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Allene Formation by the Reaction of Olefins with Propargyl Silyl Ethers Mediated by a Zirconocene Complex

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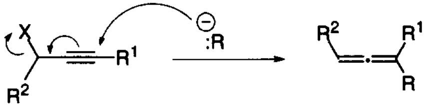
Abstract: Ethylene and styrene derivatives reacted with various propargylic ethers in the presence of zirconocene(II) to afford allenic products in high yields. The reaction proceeded *via* formation of zirconacyclopentenes by selective coupling of an olefin and a propargylic ether, which was followed by β-elimination of the siloxy group. Deuterolysis confirmed that the final product had a zirconium-carbon bond. © 1997 Elsevier Science Ltd.

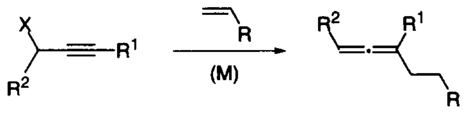
Allenes are useful precursors in organic synthesis.[1] In considering the allene structure, the usual transformation which involves the carbon-carbon bond formation is a nucleophilic 1,3-substitution reaction of a propargylic system (**A** in Scheme 1).[2] Beside this commonly used method, we would like to report herein the reactions of *non-polar* alkenes with propargylic silyl ethers (**B** in Scheme 1, where X=OTBS) which afforded various trisubstituted allenes.

Scheme 1. Carbon-carbon bond formation of a propargylic system

A: Nucleophilic 1,3-substitution by carbanions

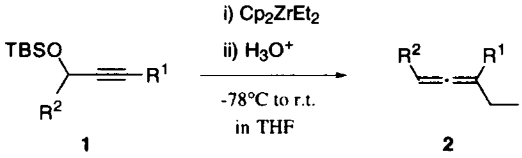


B*: Metal-mediated coupling with non-polar alkenes*



A zirconocene-ethylene complex, $Cp_2Zr(CH_2{=}CH_2)$,[3] which is generated by the reaction of Cp_2ZrCl_2 with 2 *equiv.* of EtMgBr, has been found to be a useful intermediate in various reactions. For example, when $Cp_2Zr(CH_2{=}CH_2)$ was treated by an allyl ether, it gave a 4-pentenyl alkoxyzirconium complex.[4] This reaction has been extended to the zirconium-catalyzed allylation reaction toward olefins. This prompted us to investigate the reaction of zirconocene-olefin complexes with propargylic ethers.

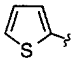
Alkylmagnesium halides, *e.g.*, ethylmagnesium bromide, do not usually react with propargylic ethers even at 50 °C. Such 1,3-substitution reactions could be catalyzed by copper (I) bromide.[1,2] However, when propargylic ethers **1** were treated with 2 *equiv.* of EtMgBr in the presence of a stoichiometric amount of Cp_2ZrCl_2, ethyl allenes **2** were obtained in high yields after hydrolysis (eq. 1). The choice of the leaving group in the propargylic position had to be considered. The corresponding chloride gave a mixture of several products and a TBSO group was the best for ease in preparation of the starting material and to attain clean reactions.



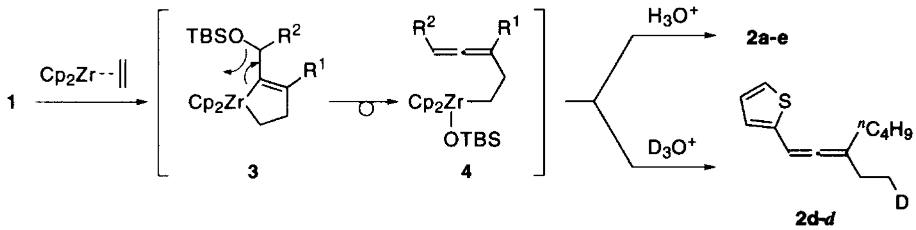
(1)

The results are shown in Table 1. Various propargylic silyl ethers with aliphatic, phenyl and trimethylsilyl groups such as R^1 and R^2 were examined. As in entry 3, the rather reactive bromine functionality on the benzene ring could tolerate the reaction conditions, and *o*-substituted bromophenyl allene **2c** was formed in 86% yield. As in entry 5, a propargyl ether derived from a silylacetylene gave successfully silyl-substituted allene **2e**. The reaction mechanism can be explained in a similar way to that of $Cp_2Zr(CH_2{=}CH_2)$ with allyl ethers,[4] in which the intermediate zirconacyclopentene **3** was formed[5] and β-siloxide elimination from **3** afforded the zirconium complex **4**. Deuterolysis of complex **4** (R^1 = *n*-C_4H_9 and R^2 = thienyl) clearly showed the high D incorporation (>99%) on the terminal carbon of the ethyl group of allenic product **2d**-*d* (eq. 2).[6] This clearly suggests that the final intermediate **4** before hydrolysis has a zirconium-carbon bond. Moreover, this indicates that the reaction does not proceed in the manner of 1,3-displacement reaction of EtMgBr toward propargylic compounds.

Table 1. Formation of ethyl allenes **2** by the reaction of $Cp_2Zr(CH_2{=}CH_2)$ with propargylic ethers[a]

Entry	R^1	R^2	Time (h)	Products	Yields (%)[b]
1	$^nC_4H_9$	$^nC_3H_7$	1	**2a**	93
2	Ph	Ph	1	**2b**	92
3	$^nC_4H_9$	*o*-BrC_6H_4	1	**2c**	86 (73)
4	$^nC_4H_9$		24[c]	**2d**	88 (64)
5	$SiMe_3$	Ph	1	**2e**	69 (54)

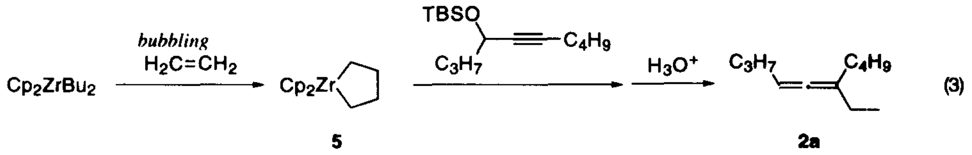
[a]All the reactions were carried out at room temperature. [b]Yields were determined by GC. In parentheses are shown isolated yields. [c]At 1h: 70%, 6h: 80%.



$(R^1{=}^nBu,\ R^2{=}2\text{-}C_4H_3S)$ (>99% D)

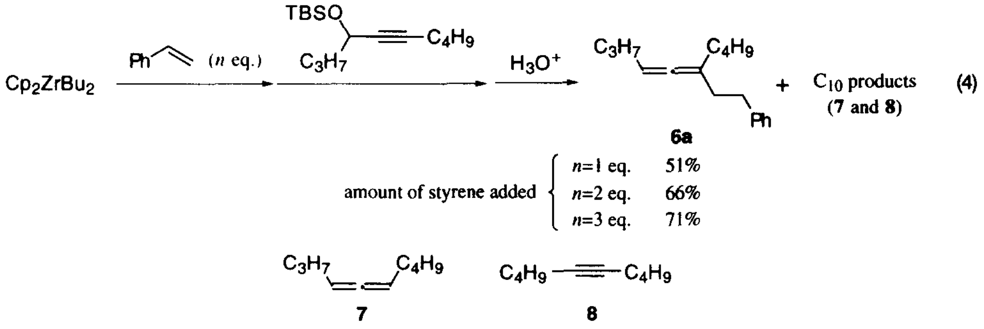
(2)

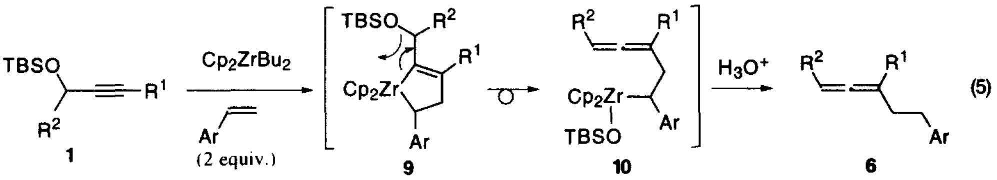
On the other hand, zirconacyclopentane **5** is known to be a precursor of the zirconocene-ethylene complex;[7] thus, the reaction was also carried out starting from ethylene to give allene **2a** as in eq. 3. The reaction proceeded with extrusion of one molecule of ethylene to be replaced by a propargyl silyl ether. In this case, it is clear that the ethyl moiety of the product came from ethylene, and noteworthy is that a *non-polar* olefin reacted



with a *polar* propargylic silyl ether mediated by a low-valent zirconium complex.

This encouraged us to further explore this reaction using other olefins. During the course of our study, styrene[8] and its derivatives were found to give the desired allenic products. When Cp_2ZrBu_2 (Negishi reagent) was treated with 1 *equiv*. of styrene and propargylic ethers, formation of **6** was observed along with a considerable amount of side-products (seemingly, **7** and **8**) without incorporation of styrene (eq. 4). These side-products came after the direct reaction of Cp_2ZrBu_2 with the propargyl ether that was reported by Taguchi and Hanzawa.[9] However, when an excess amount of styrene was used to compensate its poor coordination ability to low-valent zirconium, higher yield of the desired allenic product was achieved. Two equivalents of styrene were used for this reaction. The coupling reaction successfully took place between styrene and the alkyne moiety of propargylic ethers to form α-phenyl substituted zirconacyclopentene **9** followed by siloxide elimination to give ω-phenyl substituted allenes (eq. 5). Various styrene derivatives were employed, and allenes in moderate to high yields (Table 2) were obtaned.





For the coupling with styrene derivatives, the typical procedure is as follows. Cp_2ZrCl_2 (1 mmol) in THF (5 mL) was treated with *n*-BuLi (ca. 1.6*M* in hexane, 2 mmol) at -78°C and the solution was stirred at -78°C for 1 h. To the mixture were added styrene (2 mmol) and a propargyl silyl ether (1 mmol) successively, and the mixture was warmed to room temperature for several hours. The reaction mixture was quenched with 3*N* HCl *aq*. and all the products **6a-h** were separated on silica-gel columns.

In progress are further investigations on intramolecular reactions using enynes which have the corresponding ether moiety, the catalytic reaction which is similar to the allylic system we have reported,[4a] and further carbon–carbon bond formation reactions which utilize the remaining zirconium–carbon bond.

Table 2. Formation of allenes **6** by the coupling of aryl alkenes and propargylic ethers

Ar	R^1	R^2	Time (h)	Products	Yields (%)^a
Ph	$^{n}C_4H_9$	$^{n}C_3H_7$	1	**6a**	67 (58)
Ph	$^{n}C_4H_9$	$^{n}C_6H_{13}$	1	**6b**	91 (76)
Ph	$^{n}C_4H_9$	Ph	1	**6c**	98 (82)
p-ClC_6H_4	$^{n}C_4H_9$	$^{n}C_4H_9$	1	**6d**	— (50)
p-$MeOC_6H_4$	$^{n}C_4H_9$	$^{n}C_3H_7$	1	**6e**	60 (53)
p-FC_6H_4	$^{n}C_4H_9$	$^{n}C_3H_7$	1	**6f**	63 (46)
m-$CH_3C_6H_4$	$^{n}C_4H_9$	$^{n}C_3H_7$	1	**6g**	60 (51)
p-$CH_3C_6H_4$	$^{n}C_4H_9$	$^{n}C_3H_7$	1	**6h**	61 (55)

[a] Yields were determined by GC. In parentheses are shown isolated yields.

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6) NMR spectra for **2d**: ^{1}H NMR ($CDCl_3$, $SiMe_4$) δ 0.89 (t, J = 7.2 Hz, 3H), 1.05 (t, J = 7.4 Hz, 3H), 1.52-1.26 (m, 4H), 2.11-2.05 (m, 4H), 6.36 (t, J = 3.0 Hz, 1H), 6.85 (d, J = 3.4 Hz, 1H), 6.92 (dd, J = 5.1, 3.4 Hz, 1H), 7.08 (d, J = 5.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, $SiMe_4$) δ 12.27, 13.95, 22.51, 26.05, 29.84, 32.67, 90.28, 111.15, 123.46, 123.56, 127.27, 141.52, 201.45. ^{13}C NMR for **2d**-d: ($CDCl_3$, $SiMe_4$) δ 11.99 (CH_2D, t, $^{1}J_{C\text{-}D}$ = 19 Hz), 13.95, 22.51, 25.98, 29.85, 32.68, 90.29, 111.14, 123.46, 123.56, 127.27, 141.51, 201.45.

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