .⁶ When **9**



was treated with vinyl bromide at 50 °C for 15 h, hydrolysis of the mixture gave 2,3-diphenyl-1,3-butadiene (**10**) in 76% yield. It is interesting that 1,2-diphenyl-1,3-butadiene (**11**) was formed in 12% as a byproduct. Compound **11** was a coupling product of diphenylacetylene with vinyl bromide without skeletal rearrangement. The formation of **11** can be explained by vinylzirconation which we have already reported.⁷

The reactions described above clearly indicated that the carbon–carbon bond of vinyl bromide was selectively cleaved. In order to investigate the mechanism of this novel and selective intermolecular coupling with carbon–carbon bond cleavage, we monitored the reaction of **9** with vinyl bromide by ¹H NMR study. Results are given in eq 3 and Table 1. All compounds



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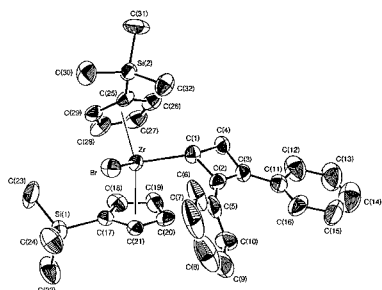
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Table 1. Observation of Intermediates of the Intermolecular Coupling of Diphenylacetylene with Vinyl Bromide^a

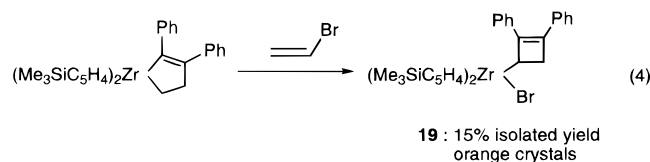
reaction conditions		ratio of 16 : 17 : 10 : 11				combined yield (%)
<i>T</i> (°C)	time (h)	16	17	10	11	
rt	1	98	tr	tr	tr	84
rt	3	95	1	2	1	93
50	1	36	38	21	5	93
50	3	25	17	48	10	90
50	6	18	3	66	13	89
50	15	1	1	84	13	90
50	24	tr	tr	86	13	87

^a The reaction was followed by ¹H NMR spectroscopy. The reaction was carried out at room temperature for 3 h, and then the mixture was warmed to 50 °C and stirred for 24 h. Yields of all intermediates were determined by GC after hydrolysis of an aliquot of the mixture using hydrocarbons as an internal standard.

**Figure 1.** Structure of the intermediate **19**. Selected bond distances (Å): C(1)–C(2) = 1.53(1); C(2)–C(3) = 1.39(1); C(3)–C(4) = 1.50(1); C(4)–C(1) = 1.59(1).

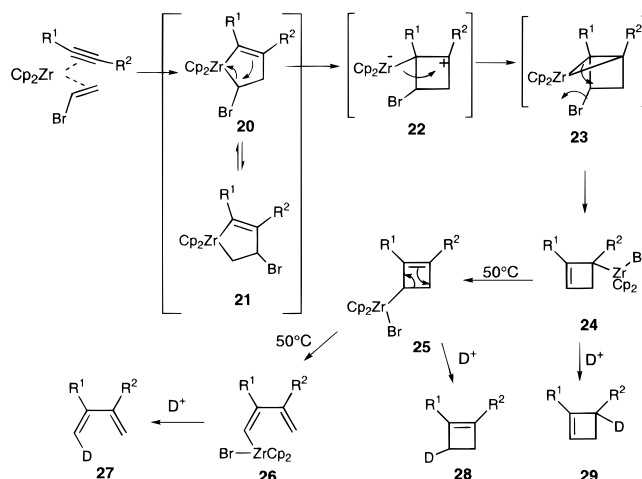
were obtained after hydrolysis of the reaction mixture. At room temperature, **16** was first formed after 1 h. Deuterolysis of the mixture gave **16D**. Its derivative **18** was characterized by X-ray study, since the NMR spectra of **18** revealed that **18** has the same ring structure as that of **12** and **16**. The derivative **18** was obtained by the reaction of **12** with benzaldehyde.

Treatment of the reaction mixture containing **12** at 50 °C caused the gradual decrease of **16**. With decrease of **16**, **17** appeared and increased. After 1 h, **17** was obtained in 38% yield. Deuterolysis instead of hydrolysis gave **17D**. When trimethylsilyl group was introduced into cyclopentadienyl ligands, the zirconium-containing intermediate **19**, which had the same ring system as **13** was obtained as crystals (eq 4). The structure of **19** was determined by X-ray study and it is shown in Figure 1.



When the reaction mixture was further heated at 50 °C, the amount of **17**, in turn, gradually decreased. Then the final product **10** was formed and became the major product at the end, as shown in Table 1.

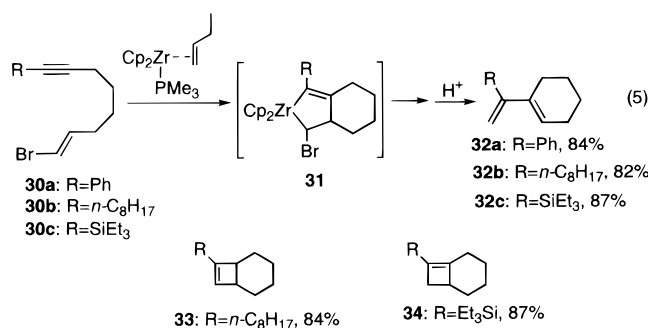
From the results obtained here, we propose the following mechanism, shown in Scheme 2, although we must await further investigations to clarify the formation of **24** from **20**. This mechanism involves (i) the formation of a zirconacyclopentene with a bromide at α -position (**20**) and (ii) the formation of **24**

Scheme 2

via **22** and **23**. iii) At 50 °C, **24** is converted into **25**. (iv) Heat treatment of **25** opens the four-membered ring to give a diene derivative **26**.

The key intermediate leading to a cyclobutene ring is **20** which has a bromide at α -position of zirconacyclopentene ring and is in equilibrium with **21**.⁸ Elimination of the bromide at β -position of zirconacyclopentene **21** gives a vinylzirconation product of alkynes without bond cleavage of a double bond of vinyl bromide as we reported.⁷ However, the elimination of the bromide from α -position of **20** leads to the bond cleavage products.

In order to check this point haloalkynes **30a–c** were prepared to fix a bromide at α -position of zirconacyclopentenes. Cyclization of **30** on zirconocene gives **31** which has a bromide at α position. As shown in eq 5, the reaction of **30a–c** with a zirconocene butene complex gave skeletal rearranged product **32a–c** in high yields. This clearly showed that the elimination



of a bromide from α -position is a key step for this skeletal rearrangement. For this *intramolecular* coupling with skeletal rearrangement of haloalkynes, similar intermediates **33** and **34** were detected in 84% and 87% yields, respectively.⁹

We are now investigating this type of reactions using other metals including late transition metal complexes.

Supporting Information Available: Details of the experimental procedure and analytical data and X-ray analysis data for **18** and **19** (25 pages). See any current masthead page for ordering and Internet access instructions.

JA970055+

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