CHAPTER III

Reaction of Aziridines with Difluoroamine

3.1 ABSTRACT

cis-2,3-Dimethylaziridine reacts with difluoroamine to give the corresponding alkene and nitrogen with retention of configuration. We have carried out DFT study of this reaction to clarify the reaction mechanism by considering a multi-step reaction pathway with possible intermediacy of several three- and four-membered cyclic intermediates and transition states (TSs). Energetics of this reaction shows that the reaction takes place in four steps including a three-membered azamine intermediate. Both energetics and stereochemical outcome of this reaction rule out the formation of a four-membered diazetine intermediate during the reaction. While the first N-N bond formation step is rate determining, the final step, asynchronous concerted cleavage of the azamine intermediate explains the stereochemistry of this reaction. The asynchronous nature of the final step makes the reaction Woodward-Hoffmann allowed as reported by Yamabe and Minato (J. Phys. Chem. A 2001, 105, 7281). Computations at HF and MP2 levels confirm the same trends in energetics. Single point energy computations at B3LYP, MP2 and QCISD levels with the 6-311+G(d,p) and cc-pVTZ basis sets show that the larger basis sets predict higher free energies of activation and less negative free energies of reaction. Intrinsic reaction coordinate (IRC) analyses reveal asynchronous nature of the first and the last steps of the reaction. The deamination of trans-2,3-dimethylaziridine was shown to follow a similar course of reaction as that of the cis isomer.
3.2 Introduction

Aziridine, a three membered heterocycle containing one nitrogen atom can be found in natural and synthetic compounds of biological interest.\textsuperscript{1} Especially 2,3-disubstituted aziridines have widespread applications as versatile intermediates in synthetic organic chemistry.\textsuperscript{2} Aziridines are susceptible to ring opening reactions, and the driving force for this is the release of their ring strain. Generally, non-activated aziridines undergo ring-opening reactions through either protonation, quartemization or through the formation of a Lewis acid adduct. With suitable choice of substituents on the carbon and nitrogen atoms, excellent stereo and regio control can be obtained in ring-opening reactions, which makes aziridines useful intermediates in organic chemistry.\textsuperscript{3,4}

Deanunation\textsuperscript{5} can be done with several reagents such as 3-nitro-N-nitrosocarbazole, nitrosyl chloride and methyl nitrite etc,\textsuperscript{6} and in majority of cases it yields alkene with the retention of configuration. In a few occasions\textsuperscript{6a} alkene with inverted stereochemistry has been formed as a product and the reaction has been exploited in the interconversion of \textit{cis-trans} isomers of alkenes. Retention or inversion of stereochemistry depends on the mechanism but there were only few attempts\textsuperscript{7,8} to investigate the mechanism of this reaction. In this chapter, we elucidate the mechanism of the deamination of aziridine by difluoroamine that results in the formation of an alkene with the retention of configuration.

Difluoroamine\textsuperscript{9} is an efficient and direct deaminating reagent, and it reacts with aziridine (1) to give alkene with 96\% stereospecificity.\textsuperscript{10} The reaction has been postulated to proceed through azamine (2) and collapse of this azamine results in the formation of alkene with evolution of nitrogen (Scheme 3.1). Mechanism of this reaction is not well understood and there is no firm experimental evidence for the proposed azamine intermediate. Moreover it was claimed\textsuperscript{11} that the elimination of nitrogen from a three membered ring should be non-stereospecific. Such situations have stimulated us to study the reaction.
mechanism with the following questions in mind; (i) what is the overall
mechanism of this reaction that leads to the retention of stereochemistry? (ii)
whether azamine intermediate indeed exists on the reaction pathway? (iii)
whether or not Woodward-Hoffmann rule controls the stereochemistry of this
reaction?

3.3 Computational details

Geometries of species at all stationary points in the potential energy
surface have been calculated with the B3LYP\textsuperscript{12,13} method using the 6-31G(d) basis
set.\textsuperscript{14} Stationary points located have been characterized by computing vibrational
frequencies; reactants, products and intermediates have all real frequencies and
the TSs have an imaginary frequency. The nature of the TSs have been confirmed
by the mode of the imaginary frequency and by IRC calculations.\textsuperscript{15} Geometry
optimizations have also been carried out at the HF\textsuperscript{16} and MP2 levels of theory\textsuperscript{17}
with the 6-31G(d) basis set for the species on the lowest energy reaction pathway
obtained at B3LYP/6-31G(d). Further single point energy calculations have been
done at the B3LYP, MP2 and QCISD\textsuperscript{18} levels with the larger basis sets
6-311++G(d,p) and cc-pVTZ on the B3LYP/6-31G(d) optimized geometries of the
species on the lowest energy reaction pathway. All calculations have been
performed with the Gaussian 98W program.\textsuperscript{19} The free energies of the species at
the HF, B3LYP and MP2 levels with the 6-31G(d) basis set have been calculated
based on their frequency calculations and for the larger basis sets they have been
computed using thermal correction data obtained at the B3LYP/6-31G(d) level. Intrinsic reaction coordinate analyses have been done for the transition structures obtained at B3LYP level. Bond orders reported here are Wiberg bond indices calculated by Natural Bond Orbital (NBO) program. From this bond orders, bond formation index $B_{Fi}$ and bond cleavage index $B_{Ci}$ are calculated as follows:

$$BF_{i} = \frac{BO_{TS} - BO_{R}}{BO_{R}} \times 100$$

$$BC_{j} = \frac{BO_{TS} - BO_{R}}{BO_{R}} \times 100$$

$B_{FC_{ave}}$ is the average percentage of all bond forming and cleaving indices of various species in the reaction step.

$$B_{FC_{ave}} = \frac{\sum_{i,j} (BF_{i} + BC_{j})}{n}$$

where $n$ is the total number of bonds that undergo major changes during the reaction.

3.4 Results and Discussion

3.4.1 Possible reaction pathways Aziridine undergoes deamination with difluoroamine to form alkene as shown in Scheme 3.1. The reaction may proceed through either one of the two intermediates, azamine (2) that has been postulated by Bumgardner et al. or diazetine intermediate (3). The detailed scheme of the reaction is given in Figure 3.1. Optimized geometries of species in the most probable pathway are presented in Figure 3.2 and other species in the reaction pathway are depicted in Figure 3.3.

Difluoroamine approaches the aziridine nitrogen in two orientations and in the first stage one molecule of HF is released with concomitant formation of an N-N bond. There are two possibilities for this: (i) the reactants form an initial complex, which yields Int1 through TS1, and (ii) the reactants form Int2a through a spiro-type TS (TS1a). The former process resembles S$_2$2-type reaction at the N atom which takes place together with the abstraction of the H atom on NHF$_2$ by the leaving F anion to give HF. There is another possibility that NHF$_2$
decomposes into NF and HF and the resultant nitrene NF attacks the aziridine to give Int1. This step has also been examined. The activation free energy for the process NHF₂ → NF + HF is found to be very high, 49.3 kcal·mol⁻¹ and therefore this possibility has not been considered further.

Figure 3.1. Reaction pathways for the deamination of cis-2,3-dimethylaziridine and NHF₂.
Computations show that the N3-N15 bond in Int1 can undergo a rotation about the newly formed N3-N15 bond through TS2 to form Int2. This brings the fluorine atom close to the hydrogen on the aziridine nitrogen and then another molecule of HF is released through TS3 to form Int3 (2). Alternatively, Int1 can undergo a hydrogen migration from N3 to N15 through TS2a to form Int2a. The H and F atoms attached to the exocyclic N atom in Int2a get closer and through TS3a one molecule of HF is released to form Int3. Int3 referred as azamine10 undergoes asynchronous concerted cycloreversion via TS4 to finally yield cis-alkene and N2. In another branch line, Int2 can undergo ring expansion through 1,2-carbon shift (TS3b) and forms Int3b. Subsequently Int3b releases one molecule of HF through TS4b to form Int4b. Int4b i.e., cis-3,4-dimethylidiazetine (3) also undergoes a concerted asynchronous cycloreversion to form trans-alkene and N2. It is interesting to note that, in the final step, both Int3 and Int4b undergo cycloreversion but the stereochemistry is retained in the former while it is inverted in the latter.
Figure 3.2. Optimized structures of complex, transition structures and intermediates in the least energy pathway of deamination of aziridines with HNF$_2$ at MP2/6-31G(d) and (B3LYP/6-31G(d)) levels of theory. Distances are in Å and dihedral angles are in degrees.
Figure 3.3. Optimized structures of transition structures and intermediates in the reaction pathway of deamination of aziridines with HNF2 at B3LYP/6-31G(d) level of theory. Distances are in Å.

3.4.2 Reaction energetics Frontier orbital energies of 1 and NHF2 were calculated to be \(-0.37\) eV (HOMO of 1), \(0.23\) eV (LUMO of 1), \(-0.51\) eV (HOMO of NHF2), and \(0.21\) eV (LUMO of NHF2) at MP2/6-31G(d) level of theory. These values show that the reaction is mainly controlled by the interaction between HOMO of 1 and LUMO of NHF2. The free energy profile of the reaction at B3LYP/6-31G(d) is shown in Figure 3.4, in which the free energies of various TSs and intermediates are expressed with reference to the reactants. Difluoroamine reacts with aziridine
through TS1 or TS1a as mentioned above. The free energies of activation for these steps are found to be 42.6 and 56.9 kcal-mol\(^{-1}\), and the free energies of reaction are 14.2 and -24.0 kcal-mol\(^{-1}\) respectively at B3LYP/6-31G(d). The computed barriers suggest that the reaction pass through TS1. The barrier for this step is unrealistically high for a reaction that takes place smoothly and inclusion of solvent effects may reduce the barrier drastically.

Int1 undergoes rotation about the N3-N15 single bond to form Int2 with a low barrier of about 3.0 kcal-mol\(^{-1}\). Following this, azamine intermediate (Int3, 2) is formed from Int2 through spiro-type TS3 and the barrier for this process is 22.3 kcal-mol\(^{-1}\). In this step, N3-N15 double bond and H14-F16 single bond are formed and N3-H14 and N15-F16 bonds are broken. Alternative step from Int1 to Int2a through 1,2-proton migration from N3 to N15 (TS2a) is a high-energy process (40.5 kcal-mol\(^{-1}\)). Int2a then leads to Int3 through TS3a with a barrier of 18.4 kcal-mol\(^{-1}\). Free energy profiles of these processes indicate that the formation of Int3 via Int2 is the energetically favourable pathway. The azamine intermediate (Int3) undergoes asynchronous concerted cleavage of the ring with a low activation barrier of 8.1 kcal-mol\(^{-1}\).

Int2 may also undergo 1,2-carbon shift to give Int3b, which is more stable than Int3, but the energy required for this step is high (33.6 kcal-mol\(^{-1}\)) probably because this TS (TS3b) has a [1,1,0] bicyclic structure. Int3b would give stable diazetine intermediate (Int4b, 3), which then may decompose through asynchronous concerted mode (TS5b) with the free energy of activation 43.9 kcal-mol\(^{-1}\) to form trans-alkene. The higher activation energy for the formation of Int3b as well as the stereochemistry of the product alkene can rule out the possible intermediacy of diazetine (Int4b) in this reaction. All these observations lead to the conclusion that the reaction takes place through three-membered azamine intermediate (Int3) and not through four membered diazetine intermediate (Int4b). Thus, the reaction pathway is reactants → complex → TS1 → Int1 → TS2 → Int2 → TS3 → Int3 → TS4 → products. The formation of Int3 from the reactants through the precursor Int2a is a high energy path. The most
probable pathway is illustrated in Figure 3.5 with relative free energies with respect to reactants at different levels of theory. The rate-determining step of the multi-step reaction is the first step via TS1. The present results nicely explain the experimental observations that the whole reaction is taking place with 96% retention of stereochemistry; i.e., when HNF2 is reacted with the cis-2,3-dimethylaziridine, cis-2-butene is the product and when trans-2,3-dimethylaziridine is reacted trans-2-butene is the product.
**Figure 3.4.** Schematic free energy profile for the deamination of cis-2,3-dimethylaziridine with NHF$_2$ at B3LYP/6-31G(d).
Figure 3.5. Schematic free energy profile for the least energy pathway with relative free energies of complex, transition states, intermediates and products with respect to reactants. Numbers are at MP2/6-31G(d), (B3LYP/6-31G(d)), and [HF/6-31G(d)].

3.4.3 Geometrical variation along the lowest energy reaction pathway

Geometries of spades along the lowest energy pathway computed at B3LYP/6-31G(d) and MP2/6-31G(d) illustrated in Figure 3.2 are informative. The initial complex between the aziridine and NHF₂ is a true minimum on the potential energy surface with a weak N₃–H–N₁₃ hydrogen-bond interaction. Figure 3.6 shows the changes of selected bond lengths along IRC for the N-N bond formation step from the complex to Int₁. The structural variations along IRC exhibit that two independent events occur in this step. One is an Sₘ₂-like displacement of F₁₇ by N₃ at the nitrogen atom, N₁₅. Smooth variation of the two bond lengths and a nearly linear alignment of N₃–N₁₅–F₁₇ at TS₁ are characteristics of Sₘ₂ displacement. The other one is the transfer of H₁₈ from N₁₅ to F₁₇. The hydrogen (H₁₈) on N₁₅ is hydrogen-bonded to the aziridine nitrogen (N₃) in the initial complex. At the early stage of the reaction the hydrogen bond is
cleaved and H18 starts to interact with F17 with the N15-H18 bond nearly intact until TS1, and then the proton transfer occurs from N15 to F17 after the TS. Thus, the step is a two-stage process with the N-N bond formation and the proton transfer occurring in different time scales.

Figure 3.6. Changes in the lengths of various bonds along the IRC around TS1 of aziridine deamination by HNF2 at B3LYP/6-31G(d). The units of IRC are amu⁻¹/² Bohr.

Figure 3.7. Changes in the lengths of various bonds along the IRC around TS4 of aziridine deamination by HNF2 at B3LYP/6-31G(d). The units of IRC are amu⁻¹/² Bohr.
On going from \textbf{Int1} to \textbf{Int2}, the dihedral angle $\angle \text{H}_{14} \text{-N}_3 \text{-N}_{15} \text{-F}_{16}$ changes from 180.0° in \textbf{Int1} through 137.6° in \textbf{TS2} to 75.3° in \textbf{Int2}. In \textbf{TS3}, further rotation around this bond takes place before liberation of an HF molecule. This TS has a distorted spiro structure where $\angle \text{H}_{14} \text{-N}_3 \text{-C}_2 \text{-C}_1 = 130.4°$ and $\angle \text{N}_{15} \text{-N}_3 \text{-C}_2 \text{-C}_1 = -114.7°$. The azamine intermediate (\textbf{Int3}) formed from \textbf{TS3} undergoes ring opening in an asynchronous concerted fashion through \textbf{TS4}. This results in the formation of N$_2$ and alkene with the retention of configuration. In Figure 3.7 are shown the changes of selected bond lengths along IRC for the final alkene-forming step. It is clearly seen that the cleavage of the C$_2$-N$_3$ bond comes ahead of that of the C$_3$-N$_3$ bond. Thus, the step is a two-stage reaction in terms of the change in bonding and hence in electronic structure.

Yamabe and Minato have previously discussed the mechanism of N$_2$ extrusion from azamine and diazetine systems and have pointed out that both of them undergo cycloreversion through asynchronous concerted mechanism. They have demonstrated that Jahn-Teller distortion occurs in the TSs and that after symmetry lowering azamine decomposition become Woodward-Hoffmann allowed while diazetine reaction doesn’t follow symmetry conservation rule. Our observation that azamine reacts in an asynchronous concerted manner with retention of configuration agrees with the symmetry lowering argument reported by the above authors.

### 3.4.4 Effect of various methods and basis sets

Table 3.1 lists the relative free energies of the complex, TSs, the intermediates, and the products at different computational methods. It is clear that all these methods and basis sets predict the first step being rate determining. Therefore, it is worthwhile to compare the effects of various levels and basis sets on the free energy of activation for the first step. With the 6-31G(d) basis set, B3LYP predicts lowest activation energy, while the HF value is the highest. With 6-311++G(d,p) and cc-pVTZ basis sets, B3LYP values are lower compared to QCISD and MP2 values. The energetics for the deamination of \textit{trans}-2,3-dimethylaziridine at the B3LYP/6-31G(d) level listed in
Table 3.1 reveals that the mechanism of trans-2,3-dimethylaziridine is basically the same as the cis-isomer.

3.4.5 Bond order analysis  Calculated bond indices listed in Table 3.2 show that the bond formation and cleavage take place in the reacting system systematically as the reaction progresses. Weak bond indices in Table 3.2 for the complex show the weak nature of the interaction between the reacting species. No major changes in bond indices are observed between Int1, TS2, and Int2, since the bond rotation is the major reaction coordinate in this step. The asynchronous nature of the concerted cycloreversion from Int3 to the final product alkene and N2 is clearly seen in the bond indices; the bond order is much larger for C2-N3 than for C1-N3 at TS4. The gradual increase in BFCave from the reactants to the products shows the progress of the reaction quantitatively. In the whole reaction, the three membered ring is intact till the last step and in the final step it cleaves concertedly. This doesn’t allow the C1-C2 bond of the ring to undergo any rotation and is responsible for the retention of the stereochemistry.

3.5 Conclusions

Deamination of cis and trans-2,3-dimethylaziridine with difluoroamine has been investigated by DFT calculations at the B3LYP/6-31G(d) level. Pathways with possible intermediacy of several three- and four-membered cyclic intermediates and TSs have been considered. Analysis of the energies of this reaction has revealed that (i) the reaction involves four steps with initial formation of a complex, (ii) the reacting system eliminates two molecules of HF in two subsequent steps resulting in the formation of azamine intermediate as suggested by earlier experimental reports, and (iii) the azamine intermediate cleaves in a concerted asynchronous way to form the corresponding alkene with retention of stereochemistry. The asynchronous nature of the step makes the reaction Woodward-Hoffmann allowed as reported by Yamabe and Minato. The formation of diazetine intermediate has been ruled out based on the energetics
and also on the observation that this intermediate inverts the stereochemistry of the reaction. The first step of the reaction is found to be rate determining and the reaction is highly exothermic. The possible involvement of nitrene in the first step was eliminated in view of very high free energy of activation for the process $\text{NHF}_2 \rightarrow \text{NF} + \text{HF}$. Computations at HF and MP2 levels with 6-31G(d) basis set also bring out the same conclusions. Single point energy computations at the B3LYP, MP2 and QCISD levels with the 6-311++G(d,p) and cc-pVTZ basis sets on the B3LYP/6-31G(d) geometries also confirm that the first step is rate determining. Geometrical changes in the first and last steps through IRC analysis and bond order analysis reveal that these are two-stage single step reactions.
Table 3.1. Relative free energies (kcal·mol⁻¹) of complex, TSs, intermediates and product for the deamination reaction of cis-2,3-dimethylaziridine at various computational methods with respect to the reactants.

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*a* Values given in the parenthesis correspond to the deamination of trans-2,3-dimethylaziridine computed at B3LYP/6-31G(d).

*b* Values obtained with single point calculations on the specified level on the B3LYP/6-31G(d) geometries.
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Table 3.2: Wiberg bond order analysis of deamination of cis-aziridines with HNF3 at B3LYP/6-31G(d).
3.6 References


