# ChemComm

#### COMMUNICATION

## **RSC**Publishing

View Article Online View Journal | View Issue

Cite this: Chem. Commun., 2013, 49, 10635

Received 24th July 2013, Accepted 25th September 2013

DOI: 10.1039/c3cc45611k

www.rsc.org/chemcomm

## Dual role of allylsamarium bromide as a Grignard reagent and a single electron transfer reagent in the one-pot synthesis of terminal olefins<sup>†</sup>

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The utility of allylsamarium bromide, both as a nucleophilic reagent and a single-electron transfer reagent, in the reaction of carbonyl compounds with allylsamarium bromide in the presence of diethyl phosphate is reported in this communication. From a synthetic point of view, a simple one-pot method for the preparation of terminal olefins is developed.

Since 1977, when Kagan<sup>1</sup> introduced samarium diiodide into organic synthesis, a lot of important individual transformations have been carried out using it as a mild, neutral, selective and versatile single-electron transfer (SET) reducing<sup>2</sup> and coupling reagent.<sup>3</sup> For example, samarium diiodide-mediated Barbier, radical-alkene/alkyne, Reformatsky, carbonyl-alkene/alkyne, Pinacol-type and other reactions have been successfully realized. Besides, samarium diiodide has been efficiently applied in the total synthesis of many natural compounds.<sup>4</sup> The active study of SmI<sub>2</sub> further promoted research of the other samarium reagents.<sup>5</sup>

In 1996, Zhang first reported the convenient preparation of allylsamarium bromide and used it successfully in Grignardtype reactions.<sup>6</sup> The subsequent research of allylsamarium bromide as a Grignard reagent has grown rapidly and received much attention from the synthetic community.<sup>7</sup> However, the possibility that allylsamarium bromide (like SmI<sub>2</sub>) can play the role of a single electron transfer reagent has been ignored for over one decade until the first report from our group appeared.<sup>8</sup>

The terminal double bond is a very important group in organic compounds and can be functionalized in many ways.<sup>9</sup> Because of the importance of terminal olefins, a lot of methods have been developed to synthesize these kinds of compounds.<sup>10</sup> This kind of transformation could be realized by addition of allylsilanes or allylstannanes to organic electrophiles with Lewis acids as catalysts.<sup>11</sup> To the best of our knowledge,

synthesis of terminal olefins using aldehyde as a substrate has not been reported. So, developing a new method using an aldehyde and an allyl metal reagent as substrates to obtain terminal olefins is desirable.

In this continuing work using allylsamarium bromide in organic synthesis by our group, we think that realization of two roles (Grignard reagent and single electron transfer reagent) for allylsamarium bromide in one reaction was definitely meaningful and challenging. Herein, we reported the efficient synthesis of terminal olefins by the reaction of allylsamarium bromide with carbonyl compounds in the presence of diethyl phosphate.

Initially, the reaction between benzaldehyde **1a** and allylsamarium bromide was selected as a model reaction to check this possibility (Table 1, entries 1–13). Firstly, a series of organophosphorus additives were examined at room temperature and the results were summarized in Table 1. From the results,

Table '	1 0	ptimization	of	reaction	conditions
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$\langle$	CHO + SmBr	additive THF	•		*	
1a 2			3a			
Entry <sup>a</sup>	Additive (equiv.)	2 (equiv.)	Time (h)	Temp. (°C)	Yield <sup>b</sup> (%)	
1	$Ph_{3}P(1.0)$	3	24	r.t	None	
2	$(EtO)_{3}P(1.0)$	3	24	r.t	None	
3	$(EtO)_{3}PO(1.0)$	3	24	r.t	None	
4	$(EtO)_2 P(O) CH_2 COOEt (1.0)$	3	24	r.t	None	
5	$(PhO)_2 P(O) H (1.0)$	3	24	r.t	12	
6	$(EtO)_2 P(O)H(1.0)$	3	24	r.t	23	
7	$(EtO)_2 P(O)H (1.0)$	3	6	65	48	
8	$(EtO)_2 P(O)H(1.0)$	3	12	65	51	
9	$(EtO)_2 P(O)H (1.5)$	3	12	65	55	
10	$(EtO)_2 P(O)H(2.0)$	3	12	65	64	
11	$(EtO)_2 P(O)H(2.0)$	3	18	65	56	
12	$(EtO)_2 P(O) H (2.0)$	2	12	65	23	
13	$(EtO)_2 P(O) H (2.0)$	4	12	65	64	

<sup>*a*</sup> Unless noted, to a solution of **1a** (0.5 mmol) in THF (3 mL) was added **2** (X mmol) in THF under a nitrogen atmosphere at room temperature, and the mixture was stirred for 1 h, then the additive (Y mmol) was added to this mixture and stirred at 65 °C. <sup>*b*</sup> Isolated yield based on **1a** after silica gel chromatography.

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Experimental procedures, characterization and spectral data of the products. See DOI: 10.1039/c3cc45611k

we could see that the reaction was dramatically influenced by the additives. With  $Ph_3P$ ,  $(EtO)_3P$ ,  $(EtO)_3PO$  and  $(EtO)_2P(O)CH_2COOEt$  as additives, no product was obtained (Table 1, entries 1–4). With  $(EtO)_2P(O)H$  as an additive, product **3a** could be obtained in low yield (Table 1, entry 6). To our delight, the yield could be further improved to 48% through increasing the temperature from room temperature to 65 °C (Table 1, entry 7). When we prolonged the reaction time to 12 h, the yield was not obviously increased (Table 1, entry 8). Then, the molar ratio of **1a**/additive/**2** was also investigated. To our delight, upon increasing the amount of diethyl phosphate, a yield of 64% was achieved (Table 1, entries 10 *vs.* 8 and 9). Thus,  $(EtO)_2P(O)H$  as an additive and 65 °C as the reaction temperature with a 1/2/3 molar ratio of **1a**/additive/**2** proved to be the optimal reaction conditions for the reaction.

With the optimized reaction conditions in hand, the substrate scope of the reaction of various aldehydes with allylsamarium bromide was subsequently explored and the results were summarized in Table 2. As shown in Table 2, good yields were obtained with aromatic aldehydes bearing electron-donating groups on the aryl ring, such as 3-methyl-, 4-methoxy-, 4-methylthio-, 4-isopropyl-, 4-tertiarybutyl-, 4-methyl-, and 3,5-dimethoxybenzaldehyde (Table 2, entries 2-8). Piperonyl aldehyde also gave the product 3i in good yield (Table 2, entry 9). With aromatic aldehydes bearing electron-withdrawing groups on the aryl ring, such as 4-chloro-, 4-bromo-, 3-chloro-, and 3,4-dichlorobenzaldehyde, the products were obtained in moderate yields (Table 2, entries 10-13). The above results showed that electron-donating groups on the aryl ring were more favorable for the reaction than electron-withdrawing groups. The reactions of 1-naphthaldehyde 1n, 2-naphthaldehyde 10 and pyrene-1-carboxaldehyde 1p with allylsamarium bromide showed quite good performance giving the desired products 3n-3p in moderate to good yields (Table 2, entries 14-16). Interestingly, terephthalaldehyde 1q could also be well tolerated and the product 3q was obtained in good yield (Table 2, entry 17). To our delight, aliphatic aldehydes 1r-1t could also react with allylsamarium bromide providing the products 3r-3t in moderate yields (Table 2, entries 18-20).

Then, we turned our attention to the reaction of allylsamarium bromide with ketones **4a** and **4b**. Unexpectedly, the conjugated olefin products **5a** and **5b** were obtained (Table 2, entries 21 and 22).

To investigate the role of diethyl phosphate and allylsamarium bromide in the reaction, studies similar to our previous work<sup>12</sup> were carried out under the optimum reaction conditions. The reaction of diethyl phosphate with allylsamarium bromide indicated that diethyl phosphate, allylsamarium bromide diethoxy(oxo)phosphate 7 or dialkylphosphinylallylsamarium bromide 8 might be the accelerant for the reaction (Scheme 1). To further identify which may be the real accelerant in the reaction, 1,1-diphenylbut-3-en-1-ol 6 was synthesized and tested in control experiments. We found that the reaction of 6 with 7 gave the desired product in moderate yield, but the reaction of 6 with (EtO)<sub>2</sub>P(O)H or 8 failed to give the product (Scheme 2).

Based on the above results, a possible mechanism is proposed. Firstly, aldehyde undergoes allylation leading to the formation of intermediate 9, then, the oxygen atom of intermediate 9 coordinates with 7 to afford transition state 10,

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	Reaction of aldenyde compe			Jillide
	R1-CHO + SmBr -	(EtO) <sub>2</sub> P(O)H	R1	$\sim$
	4 0	THF, 65°C	0	
Entry <sup>a</sup>	Substract	Product	Ja-r	Yield <sup>b</sup> (%)
1	CHO 1a		<b>3</b> a	64
2	СНО 1b		3b	75
3	CHO 1c	-0	 Зс	79
4	S CHO	s	~~ 3d	83
5	CHO 1e		3e	70
6	CHO 1f	$\chi$	3f	66
7	LCHO 1g		≫ 3g	63
8	сно		an a	69
9	CHO 1i		∽ 3i	76
10	cr Line 1j	CI	≪ 3j	59
11	Br CHO	Br	≪ 3k	55
12	CI CHO	CI	∕∼ 3I	60
13	CI CHO	CI	3m	68
14	In		an 3n	88
15	CHO 10		30	85
16	Let the second s		<u>Зр</u>	62
17	онс СНО		~~~3q	71
18	сно 1r	$\sim$	~~// 3r	42
19	CHO 1s	~~~~	∽~ 3s	51
20	Сно 11		= 3t	42



<sup>a</sup> Unless noted, to a solution of carbonyl compounds (0.5 mmol) in THF (3 mL) was added the allylsamarium reagent (1.5 mmol) in THF under a nitrogen atmosphere at room temperature, and the mixture was stirred for 1 h, then diethyl phosphate (1.0 mmol) was added to this mixture and stirred at 65  $^{\circ}$ C for 12 h. <sup>b</sup> Isolated yield based on carbonyl compounds after silica gel chromatography.



Scheme 1 The reaction of diethyl phosphate with allylsamarium bromide.



Scheme 2 Control experiments



Scheme 3 Proposed mechanism of terminal alkene of aldehydes.

which is followed by a sequential single-electron transfer process to give the intermediate 11. At last, proton capture by intermediate 11 from (EtO)<sub>2</sub>P(O)H or (EtO)<sub>2</sub>P(O)D affords the target product 3 or [D]-3 (Scheme 3).

In summary, a series of terminal alkenes were synthesized through the reaction of allylsamarium bromide with carbonyl compounds. In these reactions, single-electron transfer and nucleophilic properties of allylsamarium bromide were fully investigated. It is an efficient and experimentally simple onepot method to obtain terminal alkenes. Studies on the reaction

of allylsamarium bromide with ketones and its mechanism are underway in our laboratory and will be reported in due course.

We gratefully acknowledge the project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions and the National Natural Science Foundation of China (No. 21072143) for financial support.

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