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Ultrasound-assisted solventless synthesis of amines by *in situ* oxidation/reductive amination of benzyl halides†

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Ultrasound-assisted solventless oxidation/reductive amination of benzyl halides was developed as a facile, efficient, and environmental friendly method toward *N*-alkylated amines. Aldehydes were formed *in situ* by oxidation of organic halides with *N*-methylmorpholine *N*-oxide (NMO), followed by direct reductive amination with amines using sodium borohydride and montmorillonite K-10 catalyst as the reducing system. This green and simple procedure enables *N*-alkylated amines to be prepared in good to excellent yields with high selectivity of the monoalkylation.

Amines are key building blocks in various natural products and synthetic targets.[1] These compounds exhibit a wide range of applications, especially in pharmaceuticals, agrochemicals and catalysis.[2,3] Thus, over the years, considerable effort has been focused on the development of facile and efficient methods for their preparation. Although alkylation of amines with alkyl halides is the most simple and straightforward route toward *N*-alkylated amines, competing overalkylation often gives rise to product mixtures which complicates purification and results in low product yield.[4] While several attempts have been made to suppress the problem,[5] selectivity of monoalkylation remains difficult to control with highly reactive alkylating agents or strongly nucleophilic amines.[5]

Alternatively, reductive amination is the most applicable methods for preparation of secondary and tertiary amines. The approach is more practical since a variety of *N*-substituted amines can be efficiently prepared with higher selectivity. Generally, this reaction can be carried out *via* direct or indirect approaches.[6] In the direct method, carbonyl compound and amine are reacted in the presence of a proper reducing agent in single step, whereas an indirect reaction involves pre-formation of the imine or iminium salt intermediate before subsequent reduction in a separate step. Borohydride based reducing agents such as sodium cyanoborohydride ($NaBH_3CN$), sodium triacetoxyborohydride [$NaBH(OAc)_3$], and sodium borohydride ($NaBH_4$) are often used in the presence of Brønsted or Lewis acids to achieve selective monoalkylation of amines while minimize competing carbonyl reduction.[7]

So far, a number of available methods have been focused on conversion of carbonyl compounds into amines under the direct and indirect reductive amination.[8] The reaction with alternative reactants beyond aldehydes or ketones is rare. Only a few studies reported one-pot oxidation-imine formation/reduction sequence for conversion of alcohols into amines. A combination of an oxidizing agent with a reductant such as MnO_2/polymer-supported cyanoborohydride,[9] TEMPO–BAIB/$NaBH(OAc)_3$,[10] and TEMPO–BAIB/Hantszch ester has been attempted.[11] Although monoalkylated amines could be prepared in good yields, these methods suffer from complicated procedure, long reaction times, and requirement of expensive reagents.

Based on our previous experience on the direct oxidation of benzyl halides with *N*-methylmorpholine *N*-oxide (NMO),[12] it was envisaged that an *in situ* oxidation/reductive amination would allow a variety of monoalkylated amines to be selectively prepared from cheap and readily available benzyl halides. To the best of our knowledge, such transformation has never been previously investigated. In addition, it is much attention to design a protocol that required more green manipulation, minimized usage of ecologically harmful organic solvents, and lower costs of the processes.

Since ultrasound (US) has been proven as a powerful alternative energy to enhance the reaction rate, product yields, and selectivity in a number of organic transformations,[13] herein, an *in situ* oxidation/reductive amination of benzyl halides was investigated under solvent-free ultrasonic irradiation. The reaction involved the oxidation of benzyl halides with NMO, followed by reductive amination with $NaBH_4$ in one-pot (Scheme 1). It is noted that oxidation of organic halides with NMO proceeds *via* nucleophilic displacement of halide with

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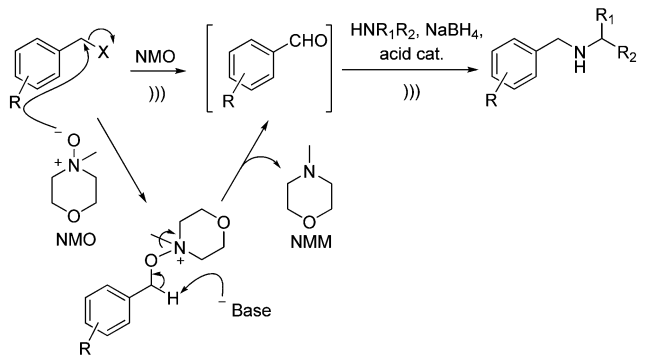


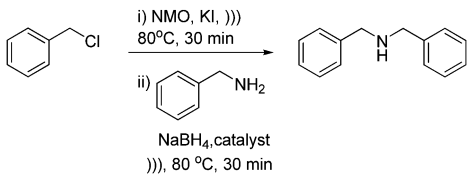
Scheme 1 Solvent-free *in situ* oxidation/reductive amination for conversion of benzylic halides into amines.

oxyanion of NMO to form an *N*-alkoxy salt. Abstraction of the proton at carbon α to the oxygen then gives an aldehyde along with *N*-methylmorpholine (NMM) by-product.

In our previous work, the NMO oxidation was carried out in ionic liquid under microwave irradiation.[12] In order to apply US as the energy source under solventless conditions, the reaction conditions were reinvestigated. Oxidation of benzyl chloride was chosen as the model reaction. Typically, a mixture of benzyl chloride, 10 mol% of KI, with various amounts of NMO was sonicated at 80 °C without addition of solvent and the progress of the reaction was monitored by GC analysis. To our delight, the reaction proceeded rapidly to yield benzaldehyde within 5 min using three-fold excess of NMO. However, the reaction rate was much slower with 1 equiv. of NMO (>90 min). Nevertheless, since excess amount of NMO may interfere with the subsequent reductive amination step, the amount of NMO was further adjusted to achieve high conversion within a reasonable time. It was found that with 1.5 equiv. of NMO, benzyl chloride was completely converted into benzaldehyde within 30 min. The effect of US in enhancing the reaction rate was further confirmed by performing the reaction under standard stirring method. It was found that with 1.5 equiv. of NMO, the reaction under vigorous stirring at 80 °C for 30 min is less effective as 68% of benzaldehyde was obtained along with the remained starting chloride.

With the optimized condition for the oxidation in hand, our attention then turned to combining the sequence with the reductive amination step. $NaBH_4$ was selected as a reducing agent due to its ease of handling, low price, and low toxicity.[14] Although $NaBH_4$ has previously been applied in several cases under neat conditions,[15] the reaction under US has never been explored. Since reductive amination was more favorable under acidic conditions, additive solid acid promoters including Amberlyst-15 resin, silica gel, Celite, and montmorillonite K-10 clay were screened for the best conversion. In a typical reaction, the reductive amination of an *in situ* prepared benzaldehyde with benzylamine was carried out by adding 100 mg of solid catalyst into the reaction vessel after benzyl chloride was completely converted into benzaldehyde. Benzylamine (1.5 equiv.) and $NaBH_4$ (2 equiv.) were then added, followed by sonication at 80 °C for further 30 min.

Table 1 Optimization for oxidation/reductive amination of benzyl chloride[a]



Entry	Catalyst	Isolated yield (%)
1	Amberlyst 15	77
2	Silica gel	70
3	Celite	44
4	Montmorillonite K-10	89
5	—	16

[a] All reactions were carried out with benzyl chloride (0.4 mmol), KI (10 mol%), NMO (0.6 mmol), benzylamine (0.6 mmol), $NaBH_4$ (0.8 mmol) and 100 mg of solid catalyst.

As shown in Table 1, Amberlyst 15 and silica gel similarly provided dibenzylamine in moderate yields (entries 1–2). The lowest yield (44%) was observed when using Celite as the catalyst (entry 3), whereas montmorillonite K-10 clay gave the highest yield (89%) of the desired amine (entry 4). Thus, this condition was selected for further study. In the absence of an acid catalyst (entry 5), only 16% of the amine product could be isolated along with the unreacted benzaldehyde. To our surprise, benzyl alcohol by-product from competing carbonyl reduction was not detected under this condition indicating that the presence of NMO and NMM by-product from the oxidation stage may has a deteriorate effect on the reactivity of $NaBH_4$ and slow down the reduction process. When the condition used in entry 4 was conducted under the conventional stirring method, dibenzylamine was obtained in only 31% yield confirming the genuine contribution of ultrasonic irradiation. Since the reaction is heterogeneous, US should facilitate mass transport and harsh mixing leading to reaction rate acceleration. It is also

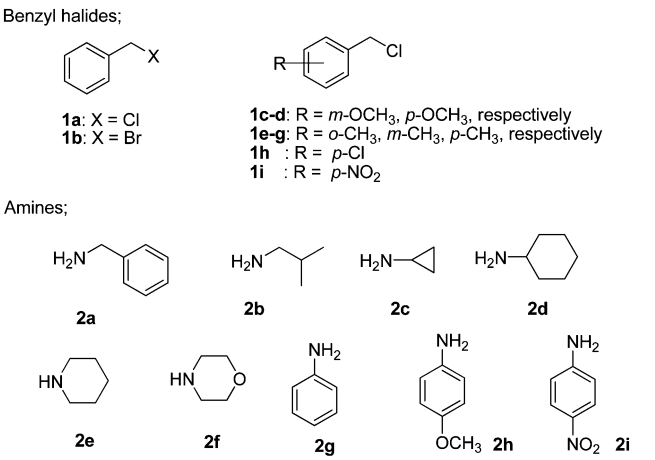


Fig. 1 Structures of benzyl halides and amines used in the synthesis.

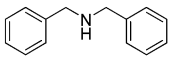
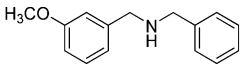
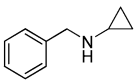
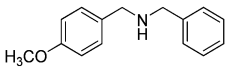
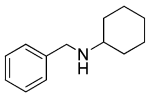
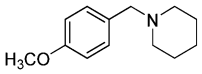
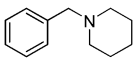
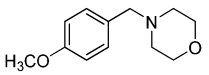
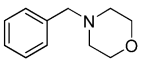
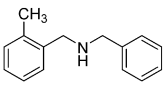
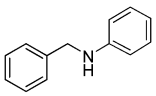
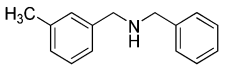
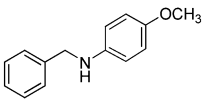
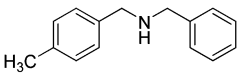
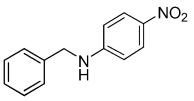
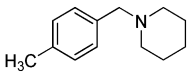
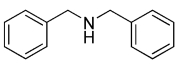
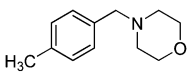
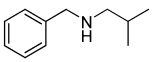
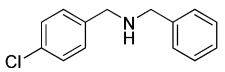
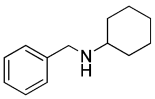
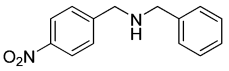
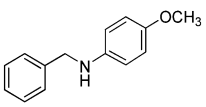
possible that local hot spots with higher temperature may catalyze the reaction.

Considering that benzyl halide also acts as an electrophile in the nucleophilic displacement with amines, a control experiment was carried out under the optimized condition, excepted that no NMO was added. Based on the GC-MS analysis of the crude product, *N*-alkylation by nucleophilic substitution proceeded with 84% conversion to yield 63% of the desired amine along with 37% of the dialkylated product. This result suggested that in the presence of NMO, competitive *N*-alkylation by nucleophilic displacement is unlikely unless there is a remained halide from the oxidation step.

Having established the optimum condition for one-pot oxidation/reductive amination sequence, further investigation on the scope and generality of the reaction was performed by reacting a range of benzyl halides (X = Cl, Br) with a variety of amines including benzylic, aliphatic, and aromatic amines (Fig. 1).[16]

According to Table 2, benzyl chloride reacted smoothly with primary and secondary aliphatic amines to afford the corresponding amines in good to excellent yields (entries 1–5). Side products from overalkylation and aldehyde reduction were not observed. However, under the standard reaction condition, the less reactive aromatic amines gave relatively low yields of the

Table 2 Synthesis of amines *via* oxidation/reductive amination of benzyl halides[a]

Entry	Benzyl halide	Amine	Product	%Yield (ref.)	Entry	Benzyl halide	Amine	Product	%Yield (ref.)
1	1a	2a		89 (ref. 17)	13	1c	2a		80 (ref. 8*d*)
2	1a	2c		85 (ref. 18)	14	1d	2a		92 (ref. 19)
3	1a	2d		87 (ref. 20)	15	1d	2e		95 (ref. 21)
4	1a	2e		86 (ref. 22)	16	1d	2f		92 (ref. 23)
5	1a	2f		96 (ref. 8*i*)	17	1e	2a		83 (ref. 24)
6[b]	1a	2g		87 (ref. 25)	18	1f	2a		82 (ref. 26)
7[b]	1a	2h		88 (ref. 8*i*)	19	1g	2a		80 (ref. 20)
8[b]	1a	2i		55 (ref. 19)	20	1g	2e		88 (ref. 27)
9[c]	1b	2a		91 (ref. 17)	21	1g	2f		92 (ref. 7*f*)
10[c]	1b	2b		86 (ref. 9)	22	1h	2a		82 (ref. 19)
11[c]	1b	2d		91 (ref. 20)	23[d]	1i	2a		77 (ref. 19)
12[b,c]	1b	2i		93 (ref. 8*i*)					

[a] Unless otherwise specified, all reactions were carried out by sonication of a mixture containing benzyl halide (0.4 mmol), KI (10 mol%), and NMO (0.6 mmol) at 80 °C for 30 min, followed by addition of amine (0.6 mmol), $NaBH_4$ (0.8 mmol) and 100 mg of montmorillonite clay 10 and sonication at 80 °C for further 30 min. [b] Reductive amination was performed at 80 °C for 60 min using 0.8 mmol of amine. [c] KI was not added. [d] Oxidation was performed at 80 °C for 60 min.

monoalkylated amines. The yield of *N*-benzylaniline was greatly improved from 53% to 87% with prolonged reductive amination step (entry 6). Under similar condition, *N*-benzyl-4-methoxyaniline was also obtained in good yield (88%, entry 7). However, due to the strong electron withdrawing effect of the nitro group, the least reactive 4-nitroaniline gave the desired amine in only 55% yield along with 40% of benzyl alcohol by-product (entry 8).

Slightly better results were obtained with the more reactive benzyl bromide. Since benzyl bromide is a good substrate for NMO oxidation, addition of KI catalyst is not necessary. The reactions of benzyl bromide with a series of amines proceeded smoothly to afford high yields of the corresponding amines (entries 9–12).

In agreement with our previous study,[12] the rate of benzyl halide oxidation was depended on electronic nature of the substituents on aromatic ring. Substrates with electron-donating groups were more reactive than those containing electron-withdrawing groups. Benzyl chlorides with electron donating groups such as $-OCH_3$ and $-CH_3$ were converted readily to the corresponding aldehydes leading to relatively high yields of the amine products (entries 13–22). However, the oxidation of 4-nitrobenzyl chloride was rather sluggish and only 77% yield of the desired amine was obtained even with prolonged oxidation step (entry 23).

It is noted that although this sequence reaction can be performed with other less reactive primary aliphatic halides, the reaction rate for the oxidation step is much slower and generally requires a longer time for completion of the reaction. In fact, 91% yield of *N*-benzyldecan-1-amine was isolated based on 54% conversion of dodecyl bromide after subjected to 60 min oxidation. Nevertheless, attempts to perform the reaction with secondary halides such as cyclohexyl bromide and 3-bromocyclohexene failed to give satisfactory results due to competitive elimination during NMO oxidation.

In summary, for the first time, a one-pot procedure for conversion of benzyl halides into amines *via* a sequential oxidation/reductive amination under solventless ultrasonic irradiation was reported. This protocol provided several benefits over the conventional mode including simple equipment set-up, used no solvent, and easy work-up. In addition, the mild oxidation with NMO is compatible with the subsequence reduction step, thus allows a clean synthesis of amine from the two step oxidation–reduction conducted in one pot. In most cases, primary benzylic halides together with a range of amines could be efficiently converted into secondary and tertiary amines in good to excellent yields without detectable side products from overalkylation or aldehyde reduction. Moreover, the crude mixture can be purified simply by applied directly onto a chromatography column. The reaction is simple, rapid and eco-friendly which could be potentially useful alternative for selective synthesis of *N*-alkylated amines.

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