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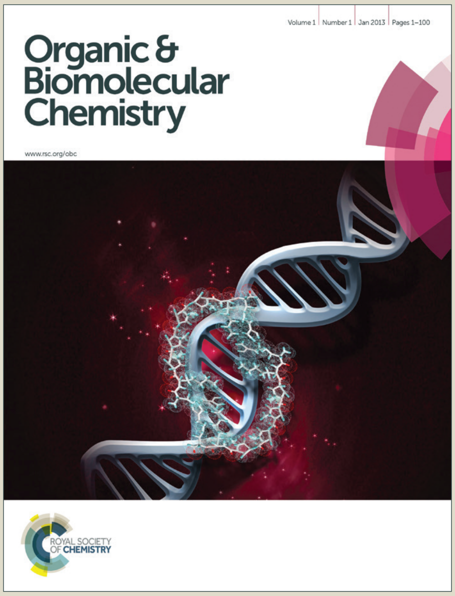

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ARTICLE TYPE

The metal tin promoted cascade reaction of ketone in aqueous media for the construction of 2-bromo-4-aryl-1,3-pentadiene

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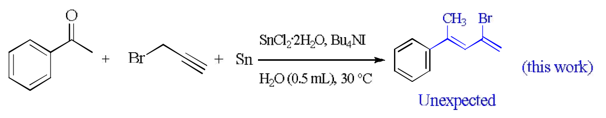
A novel type of transformation was discovered serendipitously during the Barbier-type allenylation reaction of aromatic ketone promoted by the metal tin in aqueous media. And a series of new highly functionalized 2-bromo-4-aryl-1,3-pentadiene could be obtained with good yields in this reaction. This cascade reaction shows the metal tin's unique property. And it is actually a cascade reaction which involves two steps: one is the Barbier-type allenylation of the carbonyl compound, the other is the S_N2' type addition-elimination reaction. Notably, this reaction has the advantages of simple, mild and easy to operate. Furthermore, the corresponding product could be applied to various coupling reactions or other diversified transformations.

The Barbier-type propargylation of carbonyl compounds is one of the hot research fields in organic reaction methodology. Up to date, there are many successful reports about the propargylation of aldehydes promoted by the metal (Sn, Zn, In, Ga, Mn, Ba etc.).[1] In comparison, studies on the Barbier-type allenylation of carbonyl compounds are very scant.[2] This is because that in the Barbier-type reaction, homopropargylic alcohol is mainly obtained in most cases whereas the allenylic alcohol can be rarely generated. To the best of our knowledge, only in the case of the reaction between the ketone and 1-bromobut-2-yne, the allenic alcohol can be produced.[3] Additionally, only the active metal indium, barium or metal alloy and so on, can promote this Barbier-type propargylation or allenylation reaction of aromatic ketone.[4] Moreover, the regioselectivity is relatively poorer than that of aromatic aldehyde due to the low reactivity and steric hinderance of ketones.[5]

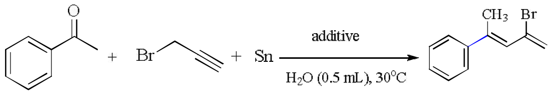
As our continuous work on the propargylation of aldehydes mediated by the metal tin for the synthesis of homopropargylic alcohols, which have been further used to construct the complicate compounds,[6] we embarked upon the propargylation reaction of the low active ketone carbonyl compounds so as to prepare the tertiary homopropargylic alcohol. As a result, we obtained an unexpected new compound, 2-bromo-4-phenyl-1,3-pentadiene (Scheme 1).



Scheme 1. A novel transformation mediated by the metal tin

Initially, our developed optimal protocol for the Barbier-type propargylation of aldehydes was directly employed to the acetophenone substrate.[6c] But unfortunately, no reaction occurred (Table 1, entry 1). When changing to use the analogous additives, $SnBr_2$ and SnI_2, the similar poor results were obtained (entries 2 and 3). To activate the propargylic bromide, the NaI or CuI was added into the reaction systems, respectively. However, the reaction was still sluggish (entries 4 and 5) with the great amount of starting material recovered. In view of the more hydrophobicity of the acetophenone than that of benzaldehyde in aqueous media, we attempted to add the surfactant $C_{12}H_{25}SO_3Na$ or phase transfer catalyst TBAI (tetrabutyl ammonium iodide) to the reaction mixture. Surprisingly, neither expected homopropargylic alcohol nor allenic alcohol were obtained, but resulted in a new unknown compound. Through a series of determination methods, such as ^1H NMR, ^{13}C NMR, DEPT (θ= 90° and 135°), HMBC, HMQC and EI-MS (Figures S1-S7), this new compound was finally defined to be a conjugated diene containing bromide atom. Moreover, the elemental analysis (EA) results further confirmed this new compound's exact structure (Anal. Calcd for $C_{11}H_{11}Br$, C 59.22, H 4.97; found: C 58.90, H 5.37). Namely, a new compound, 2-bromo-4-phenyl-1,3-pentadiene, was produced in this novel Barbier-type allenylation of acetophenone promoted by metal tin in aqueous media. Thus, it was calculated that this new compound was obtained in high yield with 80% or 85%, respectively (Table 1, entries 6 and 7). Reducing the amount of TABI from 0.5 equiv. to 0.2 equiv. or altering the Lewis acid to $SnBr_2$ or $ZnCl_2$, the reaction yields decreased dramatically (entries 8 -10). It demonstrated that this reaction was sensitive to the micro-environment of systematic acidity. Using the TBABr, the reaction yields were lower whether in the presence of $SnCl_2{\cdot}2H_2O$ or $SnBr_2$ (Table 1, entries 11-12).

Table 1. The effect of the additive on the new cascade reaction of acetophenone mediated by the metal tin[a]

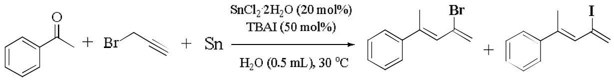


Entry	Additive (equiv.)	Diene bromide[b]
1	$SnCl_2{\cdot}2H_2O$ (0.2)	--
2	$SnBr_2$ (0.2)	--
3	SnI_2 (0.2)	trace
4	NaI (0.5)	trace
5	CuI (0.5)	trace
6	$SnCl_2{\cdot}2H_2O$ (0.2) + $C_{12}H_{25}SO_3Na$ (0.5)	80
7	$SnCl_2{\cdot}2H_2O$ (0.2) + TBAI (0.5)	85
8	$SnCl_2{\cdot}2H_2O$ (0.2) + TBAI (0.2)	62
9[c]	$SnBr_2$ (0.2) + TBAI (0.5)	26
10	$ZnCl_2$ (0.2) + TBAI (0.5)	57
11	$SnCl_2{\cdot}2H_2O$ (0.2) + TBABr (0.5)	20
12	$SnBr_2$ (0.2) + TBABr (0.5)	11

[a] Procedure: In a tube, 0.5 mL H_2O, the tin powder (45 mg, 0.375 mmol, 0.75 equiv.), additive, propargylic bromide (176 mg, 1.5 mmol, 3.0 equiv.) and acetophenone (60 mg, 0.5 mmol) were added sequentially. The mixture was stirred at 30 °C for certain time and traced by TLC. [b] Isolated yield. [c] The product was a mixture of bromide (26% yield) and iodide (9% yield)

Inspired by the above primary results, we tried to further optimize the reaction conditions. The amounts of the tin powder and propargylic bromide were then investigated (Table 2). For example, using 1.0 or 1.5 equiv. tin powders to the acetophenone, the reaction yield slightly decreased compared to that of 0.75 equiv. Sn (Table 2, entries 1-3). And in the case of 1.5 equiv. tin powder, there was small amount of iodide **3a** besides the conjugated diene bromide **2a**. When further increasing the amount of metal tin to 3.0 equiv., no expected product was obtained (entry 4). It might be because the excess tin powder led to the nearly dry reaction system in the same volume water, and then failed to stir and react with each other completely. In addition, the product yield was reduced in the presence of 0.5 equiv. metal tin (entry 5). Changing the metal tin to the indium, almost equivalent amount of homopropargylic alcohol and allenic alcohol (1:1) were obtained in a total 26% isolated yield (Table 2, entry 6). Then increasing the amount of propargylic bromide from 3.0 to 5.0 equiv., the reaction gave the decreased yield of product (Table 2, entry 7). Reducing the amount of the propargylic bromide to 1.5 equiv., not only the reaction yield had an obvious decrease, but also the competitive conjugated diene iodide **3a** was generated (entry 8). Using 1.0 equiv. the propargylic bromide, only allenic alcohol **4a** was obtained (entry 9). It was surmised that the small bromine source failed to perform the next addition-elimination reaction.

Table 2. The amount of the metal tin and propargylic bromide screening in this reaction



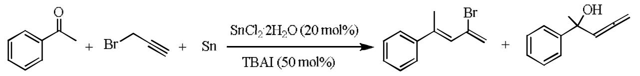
1a **2a** **3a**

Entry[a]	The amount of tin (equiv.)	Product	Yield (%)[c]
1	0.75	**2a**	85
2	1.0	**2a**	62
3	1.5	**2a**+**3a** (3:1)	80
4	3.0	--	--
5	0.5	**2a**	72
6[d]	In (0.75)	-	-
Entry[b]	The amount of propargylic bromide (equiv.)	Product	Yield (%)[c]
7	5.0	**2a**	76
8[e]	1.5	**2a**+**3a** (2:1)	66
9	1.0	**4a**	30

[a] Entries 1-7, propargylic bromide 3.0 equiv.. [b] Entries 8-10 tin 0.75 equiv. **4a** was an allenyl alcohol product. [c] Isolated yield. [d] Almost equivalent amount of homopropargylic alcohol and allenic alcohol (1:1) was obtained in a total 26% isolated yield.

Next, the solvent was also examined. As shown in Table 3, whether increasing the water amount to 1 mL or 2 mL or decreasing to 0.2 mL, the product was resulted in reduced yields (entries 2-4). Moreover, the reaction yield decreased gradually with the increasing water. To improve the reaction system's heterogeneous nature, we attempted to adopt the THF/H_2O mixture solvents. Consequently, it was found that the reaction gave the product in a sharply decreased yield (Table 3, entry 5, only 27%). And in the case of the pure THF solvent, the allenic alcohol was mainly obtained (entry 6). Interestingly, when letting the reaction mixture system in THF stand for overnight, part of the allenic alcohol compound was converted to the 2-bromo-4-phenyl-1,3-pentadiene product (Figure S8, entry 7). Additionally, the brine was also tested. But no improved result was obtained (Table 3, entry 8). Therefore, the optimal reaction condition was that: 0.75 equiv. metal tin, 3.0 equiv. propargylic bromide, 20 mol% $SnCl_2{\cdot}2H_2O$ and 50 mol% Bu_4NI, 0.5 mL water, 30 °C.

Table 3. The effect of various solvents or the amount of water on the reaction



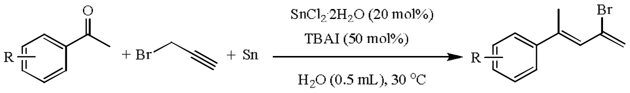
1a 2a 4a

Entry	Solvent (mL)	Product	Yield (%)[a]
1	H_2O (0.5)	**2a**	85
2	H_2O (1)	**2a**	77
3	H_2O (2)	**2a**	64
4	H_2O (0.2)	**2a**	79
5	THF/H_2O (1:1) (0.5)	**2a**	27
6	THF (0.5)	**4a**	43
7[b]	THF (0.5)	**2a**	--
8	Brine (0.5)	**2a**	58

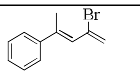
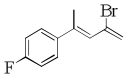
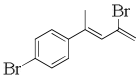
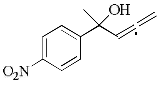
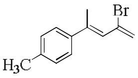
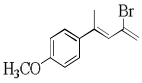
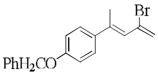
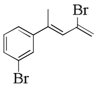
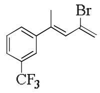
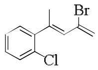
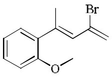
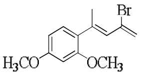
[a] Isolated yield (%). [b] Standing for overnight.

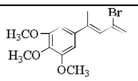
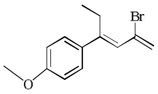
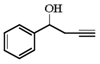
Then the various carbonyl compounds were employed to demonstrate the efficiency and scope of the present methods. The results were summarized in Table 4. In most cases of aromatic ketone derivatives, good or moderate yields were achieved while the chemical yields dramatically changed depending on the substituent on the phenyl ring. Regardless of the substituted position on the acetophenones and the substitution pattern, all reactions could proceed smoothly except for the 4-hydroxy and 2,4-dimethyl acetophenones (Table 4). Surprisingly, no conjugated diene bromide was obtained but with the allenic alcohol in 42% yield when using the 4-nitroacetophenone in this reaction (Table 4, entry 4). The reason remained unclear at present. In addition, the small amount of allenic alcohol was also obtained besides the conjugated diene product in the example of 3-bromoacetophenone (Table 4, entry 9). These two cases indicated that the aromatic ketone firstly conducted the Barbier-type allenylation in our methodology. Moreover, the reaction between the propargylic bromide and the ketones, with unsubstituted or electron-donating group substituted, could afford the conjugated diene bromide products in better yields (entries 1, 5-7, 12-13) than those of electron-withdrawing substituted acetophenones (entries 2-3 and 9-11). Nevertheless, for the 4-hydroxy or 2,4-dimethyl acetophenone, the reaction could hardly run with the great amount of starting material recovered (Table 4, entries 8 and 14). It may be due to the hydrogen-bond or slightly pH effect of hydroxy group and the relatively steric hinderance of 2-methyl group, respectively. But interestingly, this reaction could afford the corresponding 2-bromo-1,3-pentadiene in moderate yield in the cases of 2-methoxy and 2,4-dimethoxy acetophenone, even for the multi-substituted acetophenone, 3,4,5-$(CH_3O)_3C_6H_2COCH_3$ (Table 4, entries 12, 13 and 15). It remains unclear at present. For the 4-methoxy propiophenone, the good yield of diene product could be obtained (entry 16). Additionally, this reaction resulted in the major homopropargylic product (yield 60%) with small amount of the 2-bromo-4-phenyl-1,3-pentadiene in 35% yield when using the benzaldehyde as substrate (entry 17). For the aliphatic ketone, such as acetone, the reaction was hardly run (entry 18). From these results we could see that only the aromatic ketones are the most applicable substates in this cascade reaction, whereas the aromatic aldehydes or aliphatic ketone had poor performance. It may be because that the homopropargylic alcohol is mainly obtained for the highly active aromatic aldehyde in the Barbier-type propargylation or allenylation reaction. And the aliphatic aldehydes or ketones have been untouched hitherto in this type of reaction. In addition, it should be noted that the (*E*)-configuration diene products were mainly obtained with small amount of (*Z*)-isomers in the above all reactions.

Table 4. The scope of ketone substrates used under the optimal protocol in the reaction[a]



1 2

Entry	R	Product	Yield (%)[b]
1	-	 **2a**	85
2	4-F	 **2b**	67
3	4-Br	 **2c**	58
4[c]	4-NO_2	 **4d**	42
5	4-CH_3	 **2e**	65
6	4-CH_3O	 **2f**	71
7	4-$PhCH_2O$	 **2g**	54
8	4-OH	--	--
9	3-Br	 **2h**	60
10	3-CF_3	 **2i**	48
11	2-Cl	 **2j**	55
12	2-CH_3O	 **2k**	71
13	2,4-$(CH_3O)_2$	 **2l**	69
14	2,4-$(CH_3)_2$	--	--

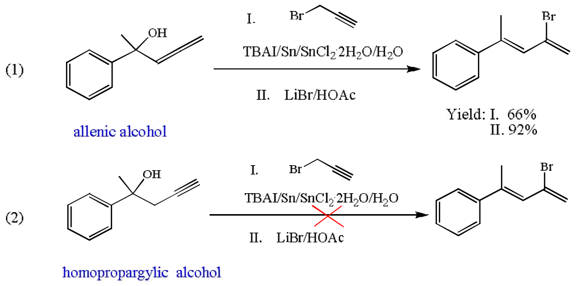
15	3,4,5-$(CH_3O)_3$	 **2m**	50
16[d]	4-CH_3O-$C_6H_4COCH_2CH_3$	 **2n**	62
17[e]	PhCHO	 **2o**	35
18	CH_3COCH_3	--	--

[a] Procedure: In a tube, H_2O 0.5 mL, the tin powder (45 mg, 0.375 mmol, 0.75 equiv.), $SnCl_2{\cdot}2H_2O$ (23 mg, 0.1 mmol, 0.2 equiv.), $^nBu_4NI$ (92 mg, 0.25 mmol, 0.5 equiv.), propargylic bromide (176 mg, 1.5 mmol, 3.0 equiv.) and aromatic ketone (0.5 mmol) were added sequentially. The mixture was then stirred at 30 °C for 6 h. After completion, the saturated sodium bicarbonate aqueous was added to quench the reaction and followed by extraction with ethyl acetate (15 mL×3) three times. Combining the organic phase, and washed it with sequential brine (5 mL) and water (5 mL), then dried by anhydrous $MgSO_4$, filtered and concentrated to obtain the residue which was purified by the silica gel chromatography, and finally affording the pure product. [b] Isolated yield; [c] Allenic alcohol. [d] The substrate is the propiophenone. [e] The substrate is the benzaldehyde, the major product is the homopropargylic alcohol in 60% yield, the side product is the 2-bromo-4-phenyl-1,3-pentadiene in 35% yield.

With respect to this novel Barbier-type allenylation reaction, we paid more attention to the reaction mechanism investigation. The ^{1}H NMR trace method was employed. The propargylic bromide shows two peaks **a** and **b** in Figure S8.(1) in D_2O (2.92 ppm, CH; 3.99 ppm, CH_2). Adding the tin powder and $SnCl_2{\cdot}2H_2O$ sequentially to the D_2O solution, the peaks of propargylic bromide has no obvious changed only with very small new allenic peaks appearing (**c** and **d**) (Figure S8.(2) and (3)). Continuing to add the TABI to the above mixture, it was observed that the peaks of propargylic bromide have almost disappeared and the new characteristic peaks of the allenic tin intermediate appeared in 4.61 ppm and 5.24 ppm (Figure S8.(4) **c″**, **d″**),[7] which are consistent with the spectrum of the allenyltin trichloride prepared by exchange reaction of tributyl allenyltin and tin tetrachloride in our group (Figure S9, CH_2, 5.14-5.16 ppm; CH, 5.65-5.68 ppm). This phenomenon demonstrated that the TBAI accelerated the formation of allenyltin intermediate by combining with the Lewis acid $SnCl_2{\cdot}2H_2O$ to form the adduct $Bu_4N^+SnCl_2I^-$ which displays stronger nucleophilicity than $SnCl_2{\cdot}2H_2O$.[2a]

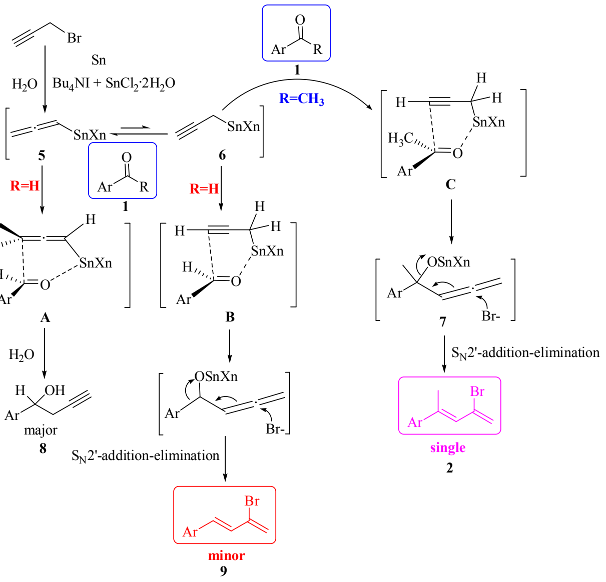
Ma and other research groups have ever reported an unexpected product (1,3-diene-3-bromide) in the reaction of allenic alcohol and hydroquinone. The reaction is believed to proceed through an S_N2' type addition-elimination process.[8] Therefore, it was inferred that the reaction herein may firstly result in the allenic alcohol or similar structural intermediate and then afford the 1,3-diene-3-bromide via similar reaction process.

In order to verify our reaction process, we performed additional four reactions using the pure allenic alcohol or homopropargylic alcohol synthesized beforehand under our reaction system and in the presence of LiBr/HOAc, respectively (Scheme 2). As a result, for the allenic *tert*-alcohol, the reaction could smoothly proceed under two different conditions and afford the corresponding 2-bromo-4-phenyl-1,3-pentadiene product in good or high yield (Figure S11, Scheme 2 (1)). In contrast, no reaction occurred in the case of homopropargylic alcohol no matter under what conditions (Scheme 2 (2)).



Scheme 2. The S_N2' type addition-elimination reaction

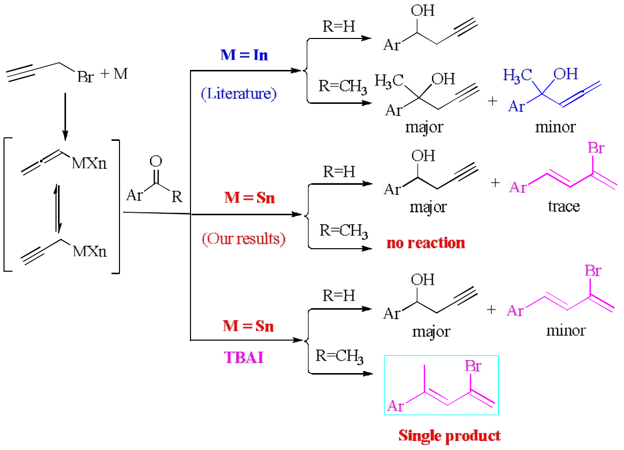
In the Barbier-type propargylation reaction of carbonyl compound mediated by the metal, the metal firstly reacts with the propargylic halide to form the allenyl organometallic or propargylic metal reagent *in-situ*, and the allenylmetal reagent is the thermo-dynamical controlled intermediate, whereas the propargylic metal reagent belongs to be the kinetic preference.[9] These two organometallic reagents could inter-convert, which depends on the steric hinderance, substitution of the organometallic substrate, solvation and nature of the metal. In addition, the chemo-selectivity of the Barbier-type propargylation or allenylation of carbonyl compounds is generally higher for the aldehydes with sole homopropargylic alcohol. But for the inert ketone, both homopropargylic alcohol and allenic alcohol could be obtained at the same time in most cases.[1,4,5] Based on that, we proposed the following possible mechanism for this cascade transformation (Scheme 3).



Scheme 3. The possible mechanism of this reaction

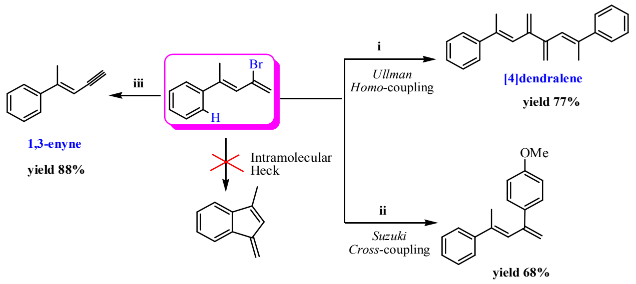
In our protocol, the allenyltin intermediate was observed in ^{1}H NMR. In this way, the homopropargylic alcohol should be mainly produced. Nevertheless, only the allenic alcohol could result in the consecutive addition-elimination under the reaction conditions. This apparent contradiction could be explained by the equilibrium between the allenyltin (**5**) and propargyltin reagents (**6**) under the reaction conditions.[10] In the case of the benzaldehyde, due to its high reactivity, the aldehyde could quickly attack the allenyltin intermediate **5** via γ-addition to produce the great amount of homopropargylic alcohol **8** as well as the minor conjugated diene **9** via the intermediate **B**. But for the inert acetophenone with a certain steric hinderance, the major reaction pathway may be dependent on the stability of the transition state under kinetic control or on orientations and steric factors (Scheme 3). Namely, the stable allenyltin **5** was converted to unstable but higher active kinetic favored propargyltin reagent **6** with the subsequent allenylation and the addition-elimination cascade reaction to give the final conjugated diene **2**. In addition, it can freely rotate for the α-carbon of propargyltin intermediate but not for the α-carbon of allenyltin. And the methyl group of aromatic ketone may bring about a repulsion when attacking the γ-carbon of the allenyltin with two hydrogen atoms. Therefore, the fine steric hinderance has an important influence on this reaction.

Based on the reported literatures, in the presence of the metal indium, the carbonyl compound, whether aromatic aldehyde or aromatic ketone, the homopropargylic alcohol is generally mainly obtained in most Barbier-type propargylation reaction. This is because that the organometallic indium reagent formed *in-situ* is so high active as to be able to react with both the aldehyde and ketone.[1-5] In comparison, for the metal tin, the case is different for the aldehyde and ketone, respectively (Scheme 4). In our reaction system, in the absence of TBAI, only aldehyde could smoothly undergo the Barbier-type propargylation reaction with high yield of homopropargylic alcohol and trace conjugated diene. But for the aromatic ketone, no reaction occurred. However, when adding the TBAI into the reaction mixture, the reactions of aldehyde and ketone exhibits both the similarities and the differences. In detail, the similarity is that the same structural conjugated dienes can be obtained in two cases of benzaldehyde and acetophenone. It may be owing to the relatively strong acidic atmosphere in Sn-promoted Barbier-type propargylation (pH=1~2), thus lead to the subsequent S_N2'-type addition elimination from allenic alcohol generated. The difference lies in that the major homopropargylic alcohol is obtained in the case of aldehyde but the diene is the single product for the acetophenone. In addition, replacing the metal tin to the indium in our protocol, the reaction produced the homopropargylic alcohol and allenic alcohol in 1:1 ratio with a total isolated yield (26%). All these results demonstrated that the IV main group metal tin displays a unique property which is different from the metal indium.



Scheme 4. The possible reaction of carbonyl compound promoted by different metals

Next, the synthetic utility of the corresponding product 1,3-pentadiene was examined (Scheme 5). With regard to the structure features, for example, containing the double bond, bromine and phenyl, the 2-bromo-4-phenyl-1,3-pentadiene was firstly attempted to perform the intramolecular *Heck* reaction catalyzed by the transition-metal Pd. But unfortunately, no cyclization product was obtained. On the contrary, a new highly cross-conjugated polyene derivative ([4]dendralene) was generated via intermolecular *homo*-coupling reaction in 77% yield.[11] And simultaneously, the small amount of oligomers was observed with bright fluorescent yellow in thin layer chromatography (TLC) plate. Apart from the dimerization, this diene could also undergo the Suzuki *cross*-coupling with the *p*-MeO-$C_6H_4B(OH)_2$.[12] Interestingly, it was easy to transform this conjugated diene bromide to 1,3-enyne with high yield (88%) in the presence of Bu_4NF (TBAF).[13] The further insight researches on cascade cyclization or other possible reactions of this conjugated diene are currently on progress in our group.



The reaction conditions: i) $Pd(OAc)_2$ (2.5 mol%), In (1.0 equiv.), LiCl (3.0 equiv.), DMF, 100 °C, 2 h; ii) $Pd(PPh_3)_4$ (5 mol%), Cs_2CO_3 (3.0 equiv.), toluene/H_2O (3/1), 80 °C, 6 h; iii) $TBAF\cdot 3H_2O$ (5.0 equiv.), THF, 60 °C, 26 h.

Scheme 5. The possible coupling reaction of the 2-bromo-4-phenyl-1,3-pentadiene

Conclusions

In summary, a novel Barbier-type allenylation reaction of aromatic ketone was developed and afforded a series of new multi-substituted 1,3-diene derivatives in good or moderate yields. Employing the metal tin and the environmentally benign water as media, the ketone carbonyl compounds could react with propargyl bromide to yield 2-bromo-4-aryl-1,3-pentadiene in the presence of TBAI in one pot. It avoids the separation of intermediate and the application of the expensive and complicated catalysts such as transition metal complex in the synthesis of conjugated diene. This reaction has a wide scope applicability of the substrates. And the mechanism was also explored. It was concluded that the metal tin possesses distinct nature which is different from the other main group metals (Zn or In). In addition, the activity differences between the aromatic aldehyde and ketone were also well illustrated in our protocol. Moreover, the TBAI plays an important role in this reaction. It acts as not only a phase transfer catalyst to improve the heterogeneous reaction system, but also an auxiliary to accelerate the formation of allenyltin intermediate. Meanwhile, the corresponding product 2-bromo-4-phenyl-1,3-pentadiene could be further applied to conduct various possible reactions for the synthesis of the functional compounds. Further studies on this new process catalyzed by the metal tin and its application for the synthesis of natural products are underway.

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Notes and references

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11 The characterizations of the *homo*-coupling product conjugated polyene are as follows: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.16 (s, 6H), 5.13 (s, 2H), 5.43 (s, 2H), 6.49 (s, 2H), 7.28-7.52 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.3, 116.6, 125.8, 126.7, 127.1, 128.3,

138.0, 143.3, 145.0; EI-MS: m/z 286.2; DEPT, HMBC and HMQC are shown in Figure S12-15.

12 The characterizations of the *Suzuki*-coupling product are as follows: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 3.95 (s, 3H), 5.35 (s, 1H), 5.81 (s, 1H), 6.07 (s, 1H), 7.04-7.07 (d, 2H), 7.45-7.72 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.4, 55.0, 113.6, 113.5, 125.8, 127.1, 127.6, 127.6, 127.7, 133.3, 138.4, 143.2, 144.54, 159.2.

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