

Efficient Solvent-Free Synthesis of Homoallylic Alcohols Mediated by Zinc–Copper Couple

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Abstract: Under solvent-free conditions, it was found that zinc–copper couple could efficiently mediate the Barbier-type reaction of ketones and allyl bromide to give the corresponding homoallylic alcohols in high to excellent yields at room temperature.

Key words: solvent-free, zinc–copper couple, ketones, allylation, homoallylic alcohols

Due to the importance in synthetic organic and pharmaceutical chemistry, homoallylic alcohols are highly featured in the organic synthesis of many biologically active molecules such as macrolides, polyhydroxylated natural products, and polyether antibiotics.¹ In order to construct these synthetically and biologically important molecules, numerous reagents and methods have been developed to prepare synthetically useful homoallylic alcohols.² Since the 1980s, it has been gradually realized that carbonyl allylation can be achieved even in aqueous media through a Barbier-type reaction.³ This discovery aroused considerable attention because of the increasing public interest in green chemistry.⁴ So far, the Barbier-type reactions have been in widespread use in preparative laboratories and in industrial applications as a mild and efficient method for the synthesis of homoallylic alcohols.

Up to the present, many metals have been reported to be effective in mediating the aqueous coupling between allyl halides and carbonyl compounds to give rise to the corresponding homoallylic alcohols. Examples include indium,⁵ antimony,⁶ lead,⁷ manganese,⁸ iron,⁹ magnesium,¹⁰ zinc,¹¹ tin,¹² gallium¹³ or organometallic compounds such as allylmercurybromide¹⁴ and allyltributylstannanes.¹⁵ Although good yields could be often obtained in these reactions, it is noteworthy that not all of the above aqueous Barbier reactions could be conducted in fully aqueous media. Most of these reactions were carried out with acidic co-reagents such as ammonium chloride, hydrobromic acid, or organic co-solvents like a mixture of tetrahydrofuran and water, ethanol and *N,N*-dimethylformamide to improve the yields. In addition, long reaction time was frequently required for full conversions. Recently, solvent-free reactions have received increasing attention because of the following advantages: short reaction time,

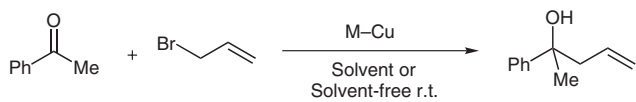
high yields, low costs, reduced pollution, and simplicity in process and handling.¹⁶ As environmentally friendly 'green' synthesis is becoming more important, chemists have been searching for solvent-free reactions under mild conditions.

So far, many reports are concerned with the allylation of aldehydes. However, successful examples for allylation of ketones were much less than those for aldehydes. Perhaps this is due to the lower electrophilicity of the carbonyl carbon.^{12f,17} Among the limited successful examples for allylation of ketones, long reaction time,^{12e} ultrasonic radiation^{12f} or heating^{13c} was indispensable to accomplish the reaction. Furthermore, the allylation of ketones resulted in lower yields in many cases.^{12g} These results stimulated us toward further research on this kind of reactions.

As part of our program to explore the synthetic applications of organozinc reagents,¹⁸ we have focused our attempts on developing rapid and novel green chemistry reactions. In our further investigations, we found that zinc–copper couple was efficient in some reactions,¹⁹ including the allylation of iminium ions to give the corresponding homoallylic amines.^{19f} In this paper, we wish to report our improvement on an efficient, rapid and practical procedure for the allylation of ketones mediated by zinc–copper couple under solvent-free conditions to give rise to the corresponding homoallylic alcohols in high to excellent yields.

To study the effect of different M–Cu couples and solvents on the yields of the reaction, a mixture of acetophenone, allyl bromide, solvent and the M–Cu couple was stirred at room temperature. The results are listed in Table 1.

From Table 1, it can be gathered that no significant formation of the desired product was observed even after prolonged stirring time when distilled water, diethyl ether or dichloromethane was used as solvent (Table 1, entries 1–4). If the solvent was *N,N*-dimethylformamide or tetrahydrofuran, acetophenone could be allylated to give the corresponding product in high yields (Table 1, entries 7 and 8). However, lower yield of homoallylic alcohol was obtained when dimethyl sulfoxide was used as solvent (Table 1, entry 6). The reaction in acetonitrile afforded very poor yields (Table 1, entry 5). When no solvent was used, to our surprise, the allylation of acetophenone proceeded smoothly at room temperature and satisfactory yields were obtained (Table 1, entries 9 and 10).

Table 1 Allylation of Acetophenone Mediated by Various M–Cu Couples under Different Conditions^a


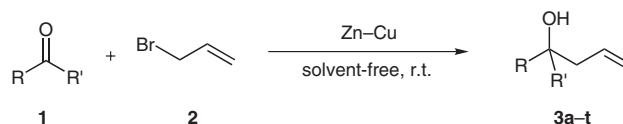
Entry	M–Cu	Solvent	Time (h)	Yield (%) ^b
1	Zn–Cu	H ₂ O	12	Trace ^c
2	Zn–Cu	H ₂ O	36	12
3	Zn–Cu	Et ₂ O	13	58
4	Zn–Cu	CH ₂ Cl ₂	16	64
5	Zn–Cu	MeCN	2	39
6	Zn–Cu	DMSO	1.5	67
7	Zn–Cu	THF	2	83
8	Zn–Cu	DMF	2	78
9	Zn–Cu	–	0.33	93
10	Zn–Cu	–	3	92
11	Cd–Cu	–	24	NR ^c
12	Fe–Cu	–	24	NR ^c
13	Mn–Cu	–	48	NR ^c
14	Al–Cu	–	48	NR ^c
15	Sn–Cu	–	1	65
16	Mg–Cu	–	1	78
17	Zn	–	0.33	85

^a Reaction conditions: M–Cu couple (3 mmol), allyl bromide (3 mmol), acetophenone (2 mmol), solvent (2 mL), r.t.

^b The isolated yields are reported. The product was identified by IR, ¹H NMR, ¹³C NMR and MS.

^c NR: no reaction. Almost all of the acetophenone was recycled.

In an effort to obtain improved yields, we screened different M–Cu couples to mediate the reaction. The M–Cu couples such as cadmium–copper couple, iron–copper couple, manganese–copper couple and aluminum–copper couple did not furnish the desired products even after prolonging the reaction time (Table 1, entries 11–14). When tin–copper couple or magnesium–copper couple was chosen as the mediator, the allylation reaction proceeded smoothly and the desired products were obtained (Table 1, entries 15 and 16). With zinc powder, the allylation yield was further enhanced to 85% at room temperature after 20 minutes (Table 1, entry 17). Among the different M–Cu couples studied, zinc–copper couple was found to be the most effective mediator for this allylation since it resulted in the highest conversion of the desired product (Table 1, entry 9). These results encouraged us to conduct further investigations on allylation reaction mediated by zinc–copper couple. According to the present

**Scheme 1**

studies, we found that zinc–copper couple could efficiently mediate the allylation of ketones under solvent-free conditions at room temperature.²⁰

Subsequently, we examined the scope of the reaction by using various ketones (Scheme 1). The results are summarized in Table 2. We first tried the reaction of allyl bromide with diphenylmethanone under solvent-free conditions. Although the steric hindrance caused by phenyl groups in diphenylmethanone always results in its low reactivity, we were lucky to obtain a satisfactory result (Table 2, entry 1). Then bis(4-chlorophenyl)methanone was used under the same conditions, and again an excellent isolated yield of 96% was obtained (Table 2, entry 2). Subsequently, a variety of ketones were examined by using the solvent-free allylation method. From Table 2, it can be seen that the allylation of ketones mediated by zinc–copper couple under solvent-free conditions usually gave products in an excellent yield. For 1-phenyl-1-propanone (Table 2, entry 3), acetophenone (Table 2, entry 4), 2-acetylnaphthalene (Table 2, entry 8), and 1-(9*H*-fluoren-7-yl)ethanone (Table 2, entry 9), the allylation could be carried out very well. Moreover, the reaction conditions were sufficiently mild not to affect the chloro (Table 2, entry 5), phenyl (Table 2, entry 7) and methoxy (Table 2, entry 6) functionalities. Aliphatic ketones could also be allylated smoothly under our conditions (Table 2, entry 10). However, allylation of alicyclic ketones gave the corresponding products in moderate yields (Table 2, entries 11–13). Further studies indicated that the heterocyclic ketones also provided the allylation products in high yields (Table 2, entries 15–19). In particular, for α,β -unsaturated ketones including cyclohex-2-enone (Table 2, entry 13), (*E*)-4-phenylbut-3-en-2-one (Table 2, entry 14) and (*E*)-4-(thiophen-2-yl)but-3-en-2-one (Table 2, entry 15), only the 1,2-addition products were obtained selectively. In addition, for benzil, the allylation proceeded smoothly and gave the single addition product (Table 2, entry 20).

It is noteworthy that no coupling products were found in our reactions. Also, the solvent-free conditions were necessary for the successful allylation of ketones, which is a great improvement in reducing chemical pollution.

In conclusion, the present study has succeeded in the novel allylation of ketones mediated by zinc–copper couple under solvent-free conditions at room temperature. Compared with previous reaction systems, the reaction reported here has the following advantages: mild conditions, short reaction time, environmentally benign and high yields.

Table 2 Alkylation Reactions Mediated by Zinc–Copper Couple under Solvent-Free Conditions^a

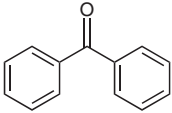
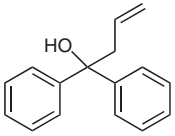
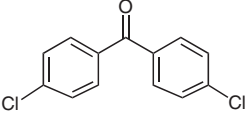
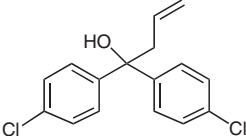
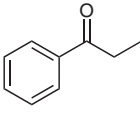
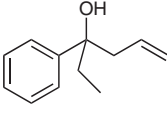
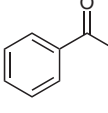
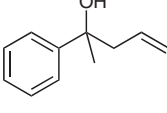
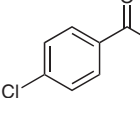
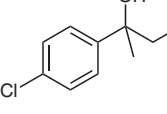
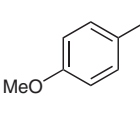
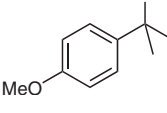
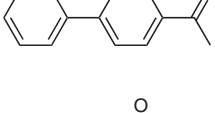
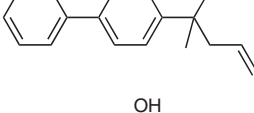
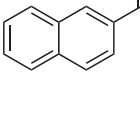
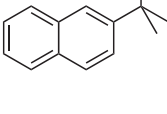
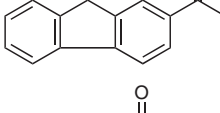
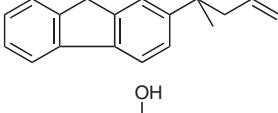
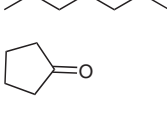
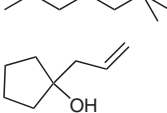
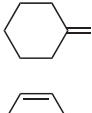
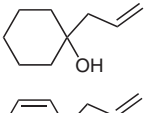
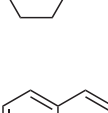
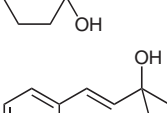
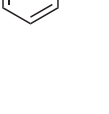
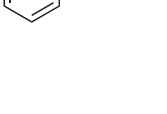


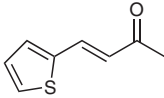
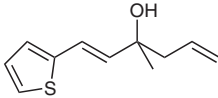
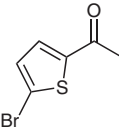
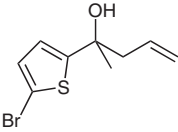
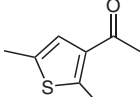
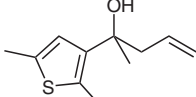
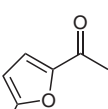
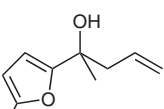
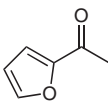
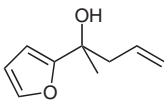
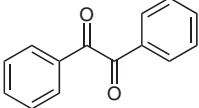
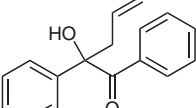
Entry	Substrate	Product ^b		Time (min)	Yield (%) ^c
1			3a	15	95 (80) ^d
2			3b	15	96
3			3c	25	94 (77) ^d
4			3d	15	93 (85) ^d
5			3e	13	92
6			3f	15	97
7			3g	13	94
8			3h	15	96
9			3i	13	93
10			3j	15	87 (74) ^d
11			3k	18	77 (70) ^d
12			3l	14	86 (71) ^d
13			3m	13	82 (78) ^d
14			3n	17	91

Table 2 Allylation Reactions Mediated by Zinc–Copper Couple under Solvent-Free Conditions^a (continued)

Entry	Substrate	Product ^b	Time (min)	Yield (%) ^c
15			20	87
16			15	86
17			13	88
18			14	83
19			18	83
20			80	96

^a All reactions were conducted on the following scale: zinc–copper couple (0.24 g), ketones (2 mmol), and allyl bromide (2.5 mmol) at r.t. for 13–80 min.²⁰

^b All products were characterized by IR, ¹H NMR, ¹³C NMR, MS, and elemental analyses.²¹

^c Yields of isolated products.

^d The yields in brackets are from the same reaction mediated by zinc powder.^{11a}

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- (20) **Preparation of the Zinc–Copper Couple:** Zinc powder (11.6 g) and distilled H₂O (80 mL) were placed into a 100-mL round-bottom flask equipped with a stir bar. With stirring, HCl acid (37%, 2 × 1 mL) was added over 10 min. Then the CuSO₄ solution (20%, 20 mL) was added dropwise with stirring and the stirring was continued for about 15 min. Finally, the mixture was filtered and the solid was washed with H₂O (3 × 30 mL), acetone (3 × 10 mL), and Et₂O (2 × 10 mL). Then the solid was transferred into a flask equipped with vacuum take-off and dried under vacuum for 3 h at 100 °C. Other M–Cu couples were also prepared in this way.
- Preparation of the Homoallylic Alcohols:** Zinc–copper couple (0.24 g), allyl bromide (2.5 mmol) and ketones (2 mmol) were placed in a dried round-bottom flask, and the mixture was stirred at r.t. and the reaction was monitored by TLC. After reaction completed, sat. brine (10 mL) was poured into the mixture, the mixture was extracted with Et₂O (3 × 10 mL) and the organic layer was separated, dried over anhyd MgSO₄, filtered, and evaporated. The pure products were obtained by flash chromatography over silica gel, and characterized by IR, ¹H NMR, ¹³C NMR and MS.
- (21) **Representative Spectroscopic Data for Compounds 3.** Compound **3i**: IR: 3475, 2976, 1670, 1456, 1269, 1101, 920, 771, 738 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 7.24–7.84 (m, 7 H), 5.60–5.70 (m, 1 H), 5.09–5.19 (m, 2 H), 3.88 (q, *J* = 6.4 Hz, 2 H), 2.65–2.76 (m, 1 H), 2.52–2.63 (m, 1 H), 2.14 (s, 1 H), 1.61 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ = 146.4, 143.3, 143.3, 141.4, 140.2, 133.7, 126.7, 126.5, 125.0, 123.4, 121.5, 119.8, 119.4, 73.8, 48.6, 37.0, 30.1, 26.8. EI–MS: *m/z* (%) = 250 (2.4) [M⁺], 209 (64.9), 193 (16.8), 165 (37.7), 43 (100), 39 (17.2). Anal. Calcd for C₁₈H₁₈O: C, 86.36; H, 7.25. Found: C, 86.36; H, 7.36. Compound **3p**: IR: 3406, 3077, 2977, 1644, 1439, 1372, 1114, 923, 796 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 6.88 (d, *J* = 3.6 Hz, 1 H), 6.63 (d, *J* = 3.6 Hz, 1 H), 5.67–5.78 (m, 1 H), 5.12–5.19 (m, 2 H), 2.57–2.67 (m, 1 H), 2.48–2.54 (m, 1 H), 2.34 (s, 1 H), 1.57 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ = 154.6, 132.8, 129.5, 122.5, 120.2, 110.5, 73.0, 48.7, 30.1. EI–MS: *m/z* (%) = 248 (0.3) [M⁺ + 2], 246 (0.2) [M⁺], 231 (0.3) [M⁺ – Me], 229 (0.3) [M⁺ – OH], 207 (33.7), 43 (100), 39 (21.7). Anal. Calcd for C₉H₁₁BrOS: C, 43.74; H, 4.49. Found: C, 43.29; H, 3.93. Compound **3q**: IR: 3439, 3072, 2922, 1662, 1445, 1369, 1142, 917, 829 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 6.54 (s, 1 H), 5.67–5.78 (m, 1 H), 5.12–5.17 (m, 2 H), 2.15–2.50 (m, 8 H), 2.04 (s, 1 H), 1.51 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ = 142.1, 134.2, 133.9, 131.3, 125.3, 119.2, 73.6, 47.7, 30.9, 29.3, 15.0. EI–MS: *m/z* (%) = 196 (2.37) [M⁺], 181 (0.04) [M⁺ – OH], 155 (24.9), 139 (10.5), 113 (5.7), 59 (9.3), 43 (100), 41 (16.2), 39 (16.9). Anal. Calcd for C₁₁H₁₆OS: C, 67.30; H, 8.22. Found: C, 66.92; H, 8.07. Compound **3r**: IR: 3411, 3077, 2981, 1684, 1373, 1097, 921, 786 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 6.05 (s, 1 H), 5.87 (s, 1 H), 5.68–5.72 (m, 1 H), 5.11–5.15 (m, 2 H), 2.64–2.69 (m, 1 H), 2.51–2.56 (m, 1 H), 2.28 (s, 3 H), 2.14 (s, 1 H), 1.51 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ = 157.3, 151.2, 133.5, 119.0, 105.8, 105.3, 70.5, 46.0, 26.3, 13.5. EI–MS: *m/z* (%) = 166 (0.7) [M⁺], 149 (1.7) [M⁺ – OH], 135 (0.7), 125 (91.5), 109 (10.3), 95 (2.1), 43 (100), 39 (20.6). Anal. Calcd for C₁₀H₁₄O₂: C, 72.26; H, 8.49. Found: C, 72.28; H, 8.64.

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