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β-Elimination of an aziridine to an allylic amine: a mechanistic study

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The base-induced rearrangement of aziridines has been examined using a combination of calculations and experiment. The calculations show that the substituent on nitrogen is a critical feature that greatly affects the favorability of both α-deprotonation, and β-elimination to form an allylic amine. Experiments were carried out to determine whether E2-like rearrangement to the allylic amine with lithium diisopropyl amide (LDA) is possible. *N*-tosyl aziridines were found to deprotonate on the tosyl group, preventing further reaction. A variety of *N*-benzenesulfonyl aziridines having both α- and β-protons decomposed when treated with LDA in either tetrahydrofuran or hexamethylphosphoramide. However, when α-protons were not present, allylic amine was formed, presumably via β-elimination.

Supporting information may be found in the online version of this paper.

Keywords: aziridine; allylic amine; α-elimination; β-elimination

INTRODUCTION

The chemistry of aziridines is rich and varied.[1] In recent years, the reactions of aziridine α-anions have been the subject of many fruitful studies.[2] In this report, the potentially competitive base-promoted E2-like rearrangement of aziridines to form allylic amines is investigated.

The base-induced E2-like rearrangement of epoxides to allylic alcohols is a well-known reaction that can occur with high regio- and stereoselectivity.[3] The analogous rearrangement of aziridines to allylic amines is virtually unknown. Allylic amines are important intermediates in the synthesis of many nitrogenous natural products. Historically, there have been a limited number of ways to make them,[4,5] but in recent years, new methods have been developed.[6–8] Given the utility and selectivity of epoxide rearrangements, it would be useful to study whether the aziridine analog is feasible.

The rearrangement of epoxides in base is mechanistically complicated.[3] Even with a bulky, non-nucleophilic base such as lithium diisopropyl amide (LDA), there are two competing reactions: α-deprotonation that initially forms the epoxide α-anion, and β-elimination to form the allylic alcohol by an E2-like reaction. The α-deprotonation is favored when epoxides have added strain, such as cyclopentene oxide,[9] or when using strong bases such as butyl lithium.[3] The α-anion behaves as a carbenoid,[10] and typically undergoes CH bond insertion reactions. Interestingly, allylic alcohols can also form through this competing pathway, as well as ketones and other products, though often with loss of selectivity. The solvent is also known to influence the mechanism; cyclopentene oxide undergoes α-elimination in ether or benzene, but β-elimination in hexamethylphosphoramide (HMPA).[11] The stereochemistry of β-elimination of 4-*tert*-butylcyclohexene oxide is *syn* in ether[12] but *anti* in HMPA.[9] The importance of the solvent-dependent aggregation state of the base on the α- versus β-elimination mechanisms for epoxide rearrangement has been studied by Collum *et al.*[13]

Because the preparation of allylic alcohols from epoxides continues to be a useful reaction, we were interested in determining whether the β-elimination of aziridines to allylic amines could also be carried out. Reports of aziridine rearrangement are few, and do not appear to occur via the stereoselective E2-like pathway. In 1993, da Zhang and Scheffold[14] reported the isomerization of the *N*-acyl aziridines derived from cyclohexene and cyclopentene to optically active allylic amines using cob(I)alamin in methanol; this transformation is thought to begin with nucleophilic addition to form an organocobalamin intermediate. While this transformation appears to be promising, this methodology has not been utilized since. Other reports of allylic amine synthesis from aziridines involve the use of chiral alkyl lithium base to remove a bridgehead proton, generating the α-anion. In their studies on the desymmetrization of achiral aziridines, Müller and Nury[15] generated some allylic amines as well as other interesting rearrangement products from simple *N*-tosyl aziridines (Scheme 1). Note that the α-anion is shown as a resonance structure of the carbene; this has been demonstrated computationally for the α-anion of cyclopentene oxide,[10] and is likely the case with the aziridine anions as well.

Additional examples, with an eye to the mechanistic and synthetic potential of the α-elimination mechanism, have been reported by O'Brien *et al.*[16,17]

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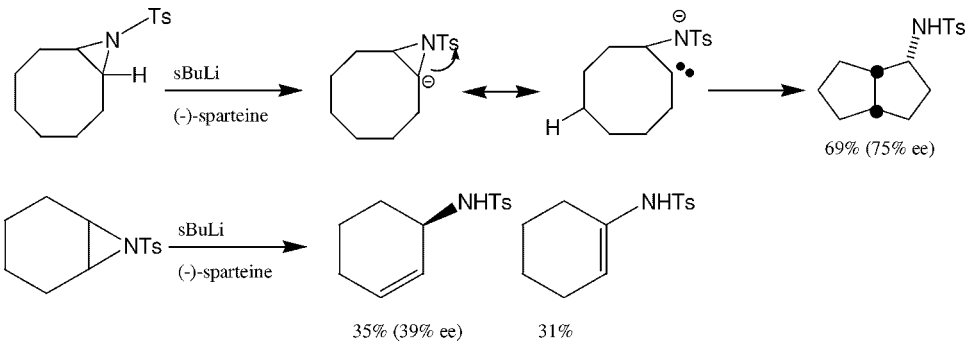

Scheme 1.

An extensive study of aziridine rearrangements was published by Mordini *et al.*[18] Cyclic and acyclic aziridines were treated with superbasic mixtures of butyl lithium/potassium *tert*-butoxide (LICKOR) or lithium diisopropylamide/potassium *tert*-butoxide (LIDACOR). A series of nitrogen substituents was investigated, with the tosyl substituent being most productive; acyl substituents could not withstand the reaction conditions. Allylic amines were generally obtained in low to moderate yield, generally below 50%. Given the use of such strong base and the presence of α-elimination products, notably the bicyclooctane shown in Scheme 1, α-elimination is likely occurring under these conditions.

RESULTS AND DISCUSSION

In order to evaluate the feasibility of the β-elimination rearrangement, a series of *ab initio* and density functional theory calculations were performed. Briefly, the calculations suggest that E2-like rearrangement of aziridines is a favorable reaction, though competing α-deprotonation may be problematic. Not surprisingly, the nitrogen substituent plays a significant role. Experimental studies described herein reveal that allylic amine is obtained when α-protons are not present on the aziridine, consistent with rearrangement via β-elimination.

Computational analysis

The computational study was modeled after Gronert's report on the gas-phase rearrangement of methyloxirane with hydroxide.[19] While hydroxide is not known to promote the E2 rearrangement of epoxides in solution, the results thus obtained are consistent with all known experimental data, and hence provide a reasonable model of the various reaction pathways. Overall, the goal of this computational study is to predict the inherent reactivity of aziridines compared to epoxides, to determine whether aziridine β-elimination might be possible. The effects of solvent are evaluated using a Self-Consistent Reaction Field, specifically Tomasi's Polarized Continuum Model,[20] using benzene as a nonpolar solvent and DMSO as a polar aprotic solvent. The role of the lithium counterion in this type of reaction is complicated, and beyond the scope of this study.

Gronert's study considered three epoxide reactions: *syn* β-elimination, *anti* β-elimination, and α-deprotonation. In the gas phase, the epoxide and base also form a stabilized ion–molecule complex. In this study, these pathways were calculated for the parent 2-methylaziridine (NH), and the sulfonamide derivative having N–SO_2H. The expectation was that the parent aziridine would be less reactive than the epoxide, due to the high energy of the unstabilized nitrogen anion produced, but the sulfonamide, having a stabilized anionic intermediate, would be at least competitive with the epoxide. Two aziridine structures were considered in each case, with the nitrogen group *cis* versus *trans* to the methyl. In addition, three conformations around the N–SO_2H bond were explored. The calculations were carried out at both the MP2/6-31+G**//MP2/6-31+G* and B3LYP/6-31+G* levels of theory. As in the Gronert study, zero point energies were included to give enthalpies at zero degrees. In general, the two computational methods give similar results, and in the ensuing analysis only the MP2 results are discussed.

In both cases, the aziridine conformers having the nitrogen substituent *trans* to the ring methyl were more stable than the *cis* conformers. For methyl aziridine, this preference is 0.8 kcal mol^{-1} at the MP2/6-31+G**//MP2-6-31+G* level of theory. For the sulfonamide derivative, the lowest energy *trans* conformation has the SO_2H proton oriented away from the ring methyl, with H–S–N–C(CH_3) = 169°. The next lowest structure is +0.3 kcal mol^{-1} and has H–S–N–C(CH_3) = −102°, while the final conformer is +2.6 kcal mol^{-1} and has H–S–N–C(CH_3) = 36°. Only two conformers of the *cis* structure were obtained, having H–S–N–C(CH_3) = −178° and +2.6 kcal mol^{-1}; and H–S–N–C(CH_3) = 47° and +6.0 kcal mol^{-1}.

Inversion of the *trans* to *cis* methyl aziridine conformers was explored. For the parent methyl aziridine, the barrier is 17.9 kcal mol^{-1} at the MP2/6-31+G**//MP2-6-31+G* level of theory. A previous computational study[21] that used a cc-pVQZ MP2 method found the barrier to be similar, 19.1 kcal mol^{-1}. The *trans* to *cis* inversion barrier calculated for the sulfonamide derivative is significantly lower, 13.7 kcal mol^{-1}.

Figure 1 shows the MP2/6-31+G* optimized structures for methyl aziridine having the NH *trans* to the methyl (Fig. 1a), as well as the ion–molecule complex formed with hydroxide (Fig. 1b); the transition states to *anti* and *syn* elimination with hydroxide (Fig. 1c and d); and the lowest energy of three possible α-anions (Fig. 1e). Selected structural parameters are shown in Table 1, and in general are not surprising. Formation of the ion–molecule complex causes only minor structural changes, and positions the base near the reactive methyl protons. The geometries for the *anti* and *syn* E2 transition states for the reactions of hydroxide with the aziridine show expected patterns, such as C–N bond lengthening, C2–C4 bond shortening as the alkene forms, and opening of the N–C3–C2 bond angle as the ring opens. Similar geometries are found for the other aziridine series, and are included in the supplemental information. In general,

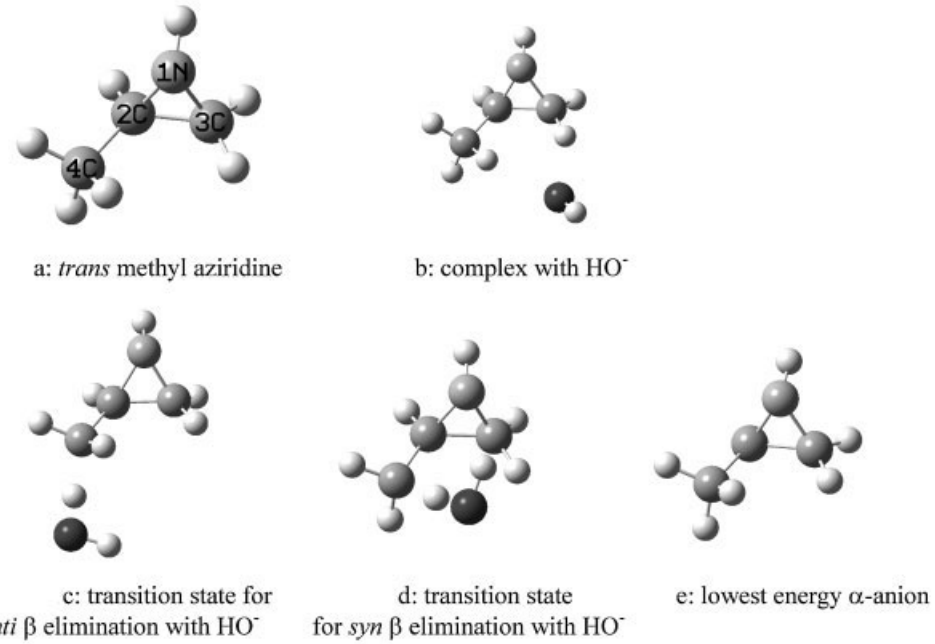

Figure 1. MP2/6-31+G* optimized geometries for *trans* methyl aziridine series of compounds. (a) *trans* methyl aziridine. (b) Complex with HO^-. (c) Transition state for anti β-elimination with HO^-. (d) Transition state for *syn* β elimination with HO^-. (e) Lowest energy α-anion.

the structural deformations are more pronounced for the sulfonamide transition states, consistent with the greater reactivity expected for the sulfonamides. For example, at the transition state to *anti* β-elimination for the *trans* sulfonamide, the C2–N bond lengthens to 1.63 Å, the C2–C4 bond shortens to 1.46 Å, and the N–C3–C2 angle opens to 66.1°. Note that the transition states for *syn* elimination of the *cis* aziridines were not found, despite numerous attempts.

The energies of a variety of pathways were calculated, and are reported in Table 2. The aziridine used for reference in both the *trans* and *cis* methyl aziridine calculations is the lower energy *trans* conformation, and for the sulfonamides, the lowest energy conformer of the *trans* structure is used. The enthalpies of ion–molecule complex formation, and activation enthalpies for E2 transition state formation, are calculated with respect to starting epoxide or aziridine plus hydroxide. A range of values is tabulated for the sulfonamides because multiple conformers around the N–S bond were considered for the transition states.

In all cases, stabilized ion–molecule complexes with hydroxide form as expected in the gas phase. The added stabilization of the complex having the NH *cis* to the ring methyl is due to an additional interaction between the N–H proton and the hydroxide oxygen that is not available in any of the other complexes. Not surprisingly, for all substrates *anti* β-elimination is more favorable than *syn* elimination in the gas phase. Note that negative activation enthalpies result because at the transition states, the charge initially localized on hydroxide is now delocalized in the transition state complex. As anticipated, methyl aziridine is calculated to be less reactive than the epoxide. The calculated activation enthalpy for *anti* elimination in the sulfonamide is significantly lower than the epoxide, suggesting that this reaction pathway could be viable and rapid. The various sulfonamide conformations all give similar transition state energies. Similar trends were found for *syn* eliminations, with the sulfonamide again having the lowest calculated barrier, compared to the aziridine plus hydroxide.

Reaction enthalpies are also reported in Table 2 for the gas phase reaction of the epoxide or aziridine plus hydroxide, forming the α-anion plus water. There are three ring protons, and hence three possible α-anions that could form from each

Table 1. Selected structural parameters for *trans* methyl aziridine series of compounds, MP2/6-31+G*

	Aziridine	Complex with HO^-	*anti* β-elim TS	*syn* β elim TS	α-Anion
rC2–N (Å)	1.48	1.49	1.54	1.51	1.53
rC3–N (Å)	1.48	1.50	1.49	1.49	1.49
rC2–C3 (Å)	1.48	1.48	1.48	1.49	1.50
rC2–C4 (Å)	1.50	1.51	1.48	1.49	1.52
rC4–H_{methyl} (Å)	1.10	1.10	1.60	1.56	
rO–H_{methyl} (Å)		2.25	1.13	1.15	
θNC3C2	59.7°	59.9°	62.7°	60.9°	61.8°
τNC2C4H			−161.3°	−32.7°	

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Table 2. Enthalpies of aziridine and epoxide reactions with hydroxide (kcal mol^{-1})

	ΔH_{rxn}, ion–molecule complex	$\Delta H^{\ddagger}$, *anti* β-elimination	$\Delta H^{\ddagger}$, *syn* β-elimination	ΔH_{rxn}, α-anion formation[a]
Methyl oxirane[19]	−15.9	−9.6	−5.0	+15.9 to +17.3
Methyl aziridine NH *trans* methyl	−11.1	−1.9	+0.5	+19.0 to +22.8
Methyl aziridine NH *cis* methyl	−23.0	−5.7	n/a	+19.2 to +25.5
Methyl aziridine NSO_2H *trans* methyl	−25.8	−18.8 to −18.2	−14.9 to −13.9	−11.3 to −3.3
Methyl aziridine NSO_2H *cis* methyl	−17.8	−17.8	n/a	−8.5 to +3.3

[a] Three isomeric α-anions can form; the range shows the variation in ΔH_{rxn} to form them.

heterocycle, and the range is tabulated. The α-deprotonation of methyl aziridine was calculated to be least favorable, and the sulfonamide the most favorable. The α-anions have significant carbenoid character. This has previously been observed computationally for α-deprotonation of cyclopentene oxide,[10] and similar results are found here. The carbenoid nature of the anions is exhibited structurally in the lengthening of the bond between the heteroatom and the carbanion/carbenoid carbon. In the three anions generated from methyl oxirane, this bond has lengthened to 1.55–1.58 Å compared to the other C–O bond in the ring, 1.42–1.44 Å. In the anions generated from the *anti* conformation of methyl aziridine, the analogous bonds are 1.53–1.57 Å versus 1.47–1.49 Å, and in the sulfonylated derivative these are 1.54–1.58 Å versus 1.47–1.49 Å. The carbenoid character of the α-anions is also apparent in the atomic charges, as calculated using Reed and Weinhold's Natural Population Analysis.[22,23] For example, in the anion generated from methyl aziridine shown in Figure 1e, the charges are −0.83 on N, −0.38 on C2, −0.33 on C3, and −0.67 on C4. The CH proton charges are all +0.15 to +0.19, and the amine proton is +0.36. These charges are more similar to the α-anion/carbenoid derived from cyclopentene oxide rather than the corresponding neutral α-hydroxycarbene, in which the oxygen does not complex to the carbene. In this anion, the anionic/carbenoid carbon was −0.22, while in the true carbene, the charge was −0.05. Further, as in the case of the cyclopentene oxide α-anion, it was not possible to find a discrete structure for the nitrogenous carbene separate from the α-anion; all starting structures either reverted to the α-anion, or gave carbene CH bond insertion products.

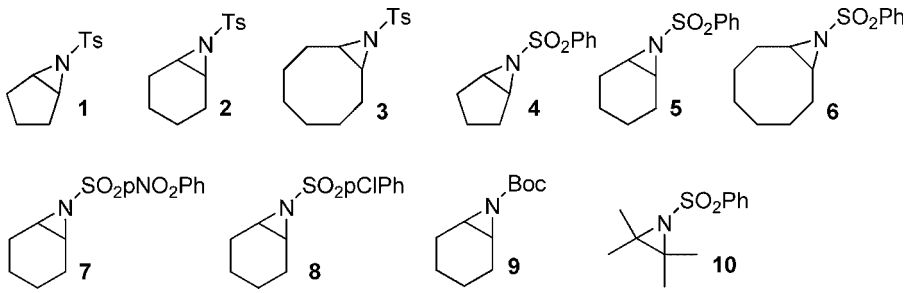
Ionic reaction coordinates are highly sensitive to the effects of solvent, so the reactions were also examined in solution using the Polarized Continuum Model,[20] in both benzene and DMSO solvent. The optimized MP2/6-31+G* gas phase structures were used for simplicity, and single point energies were calculated at MP2/6-31+G** with the PCM correction. Solvation had a minimal impact, if any, on the relative stabilities of conformers, if applicable, and on the relative stabilities of the isomeric α-anions. The calculated reaction enthalpies in solution are shown in Table 3. Not surprisingly, all the reactions have barriers in solution. This is largely due to the highly favorable solvation of hydroxide; benzene was calculated to stabilize hydroxide by −47.6 kcal mol^{-1} and DMSO stabilizes hydroxide even more, −85.9 kcal mol^{-1}. For comparison, the solvation of water is not nearly so significant, −4.0 and −9.2 kcal mol^{-1}, respectively. The trends observed in the gas phase are generally maintained in solution. *Anti* β-elimination is again the most favorable reaction, and the sulfonylated aziridines are more reactive than epoxides. One significant difference in solution is that deprotonation at the α-position becomes competitive with β-elimination in both solvents for the *trans* isomer of the sulfonylated aziridine.

To summarize the computational results, substituents that can stabilize the incipient nitrogen anion are predicted to favor all three aziridine reactions studied, compared to epoxides. It is

Table 3. Reaction enthalpies calculated in benzene and DMSO (PCM) (kcal mol^{-1})

	$\Delta H^{\ddagger}$, *anti* β-elimination		$\Delta H^{\ddagger}$, *syn* β-elimination		ΔH_{rxn}, α-anion formation[a]	
	Benzene	DMSO	Benzene	DMSO	Benzene	DMSO
Methyl oxirane	+6.9	+19.0	+11.4	+23.5	+27.0 to +28.2	+32.8 to +33.2
Methyl aziridine NH *trans* methyl	+15.0	+26.9	+17.2	+29.2	+31.2 to +34.4	+37.6 to +39.7
Methyl aziridine NH *cis* methyl	+11.9	+25.1	n/a	n/a	+31.0 to +35.7	+37.6 to +40.2
Methyl aziridine NSO_2H *trans* methyl	+1.5 to +2.7	+16.5 to +17.5	+5.6 to +7.7	+21.9 to +23.2	+6.6 to +13.9	+19.3 to +23.9
Methyl aziridine NSO_2H *cis* methyl	+1.7	+17.4	n/a	n/a	+9.5 to +19.6	+22.5 to +29.3

[a] Three isomeric α-anions can form; the range shows the variation in ΔH_{rxn} to form them.



Scheme 2.

curious, then, why β-elimination of aziridines to allylic amines has not yet been demonstrated. Certainly the role of α-deprotonation must be considered as a factor.

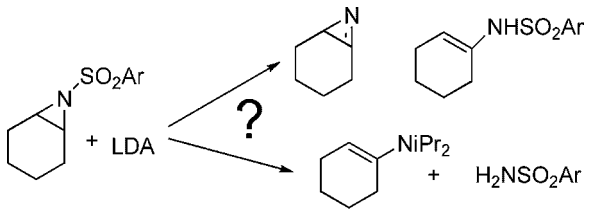
Reactions of aziridines with base

Buoyed by these promising computational results, we have also explored the rearrangements of ten aziridines with LDA. The first aziridines prepared were *N*-tosyl compounds **1**–**3** (Scheme 2); tosyl aziridines are common, and simple to make. These were easily synthesized from cyclopentene, cyclohexene, and cyclooctene with PhI = NTs, according to literature precedent.[24]

Treatment of the *N*-tosyl aziridines **1**–**3** with 2.5 molar equivalents of LDA in either THF or HMPA gave recovered aziridine. During some of the runs, a mixture of aziridine and cyclohexene oxide was used, and the epoxide rearranged successfully, showing that active LDA was in fact present. This finding is consistent with O'Brien's observation that *N*-tosyl aziridines are substantially less reactive than epoxides to lithium amide bases.[25] Because the calculations predicted so convincingly that the sulfonylated aziridines would react even more favorably than epoxides, the apparent inertness of the aziridines was surprising. However, a competing reaction of the *N*-tosyl aziridines was found: methyl deprotonation of the tosyl group. This was determined by subjecting **3** to LDA in THF, then quenching with D_2O. GC/MS analysis of the recovered aziridine showed an increase in one mass unit compared to the reactant. Further, the fragmentation was consistent with incorporation of deuterium in the tosyl group, rather than deprotonation of the aziridine bridgehead; for example, the SO_2Ar fragment increased in mass from 155 to 156. This methyl deprotonation apparently prevents or retards subsequent reactions.

Aziridines **4**–**6** do not have the reactive methyl group. Treatment with LDA in either THF or HMPA at room temperature led to degradation of the reactant without formation of the desired allylic amine. Note that the anticipated product appears to be stable to the reaction conditions; some samples of aziridine **5** were contaminated with 1–2% of the allylic amine, which persisted through the workup and into the GC analysis. Aziridines **7**–**8** with the activating electron-withdrawing groups also degraded. In some runs, a product having a much shorter GC retention time was observed, in low yield. The product could not be isolated or identified definitively, despite numerous attempts. However, a GC/MS was obtained for this product formed from **7**, and *m/z* of 96 was found, consistent with loss of the sulfonyl group. The *N*-Boc-substituted aziridine **9** was also studied. Again, only decomposition of the aziridine was observed.

It is possible that removal of the α-proton leads to formation of an unstable azirine (Scheme 3); this type of reaction has been



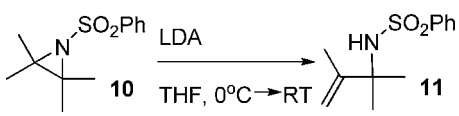
Scheme 3.

reported by Davis *et al.*[26] when certain *N*-sulfinyl aziridines were treated with LDA at −78 °C. Davis also noted that other *N*-tosyl aziridines can rearrange to vinylic amines; both processes are thought to begin with α-deprotonation of the aziridine. Note that the highly strained bicyclic azirine that would form from aziridines **5** and **7**–**9** has only recently been detected spectroscopically, *in situ*, by Banert and Meier.[27] Another possible decomposition pathway, reductive alkylation, was reported by O'Brien for aziridines treated with *sec*-butyl lithium;[17] however, the likelihood of the bulky diisopropylamide exhibiting this reaction is low.

The formation of the azirine receives some computational support, in addition to the observed GC/MS signal with *m/z* 96. The structures of a few α-anions were not obtainable at the B3LYP/6-31+G* level of theory. In one case, dissociation to the azirine and SO_2H anion was observed instead. Still, that it was found at all may give some insight into the possible decomposition of the aziridines.

The final aziridine studied differs from all others in that it possesses no α-protons on the aziridine ring. When treated with LDA in THF, **10** yields allylic amine **11** (Scheme 4).

The reaction mixtures were analyzed by GC, and **11** was the only major product observed; a few baseline impurities were also seen. In one run, rearrangement gave approximately 2/3 conversion of aziridine to allylic amine in 2 h. In an *in situ* competition experiment, **10** was shown to react faster than cyclohexene oxide. After 3 h, 1/3 of aziridine and 1/4 of epoxide had rearranged, and overnight, the aziridine was fully rearranged to allylic amine but 1/4 of the epoxide remained. While these results are promising, the reaction is not without its vagaries. In another run of **10**, the initial yellow-orange reaction mixture



Scheme 4.

turned brown within a couple hours, and only decomposition and an insoluble brown coating on the stir bar were observed. Regardless, it is unambiguous that **10** rearranges to **11**. Clearly, the allylic amine cannot be formed via α-elimination in the case of **10**, suggesting that β-elimination of an aziridine has been observed for the first time.

EXPERIMENTAL

Computational methods

Calculations were performed using Gaussian 03W.[28] Vibrational frequency analysis was carried out to verify that structures were, as appropriate, energy minima or transition states. GaussView was used to animate the imaginary frequency to ensure that the mode corresponded to the desired transition state. Using the Gronert study[19] as a guide, geometries were optimized at the MP2/6-31+G* level of theory, and single point energies were evaluated at MP2/6-31+G**. In addition, B3LYP/6-31+G* optimizations were carried out. However, several of the structures that could be obtained using the MP2/6-31+G* method could not be found. Relative enthalpies were obtained using unscaled zero point energies and energies calculated at MP2/6-31+G**/MP2/6-31+G*. The effects of solvation were modeled using the Polarized Continuum Model[20] as implemented in Gaussian 03W, by carrying out single point calculations at the MP2/6-31+G**//MP2/6-31+G* level of theory, using both benzene and DMSO as the solvent.

General methods

GC analysis was performed on an instrument with a flame ionization detector, equipped with a 30 m HP-1 capillary column. GC/MS were obtained using a 30 m HP5MS capillary column, interfaced to a mass selective detector. NMR spectra were obtained using spectrometers operating at 499.9 MHz or at 300.0 MHz.

Synthesis of aziridines

Most of the aziridines studied are known compounds and were prepared using the copper triflate-catalyzed reaction of PhI=NSO$_2$Ar with an alkene.[24] The nitrene precursors were synthesized from iodosobenzene diacetate and sulfonamides, and were recrystallized from methanol/water.[29] The aziridines were purified by column chromatography using 4:1 hexanes/ethyl acetate on silica. The *N*-Boc aziridine was prepared according to the literature.[14,18] Two of the aziridines were not previously described in the literature.

N-benzenesulfonyl-9-azabicyclo[6.1.0]nonane **6**

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.94 (d, 2H, J = 8.0 Hz) 7.62 (t, 1H, J = 7.5 Hz), 7.54 (m, 2H), 2.82 (dd, 2H, J = 17.3, 7 Hz), 2.02 (dd, 2H, J = 13.8, 3.3 Hz), 1.63–1.52 (m, 4H), 1.48–1.40 (m, 4H), 1.33–1.26 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 139.2, 133.4, 129.2, 127.8, 44.3, 26.6, 26.4, 25.4; MS (*m/z*, %) 236 (0.9), 196 (6.6), 141 (4.9), 124 (100), 77 (2.7); Anal calc. for $C_{14}H_{19}NO_2S$: C 63.36, H 7.22, N 5.28, O 12.06, S 12.08; found: C 63.45, H 7.22, N 5.11, O 11.91, S 11.94.

2,2,3,3-Tetramethyl-1-(benzenesulfonyl)aziridine **9**

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.91 (d, 2H, J = 8.0 Hz), 7.54 (t, 1H, J = 8.0 Hz), 7.49 (m, 2H), 1.48 (s, 12H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 142.9, 132.6, 129.0, 126.9, 53.6, 20.5; MS (*m/z*, %) 240 (0.4, M+1), 224 (3.1), 141 (6.5), 98 (100), 77 (36.3); Anal calc. for $C_{12}H_{17}NO_2S$: C 60.22, H 7.16, N 5.85, O 13.37, S 13.40; found: C 60.33, H 7.26, N 5.87, O 13.53, S 13.36.

Aziridine rearrangement[3]

Dry THF or HMPA (2.7 mL) was added by syringe to an oven-dried flask under N_2. The flask was cooled to 0 °C, then 0.189 mL (1.34 mmol) diisopropyl amine that had been distilled from NaOH, and 0.53 mL of 2.5 M BuLi in hexanes (1.33 mmol) were added by syringe. The solution was stirred for 15 min, at which time a solution of aziridine, or a mixture of aziridine and epoxide (total of 0.54 mmol), in 0.45 mL THF or HMPA was added by syringe. The reaction was warmed to room temperature after 30 min and stirred under N_2 for several hours. The reaction was quenched by adding 2 mL water. Solid NaCl was added to separate the phases, and the organic layer was isolated. The aqueous phase was extracted once more with ether, and the combined organic fraction was dried over Na_2SO_4. Analysis was performed by GC and GC/MS.

N-(2,3-dimethylbut-3-en-2-yl)benzenesulfonamide **11**

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.88 (d, 2H, J = 7.5 Hz), 7.54 (t, 1H, J = 7.0 Hz), 7.49 (m, 2H), 4.95 (s, 1H), 4.83 (br s, 1H), 4.80 (s, 1H), 1.64 (s, 3H), 1.34 (s, 6H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 148.5, 143.1, 132.4, 129.0, 127.4, 112.0, 59.7, 27.6, 19.0; MS (*m/z*, %) 224 (100), 198 (80.9), 141 (65.8), 98 (7.9), 77 (71.9).

CONCLUSION

A computational analysis of three reactions of aziridines with base suggest that while methyl aziridine should be less reactive than methyl oxirane towards α-deprotonation, *syn*- and *anti* β-elimination, the *N*-sulfonylated aziridine should react faster than the epoxide in all three reactions. The rearrangement of tetrasubstituted aziridine **10** to allylic amine **11** using LDA is reported. Without competing α-deprotonation as a possible reaction path, this reaction presumably occurs via an E2-like mechanism.

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