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# A practical method for the aziridination of $\alpha,\beta$ -unsaturated carbonyl compounds with a simple carbamate utilizing sodium hypochlorite pentahydrate†

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The efficient formation of *tert*-butyl *N*-chloro-*N*-sodio-carbamate by the reaction of simple *tert*-butyl carbamate with sodium hypochlorite pentahydrate (NaOCl·5H<sub>2</sub>O) would be a practical and green method for the aziridination of  $\alpha,\beta$ -unsaturated carbonyl compounds. The process described herein is transition-metal free, all of the materials are commercially available, the byproducts (NaCl and H<sub>2</sub>O) are environmentally benign and the reaction is stereoselective. The resulting aziridines are potential precursors of amino acids.

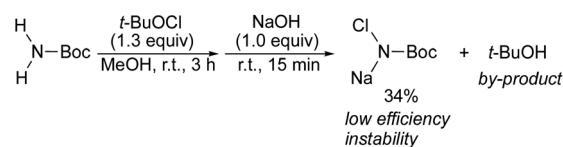
## Introduction

Aziridines containing a carbonyl functionality at the 2-position represent potential precursors of natural and unnatural  $\alpha$ - or  $\beta$ -amino acids by ring-opening reactions with suitable nucleophiles.<sup>1,2</sup> Among the possible synthetic methods for preparing such aziridines, the one-step installation of a nitrogen unit into an  $\alpha,\beta$ -unsaturated carbonyl compound would be a practical approach, and catalytic and stereoselective variants have been developed.<sup>3,4</sup> The preparation of activated aziridines that contain electron-withdrawing groups on the nitrogen, which would be readily ring-opened, from  $\alpha,\beta$ -unsaturated carbonyl compounds would be useful route to the synthesis of amino acid derivatives.<sup>4</sup> The nitrogen sources used for synthesizing these aziridines are highly oxidized, and include hypervalent iodine reagents (ArSO<sub>2</sub>N=IPh)<sup>4a,b,d</sup> and nitrogen-oxygenated agents (ArSO<sub>3</sub>-NHCO<sub>2</sub>R).<sup>4e,f,g</sup> These reagents require transition-metal catalysts or bases for the desired aziridination to be successful, and they have drawbacks such as difficulties associated with their preparation and instability. When these nitrogen sources are used in aziridination reactions, the by-products are iodobenzene and aryl sulfonates, thus making such reactions not atom-economical. *N*-Chloro-*N*-sodio-carbamates (chloramine salts) as an alternative nitrogen source were developed by our group for the aziridination of  $\alpha,\beta$ -unsaturated carbonyl compounds.<sup>5</sup>

This aziridination involved the 1,4-addition of a chloramine salt to an  $\alpha,\beta$ -unsaturated carbonyl compound, followed by cyclization of the resulting enolates accompanied by liberating

only sodium chloride as the by-product. By taking advantage of the poor solubility of chloramine salts, the use of solid-liquid phase transfer catalyst, optically active quaternary ammonium salts, realized the stereoselective aziridination.<sup>5,6</sup> Since chiral aziridines derived from enones are valuable building blocks,<sup>7</sup> tremendous efforts have been devoted to the development of the stereoselective aziridination of enones.<sup>8,9</sup> Among these, our protocols<sup>5,6</sup> are promising for producing enantioenriched aziridines. Our nitrogen sources, chloramine salts, however, are prepared by the reaction of a carbamate (benzyl carbamate or *tert*-butyl carbamate) with *tert*-butyl hypochlorite followed by treatment with sodium hydroxide, in which *tert*-butanol is by-product, and the efficiency is low. In addition, the chloramine salts are not sufficiently stable to allow them to be stored in a freezer (Scheme 1).

To overcome these problems and make it a more sustainable reaction, we envisaged the *in situ* generation of the reactive nitrogen source, a chloramine salt, using a suitable oxidant for the desired aziridination. From these points of view, we report herein on the practical aziridination of  $\alpha,\beta$ -unsaturated carbonyl compounds with a simple carbamate and an ideal oxidant in the presence of quaternary ammonium salt as a phase transfer catalyst. The optimal conditions using the oxidant were applied to the stereoselective aziridination developed by our group.<sup>5,6</sup>

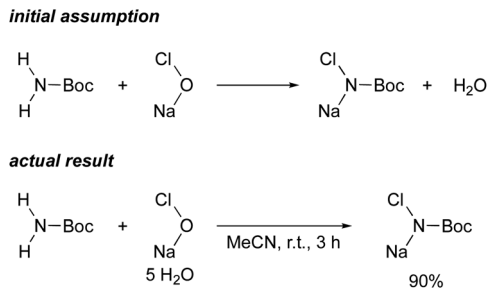


**Scheme 1** Inefficient formation and instability of chloramine salt of carbamate.

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Scheme 2 Initial assumption and actual result for efficient formation of chloramine-Boc.

## Results and discussion

In order to find an ideal oxidant, considering minimum combination of atoms required for the transformation of simple carbamate into *N*-chloro-*N*-sodio-carbamate, we concluded that sodium hypochlorite would be the ideal oxidant, because the by-product molecule is only water (Scheme 2). We recently found that sodium hypochlorite pentahydrate in the solid form<sup>10</sup> and not aqueous solution of sodium hypochlorite was the ideal oxidant for the transformation of sulfonamides into the corresponding *N*-chloro-*N*-sodiosulfonamides.<sup>11</sup> As a simple carbamate, we focused on *tert*-butyl carbamate because it contains a Boc group that can be readily removed. In fact, when *tert*-butyl carbamate was treated with NaOCl·5H<sub>2</sub>O in MeCN at room temperature for 3 h, *tert*-butyl *N*-chloro-*N*-sodio-carbamate (chloramine-Boc)<sup>12</sup> was obtained in high yield (Scheme 2).

The efficient formation of chloramine-Boc with the ideal oxidant prompted us to investigate the aziridination of  $\alpha,\beta$ -unsaturated carbonyl compounds using the simple *tert*-butyl carbamate. Although chloramine-Boc is formed in 90% yield, the use of 1.4 equivalents of H<sub>2</sub>NBoc and NaOCl·5H<sub>2</sub>O relative to the olefin substrates was found to be suitable for the desired aziridination. When benzyl acrylate (**1a**) was treated with *tert*-butyl carbamate in the presence of NaOCl·5H<sub>2</sub>O as an oxidant and benzyltriethylammonium chloride under conditions of a phase transfer catalysis, the desired aziridine **2a** was obtained in 15% yield (path a) along with the  $\beta$ -aminated ester **3a** as the main product (Table 1, Entry 1). Since the enolate derived from the 1,4-addition of *in situ* generated chloramine-Boc to **1a** would be protonated with water leading to **3a** (path b), we screened a series of dehydrating agents. Although the addition of MS3A drastically improved the yield of **2a** (Entry 2), the formation of **3a** could also be effectively reduced by using K<sub>2</sub>CO<sub>3</sub> (Entry 3). The rate of aziridination was very slow without the addition of the PTC (Entry 4) but when the reaction time was extended, 5 mol% of PTC was sufficient to allow the aziridination to proceed (Entry 5). Decreasing the amount of K<sub>2</sub>CO<sub>3</sub> resulted in a decrease in the yield of aziridine **2a** and an increase in the protonated product **3a** (Entry 6). Other additives were not effective for the aziridination (Entries 7–12).

In order to examine the superiority of NaOCl·5H<sub>2</sub>O, related oxidants, including *tert*-BuOCl, Ca(ClO)<sub>2</sub>, *N*-chlorosuccinimide

Table 1 Optimization of reaction conditions (1)<sup>a</sup>

Entry	Additive	PTC (mol%)	Time (h)	Yield <sup>b</sup> (%)	
				2a	3a
1	None	10	12	15	40
2	MS3A (800 mg)	10	12	74	25
3	K <sub>2</sub> CO <sub>3</sub> (9 equiv.)	10	12	80	9
4	K <sub>2</sub> CO <sub>3</sub> (9 equiv.)	None	24	58	7
5	K <sub>2</sub> CO <sub>3</sub> (9 equiv.)	5	18	82 <sup>c</sup>	1
6	K <sub>2</sub> CO <sub>3</sub> (6 equiv.)	5	18	60	12
7	CS <sub>2</sub> CO <sub>3</sub> (9 equiv.)	5	24	73	3
8	K <sub>3</sub> PO <sub>4</sub> (9 equiv.)	5	21	69	1
9	Et <sub>3</sub> N (9 equiv.)	5	24	33	15
10	Na <sub>2</sub> CO <sub>3</sub> (9 equiv.)	5	18	11	35
11	KHCO <sub>3</sub> (9 equiv.)	5	24	9	61
12	NaHCO <sub>3</sub> (9 equiv.)	5	24	9	47

<sup>a</sup> Reactions were performed on a 0.5 mmol scale. <sup>b</sup> Determined by <sup>1</sup>H NMR analysis of the crude product. <sup>c</sup> Isolated yield.

(NCS), and aqueous NaOCl were employed in the reaction, but the efficiencies were low compared to the solid state NaOCl (Table 2, Entries 1–4). After screening other solvents, MeCN was found to be the optimal solvent for the aziridination (Entries 5–9).

Because the Boc group on the nitrogen of the resulting aziridine can be readily detached under mild conditions, we concluded that BocNH<sub>2</sub> should be a useful nitrogen source. To examine the scope of the aziridination, other simple carbamates and amides as a nitrogen source were subjected to the conditions. Unfortunately, only benzyl carbamate could be used for the aziridination (**2a'**), albeit in low yield (Scheme 3). Trifluoroacetamide, benzamide, methanesulfonamide, benzenesulfonamide, and tosylamide had no effect on the process. Carboxamides such as trifluoroacetamide and benzamide failed to react with NaOCl·5H<sub>2</sub>O under the conditions because of the low acidity of N–H protons. Sulfonamides were converted to chloramine salts by the reaction with NaOCl·5H<sub>2</sub>O, but their low nucleophilicity did not induce the 1,4-addition to **1a**.

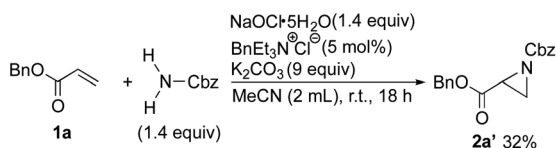
With the optimized conditions (Table 1, Entry 5) in hand, the scope of the  $\alpha,\beta$ -unsaturated esters was investigated (Table 3). Methyl and ethyl acrylates were transformed into the corresponding aziridines (Entries 1 and 2). Although, under the same conditions, the yield for the reaction of *tert*-butyl acrylate was low, increasing the amount of the catalyst used and the reaction



Table 2 Optimization of reaction conditions (2)<sup>a</sup>

Entry	Oxidant	Solvent	Time (h)	Yield <sup>b</sup> (%)	
				2a	3a
1	<i>tert</i> -BuOCl <sup>c</sup>	MeCN	18	51	23
2	Ca(ClO) <sub>2</sub> <sup>d</sup>	MeCN	24	44	0
3	NCS	MeCN	48	0	0
4	NaOCl aq. <sup>e</sup>	MeCN	18	42	21
5	NaOCl·5H <sub>2</sub> O	CH <sub>2</sub> Cl <sub>2</sub>	18	66	5
6	NaOCl·5H <sub>2</sub> O	Toluene	18	66	0
7	NaOCl·5H <sub>2</sub> O	THF	18	44	0
8	NaOCl·5H <sub>2</sub> O	DMF	24	8	0
9	NaOCl·5H <sub>2</sub> O	EtOH	6	0	0

<sup>a</sup> Reactions were performed on a 0.5 mmol scale. <sup>b</sup> Determined by <sup>1</sup>H NMR analysis of the crude product. <sup>c</sup> K<sub>2</sub>CO<sub>3</sub>: 10.4 equiv. <sup>d</sup> Ca(ClO)<sub>2</sub>: 0.7 equiv. <sup>e</sup> 13 wt% (360 μl).

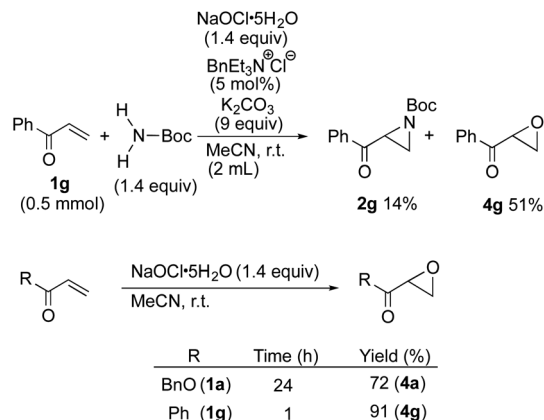
Scheme 3 Formation of *N*-Cbz aziridine.

temperature improved the efficiency (Entries 3–5). Methyl cinnamate was completely unreactive, and it was fully recovered (Entry 6). Arylmethyl acrylates were converted into the corresponding aziridines in good yields (Entries 7 and 8).

Table 3 Scope of  $\alpha,\beta$ -unsaturated esters<sup>a</sup>

Entry	R <sup>1</sup>	R <sup>2</sup>	Temp. (°C)	Time (h)	Yield <sup>b</sup> (%)	
						Product
1	Me	H	<b>1b</b>	r.t.	18	60 ( <b>2b</b> )
2	Et	H	<b>1c</b>	r.t.	18	55 ( <b>2c</b> )
3	<sup>t</sup> Bu	H	<b>1d</b>	r.t.	24	12 ( <b>2d</b> )
4	<sup>t</sup> Bu	H	<b>1d</b>	40	20	27 ( <b>2d</b> )
5 <sup>c</sup>	<sup>t</sup> Bu	H	<b>1d</b>	80	18	35 ( <b>2d</b> )
6 <sup>d</sup>	Me	Ph		r.t.	20	0
7	2-MeOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	H	<b>1e</b>	r.t.	18	75 ( <b>2e</b> )
8	9-Anthracenylmethyl	H	<b>1f</b>	r.t.	18	57 ( <b>2f</b> )

<sup>a</sup> Reactions were performed on a 0.5 mmol scale. <sup>b</sup> Isolated yield. <sup>c</sup> PTC: 10 mol%. <sup>d</sup> Recovery of olefin: 100%.

Scheme 4 Comparison of the rate of the epoxidation of an  $\alpha,\beta$ -unsaturated ester and ketone with NaOCl·5H<sub>2</sub>O.

In order to further expand the scope of substrates, an  $\alpha,\beta$ -unsaturated ketone, phenyl vinyl ketone (**1g**), which was not examined in our previous studies,<sup>5,6</sup> was employed in the present process, unexpectedly affording epoxide **4g** as a main product as well as the desired aziridine **2g** (Scheme 4).

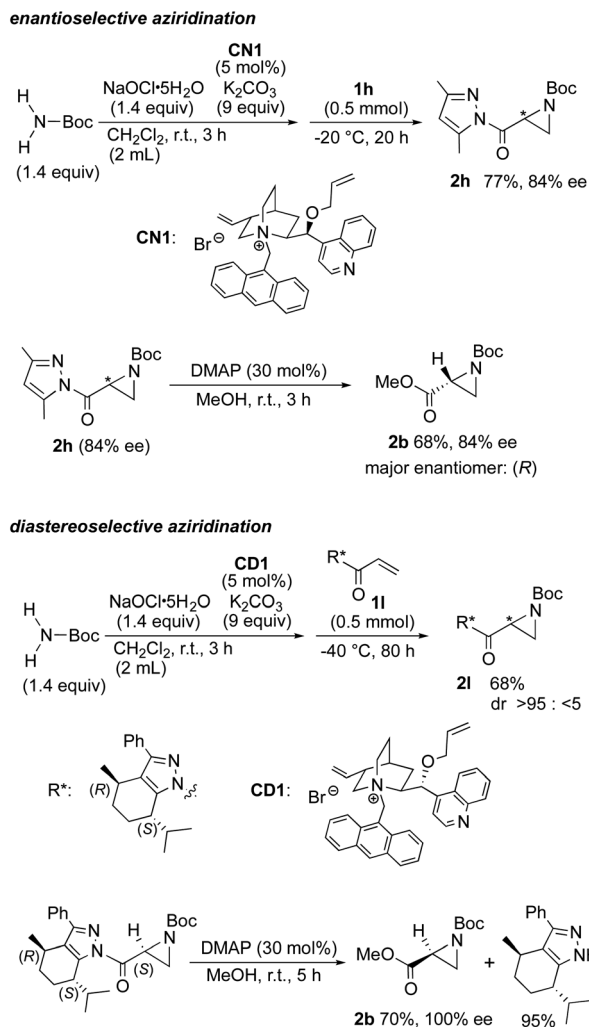
To clarify the difference between the reaction of  $\alpha,\beta$ -unsaturated esters and that of the ketone, considering that the oxygen source of the epoxide is NaOCl·5H<sub>2</sub>O, the olefins **1a** and **1g** were treated with NaOCl·5H<sub>2</sub>O. The rapid epoxidation of **1g** was observed compared with that of **1a** (Scheme 4). These

Table 4 Scope of electron-deficient olefins

Entry	EWG	Solvent	Time (h)	Yield <sup>a</sup> (%)	
1	Ph	<b>1g</b>	CH <sub>2</sub> Cl <sub>2</sub>	1	87 ( <b>2g</b> )
2		<b>1h</b>	MeCN	1	85 ( <b>2h</b> )
3		<b>1i</b>	MeCN	1	96 ( <b>2i</b> )
4		<b>1j</b>	CH <sub>2</sub> Cl <sub>2</sub>	1	76 ( <b>2j</b> )
5	Ph-SO <sub>2</sub>	<b>1k</b>	MeCN	2	66 ( <b>2k</b> )

<sup>a</sup> Isolated yields.





Scheme 5 Enantio- and diastereoselective aziridination and deprotection.

results indicate that  $\text{NaOCl}\cdot 5\text{H}_2\text{O}$  reacts with  $\alpha,\beta$ -unsaturated ketones faster than with  $\text{H}_2\text{NBoc}$ .

To avoid epoxide formation, when  $\text{H}_2\text{NBoc}$  was first treated with  $\text{NaOCl}\cdot 5\text{H}_2\text{O}$  in the presence of the PTC and  $\text{K}_2\text{CO}_3$  at room temperature for 3 h, followed by the addition of phenyl vinyl ketone (**1g**), the desired aziridine **2g** was produced in 87% yield (Table 4, Entry 1). Changing the solvent from MeCN to  $\text{CH}_2\text{Cl}_2$  improved the reaction efficiency in this case. Since the electron-deficient olefins shown in Table 4 reacted first with  $\text{NaOCl}\cdot 5\text{H}_2\text{O}$ , these conditions were employed in reactions of these substrates. Enones containing pyrazole, oxazolidinone, and carbazole moieties were smoothly transformed into the corresponding aziridines in good to excellent yields (Entries 2–4). The present method was applicable to a vinyl sulfone **1k**, affording the aziridine **2k** in good yield (Entry 5).

The robust aziridination that occurs when utilizing  $\text{NaOCl}\cdot 5\text{H}_2\text{O}$  could be applied to enantio- and diastereoselective reactions using optically active phase transfer catalysts, the conditions for which were optimized in our previous studies (Scheme 5).<sup>5,6</sup> Hybridization of our present and previous conditions using

the cinchonine-derived anthracenylmethylated ammonium salt **CN1** as a chiral PTC induced asymmetric aziridination in good yield and enantioselectivity. The resulting aziridine containing dimethylpyrazole was readily transformed into the methyl ester-substituted aziridine **2b** with no change in optical purity.

Regarding the diastereoselectivity of the reaction, the combination of an *L*-menthopyrazole chiral auxiliary and a cinchonidine-derived chiral ammonium catalyst is essential for achieving a high diastereoselectivity. When *tert*-butyl carbamate was treated with  $\text{NaOCl}\cdot 5\text{H}_2\text{O}$  in the presence of **CD1** and  $\text{K}_2\text{CO}_3$  in  $\text{CH}_2\text{Cl}_2$  at room temperature for 3 h, followed by the addition of the enone **11** containing a chiral auxiliary at  $-40^\circ\text{C}$  for 80 h, the corresponding aziridine was produced in good yield with complete diastereoselectivity. The auxiliary was easily deprotected without epimerization giving the methyl ester derivative, with the efficient recovery of *L*-menthopyrazole auxiliary which can be recycled.

## Conclusions

In conclusion, a practical and efficient process for the synthesis of valuable aziridines is reported. Although this basic transformation was previously established by our group, the use of a potential oxidant,  $\text{NaOCl}\cdot 5\text{H}_2\text{O}$  allowed it to be an efficient, sustainable and robust reaction with the stereoselectivity of the aziridination being retained. The reaction is metal free and organocatalysts can be used with a high enantio- and diastereoselectivity, and the resulting aziridines represent potential precursors of  $\alpha$ - or  $\beta$ -amino acids.

## Conflicts of interest

There are no conflicts to declare.

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