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Iron(II)-catalyzed intermolecular aziridination of alkenes employing hydroxylamine derivatives as clean nitrene sources

Georgina Kirby,^a Maxime R. Vitale,^b Laurence Grimaud,^b Guillaume Prestat,^{a*} Farouk Berhal^{a*}

The iron-catalyzed intermolecular aziridination of alkenes with hydroxylamine derivatives is described. Using simple iron(II) sources and readily available ligands, the formal (2+1) cycloaddition process proved to be efficient on both styrenes and aliphatic alkenes, providing access to a wide range of aziridines. In these particularly sustainable reaction conditions, yields up to 89 % could be obtained, with a catalyst loading which could be lowered to 5 mol % when the reaction was performed on large scale. Preliminary mechanistic studies suggest that both concerted and stepwise pathways are operating in this transformation.

Introduction

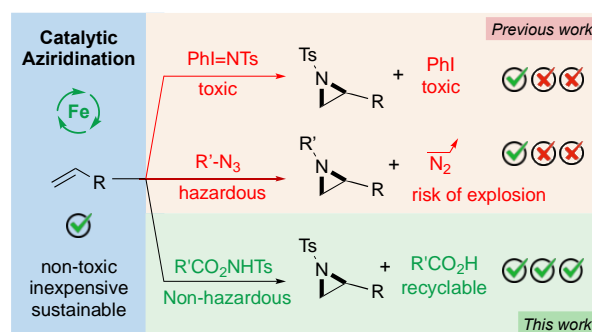
Aziridines are particularly important *N*-heterocycles. Not only can they be found in many pharmaceutical molecules or biologically relevant natural products, but they are also direct precursors of synthetically useful compounds such as amino alcohols and diamine derivatives. Consequently, different strategies have been developed to access this motif,¹ among which the formal insertion of a nitrenoid (i.e. nitrene source) onto an alkene is certainly the most elegant and efficient approach. In this latter research area, metal catalysis plays a pivotal role since it allows for the stabilization of highly reactive nitrenes through the formation of the corresponding metal-nitrenes. As of now, different catalytic systems have been developed, mostly based on rhodium,² ruthenium,³ and copper complexes.^{4,5} Despite their good reaction efficiency, these methods pose sustainability issues that ultimately question their viability. Indeed, such metal sources are rare and/or toxic. Besides, these methods rely on fairly hazardous nitrene precursors, including *ex situ* or *in situ* generated iminoiodinanes (e.g. $\text{PhI}=\text{NTs}$)⁶ and azide reagents, where the former liberates stoichiometric amounts of toxic byproducts (e.g. iodobenzene) and the latter has significant risks of explosion.

To circumvent this issue, Lebel,⁷ followed by Ess, Kurti, Falck and Jat, introduced the use of hydroxylamine derivatives in aziridination processes.⁸ Some of the many advantages offered by this original class of nitrene precursors⁹ include their straightforward and cost-effective preparation from hydroxylamine, and their propensity to form metal-nitrenes without the need for external oxidants. Yet, their use is still limited to rhodium- and copper-catalyzed processes, such that more environmentally benign catalytic systems would be welcomed.

Iron, in addition to the fact that it is cheap, has many advantages over other transition metals. This metal is largely abundant in the Earth's crust and displays very low toxicity. For these reasons, our research group has focused on the

development of original iron-catalyzed sustainable methods based on the use of valuable hydroxylamine derivatives.¹⁰ In the course of our studies, we reported an intramolecular iron-catalyzed oxyamination of alkenes,^{10a} for which the identification of a fused aziridine unveiled the involvement of a transient intramolecular aziridination step. Stimulated by this result, we decided to explore if a more challenging intermolecular version could be achieved. Worthy of note, since the pioneering work of Mansuy *et al.*, there has been some development for iron-catalyzed aziridination of alkenes.^{11,12} However, it remains limited to the use of hazardous $\text{PhI}=\text{NTs}$ or azides and, for the vast majority of reported cases, on the use of specific heme-type iron complexes. Hence, the development of more efficient and sustainable iron-catalytic systems and non-toxic reaction conditions are still needed.¹³ It prompts us to disclose here the first intermolecular aziridination of alkenes based on readily available iron-sources, simple ligands, and

SCHEME 1 Nitrogen sources for iron-catalyzed aziridination.



comparatively benign hydroxylamine derivatives (Scheme 1).

Results and discussion

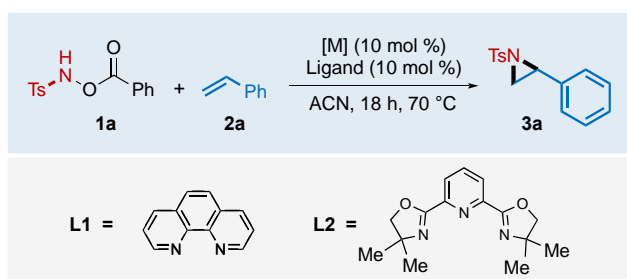
At the onset of this study, the hydroxylamine derivative **1a** (TsNHOBz) was used as a model substrate for the optimization

of the reaction conditions allowing for the aziridination of styrene **2a** (2.5 eq). Mixing these reactants with iron(II) acetate (10 mol %) in acetonitrile (ACN) for 18 h at 70 °C, afforded the desired aziridine **3a** in an encouraging 25 % yield (Table 1, entry 1). The addition of phenanthroline (20 mol %) **L1** as a ligand, significantly improved the yield to 47 % (Table 1, entry 2), then the tridentate Pybox **L2** ligand increased it further to 80 % (Table 1, entry 3).¹⁴ The nature of the iron source was next evaluated. Keeping ligand **L2**, iron(II) triflate led to a dramatic decrease of reaction efficiency (23 % yield, Table 1, entry 4), whereas iron(II) chloride and iron(III) bromide, despite showing some catalytic activity, only gave moderate yields (47 % and 50 %, respectively, Table 1, entries 5 and 6). Finally, a slightly better yield was obtained when the pivalic derivative **1b** (TsNHOPiv) was used in lieu of **1a** (83 % yield, Table 1, entry 7 vs entry 3).¹⁵

To ensure that iron is the catalyst of the process, control experiments were conducted. No aziridine was formed in the absence of the iron salt (Table 1, entry 8), while copper sources such as copper(I) iodide and copper(II) acetate only provided trace amounts of **3a** (Table 1, entries 9 and 10). These

studied for a wider range of styrene derivatives (Scheme 2). Switching from a phenyl aromatic ring to a naphthyl had a negligible impact on the reaction course, the aziridine **3b** being isolated in a good 77 % yield (Scheme 2). The effect of electron-withdrawing groups by inductive effect was investigated next. Halogen substituted styrenes reacted smoothly, even when more sterically demanding ortho-substituted derivatives were employed. Indeed, 2-, 3- and 4-chlorophenyl aziridines **3c**, **3d** and **3e** were isolated with excellent 87 %, 85 % and 87 % yields, respectively. In the same vein, the 4-fluorophenyl aziridine **3f** was efficiently formed (84 %), while the 4-bromophenyl aziridine **3g** was isolated in a slightly diminished yield (77 %). The phenyl aziridines **3h** and **3i** bearing the electron-withdrawing 4-CF₃ and 4-OAc groups were also satisfactorily obtained (70 % and 78 %, respectively). However, a more electron-withdrawing nitro group, for which a mesomeric effect particularly affects positions 2 and 4, induced a significantly lower yield (**3j**, 59 %). Potentially coordinating substituents were found to limit the catalytic activity, as shown by the fact

TABLE 1 Optimization of the reaction conditions^a

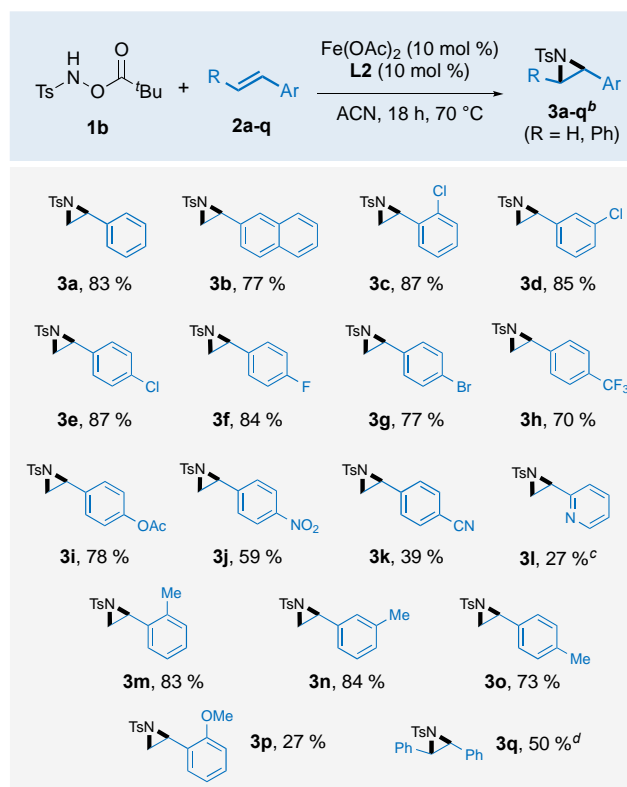


Entry	[M] (10 mol %)	Ligand (10 mol %)	Yield ^b
1	Fe(OAc) ₂	---	25 %
2	Fe(OAc) ₂	L1 (20 mol %)	47 %
3	Fe(OAc) ₂	L2	80 %
4	Fe(OTf) ₂	L2	23 %
5	FeCl ₂	L2	47 %
6	FeBr ₃	L2	50 %
7 ^c	Fe(OAc) ₂	L2	83 %
8	---	---	0 %
9	CuI	L2	trace
10	Cu(OAc) ₂	L2	trace

^a Reaction conditions: In a sealed tube, **1a** (0.27 mmol, 1 eq), styrene (0.68 mmol, 2.5 eq), [M] (0.027 mmol, 10 mol %) and ligand (0.027 mmol, 10 mol %) were mixed with ACN (C = 0.2 M) before stirring at 70 °C for 18 h. ^b Isolated yields. ^c TsNHOPiv **1b** was used in lieu of **1a**.

experiments clearly demonstrate that this aziridination process does rely on the action of a catalytically active iron complex and is not the result of contamination by residual copper salts. With these optimized reaction conditions in hand (Table 1, entry 7), the scope and limitations of this transformation were then

SCHEME 2 Scope and limitations for styrenes.^a



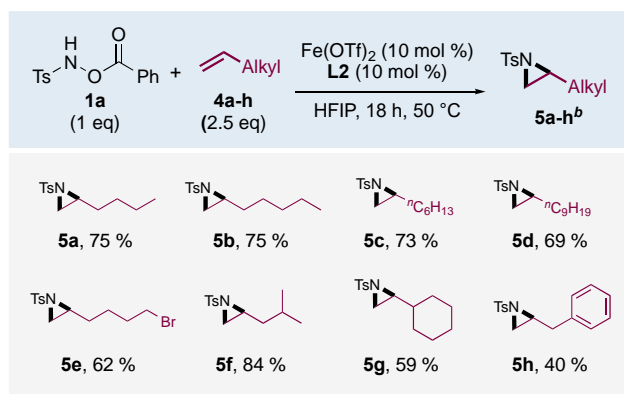
^a Reaction conditions: In a sealed tube, **1b** (0.27 mmol, 1 eq), the proper styrene (0.68 mmol, 2.5 eq), Fe(OAc)₂ (0.027 mmol, 10 mol %) and **L2** (0.027 mmol, 10 mol %) were mixed with ACN (C = 0.2 M) before stirring at 70 °C for 18 h. ^b Isolated yields. ^c Fe(OTf)₂ (10 mol %) was used instead of Fe(OAc)₂. ^d TsNHOBz **1a**, Fe(OAc)₂ (5 mol %) and **L1** (10 mol %) were employed.

that 4-cyanophenyl and 2-pyridine aziridines **3k** and **3l** were isolated in modest yields (39 % and 27 %, respectively). The influence of electron-donating functional groups was then surveyed. The ortho-methylphenyl aziridine **3m** was isolated in 83 % yield, demonstrating further that this method is amenable

to the use of hindered styrene derivatives. Meta- and para-methylphenyl aziridines **3n** and **3o** were also obtained with good yields (84 % and 73 %, respectively). Conversely, the highly electron-donating methoxy group was found to be detrimental for this process, in which case the aziridine **3p** was formed in a low 27 % yield. Finally, by slightly adapting the reaction conditions, (*E*)-stilbene led to aziridine **3q** in 50 % yield, with complete diastereoselectivity in favor of the *trans* isomer.

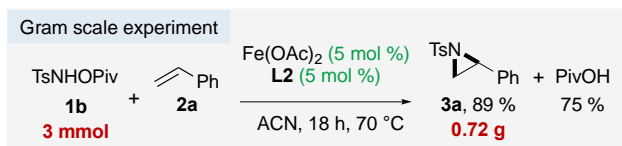
Afterwards, the efficiency of this catalytic aziridination method was assessed on more challenging non-activated aliphatic alkenes. Indeed, for those compounds allylic C-H amination is a competing process from the desired aziridination.¹⁶ While our previous conditions proved to be unsuccessful with hexene (**4a**), simply replacing iron(II) acetate with iron(II) triflate and switching the solvent from ACN to HFIP allowed for good catalytic activity to be regained.¹⁵ In these conditions, the targeted butyl-substituted aziridine **5a** was obtained in a satisfactory 75 % yield, which prompted us to evaluate other aliphatic alkenes (Scheme 3). The length of the alkyl chain showed a negligible impact on reactivity. Indeed, the *n*-pentyl, *n*-hexyl and *n*-nonyl substituted aziridines **5b**, **5c** and **5d** were isolated in good yields ranging from 69 to 75 %. Of note, the reaction was also amenable to the use of an aliphatic alkene possessing a bromine atom in terminal position (e.g. **4e**), which opens the door for further functional group manipulation with **5e** which was isolated in 62 % yield. The ramified isobutyl aziridine **5f** was obtained with an excellent 84 % yield, while the more sterically demanding cyclohexyl group only slightly impeded the formation of **5g** (59 % yield). Finally, the allyl benzene substrate was found to produce the corresponding aziridine **5h** in a moderate 40 % yield.

SCHEME 3 Scope and limitations for aliphatic alkenes.^a



^a Reaction conditions: **1a** (0.2 mmol, 1 eq), alkene (0.5 mmol, 2.5 eq), Fe(OTf)₂ (0.02 mmol, 10 mol %) and ligand **L2** (0.02 mmol, 10 mol %) were mixed in HFIP (C = 0.2 M) before stirring at 50 °C for 18 h. ^b Isolated yields.

SCHEME 4 Scale-up of the aziridination process.^a

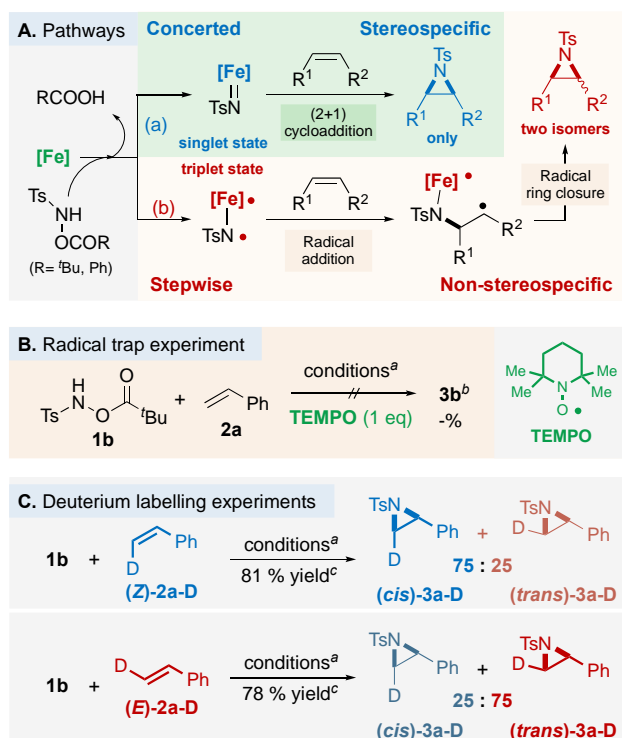


^a Reaction conditions: In a sealed tube, **1b** (3.0 mmol, 1 eq), styrene (7.4 mmol, 2.5 eq), Fe(OAc)₂ (0.15 mmol, 5 mol %) and **L2** (0.15 mmol, 5 mol %) were mixed in ACN (C = 0.2 M) before stirring at 70 °C for 18 h.

0.72 g of the desired aziridine **3a**, which corresponds to an excellent yield of 89 % (Scheme 4). Moreover, it should be noted that in such a high scale only 5 mol % of catalyst and ligand could be used and that 75 % of pivalic acid could also be easily retrieved after the reaction. It reinforces the synthetic potential of this green aziridination method, since it can operate with a fairly low iron catalyst loading and proceeds with notable atom-economy.

Finally, we tried to elucidate which kind of mechanism might be involved in such iron-catalyzed aziridination process. By direct analogy to what is described for related metal catalyzed processes,¹⁷ we propose that the *in situ* generated iron catalyst ([Fe], Scheme 5) leads to an iron-nitrene intermediate upon reaction with the hydroxylamine derivative (via the release of an equivalent amount of carboxylic acid). It remains unclear to

SCHEME 5 Mechanistic considerations and preliminary mechanistic studies.



^a Reaction conditions: In a sealed tube, **1b** (0.27 mmol, 1 eq), the adequate alkene (0.68 mmol, 2.5 eq), Fe(OAc)₂ (0.027 mmol, 10 mol %) and **L2** (0.027 mmol, 10 mol %) were mixed in ACN (C = 0.2 M) before stirring at 70 °C for 18 h. ^b No aziridination – degradation of **1b** only. ^c Isolated yields

us whether an iron(II)-nitrene or its iron(III) counterpart would be the actual catalytic species, because our optimization studies

showed that iron(III) bromide also displayed some catalytic activity. Nevertheless, because metal-nitrenes typically exist in two different spin states, we had to consider two possible reactions pathways for this transformation (Scheme 5, A). On one hand, if the metal-nitrene predominantly exists under its singlet state, a concerted (2+1) cycloaddition should take place, which would lead to a stereospecific process (Scheme 5, A-(a)). On the other hand, if the iron-nitrene complex is in its triplet state (as previously proposed by Mansuy *et al.* with iron(III)-porphyrin complexes),^{11b} a mechanism in which a radical addition followed by a radical-based ring closure would occur (Scheme 5, A-(b)). In this case, due to the stepwise nature of the process, poor to no stereoselectivity should be observed. To get more insights, we performed the model reaction of **1b** with **2a** in the presence of TEMPO to prove or invalidate the stepwise radical pathway. This additive, which is typically employed for the trapping of radical intermediates, completely inhibited the reaction such that no aziridine product was formed (Scheme 5, B). This experiment tended to support that a radical pathway was operating. However, because we could neither isolate any TEMPO adduct nor identify some by-products, we could not rule out the concerted (2+1) cycloaddition route. For this reason, we decided to perform some deuterium labelling experiments with the idea that the stereochemical outcome would be more informative (Scheme 5, C). **(Z)-2a-D** reacted with **1b** to provide the *cis*-aziridine **3a-D** as the major isomer (75 %) in a mixture of the diastereomeric *trans*-aziridine **3a-D** (25 %). In the same vein, **(E)-2a-D** led to 75 % of the *trans*-isomer in a mixture with 25 % of the *cis*-isomer. In these two cases, we could observe a partial transfer of the stereochemical information, meaning that the concerted pathway is most probably the predominant reaction mechanism. However, it appears that the stepwise pathway operates concurrently, which would, according to a non-stereospecific radical process, account for the formation of the minor diastereomers. These results are reminiscent of the recent work of Maiti, Maldivi, Latour *et al.*¹⁸ and suggest that the iron-nitrene species which is generated coexists on both the singlet and the triplet spin state and, accordingly, that the difference of energy between both remains low. Further mechanistic studies will be conducted.

Conclusions

In conclusion, we have developed a robust iron-catalyzed process in which a simple iron(II) salt and readily available ligands promote the green aziridination of alkenes. In opposition to currently available methods, hazardous reagents and reaction conditions can be avoided via the implementation of hydroxylamine derivatives as nitrene sources. This sustainable method could be applied to various styrenes and aliphatic alkenes, leading to the corresponding aziridines in good to excellent yields. The reaction could be easily scaled-up even with a catalyst loading as low as 5 mol % which does not impact the efficiency of the aziridination. The released carboxylic acid could even be recovered, which further reinforces the sustainable and atom-economical character of this method. Preliminary mechanistic studies suggest that this

iron-catalyzed aziridination process involves the formation of an iron-nitrene complex, which competitively reacts with the alkene according to a concerted (2+1) cycloaddition process or a stepwise radical mechanism. Further mechanistic studies are ongoing in our lab and will be reported in due course.

Conflicts of interest

There are no conflicts to declare.

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