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Ring Expansion of Donor–Acceptor Cyclopropane via Substituent Controlled Selective *N*-Transfer of Oxaziridine: Synthetic and Mechanistic Insights

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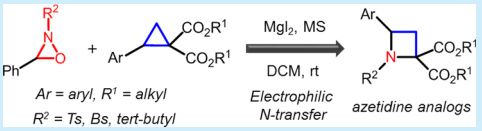
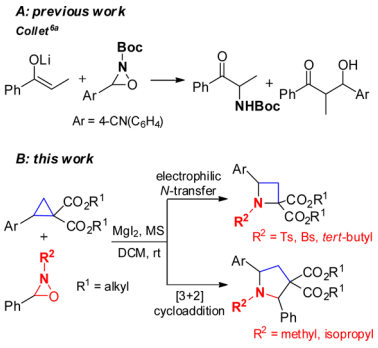
Supporting Information

ABSTRACT: A distinctive *N*-substituent controlled electrophilic *N*-transfer of oxaziridines with donor–acceptor cyclopropanes in the presence of MgI_2 is reported. Contrary to earlier reports, the oxaziridine having bulkier *N*-substituents can also give *N*-transferred product instead of the *O*-transferred one. Interestingly, the oxaziridines having α-H containing *N*-substituents lead to the pyrrolidine derivatives through [3 + 2] cycloaddition. A mechanistic reasoning for this divergent reactivity is depicted by density functional theory calculations and validated through energy decomposition analysis.



Oxaziridines, the members of the subcategory composed of oxygen–nitrogen heterocycles, were first synthesized by Emmons in 1957.[1] The presence of two electronegative atoms at adjacent positions in a three-membered strained ring makes its reactivity quite fascinating. In addition, oxaziridines are easy to prepare and have unusual physical properties.[2] As a result, the chemistry of oxaziridines has been largely exploited over the past few decades. Various distinctive reactivities of oxaziridines, like transition-metal-promoted rearrangements,[1,3] cycloadditions,[4] oxyaminations,[5] etc., are well established where oxaziridine acts as an *O*-transfer agent. However, their roles as *N*-transfer agents are yet to be established. In this context, the initial work by Collet and co-workers indicated the ability of the *N*-alkoxycarbonyl-oxaziridines to deliver the *N*-alkoxycarbonyl fragment to various nucleophiles.[6] Nevertheless, the competitive oxidation and aldol reaction hampered the amination process, resulting in low yield of the aminated product (Scheme 1A). It is necessary to mention here that the substituents on the nitrogen atom of oxaziridines play a significant role in atom transfer reactions.[7−10] Perceiving the diversity of oxaziridine reactivity developed to date, we are interested in further exploring the role of *N*-substituent over oxaziridine reactivity. We paid particular attention to establishing the *N*-transfer ability of oxaziridines to the carbon nucleophile, which can give direct access to different valuable acyclic or cyclic *N*-containing molecular entities. Our work imparts a novel *N*-transfer reactivity of oxaziridine to donor–acceptor cyclopropane[11,12] (DAC) for the synthesis of azetidine derivatives. MgI_2 catalyzes this transformation with good yield (Scheme 1B). Contrary to earlier investigations, we established the fact that bulky substituents on nitrogen of oxaziridine, such as *N*-sulfonyl and *N*-*tert*-butyl, can also be transferred to give *N*-transferred adduct. Interestingly, the oxaziridines having α-hydrogen containing an *N*-substituent like *N*-methyl, *N*-isopropyl, etc. led to [3 + 2] cycloaddition instead of *N*-transfer under same reaction conditions (Scheme 1B). A mechanistic study for this divergent reactivity is portrayed by density functional theory calculations and validated through energy decomposition analysis.

Scheme 1. Reactivity of Oxaziridine toward *N*-Transfer



The present investigation was initiated to establish the *N*-transfer process using oxaziridines to DACs (Table 1). We first examined the reaction without employing any catalyst at reflux condition in DCE but observed that both the reactants remained unreacted after a long reaction time (Table 1, entry 1). In the methodologies developed in our group to date concerning the utility of DACs,[13] MgI_2 played the role of active catalyst. With that hope, we took MgI_2 as a catalyst for the said transformation. Gratifyingly, we got the desired aminated product with 46% yield using 10 mol % of MgI_2 (Table 1, entry 2). To improve the product yield, we further optimized the other reaction parameters like the amount of catalyst and solvent (Table 1, entries 3–5, and for solvent variation see the Supporting Information, Table 1). We observed that 20 mol %

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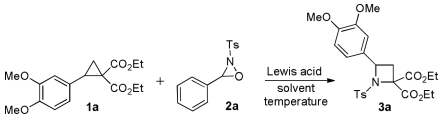
Table 1. Optimization of Reaction Conditions for Electrophilic *N*-Transfer[a]



entry	Lewis acid	LA (mol %)	temp (°C)	solvent[b]	yield (%)[c]
1			80	DCE	nr[d]
2	MgI_2	10	30	DCM	46
3	MgI_2	20	30	DCM	75
4	MgI_2	40	30	DCM	75
5	MgI_2	100	30	DCM	cm[e]
6	$Mg(OTf)_2$	20	30	DCM	nr[d]
7	$MgBr_2$	20	30	DCM	8
8	$Sc(OTf)_3$	20	30	DCM	nr[d]
9	$InCl_3$	20	30	DCM	nr[d]
10	$Yb(OTf)_3$	20	30	DCM	nr[d]
11	$CuCl_2$	20	30	DCM	nr[d]
12	$TiCl_4$	20	30	DCM	cm[e]
13	$FeCl_2$	20	30	DCM	nr[d]
14	ZnI_2	20	30	DCM	nr[d]

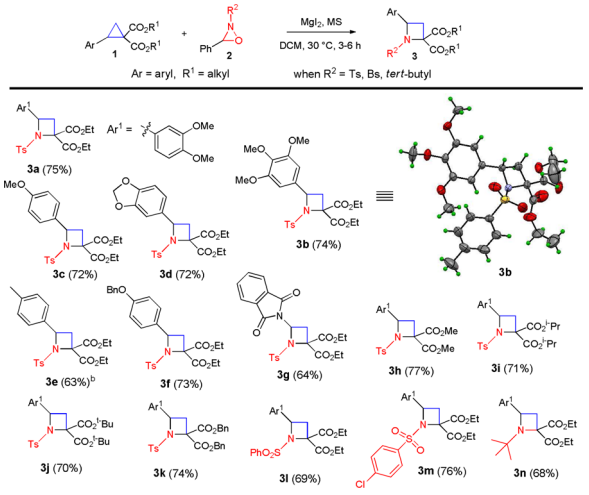
[a]Reactions were carried out with 1 equiv of **1a** and 1.5 equiv of **2a** in the presence of molecular sieves (4 Å). [b]DCM = dichloromethane. DCE = dichloroethane. [c]Isolated yield. [d]nr = no reaction. [e]cm = complex mixture.

of MgI_2 gave the best yield in DCM (Table 1, entry 3). Excess oxaziridine (1.5 equiv) was used in every case as oxaziridine itself rearranges to produce the corresponding aldehyde and imine in the presence of Lewis acid. Among the other magnesium containing Lewis acids, $MgBr_2$ gave the aminated product in trace amount (Table 1, entry 7). When we used $TiCl_4$, both the substrates readily decomposed to give a complex mixture (Table 1, entry 12). Other commercially available Lewis acids, like $Sc(OTf)_3$, $InCl_3$, $Yb(OTf)_3$, $CuCl_2$, $FeCl_2$, and ZnI_2, failed to catalyze the transformation (Table 1, entries 8−11 and 13−14).

Employing the optimized reaction conditions, (Table 1, entry 3) the scope of this transformation was assessed with various DACs and oxaziridines (Scheme 2). To our delight, DACs bearing electron donating substituents gave the best yield of the aminated compound (Scheme 2, **3a**−**3d** and **3f**). As we moved to a relatively less activated one, like *p*-tolyl-substituted DAC, it required high temperature and longer time to give the product (Scheme 2, **3e**). However, phenyl-substituted DAC remained unreacted at the same reaction conditions (like **3e**) after 8 h. A range of ester-substituted DACs worked smoothly affording the desired aminated products in good yield (Scheme 2, **3h**−**3k**). The DAC bearing heteroatom containing donor substituents, like *N*-phthalimide-substituted DAC, also gave the *N*-transferred adduct (Scheme 2, **3g**). To examine the feasibility and control over the said transformation due to changes in *N*-substituents of oxaziridines, we carried out the amination reaction with different *N*-sulfonyl and *N*-alkyl oxaziridines. As expected we obtained the aminated adduct with *N*-benzenesulfonyl-, *N*-(4-chlorophenyl)sulfonyl-, and *N*-*tert*-butyl-substituted oxaziridines in good yield (Scheme 2, **3l**−**3n**). In all the cases selectively *N*-transferred adduct was formed, *O*-transferred adduct was not observed.

Excitingly, the other *N*-alkyl-substituted oxaziridines with *α*-hydrogen like *N*-methyl, *N*-isopropyl, etc. produced pyrrolidine derivatives (**4a**−**4f**) by [3 + 2] cycloaddition reactions between

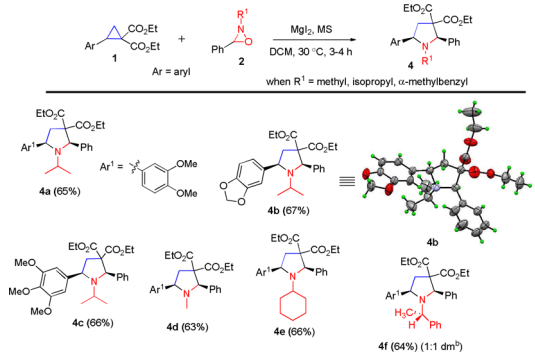
Scheme 2. Scope of *N*-Transfer[a]



[a]Unless otherwise specified, all reactions were carried out in DCM at 30 °C with 1 equiv of **1** and 1.5 equiv of **2** in the presence of MgI_2 (20 mol %) and molecular sieves (4 Å). [b]Reaction was carried out at 40 °C in DCM while the other conditions remained the same.

DACs and *in situ* generated imine instead of giving *N*-transferred adduct (Scheme 3; for details see the Supporting

Scheme 3. Scope of [3 + 2] Cycloaddition[a]



[a]Reactions were carried out with 1 equiv of **1** and **2** in the presence of MgI_2 (20 mol %) and molecular sieves (4 Å). [b]dm = diastereomeric mixture.

Information). The structure of **3b** and **4b** was confirmed unambiguously using single crystal X-ray analysis (Scheme 2 and Scheme 3 respectively; also see the Supporting Information).[14]

A plausible mechanism is proposed to describe the electrophilic *N*-transfer (Figure 1a) and verified through density functional theory based calculations at the wB97XD/def2-SVP level.[15] In the presence of MgI_2, DAC ($\mathbf{A_1}$) undergoes nucleophilic ring opening to give the reactive open chain intermediate $\mathbf{A_3}$ (see Figure S1). $\mathbf{A_3}$ can act as a nucleophile to attack the *N*-atom of the activated oxaziridine $^{O}\mathbf{B_2}$ (oxaziridine ($\mathbf{B_1}$) activated by MgI_2) leading to the formation of intermediate $^{O}\mathbf{C_2}$. The intermediate $^{O}\mathbf{C_2}$ undergoes structural rearrangements (via **TS-**$^{O}\mathbf{C_{2-3}}$, $^{O}\mathbf{C_3}$, **TS-**$^{O}\mathbf{C_{3-4}}$) and finally follows S_N2 ring closure to give the *N*-transferred adduct. Two successive S_N2 pathways are followed during the whole process; the first one is S_N2 ring opening of DAC, and the second one is S_N2 ring closure. This was experimentally

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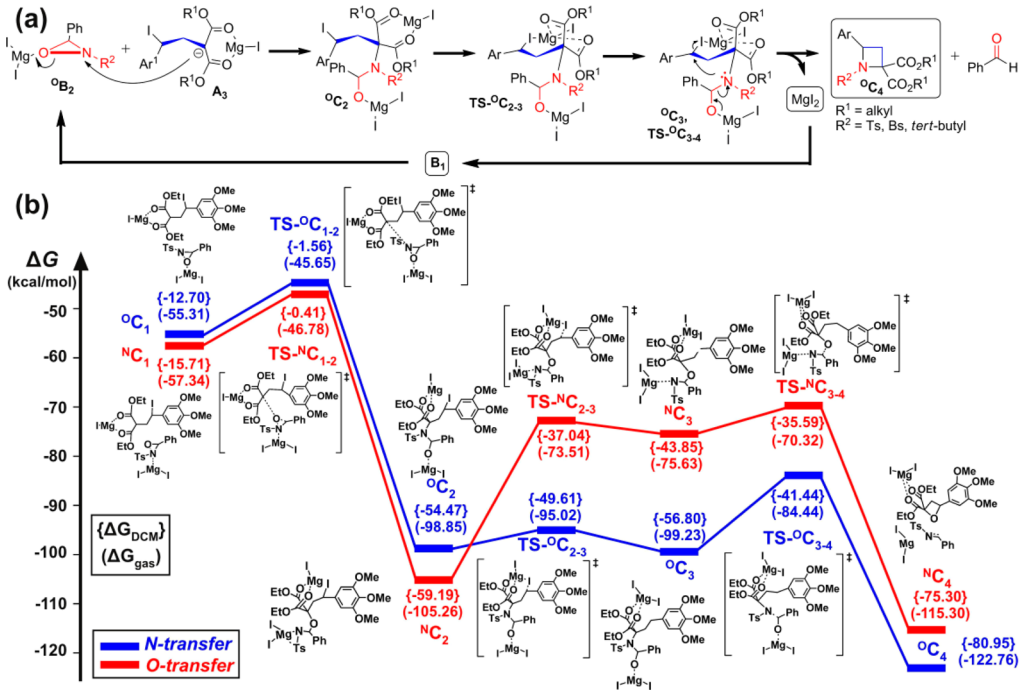

Figure 1. (a) Plausible mechanism of electrophilic *N*-transfer. (b) Reaction profile for the competing *N*-transfer and *O*-transfer pathways.

proved when the said transformation was performed with enantiomerically pure (*S*)-DAC where (*S*)-enantiomer of the azetidine derivative was obtained in excess (see the Supporting Information).

As a catalyst, MgI_2 can coordinate with oxaziridine ($\mathbf{B_1}$) through either *N*-atom ($^{N}\mathbf{B_2}$) or *O*-atom ($^{O}\mathbf{B_2}$) (see Figure S2), but not with the electropositive C1 atom (N1, −0.41; O1, −0.41; C1, 0.29 |e|). During the reaction, $\mathbf{A_3}$ and $\mathbf{B_2}$ will generate dispersion complexes, viz., $^{O}\mathbf{C_1}$ (complex of $\mathbf{A_3}$ and $^{O}\mathbf{B_2}$) and $^{N}\mathbf{C_1}$ (complex of $\mathbf{A_3}$ and $^{N}\mathbf{B_2}$) (see Figure 1b). Between two dispersion complexes, $^{N}\mathbf{C_1}$ is slightly more stable than $^{O}\mathbf{C_1}$, which indicates the more reactive nature of $^{O}\mathbf{C_1}$. It may be noted that the $^{O}\mathbf{C_1}$ and $^{N}\mathbf{C_1}$ will eventually result in the *N*-transfer and *O*-transfer products, respectively. The C3 atom is nucleophilic (−0.39 |e|) in both $^{O}\mathbf{C_1}$ and $^{N}\mathbf{C_1}$. For $^{O}\mathbf{C_1}$, in the following step a nucleophilic attack of C3 occurs to the *N*-atom of oxaziridine, which results in the breaking of the N−O bond and the formation of a new C−N bond. The C−N bond distance changes from 3.184 Å (in $^{O}\mathbf{C_1}$) to 2.553 Å in the transition state (TS) (**TS-**$^{O}\mathbf{C_{1-2}}$, $\Delta^{\ddagger}G_{1-2}$ = 9.66 kcal/mol) and becomes 1.447 Å in the corresponding intermediate ($^{O}\mathbf{C_2}$). On the other hand, for $^{N}\mathbf{C_1}$ the C3 attacks the *O*-atom and forms a new C−O bond and breaks the N−O bond in $^{N}\mathbf{C_2}$ through **TS-**$^{N}\mathbf{C_{1-2}}$ ($\Delta^{\ddagger}G_{1-2}$ = 10.56 kcal/mol).

The subsequent step has three possible pathways. The first one is a highly concerted mechanism where removal of iodine and side products (benzaldehyde and benzylidenimine) and the formation of 4-membered ring take place simultaneously. The second possibility includes the initial removal of side products followed by a 4-membered ring formation through iodine removal. Our attempts to locate the TS for prior removal of side product remain unsuccessful as the energy of the fragments increases monotonically in the relaxed surface scan. The third possibility may allow shifting of the iodine atom from C1 to reunite with MgI, leaving a positive charge on the C1 atom and thereby facilitating the nucleophilic attack of N1 atom (in $^{O}\mathbf{C_2}$) or the O1 atom (in $^{N}\mathbf{C_2}$) to the C1 atom. The relaxed surface scan suggests the initial removal of iodine and regeneration of MgI_2, followed by formation of the 4-membered rings and removal of the side products which supports the third possibility. In $^{O}\mathbf{C_2}$ the natural charge on the C1 atom is −0.29 |e|, which changes to −0.02 |e| in TS (**TS-**$^{O}\mathbf{C_{2-3}}$) corresponding to the iodine removal and gradually becomes positive (0.08 |e|) in the corresponding intermediate, $^{O}\mathbf{C_3}$. This step has a small activation barrier ($\Delta^{\ddagger}G_{2-3}$ = 3.84 kcal/mol), and the reaction energy is slightly exergonic ($\Delta_r G_{2-3}$ = −0.38 kcal/mol). Like the *O*-coordinated system, in the *N*-coordinated system also the C1 atom gradually becomes positively charged (−0.37 in $^{N}\mathbf{C_2}$ to 0.02 in **TS-**$^{N}\mathbf{C_{2-3}}$ to 0.06 |e| in $^{N}\mathbf{C_3}$). Interestingly, this step has a high activation barrier ($\Delta^{\ddagger}G_{2-3}$ = 31.76 kcal/mol) and the reaction energy is highly endergonic ($\Delta_r G_{2-3}$ = 29.63 kcal/mol). The huge difference between the two activation barriers for the iodine removal step eventually makes this step as the determining step to selectively produce *N*-transfer product rather than *O*-transfer product. Energy decomposition analysis (EDA) shows that in **TS-**$\mathbf{C_{2-3}}$ and $\mathbf{C_3}$ the interaction between MgI_2 and the remaining unit is mostly guided by electrostatic interaction (ΔE_{elstat}), whereas for $\mathbf{C_2}$ structures ΔE_{orb} is the major contributor toward the total interaction energy (ΔE_{int}) (see Table 10 in the Supporting Information). The change in dissociation energy (ΔD_e) is small (−4.42 kcal/mol) for the $^{O}\mathbf{C_2}$ → **TS-**$^{O}\mathbf{C_{2-3}}$ step, while for the $^{N}\mathbf{C_2}$ → **TS-**$^{N}\mathbf{C_{2-3}}$ process ΔD_e is large (−24.81 kcal/mol). It indicates that a large amount of energy is required to generate the ^{N}**TS-**$\mathbf{C_{2-3}}$ from $^{N}\mathbf{C_2}$, and therefore $^{N}\mathbf{C_2}$ → **TS-**$^{N}\mathbf{C_{2-3}}$ is a high energetic pathway compared to the $^{O}\mathbf{C_2}$ → **TS-**$^{O}\mathbf{C_{2-3}}$.

In the next step another nucleophilic attack can occur from the N1 (or O1) atom to the C1 atom to produce the *N*-transfer (or *O*-transfer) product. In $^{O}\mathbf{C_3}$, C−N bond breaking occurs to remove benzaldehyde (through **TS-**$^{O}\mathbf{C_{3-4}}$, $\Delta^{\ddagger}G_{3-4}$ = 14.78 kcal/mol), and thereafter a concomitant nucleophilic attack occurs from N1 (−0.78 |e|) to C1, which produces the 4-membered *N*-transfer product ($^{O}\mathbf{C_4}$). The transition mode indicates the removal of benzaldehyde only and discards the

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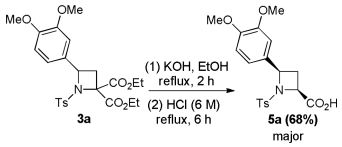
possibility of any concerted pathway where nucleophilic attack and removal of the side product can occur simultaneously. For $^{N}C_3$ the benzylideneimine removal occurs through **TS-$^{N}C_{3-4}$** and *O*-transfer product ($^{N}C_4$) gets formed.

To check the potentiality of the azetidine dicarboxylate molecule for further synthetic application, we performed the decarboxylation reaction. Following a two-step process in the presence of KOH, ethanol, and HCl, **3a** can be easily converted to **5a** (cis-isomer as major) in 68% isolated yield (Scheme 4).[16] The monodecarboxylated **5a** contains the structural scaffold of bioactive molecules like azetidine carboxylic acid and mugenic acid.

Scheme 4. Monodecarboxylation of 3a



In conclusion, we have discovered the *N*-substituent directed dual reactivity of oxaziridine toward DAC. The scope of electrophilic *N*-transfer by oxaziridine is developed through this first example with DAC that gives easy access to the biologically important azetidine molecule. The overall reaction profile suggests that the iodine removal step from the C1 atom is the rate- as well as the product-selectivity-determining step and is decisive to form the *N*-transfer product rather than other possible products in the case of tosyl group containing oxaziridine. Further examination on the scopes and limitations of our methodology for synthetic application including asymmetric version are in progress.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02417.

^{1}H, ^{13}C NMR, and IR spectra, mass data of all new compounds, single-crystal X-ray data, and DFT and EDA calculations (PDF)

Crystallographic data for **3b** (CIF)

Crystallographic data for **4b** (CIF)

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Notes

The authors declare no competing financial interest.

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(14) (a) CCDC 1408435 contains supplementary crystallographic data for the compound **3b**. (b) CCDC 1451620 contains supplementary crystallographic data for the compound **4b**.

(15) Please see the Supporting Information for the computational details.

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