

α -Amination of Aldehydes Catalyzed by In Situ Generated Hypoiodite**

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Direct functionalization of organic molecules using metal-free oxidative transformations has long been one of the most challenging research targets.^[1] Over the past two decades, immense research interests were directed toward the application of hypervalent iodine compounds in organic synthesis. The interest was partly due to the low toxicity, simple handling, commercial availability, and mild reactivity of hypervalent iodine reagents.^[2] The most notable feature of such iodine compounds is their catalytic activity; they work effectively in combination with stoichiometric amounts of common co-oxidants, as evidenced in the development of new reactions.^[3,4] Recent progress has focused on the construction of C–O and C–N bonds by employing in situ generated hypervalent iodine as the catalyst. Examples include α -oxygenation reaction of ketones reported by Ochiai and co-workers,^[3b] dearomatization of phenols by Kita and co-workers,^[3h] and the oxidative cycloetherification of ketophenols by Ishihara and co-workers^[3i] for the installation of C–O bonds and the spirocyclization of amides by Kita and co-workers,^[4a] the cross-amination of unactivated arenes by Antonchick and co-workers,^[4b] and the oxidative amination of heteroarenes by Nachtsheim and co-workers^[4c] for the construction of C–N bonds. Despite the progress made in forming C–O or C–N bonds, the development of methods for the formation of C–N bonds of α -amino acid derivatives has lagged behind, even though there is a significant interest in doing so, because

α -amino acid derivatives are central building blocks for pharmaceutical agents and natural products with biological activities.^[5] Accordingly, novel methodologies to install C–N bonds still remain a hot research topic. For instance, a new methodology has been reported for the synthesis of α -amino acetals, involving the use of a copper catalyst.^[6] However, this approach was plagued by major problems that needed to be solved, especially in regard to its narrow substrate scope.

Therefore, we aimed to realize the synthesis of α -amino acetals catalyzed by an active cationic iodine species that is generated in situ. This process is mainly carried out with readily available and environmentally benign co-oxidants, such as molecular oxygen or hydrogen peroxide, which were already used in similar oxidation processes.^[7] We herein report a method for the α -amination of a divergent group of aldehydes. The reaction utilizes secondary amines as the nucleophilic nitrogen source, and is catalyzed by in situ generated hypoiodite, which is prepared with commercially available hydrogen peroxide (30 wt % in water) or sodium percarbonate (H_2O_2 20–30 %). Sodium percarbonate is regarded as a “solid form” or “dry carrier” of hydrogen peroxide and is used for the preparation of hypervalent iodine compounds.^[8] This novel approach has a number of advantages, which include being a metal-free system, working under milder reaction conditions, accommodating a wide scope of substrates, which include bulky aldehydes or secondary amines, and avoiding the generation of toxic by-products derived from the co-oxidant.

In an initial study, which was aimed at optimizing the reaction conditions as well as the choice of the co-oxidant, dibenzylamine **1a** and phenylacetaldehyde **2a** were used as the substrates in the presence of molecular iodine and methanol (Table 1). Interestingly, each reaction afforded the desired product **3a** in moderate to good yield. According to the results of reactions in which molecular oxygen and hydrogen peroxide (30 wt % in water) were used as the co-oxidants (Table 1, entries 1–7), methanol was a better solvent than 1,2-dichloroethane with regard to product formation and yield. Even at 20 °C, product **3a** was generated in 50–67 % yield in methanol (Table 1, entries 3 and 7). Gratifyingly, desired product **3a** was obtained in 83 % yield when the co-oxidant was changed to sodium percarbonate and dichloroethane was used as the solvent (Table 1, entry 8). Further exploration of the reaction with sodium percarbonate showed that it proceeded smoothly, even at room temperature, although the yield decreased slightly (Table 1, entry 9). Increasing the temperature to 80 °C resulted in a significantly lower yield (61 %; Table 1, entries 10 vs. 8 and 9). Thus, the optimal temperature was established to be 40 °C. The nature of the solvent also played an important role in the reaction. Using the sodium percarbonate system, $(\text{CH}_2\text{Cl})_2$ was the most suitable solvent, giving isolated compound **3a** with the highest yield of 83 % (Table 1, entry 8). However, use of methanol, MeCN, and 1,4-dioxane as solvents provided the desired product in low to moderate yields of 46, 74, and 68 %, respectively (Table 1, entries 11–13). These initial studies showed that the ideal ratio of **1a**:**2a** was 1:1.5 (Table 1, entries 9, 14, and 15). Based on these results, the optimized

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Table 1: Optimization of the reaction conditions.^[a]

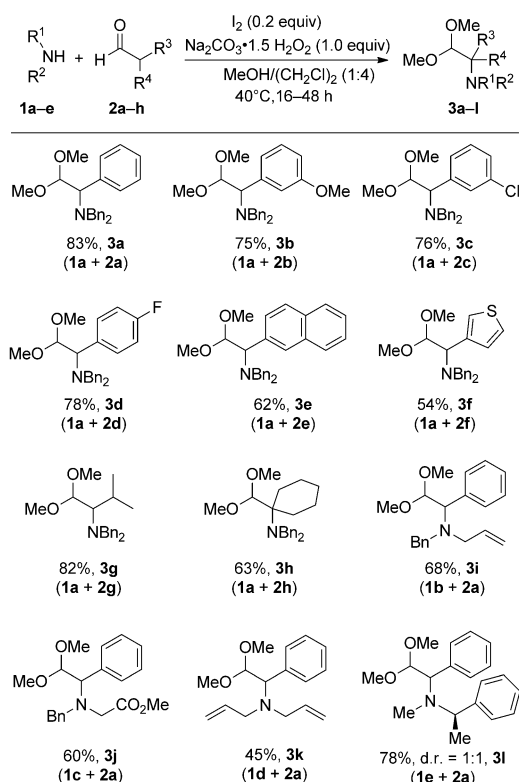
Entry	Oxidant (equiv)	Solvent	T [°C]	t [h]	Yield [%] ^[b]
1	O ₂ (1 atm)	(CH ₂ Cl) ₂	40	16	45
2	O ₂ (1 atm)	(CH ₂ Cl) ₂	20	24	40
3	O ₂ (1 atm)	MeOH	20	24	50
4	30% H ₂ O ₂ (1.5)	(CH ₂ Cl) ₂	40	16	41
5	30% H ₂ O ₂ (1.5)	(CH ₂ Cl) ₂	20	24	39
6	30% H ₂ O ₂ (1.5)	MeOH	40	24	64
7	30% H ₂ O ₂ (1.5)	MeOH	20	24	67
8	Na₂CO₃·1.5 H₂O₂ (1.0)	(CH₂Cl)₂	40	16	83
9	Na ₂ CO ₃ ·1.5 H ₂ O ₂ (1.0)	(CH ₂ Cl) ₂	20	24	79
10	Na ₂ CO ₃ ·1.5 H ₂ O ₂ (1.0)	(CH ₂ Cl) ₂	80	24	61
11	Na ₂ CO ₃ ·1.5 H ₂ O ₂ (1.0)	MeOH	40	16	46
12	Na ₂ CO ₃ ·1.5 H ₂ O ₂ (1.0)	MeCN	40	16	74
13	Na ₂ CO ₃ ·1.5 H ₂ O ₂ (1.0)	1,4-dioxane	40	16	68
14 ^[c]	Na ₂ CO ₃ ·1.5 H ₂ O ₂ (1.0)	(CH ₂ Cl) ₂	40	24	74
15 ^[d]	Na ₂ CO ₃ ·1.5 H ₂ O ₂ (1.0)	(CH ₂ Cl) ₂	40	24	61

[a] Reaction conditions: dibenzylamine **1a** (0.5 mmol, 1.0 equiv), phenylacetaldehyde **2a** (0.75 mmol), iodine (0.2 equiv), oxidant (1.0 equiv), MeOH (0.5 mL), solvent (2.0 mL). [b] Isolated yields based on dibenzylamine. [c] Dibenzylamine **1a** (0.5 mmol, 1.0 equiv), phenylacetaldehyde (0.5 mmol). [d] Dibenzylamine **1a** (0.75 mmol), phenylacetaldehyde (0.5 mmol, 1.0 equiv). The entry highlighted in bold marks optimized reaction conditions.

conditions for the synthesis of α -amino acetals employing our method include: use of sodium percarbonate as the co-oxidant, conduction of the reaction at 40 °C, use of (CH₂Cl)₂ as the solvent, use of secondary amine and aldehyde in a ratio of 1:1.5, adjustment of the solvent ratio of MeOH/(CH₂Cl)₂ to 1:4 (v/v), and use of 0.2 equivalents of molecular iodine as the precatalyst.

Next, our studies focused on the investigation of the scope of our α -amination reaction by employing aldehydes that contain a short carbon chain or a bulky group. A dozen reactions were carried out using the optimized reaction conditions (Scheme 1).

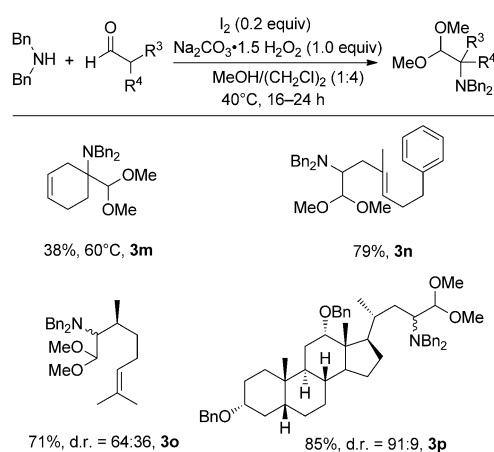
The bulky mono- α -substituted acetaldehydes **2a–g** reacted smoothly to afford the corresponding α -amino acetals. When di- α -substituted acetaldehyde **2h** was used, a new C–N bond was directly constructed at the tertiary carbon center. For the single-ring-substituted phenylacetaldehydes with a substituent such as a methoxy or halo group, the reaction provided the α -amino acetals **3b–d** in good yields (75–78%). An aldehyde with a larger aromatic group, such as naphthyl, was also suitable for this reaction and the desired product **3e** was obtained in a moderate yield of 62%. It is worth noting that, as a result of the mild reaction conditions, the reaction showed good tolerance for heteroaromatic substituents. For example, the amination of 2-(thiophen-3-yl)acetaldehyde afforded α -amino acetal **3f** in a moderate yield of 54%. The reaction was also very effective with branched aldehydes, such as **2g**, which contains an isopropyl group at the α -position. The substrate was aminated to provide the desired product **3g** in a good yield of 82%. It is gratifying that di- α -substituted acetaldehydes, such as cyclo-



Scheme 1. Scope of aldehydes and secondary amines. Reaction conditions: secondary amines **1** (0.5 mmol, 1.0 equiv), aldehydes (0.75 mmol), iodine (0.2 equiv), sodium percarbonate (1.0 equiv), MeOH (0.5 mL), (CH₂Cl)₂ (2.0 mL). Yields of isolated products based on secondary amines **1**. Compound numbers of corresponding starting materials given in brackets underneath the products.

hexane carbaldehyde **2h** also worked well in this reaction, which directly created a new quaternary carbon center that bears a C–N bond. We further expanded the scope of this reaction by investigating the effects of different functionalities on secondary amines. Secondary amines that contain an allylic substituent or ester functionality were also suitable for this reaction, affording the corresponding α -amino acetals **3i–k** in moderate yields. The secondary amine **1e**, which features a stereogenic center, was also applied to this reaction, and furnished the desired product **3l** in a good yield of 78% as a mixture of two diastereomers (1:1). The two optically active α -amino acetals were easily separated by column chromatography on silica gel.

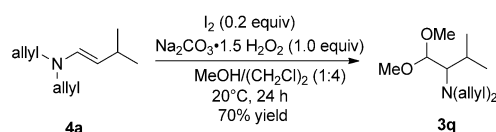
This newly discovered approach to prepare C–N bonds also provides a route to critical intermediates needed to construct complex molecules or to improve biological activities by introducing novel functional groups to natural products or drugs. For example, a Diels–Alder adduct^[9] and a Claisen rearrangement adduct^[10] were readily converted to the desired α -amino acetals **3m** and **3n** in 38% and 79% yields, respectively (Scheme 2). It is especially noteworthy that aldehydes derived from natural sources, such as (S)-(-)- β -citronellol and deoxycholic acid, were also suitable for this reaction. Furthermore, the diastereoselectivity of the formation of α -amino acetals **3p** was 91:9, and the two diastereo-



Scheme 2. Functionalization of complex molecules. Reaction conditions: dibenzylamine **1a** (0.5 mmol, 1.0 equiv), aldehydes (0.75 mmol), iodine (0.2 equiv), sodium percarbonate (1.0 equiv), MeOH (0.5 mL), (CH₂Cl)₂ (2.0 mL). Yields of isolated products based on dibenzylamine **1a**.

mers were easily separated by column chromatography on silica gel (Scheme 2).

In order to better understand the reaction mechanism and to determine the active intermediates involved, the following control experiments were conducted: 1) The enamine **4a** (*N,N*-diallyl-3-methylbut-1-en-1-amine)^[11] was utilized for this reaction, affording the desired product **3q** in 70% yield (Scheme 3). This showed that an enamine is a possible



Scheme 3. Control experiment. Use of an enamine.

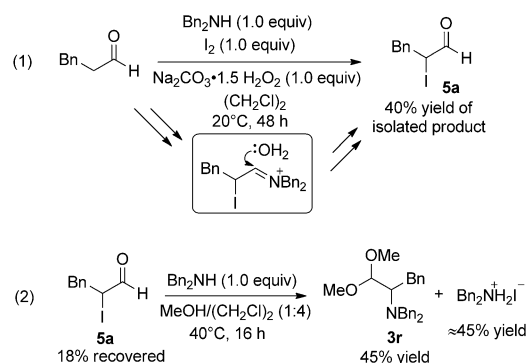
intermediate in this α -amination. 2) The reaction of **1a** and **2a** was also studied in (CH₂Cl)₂ and methanol at 40°C using iodized salts of different oxidation states (Table 2). The use of molecular iodine (I₂) or sodium iodate (NaIO₃) did not result in the formation of the desired product **3a** (Table 2, entries 1

Table 2: Control experiments. Use of iodized salts at different oxidation states.^[a]

Entry	Additive [equiv]	Yield [%] ^[b]
1	I ₂ (1.0)	0
2	I ₂ (1.0) + KOH (2.0)	70
3	NaIO ₃ (1.0)	0
4	NaIO ₄ (1.0)	trace

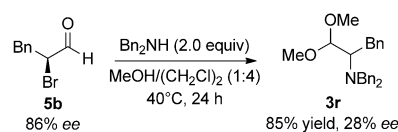
[a] Reaction conditions: Dibenzylamine **1a** (0.5 mmol, 1.0 equiv), phenylacetaldehyde (0.75 mmol), additive (1.0 equiv), MeOH (0.5 mL), (CH₂Cl)₂ (2.0 mL) at 40°C for 16 h. [b] Isolated yields based on dibenzylamine **1a**.

and 3). Only a trace amount of product was detected when sodium periodate (NaIO₄) was used (Table 2, entry 4). In contrast, when a mixture of molecular iodine and two equivalents of potassium hydroxide was employed in this reaction, the desired product was obtained in a good yield of 70% (Table 2, entry 2). As a result, an in situ generated hypoiodite (IO⁻) or iodite (IO₂⁻)^[12] was suggested to be the active intermediate (see the Supporting Information). 3) When the reaction was carried out in the absence of methanol [Scheme 4, Eq. (1)], no α -amino aldehyde was detected and only α -iodo aldehyde was isolated. This showed

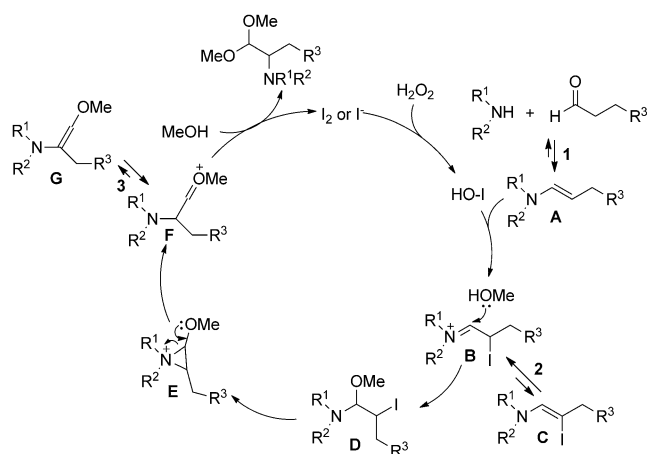


Scheme 4. Control experiment. Reaction in the absence of methanol.

that a) dibenzylamine serves as the catalyst and not a reactant in the reaction; b) the reaction of hypoiodite acid (from the oxidation of molecular iodine) with enamine led to the formation of the α -iodo iminium ion intermediate, and c) hypoiodite (IO⁻) is possibly the active intermediate. Meanwhile, further reaction of dibenzylamine with α -iodo aldehyde **5a** in the presence of methanol afforded the desired α -amino acetal [Scheme 4, Eq. (2)]. 4) To clarify how α -iodo aldehyde was converted into the corresponding α -amino acetal, three possible pathways were proposed: a) configuration inversion of the product through intermolecular nucleophilic substitution, b) configuration retention of the product through double nucleophilic substitution, or c) intramolecular amino migration (see the Supporting Information). Studying the stereochemical outcome of the reaction may provide a clue to the mechanism. Therefore, the easily available optically active α -bromo aldehyde **5b** (86% *ee*) was treated with dibenzylamine and methanol, and the desired α -amino acetal **3r** was obtained in 85% yield. However, the enantioselectivity of the resulting product was only 28% *ee* (Scheme 5). This result showed that a reversible step involving the stereogenic center may exist in the reaction process, thus supporting the amino migration mechanism.



Scheme 5. Control experiment. Use of an optically active α -bromo aldehyde.



Scheme 6. Proposed mechanism for α -amination of aldehydes catalyzed by in situ generated hypoiodite.

On the basis of these control experiments and reports on the intermediates of the active cationic iodine species,^[2–4,7] a mechanism for the α -amination of aldehydes catalyzed by in situ generated hypoiodite is proposed (Scheme 6). In the first step, the active cationic iodine species, hypoiodite acid, which is thought to function as a one-electron oxidizing reagent or electrophilic reagent, is formed by oxidation of iodine (I_2) or iodide (I^-) with hydrogen peroxide. In the second step, the hypoiodite reacts with enamine **A** to provide iminium ion **B**, the existence of which was confirmed by the control experiment shown in Scheme 4, in which the hydrolysis of the intermediate **B** led to the corresponding α -iodo aldehyde. In the third step, methanol attacks iminium ion **B** to give the iodo-substituted intermediate **D**, which undergoes intramolecular cyclization to afford aziridinium ion **E**. Finally, an additional methanol molecule captures the ring-opened intermediate **F** to afford the desired product.

In conclusion, our group has discovered a highly efficient α -amination of sterically divergent aldehydes catalyzed by in situ generated hypoiodite. Furthermore, the use of secondary amines as nitrogen source for the synthesis of α -amino acetals was demonstrated. This reaction has apparent advantages, such as mild reaction conditions, non-toxicity, and easy handling, and sodium percarbonate is used as an environmentally benign co-oxidant. The reaction tolerates a wide range of functionalities, such as benzyl, allyl, or ester groups, as well as bulky aldehydes and secondary amine derivatives. Further development of this unprecedented method to form C–N bonds in aldehydes, particularly with emphasis on the asymmetric synthesis of α -amino acetals, as well as its application to the synthesis of complex molecules are in progress.

Experimental Section

Typical procedure for the α -amination of aldehydes catalyzed by in situ generated hypoiodite (for dibenzylamine **1a** and phenylacetaldehyde **2a** as a model system): Iodine (25 mg, 0.1 mmol) was added to a mixture of sodium percarbonate (79 mg, 0.5 mmol), **1a** (98 mg, 0.5 mmol), and **2a** (90 mg, 0.75 mmol) in methanol (0.5 mL)/dichloro-

ethane (2.0 mL) at room temperature. The mixture was stirred at 40 °C until **1a** was completely consumed, according to TLC analysis of the reaction mixture. A small amount of silica gel was added to the mixture, which was subsequently concentrated. The crude product was purified by flash chromatography (silica gel; ethyl acetate or diethyl ether/hexane = 1:100, v/v) to afford the desired product **3a** as a light-yellow oil (0.150 g, 83 %).

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