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Copper Catalyzed C-C Bond Formation Reaction of Allylzirconation Products of Alkynes

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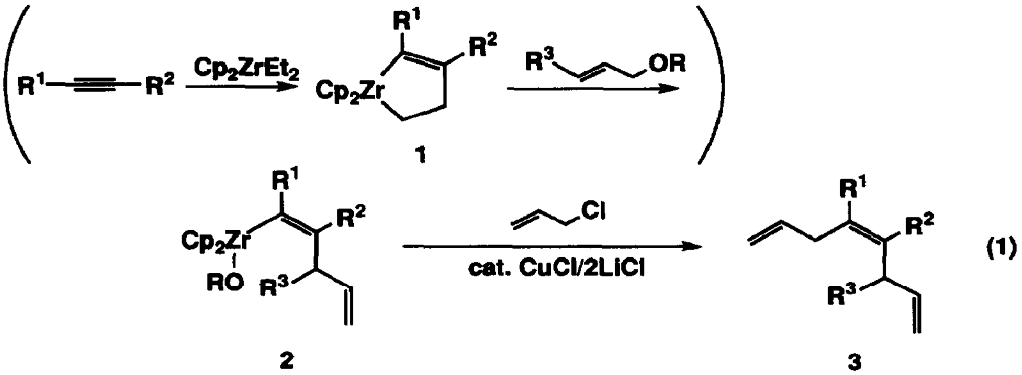
Abstract: Reaction of allylzirconation products of alkynes with allyl chloride was catalyzed by copper salts to give stereodefined 1,4,7-trienes.

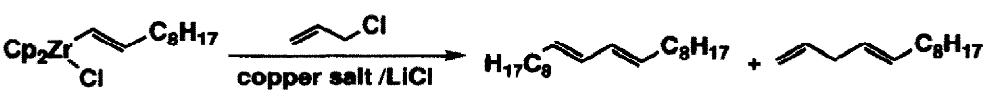
Recently we have reported the allylzirconation reaction of alkynes via zirconacyclopentenes.[2] The carbon-carbon bond formation proceeded exclusively at γ-position of allylic compounds. In order to use the allylzirconation product for further reactions, we investigated C-C bond formation reactions of it. During the course of our study, we found a copper catalyzed allylation reaction of alkenylzirconium compounds with allyl chloride. We would like to describe here the selective preparation of 1,4,7-trienes by the allylation reaction of allylzirconation products of alkynes.



Typical procedure is as follows. To a solution of allylzirconation product **2**, prepared *in situ* as previously reported[2a] using 1 mmol of 5-decyne, 1.2 equiv of Cp_2ZrCl_2, 2.4 mmol of EtMgBr, 5 mL of THF and 1.25 mmol of allyltrimethylsilyl ether, was added 1.5 mmol of allyl chloride and 0.1 mmol of CuCl. After stirring the mixture at 50°C for 1 h, cis-4,5-dibutyl-1,4,7-octatriene (**3**: $R^1 = R^2 =$ n-Bu, $R^3 =$ H) was obtained in 87 % yield.[3] Dimerization product, 4,5,6,7-tetrabutyl-1,4,6,9-decatetraene was not detected.

Alkenylzirconocene compounds prepared by hydrozirconation reaction are known to be transferred to cuprates, which react, in turn, with α,β-unsaturated ketones as reported by Lipshutz et al.[4] It was reported that, however, when alkenylzirconocene compounds were treated with 1 equiv of CuCl, dimerization proceeded to afford dienes.[5] Although the yield is relatively low, CuCN also gives dimerization products. Interestingly, allylzirconation products **2** prepared in situ did not give dimerization products at all in the presence of catalytic amount (10 mol %) of CuCl or CuCN. Addition of allyl chloride to the mixture led to a clean C-C bond formation reaction as described above. In order to elucidate the effect of copper salt, we investigated the reaction of alkenylzirconocene, $Cp_2ZrCl(CH{=}CHC_8H_{17})$ (**4**), prepared from 1-octyne and Cp_2ZrHCl. The results are summarized in Table 1.

Table 1. The effect of copper salt and LiCl on the reaction of **4** with allyl chloride



(2)

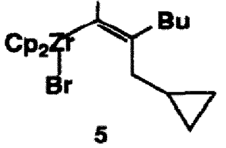
Copper salt	LiCl		Time/h		
CuCN (1 eq)	-	-	3	42	-
CuCN (1 eq)	2 eq	-	3	54	-
CuCN (1 eq)	-	1 eq	3	28	15
CuCN (1 eq)	2 eq	1 eq	1	27	59
CuCN (10 mol %)	2 eq	1 eq	1	4	75

The reactions were carried out in THF at room temperature. Alkenylzirconocene was prepared by the reaction of 1-decyne with Cp_2ZrHCl. Yields were based on 1-decyne.

Knochel reported that addition of LiCl enhanced the solubility of copper salt.[4a,6] We observed the similar effect of LiCl in the case of dimerization using CuCN. However, surprisingly, the addition of LiCl to the mixture of **4**, CuCN and allyl chloride could change the major product. In addition, in the presence of a catalytic amount of CuCN the allylation product was formed in 75% yield. Dimerization product, 9,11-icosadiene was obtained only in 4 % yield. This is because dimerization requires a stoichiometric amount of copper salt. On the other hand allylation of alkenylzirconocene with allyl chloride can be catalytic. Thus, the catalytic amount of CuCN could minimize the formation of dimerization product. Furthermore, in the case of **2**, dimerization product was not formed because of the α-substituted alkenyl moiety.[7]

The solution of allylzirconation product **2** prepared *in situ* contains LiCl or MgX_2. Therefore additional LiCl was not necessary. Only catalytic amount of copper salt was required for the reaction of **2** with allyl chloride. Copper catalyzed allylation of *alkyl*zirconium compounds has been reported by Lipshutz et al.[8]

The present copper catalyzed allylation could be used for other trisubstituted alkenylzirconium compounds such as **5** which was prepared *in situ* by a reaction of zirconacyclopentene **1**[9] with homoallyl bromide.[10] The corresponding allylation products **6** was formed in 70% yield.



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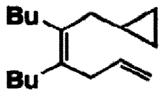

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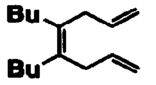
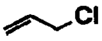
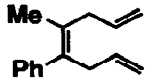
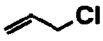
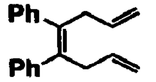
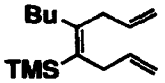
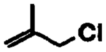
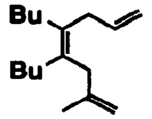
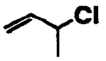
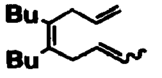
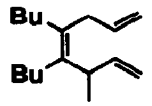
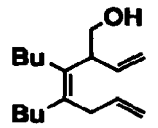
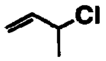
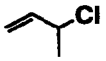
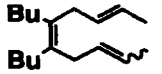
Table 2. Preparation of 1,4,7-Trienes by Double Allylation of Alkynes

Alkynes	1st Allylation			2nd Allylation			Product	Yield[a] /%
	Allyl compound	Temp /°C	Time /h	Allyl compound	Temp /°C	Time /h		
Bu—≡—Bu		50	1		50	1		87 (79)
Ph—≡—Me		50	3		50	3		87 (81)
Ph—≡—Ph		50	1		50	1		95 (84)
Bu—≡—TMS		r.t.	1		50	1		72 (50)
Bu—≡—Bu		50	1		50	1		95 (81)
Bu—≡—Bu		50	1		50	1		90[b] (67)
Bu—≡—Bu		50	1		r.t.	3		92[c] (70)
Bu—≡—Bu		50	6		r.t.	1		72 (54)
Bu—≡—Bu		50	1		50	1		64[d] (54)

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[a] GC yield. Isolated yields were provided in parentheses.[b] A mixture of trans and cis isomers in a ratio of 4.6 :1. Combined yield. [c] Regio isomer, 4,5-dibutyl-1,4,7-nonatriene, was obtained in 12%. Combined yield. [d] First allylation gave only trans isomer. Second allylation afforded a mixture of trans and cis in a ratio of 3 :1.

Combination of copper catalyzed allylation reported here and allylzirconation reaction of alkynes previously reported provided a convenient one pot procedure to prepare stereodefined 1,4,7-octatrienes.[11] Results are shown in Table 2. Double allylation products were obtained in high yields. It is noteworthy that the stereochemistry of the tetrasubstituted alkene moiety was maintained during the copper catalyzed allylation reaction.

Allyltrimethylsilyl ether was a suitable first allylation reagent. This reaction is a substitution reaction of an ethylene moiety of zirconacyclopentenes **1**[9] by allylic compounds. Although allyl chloride gave high yields of 1st allylzirconation products, allyl chloride remained in the reaction mixture after 1st allylation easily reacts with **2** in the presence of copper salt. In the case of unsymmetric double allylation, high reactivity of allyl chloride causes the formation of undesired symmetric allylation products. In order to avoid it, allyltrimethylsilyl ether was used. It reacted with zirconacyclopentenes **1** but not with **2** even in the presence of copper salt.

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3. **3** (R^1=R^2=n-Bu, R^3= H): Yield: 87%, ^{1}H-NMR: 0.90 (t, J = 6.9Hz, 6H); 1.2-1.4 (m, 8H); 2.00 (t, J = 7.6Hz, 4H); 2.75 (d, J = 15.2Hz, 4H); 5.75 (tdd, J = 17, 10, 6.2Hz, 2H); 4.9-5.1 (m, 4H). ^{13}C-NMR: 14.06, 23.02, 31.23, 31.57, 36.15, 114.48, 132.22, 137.18. IR(neat): 3079, 3003, 2957, 2930, 2860, 1638, 1458, 1379, 993, 908, 729 cm^{-1}.
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