The Solvent-Free Addition Reaction of Allylzinc Bromide and Carbonyl Compounds

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The reactivity of organozincs could be enhanced dramatically under solvent-free conditions. Allylzinc bromide can react rapidly with aldehydes and ketones to give homoallylic alcohols in high yields in the absence of a catalyst under solvent-free conditions in an open atmosphere at room temperature.

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Introduction

Allylation of carbonyl compounds to produce homoallylic alcohols plays a very important role in the organic synthesis of many biologically active molecules such as macrolides, polyhydrosylated natural products, and polyether antibiotics.^[1] The allylation of carbonyl compounds by using allylic metal reagents is a very important class of C–C bond-forming reaction.^[2] More recently, allylic organometallic compounds, such as allylchromium,^[3] -indium,^[4] -magnesium,^[5] -aluminum,^[6] -silane,^[7] -boronate,^[8] -stannane,^[9] and so on, have been examined. However, many allylmagnesium and allyllithium reagents are often very difficult to handle, and the reactions have to be performed under strictly anhydrous, oxygen-free, and low-temperature conditions for prolonged lengths times.

Organozinc reagents have been known for more than 150 years.^[10] However, their application to organic synthesis is limited to very specific reactions as a result of their moderate reactivity. These reagents were soon replaced by the more-active organomagnesium and organolithium reagents, which had broad applications in organic synthesis. However, it soon became clear that this high reactivity had some drawbacks, as low chemoselectivity was observed and only R groups bearing relatively few functional groups were tolerated. It was noticed that organozinc reagents were easily prepared and had higher functional group compatibility in comparison with organolithium and Grignard reagents. Furthermore, the low reactivity of zinc organometallic reagents can be increased by adding a transition-metal cata-

[b] State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, P. R. China lyst.^[11,12] Organozinc compounds are today one of the most useful classes of organometallic reagents. The applications of organozinc compounds range from the preparation of biologically relevant molecules, asymmetric synthesis, and new materials to combinatorial chemistry.

There are three main classes of organozinc reagents: organozinc halides (RZnX), diorganozinc reagents (R2Zn), and triorganozincates.^[13] Organozinc halides are readily available by the direct insertion of zinc dust into organic halides.^[14] Diorganozinc reagents require different methods of preparation, like iodine-zinc and boron-zinc exchange.^[15] Diorganozinc reagents display enhanced chemical reactivity in comparison to alkylzinc halides. In 1978, Mukaiyama first reported that Et₂Zn could react smoothly with benzaldehyde in the presence of a transition-metal catalyst.^[16] Since then, much attention has been given to the reaction,^[17] especially with regard to the enantioselective addition reaction of diorganozinc compounds to aldehydes and ketones.^[18] Organozinc halides are very unreactive to most organic electrophiles. The low reactivity of zinc organometallic reagents can be increased by adding a transitionmetal catalyst like Cu, Pd, Ni, Co, or Mn.^[19] In 1988, Knochel^[12] found that functional organozinc iodides RZnI could undergo transmetalation into organozinc-copper reagents [RCu(CN)ZnI] with the THF-soluble copper salt CuCN·2LiCl. This report greatly extended the application range of organozinc reagents in organic synthesis. Organozinc-copper reagents have been successfully used in coupling reactions with organic halides, 1,2-addition reactions with aldehydes or ketones, and 1,4-addition reactions with α , β unsaturated carbonyl compounds or nitro olefins.^[19a,20] However, stoichiometric toxic CuCN·2LiCl must be used in most reactions. In recent years, many green and efficient ways have been applied to the preparation and reactions of organozinc reagents, such as the use of Cu(OAc)₂·2LiCl instead of CuCN·2LiCl,^[21] nickel(II) catalysts,^[22] ionic liquids.^[23] and electrochemical methods.^[24] We also have re-



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ported^[25] the transition-metal-catalyzed stereoselective synthesis of (E)-stilbenes with the use of organozinc reagents and carbonyl compounds.

In this paper, we report the reactions of allylzinc bromide and carbonyl compounds to give homoallylic alcohols under solvent-free conditions. We find that the reactivity of the organozinc reagent could be enhanced dramatically in the absence of solvent (THF). Allylzinc bromide can react with various aldehydes and ketones to give homoallylic alcohols in a very short time without any catalysts. The reaction of organozinc reagents always requires strict reaction conditions such as a nitrogen atmosphere, anhydrous solvents, and low temperature. However, the reaction of allylzinc bromide with carbonyl compounds proceeds well in an open atmosphere at room temperature following our present route. The yields are high and the reaction time is very short.

Results and Discussion

FULL PAPER

We initially studied the reactions of allylzinc bromide and aldehydes under solvent-free conditions. The range of different types of aldehydes that participate in this reaction is summarized in Table 1. From the results, it can be seen that most of the reactions were complete after 2 min at room temperature, and side reactions such as couplings were not observed. In general, allylation of a number of aromatic aldehydes (Table 1, Entries 1-10, 16, 17) gave the corresponding products in good to excellent yields under solvent-free conditions. Aliphatic aldehydes were also allylated smoothly under the same conditions in good yields (Table 1, Entries 14 and 15). 9-Anthranylaldehyde gave a moderate yield (58%) under similar conditions (Table 1, Entry 10). The low yield of 9-anthranylaldehyde is attributed to its steric hindrance. Further studies indicated that heteroaromatic aldehydes could provide the allylation products in high yields (Table 1, Entry 11). It was noteworthy that cinnamaldehydes solely gave 1,2-addition products (Table 1, Entries 12 and 13). Thus, we can conclude that electron-withdrawing or electron-donating groups on the aromatic ring do not affect significantly the reaction, and all reactions were complete in a few minutes at room temperature.

Encouraged by these preliminary results, we further investigated the allylation of some ketones under the same conditions. The results are summarized in Table 2. It was found that the solvent-free allylation of various ketones also provided homoallylic alcohols in satisfactory yield. However, the yield and the rate of the reaction decreased slightly relative to those with aldehydes. Benzophenone provided the allylation products only in a moderate yield under the same conditions. This is attributed to steric hindrance from the two phenyl groups (Table 2, Entry 2). In this case, an excess amount of allylzinc bromide was necessary (with 1.5 equiv. of allylzinc bromide) to increase the conversion of benzophenone. When an α , β -unsaturated ketone was used, the 1,2-addition product was obtained exclusively (Table 2, Entry 7).

Table 1. The addition reactions of allylzinc bromide and aldehydes. $\ensuremath{^{[a]}}$

//	ZnBr +	solvent free	→	ОН	~
	1	2 min, r.t.	F	₹ ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	~
Entry	R	Product		Time [min]	Yield ^[b] [%]
1	o-HOC₀H₄	ОН	3a	2	82
2	2,4-Cl ₂ C ₆ H ₃	CI-CI	3b	2	96
3	<i>p</i> -ClC ₆ H ₄	CI-OH	3c	2	88
4	o-MeOC ₆ H ₄	OCH ₃	3d	2	87
5	$m ext{-BrC}_6 ext{H}_4$	Br OH	3e	2	91
6	<i>p</i> -BrC ₆ H ₄	Br	3f	2	86
7	<i>p-t</i> BuC ₆ H ₄	/Bu	3g	2	76
8	<i>p</i> -MeOC ₆ H ₄	Н3СО-	3h	2	90
9	Ph	OH OH	3i	2	87
10		HO	3j	10	58
11	$\overline{\mathbb{C}}$	OH OH	3k	2	89
12	C ₆ H ₄ CH=C(Br)	OH Br	31	2	69
13	C ₆ H ₄ CH=C(Me)	OH CH ₃	3m	2	76
14	CH ₃ (CH ₂) ₅	OH	3n	2	67
15	$C_6H_4CH_2$	OH OH	30	2	87
16	<i>p</i> -O ₂ NC ₆ H ₄	O ₂ N-	3p	2	82
17	p-F ₃ CC ₆ H ₄	F ₃ C	3q	2	78

[a] Reaction conditions: allylzinc bromide (10 mmol) was treated with the aldehyde (8 mmol) for 2 min in an open atmosphere at room temperature. [b] Isolated yield.

Table 2. The addition reactions of allylzinc bromide and ketones.[a]

*	ZnBr	+	R^{O} R^{1}	solvent free	→	R^{OH}	//
	1		4	,		5a-m	
Entry	R	R^1		Product		Time [h]	Yield ^[b] [%]
1	Ph	Me		CH ₃	5a	2	78
2	Ph	Ph		OH	5b	3	80
3	Ph	Et		OH C ₂ H ₅	5c	2	82
4	CH ₃ (CH ₂) ₄	Me	\sim		5d	2	71
5)	\langle	OH	5e	3	65
6				OH	5f	3	68
7)	$\left\langle \right\rangle$	OH	5g	2	70
8	<i>p</i> -ClC ₆ H ₄	Me	ci—	OH CH ₃	5h	1	83
9	<i>p</i> -MeC ₆ H ₄	Me	Н₃С—	OH CH ₃	[≈] 5i	1	80
10	<i>p</i> -BrC ₆ H ₄	Me	Br—	CH ₃	≷5j	1	77
11	<i>p</i> -MeOC ₆ H ₄	Et	H ₃ CO-	OH C ₂ H ₅	5k	2	67
12	<i>p</i> -MeOC ₆ H ₄	Me	H ₃ CO-	CH ₃	51	2	75
13	S	Me		OH CH ₃	5m	1	80

[a] Reaction conditions: allylzinc bromide (10 mmol) was treated with the ketone (8 mmol) for 1-3 h at room temperature in an open atmosphere at room temperature. [b] Isolated yield.

Removal of the solvent (THF) plays a major role in the reaction. By using the reaction of allylzinc bromide with 2,4-dichlorobenzaldehyde as an example, we investigated the effect of the solvent on the reaction. We initially studied the reactions of allylzinc bromide and 2,4-dichlorobenzaldehyde in THF. The yield was low (50%) in the presence of THF, even after a long reaction time (16 h). To our surprise, the reactivity of the organozinc reagents could be enhanced dramatically in the absence of THF. Allylzinc bromide can react with 2,4-dichlorobenzaldehyde in 2 min without any catalysts under solvent-less conditions, and the yield was very high (96%). The reason^[26] is probably that the micro-environment and the higher concentration of reactants in the absence of solvent led to more favorable kinetics than in solution.



We have also investigated the same reaction of zinc reagents of substituted allyl bromide (1-bromo-3-methyl-2-butene and 2,3-dibromo-1-propene) with aromatic aldehydes and heteroaromatic aldehydes, but no reaction occurred. No desired products were obtained under the same conditions. The reason is due to the low reactivity of α , γ -substituted allylzinc reagents.

Conclusions

In conclusion, we present herein a rapid, efficient method for obtaining a variety of homoallylic alcohols by the addition of allylzinc bromide to carbonyl compounds under solvent-free conditions. The advantages of this environmentally benign procedure include short reaction times, excellent yields, operational simplicity, and broad applicability to both ketones and aldehydes.

Experimental Section

General Methods: IR spectra were measured by using an Alpha Centauri FTIR spectrophotometer. ¹H NMR spectra (400 MHz) were recorded in CDCl₃ by using a Bruker AC-E 400 MHz spectrometer. Mass spectra were performed with a QP-1000A GC–MS spectrometer by EI ionization at 70 eV. Purification of the products was performed by flash chromatography with 200–400 mesh silica gel [petroleum ether (b.p. 60–90 °C)/ethyl acetate, 15:1]. All chemicals were obtained from commercial sources. The spectral data of new compounds **31** and **5k** are given below. The spectral date of other known products **3a**,^[27] **3b**,^[28] **3c**,^[2a] **3d**,^[29] **3e**,^[3a] **3g**,^[31] **3h**,^[29,31] **3i**,^[31] **3j**,^[32] **3k**,^[29,31] **3m**,^[33] **3n**,^[34] **3o**,^[29] **3g**,^[35] **3q**,^[36] **5a**^[29,31] **5b**,^[29] **5c**,^[37] **5d**,^[29] **5e**,^[29,31] **5f**,^[38] **5g**,^[29] **5h**,^[28] **5**,^[39] **5**,^[36] **5**,^[40] and **5m**^[29,31] are consistent with those reported in the literature.

Typical Procedure for the Synthesis of 1-Phenyl-3-buten-1-ol (3i): Allylzinc bromide was prepared under a nitrogen atmosphere by using Knochel's procedure,^[12] which was slightly modified. In a flame-dried round-bottom flask fitted with magnetic bar and dropping funnel was placed zinc powder (0.78 g, 12 mmol), and the flask was flushed with dry nitrogen. Zinc powder was heated to 60-70 °C. 1,2-Dibromoethane (0.1 mL, 1.2 mmol) and THF (2 mL) was added, and the temperature was maintained for 10 min. The reaction mixture was then cooled to room temperature. Trimethylsilyl chloride (0.1 mL, 0.8 mmol) and THF (1 mL) was added. The mixture was stirred at room temperature for 15 min. After this step, allyl bromide (1.21 g, 10 mmol) in THF (5 mL) was added dropwise over 30 min, and the mixture was stirred for 2 min.

Procedure for the Addition Reaction of Allylzinc Bromide to the Carbonyl Compounds: The THF solvent was evaporated from the allylzinc bromide solution in vacuo. In an open atmosphere, benzaldehyde (0.85 g, 8 mmol) was added immediately. The resulting mixture was stirred for 2 min at room temperature. After the reaction was complete, as indicated by TLC, saturated aqueous ammonium chloride was poured into the mixture, which was then stirred for 10 min. Ethyl ether was added to the reaction mixture, and the organic layer was separated. The organic extracts were dried with anhydrous MgSO₄. The residue was purified by flash chromatography on silica gel to obtain the pure product.

2-Bromo-1-phenylhexa-1,5-dien-3-ol (3l): Oil. ¹H NMR (400 MHz, CDCl₃): *δ* = 7.61–7.25 (m, 5 H), 7.08 (s, 1 H), 5.85–5.77 (m, 1 H),

5.24–5.16 (m, 2 H), 4.33 (q, ${}^{3}J_{H,H} = 6.0$ Hz, 1 H), 2.63–2.52 (m, 2 H), 2.18 (s, 1 H, OH) ppm. 13 C NMR (100 MHz, CDCl₃): $\delta = 135.0, 133.2, 129.1, 129.0, 128.2, 128.1, 118.8, 76.5, 40.4, 30.9 ppm. IR: <math>\tilde{v} = 3388, 3073, 2931, 1829, 1642, 1435, 1172, 1084, 983, 915, 734, 621 cm^{-1}$. MS (EI): m/z (%) = 254 (10.6) [M⁺ + 2], 252 (10.6) [M⁺], 211 (77.0), 193 (22.6), 131 (100.0), 103 (58.3), 91 (4.9), 77 (54.4), 51 (25.6), 39 (44.9). C₁₂H₁₃BrO (253.14): calcd. C 56.93, H 5.17; found C 56.71, H 5.34.

3-(4-Methoxyphenyl)hex-5-en-3-ol (5k): Oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.29–7.25 (m, 2 H), 7.16–7.12 (m, 2 H), 5.69–5.48 (m, 1 H), 5.16–5.07 (t, ³J_{H,H} = 9.2 Hz, 2 H), 2.75–2.41 (m, 2 H), 2.33 (s, 3 H), 1.96 (s, 1 H), 1.87–1.77 (m, 2 H), 0.80–0.76 (m, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 142.7, 135.8, 133.7, 128.7, 125.3, 119.3, 75.8, 46.8, 35.2, 20.9, 7.8 ppm. IR: \tilde{v} = 3471, 3067, 2962, 2930, 1642, 1448, 988, 922, 813 cm⁻¹. MS (EI): *m*/*z* (%) = 189 (0.6) [M⁺ – OH], 165 (0.1), 149 (54.7), 119 (25.9), 105 (3.0), 91 (23.0), 77 (5.5), 57 (100.0), 41 (16.2). C₁₃H₁₈O₂ (206.28): calcd. C 75.69, H 8.79; found C 75.88, H 8.58.

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