β-Hydride Elimination from α-Positioned Methyl Group of Bicyclic Zirconacyclopentanes Assisted by Aldehyde

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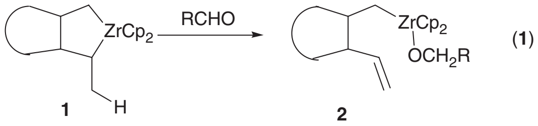
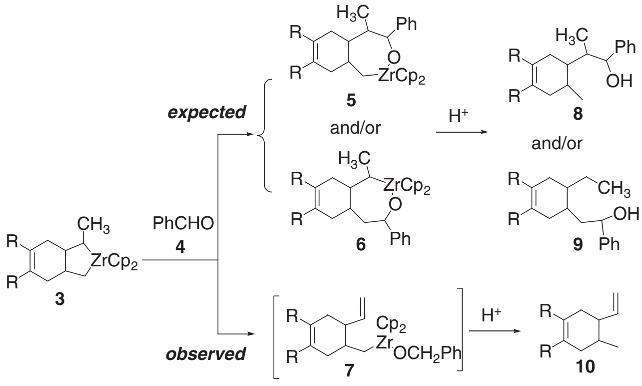
β-Hydrogen elimination from α-methylated bicyclic zirconacyclopentanes was promoted by benzaldehyde at low temperature. Treatment of the resulting mixture with allyl bromide and benzoyl chloride in the presence of CuCl introduced new olefin or phenylcarbonyl moieties in the product.

β-Hydride elimination is one of the fundamental reactions of organometallic compounds.[1,2] Zirconacyclopentanes **1**, can be readily prepared by coupling of alkenes or dienes on zirconocene.[3] Although β-hydride elimination reactions of zirconacycles has been reported,[4] organic compound-assisted β-hydrogen elimination reactions of zirconacyclopentane have not been reported yet, to the best of our knowledge. In this paper we would like to report aldehyde assisted β-hydrogen elimination of α-methylated bicyclic zirconacyclopentanes. (Eq 1)[5]



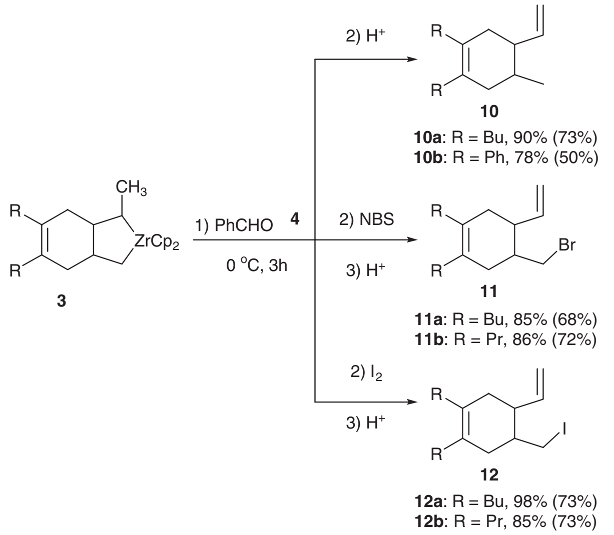
We have reported that aldehydes can insert into the Zr–C^{sp3} bonds of zirconacyclopentanes to afford 7-membered oxazirconacycles.[6] Initially, in order to investigate the regioselectivity of insertion reactions of aldehydes into zirconacyclopentanes bearing a substituent at the α-position, we treated bicyclic zirconacyclopentanes **3**, prepared in situ via zirconocene-mediated stereoselective cyclization of 1,4,7-trienes,[7] with benzaldehyde **4**.



Scheme 1.

As given in Scheme 1, oxazirconacycles **5** and/or **6** were expected. However, interestingly, totally no formation of **8** and/or **9** was observed in most cases after hydrolysis. 2-Methyl-1-vinyl cycloalkenes **10** were formed in high yields with high chemo- and stereoselectivities. The aldehyde moiety was not incorporated in the product.

A typical procedure is as follows. To a THF solution of in situ prepared bicyclic zirconacyclopentanes **3** by the reaction of 1,4,7-trienes and Cp_2ZrBu_2 was added one equivalent of benzaldehyde **4** at 0 °C. The reaction mixture was then stirred at the same temperature for 3 h. Hydrolysis of the reaction mixture with aqueous 3N HCl afforded **10** (Scheme 1) in high yields based on 1,4,7-trienes (**10a**: R = Bu, a mixture of two *cis* and *trans* isomers in a ratio of 13:1, 90% GC yield; **10b**: R = Ph, a mixture of two *cis* and *trans* isomers in a ratio of 5:1, 78% GC yield).



Scheme 2.

Quench of the reaction mixture with NBS generated brominated vinylcyclic compounds **11a** and **11b** as mixtures of *cis* and *trans* isomers in the ratios of 16:1 and 17:1, respectively (Scheme 2). Iodinated vinylcycloalkenes **12** were also obtained in excellent yields when the reaction mixture was terminated with I_2 (**12a**: R = Bu, a mixture of two *cis* and *trans* isomers in a ratio of 20:1, 98% GC yield; **12b**: R = Pr, a mixture of two *cis* and *trans* isomers in a ratio of 25:1, 85% GC yield).

Formation of these brominated and iodinated products (**11** and **12**) indicates that there exists a Zr–C bond in the organometallic intermediate, which can be, in addition to bromination and iodination reactions, further utilized for new carbon–carbon bond formation (Eq 2). In fact, the reaction intermediates could react with a variety of electrophiles in the presence of CuCl to afford vinylcycloalkene derivatives **13**. Reactions of **3a**, **3b**, and **3c** with one equiv. of allyl bromide in the presence of one equivalent of CuCl afforded **13a**, **13b**, and **13d** in 80%, 87%, and 76% GC yields, respectively (Table 1). Acylated derivative **13c** was obtained in 90% yield when **3b** was treated with benzoyl chloride in the presence of CuCl.

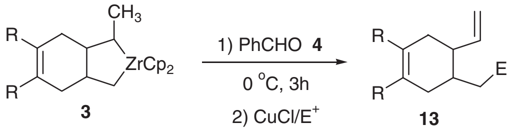
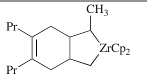
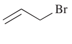
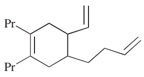
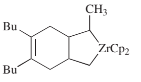
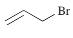
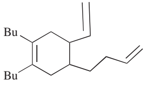
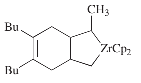
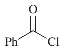
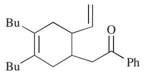
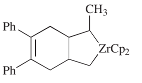
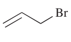
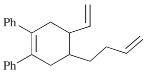


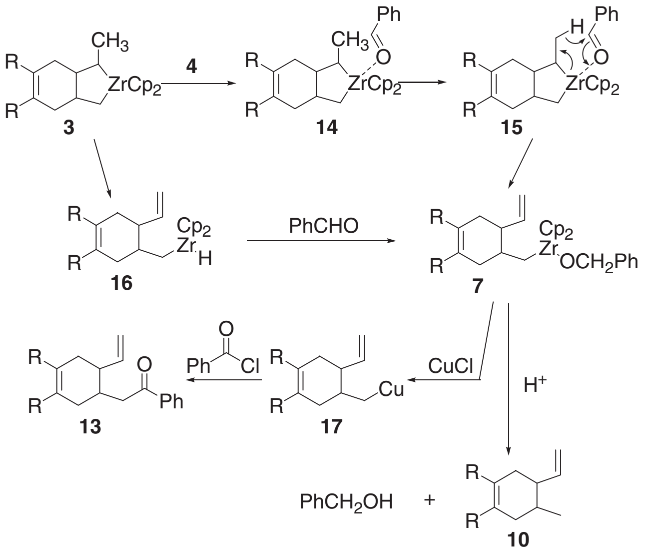
Table 1. Reactions of the PhCHO-induced β-hydrogen elimination intermediates with electrophiles

Zirconacyclopentane	Electrophile	Product	Yield/%[a]
 **3a**		 **13a**[b]	80 (70)
 **3b**		 **13b**[c]	87 (54)
 **3b**		 **13c**[d]	90 (78)
 **3c**		 **13d**[e]	76 (45)

[a] GC yields. Isolated yields are given in parentheses. Combined yields are given. [b] A mixture of *cis* and *trans* isomers in 12:1. [c] A mixture of *cis* and *trans* isomers in 20:1. [d] A mixture of *cis* and *trans* isomers in 9:1. [e] A mixture of *cis* and *trans* isomers in 16:1.

In order to understand the reaction mechanism, we firstly tried to find out the fate of the aldehyde after the reaction completed, since the aldehyde was obviously not incorporated in the product. As expected, the formation of benzyl alcohol was observed in the yield of 19% after hydrolysis of the reaction mixture.

Based on the above results, a proposed reaction mechanism is given in Scheme 3. One possible way is the direct abstraction of β-hydrogen from the methyl group by aldehyde via **15**. The other path is hydrozirconation of benzaldehyde via **16**. Monitoring of the reaction mixture of **3c** with benzaldehyde by NMR revealed the formation of **7c** (R = Ph). In the ^{13}C NMR of the mixture there were two singlets at 111.07 and 110.88 ppm assignable to the two Cp rings. The methylene carbon attached to Zr and the carbon of CH_2 attached to oxygen appeared at 40.92 and 76.26 ppm, respectively.[6b] It is noteworthy that the intermediates **7** are thermally stable; no decomposition of **7c** was detected even heated at 50 °C for 6 h. The complex **7**, in turn, reacted with various electrophiles via transmetalation to the copper derivative **17**.



Scheme 3.

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References and Notes

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