



Communication

An efficient Bi/NH₄I-mediated addition reaction for the highly diastereoselective synthesis of homoallylic alcohols in aqueous media



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ABSTRACT

An efficient water-based bismuth-mediated addition reaction of carbonyl compound with cyclic allylic halide was developed. The reactions proceeded smoothly in aqueous DMF in the presence of ammonium iodide to afford the corresponding *syn*-homoallylic alcohols in moderate to good yields with excellent diastereoselectivities (>99:1 *syn:anti*). Reversal of product diastereoselectivity was observed when heteroaryl aldehyde possessing an adjacent chelating nitrogen atom was employed as substrate.

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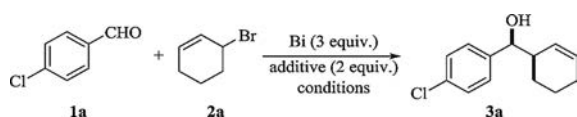
Homoallylic alcohols, which play an important role in organic synthesis, are not only structural units widely existed in complex molecules, but also versatile intermediates broadly employed in synthetic organic chemistry [1,2]. In general, metal-mediated addition reactions of carbonyl compounds with allylic halides function as one of the most efficient methods for accessing homoallylic alcohols [1,2]. Among the various allylic halides used for the addition reactions, cyclic allylic halides serve as efficient and special allylating agents for organic synthesis, which could react with carbonyl compounds to afford the homoallylic alcohols, potentially in a diastereoselective manner [3–6]. For examples, Knochel and co-workers have shown that cyclic allylic zinc [3] and aluminium [4] reagents, which could be pre-generated by metal insertion into cyclic allylic halides under strictly moisture- and air-free conditions, could be diastereoselectively converted into the corresponding *syn*-homoallylic alcohols upon treatment with carbonyl compounds. In addition, the Khan group [5] has reported that the addition reaction using cyclic allylic halide as substrate could also work well by employing indium as reaction mediator, though the diastereoselectivity of product is only proximate to

90:10. Very recently, we described that the analogous addition reaction could also be achieved with high diastereoselectivity (>99:1 *syn:anti*) by utilizing metallic bismuth and iron as reaction promoter [6]. However, all the above-mentioned addition reactions using cyclic allylic halides as substrates should be carried out under water-free conditions which required tedious manipulations. In continuation of our tasks to develop metal-mediated organic transformations in aqueous media [7–9], based on the previous reports [10–13], here we report an efficient bismuth-mediated addition reaction of carbonyl compounds with cyclic allylic halides in aqueous media, which proceeded smoothly in the presence of ammonium iodide to afford the corresponding homoallylic alcohols in moderate to good yields with excellent diastereoselectivities. In addition, reversal of product diastereoselectivity was observed when heteroaryl aldehyde possessing an adjacent chelating nitrogen atom was employed as substrate.

At the outset, the model reaction involving 4-chlorobenzaldehyde (**1a**) and 3-bromocyclohexene (**2a**) was performed in the presence of bismuth (3 equiv.) and various additives (2 equiv.) in aqueous DMF at room temperature for 24 h, attempting to find the optimum reaction conditions. As summarized in Table 1, among the several additives screened (such as LiCl [14], LiI [15], NaI [16], NH₄Cl [17], NH₄Br [18], and NH₄I [19]; entries 2–7), the use of NH₄I as reaction additive afforded the desired product **3a** with the highest product yields (95% NMR yield, 93% isolated yield; entry 7). In sharp contrast, the reaction proceeded sluggishly in the absence

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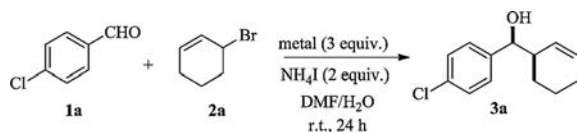
Table 1
Optimization of reaction conditions.^a

Entry	Additive	Conditions	Yield (%) ^b
1	–	DMF/H ₂ O, r.t., 24 h	15
2	LiCl	DMF/H ₂ O, r.t., 24 h	22
3	LiI	DMF/H ₂ O, r.t., 24 h	79
4	NaI	DMF/H ₂ O, r.t., 24 h	58
5	NH ₄ Cl	DMF/H ₂ O, r.t., 24 h	75
6	NH ₄ Br	DMF/H ₂ O, r.t., 24 h	78
7	NH ₄ I	DMF/H ₂ O, r.t., 24 h	95 ^c
8	NH ₄ I	DMF/H ₂ O, r.t., 12 h	89
9	NH ₄ I	DMF/H ₂ O, r.t., 48 h	80
10	NH ₄ I	DMF/H ₂ O, 60 °C, 24 h	70
11	NH ₄ I	DMF/H ₂ O, 120 °C, 24 h	67
12	NH ₄ I	THF/H ₂ O, r.t., 24 h	49
13	NH ₄ I	CH ₃ CN/H ₂ O, r.t., 24 h	22
14	NH ₄ I	MeOH/H ₂ O, r.t., 24 h	11
15	NH ₄ I	acetone/H ₂ O, r.t., 24 h	33
16	NH ₄ I	DMA/H ₂ O, r.t., 24 h	90
17	NH ₄ I	DMSO/H ₂ O, r.t., 24 h	89

^a The reactions were performed at room temperature (or 60–120 °C) for 24 h (or 12–48 h) by using 4-chlorobenzaldehyde (**1a**, 1 mmol), 3-bromocyclohexene (**2a**, 3 mmol), Bi (3 mmol), and additive (2 equiv.) in a mixture of organic solvent (2 mL) and water (1 mL).

^b Yields were determined by NMR analysis of crude reaction mixture after work-up by using 1,4-dimethoxybenzene as an internal standard.

^c 93% isolated yield; 81% isolated yield on a 10 mmol scale.

Table 2
Optimization of reaction conditions by using different metals.^a

Entry	Metal	Yield (%) ^b
1	Bi	95 ^c
2	Mg	<5
3	Zn	<5
4	Sm	<5
5	Cr	<5
6	Fe	<5
7	Al	<5
8	Pb	<5
9	In	58 ^d
10	–	0

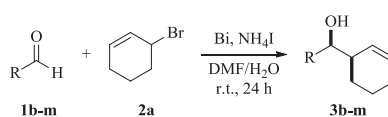
^a The reactions were performed at room temperature for 24 h by using aldehyde **1a** (1 mmol), 3-bromocyclohexene (**2a**, 3 mmol), Bi (3 mmol), and NH₄I (2 mmol) in DMF (2 mL) and water (1 mL).

^b Yields were determined by NMR analysis of crude reaction mixture after work-up by using 1,4-dimethoxybenzene as an internal standard.

^c >99:1 *syn:anti*.

^d 87:13 *syn:anti*.

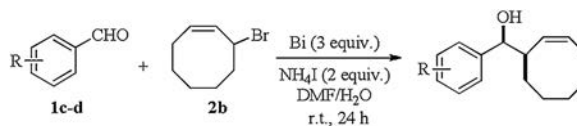
of an additive (entry 1). It should be mentioned that the use of LiI, NH₄Cl, and NH₄Br as reaction additive also delivered the product **3a** in reasonable yields (entries 3, 5, and 6). By using NH₄I as optimum reaction additive, it was observed that conducting the reactions with reduced or prolonged reaction time led to decreased product yield (entries 8 and 9). Moreover, the addition reaction was found to be sensitive to temperature, as eroded reaction performance was detected when the reactions were carried out

Table 3
Substrate scope study by employing different aldehydes.^a

Entry	Aldehyde	Product	Yield (<i>syn:anti</i>) ^b
1	1b	3b	96% (>99:1)
2	1c	3c	91% (>99:1)
3	1d	3d	94% (>99:1)
4	1e	3e	92% (>99:1)
5	1f	3f	74% (>99:1)
6	1g	3g	69% (>99:1)
7	1h	3h	57% (>99:1)
8	1i	3i	88% (>99:1)
9	1j	3j	71% (>99:1)
10	1k	3k	69% (>99:1)
11	1l	3l	54% (>99:1)
12	1m	3m	52% (>99:1)

^a The reactions were performed at room temperature for 24 h by using aldehyde **1b-m** (1 mmol), 3-bromocyclohexene (**2a**, 3 mmol), Bi (3 mmol), and NH₄I (2 mmol) in DMF (2 mL) and water (1 mL).

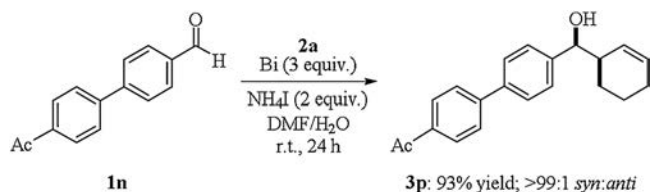
^b Isolated yield.



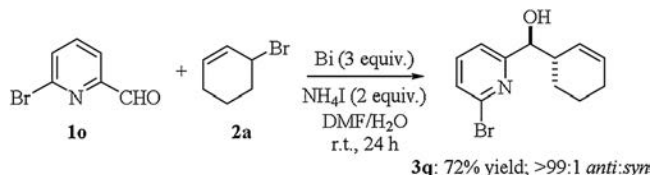
3n (R = CN): 88% yield; >99:1 *syn:anti*
3o (R = CO₂Me): 91% yield; >99:1 *syn:anti*

Scheme 1. Bismuth-mediated highly diastereoselective addition reaction using (Z)-3-bromocyclooct-1-ene (**2b**) as substrate.

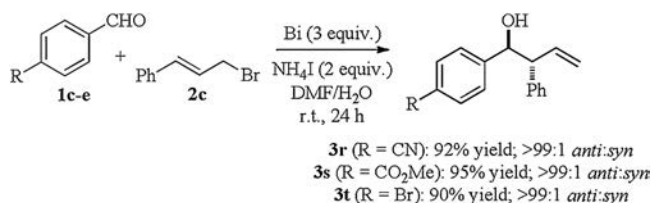
at elevated temperature (entries 10 and 11). Furthermore, survey of other aqueous solvent systems showed that the reactions worked more efficiently in aqueous media containing more polar organic solvents (DMA and DMSO; entries 16 and 17) than in aqueous media using relatively less polar organic solvents (THF, CH₃CN, etc.; entries 12–15). In view that the highest product yield was obtained



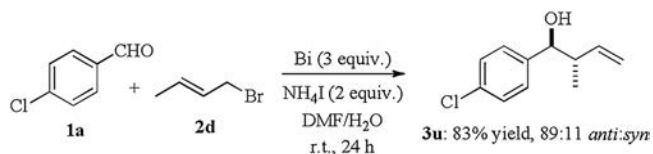
Scheme 2. Bismuth-mediated selective addition reaction of formyl group of substrate **1n** in the presence of acetyl group.



Scheme 3. Bismuth-mediated highly diastereoselective addition reaction using 6-bromopicolinaldehyde (**1o**) as substrate with inversion of product stereochemistry.



Scheme 4. Bismuth-mediated highly diastereoselective addition reaction using (*E*)-cinnamyl bromide (**2c**) as substrate.



Scheme 5. Bismuth-mediated diastereoselective addition reaction using (*E*)-crotyl bromide (**2d**) as substrate.

by employing DMF/H₂O as reaction media, thus the following reactions were performed in aqueous DMF by utilizing NH₄I as reaction additive (entry 7). More importantly, the desired product **3a** was obtained with excellent diastereoselectivity (>99:1 *syn:anti*) under the optimized reaction conditions, with the formation of *syn*-**3a** as the exclusive diastereomer. Additionally, a 10 mmol scale of the model reaction by using 1.4 g aldehyde **1a** could also work with a good efficiency to provide the corresponding product **3a** in 81% yield (entry 7, footnote c).

Under the above optimized reaction conditions, various metals were investigated to see their efficiency in mediating the present addition reactions in aqueous media. As outlined in Table 2, it was found that bismuth served as the most efficient mediator for the

addition reaction (entry 1). In comparison, employment of most of the other metals almost did not lead to the generation of the desired product (entries 2–8). Only the use of indium as reaction promoter gave the product **3a** in 58% yield with reduced diastereoselectivities (87:13 *syn:anti*; entry 9).

Subsequently, the substrate scope of the addition reaction was evaluated by applying the optimized reaction conditions (Bi, NH₄I, DMF/H₂O, r.t., 24 h) to a wide variety of aldehydes in aqueous media. As listed in Table 3, the addition reactions employing various aldehydes proceeded smoothly to furnish the corresponding homoallylic alcohols in modest to good yields. Generally, the reaction worked with enhanced performance by using aryl aldehydes **1b–e** bearing electron-withdrawing groups (entries 1–4) than by utilizing aryl aldehydes **1g–h** containing electron-donating substituents (entries 6 and 7). 2-Thiophenecarboxaldehyde (**1j**) and 3-pyridinecarboxaldehyde (**1k**) possessing heteroatoms worked with equal success to produce the expected products **3j–k** in good yields (69%–71% yields; entries 9 and 10). In the case of α , β -unsaturated aldehyde of cinnamyl aldehyde (**1l**), the addition reaction proceeded regioselectively at the C–O double bond, leaving the C–C double bond untouched (entry 11). As for less reactive alkyl substituted aldehyde of 3-phenylpropanal (**1m**), an acceptable yield of 52% was obtained for the anticipated product **3m** (entry 12). Moreover, the reaction proved compatible with functional groups such as nitro, cyano, methoxycarbonyl, and bromide (entries 1–4).

Apart from six-membered 3-bromocyclohexene (**2a**), eight-membered allylic bromide of (*Z*)-3-bromocyclooct-1-ene (**2b**) was also demonstrated to be an appropriate allylating agent for the reaction, which reacted with representative aryl aldehydes **1c–d** in aqueous media, leading to the expected products **3n–o** as *syn*-diastereomers in 88%–91% yields (Scheme 1).

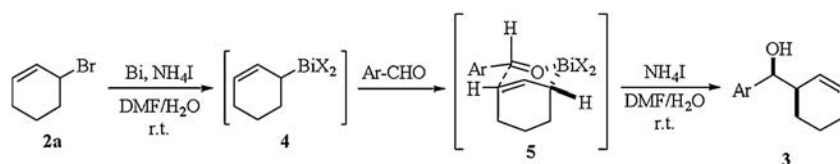
In addition, the mild reaction conditions also entailed the addition reaction to selectively occur at the formyl group of aryl aldehyde **1n** which contains an acetyl group, giving rise to the desired homoallylic alcohol **3p** in 93% yield, with the acetyl group remaining intact (Scheme 2).

Analogous to previous reports [6], when 6-bromopicolinaldehyde (**1o**) possessing a proximal chelating nitrogen atom was subjected to the addition reaction with 3-bromocyclohexene (**2a**) in aqueous media under the well-established reaction conditions, the target product **3q** was produced in 72% yield, with the *anti*-**3q** being the exclusive diastereomer (Scheme 3).

Besides cyclic allylic halides, acyclic allylic bromide of (*E*)-cinnamyl bromide (**2c**) was also proven to be an appropriate allylating reagent for the addition reaction. As shown in Scheme 4, it reacted with typical aryl aldehydes **1c–e** with high efficiency, generating the *anti*-diastereomer **3r–t** in 90%–95% yields.

In addition to (*E*)-cinnamyl bromide (**2c**), sterically less congested (*E*)-crotyl bromide (**2d**) was also employed as a starting material for the present reaction (Scheme 5). As expected, the reaction proceeded smoothly under optimized reaction conditions to give the desired product **3u** in 83% yield, but with slightly reduced diastereoselectivity (89:11 *anti:syn*).

A possible reaction mechanism is proposed in Scheme 6. Initially, allylic bromide **2a** reacts with bismuth powder in the



Scheme 6. Proposed reaction mechanism.

presence of NH_4I to generate an allylic bismuth intermediate **4**. The *in situ* formed organobismuth species **4** subsequently undergoes reaction with aryl aldehyde *via* a Zimmerman-Traxler six-membered ring transition state **5** and followed by hydrolysis to afford the desired product **3** as a *syn*-diastereomer.

In summary, an efficient bismuth-mediated addition reaction of cyclic allylic halide with aldehyde was developed. The reactions employing a variety of structurally varied aldehydes proceeded efficiently in the presence of bismuth and ammonium iodide in aqueous media at room temperature, leading to the desired products of homoallylic alcohols in modest to high yields with compatibility to various functional groups. Bismuth was found to be the mediator of choice among the several metals evaluated. In case where cinnamyl aldehyde and substrate **1n** were used as electrophiles, the addition reactions occurred regioselectively at the formyl group, leaving C—C double bond and acetyl group untouched. More importantly, the reactions proceeded with exclusive diastereoselectivity to afford the corresponding homoallylic alcohols as *syn*-diastereomer. Only in a case where aldehyde of 6-bromopicolinaldehyde containing an adjacent chelating nitrogen atom was used, the reaction proceeded with the inversion of diastereoselectivity to afford the desired product as *anti*-diastereomer.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.ccl.2019.07.030>.

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