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Hydrogen peroxide/dimethyl carbonate: a green system for epoxidation of *N*-alkylimines and *N*-sulfonylimines. One-pot synthesis of *N*-alkyloxaziridines from *N*-alkylamines and (hetero)aromatic aldehydes†

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A green method for epoxidation of imines using an environmentally benign oxidant system, H₂O₂/dimethyl carbonate, was developed. *N*-Alkyloxaziridines were prepared in high yields from *N*-alkylamines and (hetero)aromatic aldehydes in one-pot fashion, whereas *N*-sulfonyloxaziridines have been prepared by using the same oxidant system and 5 mol% of Zn(OAc)₂·2H₂O as catalyst.

Oxaziridines, first reported by Emmons in 1957,¹ exhibit unusual and distinctive reactivity, which is linked to the nature of their *N*-substituent. For example, *N*-sulfonyloxaziridines have been used as electrophilic oxygenating agents for enolates,² alkenes³ and sulfides.⁴ *N*-Alkyloxaziridines undergo cycloaddition reactions with a variety of heterocumulenes,^{5,6} alkenes,⁷ alkynes,⁸ nitriles⁹ and arynes¹⁰ leading to various five-membered ring heterocycles. In addition, oxaziridines are useful as precursors of nitrones,¹ amides,¹¹ secondary amines¹² and *N,N*-disubstituted hydroxylamines.^{1,13} Within the past decade, the chemistry of oxaziridines has been significantly expanded and now encompasses some new interesting reaction types, among which the enantioselective oxyamination of alkenes with *N*-sulfonyloxaziridines, catalyzed by Cu(II)¹⁴ and Fe(II)¹⁵ complexes, and the enantioselective Lewis-base catalyzed cycloaddition of *N*-sulfonyloxaziridines with ketenes can be mentioned.¹⁶

Oxaziridines can be readily prepared from imines, through a number of methods including oxidation with peracids,¹⁷ particularly *m*-chloroperbenzoic acid (MCPBA),^{18,19} oxidation with O₂ in the presence of transition metals,²⁰ oxidation with H₂O₂ in combination with acetic anhydride,¹ nitriles,^{21,22} and urea²³

and oxidation with buffered oxone.²⁴ Perfluoro-oxaziridines have also been prepared by the oxidation of the corresponding perfluoro-imines with H₂O₂ in the presence of a base.²⁵ These methods usually use toxic solvents²⁶ such as CH₃CN^{11,17} and CH₂Cl₂.^{19b} Furthermore, most of them generate stoichiometric amounts of undesirable waste, and require tedious work-up and purification.

Recently, such synthetic routes utilizing hazardous solvents and reagents and generating toxic waste have become discouraged and there have been much efforts to develop safer and environmentally-benign alternatives. This green chemistry approach was introduced in 1990 with the aim at developing cleaner processes through the design of innovative and environmentally benign chemical reactions. In recent years, increasingly stringent environmental requirements have led to a great interest in the application of sustainable and green oxidations. The concept of green chemistry has been rapidly expanding and important advances have been achieved in this field.²⁷ Interest in new synthetic methods has also been extended to many relevant classes of chemical compounds, such as oxaziridines. In this case, two attempts of eco-friendly synthesis of *N*-alkyloxaziridines were described in the literature. The first one consisted in the oxidation of imines with H₂O₂ in acetonitrile, catalyzed by 2 mol% of sodium tungstate,^{11,27b} and the other one described a chemo-enzymatic synthesis of *N*-alkyloxaziridines using H₂O₂/octanoic acid system as oxidant of *N*-alkylimines.¹⁷ In both cases, the conversions of imines to oxaziridines did not reach completion and tedious work-up and further purification were needed. Furthermore, these methods did not avoid the use of toxic solvents, such as CH₃CN, and are limited to the synthesis of *N*-alkyloxaziridines rather than other types of oxaziridines.

Among environmentally-friendly oxidation reagents, hydrogen peroxide is particularly attractive, both for its high oxygen content and the nature of its by-products (water and O₂). Moreover, diluted aqueous solutions of hydrogen peroxide are stable and they can be easily handled and stored. On the other

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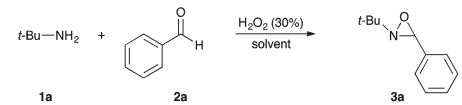


hand, dimethyl carbonate (DMC) is an interesting green solvent and reagent alternative in organic synthesis due to its high biodegradability and low toxicity defined as the absence of associated irritating or mutagenic effects.²⁸ Furthermore, its industrial production does not require phosgene but only methanol and CO.²⁹ As reported by Rüschen, Klaas using DMC with large excess of hydrogen peroxide solution (60%) under chemo-enzymatic catalysis, alkenes were epoxidized with moderate to high yields.³⁰ These authors assume that the active oxidant is the monoperoxy carbonic acid methyl ester (MeO-CO-OOH) generated by the reaction of hydrogen peroxide with DMC, and decomposes to CO₂ and methanol after epoxidation of alkenes. In general, *O*-alkylmonoperoxy-carbonic acids (RO-CO-OOH) are known to be effective epoxidizing reagents of olefins.^{31–34} They are generated *in situ* by the reaction of ethyl chloroformate,³¹ alkoxycarbonyl-1,2,4-triazoles,³² alkoxycarbonylimidazoles³³ or dialkyl carbonates using hydrogen peroxide solution,^{30,34} and they could be utilized without isolation because of their instability. In some cases, *O*-alkylmonoperoxy-carbonic acids have been isolated³⁴ or detected.³² We think that the H₂O₂/DMC system is still under investigated in synthetic chemistry. Indeed, since the report of Rüschen, Klaas in 1999, no other reactions using this green oxidant system have been described in the literature.

In this paper we describe a simple, efficient and eco-friendly synthesis of oxaziridines by use of the green 30% H₂O₂/DMC system. *N*-Alkylloxaziridines have been prepared quantitatively in one-pot synthetic route from the corresponding alkylamines and aldehydes, under mild and neutral conditions, whereas *N*-sulfonyloxaziridines have been prepared with high yields from the corresponding *N*-sulfonylimines under basic conditions, in the presence of Zn(OAc)₂·2H₂O as a catalyst.

With the aim of synthesizing *N*-alkylloxaziridines in a one-pot fashion, we investigated the reaction of *t*-butylamine **1a** (1.0 and 1.5 mmol) with benzaldehyde **2a** (1 mmol) and 30% hydrogen peroxide solution, in the presence of a variety of solvents, affording 2-*t*-butyl-3-phenyloxaziridine **3a** (Table 1). We found that, when the one-pot reaction was run in H₂O, CH₂Cl₂, toluene or DMPU, no transformation into the oxaziridine was observed (Table 1, entries 8–11). These solvents are indeed known to be inert towards H₂O₂. Accordingly, these results indicate that hydrogen peroxide itself is not sufficiently reactive to epoxidize the intermediate imine, whereas, when the reaction was run in DMC, acetonitrile, ethyl acetate, methanol or propylene carbonate (Table 1, entries 1–7), a moderate to high conversion into the oxaziridine was observed. Solvents such as acetonitrile, dialkyl carbonates or ethyl acetate can react with H₂O₂. Indeed, peroxyimidic acids, generated *in situ* by perhydrolysis of a nitrile, are known to be effective epoxidizing reagents of olefins and imines (Payne oxidation).^{22,35} Perhydrolysis of ethyl acetate may also generate peracetic acid as the oxidant of the imine.^{17,36} In this case, oxaziridine **3a** was formed with a moderate yield after 24 h (Table 1, entry 5). The use of methanol as solvent provided the oxaziridine **3a** in 50% yield after 24 h (Table 1, entry 6). As shown in Table 1, the best result for the one-pot synthesis of

Table 1 Investigation of solvents on the model reaction^a

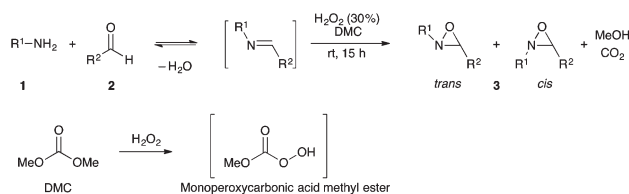


Entry	Equiv. H ₂ O ₂	Equiv. <i>t</i> -BuNH ₂	Solvent	Time (h)	Conversion 3a ^b (%)
1	5	1	DMC	24	88
2	3	1.5	DMC	24	85
3	5	1.5	DMC	15	100
4	5	1.5	CH ₃ CN	20	98
5	5	1.5	EtOAc	24	61
6	5	1.5	CH ₃ OH	24	50
7	5	1.5	PC ^c	18	92
8	5	1.5	H ₂ O	10	0 ^d
9	5	1.5	CH ₂ Cl ₂	10	0 ^d
10	5	1.5	Toluene	10	0 ^d
11	5	1.5	DMPU ^e	10	0 ^d

^a Conditions: **1a**, 1 mmol of **1b**, H₂O₂ (30%), solvent (1 mL), rt. ^b Determined by ¹H NMR analysis of crude product. ^c Propylene carbonate. ^d The oxaziridine was not detected (TLC, ¹H NMR). ^e 1,3-Dimethyltetrahydropyrimidin-2(1*H*)-one.

oxaziridine **3a** was achieved when the reaction was performed by stirring a mixture of *t*-butylamine (1.5 mmol), benzaldehyde (1 mmol) and aqueous solution of H₂O₂ (30%, 5 mmol) in 1 mL of DMC for 15 h, furnishing quantitatively oxaziridine **3a** (Table 1, entry 3). We assume that the active oxidant is the monoperoxy-carbonic acid methyl ester (MeO-CO-OOH) generated by the reaction of H₂O₂ with DMC for the following reasons: (i) *O*-alkylperoxy-carbonic acids have already been reported in the literature,^{31–34} among which *O*-benzylperoxy-carbonic acid, prepared from dibenzyl dicarbonate and H₂O₂, was isolated and characterized;³⁴ (ii) H₂O₂ itself is not sufficiently reactive for epoxidation; this hypothesis is supported by the results given in Table 1 (entries 8–11).

The optimized conditions found for the one-pot synthesis of oxaziridine **3a** (Table 1, entry 3) were chosen as model conditions for our continuing studies. The substrate scope was then investigated, and a variety of *N*-alkylloxaziridines were prepared from the corresponding aldehydes and alkylamines, using the 30% H₂O₂/DMC system (Scheme 1). The condensation of alkylamine **1** with aldehyde **2** provided the imine intermediate, which underwent epoxidation by the oxidizing agent to afford oxaziridine **3**. In general, the synthesis of an imine requires removal of water by use of dehydrating agents, such as molecular sieves,^{37,38} to shift the equilibrium in favor of the imine formation. In our case, the total conversion of



Scheme 1 One-pot synthesis of *N*-alkylloxaziridines.



amine and aldehyde into the imine is assured by the consumption of the latter through its oxidation. ^1H NMR analysis showed total conversion of alkylamines **1** and aldehydes **2** into oxaziridines **3**. Pure products were obtained in excellent yields after washing with a saturated solution of sodium sulfite and extraction with ethyl acetate (Table 2). Consequently, additional purification methods such as column chromatography or recrystallization were not needed. Noteworthy, the present oxidation is scalable as the reaction with 1 g of benzaldehyde (10 mmol) with 15 mmol of *t*-butylamine in 10 mL of DMC, in the presence of 5 mL of 30% H_2O_2 , reached completion after 18 h and afforded oxaziridine **3a** in 97% yield.

We found that excess of *N*-alkylamines and H_2O_2 is necessary to ensure complete consumption of the starting aldehydes in a reasonable time. The reaction time is attractive if we consider that the one-pot route to *N*-alkyloxaziridines allows avoiding prior imine synthesis and related work-up. As described in the literature, *N*-alkylimines were prepared in 18 h at room temperature using CH_2Cl_2 as a solvent, activated molecular sieves and 2 equiv. of alkylamines with regard to aldehydes,³⁷ and in 48 h by heating an equimolecular mixture of amine and aldehyde in dry toluene, in the presence of activated molecular sieves.³⁸

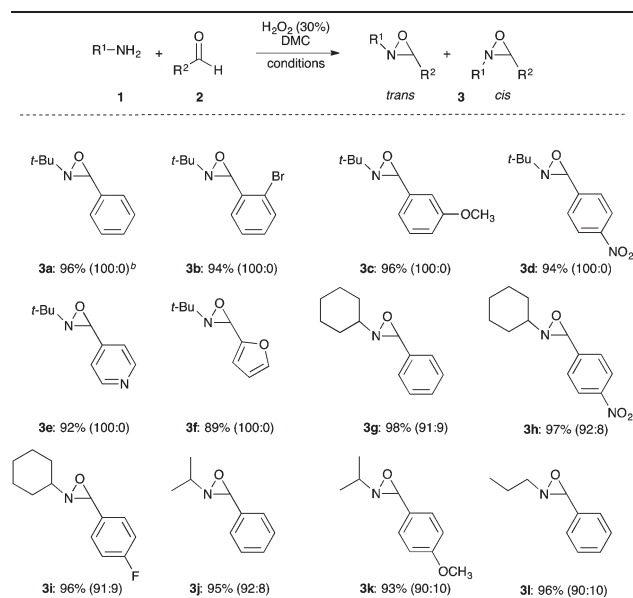
It was demonstrated that commercial aqueous H_2O_2 solution in moderate concentration (30%) can be used successfully instead of more concentrated solutions.³⁰ Moreover, this oxidation does not require a catalyst to take place. No significant amount of by-products, resulting from the oxidation of aldehydes and amines with the DMC/ H_2O_2 system, were formed in

this reaction. Indeed, the oxidation of aldehydes with hydrogen peroxide requires the presence of selenium oxychloride as catalyst.³⁹ As for alkylamines, they can be easily oxidized by peracids⁴⁰ or by the $\text{H}_2\text{O}_2/\text{Na}_2\text{WO}_4$ system.^{27b,41} Consequently, the one-pot route from aldehydes and amines to *N*-alkyloxaziridines probably cannot be achieved by the use of peracids or $\text{H}_2\text{O}_2/\text{Na}_2\text{WO}_4$. Thus, the present work represents the first example of a one-pot route to *N*-alkyloxaziridines from *N*-alkylamines and aldehydes.⁴²

In this work, *N*-*t*-butyloxaziridines were formed exclusively in the *trans*-isomer form (Table 2). The less stable *cis*-isomer is less favoured because of the bulkiness of the *t*-butyl group. Oxaziridines with smaller *N*-substituents were produced as mixtures of *trans* and *cis*-isomers though. These stereoselectivity results are in agreement with the other methods described in the literature.^{17,22,43,44} The one-pot synthesis of *N*-alkyloxaziridines, described in this work, provided a high stereoselectivity, affording the *trans*-isomer as a major product (100:0–90:10, Table 2). The *cis/trans* ratio was determined by ^1H NMR analysis. Indeed, *cis* and *trans*-oxaziridines isomers are known to give different ^1H and ^{13}C NMR spectra.^{17,22,43,44} NMR data of *cis* and *trans*-oxaziridines isomers is provided in ESI.†

Encouraged by the excellent results obtained using the $\text{H}_2\text{O}_2/\text{DMC}$ system for the synthesis of *N*-alkyloxaziridines, we investigated the preparation of other synthetically important oxaziridines, such as *N*-sulfonyloxaziridines. Our initial attempts to perform the oxidation of *N*-sulfonylimines into *N*-sulfonyloxaziridines under the same conditions previously described ($\text{H}_2\text{O}_2/\text{DMC}$ system, neutral conditions and without catalysis) were unsuccessful (no conversion of the *N*-sulfonylimine was observed). Therefore, a systematic study was undertaken to define the best reaction conditions for the synthesis of these oxaziridines (Table 3). We investigated the influence

Table 2 One-pot preparation of *N*-alkyloxaziridines from alkylamines and aromatic aldehydes^a



^a Reaction conditions: alkylamine (1.5 mmol), aldehyde (1 mmol), H_2O_2 (30%) (5 mmol), DMC (1 mL), rt, 15 h (reaction monitored by TLC). ^b Isolated yields (*trans/cis* selectivity determined by ^1H NMR analysis).

Table 3 Optimization of the conditions on the model reaction^a

Reaction scheme showing the optimization of the conditions on the model reaction, yielding **5a**.

Entry	Equiv. H_2O_2	Catalyst	Base	Time (h)	Conversion 5a ^b (%)
1	5	—	—	10	0 ^c
2	10	—	Na_2CO_3	24	62
3	5	$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$	—	10	0 ^c
4	5	TBAB	Na_2CO_3	24	23
5	5	$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$	Na_2CO_3	24	86
6 ^d	5	$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$	Na_2CO_3	10	0 ^c
7 ^e	10	$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$	Na_2CO_3	24	86
8	5	$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$	AcONa	10	0 ^c
9	5	$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$	NaOH	24	66
10	5	$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$	Imidazole	10	0 ^c
11	10	$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$	Na_2CO_3	14	99

^a Conditions: 0.5 mmol of **4a**, catalyst (5 mol%), base (1.2 equiv.), H_2O_2 (30%), DMC (1.5 mL), rt. ^b Determined by ^1H NMR analysis of crude product. ^c The oxaziridine was not detected by TLC. ^d Reaction carried out in MeOH or in CH_2Cl_2 instead of DMC. ^e 0.5 equiv. of Na_2CO_3 was used instead of 1.2 equiv.



of basic medium and that of catalysis with $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and TBAB (tetra-*n*-butyl ammonium bromide) on the model reaction, based on the following precedents: (i) the epoxidation of *N*-sulfonylimines with MCPBA,^{18a,19} $\text{CCl}_3\text{CN}/\text{H}_2\text{O}_2$ ²² and Oxone®²⁴ requires basic medium; (ii) the epoxidation of *N*-sulfonylimines with $\text{CCl}_3\text{CN}/\text{H}_2\text{O}_2$ requires the use of TBAB as a phase transfer catalyst;²² (iii) $\text{Zn}(\text{OAc})_2$ is a non-toxic compound (food additive E650) that showed high catalytic activity in the methoxycarbonylation of aromatic diamines with DMC.⁴⁵

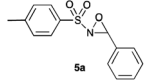
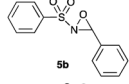
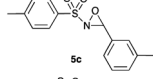
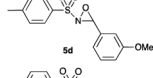
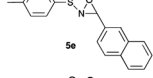
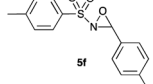
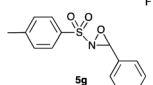
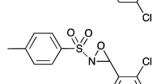
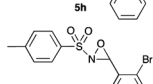
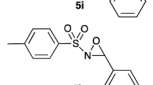
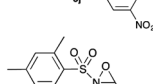
Optimization studies led us to conclude that the basic medium is essential for the epoxidation of *N*-sulfonylimine **4a** (Table 3, entries 1 and 2), but it is not sufficient for completion of the reaction in less than 24 h. The reaction did not work when using bases that are soluble in DMC, such as sodium acetate and imidazole (Table 3, entries 8 and 10). To improve the efficiency of this reaction, we tried two catalysts, *i.e.* TBAB as a phase transfer catalyst and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ as an activating reactant of DMC. The use 5 mol% of TBAB did not lead to any improvement of the reaction (Table 3, entry 4), whereas 5 mol% of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ would work best for this reaction (Table 3, entries 5 and 11). Thereafter, the reaction reached completion in 14 h when 10 equiv. of H_2O_2 were used (Table 3, entry 11).

Hence, the optimized conditions found for the synthesis of *N*-sulfonyloxaziridines starting from *N*-sulfonylimines (1.2 equiv. of Na_2CO_3 , 5 mol% of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, 10 equiv. of 30% H_2O_2 , DMC, rt) were chosen as model conditions for our continuing studies. The substrate scope was then investigated. A variety of *N*-sulfonylimines **4a–k** were tested under the optimized conditions, and representative results are summarized in Table 4. *N*-Sulfonyloxaziridines **5a–k** were obtained in high yields after washing with sodium sulfite, extraction with ethyl acetate and filtration through a short pad of silica gel. There was not much difference in reaction time and yields with various functional groups on the benzene ring of the imine system. In all cases, the reaction produced only one *N*-sulfonyloxaziridine isomer, namely, the thermodynamically favored *trans*-oxaziridine, as for the existing methods.^{18a,19,22}

In order to demonstrate the applicability of the present method, a gram scale oxidation of imine **4f** was carried out, using 2 g of **4f** (7.2 mmol), 10 mL of DMC, 0.9 g of Na_2CO_3 , 7 mL of H_2O_2 (30%) and 80 mg of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (5 mol%). The reaction reached completion in 12 h and afforded oxaziridine **5f** in 92% yield.

As for epoxidation of imines with peracids,^{18a} we postulated that the reaction proceeds in two steps according to a Baeyer–Villiger type mechanism, rather than the concerted oxygen transfer (epoxidation of olefins). A plausible mechanism illustration is proposed in Fig. 1. The addition of H_2O_2 to DMC, in the presence of Na_2CO_3 , would generate the methoxy carbonyl peroxydate **6** as an active oxidant, which would react with the electrophilic *N*-sulfonylimine to give intermediate **7**. The latter undergoes intramolecular cyclisation by attack of the sulfonamide anion on the electrophilic oxygen of the methoxy carbonyl peroxide moiety. The role of Na_2CO_3 may be explained by

Table 4 Synthesis of *N*-sulfonyloxaziridines^a

Entry	Time (h)	Oxaziridine 5	Yield 5 (%)
1	14		91
2	13		86
3	16		88
4	14		94
5 ^b	17		87
6	18		89
7 ^b	15		88
8 ^b	18		90
9 ^b	15		85
10	14		83
11	14		93

^a Reaction conditions: *N*-sulfonylimine (0.5 mmol),⁴⁶ $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (5 mol%), Na_2CO_3 (1.2 equiv.), H_2O_2 (30%, 10 equiv.), DMC (1.5 mL), rt. ^b Reaction carried out in 3 mL of DMC instead of 1.5 mL to solubilize the imine.

the generation of the sulfonylamide anion instead of the *N*-H sulfonamide in **7**, which would not be nucleophilic enough because of the adjacent electron-withdrawing sulfonyl group. On the other hand, the role of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ may be explained by its ability to activate the carbonyl group of the DMC and intermediates **6** and **7** to increase the rate of the oxidation.

The influence of the pH of the reaction media was studied in the synthesis of *N*-alkyloxaziridines, in order to get more insight into the mechanism of the oxidation of the alkylimine. The oxidation of isolated *N*-alkylimines was investigated under



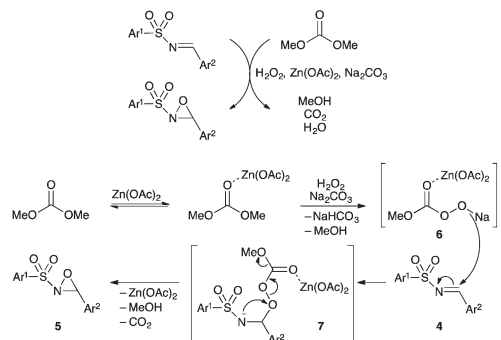


Fig. 1 Postulated reaction mechanism for the Baeyer–Villiger-type oxidation of *N*-sulfonylimines in basic medium under $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ catalysis.

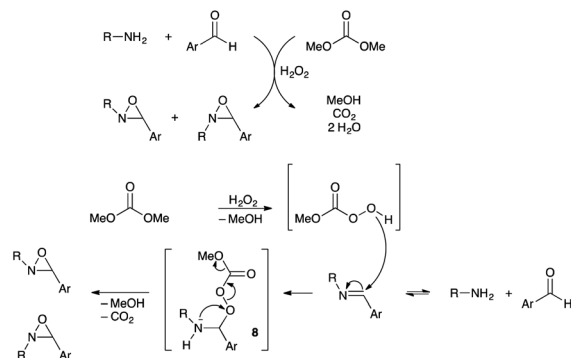


Fig. 2 Proposed reaction mechanism for the one-pot Baeyer–Villiger-type oxidation of *N*-alkylimines in neutral medium without catalyst.

different pH conditions (Table 5). When the pH was adjusted to 8.5 by adding 1.2 equiv. of Na_2CO_3 , or to 7.0 by adding 0.5 equiv. of *t*- BuNH_2 , the obtained results were quite similar to those observed without addition of a base, in both reaction time and conversion (Table 5, entries 1–3). A similar trend was reported for the epoxidation of olefins with the *O*-ethylperoxy-carbonic acid in acidic and basic media.³¹

Based on the previous control experiments, we assume that the basic media is not crucial for the one-pot synthesis of *N*-alkyloxaziridines because the N–H group in the intermediate **8** may be sufficiently nucleophilic for the cyclisation step (Fig. 2). The excess of *N*-alkylamine used in the optimized conditions (1.5 equiv.) is believed to be necessary to ensure the complete consumption of the aldehyde by shifting the equilibrium towards the imine formation and ensure, accordingly, the total conversion of the imine into the corresponding oxaziridine. This hypothesis is in agreement with the following results: (i) in the presence of 1 equiv. of *t*- BuNH_2 , the conversion of benzaldehyde into the oxaziridine was not complete after 24 h of reaction (Table 1, entry 1), (ii) the oxidation of *N*-propylimine, in the presence of *t*- BuNH_2 (1 equiv.), furnished a mixture of *N*-propyloxaziridine **3l** (64%) and *N*-*t*-butyl-

oxaziridine **3a** (33%) (Table 5, entry 4), demonstrating the equilibrium taking place in the reaction conditions (Fig. 2).

For the first time, an eco-friendly one-pot synthesis of *N*-alkyloxaziridines from the corresponding *N*-alkylamines and aldehydes has been developed. In this approach, only green DMC is used as solvent and reagent in the presence of an aqueous solution of hydrogen peroxide (30%). Monoperoxy carbonic acid methyl ester, generated *in situ* by perhydrolysis of DMC, is the active oxidant, which decomposes, after epoxidation of the imine intermediate, to carbon dioxide and methanol. The method has been expanded to the preparation of *N*-sulfonyloxaziridines from the corresponding *N*-sulfonylimines. In this case, the reaction was carried out in basic medium under catalysis with 5 mol% of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$. All oxaziridines were obtained in high yields and high purity under simple and minimum manipulation. This procedure appears to be better than the existing methods on cost, ease of manipulation and greenness, and will provide a novel approach to an environmentally benign process for the preparation of oxaziridines.

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Table 5 Influence of the pH on the oxidation of *N*-alkylimines^a

Entry	R	Additive	Time (h)	Conversion (%) ^b	By-product ^b (%)
1	<i>t</i> -Bu	—	12	96	PhCHO (4%)
2	<i>t</i> -Bu	Na_2CO_3 (1.2 equiv.)	12	>99	PhCHO (<1%)
3	<i>t</i> -Bu	<i>t</i> - BuNH_2 (0.5 equiv.)	10	100	—
4	<i>n</i> -Pr	<i>t</i> - BuNH_2 (1 equiv.)	10	64 (3l)	3a (33%), PhCHO (3%)

^a Conditions: imine (1 mmol), H_2O_2 (30%, 5 mmol), DMC (1 mL), additive, rt. ^b Determined by ^1H NMR analysis of crude product.



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