Allylzirconation of Alkynes by the Reactions of Zirconocene-Alkyne Complexes with Allylic Ethers

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Abstract: Reactions of zirconocene-alkyne complexes with allylic ethers afforded allylzirconation products of alkynes in high yields.

Although allylmetalation of alkynes is very attractive reaction for organic synthesis, only allylmetals containing Li, Mg, B, Zn or Al have been used.[2,3] No precedents have been reported for allylzirconation of alkynes. Mechanistic studies of these allylations suggested six-centered or four-centered intermediate stage was plausible.[3] We describe here novel type of allylzirconation of alkynes by the reactions of zirconocene-alkyne complexes with allylic ethers.

Zirconium mediated allylzincation of alkynes[4] or zirconium catalyzed allylalumination reaction[5] has been reported by Negishi. However, allylzirconocene compounds, which are easily prepared by the reaction of Cp_2ZrCl_2 with allyl Grignard[6] or oxidative addition of allylic ethers to 'zirconocene equivalent'[7-9] (Cp_2ZrBu_2: Negishi reagent[10]), are inert for allylzirconation of alkynes.

Recently we found that zirconium-ethylene complex reacted with allylic ether to afford allylzirconation product of ethylene.[11] Furthermore, this reaction could be catalytic as an allylation reaction in the presence of EtMgBr.[11] This reaction proceeded via a five membered zirconacyclopentane intermediate. During the course of our study on this mechanism we demonstrated that zirconacyclopentene compounds reacted with allylic ethers to give allylated products via β,β'-C-C bond fission reactions. These informations led us to allylzirconation reaction of alkynes by the reactions of zirconocene-alkyne complexes with allylic ethers.

Preparation and reactions of zirconocene-alkyne complexes have been already investigated by several groups.[12-19] Zirconocene-alkyne complexes have been prepared by the following two methods:(i) Adding alkyne and stabilizing reagent such as PMe_3[12,14,17] and DMAP[18] to Cp_2ZrBu_2 (Negishi reagent) and (ii) Hydrozirconation of alkynes producing $Cp_2Zr(CR=CHR)Cl$, followed by methylation with MeLi and β-hydrogen abstraction from alkenyl ligand.[13,15,16] The method (i) is very convenient for our purpose. For terminal alkynes, however, the method (i) does not give alkyne-complexes in good yields. The method (ii) is useful for terminal alkyne complexes.
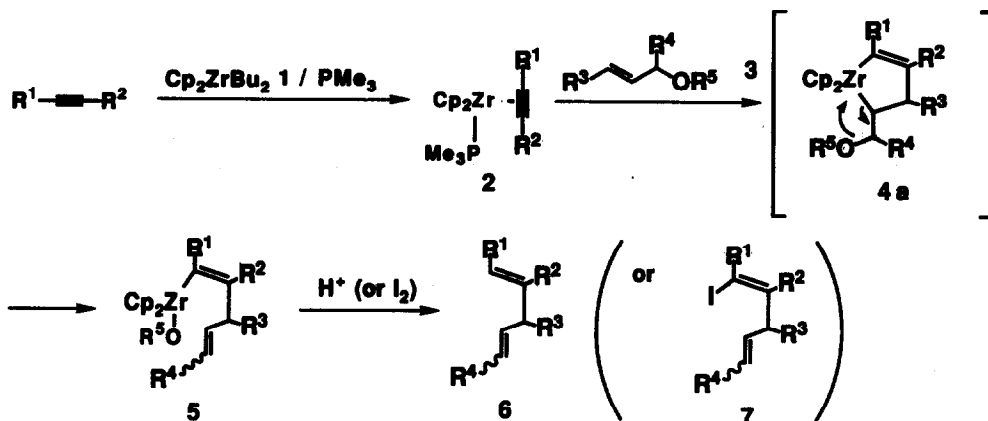
Typical procedure is as follows. To Cp$_2$ZrBu$_2$ prepared from Cp$_2$ZrCl$_2$(1.25 mmol, 0.365 g) and 2 equiv of n-BuLi (2.5 mmol, 1.56 ml 1.6 M) in 5 ml of THF at -78°C was added 1.5 mmol of PMe$_3$ (1.25 ml of 1.0M solution in THF) at -78°C. The mixture was warmed up to room temperature and stirred for 1 hr. And then to this was added 1-trimethylsilylphenylacetylene (1mmol, 0.174 g) at room temperature. Zirconocene alkyne complex was cleanly formed. After addition of 2 mmol of allylphenyl ether (0.268 g), the mixture was stirred for 3h at 35°C. Hydrolysis of this resulting mixture gave 1-trimethylsilyl-2-phenyl-1,4-pentadiene in 97% yield based on alkyne with 98% of regioselectivity. Iodination of this mixture afforded 1-iodo-1-trimethylsilyl-2-phenyl-1,4-pentadiene in 94 % yield.

Results are shown in Table. Trimethylsilylated-1-alkynes gave regioselective allylzirconation products in high yields. Since trimethylsilyl group stabilizes α-carbanions, α-silyl-alkenylzirconium compounds such as 5 (R^1 = TMS) are favorable as products. This is the reason for high regioselectivities in the case of trimethylsilylated-1-alkynes. This type of regioselectivity or orientation was also observed for other allylmetalation such as allylzincation[20] and for reactions of alkynes on zirconium.[16] Unsymmetrical alkyne, 1-phenylpropyne, did not show a high regioselectivity. It is noteworthy that carbon-carbon bond formation occurred only at γ-position of allylic ethers.

The mechanism involving zirconacyclopentene intermediate is plausible for this allylzirconation by the reaction of zirconocene-alkyne complexes with allylic ethers. First, allylzirconocene compounds did not give allylzirconation products of alkynes as described above. Secondly, formation of zirconacyclopentene compound has been reported in the reaction of zirconocene-cyclopentyne complex with α-substituted allylic ether.[19] Two possible isomers 4a and 4b can be considered as zirconacyclopentene intermediates. Even though 4b is formed, transformation of 4b via β–β'-C-C bond cleavage of zirconacyclopentenes[20-22] affords 4a under some conditions as observed for allylation of alkenes.[11] When -CH$_2$OR group occupies α-position of zirconacyclopentene such as the complex 4a, elimination of OR group occurs to give allylzirconation product 5. The complex 5a (R^1= TMS, R^2= Ph, R^3= H, R^4= H, R^5= Ph) was quantitatively formed and characterized by ^{1}H NMR and ^{13}C NMR spectroscopies. The ^{1}H NMR spectrum[23] of 5a showed a singlet

peak at 6.03 ppm assigned to Cp and its ^{13}C NMR spectrum clearly indicated all carbons of **5a** at 3.94, 50.89, 112.00, 115.94, 118.47, 119.87, 126.25, 127.89, 129.00, 129.72, 136.96, 148.70, 158.29, 164.78, 185.21, which are consistent with **5a**.
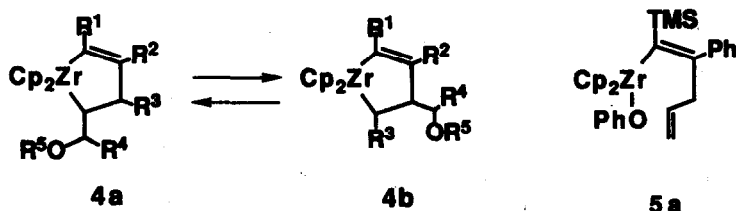
The mechanism involving five membered zirconacyclopentenes for allylzirconation of alkynes is quite different from a mechanism involving four-centered or six-centered transition state proposed previously for allylmetalation reactions of alkynes using allylmetals.

Further investigations are now in progress in this area.

Table. Allylzirconation Reactions of Alkynes by the Reactions of Zirconocene Alkyne Complexes with Allylic Ethers[a]

Run	R[1]	R[2]	R[3]	R[4]	R[5]	Temp /°C	Time /h	Protonolysis Product 6		Iodinolysis Product 7	
								Yield /%	Isomerical purity/%	Yield /%	Isomerical purity/%
1	TMS	Hex	H	H	Ph	35	3	81	97	84	99
2	TMS	Hex	H	H	Et	35	6	80	95	72	96
3	TMS	Hex	H	H	Allyl	35	3	94	>99	88	>99
4	TMS	Hex	Pr	H	Ph	50	48	72	>99	75	>99
5	TMS	Hex	H	C$_5$H$_{11}$	Bn	35	24	80	b	77	b
6	TMS	Ph	H	H	Ph	35	3	97	98	94	98
7	Ph	Ph	H	H	Ph	35	24	97	>99	87	>99
8	Pr	Pr	H	H	Ph	35	1	67	>99	71	>99
9	Ph	Me	H	H	Ph	35	24	76	62	76	60
10[c]	H	Hex	H	H	Allyl	35	24	73	d	56	e

[a]Yields were determined by GC. Unless otherwise mentioned, the alkyne complex was prepared by the method (i) with PMe$_3$. [b]cis:trans = 58:42. [c]Terminal alkyne complex was prepared by the method (ii)[15]. [d]2-hexyl-1,4-pentadiene:(E)-1,4-undecadiene = 78:22. [e]1-iodo-2-hexyl-1,4-pentadiene:(Z)-5-iodo-1,4-undecadiene = 81:19.

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23   ^{1}H NMR data for 5a: 0.02(s, 9H), 2.76(ddd, $J=6.3$, 1.6, 1.3Hz, 2H) 4.87-4.96(m, 2H), 5.69-5.84(m, 1H), 6.03(s, 10H), 6.59-6.64(m, 2H), 6.85-6.91(m, 1H), 7.04-7.26(m, 7H).