Pergamon

Tetrahedron Letters 41 (2000) 7471–7474

TETRAHEDRON
LETTERS

Formation of cyclopentadiene derivatives by reaction of zirconacyclopentadienes with 1,1-dihalo compounds

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Received 12 April 2000; accepted 24 July 2000

Abstract

Zirconacyclopentadienes reacted with benzal halides in the presence of CuCl and dimethylpropyleneurea to give pentasubstituted cyclopentadienes in moderate to good yields. Treatment of zirconacyclopentadienes with 1,1-dibromo-1-alken-3-yne and 1,1-dibromo-1,3-alkadiene afforded fulvene derivatives in good yields.

Cyclopentadienes or fulvenes are important as intermediates in organic synthesis and as ligands in coordination chemistry and homogeneous catalysis for olefin polymerization.[1] One convenient preparative method is the coupling of three components such as two alkynes and a one-carbon unit in one-pot. Recently we have reported the formation of cyclopentadienes by the reaction of five-membered zirconacyclic compounds with a one-carbon unit building block; for example, the reaction of zirconacyclopentadienes with propynoates through double Michael additions,[2] and nucleophilic attack of zirconacyclopentenes to acyl halides in the presence of CuCl followed by elimination.[3] On the other hand, the use of 1,1-dihalo compounds as a one-carbon unit is one direct replacement of the zirconium metal of zirconacycles. However, there is no report on the reaction of zirconacyclopentadienes[4] with 1,1-dihalo compounds to give five-membered cyclic compounds (Eqs. (1) and (2)), to the best of our knowledge, although the reactions with $RPCl_2$,[5] $SOCl_2$,[5] $BiCl_3$,[5] R_2SnCl_2,[5,6] R_2GeCl_2,[5,6] and $RHSiCl_2$,[7] have been reported. This prompted us to investigate the reaction of zirconacyclopentadienes with 1,1-dihalo compounds. During the course of our study, we found that benzal halides, 1,1-dihaloenyne or 1,1-dihalodiene could be used as a one-carbon unit to react with zirconacyclopentadienes. We would like to report here the first example of the formation of cyclopentadienes or fulvenes by the reaction of zirconacyclopentadienes with benzal halides or 1,1-dihalo alkene derivatives.

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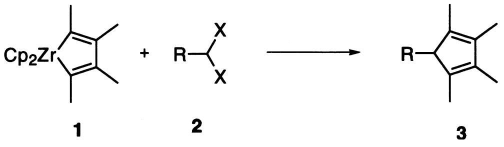
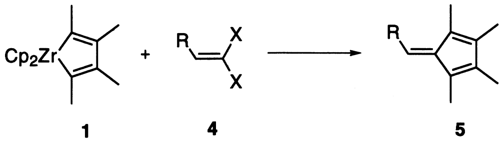
0040-4039/00/$ - see front matter
PII: S0040-4039(00)01277-6

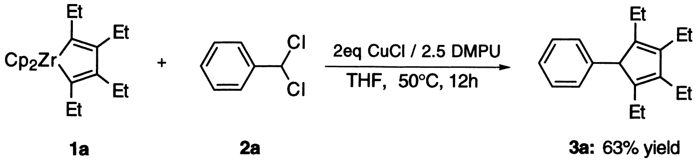


(1)



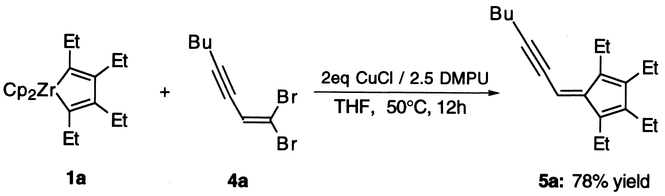
(2)

We first tried the reaction of tetraethylzirconacyclopentadiene **1a** with 1,1-dihaloalkanes such as dibromomethane. Unfortunately, the desired cyclopentadiene was not obtained under various conditions. Recently, we have reported the reaction of zirconacyclopentadienes with a benzyl halide moiety for the formation of seven- to nine-membered ring compounds.[8] Therefore, we used benzal halides such as benzal chloride **2a**, 3-chlorobenzal chloride **2b** and benzal bromide **2c** as 1,1-dihalo compounds. As shown in Eq. (3), **2a** was added at 0°C to the solution of **1a** in THF in the presence of 2 equiv. of CuCl and 2.5 equiv. of DMPU. The mixture was warmed to 50°C and was stirred at 50°C for 12 h. The desired product, 1,2,3,4-tetraethyl-5-phenylcyclopenta-1,3-diene **3a** was formed in 61% yield. It is noteworthy that two double bonds in the cyclopentadiene **3a** stayed at the same positions as in **1a**. During the reaction or work-up, no double bond isomerization occurred.



(3)

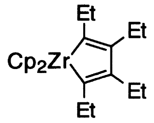
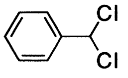
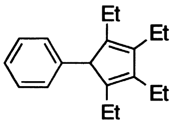
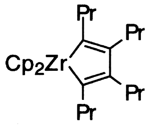
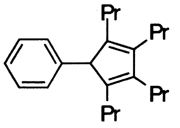
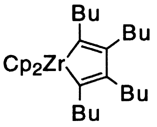
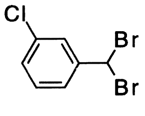
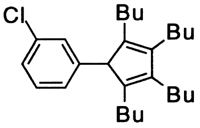
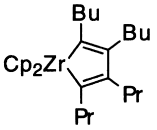
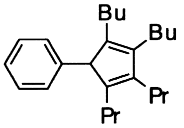
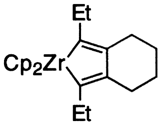
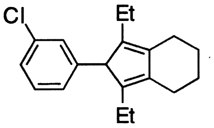
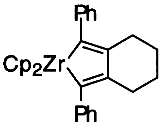
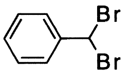
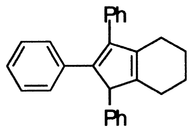
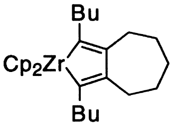
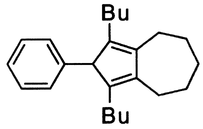
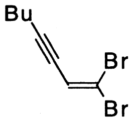
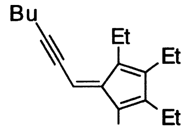
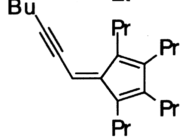
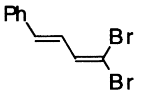
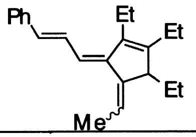
Results are shown in Table 1. In the case of benzal bromide **2c** instead of benzal chloride **2a**, the reaction proceeded even at room temperature. The use of 3-chlorobenzal bromide afforded products within 1 h even at room temperature. When bicyclic zirconacyclopentadienes **1e**–**f** with a six-membered side ring were used, isomerization of two double bonds in the products **3e**–**f** was observed. This is due to the stability of the positional isomers. In contrast, in the case of bicyclic zirconacyclopentadiene **1g** with a seven-membered side ring, such isomerization of the double bonds in the product was not observed, although the yield was low.



(4)

As for 1,1-dihaloalkenes, we first tried to use very simple 1,1-dibromoethylene. However, the desired product was not obtained. And then we turned our attention to the more reactive 1,1-dihaloenynes or 1,1-dihalodienes such as **4a** and **4b**. The zirconacyclopentadiene **1a** reacted with **4a** in the presence of 2 equiv. of CuCl and 2.5 equiv. of DMPU to afford alkynylated fulvene **5a** in 78% yield (Eq. (4)). The results of the reactions with **4a** and **4b** are shown in Table 1. It is interesting to note that the two double bonds in the ring showed no isomerization for **5a** and **5b**, whereas **5c** showed that one of two double bonds in the ring isomerized to an exocyclic double bond. It is not clear why one double bond of **5c** isomerized outside.

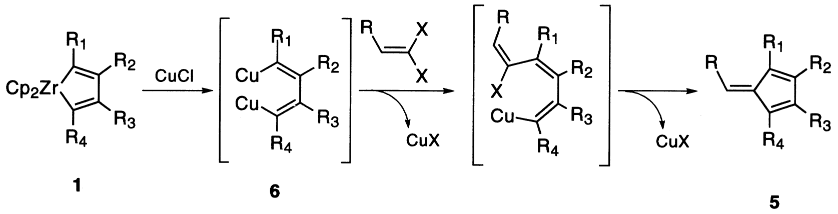
Table 1
Reaction of zirconacyclopentadienes with benzal halides or alkenyl dibromide

Zirconacyclopentadiene	Benzal Halide	Product	T/°C	Time/h	Yield (%)[a]
 **1a**	 **2a**	 **3a**	50	12	61 (51)
 **1b**	**2a**	 **3b**	50	12	62 (47)
 **1c**	 **2b**	 **3c**	rt	1	76 (46)
 **1d**	**2a**	 **3d**	50	12	50 (35)
 **1e**	**2b**	 **3e**[b]	rt	12	59 (40)
 **1f**	 **2c**	 **3f**	rt	18	88 (52)
 **1g**	**2c**	 **3g**	rt	72	35 (21)
1a	 **4a**	 **5a**	50	12	78 (65)
1b	**4a**	 **5b**	50	12	80 (57)
1a	 **4c**	 **5c**	50	12	77 (62)

[a] Isolated yields are in parentheses. [b] After isolation, the double bonds gradually isomerized.

The mechanism of the copper-mediated coupling reaction of zirconacyclopentadienes has been well discussed. The mechanism of the reactions of zirconacyclopentadienes with **2** or **4** can be explained in a similar way to that we have reported for other copper-mediated reactions of zirconacyclopentadienes.[9] It involves transmetalation of zirconacyclopentadienes to Cu to form dicopper compounds. Coupling reaction with one carbon–halogen bond of **2** or **4** affords 5-halo-1,4-pentadienylcopper. Subsequent intramolecular coupling reaction gives a cyclopentadiene or a fulvene derivative. According to this mechanism, CuCl is regenerated. Therefore, a catalytic reaction might be expected. However, the use of 2 equiv. of CuCl was required in these reactions because the yields were very low when a catalytic amount of CuCl was used. In the reactions described here, monocyclic zirconacyclopentadiene with phenyl and silyl groups did not give satisfactory results. One reason is that the transmetalation of phenyl-substituted or silyl-substituted zirconacyclopentadienes to copper is very slow, as we observed before.[9d] In addition, the coupling reaction of dienylcopper derivatives **6** with benzal chloride is much slower than in the case of benzyl chloride where the coupling reaction with **6** proceeds fast, even at room temperature.

In conclusion, the reactions of zirconacyclopentadienes with 1,1-dihalo compounds provided novel preparative methods of pentasubstituted arylcyclopentadienes and fulvenes with an alkynyl or an alkenyl moiety (Scheme 1).



Scheme 1.

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