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A brief survey on the copper-catalyzed allylation of alkylzinc and Grignard reagents under Barbier conditions

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The same regioselectivity can be obtained in the CuI catalyzed allylic coupling of *n*-butylzinc reagents prepared by either pre-transmetallation or *in situ* transmetallation of Grignard reagents in the presence of allylic partner and catalyst. *n*-Butylzinc bromide and di-*n*-butylzinc undergo γ-selective allylation whereas tri-*n*-butylzincate gives preferential α-selectivity. The regioselectivity obtained in the reaction of *n*-butyl bromide and *E*-crotyl chloride in the presence of Mg and CuCN is parallel to the coupling of preformed *n*-butylmagnesium bromide. It is remarkable that the regiochemical outcome of copper catalyzed alkyl-allyl coupling can be controlled by using Grignard reagents prepared under Barbier conditions and alkylzincs prepared by *in situ* transmetallation. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: alkyl Grignard reagents; alkylzinc reagents; allylic coupling; Barbier–Grignard coupling

INTRODUCTION

The alkylation of allylic electrophiles with organometallics is an important class of reactions for the formation of new C–C bonds. Considerable progress has been made in controlling the regiochemistry and stereochemistry of the copper-mediated and especially copper catalyzed allylic substitution of alkyl Grignard reagents[1–9] and alkylzinc reagents (Scheme 1).[10,11]

The regiochemistry of the copper catalyzed alkyl Grignard reagent-allyl coupling has been found[12–19] to depend on the structure of Grignard reagent, the allylic compound and copper catalyst, as well as reaction conditions. Findings from the allylic coupling of alkylcopper, dialkyl- and alkylcyanocuprates derived from organolithiums and Grignard reagents were found mainly to be consistent with the copper-catalyzed coupling of Grignard reagents.[20–23]

Dialkylzincs and alkylzinc halides were reported to undergo γ-selective allylation in THF in the presence of a copper catalyst,[24,26] a coordinating additive[27,28] or a copper catalyst and a coordinating additive.[25,29–31] α-Selective allylic substitution of a lithium trialkylzincate in THF in the presence of a coordinating additive was also observed.[27] Dialkyl- and alkylcyanozinc halocuprates react with allylic substrates with high γ-selectivity.[11]

Asymmetric γ-selective substitution of allylic substrates with a chiral leaving group or with a chiral group at the γ-position, by alkylcopper[32–38] and -zinc reagents,[39,40] has also been reported. Enantioselective allylic substitution of alkyl Grignard reagents[41–43] and also diethylzinc[44–49] in the presence of a copper catalyst coordinated to a chiral ligand has attracted great interest in recent years.

Although nonsymmetric copper-catalyzed allylic substitution of Grignard reagents has been well established, α- or γ-selective conditions on the corresponding substitution of organozincs has not been well demonstrated. Because of the great utility of organozincs in organic synthesis, we planned to undertake a thorough study of the copper catalyzed alkylzinc-allyl coupling with the aim of developing full regiocontrol depending on coupling partners and copper catalyst as well as other reaction parameters.

EXPERIMENTAL

General

All reactions were carried out under a positive pressure of dry nitrogen,[50] using freshly distilled THF over sodium benzophenone dianion under anhydrous conditions.

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Reagents and solvents were handled using standard syringe-septum cap techniques. Quantitative glpc analysis were performed on a Unicam 610 gas chromatograph equipped with a DB-1 glass capillary column packed with dimethyl polysiloxane and Thermo Finnigan Trace gas chromatograph equipped with a ZB-5 capillary column packed with phenylpolysiloxane using internal standard technique. Yields and product ratios are given as average of at least three experiments.

n-Butyl bromide and *E*-crotyl chloride were obtained commercially and purified using literature procedures. Magnesium turnings for Grignard reactions were used without purification. Zinc chloride was dried under reduced pressure and used as a THF solution prepared prior to use. Copper (I) iodide[51] and copper (I) cyanide[52] were purified according to the published procedures, dried under reduced pressure and kept under nitrogen. *n*-Butylmagnesium bromide was prepared in THF according to standard procedure and its concentration was found by titration prior to use.[53] For authentic samples, *E*-2-octene was purchased and 3-methyl-1-heptene was synthesized.[54]

Procedure for copper catalyzed allylic coupling of *n*-butylzinc reagents 2, 3 and 4 prepared by pre-transmetallation

n-Butylzinc chloride (**2**), di-*n*-butylzinc (**3**) and bromomagnesium tri-*n*-butylzincate (**4**) were prepared by dropwise addition of *n*-butylmagnesium bromide (**1**) (1.1, 2.2 or 3.3 mmol, respectively, 0.9 M, 1.2 ml, 2.4 ml or 3.6 ml, respectively) to a stirred solution of $ZnCl_2$ in THF (1.1 mmol, 0.64 M, 1.7 ml) at 0 °C and stirring at this temperature for 20 min. The reaction mixture was allowed to come to room temperature; CuI (0.2 mmol, 0.038 g) and *E*-crotyl chloride, **5** (1 mmol, 0.1 ml), were added. The mixture was stirred at room temperature for 4 h. Following the addition of internal standard nonane, the mixture was quenched with aqueous NH_4Cl, extracted with Et_2O and organic layer was dried. GC samples were taken for analysis.

Procedure for copper catalyzed allylic coupling of *n*-butylzinc reagents 2, 3 and 4 prepared by *in situ* transmetallation

Addition method A

To a stirred mixture of $ZnCl_2$ in THF (1.1, 2.2 or 3.3 mmol for **2**, **3** and **4**, respectively) and **5** (1 mmol) at 0 °C, **1** (1 mmol) was added dropwise and stirring continued for another 20 min at this temperature. The reaction mixture was allowed to come to room temperature and CuI (0.2 mmol) was added. The mixture was stirred at room temperature for 4 h. The work-up procedure given for the coupling of preformed *n*-butylzinc reagents was used.

Addition method B

To a stirred mixture of required amounts of $ZnCl_2$ in THF, **5** and CuI at O °C, **1** was added dropwise, stirring continued for another 20 min at this temperature. The reaction mixture was allowed to come to room temperature and stirred for 4 h. The same work-up procedure was used as given for addition method A.

Procedure for copper catalyzed allylic coupling of *n*-butylmagnesium bromide 1

Addition method A

n-Butylmagnesium bromide **1** (1.1 mmol, 0.9 M, 1.2 ml) was added dropwise to a stirring mixture of **5** (1 mmol, 0.1 ml) and copper catalyst (0.2 mmol) at room temperature. Stirring continued at that temperature for 4 h. The work-up procedure was the same as given for coupling of *n*-butylzinc reagents.

Procedure for copper catalyzed *in situ n*-butyl-*E*-crotyl coupling

Addition method B

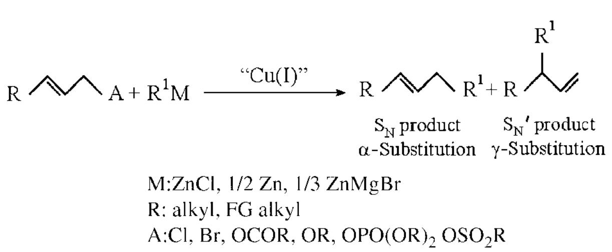
n-Butyl bromide (10 mmol, 1.1 ml) in THF (5 ml) and **5** (5 mmol, 0.5 ml) in THF (5 ml) were added separately to Mg (12 mmol, 0.288 g) and copper catalyst (1 mmol) mixture at room temperature. The reaction was started by first adding a few drops of *n*-butyl bromide. After controlled addition (the addition rate was kept to approximately 0.3–0.5 ml/minute), the reaction mixture was stirred at room temperature for 4 h. The work-up procedure was the same as given for coupling of **1**.

RESULTS AND DISCUSSION

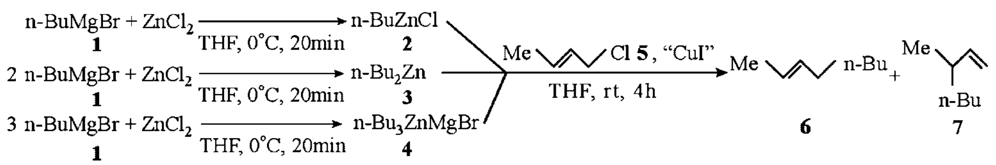
First, we investigated the effect of organozinc type on the regioselectivity of allylic coupling. For a model reaction, we reacted Grignard reagent-derived *n*-butylzinc chloride (**2**), di-*n*-butylzinc (**3**) and tri-*n*-butylzincate (**4**) with *E*-crotyl chloride (**5**) in THF in the presence of a Cu(I) catalyst. (Scheme 2).

We were also interested to see if the preparation of alkylzincs by pre-transmetallation or *in situ* (merged) transmetallation would make a change in the regiochemical outcome of the allylic coupling. For this purpose, we also tried *in situ* transmetallation of Grignard reagent[55,56] either in the presence of an allylic partner or in the presence of an allylic partner and catalyst (Scheme 3).

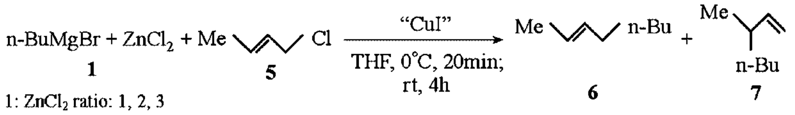
Table 1 summarizes the regioselectivites obtained in the allylation of *n*-butylzinc reagents (**2, 3** and **4**) obtained by



Scheme 1. Copper-catalyzed allylic substitution of alkylzinc reagents.



Scheme 2. Copper-catalyzed allylic substitution of *n*-butylzinc reagents prepared by pre-transmetallation.



Scheme 3. Copper-catalyzed allylic substitution of *n*-butylzinc reagents prepared by *in situ* transmetallation.

Table 1. Copper-catalyzed (20 mol% CuI) allylic coupling of *n*-butylzinc chloride (**2**), di-*n*-butylzinc (**3**) and bromomagnesium tri-*n*-butylzincate (**4**) prepared by pre-transmetallation[a]

Entry	*n*-Butylzinc reagent	Total yield, %	**6**:**7** ratio
1	**2**	74	9:91
2	**2**[b]	65	8:92
3	**3**	82	13:87
4	**3**	71[c]	7:93
5	**4**	93	65:35
6	**4**	84[c]	67:33

[a] **2**, **3** and **4** were prepared by adding the Grignard reagent to $ZnCl_2$ in THF at 0 °C. CuI and **5** were added at room temperature. See the Experimental section for details.

[b] **2** was prepared using $ZnCl_2$. TMEDA complex.

[c] The reaction was performed at 0 °C.

pre-transmetallation of *n*-butylmagnesium bromide (**1**) with one, two or three equivalents of $ZnCl_2$, respectively at 0 °C. Allylation was carried out by addition of *E*-crotyl chloride (**5**) and catalyst to the *n*-butylzinc reagent and stirring the reaction mixture at room temperature. With the optimized 20 mol% CuI, an $\alpha:\gamma$ ratio of 9 : 91 with a total yield of 74% was obtained (entry 1). Using $ZnCl_2$ TMEDA for transmetallation (entry 2) decreased the yield. Di-*n*-butylzinc (**3**) gave the same yield and γ-regioselectivity (entry 3) in the experimental limit. However, coupling of tri-*n*-butylzincate (**3**) gave preferential α-selectivity with an $\alpha:\gamma$ ratio of 65 : 35 and a high yield of 93% (entry 5). Carrying out the coupling at 0 °C decreased the yield slightly, but did not change the regioselectivity (entries 3 and 4; 5 and 6).

To investigate the influence of *in situ* transmetallation on the allylic coupling, *n*-butylzinc reagents (**2**, **3** and **4**) were prepared by the addition of one, two or three equivalents of *n*-butylmagnesium bromide **1**, respectively, to $ZnCl_2$ in the presence of *E*-crotyl chloride (**5**) in THF at 0 °C and, after stirring for 20 min at 0 °C, the catalyst was added (method A). The addition of *n*-butylmagnesium bromide to $ZnCl_2$ was also tried in the presence of **5** and catalyst in THF at 0 °C (method B).

Table 2. Copper-catalyzed (20 mol% CuI) allylic coupling of *n*-butylzinc chloride **2**, di-*n*-butylzinc (**3**) and bromomagnesium tri-*n*-butyl zincate (**4**) prepared by *in situ* transmetallation[a]

Entry	**1**:$ZnCl_2$ ratio	Addition method[b]	Total yield, %	**6**:**7** ratio
1	1	A	52	12:88
2	1	B	82	10:90
3	2	A	74	8:92
4	2	B	84	30:70
5	3	A	86	88:12
6	3	B	83	31:69

[a] Molar ratio of **1**:$ZnCl_2$ was 1, 2 and 3, respectively, for *in situ* preparation of **2**, **3** and **4**.

[b] (A) The Grignard reagent was added to $ZnCl_2$ and **5** in THF at 0 °C; the reaction mixture was allowed to come to room temperature and CuI was added. (B) The Grignard reagent was added to $ZnCl_2$, **5** and CuI at 0 °C and the reaction mixture was allowed to come to room temperature. See the Experimental section for details.

The results summarized in Table 2 show the following features of CuI-catalyzed allylic coupling of alkylzincs prepared by *in situ* transmetallation of alkyl Grignard reagents:

(1) Method B gave higher yields than those obtained with method A in the coupling of *in situ* *n*-butylzinc reagents **2** and **3** (entries 1 and 2; 3 and 4); and **2** and **3** were allylated with a yield of 82 and 84%, respectively. The addition method did not change the γ-selectivity ($\alpha:\gamma = 12:88$) obtained in the coupling of **2**. However, in the coupling of **3**, the $\alpha:\gamma$ ratio of 8 : 92 obtained by method A, decreased to 30 : 70 by method B.

(2) Coupling of **4** using method A resulted in α-selectivity ($\alpha:\gamma = 88:12$) with a yield of 86% (entry 5); however using method B gave the selectivity obtained in the coupling of **3** using method B (entries 4 and 6). These results indicate that the same catalytic organocopper species derived from Grignard reagent are possibly present in the reaction mixture of **3** and **4** if *in situ* organomagnesium to organozinc transmetallation is carried out in the presence of copper catalyst at higher **1**:$ZnCl_2$ ratios.

(3) A remarkably parallel regiochemical outcome was obtained in the coupling of pre-prepared and *in situ* prepared **2, 3** or **4**. Allylation yields of *in situ* prepared *n*-butylzincs are as high as those found from pre-prepared reagents. The $\alpha:\gamma$ ratios in the coupling of preformed and *in situ* formed *n*-butylzinc chloride **2** are 9 : 91 (Table 1, entry 1) and 12 : 88 (Table 2, entry 1), respectively. In addition, a higher α-selectivity ($\alpha:\gamma = 88:12$, Table 2, entry 5) was obtained in the coupling of **4** prepared by *in situ* transmetallation compared with the coupling of **4** prepared by pre-transmetallation ($\alpha:\gamma = 65:35$, Table 1, entry 5).

(4) The γ-selective allylic coupling of Grignard reagent-derived alkylzinc halides can be simplified by carrying out the transmetallation in the presence of both allylic substrate and copper catalyst. However for γ-selective coupling of trialkyl zincates, *in situ* transmetallation should be carried out only in the presence of allylic substrate. We tried *in situ* transmetallation also in the presence of a catalytic amount of $ZnCl_2$, however the use of 10 mol% $ZnCl_2$ in the addition method A resulted in poor regioselectivity ($\alpha:\gamma = 43:57$) with a yield of 95% at 0 °C.

Next we studied one pot reaction of *n*-butyl bromide, *E*-crotyl chloride and Mg in the presence of copper catalyst with the interest of the effect of Barbier–Grignard type allylic substitution on the outcome of the reaction (Scheme 4, route b). However, in the coupling of *in situ* formed *n*-butylmagnesium bromide with *E*-crotyl chloride, *in situ* formed crotylmagnesium chloride might also react with *n*-butyl bromide as well as homocoupling of both Grignard reagents.

For comparison, we first carried out coupling of preformed *n*-butylmagnesium bromide (**1**) with *E*-crotyl chloride (**5**) in THF at room temperature. Two different methods for the addition of coupling partners were tried. The Grignard reagent was added slowly to a solution of **5** and catalyst (method A), or a solution of **5**, and subsequently catalyst were added to the Grignard reagent (method B). It is interesting to find that the coupling also takes place in the absence of catalysis and method A gave a total yield of 80% and an $\alpha:\gamma$ ratio of 84 : 16. In the presence of optimized 20 mol% CuI, an almost quantitative yield was obtained, but α- and γ-substituted products, **6** and **7**, were formed in a ratio of 59 : 41 using method A. Method B lowered the coupling yield to 82%, but a higher $\alpha:\gamma$ ratio of 80 : 20 was obtained. As expected,[19] a change in regioselectivity took place in the coupling catalyzed by 20 mol% CuCN, and **6** and **7** were formed in a ratio of 13 : 87 with a total yield of 93%.

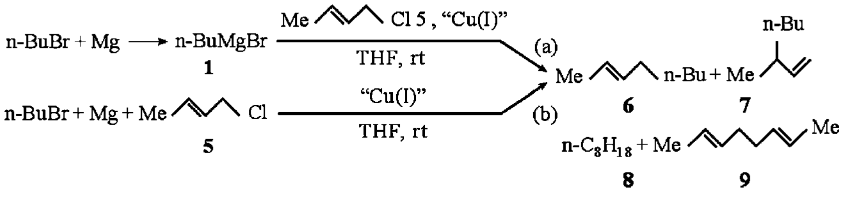
Before carrying out copper-catalyzed *n*-butylmagnesium bromide–crotyl chloride substitution under Barbier conditions, the copper-catalyzed reaction of preformed *E*-crotylmagnesium chloride with *n*-butyl bromide was run in THF at room temperature using method A, i.e. adding the Grignard reagent to *n*-butyl bromide and catalyst. In the presence of 20 mol% CuI or CuCN, we obtained **6** and **7** in a ratio of 97 : 3 (with a total yield of 36%) and 76 : 24 (with a total yield of 38%) respectively. For the one-pot coupling between *n*-butyl bromide and *E*-crotyl chloride in the presence of Mg and CuI or CuCN as a catalyst, we used two different addition methods. Solutions of *n*-butyl bromide and crotyl chloride (**5**) in THF were added separately to Mg and then the catalyst was added (method A), or solutions of *n*-butyl bromide and *E*-crotyl chloride (**5**) were added to Mg and catalyst (method B). The results of Barbier–Grignard type *n*-butyl-*E*-crotyl coupling can be summarized as follows:

(1) Addition methods gave the same total yield of 50% in a reaction catalyzed by optimized 20 mol% CuI. Method A and method B resulted in γ-selectivity with a $\alpha:\gamma$ ratio of 28 : 72 and 37 : 63, respectively. (The yields of homo coupled products **8** and **9** were not determined.)

(2) Compared with the α-selectivity ($\alpha:\gamma = 97:3$) obtained in the CuI catalyzed coupling of *E*-crotyl magnesium chloride, the Grignard reagent formed in the *n*-butyl bromide-*E*-crotyl chloride coupling can be postulated to be *n*-butylmagnesium bromide.

(3) However, $\alpha:\gamma$ ratio of 59 : 41 obtained in the CuI catalyzed allylic coupling of preformed *n*-butylmagnesium bromide does not seem to support this conclusion. The change of regioselectivity in the preformed and *in situ* formed *n*-butylmagnesium bromide may be attributed to the crucial role of addition order on the $\alpha:\gamma$ ratio in allylic coupling reactions. Addition of coupling partners separately to Mg and CuI possibly leads to formation of *n*-butylmagnesium bromide as a key intermediate, resulting in an increased $\alpha:\gamma$ ratio.

(4) In a reaction catalyzed by 20 mol% CuCN, the total yield increased to 86% and an $\alpha:\gamma$ ratio of 10 : 90 was obtained. This regiochemical outcome is parallel to the CuCN-catalyzed coupling of preformed *n*-butylmagnesium



Scheme 4. Copper-catalyzed allylic substitution of preformed *n*-butylmagnesium bromide (route a) or *in situ* formed *n*-butylmagnesium bromide (route b).

bromide with a yield of 93% and an $\alpha:\gamma$ ratio of 13 : 87. In addition, CuCN-catalyzed coupling of *E*-crotyl magnesium chloride gave α-selectivity ($\alpha:\gamma = 76:24$). These results confirm, even at a supportive level, that *n*-butylmagnesium bromide forms to a higher extent than *E*-crotyl magnesium bromide in a one pot reaction of *n*-butyl bromide and crotyl chloride in the presence of the Mg–CuCN combination. Our work is the first successful alkyl–allyl coupling under Grignard–Barbier conditions.

We have shown that the same regiocontrol is obtained in the CuI-catalyzed allylic coupling of *n*-butylzinc chloride, di-*n*-butylzinc and tri-*n*-butylzincate prepared by either pre-transmetallation or *in situ* transmetallation of Grignard reagents. The reaction of *n*-butyl bromide and *E*-crotyl chloride in the presence of magnesium and CuCN catalyst gives the same regioselectivity as observed in the CuCN-catalyzed reaction of *n*-butylmagnesium bromide with an allylic partner. It is remarkable that the regiochemical outcome of copper-catalyzed alkyl–allyl coupling can be controlled using Grignard reagents prepared under Barbier conditions or alkylzincs prepared by *in situ* transmetallation.

Studies on the scope and synthetic application of alkyl–allyl coupling under Barbier conditions and on the role of copper catalysts in controlling the regiochemistry of alkylzinc–allyl coupling are currently under progress in our laboratory.

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