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Barbier-type reaction mediated with tin nano-particles in water

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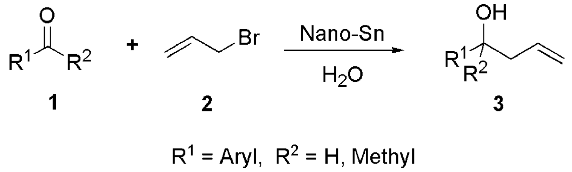
Abstract—Tin nano-particles are employed in the Barbier-type allylation reaction of carbonyl compounds in water to afford the corresponding homoallylic alcohols in good yields. The in situ generated allylation intermediates, allyltin(II) bromide and diallyltin dibromide, have been directly observed by using ^1H NMR. A mechanism is proposed based on this observation.

1. Introduction

The classical Barbier-type reaction has not been used as extensively as Grignard-type reaction even though the latter involves an extra step to prepare the organometallic reagents.[1] This is because many side reactions can also be mediated by the metal at the same condition. In order to extend the application of Barbier-type reactions and fully take its advantage, Barbier-type reactions in aqueous media were developed in the recent years.[2] The importance of this type of reaction has been gradually recognized not only because the tedious protection–deprotection processes can be simplified for certain functional groups containing acidic hydrogen atoms, but also because there is a growing public interest in Green Chemistry.[3] Many metal mediators as well as their salts[4] have been used in the Barbier-type allylation reactions to enhance the reaction yield and improve the stereoselectivity.[5] The dimension of metal particles should affect on metal-mediated allylation of carbonyl compounds in aqueous media because the key intermediate is believed to be generated on the metal surface.[2b] However, the metal particles smaller than the regular powder, for example, nanometer-scale particles,[6] have been not been well studied as a reagent in organic reactions.[7,8] As suggested by our previous study,[7] the yield of the Barbier-type allylation reaction can be improved by applying nano-scale metal particles. In order to further test this idea and explore the mechanism of Barbier-type reactions in water, we recently studied the allylation mediated by tin nano-particles with different sizes (Scheme 1). The details of this study are described below.



Scheme 1.

2. Results and discussion

2.1. TEM and XRD of 20-nm and 100-nm tin particles

In order to further study the mechanism of Barbier-type allylation reaction mediated by metal nano-particles and the effect of the size of nano-particles on this reaction, tin nano-particles with different sizes were prepared. Tin nano-particles with an average diameter of 20-nm were prepared by γ-radiation (method A), and tin nano-particles with an average diameter of 100-nm were prepared conveniently by reduction of $SnCl_2$ with KBH_4 in water at the presence of cetyl trimethylaminoium bromide (CTAB) (method B). Both of the two kinds of tin nano-particles were characterized by transmission electron microscopy (TEM) and X-ray powder diffraction (XRD). The average size of two kinds of nano-particles is illustrated by the TEM images (Fig. 1). As shown in Figure 2, both 20- and 100-nm tin particles are polycrystalline and their XRD patterns are consistent with that of metallic tin.[9]

Keywords: Tin; Nano-particles; Barbier-type reaction; Mechanism; Water.

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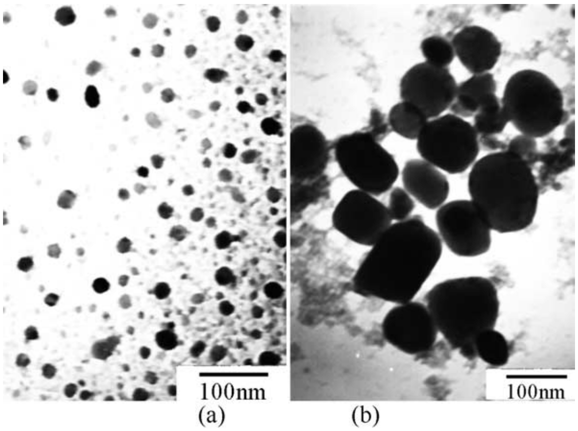


Figure 1. (a) A TEM image of 20-nm tin particles prepared with method A; (b) A TEM image of 100-nm tin particles prepared with method B.

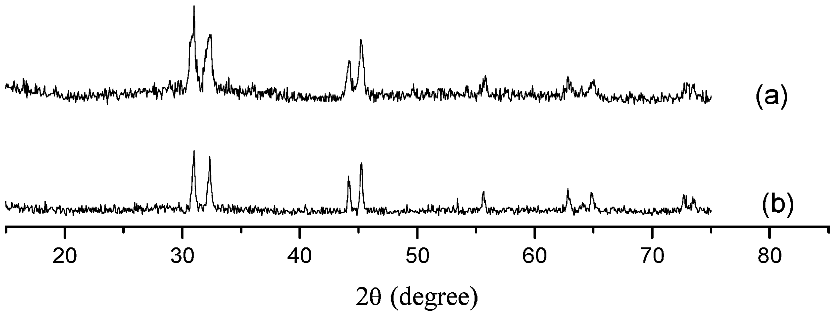


Figure 2. (a) XRD pattern of 20-nm tin particles; (b) XRD pattern of 100-nm tin particles.

2.2. Allylation reaction mediated by tin nano-particles in water

As shown in Table 1, tin nano-particles were found to be more effective than regular tin in mediating the allylation reaction.[7a] When 100-nm tin particles were employed the corresponding homoallylic alcohol was obtained in a yield of 98% (entry 7 in Table 1). When 20-nm tin nano-particles were used, the corresponding homoallylic alcohol was yielded quantitatively (entry 6 in Table 1).

Table 1. Allylation of benzaldehyde mediated by various metals in water

Entry	Metal	Size	Yield (%)[a]/ Time (h)
1	Fe	Regular[b]	Polymerization
2	Mg	Regular	—
3	Al	Regular	—
4	Zn	Regular	20/24
5	Sn	Regular	93/15
6	Sn	20-nm	95/1.5 (100/6.0)
7	Sn	100-nm	90/1.5 (98/9.0)

[a] Determined by ^{1}H NMR.
[b] The diameter of regular tin is about 80 μm.

Subsequently, tin nano-particles with average diameters of 20- and 100-nm were employed in the allylations of various aldehydes and ketones. As summarized in Table 2, this reaction usually generates the corresponding homoallylic alcohol in a high yield (mostly higher than 90%). Both of the aldehydes (entries 1–11 in Table 2) and ketones (entries 12–14 in Table 4) can be allylated in this reaction. Furthermore, both aromatic (entries 1–9 and 14 in Table 2) and aliphatic (entries 10–13 in Table 2) carbonyl compounds are reactive. The ketone with hydroxyl group is successfully employed in this reaction without protection (entry 13 in Table 2), yielding the corresponding homoallylic alcohol. Interestingly, the allylation of 4-nitrobenzaldehyde mediated by 20 nm tin particles generates the corresponding homoallylic alcohol in an excellent yield (entry 9 in Table 2). In comparison, the reaction between 4-nitrobenzaldehyde and allyl bromide usually only yields N-alkylation products[10] when mediated by metals in aqueous media. 20-nm particles usually give rise to a higher yield of the homoallylic alcohol than 100-nm tin particles do. But the difference is small.

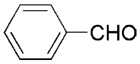
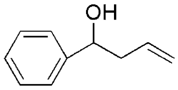
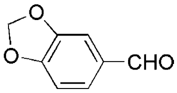
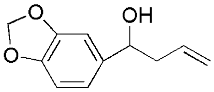
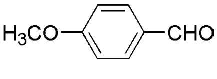
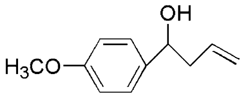
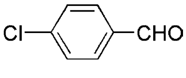
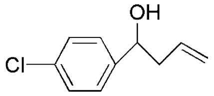
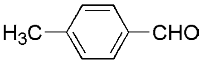
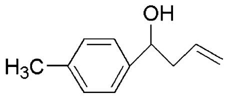
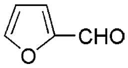
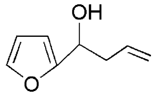
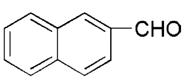
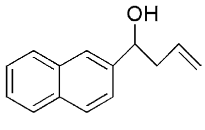
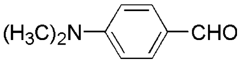
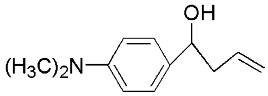
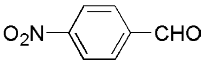
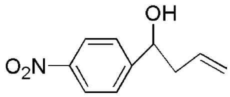
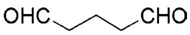
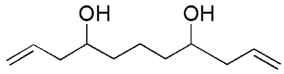
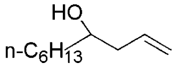
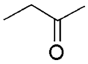
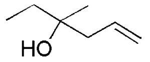
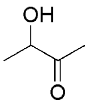
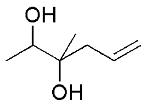
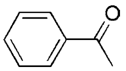
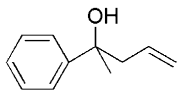
2.3. Regioselectivity and diastereoselectivity of the allylation reaction mediated by tin nano-particles

Additionally the regioselectivity and diastereoselectivity were studied for the nanometer-sized tin mediated allylation in the reaction of benzaldehyde and substituted allyl bromide (Scheme 2). As indicated in Table 3, the reaction between benzaldehyde and ethyl 4-bromo-2-butenate exclusively affords γ-adduct no matter whether tin is regular or nanometer sized (entries 1–3 in Table 4). The *syn* product is more favored by smaller tin particles. When 20-nm tin particles mediates the allylation reaction, the ratio of *syn* to *anti* homoallylic alcohol is as high as 94:6. The regular tin mediated reaction between benzaldehyde and crotyl bromide favors α-adduct (entry 4 in Table 4). On the other hand, the reaction mediated by tin nano-particles affords γ-adduct with a high selectivity (entries 5 and 6 in Table 3, 90% for 100 nm tin particles and almost 100% for 20 nm tin particles). Interestingly, when 20-nm diameter tin aggregates into bigger particles, both α- and γ-products are yielded in a ratio of 33:52 (entry 7 in Table 3).

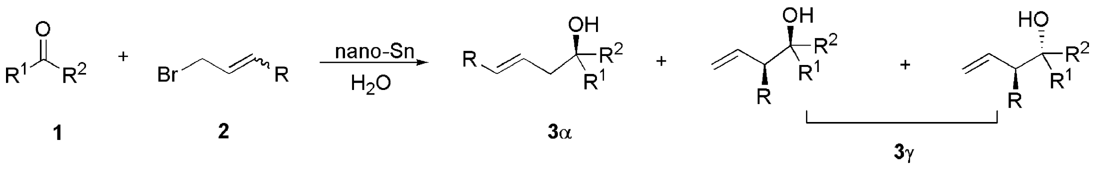
2.4. The detection of the intermediates and a proposed mechanism

Different mechanisms have been proposed for the aqueous Barbier type reactions involving the intermediates of a radical,[2b] a radical anion,[11] and an allylmetal species.[12] Direct observation of an intermediate is obviously important to establish a specific mechanism. However, as we know, no

Table 2. Allylation reactions mediated by tin nano-particles in water

Entries	Substrates	Products	Diameter of nano-Sn	Yield (%)[a]/Time (h)
1			20-nm 100-nm	95/1.5 90/1.5
2			20-nm 100-nm	99/3.0 96/3.0
3			20-nm 100-nm	99/2.0 95/2.0
4			20-nm 100-nm	99/2.0 95/2.0
5			20-nm 100-nm	96/3.0 89/3.0
6			20-nm 100-nm	96/3.0 92/3.0
7			20-nm 100-nm	99/3.0 96/3.0
8			20-nm 100-nm	95/3.0 81/3.0
9			20-nm 100-nm	95/3.0 86/3.0
10			20-nm 100-nm	90/1.5 90/1.5
11	*n*-C6H13CHO		20-nm 100-nm	99/1.5 99/1.5
12			20-nm 100-nm	85/1.5 81/1.5
13			20-nm 100-nm	81/3.0 79/3.0
14			20-nm 100-nm	65/4.0 59/4.0

[a] The yield was determined by ^{1}H NMR.



Scheme 2.

Table 3. Regioselectivity and diastereoselectivity of the allylation reaction mediated by tin nano-particles in water

Entry	R_1	R_2	R	Av size of Sn	Time (h)	Yield (%)[a]	α(*Z*/*E*)	γ(*anti*/*syn*)[b]
1	Ph	H	$COOCH_2CH_3$	Regular	24	58	—	(26:74)
2	Ph	H	$COOCH_2CH_3$	100-nm	12	55	—	(19:81)
3	Ph	H	$COOCH_2CH_3$	20-nm	12	61	—	(6:94)
4	Ph	H	CH_3	Regular	24	76	54(53:47)	22(37:63)
5	Ph	H	CH_3	100-nm	12	70	7(60:40)	63(49:51)
6	Ph	H	CH_3	20-nm	12	80	Trace	(44:56)
7	Ph	H	CH_3	20-nm	24	85	33(74:26)	52(33:67)[c]

[a] Isolated yield.

[b] The ratio of *syn* isomer to *anti* isomer (E isomer to Z isomer) was determined by ^1H NMR, ^{13}C NMR and isolation.

[c] The reaction was mediated by aggregated tin nano-particle.

Table 4. Allylation of carbonyl compounds by tin nano-particles in different solvent

Entry	Solvent	Metal	Yield (%)
1	—	Regular	0
2	—	20-nm	0
3	—	100-nm	0
4	CH_3OH	20-nm	0
5	CH_3OH	100-nm	0
6	Ethyl ether	20-nm	0
7	Ethyl ether	100-nm	0
8	H_2O	20-nm	95
9	H_2O	100-nm	90

Determined by ^1H NMR.

in situ allylation intermediate was reported to be observed in distilled water at room temperature in the allylation reaction mediated by metal tin. The following experiment was designed to search for the intermediate. 100-nm tin particles (178 mg, 1.5 mmol) and allyl bromide (0.18 mL, 2 mmol) were mixed in water (2–4 mL) at room temperature. After stirring for 15 min, the black mixture changed to milk-white. Then benzaldehyde was added to this mixture and the corresponding homoallylic alcohol was obtained in a good yield. This result implies that the milk-white substance should be the intermediate of the allylation. To identify the structure of the white substance, allyl bromide and the tin nano-particles (20 or 100 nm) were stirred in D_2O at room temperature and then monitored by using ^1H NMR. In the ^1H NMR spectrum two doublets at 2.16 and 2.48 ppm were observed (Fig. 3A, a), which are assigned to be the signals due to allyltin (II) bromide (**4**) and diallyltin dibromide (**5**), respectively.[12] The interconversion between allyltin (II) bromide (**4**) and diallyltin dibromide (**5**) was further studied by using tin nano-particles of different sizes. When a mixture of 1 mmol of allyl bromide and 0.5 mmol of 20-nm tin particles was stirred in D_2O at room temperature the ratios of **4** to **5** were 42/58 (0.5 h), 28/72 (1 h), 16/84 (1.5 h) and 8/92 (24 h), respectively (Fig. 3A, b–e). The ratio of **4** to **5** decreased due to the transformation of **4** to **5**. When 1 mmol of allyl bromide and 0.5 mmol of 100-nm tin were stirred in D_2O at room temperature, two intermediates, **4** and **5**, were generated immediately as indicated by the appearance of two doublets at 2.16 ppm and at 2.48 ppm in the ^1H NMR spectrum. The ratio of **4** to **5** were 1/99 (10 min) (Fig. 3A, f) and 0/100 (25 min) (Fig. 3A, g). After addition of another 1 mmol of 100-nm tin particles, the ratios of **4** to **5** were 55/45 (35 min), 36/64 (60 min) and 0/100 (15 h), respectively, as shown in Figure 3A, h–j. This indicates **5** can be converted to **4** by the addition of tin metal and also suggests that **5** is more stable in the aqueous solution.[12d] In comparison, when regular tin was stirred with allyl bromide in D_2O at room temperature, neither **4** nor **5** was observed in ^1H NMR spectrum. The absence of allyltin intermediates suggests that the mechanism of allylation reaction mediated by regular tin at neutral condition and room temperature involves not an allyltin intermediate but a radical or a radical anion.[2b] In fact, the allylation reaction mediated by regular tin requires heat (or ultrasonic irradiation) or the use of catalyst (HBr or Al) to promote the formation of covalent organometallic intermediates.[12d,13] Compared with regular tin, nanometer sized tin particles have a higher surface energy, which favors the formation of allyltin intermediates.

It is noted that water plays an important role in the allylation reaction. The reaction occurs only when water is used as solvent or as a catalyst regardless of the presence of organic solvent (entries 8 and 9 in Table 4). In anhydrous methanol or diethyl ether, or in a solvent-free condition,[14] no allylation product is yielded (entries 1–7 in Table 4). However, it is still not clear how water molecules participate in the reaction.

As shown in Figure 3B, when allyl bromide is replaced with crotyl bromide, two peaks are observed at 2.16 and 2.46 ppm, respectively in the ^1H NMR spectrum. The two peaks split into asymmetric multiplets rather than doublets, which are observed in the ^1H NMR spectrum of the reaction mixture of allyl bromide and tin nano-particles. This indicates that a covalent bond is formed between tin atom and γ-C when crotyltin (II) bromide and dicrotyltin dibromide are generated.[15]

As shown in Scheme 3, the formation of a γ-C–Sn bond can be explained by assuming that a π complex (**I**) is formed as a transition state. In this mechanism, allyl bromide binds the surface of tin nano-particles and generates the π-complex (**I**) first. Then the π electrons delocalize toward the γ-C and give rise to the formation of γ-C–Sn bond. Quantum chemistry calculation also indicates that the π complex transition state (**I**) is favored in energy.[16] Intermediate **4** can be further converted to **5** in the presence allylic bromide, and intermediate **5** can be converted to **4** in the presence of excessive tin. Both intermediate **4** and **5** can react with a carbonyl compound to give the corresponding homoallylic alcohol.

Most of experimental results can be explained based on this mechanism. For example, the allylation of 4-nitrobenzaldehyde yields reduction or polymerization products instead of

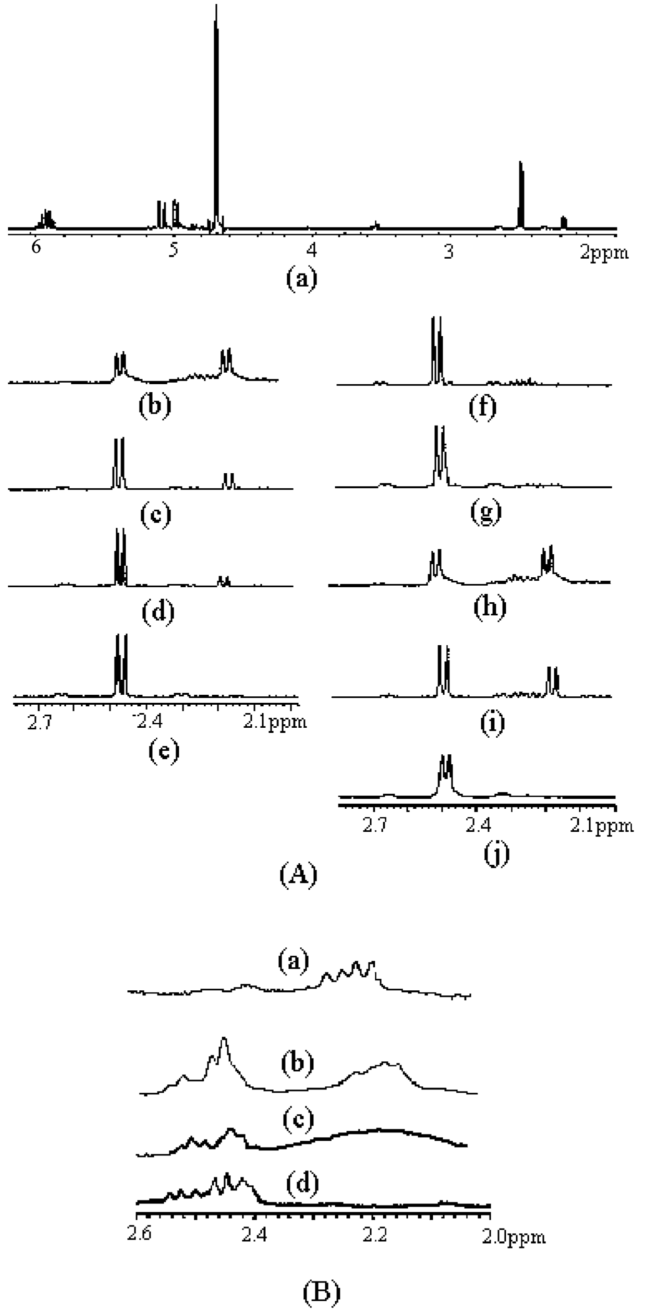


Figure 3. (A). Partial ^{1}H NMR spectra for the mixture of allyl bromide and nano-tin stirred in D_2O solution for different periods of time. (a–e) for 20-nm: (a) 1.5 h; (b) 0.5 h; (c) 1 h; (d) 1.5 h; (e) 24 h. (f–j) for 100-nm: (f) 15 min; (g) 25 min; (h) 35 min; (i) 60 min; (j) 15 h). (B) Partial ^{1}H NMR spectra of for the mixture of crotyl bromide and tin nano-particles stirred in D_2O solution for different periods of time. (a) 15 min; (b) 45 min; (c) 1.5 h; (d) 6 h.

homoallylic alcohol when mediated with regular tin[10] since the formation of allyltin intermediates is too slow to compete with the side reactions. When mediated with tin nano-particles, the allyltin intermediates are generated faster. Therefore the corresponding homoallylic alcohol is obtained in a high yield.

The selective formation of γ-addition product in the allylation reaction mediated with tin nano-particles (entries 5 and 6 in Table 3) can be explained by a γ-C bonded crotyltin (II) bromide intermediate (**4** in Scheme 3), which should be more stable than the α-C bonded crotyltin bromide because the γ-C is a secondary carbon. On the other hand, α-addition product is the major in the allylation reaction mediated by regular tin. This suggests again that the mechanism of allylation reaction mediated by regular tin at neutral condition and room temperature involves an intermediate rather than allyltin.[17] However, the allylation of benzaldehyde with ethyl-4-bromo-2-butenate only yields the γ-addition products no matter whether regular tin or nanometer-sized tin is used as a mediator (entries 1–3 in Table 3). This implies that γ-C bonded allyltin intermediates are formed when allyl group is conjugated with an electron-withdrawing group (such as an ester) regardless of the dimension of metallic tin (regular powder or nano-particles). The exclusive formation of γ-C bonded allyltin intermediates is due to the electron-withdrawing character of ester group, which can stabilize the high electron density on the Sn-bonded carbon.[18]

3. Conclusion

In conclusion, the allylation reaction mediated with tin nano-particles of different size in water has been systematically investigated. More importantly, the in situ generated allylation intermediates (**4** and **5** in Scheme 3) have been directly observed using ^{1}H NMR. A mechanism involving the allyltin intermediates is proposed. Further research is in progress in our laboratory to control the regioselectivity and stereoselectivity in allylation reactions by adjusting the dimension of the metal nano-particles.

4. Experimental

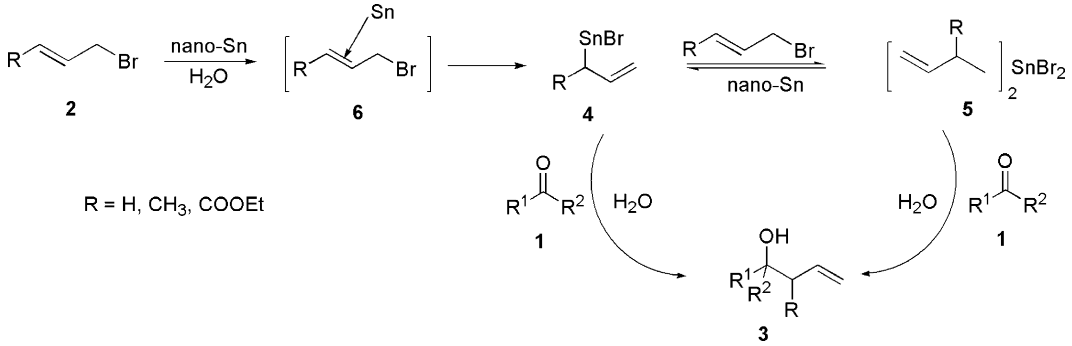
Analytical thin-layer chromatography (TLC) plates were commercially available. Solvents were reagent grade unless otherwise noted. Tin powder (150 mesh, 99.99%, 100 g packing) was freshly opened for use. Carbonyl compounds were further purified by redistillation or recrystallization from commercial chemicals when necessary.

4.1. General method for preparation of 20-nm tin particles

Method A. To 1L of a solution of 2-propanol in water (2.0 mol/L) were added 2.25 g (0.01 mol) of $SnCl_2 \cdot 2H_2O$ and 20 g (0.5 mol) of NaOH. The reaction mixture was stirred until $SnCl_2$ and NaOH were dissolved. The solution was bubbled with nitrogen over 20 min and then irradiated with a γ-ray (^{60}Co) source for about 12 h (2.5×10^4 Gy). The 20-nm tin particles were obtained from the solution by centrifugation. The tin nano-particles were washed with water and alcohol, respectively, and dried under vacuum.

4.2. General method for preparation of 100-nm tin particles

Method B. A solution of potassium borohydride (0.80, 15 mmol) in water (20 mL) was slowly added to a stirred solution of $SnCl_2 \cdot 2H_2O$ (2.25 g, 10 mmol) and cetyltrimethylaminoium bromide (0.36 g, 2 mmol) in 100 mL



Scheme 3. A proposed mechanism for the allylation reaction mediated by tin nano-particles.

of water. The mixture was stirred at room temperature for 15 min and in-situ tin nano-particles were yielded. The mixture of in-situ tin nano-particles was centrifuged to give 100-nm tin particles. The tin nano-particles were washed with water and alcohol, respectively, and dried under vacuum.

4.3. Details of in situ NMR experiments

In a typical procedure, tin nano-particles (178 mg, 1.5 mmol) and allyl bromide (0.14 mL, 1.5 mmol) were added into 2 mL of D_2O at room temperature. After the mixture was stirred for 10 min, the solution turned milky white. The milky white solution was briefly evacuated, purged with nitrogen, and transferred via cannula to a NMR tube.

4.4. General method for allylation of carbonyl compounds in aqueous media

To a mixture of carbonyl compound (1 mmol) in water (4 mL) was added tin nano-particles (0.118 g 1 mmol–0.177 g 1.5 mmol) and allyl bromide (0.14 mL 1.5 mmol) at room temperature. The mixture was stirred for 0.5–4 h and quenched with 1 N HCl (1 mL) solution. The mixture was extracted with ether (3×10 mL), and the combined organic layer was washed with saturated aqueous $NaHCO_3$ solution and dried over magnesium sulfate. The organic solvent was evaporated, and the corresponding homoallylic alcohol was yielded. The product was usually pure enough without further purification according to the ^1H NMR spectrum, and was further purified by flash chromatography on silica gel only when necessary.

4.5. Spectroscopic data

IR (Perkin–Elmer, 2000FTIR), ^1H NMR (CD_3Cl, 500 or 400 MHz), ^{13}C NMR ($CDCl_3$, 125.7 or 100 MHz) and MS–GC (HP 5890(II)/HP5972, EI.

4.5.1. *syn*-Ethyl-2-[hydroxy(phenyl)methyl]but-3-enoate (entry 1, Table 3). IR(NaCl, cm^{-1}): 3482, 1728, 1638, 1318, 1176, 1027, 765, 701. ^1H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.17–7.33 (m, 5H), 5.75–6.90 (m, 1H), 5.06–5.25 (m, 2H), 4.91 (d, $J=6.4$ Hz, 1H), 3.95 (q, $J=7.0$ Hz, 2H), 3.22–3.41 (m, 1H), 3.10 (s, 1H), 1.02 (t, $J=7.0$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 172.5, 140.7, 132.0, 128.2, 127.9, 126.5, 120.5, 74.0, 60.9, 58.4, 14.0. HRMS (EI) *m/z* calcd for $C_{13}H_{16}O_3$: 220.1099. Found: 220.1052.

4.5.2. *anti*-Ethyl-2-[hydroxy(phenyl)methyl]but-3-enoate (entry 1, Table 3). IR(NaCl, cm^{-1}): 3450, 1731, 1635, 1304, 1176, 1035, 760, 700; ^1H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.17–7.26 (m, 5H), 5.51–5.67 (m, 1H), 4.90–5.02 (m, 2H), 4.84 (d, $J=8.4$ Hz, 1H), 4.10 (q, $J=7.2$ Hz, 2H), 3.31–3.38 (m, 1H), 2.35–2.2.68 (br, 1H), 1.16 (t, $J=7.2$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 173.0, 141.2, 132.2, 128.4, 128.0, 126.7 119.5, 75.3, 61.1, 57.9, 14.1. HRMS (EI) *m/z* calcd for $C_{13}H_{16}O_3$: 202.0994 (M−18). Found: 202.0996 (M−18).

4.5.3. Phenyl-3-penten-1-ol (mixture of *Z* and *E*) (entry 4, Table 3). IR (film, cm^{-1}): 3432, 3083, 1644. ^1H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.29–7.39 (m, 5H), 5.53–5.72 (m, 1H), 5.40–5.50 (m, 1H), 4.65–4.72 (m, 1H), 2.42–2.65 (m, 3H), 1.61–1.73 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 144.2, 144.1, 129.2, 128.4, 127.5, 127.4, 126.9, 126.0, 125.9, 125.8, 73.9, 73.6, 42.7, 36.9, 18.1, 13.0. HRMS (EI) *m/z* calcd for $C_{11}H_{14}O$: 162.1045. Found: 162.1049.

4.5.4. 2-Methyl-1-phenyl-3-buten-1-ol (mixture of *syn* and *anti*) (entry 4, Table 3). IR (film, cm^{-1}): 3417, 3080, 1640. ^1H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.27–7.39 (m, 5H), 5.64–5.88 (m, 1H), 5.13–5.23 (m, 2×0.37H) (*anti*), 4.99–5.09 (m, 2×0.63H) (*syn*), 4.57 (d, $J=5.84$ Hz, 1×0.63H) (*syn*), 4.32 (d $J=7.64$ Hz, 1×0.37H) (*anti*), 2.35–2.62 (m, 1H), 1.99–2.19 (br, 1H), 1.02 (q, $J=6.87$ Hz, 3×0.63H) (*syn*), 0.90 (d, $J=6.83$ Hz, 3×0.37H) (*anti*). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 14.1 (*syn*), 16.5 (*anti*), 44.6 (*syn*), 46.2 (*anti*), 77.1 (*syn*), 77.4 (*anti*), 115.5 (*syn*), 116.8 (*anti*), 126.5 (*syn*), 126.9 (*anti*), 127.4 (*syn*), 127.7 (*anti*), 128.1 (*syn*), 128.3 (*anti*), 140.3 (*syn*), 140.6 (*anti*), 142.4 (*anti*), 142.6 (*syn*). HRMS (EI) *m/z* calcd for $C_{11}H_{14}O$: 162.1045. Found: 162.1042.

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