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REGULAR ARTICLE

Active bismuth mediated allylation of carbonyls/*N*-tosyl aldimines and propargylation of aldehydes in water

MICKY LANSTER SAWKMIE[a], DIPANKAR PAUL[a], SNEHADRINARAYAN KHATUA[b] and PARESH NATH CHATTERJEE[a,*]

[a]Department of Chemistry, National Institute of Technology Meghalaya, Bijni Complex, Laitumkhrah, Shillong, Meghalaya 793 003, India
[b]Centre for Advanced Studies, Department of Chemistry, North Eastern Hill University, Shillong, Meghalaya 793 022, India
E-mail: paresh.chatterjee@nitm.ac.in

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Abstract. Active bismuth is synthesized by the chemical reduction of bismuth trichloride using freshly prepared sodium stannite solution as the reducing agent at room temperature. The as-synthesized active bismuth is applied as a reagent for the synthesis of homoallyl alcohol/homopropargyl alcohol from allyl bromide/propargyl bromide and carbonyl compounds in water at 50 °C. The homoallyl amines are also synthesized from *N*-tosyl aldimines and allyl bromide using active bismuth reagent in good yields. No assistance of organic co-solvent, co-reagent, phase transfer catalyst or inert atmosphere is required for this reaction. The waste bismuth material obtained after the completion of the organic reaction can be reduced to active bismuth by sodium stannite solution and successfully reused for mediating the allylation of aldehydes.

Keywords. Active bismuth; allylation; crotylation; propargylation; carbonyl; *N*-tosyl aldimine; homoallyl alcohol; homoallyl amine; homopropargyl alcohol.

1. Introduction

Metal-mediated Barbier allylation reaction of carbonyls is a very important C-C bond forming reaction in organic synthesis,[1] driven in part by the versatility of the homoallyl alcohols as synthetic intermediates.[2] Numerous metals, such as antimony, cerium, magnesium, manganese, indium, tin and zinc are known to participate in this fundamental C-C bond forming reaction.[3] In view of elemental resources, it is desired to explore various elements for catalyzing or mediating organic transformations. Among group 15 elements, bismuth is inexpensive, safe and environmentally-benign compared to arsenic and antimony with enhanced metallic character. It is also used in cosmetics and anti-viral creams and as a component of oral gastrointestinal formulations.[4] The commercially available bismuth powder has been reported for the reductive allylation of aldehydes under varying reaction conditions.[5] Wada *et al.,* reported several bimetallic reducing systems consisting of a metal and $BiCl_3$ for the allylation of carbonyls. They include Al-$BiCl_3$, Mg-$BiCl_3$, Fe-$BiCl_3$ and Zn-$BiCl_3$ systems.[5b, 6] Bismuth nanoparticles[7] as well as ball milling technique[8] have also been used to carry out the bismuth mediated allylation of carbonyls. Shi-Hui *et al.,* demonstrated Barbier allylation of aldehydes promoted by *in situ* generated active Bi(0) from $BiCl_3$ and sodium borohydride.[9] Herein, we report a versatile method for Barbier-type reaction of various carbonyls and *N*-tosyl aldimines in water mediated by freshly prepared active Bi(0) (Scheme 1). The active Bi(0) is synthesized *via* a simple reduction of $BiCl_3$ by freshly prepared sodium stannite (Na_2SnO_2) solution at room temperature.[10] Moreover, for the first time, we demonstrate active Bi(0) mediated allylation of *N*-tosyl aldimines as well as propargylation of aldehydes in water to achieve the corresponding homoallyl amines

*For correspondence
MICKY LANSTER SAWKMIE and DIPANKAR PAUL have contributed equally to this work.

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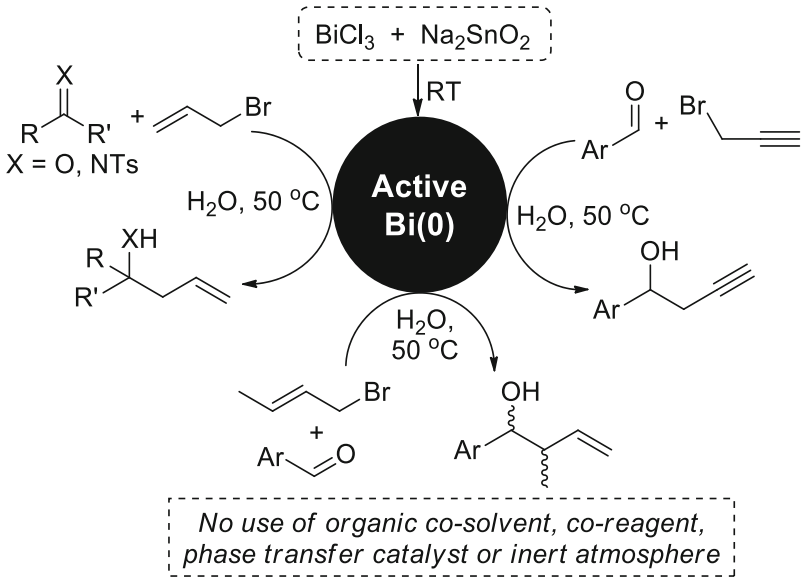


Scheme 1. Active bismuth mediated Barbier-type reaction of carbonyls and *N*-tosyl aldimines.

and homopropargyl alcohols, respectively. The importance of homoallyl amines and homopropargyl alcohols as versatile building blocks for the synthesis of valuable organic moieties is well established.[11] We find success in active Bi(0) mediated crotylation of aldehydes with 100% γ-regioselectivity. The synthetic protocol does not require an organic co-solvent, co-reagent, phase transfer catalyst or inert atmosphere. It is noteworthy to point out that the resulting white bismuth material after the completion of the reaction can be reduced to Bi(0) by Na_2SnO_2 solution and can be used to mediate the allylation of aldehydes, thereby making the method economical. Versatility, practicality and the economic use of this method of Barbier reaction provides excellent value for laboratory applications.

2. Experimental

2.1 *General remarks*

All reagents and solvents are of AR grade and purchased from Sigma-Aldrich, Alfa Aeser, Spectrochem and Sisco Research Laboratories Pvt. Ltd., and used without further purification unless otherwise stated. Propargyl bromide (80% solution in toluene) from Alfa Aeser was used as a reagent for propargylation. All the Barbier reactions were done in double-distilled water under air atmosphere. Reactions were monitored by thin-layer chromatography (TLC) on silica gel 60 F_{254}. Purification of organic products was performed by column chromatography using 100–200 mesh silica gel as the stationary phase and petroleum ether 60–80 °C/ethyl acetate as the eluent. The phase purity of synthesized Bi(0) material was characterized by recording X-ray diffraction data using PW1710 diffractometer (Philips, Holland) and analyzed with JCPDS software. ^{1}H and ^{13}C NMR spectra were measured on a Bruker NMR spectrometer. Chemical shifts are reported in ppm from tetramethylsilane (TMS), with the solvent resonance as the internal standard (chloroform δ 7.26 ppm). Data are reported as follows: chemical shifts, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, br=broad, dd=double doublet, m=multiplet), coupling constant (in Hz), integration.^{13}C NMR spectra were recorded with proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (chloroform δ 77.0 ppm). Elemental analyses were carried out using a CHNS/O Analyzer Perkin Elmer 2400 Series II instrument.

2.2 *Preparation of sodium stannite (Na_2SnO_2) solution*[12]

In a 100 mL beaker, $SnCl_2.2H_2O$ (677 mg, 3 mmol) and distilled water (8 mL) were taken and mixed well using a magnetic bar. Then 8 mL of 5 (M) NaOH solution was added slowly with continuous stirring until the milky white suspension turned into a colorless Na_2SnO_2 solution.

2.3 *Preparation of active Bi(0)*[10]

In a 50 mL round bottom flask, $BiCl_3$(630 mg, 2.0 mmol) was taken and 2 mL of distilled water was added to it which forms a milky white suspension of BiOCl. Then 16 mL of the freshly prepared Na_2SnO_2solution was added drop-wise to the milky white suspension of BiOCl with constant stirring at room temperature. Instantaneously, a black precipitate of Bi(0) metal was formed and the stirring was continued for 5 min. The resultant mixture was allowed to stand and the supernatant is decanted followed by washing of the black

precipitate with distilled water until the washing was pH neutral. The as-synthesized Bi(0) was used to mediate the Barbier reaction.

2.4 *Typical procedure for the active Bi(0) mediated synthesis of homoallyl alcohol*

In a 50 mL round bottom flask, 418 mg (2.0 mmol) of active Bi(0) was synthesized according to the above-mentioned procedure and washed several times to make it pH neutral. After that, 5 mL of distilled water was added, followed by the addition of 340 μL (4.0 mmol) of allyl bromide **2a**. The reaction mixture was stirred for 10 min at room temperature and 4-chlorobenzaldehyde **1a** (140 mg, 1 mmol) was added to it. The reaction mixture was placed in a pre-heated oil bath at 50 °C. The progress of the reaction was monitored by TLC. After the reaction was completed, the reaction mixture was filtered through a celite bed, followed by washing of the residue by ethyl acetate (2 × 10 mL). Finally, the filtrate was further extracted by ethyl acetate (2 × 10 mL) and washed with water (2 × 10 mL), brine (2 × 10 mL) and dried over anhydrous Na_2SO_4. The combined organic solvent was removed under reduced pressure and the crude product purified by column chromatography over silica gel (100–200 mesh, eluent: petroleum ether 60–80 °C/ethyl acetate) to afford the corresponding homoallyl alcohol **3a** in 81% yield.

2.5 *Typical procedure for the active Bi(0) mediated synthesis of homoallyl amine*

In a 50 mL round bottom flask, 418 mg (2.0 mmol) of active Bi(0), synthesized according to the above-mentioned procedure, was taken and washed several times to make it pH neutral. After that, 5 mL of distilled water was added, followed by the addition of 340 μL (4.0 mmol) of allyl bromide **2a**. The reaction mixture was stirred for 10 min at room temperature and *N*-benzylidene-4-methylbenzenesulfonamide**1t** (259 mg, 1 mmol) was added to it. The reaction mixture was placed in a pre-heated oil bath at 50 °C. The progress of the reaction was monitored by TLC. After the reaction was completed, the reaction mixture was filtered through a celite bed, followed by washing of the residue by ethyl acetate (2 × 10 mL). Finally, the filtrate was further extracted by ethyl acetate (2 × 10 mL) and washed with water (2 × 10 mL), brine (2 × 10 mL) and dried over anhydrous Na_2SO_4. The combined organic solvent was removed under reduced pressure and the crude product purified by column chromatography over silica gel (100–200 mesh, eluent: petroleum ether 60–80 °C/ethyl acetate) to afford the corresponding homoallyl amine **3t** in 66% yield.

2.6 *Typical procedure for the active Bi(0) mediated synthesis of homopropargyl alcohol*

In a 50 mL round bottom flask, 418 mg (2.0 mmol) of active Bi(0), synthesized according to the above-mentioned procedure, was taken and washed several times to make it pH neutral. After that, 5 mL of distilled water was added followed by the addition of 378 μL (4.0 mmol of 80% solution) of propargyl bromide **2e**. The reaction mixture was stirred for 10 min at room temperature and 4-chlorobenzaldehyde **1a** (140 mg, 1 mmol) was added to it. The reaction mixture was placed in a pre-heated oil bath at 50 °C. The progress of the reaction was monitored by TLC. After the reaction was completed, the reaction mixture was filtered through a celite bed followed by washing of the residue by ethyl acetate (2 × 10 mL). Finally, the filtrate was further extracted by ethyl acetate (2 × 10 mL) and washed with water (2 × 10 mL), brine (2 × 10 mL) and dried over anhydrous Na_2SO_4. The combined organic solvent was removed under reduced pressure, and the crude product was purified by column chromatography over silica gel (100–200 mesh, eluent: petroleum ether 60–80 °C/ethyl acetate) to afford the corresponding homopropargyl alcohol **4a** in 80% yield.

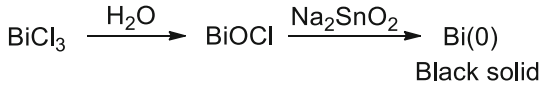
All products gave satisfactory spectral data and were compared with authentic samples wherever possible. Compounds**3a**,[12] **3b**,[13] **3c**,[14] **3d-e**,[12] **3f**,[15] **3g**,[12] **3h**,[15] **3i**,[14] **3j**,[16] **3k**,[15] **3l**,[13] **3m**,[17] **3n**,[5f] **3o**,[17] **3p**,[5f] **3q**,[16] **3r**,[15] **3s**,[12] **3t**,[18] **3u**,[18] **3w-y**,[19] **4a-b**,[20] **4c**,[21] are reported in literature. The characterization data for the new compound **3v** is given below.

2.7 *Analytical data of the new compound*

4-Methyl-*N*-(1-(naphthalen-1-yl)but-3-enyl)benzenesulfonamide (**3v**): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.91–7.89 (m, 1H), 7.81–7.79 (m, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.48–7.44 (m, 4H), 7.31–7.25 (m, 2H), 6.98 (d, J = 8.0 Hz, 2H), 5.60–5.50 (m, 1H), 5.23–5.20 (m, 1H), 5.12–5.07 (m, 3H), 2.65–2.63 (m, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 142.9, 137.1, 135.8, 133.7, 133.1, 129.8, 129.1, 128.9, 127.9, 127.1, 126.2, 125.5, 125.0, 124.2, 122.4, 119.4, 53.2, 41.2, 22.7. Anal. Cacld (%) for $C_{21}H_{21}NO_2S$: C 71.77; H 6.02; Found: C 71.81; H 5.98.

3. Results and Discussion

First, we have synthesized active Bi(0) (here after represented as Bi*) *via* a redox-driven path (Scheme 2).[10] Freshly prepared Na_2SnO_2 solution can easily reduce $BiCl_3$ in water at room temperature (Standard reduction potential of $Bi^{3+}/Bi(0) = 0.308$ V and standard reduction potential of $SnO_3^{2-}/SnO_2^{2-} = -0.93$ V). The reduction takes place spontaneously to give a black precipitate of Bi* (Figure 1d), which is confirmed by the powder XRD analysis. The XRD pattern of the as-synthesized Bi* was found to be in excellent agreement with the diffraction pattern of crystalline Bi(0) (Figure 2). The observed diffraction peaks at 2θ = 22.73°, 27.31°, 38.19°, 39.80°, 44.80°, 46.13°, 48.96°, 56.21°, 59.43°, 61.36°, 62.34°, 64.79°, 67.69° corresponds to the (033), (012), (104),



Scheme 2. Synthesis of active Bi(0).

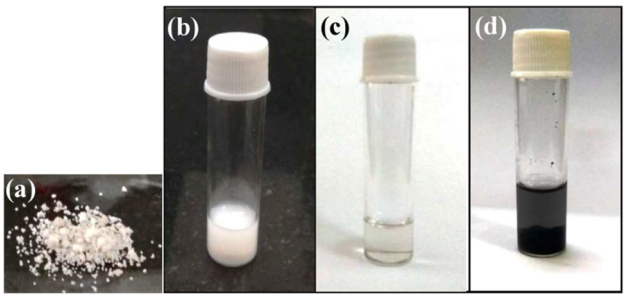


Figure 1. Photographs of (a) $BiCl_3$ (b) BiOCl (c) freshly prepared Na_2SnO_2 solution and (d) active Bi(0).

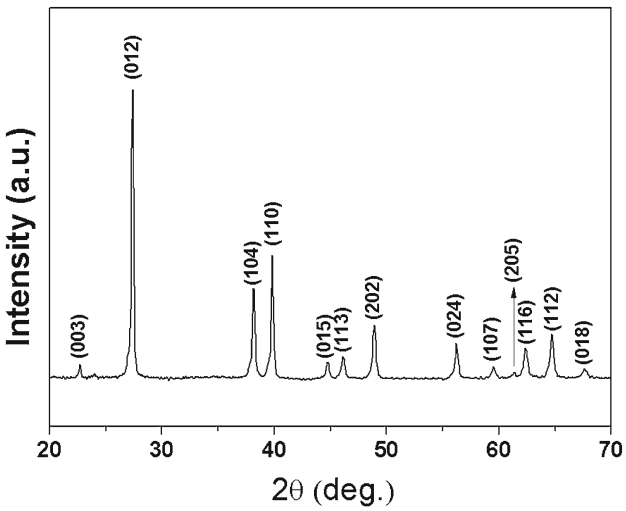


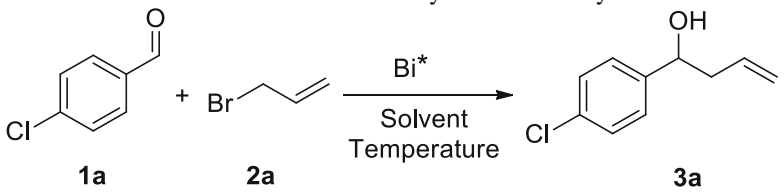
Figure 2. XRD pattern of the synthesized Bi(0).

(110), (015), (113), (202), (024), (107), (205), (116), (112) and (018) planes of Bi(0) (JCPDS 05-0519).

After confirming the identity of the black Bi(0), we applied the metallic bismuth for Barbier allylation of carbonyls and *N*-tosyl aldimines and propargylation of aldehydes. In this regard, we chose 4-chlorobenzaldehyde **1a** as the model electrophile and allyl bromide **2a** as the model allylating reagent to optimize the reaction conditions. To begin our investigation, we tested several aprotic and protic solvents in addition to their aqueous mixture (Table 1, entries 1–12). We found that DMF, MeCN and THF afforded moderate yields of the homoallyl alcohol **3a** at room temperature (Table 1, entries 1–3), whereas use of water as the only solvent afforded a better result (Table 1, entries 5). On realizing the positive effect of water on the progress of the reaction, we carried out the Barbier reaction in 1:1 mixture of the specified solvent with water (Table 1, entries 6–9) at room temperature. Although the yield of the homoallyl alcohol **3a** improved in the aqueous mixture of the solvents, the result was still below our expectation. This prompted us to assess the effect of temperature in this C-C bond forming reaction in view of achieving a better yield of **3a**. In this regard, we tested the two most promising water-organic solvent combinations *viz.* MeCN-H_2O and THF-H_2O at 50 °C and we were pleased to observe that the reaction performed significantly better (Table 1, entries 10–11). However, it is advantageous to avoid the use of organic solvents such as MeCN and THF in a synthetic organic reaction for economic and environmental benefits. This led us to carry out the reaction in water as the only solvent at 50 °C and the reaction proceeded remarkably well to yield 81% of the corresponding homoallyl alcohol **3a** (Table 1, entry 12) in 30 min. Further increase in reaction temperature to 70 °C did not improve the yield of **3a** (Table 1, entry 13). We found that the reaction mixture was strongly acidic after the completion of the reaction which may increase the electrophilicity of the reacting aldehyde.[6c,9] Recent literature of Barbier allylation reaction mediated by *in situ* generated Bi(0) shows that the molar ratio of the allyl bromide **2a** to Bi(0) plays a crucial role.[6c] Prompted by this information, we varied the amount of aldehyde **1a**, allyl bromide **2a** and our in-house synthesized Bi* in the allylation reaction as illustrated in Table 1 (entries 14–15). We noted that the highest yield of **3a** is obtained when the molar ratio of **1a**:**2a**:Bi* is taken as 1:4:2 (Table 1, entry 12). The yield of the homoallyl alcohol **3a** was found to be only 21% after 2 h of reaction when commercially available bismuth powder was used instead of Bi* (Table 1, entry 16). The low reactivity of the commercially available bismuth powder can be attributed to the aerial oxidation of the metallic surface over time.[22]

After optimizing the reaction conditions of Barbier allylation mediated by our in-house synthesized Bi*, we interested ourselves in exploring the substrate scope of this reaction and to study the effect of several substituents present at varying positions of the electrophile. We noticed that substituents such as -Cl, -Br, -Me, did not affect the reaction significantly, irrespective of their position in the aromatic ring of the aldehyde **1** (Table 2, entries 1–5 and 8). However, the presence of -NO_2 group as a substituent causes a noticeable decline in the yield of the corresponding homoallyl alcohol **3f** (Table 2, entry 6). The presence of electron-donating groups on the aromatic ring such as –OMe and -OH was found to decrease the yield of the corresponding homoallyl alcohol marginally (Table 2, entries

Table 1. Optimization of reaction conditions for Barbier allylation of aldehyde **1a**.[a]



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

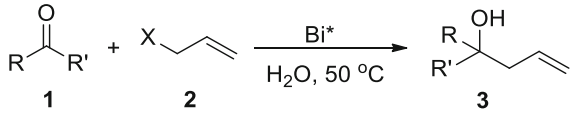
Entry	Solvent	Temperature (°C)	Time (h)	Yield **3a** (%)
1	DMF	RT	10	50
2	MeCN	RT	10	55
3	THF	RT	10	57
4	EtOH	RT	24	29
5	H_2O	RT	6	68
6	DMF-H_2O (1:1)	RT	10	61
7	MeCN-H_2O (1:1)	RT	10	64
8	THF-H_2O (1:1)	RT	10	66
9	EtOH-H_2O (1:1)	RT	24	45
10	MeCN-H_2O (1:1)	50	10	70
11	THF-H_2O (1:1)	50	10	76
12	H_2O	50	0.5	81
13	H_2O	70	0.5	80
14[c]	H_2O	50	0.5	42
15[d]	H_2O	50	0.5	69
16[e]	H_2O	50	2	21

[a] Reaction conditions: **1a** (1 mmol), **2a** (4 mmol), Bi* (2 mmol), Solvent (5 mL)
[b]Isolated yields
[c]Molar ratio –**1a** (1 mmol): **2a** (1 mmol): Bi* (1 mmol)
[d]Molar ratio –**1a** (1 mmol): **2a** (2 mmol): Bi* (1 mmol)
[e]Commercially available bismuth powder was used instead of Bi*.

9–11). The reaction also performs well in the case of 1-naphthaldehyde **1l** and terephthalaldehyde **1m**, giving rise to good yields (Table 2, entries 12–13). Next, we have extended the substrate scope by including the allylation of aliphatic aldehydes **1n-p**, which react equally well to give the desired homoallyl alcohols **3n-p** in very good yields (Table 2, entries 14–16). Cinnamaldehyde **1q** as a representative α,β-unsaturated aldehyde reacts under the optimized reaction conditions to give the 1,2-addition product **3q** exclusively (Table 2, entry 17). Our method worked well for heterocyclic aldehyde e.g., 2-thiophenecarboxaldehyde **1r** producing 72% of the desired homoallyl alcohol **3r** in presence of NH_4Cl as an additive (Table 2, entry 18). Acetophenone **1s**, a weaker electrophile, is also demonstrated to give the desired allylation product **3s** although in lower yield after prolonged reaction time (Table 2, entry 19). When allyl chloride **2b** and allyl alcohol **2c** were employed as allylating reagents instead of allyl bromide **2a** in our reaction conditions, the expected product **3a** did not form at all (Table 2, entries 20–21) and the unreacted aldehyde **2a** was recovered almost quantitatively after 24 h. It is noteworthy to mention that the resulting white precipitate after the completion of the reaction could be reduced again to Bi* by freshly prepared Na_2SnO_2 solution and the active metal, regenerated in this way, could also efficiently mediate the allylation of aldehydes in very good yield (Table 2, entry 22). We also applied our current method toward the large scale synthesis of homoallyl alcohol **3a** using 10 mmol of 4-chlorobenzaldehyde **1a**, 40 mmol of allyl bromide **2a** and 20 mmol of Bi* in water at 50 °C to obtain 78% isolated yield (Table 2, entry 23). As the method described here does not involve any suitable co-reagent capable of inducing enantiomeric purity in the products, hence the homoallyl alcohols are obtained as a racemic mixture.

Allylation of *N*-tosyl aldimines in water is considered a challenging prospect due to their proneness to hydrolyze in the reaction medium. Although there are reports of allylation of *N*-tosyl aldimines in water,[23] bismuth mediated protocols have not been developed so far. Our Bi* mediated method for the allylation of aldehydes can also be applied fruitfully for the allylation of *N*-tosyl aldimines. In our optimized reaction conditions, *N*-tosyl aldimines **1t-v** reacted smoothly to produce the corresponding homoallyl amines **3t-v** in good yields in 1 h (Scheme 3).[24]

Table 2. Substrate scope of Bi* mediated Barbier allylation of carbonyls.[a]



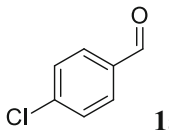
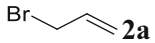
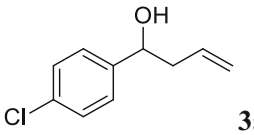
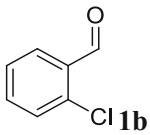
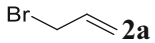
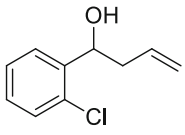
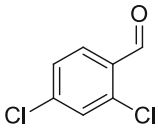
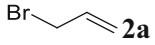
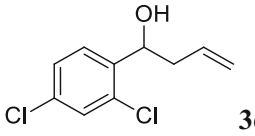
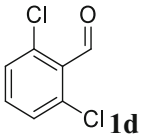
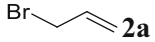
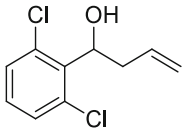
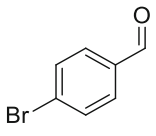
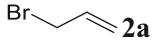
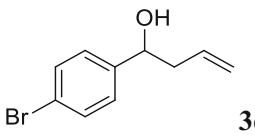
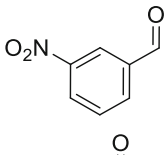
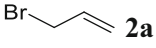
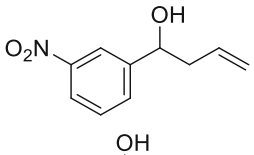
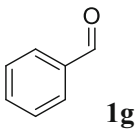
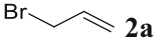
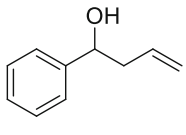
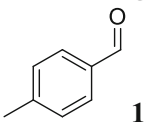
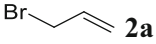
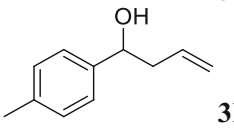
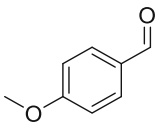
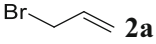
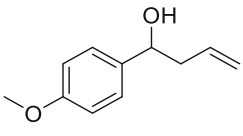
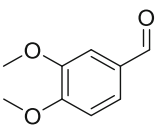
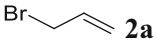
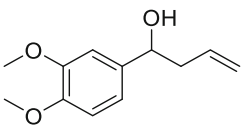
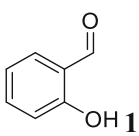
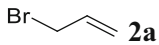
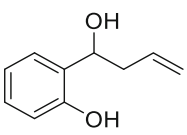
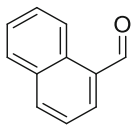
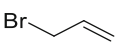
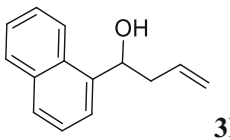
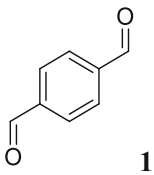
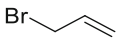
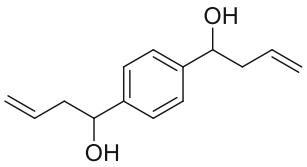
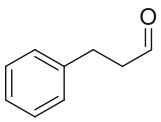
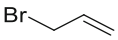
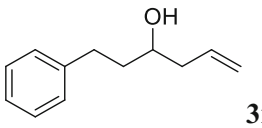
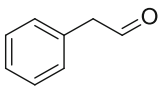
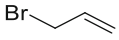
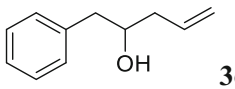
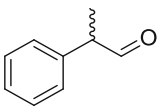
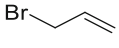
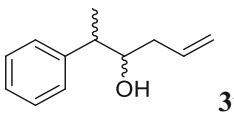
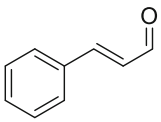
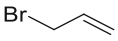
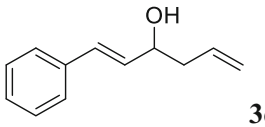
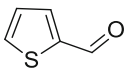
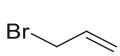
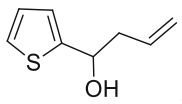
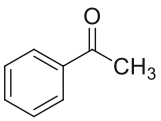
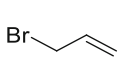
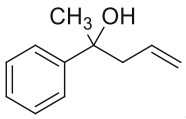
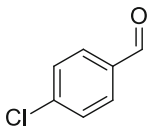
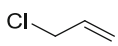
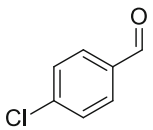
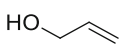
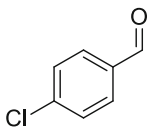
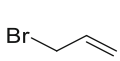
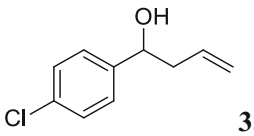
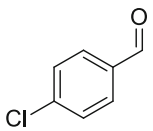
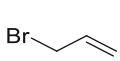
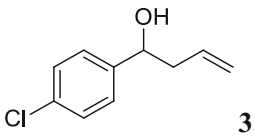
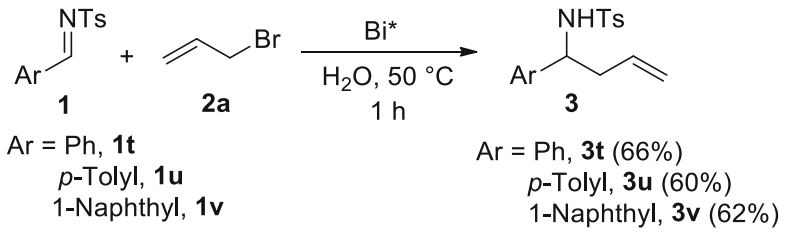
Entry	Substrate **1**	Allylating agent **2**	Product **3**	Time (h)	Yield (%)[b]
1.	 **1a**	 **2a**	 **3a**	0.5	81
2.	 **1b**	 **2a**	 **3b**	1	79
3.	 **1c**	 **2a**	 **3c**	1	78
4.	 **1d**	 **2a**	 **3d**	1	70
5.	 **1e**	 **2a**	 **3e**	1	80
6.	 **1f**	 **2a**	 **3f**	4	60
7.	 **1g**	 **2a**	 **3g**	1	81
8.	 **1h**	 **2a**	 **3h**	1	78
9.	 **1i**	 **2a**	 **3i**	1	70
10.	 **1j**	 **2a**	 **3j**	1	68
11.	 **1k**	 **2a**	 **3k**	1	72

Table 2. (*contd.*)

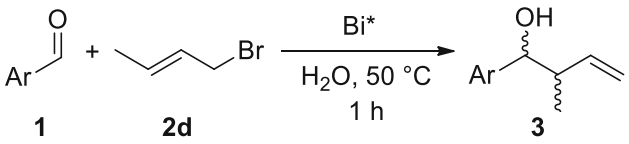
12.	 **1l**	 **2a**	 **3l**	1	74
13.	 **1m**	 **2a**	 **3m**	4	62
14.	 **1n**	 **2a**	 **3n**	1	78
15.	 **1o**	 **2a**	 **3o**	1	79
16.	 **1p**	 **2a**	 **3p**	1	76
17.	 **1q**	 **2a**	 **3q**	2	62
18.[c]	 **1r**	 **2a**	 **3r**	1	72
19.	 **1s**	 **2a**	 **3s**	6	50
20.	 **1a**	 **2b**	No product	24	-
21.	 **1a**	 **2c**	No product	24	-
22.[d]	 **1a**	 **2a**	 **3a**	1	80
23.[e]	 **1a**	 **2a**	 **3a**	2	78

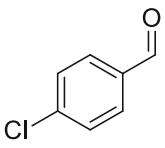
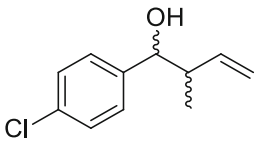
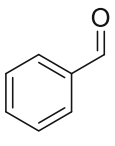
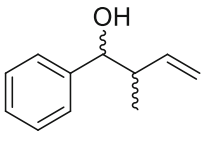
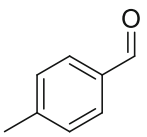
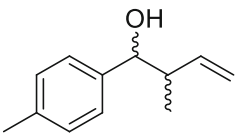
[a]Reaction conditions: **1** (1 mmol), **2** (4 mmol), Bi* (2 mmol), H_2O (5 mL), Temp. 50 °C.
[b]Isolated yields. [c]5 mL saturated NH_4Cl solution was used as a solvent instead of H_2O.
[d]Bi* reproduced from the resulting white precipitate of the first time reaction (entry 1).
[e]Reaction conditions: **1** (10 mmol), **2** (40 mmol), Bi* (20 mmol), H_2O (50 mL), Temp. 50 °C.



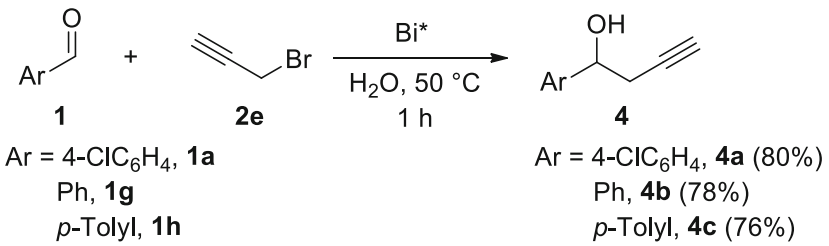
Scheme 3. Allylation of *N*-tosyl aldimines in water.

Table 3. Active Bi* mediated crotylation of aldehydes in water.



Entry	Substrate **1**	Product **3**	Yield % (*syn:anti*) [b]
1.	 **1a**	 **3w**	84 (78:22)
2.	 **1g**	 **3x**	72 (76:24)
3.	 **1h**	 **3y**	68 (73:27)

[a] Reaction conditions: **1** (1 mmol), **2d** (4 mmol), Bi* (2 mmol), H_2O (5 mL), Temp. 50 °C, 1 h.
[b] Isolated yields. The ratio of diastereoselectivity was determined by ^{1}H NMR spectra.



Scheme 4. Propargylation of aldehydes in water.

To extend the scope of the developed method, we have carried out crotylation of aldehydes using the in-house synthesized active Bi* and crotyl bromide **2d**. The reaction proceeds smoothly under the optimized reaction conditions to generate very good yields of the corresponding homoallyl alcohols **3w-y** in 1 h with 100% regioselectivity. The diastereoselectivity (determined by ^{1}H NMR) observed in our method are comparable with previously reported methods[5b–c] with *syn*-isomer being the major product (Table 3).

In our attempt to ascertain the versatility of the developed protocol, propargyl bromide **2e** has also been tested in the optimized reaction conditions as a viable reagent for Barbier type reaction. We find that the aldehydes **1a, 1g–h** generate the desired homopropargyl alcohols **4a**, **4b** and **4c** in good yields in 1 h (Scheme 4). As per our

Table 4. Comparison of present method with other Bi(0) mediated Barbier type reactions

Parameters			References[†]							
			5a	5b	5c[‡]	5d[Δ]	5e	5f	5g	Present work
Reaction conditions		Bismuth reagent used	Bi shot/powder	Bi shot/powder	Metallic Bi	Bi powder	Bi(0)	Bi powder	Bi(0)	Bi*
		Green solvent	**X**	**X**	**X**	NS	√	√	**X**	√
		Reaction temp.	RT	RT	RT	RT	RT	RT	60 °C	50 °C
		Additive free	√	**X**	**X**	√	**X**	**X**	√	√
		Reaction time (h)	4–12	5–28	20–34	3	5–16	12	4–8	**0.5–6**
		Inert atmosphere free	**X**	**X**	**X**	-	√	**X**	**X**	√
Substrate scope	Electrophiles	Aromatic aldehyde with EDG	√	√	√	√	√	√	√	√
		Aromatic aldehyde with EWG	**X**	**X**	√	**X**	√	√	**X**	√
		Heteroaromatic aldehyde	**X**	**X**	**X**	**X**	**X**	√	**X**	√
		α,β-conjugated aldehyde	√	√	√	√	√	√	**X**	√
		Aliphatic aldehyde	√	√	√	**X**	√	√	**X**	√
		Aldehyde with naphthyl ring	**X**	**X**	**X**	**X**	√	√	**X**	√
		Aromatic ketone	**X**	√	**X**	**X**	**X**	**X**	**X**	√
		Aldimine	**X**	**X**	**X**	**X**	**X**	**X**	**X**	√
	Alkylating agent	Allyl bromide	√	√	**X**	√	√	√	√	√
		Allyl chloride	**X**	√	**X**	**X**	√	**X**	**X**	**X**
		Allyl alcohol	**X**	**X**	√	**X**	**X**	**X**	**X**	**X**
		Crotyl bromide	**X**	√	**X**	**X**	**X**	**X**	**X**	√
		Propargyl bromide	**X**	**X**	**X**	**X**	**X**	**X**	**X**	√
Yield (%)			53–98	40–98	50–91	81–94	10–98	62–99	37–98	**50–81**

[†]The details of the references 5a–g are cited in the manuscript.
[‡]Substituted allyl alcohols were converted to their respective allyl iodides using *in situ* generated TMS-I (TMS-Cl + NaI) reagent before allylation reaction. [Δ]Only 3 successful entries were reported with metallic Bi reagent & reactions were performed at or below RT. NS= No solvent.

knowledge of relevant literature, Bi(0) mediated propargylation of aldehydes is not reported so far. The method described herein offers a novel alternative for the synthesis of homopropargyl alcohol-mediated by Bi* in water.

In order to establish the advantages of our present method in comparison with the similar Bi(0) mediated allylation reactions in the literature, we summarize our results along with the existing reports in Table 4. It is clear from the comparison that our protocol not only develops the desired homoallyl alcohols in a green solvent without any additive and in mild reaction conditions, but also covers several carbonyl substrates for allylation/crotylation reaction. In addition, allylation of *N*-tosyl aldimines and propargylation of aromatic aldehydes can also be achieved by using our protocol. Broad substrate scope and simple reaction procedure mark it as an attractive synthetic protocol in organic synthesis.

4. Conclusions

In conclusion, we have presented a versatile, practical and economical method for Barbier reaction mediated by active Bi(0) in water. No assistance of organic co-solvent, co-reagent, phase transfer catalyst, or inert atmosphere is necessary for this reaction. The method can be applied for the allylation of aromatic, aliphatic as well as α,β-unsaturated aldehydes in addition to *N*-tosyl aldimines. The method also works efficiently for the propargylation of aromatic aldehydes producing a very good yield of the corresponding homopropargyl alcohols. The resulting white bismuth material after the completion of the organic reaction can be reduced again to Bi(0) and can be reused for the subsequent batch of Barbier allylation of aldehydes. The active Bi(0) mediated versatile C-C bond forming reaction presented in this paper is a meaningful addition to the existing methods in the literature.

Supplementary Information (SI)

^{1}H and ^{13}C NMR data of the known compounds and ^{1}H and ^{13}C NMR spectra of the new compound are included in the supplementary information. Supplementary information is available at www.ias.ac.in/chemsci.

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