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Access to functionalized imidazolidin-2-one derivatives by iron-catalyzed oxyamination of alkenes

Anne-Doriane Manick,[a] Sidonie Aubert,[a] Boubacar Yalcouye,[a] Thierry Prangé,[b] Farouk Berhal*[a] and Guillaume Prestat*[a]

Abstract: Functionalized imidazolidin-2-one were prepared using an iron catalyzed alkene oxyamination reaction. This atom-economical process is using hydroxylamine derivatives without addition of any external oxidant. The conditions developed are efficient on mono-, di- and tri-substituted double bonds leading to good yields and diastereoselectivities and allow the access to a large scope of diaminoalcohol precursors. Mechanistic pathway was studied and appeared to involve both a fused aziridine and a carbocationic species.

Introduction

Imidazolidinone scaffolds are important building blocks found in many biologically active drugs and natural products. The vitamin B_7 and the marine sponge alkaloid Agelastatin[1] (antitumor activity) as well as the angiotensin-converting-enzyme inhibitor Imidapril (treatment of chronic heart failure) are some representative examples of this class of compounds (Figure 1).[2] Furthermore, 4-methylene-oxy-functionalized imidazolidin-2-one are important precursors of 1,2,3-diamino-alcohol derivatives and are used as versatile intermediates for the preparation of pharmaceuticals or bioactive products such as Tamiflu (influenza A/B treatment)[3] and Balanol (potent protein kinase A and B inhibitor, Figure 1).[4] The classical routes for the synthesis of diamino-alcohol moieties involve multistep processes with several protection and deprotection reactions, consuming a large amount of resources. During the last decades, the concept of sustainable chemistry has emerged with the idea of minimizing negative environmental impacts of chemical processes.[5] Thus, the development of atom- and step-economical methodologies is, today more than ever, an essential scientific and societal concern.[6] In this context, following our research program dedicated to the development of domino reactions and hetero-functionalization of alkenes,[7] we became interested in the preparation of 1,4-disubstituted imidazolidin-2-one scaffolds *via* an atom-economical approach.

Vicinal amino-oxygenation of alkenes has become a powerful reaction for the access of amino-alcohol moieties in a single step from olefins.[8] Since the pioneer work reported by Sharpless for asymmetric amino-hydroxylation of alkenes,[9] great progresses have been made in intramolecular or intermolecular versions, using various metals such as Os,[10] Rh,[11] Pd,[12] Pt,[13] Cu,[14] Fe,[15] Au,[16] or Ag.[17] The group of Hao Xu reported recently an iron-catalyzed intramolecular amino-oxygenation of alkenes using hydroxylamine derivatives.[18] This original approach fits in perfectly with the field of sustainable chemistry as a totally atom-economic process in which all the atoms of the substrate are conserved on the product using an environmentally benign metal catalyst. Moreover, the process is also step-economical as cyclization and formation of carbon-nitrogen and carbon-oxygen bonds occurred in a single step. Despite the great potential of this reaction, only the synthesis of oxazolidinone compounds has been reported to date. In order to get a broader scope, we describe herein the iron-catalyzed intramolecular amino-oxygenation of allyl-benzoyloxy urea derivatives for the synthesis of 4-methylene-oxy-functionalized imidazolidin-2-one products as 1,2,3-diaminoalcohol precursors.

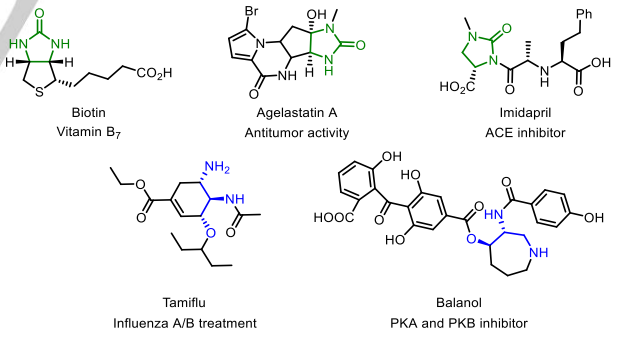

Figure 1. Imidazolidinone and diamino-alcohol in bioactive compounds.

Results and Discussion

We initiated the reaction optimization using compound **1a** as model substrate, iron(II) acetate as catalyst and acetonitrile as solvent. The target product **2a** was isolated in a poor 26 % yield (Table 1, entry 1). A screening of potential ligands was conducted using first a series of bidentate nitrogen-based derivatives. The addition of 2,2'-biquinoline **L1** and 2,2'-bipyridine **L2** increased the yield and product **2a** was obtained in 34 % and 39 % respectively (Table 1, entries 2 and 3). Functionalized phenanthrolines were then tested. The use of 1,10-phenanthroline **L3** led to a moderate 39 % yield (Table 1,

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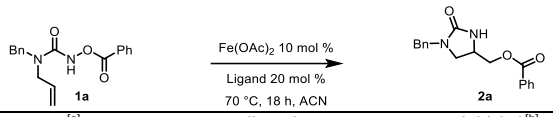
entry 4) whereas the electron-rich 3,4,7,8-tetramethyl-1,10-phenanthroline **L4** induced a dramatic decrease in the reaction efficiency (14 % yield, Table 1, entry 5). The more electron-rich 4,7-dimethoxy-1,10-phenanthroline **L5** and the electron-poor 3,5,6,8-tetrabromo-1,10-phenanthroline **L6** gave yields close to that observed in the presence of ligand **L3** (respectively 40 % and 34 % yield, Table 1, entries 6 and 7). Tridentate nitrogen-based ligands were then screened. The 2,2':6',2''-terpyridine **L7** gave a moderate 34 % yield whereas the pybox derivative **L8** gave a poor 20 % yield (Table 1, entries 8 and 9). Finally, the diketone-based 1,3-diphenylpropanedione ligand **L9** was tested affording the target product **2a** in a moderate 37 % yield (Table 1, entry 10). The best yields were thus obtained with ligands **L2**, **L3** and **L5** and the 1,10-phenanthroline ligand **L3** was selected to continue the optimization.

Table 1. Screening of ligands.

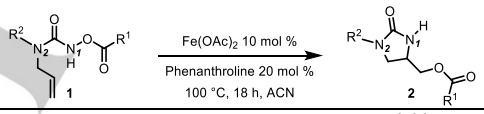


entry[a]	ligand	yield (%)[b]
1	---	26
2	L1	34
3	L2	39
4	L3	39
5	L4	14
6	L5	40
7	L6	34
8	L7	34
9	L8	20
10	L9	37

[a] Reactions were carried out under Ar using **1a** (1 equiv), $Fe(OAc)_2$ (10 mol %), ligand (20 mol %), in ACN for 18 h at 70 °C. [b] Isolated yields.

The nature of solvent and catalyst as well as the effect of additives were then studied. No improvement was observed by using other classical polar and non-polar solvents or other iron complexes (see Supporting Information). The effect of the temperature on the reaction course was also investigated. A slight increase in the yield and a cleaner reaction were observed at 100 °C (41 % yield, Table 2, entry 1). Having in hand the optimized reaction conditions in terms of catalyst, solvent and temperature (iron(II)-acetate, 1,10-phenanthroline, ACN, 100 °C), we turned our attention to the effects of the *N-**1*** and *N-**2*** substitution. First, the benzoyl moiety on the *N-**1*** atom was modulated. Different electron-rich and electron-poor aryl groups were evaluated leading to yields between 23 and 52 % (Table 2, entries 1-6). While 2,4,6-trimethyl- and 2,4-dichloro-benzoyl were found almost as efficient (52 and 50 % yield respectively, entries 5 and 6) the latter substituent was chosen for the following studies since this moiety is easier to remove. The addition of 2,4-dichlorobenzoic acid or the corresponding sodium salt to the reaction mixture, as an external nucleophile, did not increase significantly the yield (53 % vs. 50 %, Table 2, entry 6 vs. 7 and 8). Interestingly, the use of an acetate group instead of a benzoate derivative led to a similar result (50 %, Table 2, entry 9 vs. 6). A control experiment in the absence of iron catalyst was performed and surprisingly the target product was obtained, although in a poor 16 % yield (Table 2, entry 10). This result suggests a cleavage of the N-O bond under thermic conditions generating reactive species, which could undergo insertion on the double bond to afford the target compound. The substituent on the *N-**2*** atom was then modulated. By using the 3,4-dimethoxybenzyl derivative, a decrease in the reaction efficiency was observed (43 %, Table 2, entry 11). A satisfying yield was obtained for the substrate **1i** with *N-**2*** bearing a simple hydrogen atom (67 % yield, Table 2, entry 12). Finally, the best yields were obtained for products **2j** and **2k** respectively 75 % and 76 % with *N-**2*** bearing a methyl or an allyl moiety (entries 13 and 14).

Table 2. Study of *N-**1*** and *N-**2*** substitution.



entry[a]	R^1	R^2	substrate	yield (%)[b]	product
1		Bn	**1a**	41	**2a**
2		Bn	**1b**	42	**2b**
3		Bn	**1c**	23	**2c**
4		Bn	**1d**	45	**2d**
5		Bn	**1e**	52	**2e**
6		Bn	**1f**	50	**2f**
7[c]		Bn	**1f**	53	**2f**
8[d]		Bn	**1f**	53	**2f**
9	Me	Bn	**1g**	50	**2g**
10[e]		Bn	**1f**	16	**2f**
11		3,4-diMeO-Bn	**1h**	43	**2h**
12		H	**1i**	67	**2i**
13		Me	**1j**	75	**2j**
14		Allyl	**1k**	76	**2k**

[a] Reactions were carried out under Ar using substrate **1** (1 equiv), $Fe(OAc)_2$ (10 mol %), phenanthroline (20 mol %), in ACN for 18 h at 100 °C. [b] Isolated yields. [c] 1 equiv of 2,4-dichlorobenzoic acid was added. [d] 1 equiv of 2,4-dichlorobenzoic acid sodium salt was added. [e] Without iron at 100 °C.

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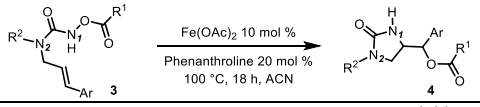
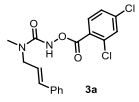
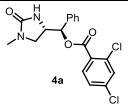
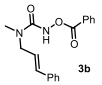
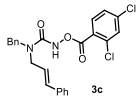
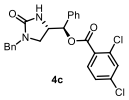
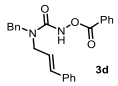
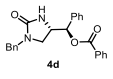
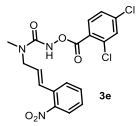
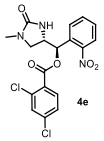
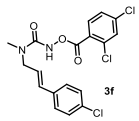
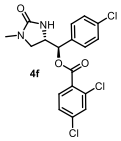
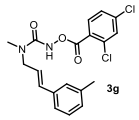
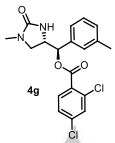
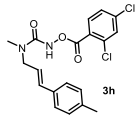
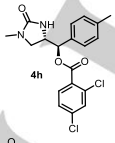
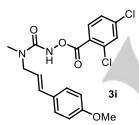
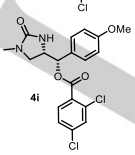
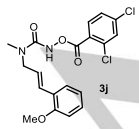
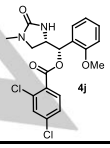
To study the scope of this transformation special attention was paid to disubstituted alkenes which represent a challenge for oxyamination reactions catalyzed by other metals.[7e,19] We began our investigations by replacing the reactive allyl appendage by a cinnamyl group (Table 3).

Table 3. Exploration of the scope for styryl derivatives.



3 4

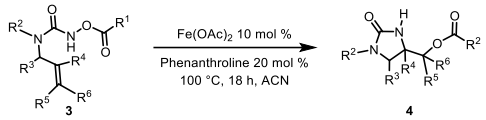
entry[a]	substrate	major product	yield (%)[b]	anti:syn[c]
1			74	96:4
2			75	92:8
3			55	92:8
4			47	94:6
5			45	94:6
6			76	94:6
7			76	80:20
8			76	70:30
9			75	12:88
10			61	38:62

[a] Reactions were carried out under Ar using substrate (1 equiv), $Fe(OAc)_2$ (10 mol %), phenanthroline (20 mol %), in ACN for 18 h at 100 °C. [b] Isolated yields. [c] dr determined by ^1H NMR on the crude mixture.

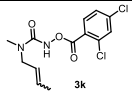
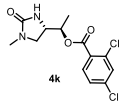
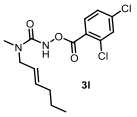
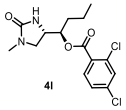
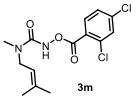
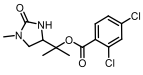
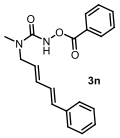
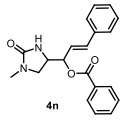
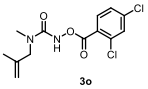
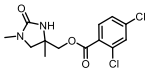
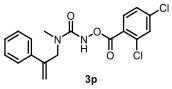
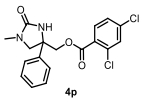
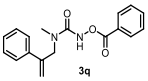
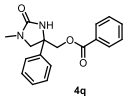
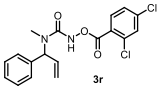
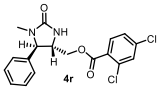
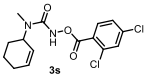
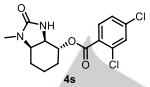
Substrate **3a** was thus submitted to the reaction conditions. Gratifyingly, excellent diastereoselectivity and good yield were observed for the phenyl-substituted product **4a** (96:4 dr, 74% yield, Table 3, entry 1). The impact of the substitution on *N-**1*** and *N-**2*** atoms on the reaction outcome with cinnamyl substrates was also explored. Switching from the 2,4-dichlorobenzoyl to a simple benzoyl on *N-**1*** did not impact the yield of the reaction and only a slight decrease of the dr, from 96:4 to 92:8, was obtained for **4b** vs **4a** (Table 3, entry 2 vs 1). As previously observed (Table 2), replacing the methyl on *N-**2*** by a benzyl group induced a significant drop in the yield. Indeed, compounds **4c** and **4d** were isolated in 55 % and 47 % yield respectively still in high dr (Table 3, entries 3 and 4 vs 1 and 2). These results clearly demonstrated that the diastereoselectivity is poorly influenced by the *N-**1*** and *N-**2*** substitution, while the yield is dramatically affected. Disubstituted *E*-alkenes bearing electron-donating and electron-withdrawing styryl groups were then evaluated (Table 3). The electron-deficient substrates **3e** and **3f** reacted smoothly affording 2-nitrophenyl **4e** and 4-chlorophenyl **4f** products in a good 94:6 dr and moderate to good yields, 45 % from the sterically demanding substrate **3e** and 76 % from **3f** (Table 3, entries 5 and 6). On the contrary, the electron-rich products 3-methylphenyl **4g**, 4-methylphenyl **4h**, 4-methoxyphenyl **4i** and 2-methoxyphenyl **4j** were isolated in good yields (from 61 % to 76 %) but in moderate to poor dr (from 38:62 to 12:88, Table 3, entries 7-10). These results highlighted the influence of the electronic effects of the styryl moiety on the selectivity of the transformation and could suggest different mechanistic pathways for electron deficient and electron rich alkenes.

To explore more deeply the scope, we then focused on diversely functionalized olefins (Table 4). Good yields and moderate dr were obtained for the crotyl, propyl and prenyl derivatives **4k**, **4l** and **4m** (71 %, 75 % and 72 % yield respectively, Table 4, entries 1-3). The styryl product **4n**, which can be seen as an interesting scaffold for post-functionalization, was isolated in a moderate 47 % yield and a poor 60:40 dr (Table 4, entry 4). The methallyl substrate **3o** led to product **4o** in a good 68 % yield unlike the phenyl analogue **4p**, which was isolated in a poor 34 % yield (Table 4, entries 5 and 6). The yield of this latter compound could be increased to 56 % by changing the 2,4-dichlorobenzoyl group on *N-**1*** to a simple benzoyl derivative (Table 4, entry 7 vs 6). The vinyl benzyl compound **3r** also underwent the transformation and gave product **4r** in moderate yield and dr (50 %, 70:30, Table 4, entry 8). Finally, the cyclohexyl substrate **3s** led to a unique diastereoisomer with a moderate 41 % yield which highlighted the impact of the conformation on the diastereoselectivity (Table 4, entry 9).

Table 4. Exploration of the reaction scope.

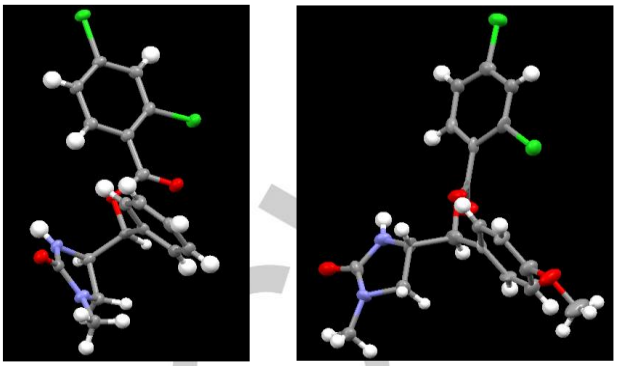


3 4

entry[a]	substrate	major product	yield (%)[b]	anti:syn[c]
1	 3k Mixture *E*:*Z* = 80:20	 4k	71	60:40
2	 3l	 4l	75	80:20
3	 3m	 4m	72	---
4	 3n	 4n	47	60:40
5	 3o	 4o	68	---
6	 3p	 4p	34	---
7	 3q	 4q	56	---
8	 3r	 4r	50	70:30
9	 3s	 4s	41	>98:2

[a] Reactions were carried out under Ar using substrate (1 equiv), $Fe(OAc)_2$ (10 mol %), phenanthroline (20 mol %), in ACN for 18 h at 100 °C. [b] Isolated yields. [c] dr determined by ^1H NMR on the crude mixture.

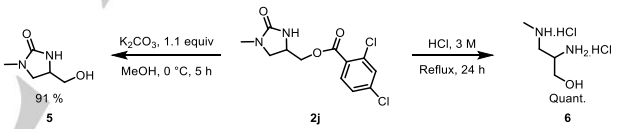
The stereochemistry was assigned using single crystal X-Ray diffraction for compounds **4a**, **4i**, **4k**, **4l** and **4s** and NMR correlations were used for the other products (Figure 2).[20] The major stereoisomer comes from a global anti-addition except, surprisingly, for the methoxy derivatives **4i** and **4j**.



Single Crystal X-Ray of compound **4a** Single Crystal X-Ray of compound **4i**

Figure 2. Single crystal X-Ray analysis for compounds **4a** and **4i**.

Finally, our reaction conditions were applied on a 1 gram scale experiment (3.3 mmol) using substrate **1j**, which afforded compound **2j** in 74 % yield as expected. To demonstrate the easy access to interesting building blocks from the functionalized imidazolidinone products synthesized, the cleavage of the protective groups was carried out on compound **2j**. The ester moiety was easily removed in the presence of potassium carbonate with an excellent 91 % yield. Furthermore, the urea was cleaved using an aqueous 3 M HCl solution to afford the diamino-alcohol salt **6** in a quantitative yield (Scheme 1).

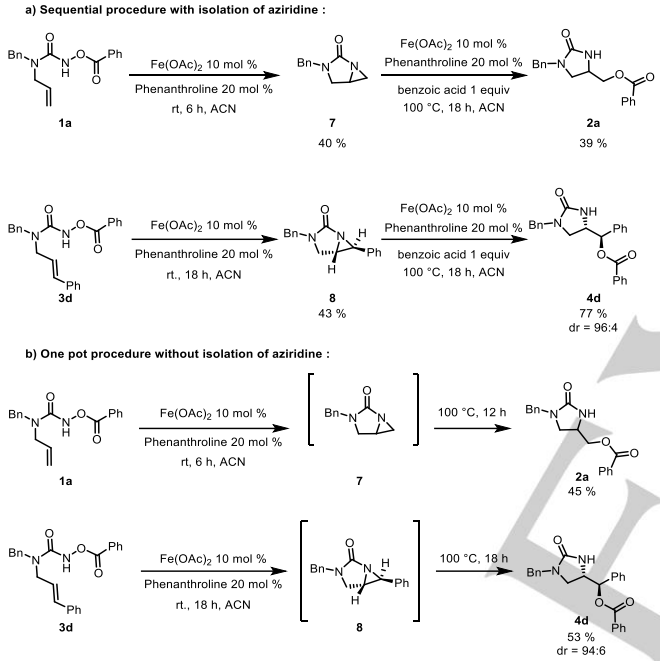


5 2j 6

Scheme 1. Deprotection reactions.

Regarding the mechanism of this transformation, the group of Hao Xu proposed an iron nitrenoid as key intermediate, which one could undergo either an olefin aziridination or a direct oxyamination reaction through carbo-radical species.[18] The authors emphasized that the rate of aziridination versus oxyamination depends on the counterion and ligand combinations. In order to postulate a mechanism applicable to our conditions, we conducted various control experiments. First, substrate **1a** was submitted to our reaction conditions decreasing the temperature from 100 °C to rt. This allowed the isolation of the aziridine **7** in 40 % yield.[21] The pure aziridine was next submitted to the oxyamination reaction conditions in the presence of 1 equivalent of benzoic acid. The expected product **2a** was isolated in 39 % yield (Scheme 2-a). Similarly, the *E*-styryl substrate **3d** afforded at rt the corresponding aziridine **8** which was isolated with a moderate 43 % yield as the single *trans*-isomer.[21] The pure aziridine **8** was then subjected to the reaction conditions in the presence of 1 equivalent of benzoic acid and the compound **4d** was obtained in a good 77 % yield and excellent 96:4 dr (Scheme 2-a). These experiments demonstrated that the aziridines **7** and **8** can be

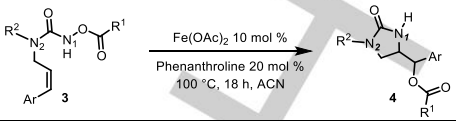
opened in the reaction conditions and are possible intermediates in this transformation. We then conducted a one pot procedure involving independently substrates **1a** and **3d**. The reaction was launched at room temperature and after observation of the aziridine intermediate (based on TLC analysis), the solution was heated at 100 °C without addition of any additive. The oxyamination products **2a** and **4d** were isolated in respectively 45 % and 53 % yield (94:6 dr for **4d**, Scheme 2-b). These results are similar to the ones obtained under the standard conditions (see Table 2, entry 1 and Table 3, entry 4). Therefore, we hypothesized that for these substrates the reaction proceeded through an aziridination followed by a S_N2 type opening route although the intermediate aziridine was not detected under these conditions.

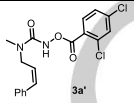
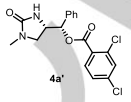
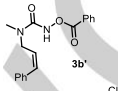
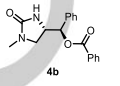
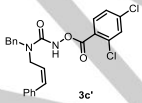
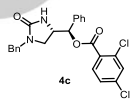
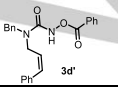
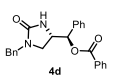


Scheme 2. Mechanistic study.

To gain more insights on the mechanism, the influence of the alkene's geometry was also investigated. Compound **3a'**, *Z*-isomer of **3a**, was submitted to the reaction conditions and afforded the expected products in a similar yield (76 %, Table 5, entry 1) with a lower dr (40:60 vs 96:4). The reaction of *Z*-**3a'** provided as the major product the opposed isomer than the one observed starting with the *E* isomer **3a**. The *Z* isomers **3b'**, **3c'** and **3d'** were then studied. Yields were obtained between 49 % and 66 % with dr from 55:45 to 75:25 (Table 5, entries 2-4). Surprisingly, the diastereoselectivity of the *Z*-substrates were clearly dependent of the *N*-***1*** and *N*-***2*** functional groups and inconsistent with *E*-substrates (Table 5 entries 1-4 vs Table 3 entries 1-4).

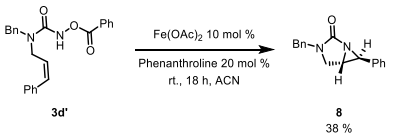
Table 5. Study of the influence of the alkene geometry.



entry[a]	substrate	major product	yield (%)[b]	anti:syn[c]
1			76	40:60
2			66	55:45
3			50	60:40
4			49	75:25

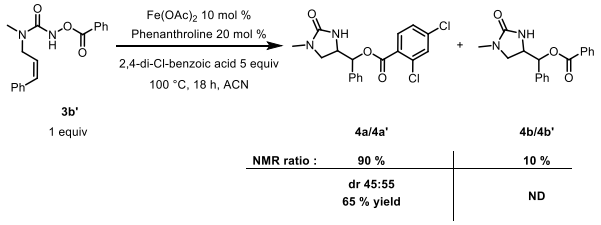
[a] Reactions were carried out under Ar using substrate (1 equiv), $Fe(OAc)_2$ (10 mol %), phenanthroline (20 mol %), in ACN for 18 h at 100 °C. [b] Isolated yields. [c] dr determined by ^1H NMR on the crude mixture.

The *Z*-styryl substrate **3d'** was thus submitted to our reaction conditions at rt. To our great surprise, the *trans*-aziridine **8** was then isolated as the sole product.[21] Yields and stereochemistry of the aziridine isolated were thus equivalent starting from either *Z* or *E* substrates demonstrating thereby a stereo-convergent formation of the aziridine at rt (Scheme 3 vs Scheme 2). This result clearly ruled out an aziridination/opening mechanism for the *Z*-substrates under our standard conditions (100°C).



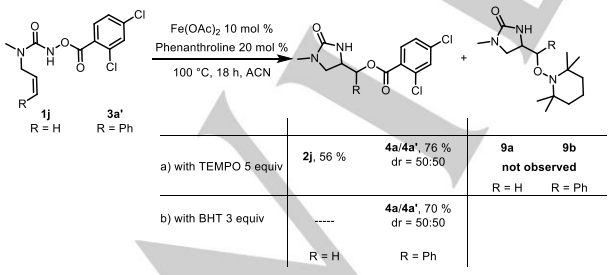
Scheme 3. Aziridine formation from substrate **3d'**.

Interestingly, the treatment of the *Z*-styryl derivative **3b'** with five equivalents of 2,4-dichlorobenzoic acid as external nucleophile under the same reaction conditions gave a 90:10 mixture of the oxyaminated products **4a/4a'** and **4b/4b'** with 65 % yield and 45:55 dr for **4a/4a'** (Scheme 4). Analogous results were obtained under standard conditions on substrate **3a'** (see Table 5, entry 1 vs Scheme 4) which demonstrated a non-stereoselective outer sphere addition of the carboxylic acid for this substrate.



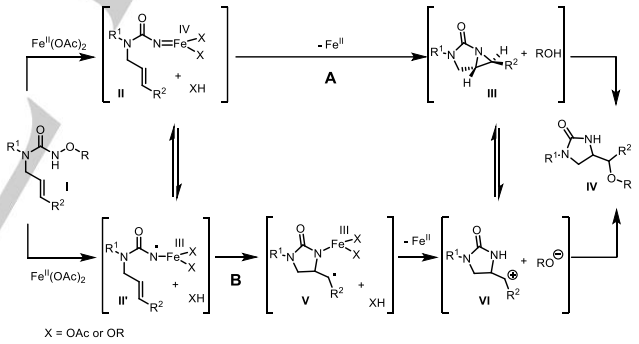
Scheme 4. Competitive study on compound **3b'** with 2,4-dichlorobenzoic acid as external nucleophile.

All these observations led us to conclude that the mechanistic pathway is likely to be substrate dependent and influenced by the configuration of the double bond, the temperature, as well as by conformational and electronic effects. Therefore, the aziridination/opening route cannot be considered as the only path leading to the oxyamination products. Based on the mechanism proposed by Hao Xu, carbo-radical species could be involved. Previous studies have shown that nitrenoid intermediates can be generated by cleavage of the N-O bond from hydroxylamine derivatives[22] and that nitrene singlet and triplet species are close in energy and could interconvert rapidly depending on the nature of the substrate.[23] This feature could explain the difference of dr from one product to another. To investigate the formation of radical species as potential intermediates, we next introduced a radical trap and a radical inhibitor in the reaction mixture (Scheme 5). Addition of 5 equivalents of TEMPO on compound **1j** induced a decrease in the yield and compound **2j** was isolated in 56 %. However the formation of compound **9a** was not observed. Under the same conditions compound **3a'** led to **4a/4a'** with identical yield than in standard conditions and with a slight difference of dr (50:50 vs 40:60) but without observation of product **9b** (Scheme 5-a). Compound **3a'** was also subjected to the reaction conditions in presence of an excess of BHT giving products **4a/4a'** in 70 % yield and 50:50 dr (Scheme 5-b). Thus, negligible differences were obtained by addition of radical scavengers on **1j** or **3a'** compared with standard conditions, which led us to conclude that a long-lived radical species was not involved in this mechanism.



Scheme 5. Study of radical inhibitors addition

Having ruled out this hypothesis, the formation of a different reactive species needed to be envisaged to explain the formation of the functionalized imidazolidinone products in a non-stereoselective manner. The scope of the reaction revealed a rather different behavior for electron-deficient and electron-rich styryl substrates (Table 3). While the nitro- and chloro-phenyl compounds **3e,f** led to high dr, the methyl and methoxy analogues **3g-j** constantly provided moderate dr, with opposite isomer as major product for the methoxy derivatives (Table 3). Considering the loss of diastereoselectivity observed with the substrates bearing electron-donating styryl groups, a carbocationic intermediate was considered as plausible reactive species for the transformation. Based on our results we therefore propose the following mechanism.[24] Insertion of the iron catalyst into N-O bond of substrate **I** generates both a singlet nitrene iron(IV) **II** and a triplet nitrene iron(III) species **II'** close in energy or in equilibrium.[23, 25] Two competitive pathways can then occur (Scheme 6). Electron-neutral and electron-poor *E*-substrates react according to pathway **A**. The nitrene species evolves through a concerted process affording the *trans*-aziridine **III**, which gives through a S_N2 type ring opening the *anti*-product **IV**. In pathway **B**, the iron nitrene **II'** generates a short-lived carbo-radical species **V**, which is rapidly oxidized to the corresponding carbocationic intermediate **VI**. Final product **IV** is then formed by direct non-stereoselective nucleophilic addition onto the carbocation or via the *trans*-aziridine derivative **III**. Pathway **B** is preferentially followed with *Z*-alkenes for which steric hindrance disfavors the direct concerted aziridination and electron-rich substrates that stabilize the intermediate carbocation.



Scheme 6. Postulated mechanism.

Conclusions

To conclude, we developed sustainable conditions for the atom-economical preparation of 4-methylene-oxy-functionalized imidazolidin-2-one derivatives. Moderate to good yields with good to excellent diastereoselectivities were obtained. This process is efficient for mono- di- and tri-substituted alkenes, which represent an important breakthrough in comparison with other oxyamination processes using palladium as metal catalyst. Several control experiments were performed to propose competing mechanistic pathways involving both a fused aziridine and a carbocation as potential intermediates. Studies are currently ongoing to extend the scope of this reaction to the formation of bigger ring size heterocycles and to better clarify the mechanism.

Experimental Section

Typical procedure for iron oxyamination reaction:

In a sealed tube, 10 mol % of $Fe(OAc)_2$ and 20 mol % of phenanthroline were placed in ACN (C = 0.1 mol/L) under argon. The solution was stirred 30 min at room temperature and 1.0 equiv of the desired alkene substrate was added. The solution was stirred 18 h at 100 °C. The reaction was then quenched with a saturated aqueous solution of $NaHCO_3$. The aqueous layer was extracted with DCM (3 times) and the combined organic phases were then dried with $MgSO_4$, filtrated and the solvent was removed under vacuum. The crude residue was purified by silica gel flash chromatography using pentane/EtOAc as eluent (9:1 to 0:10).

Acknowledgements

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Keywords: iron • alkenes • oxyamination • imidazolidinone • aziridine

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[20] See Supporting Information for details. (**4a** CCDC1539353; **4i** CCDC1539351; **4k** CCDC1539350; **4l** CCDC1539352; **4s** CCDC1539354)

[21] A complete conversion of the alkene to the aziridine was observed by ^{1}H NMR. Instability of the aziridine towards column chromatography rationalized the limited isolated yield.

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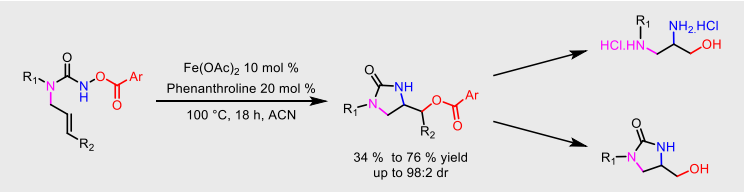

The iron-catalyzed intramolecular oxyamination of allyl-benzoyloxy urea derivatives is described. This atom-economical process is using hydroxylamine derivatives without addition of any external oxidant, affording functionalized imidazolidin-2-one products as potential 1,2,3-diaminoalcohol precursors. Mechanistic studies highlighted the corresponding fused aziridine as a viable intermediate to explain this transformation.

Anne-Doriane Manick, Sidonie Aubert, Boubacar Yalcouye, Thierry Prangé, Farouk Berhal and Guillaume Prestat**

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