REACTIONS OF ZIRCONACYCLOPENTADIENES WITH PROPARGYL HALIDES LEADING TO (BUTA-2,3-DIEN-1-YL)BENZENES

Martin KOTORA[1], Yoshinori NOGUCHI[2] and Tamotsu TAKAHASHI[3,*]

Catalysis Research Center and Graduate School of Pharmaceutical Sciences, Hokkaido University, Kita-ku, Sapporo 060, Japan; e-mail: [1] martin@cat.hokudai.ac.jp, [2] ynog@cat.hokudai.ac.jp, [3] tamotsu@cat.hokudai.ac.jp

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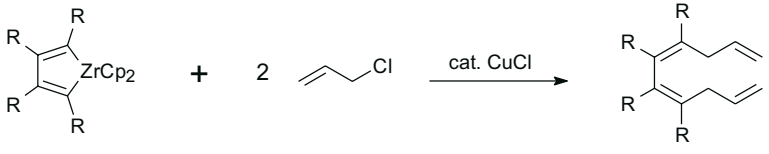
The reaction of 1,1-bis(η^5-cyclopentadienyl)-1-zirconacyclopenta-2,4-dienes with propargyl halides in the presence of a catalytic or a stoichiometric amount of CuCl afforded benzene derivatives. This reaction involves S_N2' type of attack of organocopper intermediate to propargyl halide followed by intramolecular carbometallation, and coupling with the second molecule of propargyl halide.

Key words: Zirconacyclopentadienes; Allenes; Benzenes; Propargyl chloride; Cyclotrimerization; Alkynes.

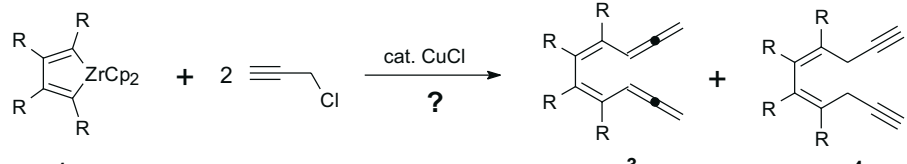
Recently we have reported several C–C bond formation reactions of 1,1-bis(η^5-cyclopentadienyl)-1-zirconacyclopenta-2,4-dienes[1–3], such as copper(I) chloride catalyzed diallylation with allyl chlorides[2] and copper(I) chloride mediated formation of benzene derivatives[3]. The former reaction, which was the first general example of C–C bond formation of 1,1-bis(η^5-cyclopentadienyl)-1-zirconacyclopenta-2,4-dienes (Scheme 1), afforded the diallylated products **2** that were used as starting materials for the preparation of eight-membered ring compounds[2]. Our further attention



SCHEME 1 **1** **2**

was turned to the reaction of zirconacyclopentadienes **1** with propargyl halides in the presence of copper halides. The reaction was expected to

yield deca-1,2,4,6,8,9-hexaene (**3**) or deca-4,6-dien-1,9-diyne (**4**) (Scheme 2). Surprisingly, the reaction of zirconacyclopentadienes with propargyl halides in the presence of CuCl did not result in the formation of the expected diallenylated products; instead, benzene derivatives were obtained. In this paper we would like to report novel type of benzene derivative formation by the reaction of zirconacyclopentadienes with propargyl halides.



1

SCHEME 2

EXPERIMENTAL

All reactions involving organozirconium compounds were carried out under nitrogen. Tetrahydrofuran was dried over sodium and benzophenone. Zirconocene dichloride was purchased from Aldrich Chemical Company, Inc. Butyllithium (1.6 M solution in hexane) was purchased from Kanto Chemicals Co. Ltd. Hex-3-yne, dodeca-3,9-diyne, and 1-trimethylsilylprop-1-yne were purchased from TCI Co. Ltd. 1,8-Diphenyl-1,7-octadiyne was prepared according to literature[4]. Zirconacyclopentadienes were prepared *in situ* according to previously published procedures[5].

^{1}H and ^{13} NMR spectra were recorded for $CDCl_3$ or C_6D_6 (containing 1% TMS) solutions at 25 °C on a Bruker ARX 400 NMR spectrometer. IR spectra were recorded on a Shimadzu FTIR-4200 spectrometer. GC analysis was performed on a Shimadzu GC-14A equipped with fused silica capillary column Shimadzu CBP1-M25-O25 and a Shimadzu C-R6A-Chromatopac integrator.

Reactions of Zirconacyclopentadienes **1** with Propargyl Chloride. General Procedure

To a solution of zirconacyclopentadiene[5a,5b] (1 mmol) in THF (5 ml) were added propargyl chloride (2.2 mmol, 164 mg, 158 μl) and CuCl (0.1 or 1 mmol, 10 or 99 mg). The reaction mixture was stirred at 0 or 20 °C till the consumption of the starting material. The reaction mixture was quenched with 3 M HCl and the product was extracted with hexane (4 × 5 ml). Yields were determined by GC analysis using suitable hydrocarbons as internal standards. The combined organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. Column chromatography on silica gel (hexane) afforded the products. Purity in all cases was ≈97% (GC).

1-(Buta-2′,3′-dien-1′-yl)-2,3,4,5-tetraethylbenzene (**5a**). Isolated 80 mg (33%) of the title compound as a colorless oil. ^{1}H NMR ($CDCl_3$): 1.15 t, 6 H, J = 7.2 (CH_3); 1.17 t, 3 H, J = 7.4 (CH_3); 1.23 t, 3 H, J = 7.6 (CH_3); 2.59–2.70 m, 8 H (CH_2); 3.35 dt, 2 H, J = 7.0, 3.0 (CH_2); 4.69 dt, 2 H, J = 7.0, 3.0 (=CH_2); 5.26 tt, 1 H, J = 7.0, 7.0 (=CH-); 6.92 s, 1 H (=CH-). ^{13}C NMR ($CDCl_3$): 15.36, 15.55, 15.58, 15.89, 21.73, 21.84, 22.18, 25.62, 32.59, 74.63,

90.06, 127.64, 135.61, 137.76, 138.08, 139.56, 140.02, 208.82. HRMS: calculated for $C_{18}H_{26}$ 242.2033, found 242.2031.

6-(Buta-2′,3′-dien-1′-yl)-5,8-diethyl-1,2,3,4-tetrahydronaphthalene (**5b**). Isolated 34 mg (14%) of the title compound as a colorless oil. ^{1}H NMR ($CDCl_3$): 1.11 t, 3 H, J = 7.5 (CH_3); 1.20 t, 3 H, J = 7.5 (CH_3); 1.75–1.81 m, 4 H (CH_2); 2.55 q, 2 H, J = 7.5 (CH_2); 2.64 q, 2 H, J = 7.5 (CH_2); 2.67–2.75 m, 2 H (CH_2); 2.75–2.80 m, 2 H (CH_2); 3.35 dt, 2 H, J = 7.0, 3.0 (CH_2); 4.69 dt, 2 H, J = 7.0, 3.0 (=CH_2); 5.24 tt, 1 H, J = 7.0, 7.0 (=CH-); 6.90 s, 1 H (=CH-). ^{13}C NMR ($CDCl_3$): 14.11, 14.28, 21.33, 22.90, 23.26, 25.51, 26.52, 26.93, 32.56, 74.72, 90.21, 126.45, 133.41, 134.95, 135.22, 137.87, 139.66, 208.86. HRMS: calculated for $C_{18}H_{24}$ 240.1877, found 240.1878.

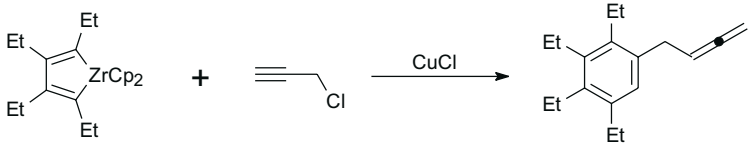
5-(Buta-2′,3′-dien-1′-yl)-1,4-bis(trimethylsilyl)-2,3-dimethylbenzene (**5c**). Isolated 97 mg (32%) of the title compound as a colorless oil. ^{1}H NMR ($CDCl_3$): 0.32 s, 9 H (CH_3); 0.42 s, 9 H (CH_3); 2.32 s, 3 H (CH_3); 2.35 s, 3 H (CH_3); 3.47 dt, 2 H, J = 7.0, 3.0 (CH_2); 4.66 dt, 2 H, J = 7.0, 3.0 (=CH_2); 5.23 tt, 1 H, J = 7.0, 7.0 (=CH-); 7.21 s, 1 H (=CH-). ^{13}C NMR ($CDCl_3$): 0.01 (3C), 3.91 (3C), 18.25, 20.78, 35.65, 75.10, 91.34, 133.75, 138.32, 139.60, 139.79, 142.37, 142.83, 208.87. HRMS: calculated for $C_{18}H_{30}Si_2$ 302.1884, found 302.1874.

6-(Buta-2′,3′-dien-1′-yl)-5,8-diphenyl-1,2,3,4-tetrahydronaphthalene (**5d**). Isolated 74 mg (22%) of the title compound as a colorless oil. ^{1}H NMR ($CDCl_3$): 1.55–1.70 m, 4 H (CH_2); 2.34–2.42 m, 2 H (CH_2); 2.58–2.66 m, 2 H (CH_2); 2.98–3.05 m, 2 H (CH_2); 4.50–4.55 m, 2 H (=CH_2); 5.0–5.1 m, 1 H (=CH-); 7.07 s, 1 H (=CH-); 7.17–7.44 m, 10 H (Ph). ^{13}C NMR ($CDCl_3$): 22.90, 23.11, 28.63, 29.17, 33.04, 74.64, 89.71, 126.66, 126.68, 127.69. 127.97 (2C), 128.34 (2C), 129.33 (2C), 129.44 (2C), 132.88, 135.12, 135.58, 140.39, 140.59, 141.32, 142.19, 208.78. HRMS: calculated for $C_{26}H_{24}$ 336.1877, found 336.1891.

Pentaethyl-(2-ethyl-2,3-butadien-1-yl)benzene (**6**). Isolated 69 mg (23%) of the title compound as a colorless oil. ^{1}H NMR ($CDCl_3$): 1.07 t, 3 H, J = 7.3 (CH_3); 1.13 t, 6 H, J = 7.3 (CH_3); 1.15 t, 6 H, J = 7.3 (CH_3); 1.17 t, 3 H, J = 7.3 (CH_3); 1.95–2.15 m, 2 H (CH_2); 2.57 q, 4 H, J = 7.3 (CH_2); 2.62 q, 6 H, J = 7.3 (CH_2); 3.26 t, 2 H, J = 4.0 (CH_2); 4.35 tt, 2 H, J = 4.0, 4.0 (=CH_2). ^{13}C NMR ($CDCl_3$): 12.30, 15.52 (2C), 15.86 (2C), 15.93, 22.14 (2C), 22.25, 22.55 (2C), 25.56, 32.45, 76.41, 105.77, 133.27, 137.44 (2C), 137.88, 138.58 (2C), 205.91. HRMS: calculated for $C_{22}H_{34}$ 298.2659, found 298.2657.

RESULTS AND DISCUSSION

The reaction of zirconacyclopentadiene **1a** with 2.2 equivalents of propargyl chloride in the presence of a catalytic amount of CuCl (10 mole %) afforded 1-(buta-2′,3′-dien-1-yl)-2,3,4,5-tetraethylbenzene **5a** in 80% yield (Scheme 3).

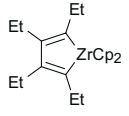
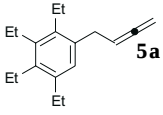
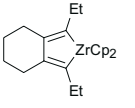
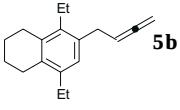
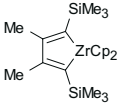
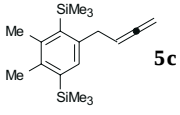
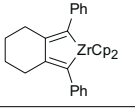
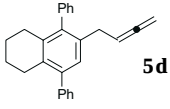


1a **5a**

SCHEME 3

Then this reaction was studied using various zirconacyclopentadienes under various conditions. The results we obtained are summarized in Table I. Generally, the best yields of products were obtained at room temperature with a catalytic amount of CuCl (10 mole %). However, the difference in yields between catalytic and stoichiometric reactions was not significant in some cases. The reaction of zirconacyclopentadiene **1a** gave the best results at room temperature and with the catalytic amount of CuCl. The reaction of zirconacyclopentadiene **1b** afforded the best yield of the product at 0 °C and catalytic amount of CuCl. The reaction of zirconacyclopentadiene **1d** did not show any significant difference in yields under any conditions. The only exception was zirconacyclopentadiene **1c** which afforded products only in the presence of stoichiometric amount of CuCl. It is noteworthy that in neither of cases products of the reaction of a zirconacyclopentadiene with one equivalent of propargyl chloride were detected or iso-

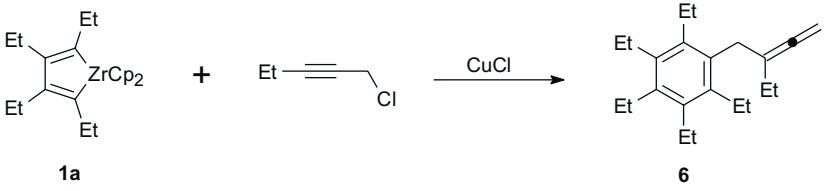
TABLE I
Reaction of zirconacyclopentadienes with propargyl chloride

Zirconacyclopentadienes[a]		T, °C	t, h	CuCl equiv.	Product	Yield, %[b]
	**1a**	20	3	0.1	 **5a**	80
		20	6	2		73
		0	3	2		69
	**1b**	0	3	0.1	 **5b**	53
	**1c**	20	1	2	 **5c**	41
	**1d**	0	12	0.1	 **5d**	45

[a] Zirconacyclopentadienes were prepared *in situ* (ref.[5a,5b]). [b] GC yields.

lated. The use of other transition metal salts such as $PdCl_2$ did not result in any detectable reaction.

Reaction of zirconacyclopentadiene **1a** with propargyl bromide afforded a lower yield of the product (49% GC yield). The reaction of tetraethylzirconacyclopentadiene **1a** with 1-chloropent-2-yne in the presence of the catalytic amount of CuCl (10 mole %) at 20 °C afforded only a small amount of the expected product **6** (29% GC yield) (Scheme 4). The reactions with substituted propargyl halides (3-bromo-1-trimethylsilylprop-1-yne and 1-phenyl-3-chloroprop-1-yne) did not afford any expected products.

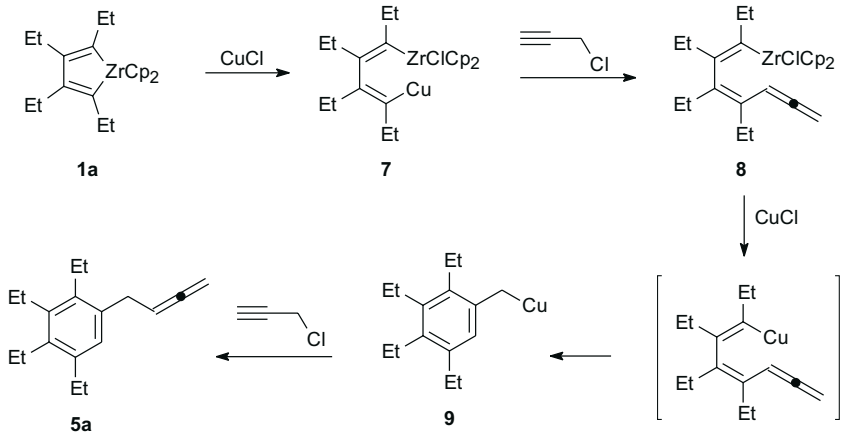


SCHEME 4

The formation of benzene derivative **5a** can be rationalized by the following reaction mechanism (Scheme 5). In the first step the C–Zr bond is transmetallated to the C–Cu bond to give **7** followed by S_N2' reaction with propargyl chloride to give the intermediate **8** containing an allenyl moiety. This intermediate after transmetallation of the second C–Zr bond to the C–Cu bond undergoes intramolecular addition to the allenyl moiety forming benzylcopper compound **9**. The benzylcopper **9** reacts with the second molecule of propargyl chloride by S_N2' reaction to give the final product **5a**. Absence of the products of hydrolysis of **8** and **9** indicates that the reactions from **8** to **9** and from **9** to **5a** are very fast. The transmetallation of both Zr–C bonds during the course of the reaction is essential, because the Zr–C bond are usually unreactive towards such insertion reactions[6]. It is well known that organocopper compounds react with propargyl derivatives by S_N2' reaction affording allene derivatives[7]. The S_N2' type of mechanism was observed in the reaction of other organozirconium compounds with allyl halides in the presence of copper chloride[8]. It is also known that intramolecular addition of organometallic compounds (organomagnesium[9] or -lithium[10]) to allenyl moiety proceeds at the terminal double bond of the allenyl moiety.

The difference between the reaction with allyl halides and the reaction with propargyl halides might be explained by a favorable orbital alignment

of the terminal double bond of the allene moiety and by a strong driving force to form the benzene ring.



SCHEME 5

REFERENCES

1. a) Kotora M., Xi Z., Takahashi T.: *J. Synth. Org. Chem.* **1997**, *55*, 36; b) Takahashi T., Sun W.-H., Xi C., Kotora M.: *Chem. Commun.* **1997**, 2069; c) Kotora M., Umeda C., Ishida T., Takahashi T.: *Tetrahedron Lett.* **1997**, *38*, 8355.
2. Takahashi T., Kotora M., Kasai K., Suzuki N.: *Organometallics* **1994**, *13*, 4183.
3. Takahashi T., Xi Z., Yamazaki A., Liu Y., Nakajima K., Kotora M.: *J. Am. Chem. Soc.* **1998**, *120*, 1672.
4. a) Sonogashira K., Tohda T., Hagihara N.: *Tetrahedron Lett.* **1975**, 4467; b) Takahashi S., Kuroyama Y., Sonogashira K., Hagihara N.: *Synthesis* **1980**, 627.
5. a) Negishi E., Cederbaum F. E., Takahashi T.: *Tetrahedron Lett.* **1987**, *28*, 917; b) Negishi E., Holms S. J., Tour J. M., Miller J. A., Cederbaum F. E., Swanson D. R., Takahashi T.: *J. Am. Chem. Soc.* **1989**, *111*, 3336; c) Xi Z., Hara R., Takahashi T.: *J. Org. Chem.* **1995**, *60*, 4444.
6. Wipf P., Xu M., Takahashi H., Jahn H., Coish P. D. G.: *Pure Appl. Chem.* **1997**, *69*, 639.
7. a) Trost B. M., Fleming I. (Eds): *Comprehensive Organic Synthesis*, Vol. 5. Pergamon Press, Oxford 1991; b) Lipshutz B. H., Sengupta S.: *Org. React.* **1992**, *41*, 135.
8. Takahashi T., Kotora M., Kasai K., Suzuki N.: *Tetrahedron Lett.* **1994**, *35*, 5685.
9. Richey H. G., Jr., Kossa W. C., Jr.: *Tetrahedron Lett.* **1969**, 2313.
10. a) Crandall J. K., Ayers T. A.: *J. Org. Chem.* **1992**, *57*, 2993; b) Crandall J. K., Ayers T. A.: *Tetrahedron Lett.* **1992**, *33*, 5311.