Synthesis of Oxazolidinones and 1,2-Diamines from *N*-Alkyl Aziridines

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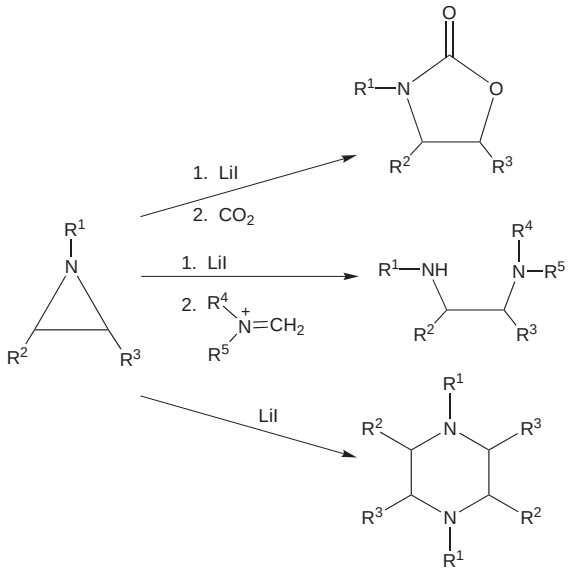
Abstract: Reactions of *N*-alkyl-substituted aziridines with LiI followed by an electrophile are discussed. In the first series of reactions, the electrophile is carbon dioxide and the product is an oxazolidinone. In all cases, either no reaction occurred or a high yield of product was obtained. HMPA had to be added to some reactions to dramatically improve the regiochemistry. Net retention of stereochemistry was observed. In the second series of reactions, the electrophile is an iminium salt and the product is a 1,2-diamine. Here the reaction is highly regioselective in THF without the addition of HMPA. Unlike the oxazolidinone chemistry, the diamine formation works equally well with or without the addition of LiI. With respect to the regiochemistry, the results are the same with and without added LiI. However, with respect to the stereochemistry, in the presence of added LiI, the reaction with the iminium salt goes with net retention of stereochemistry. In contrast, with no added LiI, in some cases the reaction goes with net retention and in some cases with net inversion of stereochemistry.

Key Words: heterocycles, ring opening, aziridines, oxazolidinones, diamines

Because *N*-alkyl-substituted aziridines are readily available and highly reactive three-membered heterocyclic ring systems,[1] we have been interested in their conversion to other organic compounds, especially to oxazolidinones[2] and 1,2-diamines[3] (Scheme 1). These conversions involve reacting the aziridine with LiI followed by an electrophile. It was found that when no electrophile is added to the reaction mixture, after the aqueous work-up, a six membered ring dimer of the aziridine (a piperazine) is obtained. Unlike many reactions of aziridines,[4] for our reactions, neither an electron-withdrawing group nor pre-formation of an aziridinium salt is required.

In this paper, we summarize our previously reported results. In addition, we discuss the synthesis of the aziridines, give yields and isomeric ratios for all reactions, and give full experimental and spectroscopic details. Most importantly, for the first time, we show that the diamine formation reaction can be done with or without the addition of LiI. Although the regiochemistry is the same with and without added LiI, the stereochemistry is not.



Scheme 1

Synthesis of Aziridines and Iminium Salts

As shown in Scheme 2, almost all the aziridines were synthesized from the corresponding epoxide and primary amine. The epoxide was treated with the primary amine in the presence of lithium perchlorate to afford the 1,2-aminoalcohol. Then, the aminoalcohol was cyclized using triphenylphosphine and bromine.[5] The exception to this was *cis*-2,3-diphenylaziridine, which was prepared by the treatment of tribenzylamine *N*-oxide with *n*-butyllithium.[6]

Also as shown in Scheme 2, the iminium salts were synthesized from the corresponding secondary amine. The secondary amine was treated with MeOH and paraformaldehyde to generate a *gem*-aminoether, which, without any purification, was added to methyltrichlorosilane to yield the iminium salt.[7]

Conversion of an Aziridine to an Oxazolidinone

Oxazolidinones are important as chiral auxiliaries and as protecting groups in organic synthesis, as ligands for metal catalysts, and as biologically active pharmaceutical agents.[8–13] In spite of these facts, there are very few reports in the literature of the conversion of a readily available *N*-alkyl aziridine, such as **1**, and carbon dioxide (CO_2) into an oxazolidinone, such as **2** or **3**

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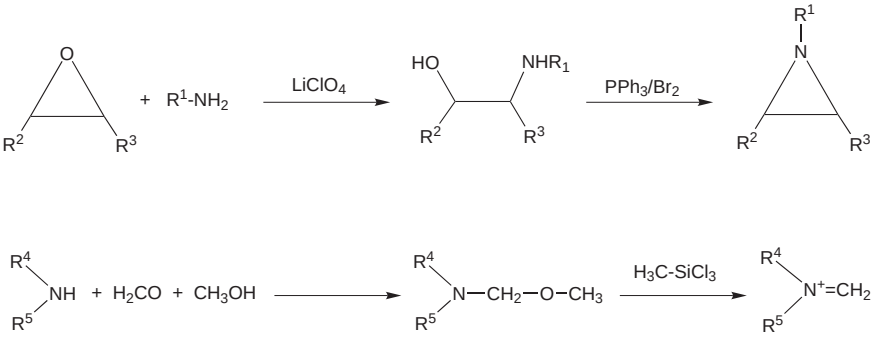
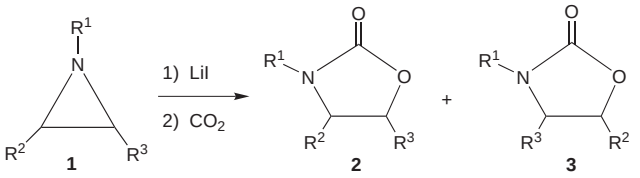


Scheme 2

(Scheme 3).[14–17] The primary obstacles for this direct conversion are the relative inertness of CO_2, and the large amount of polymer typically formed.[18–24] In contrast, CO_2 has been successfully utilized in the ring expansion of an epoxide to a carbonate.[25]

As shown in Scheme 3 and Table 1, we have accomplished the transformation of an *N*-alkyl aziridine to an oxazolidinone in good yield. The R_1 and R_2 groups on the aziridine were varied in order to determine the regiochemistry of this reaction. These reactions were run by heating aziridine **1** with LiI and then bubbling CO_2 into the solution for an extended period of time at room temperature to give the product. When the reaction of **1a** was run without the addition of LiI, or in the presence of $LiClO_4$ or I_2 in place of LiI, no product was obtained and the starting aziridine was recovered. Thus, the presence of I^- ion is important for the reaction to occur.



a $R^1 = CH_2Ph$ $R^2 = CH_3$ $R^3 = H$
b R^1 = pentyl $R^2 = CH_3$ $R^3 = H$
c $R^1 = CH_2Ph$ R^2 = Ph $R^3 = H$
d R^1 = Ph R^2 = Ph $R^3 = H$
e R^1 = Ph R^2 = butyl $R^3 = H$
f $R^1 = CH_2Ph$ $R^2, R^3 = -(CH_2)_4-$
g $R^1 = CH_2Ph$ $R^2 = CH_3$ $R^3 = CH_3$
h $R^1 = CH_2Ph$ R^2 = Ph R^3 = Ph

Scheme 3

When R_1 and R_2 are both alkyl groups and R_3 is H, about a 2:1 mixture of the two regioisomers was obtained. In contrast, when R_1 is an alkyl group and R_2 is a phenyl, there is formation of exclusively one product, the regioisomer in which the more substituted carbon-nitrogen is carboxylated. Finally, when R_1 is a phenyl group, regardless of R_2, no reaction is observed and the starting aziridine can be isolated in high yield.

Table 1 Products and Yields for the Reactions of **1** with LiI and CO_2

Aziridine	Product(s) and Ratio	Overall Yield
1a	61% **2a** 39% **3a**	83%
1b	66% **2b** 34% **3b**	86%
1c	**3c**	99%
1d		no reaction
1e		no reaction

Hoping that a higher pressure/concentration of CO_2 might allow for a more facile reaction, and thus, only one regioisomer of the product, the reaction conditions were changed from two separate steps at atmospheric pressure to one step under a higher pressure. The aziridine, 0.25 equivalents, 1 equivalent, or 2 equivalents of LiI, and an excess of powdered dry ice were mixed together in a sealed thick-walled flask. For the reactions of compounds **1a** and **1c**–**e**, the results from this higher-pressure reaction, regardless of the amount of LiI, are no different from those reported in Table 1 for the reaction in which CO_2 was bubbled into the reaction mixture.

In another effort to obtain only one product rather than a mixture from the reaction of **1a**, one equivalent of hexamethylphosphoramide (HMPA) was added as a co-solvent. HMPA has been shown to be a potent lithium-complexing agent. Many lithium-complexing agents have been shown to activate organolithium reagents by increasing the ion pair separation.[26] It was hypothesized that by increasing the ion pair separation of the LiI, the I^- ion would be more reactive and a reduction in the mixture of isomers might occur.

As shown in Table 2, the reaction of aziridine **1a** with LiI and CO_2 under the higher pressure/concentration conditions with added HMPA generated oxazolidinone **2a** and only a very small amount of **3a**. To further test our hypothesis, the same reaction with compound **1b** was run, and oxazolidinone **2b** and only a very small amount of **3b** was obtained. Unfortunately, adding HMPA to the reactions of **1d** and **1e** still gave only the starting material and no oxazolidinone.

Table 2 Products and Yields for the Reactions of **1** with LiI, HMPA, and CO_2

Aziridine	Product(s) and Ratio	Overall Yield
1a	97% **2a** 3% **3a**	91%
1b	95% **2b** 5% **3b**	88%
1d		no reaction
1e		no reaction

In order to determine the stereochemistry of this conversion, 2,3-disubstituted aziridines **1f**, **1g**, and **1h** were used under the CO_2 bubbling reaction conditions. In all cases, either no reaction occurred or less than a 20% yield of product was obtained.

Switching to the higher-pressure reaction conditions, using a single equivalent of LiI, improved the yields a great deal, but unfortunately, mixtures of *cis* and *trans* isomers of the products were formed. Hypothesizing that a stereochemical mixture might be due to an intermediate undergoing multiple S_N2 reactions with the I^- ion to scramble the stereochemistry, the reaction was attempted using 0.25 equivalents of LiI. As shown in Table 3, high yields and very clean reaction products were obtained.

Table 3 Products and Yields for the Reactions of **1** with LiI and CO_2

Aziridine	Product	Yield
1f	**2f**	90%
cis-**1g**	*cis*-**2g**	86%
trans-**1g**	*trans*-**2g**	84%
cis-**1h**		no reaction
trans-**1h**		no reaction

When the carbons were substituted by two phenyl groups, no reaction occurred and the starting aziridine was recovered unchanged even in refluxing THF. However, when the carbons were substituted by two alkyl groups, either *cis* or trans, net retention of stereochemistry was observed.[27–29]

Conversion of an Aziridine to a 1,2-Diamine

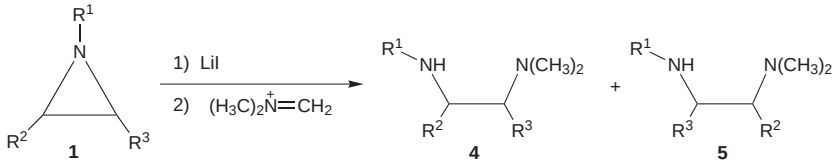
1,2-Diamines, also known as vicinal diamines, are biologically and medically important compounds. In addition, they are prominent in organic synthesis as starting materials, as chiral auxiliaries, and as chiral ligands to a variety of metal complexes.[30–34]

Although there are known conversions of aziridines to 1,2-diamines, the number of reactions that start with an *N*-alkyl aziridine is rather small.[4,30,35–40] Most of these aziridine to diamine reactions require an electron-withdrawing group on the nitrogen, and usually a strong nucleophile, such as azide, to open the ring. Alternatively, the aziridine first can be converted to an aziridinium ion, which can then be ring-opened with a large variety of nucleophiles.[41–44] As shown in Scheme 4 and Table 4, we have accomplished the conversion of an *N*-alkyl aziridine to a 1,2-diamine using neither an electron-withdrawing group nor pre-formation of an aziridininum ion.

Using $(CH_3)_2N^+{=}CH_2$ as the iminium salt, the R_1 and R_2 groups of the aziridine were varied to determine the regiochemistry of this transformation. These reactions were run by refluxing the aziridine and LiI, and then stirring with the iminium salt at room temperature for an extended period.

Table 4 Products and Yields for the Reactions of **1** with LiI and Dimethylmethylene Iminium Chloride

Aziridine	Product	Yield
1a	**4a**	85%
1b	**4b**	71%
1c	**5c**	71%
1d	**5d**	16%
1e	**5e**	22%



a $R^1 = CH_2Ph$ $R^2 = CH_3$ $R^3 = H$
b R^1 = pentyl $R^2 = CH_3$ $R^3 = H$
c $R^1 = CH_2Ph$ R^2 = Ph $R^3 = H$
d R^1 = Ph R^2 = Ph $R^3 = H$
e R^1 = Ph R^2 = butyl $R^3 = H$
f $R^1 = CH_2Ph$ $R^2, R^3 = -(CH_2)_4-$
g $R^1 = CH_2Ph$ $R^2 = CH_3$ $R^3 = CH_3$
h $R^1 = CH_2Ph$ R^2 = Ph R^3 = Ph

Scheme 4

For compounds **1a** and **1b**, when the nitrogen and a carbon are both substituted by alkyl groups, it is the less substituted carbon-nitrogen bond that is broken to give products **4a** and **4b**, respectively. Unlike the reactions of alkyl substituted aziridines with LiI and CO_2 using only THF as the solvent, for the iminium reactions, at most only a trace of the other regioisomer can be detected by ^1H NMR spectroscopy or GC–MS. When carbon-2 is substituted by a phenyl group as in **1c**, the more substituted carbon-nitrogen bond is broken to give **5c**. This change in regiochemistry also was observed in the oxazolidinone chemistry.

In contrast to the oxazolidinone chemistry, an *N*-phenyl aziridine does react under the iminium reaction conditions. With **1d** (the diphenyl case), the more substituted carbon-nitrogen bond is broken to give **5d**. Unfortunately, the isolated yield is very low and a large amount of intractable material is obtained. For aziridine **1e**, in which the nitrogen is substituted by a phenyl and the carbon by an alkyl, it is also the more substituted carbon-nitrogen bond that is broken to give **5e**. Only a trace of **4e** was observed. As with **1d**, the yield is rather low. For the two *N*-phenyl aziridines, the lack of reactivity with CO_2 and the low yield in the reaction with the iminium salt probably is due to the reduced nucleophilicity/basicity of a phenyl-substituted nitrogen (an aniline derivative) versus an alkyl-substituted nitrogen (an alkyl amine derivative).

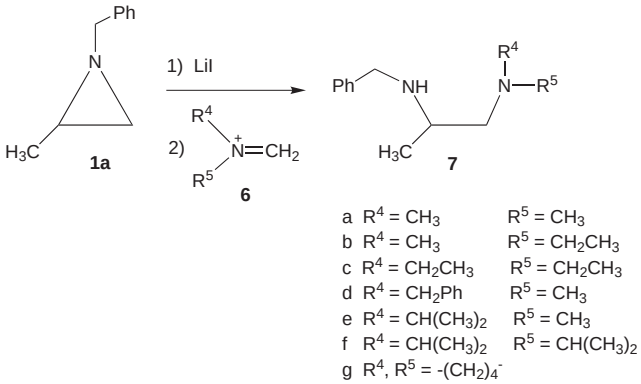
To determine the stereochemistry of this transformation, we studied 2,3-disubstituted aziridines **1f** and **1g**. Compound **1h** was not used because, as discussed above, it is inert to our LiI reaction conditions. The reaction of aziridine **1f** gives 1,2-diaminocyclohexane **4f** as the product. If the two amino groups are *trans*, a large diaxial coupling between the hydrogen at C-1 and the hydrogen at C-2 should be observed. In contrast, if the two amines are *cis*, the *J* value will be small.[44] A *J* value of 2.4 Hz was obtained, which indicates that the two amino groups are *cis*. Thus, this transformation goes with net retention of stereochemistry.

For 2,3-dimethylaziridine **1g**, the reaction is stereospecific, i.e., the *cis* stereoisomer of the starting material gives one stereoisomer of the product and the *trans* stereoisomer of the starting material gives the other stereoisomer of the product. (This was determined by the differences in the chemical shifts of the two products. The product from *cis*-**1g** has its methyl groups at 1.09 ppm and 1.14 ppm and the hydrogens at C-1 and C-2 at 2.3 ppm and 2.9 ppm. The product from *trans*-**1g** has its methyl groups at 0.8 ppm and 1.0 ppm and the hydrogens at C-1 and C-2 at 2.2 ppm and 2.3 ppm.)

The stereochemistry of the product diamine was determined by the chemical shifts and coupling constants of the hydrogens at C-1 and C-2.[45] We found that *cis*-**1g** generates *erythro*-**4g** and that *trans*-**1g** generates *threo*-**4g**. Thus, as with the cyclohexane case, this reaction goes with net retention of stereochemistry.

For the reaction with CO_2, it was found that the stereospecificity improved as the amount of LiI added was decreased. In contrast, for the reaction with the iminium salt, the product is stereospecific even when one equivalent of LiI was added.

As shown in Scheme 5 and Table 5, aziridine **1a** was reacted with a variety of iminium salts (**6**) to determine the variety of substituents that could be used.



Scheme 5

Table 5 Products and Yields for the Reactions of **1a** with LiI and Various Dialkylmethylene Iminium Chlorides **6**

Dialkylmethylene iminium chloride	Product	Yield
6a	**7a** (= **4a**)	85%
6b	**7b**	69%
6c	**7c**	63%
6d	**7d**	78%
6e	**7e**	65%
6f	**7f**	0%
6g	**7g**	80%

In all cases, the methylene is lost and the two alkyl groups are retained in the product diamine (**7**). This result implies that the iminium salts are stable to hydrogen scrambling under the reaction conditions. All reactions proceed in good yield except for the diisopropyl case (**6f**), which does not react at all. We suspect this lack of reactivity is due to the large size of the two isopropyl groups.

Because a *gem*-aminoether, as shown in Scheme 2, is the immediate precursor to the iminium salt, it was of interest to determine if an aminoether would undergo similar reactions with an aziridine. Although the aminoethers have the advantage of being less air-sensitive than the iminium salts, in most cases, they were very difficult to isolate due to their volatility. An exception is the aminoether corresponding to iminium salt **6d**, which has a benzyl substituent. It was found that the yield was much higher when using the iminium salt (78% yield) than when using the aminoether (53% yield).

Conversion of an Aziridine to a 1,2-Diamine Without Using LiI

As discussed above, no reaction occurred when an aziridine and CO_2 are mixed in the absence of LiI. In contrast, simply stirring an *N*-alkyl aziridine and an iminium salt at room temperature generates a diamine. Comparing the data in Tables 6 and 7 with the data in Tables 4 and 5 shows that the product is exactly the same and the yield is nearly the same in the presence of and in the absence of added LiI.

Table 6 Products and Yields for the Reactions of **1** with Dimethylmethylene Iminium Chloride

Aziridine	Product	Yield
1a	**4a**	98%
1b	**4b**	76%
1c	**5c**	79%
1d	**5d**	10%
1e	**5e**	46%

Table 7 Products and Yields for the Reactions of **1a** with Various Dialkylmethylene Iminium Chlorides **6**

Dialkylmethylene iminium chloride	Product	Yield
6a	**7a (= 4a)**	98%
6b	**7b**	74%
6c	**7c**	76%
6d	**7d**	94%
6e	**7e**	73%
6f	**7f**	0%
6g	**7g**	70%

The similarity of the results with and without added LiI naturally raised concern about the reactivity of compound **1** and LiI. In other words, were **1** and LiI actually reacting to give an intermediate, or was LiI not doing anything and so its presence made no difference to the reaction? When a dilute solution of compound **1** is concentrated, compound **1** is stable and can be isolated. However, as discussed above (Scheme 1), when the reaction solution of **1** with LiI is concentrated, a piperazine, which is a six-membered ring dimer of compound **1**, is formed. Therefore, immediately after compound **1** was refluxed with LiI, some of the reaction solution was removed and concentrated. For all the aziridines except **1h**, which does not react with LiI, the resulting product was not **1** but was exclusively the dimer of **1**. Thus, it is believed that a reaction with LiI did occur prior to the addition of the iminium salt. Therefore, these two different reactions (the reaction with and the reaction without added LiI) give similar results.

There are two major exceptions to the similarity of these two reactions:

(1) For the reaction of cyclohexane derivative **1f**, in the presence of LiI, the product diamine **4f** has *cis* stereochemistry (Scheme 4). In contrast, for the reaction without added LiI, a *J* value of 9.7 Hz was obtained, which indicates that the two amino groups are *trans*. Thus, unlike the reaction with LiI, this transformation goes with net inversion of stereochemistry.

(2) With either *cis*- or *trans*-diphenylaziridine **1h**, as mentioned above, there is no reaction with LiI. However, the direct reaction of **1h** with the dimethylmethylene iminium chloride does generate diamine **4h**. This reaction is stereospecific, i.e., the ^{1}H NMR spectrum of the product from *cis*-**1h** has the hydrogens at C-1 and C-2 at 3.2 ppm and 4.2 ppm and the ^{1}H NMR spectrum of the product from *trans*-**1h** has the hydrogens at C-1 and C-2 at 3.7 ppm and 4.0 ppm. As with dimethylazirdine **1g**, based on the chemical shifts and coupling constants,[45] *cis*-**1h** generates *erythro*-**4h** and *trans*-**1h** generates *threo*-**4h**. Thus, this reaction, which does not require LiI, goes with net retention of stereochemistry.

The formation of an oxazolidinone or a 1,2-diamine from a readily available *N*-alkyl substituted aziridine was studied. Our reaction involves starting with an *N*-alkyl aziridine and LiI, and then adding an electrophile. When the electrophile is CO_2, an oxazolidinone is formed. When the electrophile is an iminium salt, after an aqueous work-up, a 1,2-diamine is formed. It was found that when the aziridine is substituted by only alkyl groups, it is the less substituted carbon-nitrogen bond that is broken; whereas, when the aziridine is substituted by a phenyl group at either the nitrogen or the carbon, it is the more substituted carbon-nitrogen bond that is broken. For a 2,3-disubstituted aziridine, the reaction with CO_2 or with the iminium salt goes with net retention of stereochemistry.

It was also discovered that the iminium salt reaction works without added LiI. Here the regiochemistry is the same as in the presence of LiI. In addition, for a 2,3-disubstituted aziridine with no added LiI, the reaction goes with net retention. However, the cyclohexane-substituted aziridine goes with net inversion of stereochemistry.

Note Added to the Proof

In a paper published after this paper was accepted (Miller, A. W.; Nguyen, S. T. *Org. Lett.* **2004**, *6*, 2301), it was found that CO_2 in the presence of a (salen)Cr(III) complex can be used to convert an aziridine into an oxazolidine. For a 2-phenylaziridine, they found results very similar to ours. For a 2-alkylaziridine, our major product is the 4-alkyloxazolidinone and their major product is the 5-alkyloxazolidinone, and thus, the two methods are complementary. No comparison of stereochemistry between the two methods can be made because the only 2,3-disubstituted compound used by Miller and Nguyen is the cyclohexane derivative.

All reactions were carried out using oven-dried glassware that was cooled under an Ar atmosphere or in a desiccator. All reactions were carried out under an Ar atmosphere unless otherwise noted. In all cases, the product is an oil that could be easily purified (when necessary) by using a short alumina column in a disposable pipette, eluting with CH_2Cl_2 and EtOAc, to give the corresponding product. All yields, except where it is indicated that an inseparable mixture was obtained, are of isolated material.

THF was freshly distilled from potassium benzophenone ketyl. Benzyl bromide was distilled prior to use. Et_3N was distilled from barium oxide. All other chemicals were purchased from Aldrich and used without further purification, unless otherwise noted. Appropriate precautions were taken because 2-methylaziridine, according to Aldrich, is highly toxic and a cancer suspect agent.

All NMR spectra were recorded on a Bruker 250 MHz NMR spectrometer in $CDCl_3$, unless otherwise noted, with chemical shifts referenced to TMS at 0.00 ppm. All GC–MS spectra were recorded on a Hewlett Packard 6890, equipped with a SPB-1 capillary column. The initial injection temperature was 70 °C; the temperature was then raised to 315 °C at 10 °C/min and held at 315 °C for 5 min. IR spectra were recorded on a Perkin Elmer Spectrum One FTIR spectrophotometer using a KBr cell with a path length of 0.05 mm. All spectra were recorded in $CHCl_3$ unless otherwise noted. HRMS spectra were obtained on an Ion Spec FT-ICR using electrospray ionization. Spectroscopic data for compounds **2a**, **2f**, **3a**, **3c**, **4**, **5**, and **7** have been reported previously.[5,19,23,27,28]

CO_2-Bubbling Method for the Conversion of an Aziridine to an Oxazolidinone; General Procedure

A mixture of the aziridine and LiI in THF (30 mL) was allowed to reflux for 15 min. CO_2 was then bubbled through this reaction mixture for 4 h at r.t. After this time, the mixture was added to Et_2O (50 mL) and washed with 10% sodium bisulfite (25 mL). The ethereal solution was washed with water (3 × 30 mL). The ethereal solution was dried with anhyd K_2CO_3, filtered, and evaporated to dryness yielding the corresponding oxazolidinone.

Reaction of Aziridine 1a

The reaction of aziridine **1a** (0.15 g, 1.0 mmol), LiI (0.20 g, 1.5 mmol), and CO_2 generated **2a** (0.098 g, 0.51 mmol, 51% yield) and **3a** (0.062 g, 0.32 mmol, 32% yield).

Reaction of Aziridine 1b

The reaction of aziridine **1b** (0.13 g, 1.0 mmol), LiI (0.20 g, 1.5 mmol), and CO_2 generated **2b** (0.097 g, 0.57 mmol, 57% yield) and **3b** (0.049 g, 0.29 mmol, 29% yield). Compounds **2b** and **3b** were obtained as an inseparable mixture, and thus, the reported data are for a mixture of both **2b** and **3b**.

IR: 1747 cm^{-1}.

^1H NMR: δ = 0.91 (t, *J* = 6.7 Hz, 3 H), 1.27 (d, *J* = 5.9 Hz, 2 H), 1.30–1.39 (m, 0.33 H), 1.43 (d, *J* = 6.1 Hz, 0.67 H), 1.46–1.58 (m, 1.67 H), 1.63 (br s, 0.67 H), 2.83 (d, *J* = 4.9 Hz, 0.33 H), 2.93–3.17 (m, 1.33 H), 3.20–3.30 (m, 0.67 H), 3.33–3.47 (m, 0.67 H), 3.63 (t, *J* = 8.5 Hz, 0.33 H), 3.79–3.95 (m, 1.33 H), 4.39 (t, *J* = 7.3 Hz, 0.67 H), 4.58–4.68 (m, 0.33 H).

^{13}C NMR: δ = 14.09, 18.30, 20.87, 22.47, 27.19, 28.89, 29.02, 41.72, 44.21, 50.96, 51.47, 68.98, 69.90, 158.21.

MS: *m*/*z* = 171 (5.4), 156 (19.0), 142 (34.8), 115 (28.8), 114 (82.6), 70 (100), 56 (9.8).

HRMS: *m*/*z* calcd for $C_9H_{18}NO_2^+$: 172.1337; found: 172.1331.

Reaction of Aziridine 1c

The reaction of aziridine **1c** (0.21 g, 1.0 mmol), LiI (0.20 g, 1.5 mmol), and CO_2 generated **3c** (0.25 g, 0.99 mmol, 99% yield).

Reaction of Aziridine 1d

The reaction of aziridine **1d** (0.20 g, 1.0 mmol), LiI (0.20 g, 1.5 mmol), and CO_2 generated no oxazolidinone. Aziridine **1d** (0.19 g, 0.95 mmol) was recovered.

Reaction of Aziridine 1e

The reaction of aziridine **1e** (0.18 g, 1.0 mmol), LiI (0.20 g, 1.5 mmol), and CO_2 generated no oxazolidinone. Aziridine **1e** (0.18 g, 1.0 mmol) was recovered.

High Pressure CO_2 Method for the Conversion of an Aziridine to an Oxazolidinone with or without Added HMPA; General Procedure

A mixture of the aziridine, LiI, and HMPA (when needed) in THF (15 mL) was added to a 25 mL heavy walled round bottom flask that contained a threaded Teflon plug (Ace Glass). This reaction mixture was then cooled to –78 °C, and powdered dry ice (CO_2, 8.0 g 180 mmol) was added in two portions. The round bottom flask was then capped with the threaded Teflon plug and allowed to warm to r.t. The reaction mixture was stirred overnight at r.t., unless otherwise noted. After that, the mixture was again cooled to –78 °C and the pressure was released by slowly removing the Teflon plug. The mixture was added to Et_2O (50 mL) and washed with 10% sodium bisulfite (25 mL). The ethereal solution was washed with water (3 × 30 mL). The ethereal solution was dried with anhyd K_2CO_3, filtered, and evaporated to dryness yielding the corresponding oxazolidinone.

Reaction of Aziridine 1a with Added HMPA

The reaction of aziridine **1a** (0.059 g, 0.40 mmol), LiI (0.056 g, 0.40 mmol), and CO_2 with added HMPA (0.072 g, 0.40 mmol) generated **2a** (0.067 g, 0.35 mmol, 88% yield) and **3a** (0.002 g, 0.01 mmol, 3% yield).

Reaction of Aziridine 1b with Added HMPA

Aziridine **1b** (0.051 g, 0.40 mmol), LiI (0.056 g, 0.40 mmol), and CO_2 with added HMPA (0.072 g, 0.40 mmol) generated **2b** (0.058 g, 0.34 mmol, 84% yield) and **3b** (0.002 g, 0.01 mmol, 4% yield).

2b

IR: 1747 cm^{-1}.

^1H NMR: δ = 0.91 (t, *J* = 6.7 Hz, 3 H), 1.27 (d, *J* = 5.9 Hz, 3 H), 1.30–1.39 (m, 4 H), 1.46–1.58 (m, 2 H), 2.93–3.17 (m, 1 H), 3.33–3.47 (m, 1 H), 3.79–3.95 (m, 2 H), 4.39 (t, *J* = 7.3 Hz, 1 H).

^{13}C NMR: δ = 14.09, 18.30, 22.47, 27.19, 41.72, 50.96, 68.98, 158.21.

Reaction of Aziridine 1f

The reaction of aziridine **1f** (0.075 g, 0.40 mmol), LiI (0.014 g, 0.10 mmol), and CO_2 generated **2f** (0.083 g, 0.36 mmol, 90% yield).

Reaction of Aziridine *cis*-1g

The reaction of aziridine *cis*-**1g** (0.064 g, 0.40 mmol), LiI (0.014 g, 0.10 mmol), and CO_2 at 70 ºC generated *cis*-**2g** (0.070 g, 0.34 mmol, 86% yield).

IR: 1739 cm^{-1}.

^1H NMR: δ = 1.10 (d, *J* = 6.2 Hz, 3 H), 1.33 (d, *J* = 5.6 Hz, 3 H), 3.65 (pent, *J* = 6.8 Hz, 1 H), 4.03 (d, *J* = 14.9 Hz, 1 H), 4.61 (pent, *J* = 6.7 Hz, 1 H), 4.82 (d, *J* = 15.5 Hz, 1 H), 7.26–7.34 (m, 5 H).

^{13}C NMR: δ = 12.61, 15.05, 45.85, 53.19, 73.78, 127.96–128.88, 136.40, 158.08.

MS: *m*/*z* = 205 (30.4), 150 (40.8), 106 (33.7), 92 (14.1), 91 (100), 79 (14.2), 65 (20.7), 56 (17.9).

HRMS: *m*/*z* calcd for $C_{12}H_{16}NO_2^+$: 206.1181; found: 206.1171.

Reaction of Aziridine *trans*-1g

The reaction of aziridine *trans*-**1g** (0.064 g, 0.40 mmol), LiI (0.014 g, 0.10 mmol), and CO_2 at 70 ºC generated *trans*-**2g** (0.068 g, 0.33 mmol, 84% yield).

^{1}H NMR: δ = 1.18 (d, *J* = 6.2 Hz, 3 H), 1.33 (d, *J* = 6.1 Hz, 3 H), 3.18 (pent, *J* = 6.5 Hz, 1 H), 4.09 (d, *J* = 14.9 Hz, 1 H), 4.11 (pent, *J* = 6.5 Hz, 1 H), 4.76 (d, *J* = 15.2 Hz, 1 H), 7.26–7.34 (m, 5 H).

^{13}C NMR: δ = 17.46, 19.32, 45.90, 57.46, 127.96–128.93, 136.19, 158.08.

^{13}C NMR (CD_3CN): δ = 17.55, 19.32, 46.25, 58.65, 78.47, 128.47–129.61, 138.05.

The determination of the stereochemistry of oxazolidinones *cis*-**1g** and *trans*-**1g** was accomplished by comparing the ^{1}H NMR spectrum for each compound. It has been shown in the literature[29] that for similar oxazolidinones, the methyl groups at C-4 and C-5 are at higher field in the *cis* isomer than in the *trans* isomer. In addition, the methine protons at C-4 and C-5 are at lower field in the *cis* isomer than in the *trans* isomer.

Reaction of Aziridine *cis*-1h

The reaction of aziridine *cis*-**1h** (0.11 g, 0.40 mmol), LiI (0.054 g, 0.40 mmol), and CO_2 at 70 ºC generated no oxazolidinone. Aziridine *cis*-**1h** (0.10 g, 0.36 mmol) was recovered.

Reaction of Aziridine *trans*-1h

The reaction of aziridine *trans*-**1h** (0.11 g, 0.40 mmol), LiI (0.054 g, 0.40 mmol), and CO_2 at 70 ºC generated no oxazolidinone. Aziridine *trans*-**1h** (0.11 g, 0.40 mmol) was recovered.

Conversion of an Aziridine to a Diamine in the Presence of Lithium Iodide; General Procedure

A mixture of the aziridine and LiI in THF (30 mL) was allowed to reflux for 15 min. This reaction was cooled to r.t. Then the iminium salt was added and the solution was stirred at 25 °C. After 20 h, the reaction mixture was added to Et_2O (50 mL). Then the mixture was treated with water (100 mL) and made acidic (pH = 2 or 3, as determined by pH paper) with HCl. The water was removed and made basic (pH = 10 or 11, as determined by pH paper) with NaOH. Finally, the water was extracted with Et_2O (3 × 50 mL). The Et_2O solutions were mixed together, dried with anhyd K_2CO_3, filtered, and evaporated to dryness.

Reaction of Aziridine 1a with Lithium Iodide and *N,N*-Dimethylmethylene Iminium Chloride

The reaction of aziridine **1a** (0.15 g, 1.0 mmol), LiI (0.20 g, 1.5 mmol), and *N,N*-dimethylmethylene iminium chloride (0.10 g, 1.0 mmol) generated **4a** (0.16 g, 0.85 mmol, 85% yield).

Reaction of Aziridine 1b with Lithium Iodide and *N,N*-Dimethylmethylene Iminium Chloride

The reaction of aziridine **1b** (0.13 g, 1.0 mmol), LiI (0.20 g, 1.5 mmol), and *N,N*-dimethylmethylene iminium chloride (0.10 g, 1.0 mmol) generated **4b** (0.12 g, 0.71 mmol, 71% yield), plus a trace amount of an isomeric compound that is believed to be **5b**.

Reaction of Aziridine 1c with Lithium Iodide and *N,N*-Dimethylmethylene Iminium Chloride

The reaction of aziridine **1c** (0.21 g, 1.0 mmol), LiI (0.20 g, 1.5 mmol), and *N,N*-dimethylmethylene iminium chloride (0.10 g, 1.0 mmol) generated **5c** (0.18 g, 0.71 mmol, 71% yield), plus a trace amount of an isomeric compound that is believed to be **4c**.

Reaction of Aziridine 1d with Lithium Iodide and *N,N*-Dimethylmethylene Iminium Chloride

The reaction of aziridine **1d** (0.20 g, 1.0 mmol), LiI (0.20 g, 1.5 mmol), and *N,N*-dimethylmethylene iminium chloride (0.10 g, 1.0 mmol) generated **5d** (0.04 g, 0.16 mmol, 16% yield), plus a trace amount of an isomeric compound that is believed to be **4d**.

Reaction of Aziridine 1e with Lithium Iodide and *N,N*-Dimethylmethylene Iminium Chloride

The reaction of aziridine **1e** (0.18 g, 1.0 mmol), LiI (0.20 g, 1.5 mmol), and *N,N*-dimethylmethylene iminium chloride (0.10 g, 1.0 mmol) generated **5e** (0.05 g, 0.22 mmol, 22% yield), plus a trace amount of an isomeric compound that is believed to be **4e**.

Reaction of Aziridine 1f with Lithium Iodide and *N,N*-Dimethylmethylene Iminium Chloride

The reaction of aziridine **1f** (0.19 g, 1.0 mmol), LiI (0.20 g, 1.5 mmol), and *N,N*-dimethylmethylene iminium chloride (0.10 g, 1.0 mmol) generated *cis*-**4f** (0.19 g, 0.83 mmol, 83% yield).

Reaction of Aziridine 1g with Lithium Iodide and *N,N*-Dimethylmethylene Iminium Chloride

The reaction of aziridine *trans*-**1g** (0.16 g, 1.0 mmol), LiI (0.20 g, 1.5 mmol), and mmol) *N,N*-dimethylmethylene iminium chloride (0.10 g, 1.0 mmol) generated one stereoisomer **4g** (0.18 g, 0.90 mmol, 90% yield) and the reaction of aziridine *cis*-**1g** (0.16 g, 1.0 mmol), LiI (0.20 g, 1.5 mmol), and *N,N*-dimethylmethylene iminium chloride (0.10 g, 1.0 mmol) generated the other stereoisomer of **4g** (0.19 g, 0.94 mmol, 94% yield).

Reaction of Aziridine 1a with Lithium Iodide and *N,N*-Ethylmethylmethylene Iminium Chloride (6b)

The reaction of aziridine **1a** (0.15 g, 1.0 mmol), LiI (0.20 g, 1.5 mmol), and *N,N*-ethylmethylmethylene iminium chloride (**6b**, 0.11 g, 1.0 mmol) generated **7b** (0.14 g, 0.69 mmol, 69% yield).

Reaction of Aziridine 1a with Lithium Iodide and *N,N*-Diethylmethylene Iminium Chloride (6c)

The reaction of aziridine **1a** (0.15 g, 1.0 mmol), LiI (0.20 g, 1.5 mmol), and *N,N*-diethylmethylene iminium chloride (**6c**, 0.12 g, 1.0 mmol) generated **7c** (0.14 g, 0.63 mmol, 63% yield).

Reaction of Aziridine 1a with Lithium Iodide and *N,N*-Benzylmethylmethylene Iminium Chloride (6d)

The reaction of aziridine **1a** (0.15 g, 1.0 mmol), LiI (0.20 g, 1.5 mmol), and *N,N*-benzylmethylmethylene iminium chloride (**6d**, 0.17 g, 1.0 mmol) generated **7d** (0.21 g, 0.78 mmol, 78% yield).

Reaction of Aziridine 1a with Lithium Iodide and *N,N*-Isopropylmethylmethylene Iminium Chloride (6e)

The reaction of aziridine **1a** (0.15 g, 1.0 mmol), LiI (0.20 g, 1.5 mmol), and *N,N*-isopropylmethylmethylene iminium chloride (**6e**, 0.12 g, 1.0 mmol) generated **6e** (0.14 g, 0.65 mmol, 65% yield).

Reaction of Aziridine 1a with Lithium Iodide and *N,N*-Diisopropylmethylene Iminium Chloride (6f)

The reaction of aziridine **1a** (0.15 g, 1.0 mmol), LiI (0.20 g, 1.5 mmol), and *N,N*-diisopropylmethylene iminium chloride (**6f**, 0.15 g, 1.0 mmol) gave **1a** (0.13 g) and a dimer of **1a** in a 1:6 ratio.

Reaction of Aziridine 1a with Lithium Iodide and *N,N*-Piperidylmethylene Iminium Chloride (6g)

The reaction of aziridine **1a** (0.15 g, 1.0 mmol), LiI (0.20 g, 1.5 mmol), and *N,N*-piperidylmethylene iminium chloride (**6g**, 0.13 g, 1.0 mmol) generated **7g** (0.19 g, 0.80 mmol, 80% yield).

Reaction of Aziridine 1a with Lithium Iodide and Benzyl Methoxymethyl Methylamine

The reaction of aziridine **1a** (0.15 g, 1.0 mmol), LiI (0.20 g, 1.5 mmol), and benzyl methoxymethyl methylamine (0.17 g, 1.0 mmol) gave **7d** (0.14 g, 0.53 mmol, 53% yield).

Conversion of an Aziridine to a Diamine in the Absence of Added Lithium Iodide; General Procedure

A mixture of the aziridine and the iminium salt in THF (30 mL) was allowed to stir at 25 °C. After 20 h, the reaction mixture was added to Et_2O (50 mL). Then the mixture was treated with water (100 mL) and made acidic (pH = 2 or 3, as determined by pH paper) with HCl. The water was removed and made basic (pH = 10 or 11, as determined by pH paper) with NaOH. Finally, the water was extracted with Et_2O (3 × 50 mL). The Et_2O solutions were mixed together, dried with anhyd K_2CO_3, filtered, and evaporated to dryness.

Reaction of Aziridine 1a with *N,N*-Dimethylmethylene Iminium Chloride

The reaction of aziridine **1a** (0.15 g, 1.0 mmol) and *N,N*-dimethylmethylene iminium chloride (0.10 g, 1.0 mmol) generated **4a** (0.19 g, 0.98 mmol, 98% yield), plus a trace amount of an isomeric compound that is believed to be **5a**.

Reaction of Aziridine 1b with *N,N*-Dimethylmethylene Iminium Chloride

The reaction of aziridine **1b** (0.13 g, 1.0 mmol) and *N,N*-dimethylmethylene iminium chloride (0.10 g, 1.0 mmol) generated **4b** (0.13 g, 0.76 mmol, 76% yield), plus a trace amount of an isomeric compound that is believed to be **5b**.

Reaction of Aziridine 1c with *N,N*-Dimethylmethylene Iminium Chloride

The reaction of aziridine **1c** (0.21 g, 1.0 mmol) and *N,N*-dimethylmethylene iminium chloride (0.10 g, 1.0 mmol) generated **5c** (0.20 g, 0.79 mmol, 79% yield), plus a trace amount of an isomeric compound that is believed to be **4c**.

Reaction of Aziridine 1d with *N,N*-Dimethylmethylene Iminium Chloride

The reaction of aziridine **1d** (0.20 g, 1.0 mmol) and *N,N*-dimethylmethylene iminium chloride (0.10 g, 1.0 mmol) generated **5d** (0.02 g, 0.10 mmol, 10% yield), plus a trace amount of an isomeric compound that is believed to be **4d**.

Reaction of Aziridine 1e with *N,N*-Dimethylmethylene Iminium Chloride

The reaction of aziridine **1e** (0.18 g, 1.0 mmol) and *N,N*-dimethylmethylene iminium chloride (0.10 g, 1.0 mmol) generated **5e** (0.10 g, 0.46 mmol, 46% yield), plus a trace amount of an isomeric compound that is believed to be **4e**.

Reaction of Aziridine 1f with *N,N*-Dimethylmethylene Iminium Chloride

The reaction of aziridine **1f** (0.19 g, 1.0 mmol) and *N,N*-dimethylmethylene iminium chloride (0.10 g, 1.0 mmol) generated *trans*-**4f** (0.19 g, 0.81 mmol, 81% yield).

IR: 3065 (w), 3028 (w), 2936 (m), 2858 (m), 2822 (m), 2776 (m), 2247 (w), 2200 (w), 1495 (w), 1453 (w), 1378 (w), 1359 (w), 1339 (w), 1180 (w), 1130 (w), 1042 (w), 918 (s), 899 (s), 749 (s), 732 (s) cm^{-1}.

^1H NMR: δ = 1.15–1.34 (m, 3 H), 1.65–1.78 (m, 3 H), 2.11–2.26 (m, 8 H), 2.60 (td, *J* = 4.0, 9.8 Hz, 1 H), 3.71 (d, *J* = 13.1 Hz, 1 H), 3.84 (td, *J* = 4.1, 9.6 Hz, 1 H), 3.90 (d, *J* = 13.0 Hz, 1 H), 7.22–7.34 (m, 5 H).

^{13}C NMR: δ = 20.71, 24.25, 26.02, 31.59, 36.19, 38.60, 50.84, 62.73, 65.96, 127.07–128.59, 140.45.

MS: *m*/*z* = 231 (20.6), 187 (65.0), 141 (37.2), 124 (54.0), 106 (42.5), 96 (49.1), 91 (100), 84 (61.7), 58 (67.7).

HRMS: *m*/*z* calcd for $C_{15}H_{25}N_2^+$: 233.2018; found: 233.2055.

Reaction of Aziridine *trans*-1g with *N,N*-Dimethylmethylene Iminium Chloride

The reaction of aziridine *trans*-**1g** (0.16 g, 1.0 mmol) and *N,N*-dimethylmethylene iminium chloride (0.10 g, 1.0 mmol) generated 0.18 g (0.90 mmol, 90% yield) of the same product as is obtained in the presence of LiI.

Reaction of Aziridine *cis*-1g with *N,N*-Dimethylmethylene Iminium Chloride

The reaction of aziridine *cis*-**1g** (0.16 g, 1.0 mmol) and *N,N*-dimethylmethylene iminium chloride (0.10 g, 1.0 mmol) generated 0.19 g (0.93 mmol, 93% yield) of the same product as is obtained in the presence of LiI.

Reaction of Aziridine *trans*-1h with *N,N*-Dimethylmethylene Iminium Chloride

The reaction of aziridine *trans*-**1h** (0.28 g, 1.0 mmol) and *N,N*-dimethylmethylene iminium chloride (0.10 g, 1.0 mmol) generated *threo*-**4h** (0.17 g, 0.50 mmol, 50% yield).

IR: 3064 (w), 3029 (m), 2956 (w), 2865 (w), 2824 (m), 2781 (m), 2250 (m), 1494 (w), 1454 (m), 1367 (w), 1250 (w), 1029 (w), 918 (s), 732 (s), 651 (s) cm^{-1}.

^1H NMR: δ = 2.07 (s, 6 H), 3.46 (d, *J* = 13.5 Hz, 1 H), 3.69 (d, *J* = 10.8 Hz, 1 H), 3.76 (d, *J* = 13.5 Hz, 1 H), 4.04 (d, *J* = 10.7 Hz, 1 H), 6.92–7.35 (m, 15 H).

^{13}C NMR: δ = 40.66, 51.13, 61.34, 74.33, 126.91–130.07, 133.25, 140.84, 141.32.

MS: *m*/*z* = 331 (0.1), 196 (13.2), 135 (13.2), 134 (100), 118 (6.9), 91 (47.1), 77 (4.9), 65 (8.0); HRMS: *m*/*z* calcd for $C_{23}H_{27}N_2^+$: 331.2174; found: 331.2140.

Reaction of Aziridine *cis*-1h with *N,N*-Dimethylmethylene Iminium Chloride

The reaction of aziridine *cis*-**1h** (0.28 g, 1.0 mmol) and *N,N*-dimethylmethylene iminium chloride (0.10 g, 1.0 mmol) generated *erythro*-**4h** (0.06 g, 0.18 mmol, 18% yield).

IR: 3064 (w), 3029 (m), 2956 (w), 2865 (w), 2824 (m), 2781 (m), 2250 (m), 1494 (w), 1454 (m), 1367 (w), 1250 (w), 1029 (w), 918 (s), 732 (s), 651 (s) cm^{-1}.

^1H NMR: δ = 2.09 (s, 6 H), 3.21 (d, *J* = 6.0 Hz, 1 H), 3.38 (d, *J* = 13.4 Hz, 1 H), 3.69 (d, *J* = 13.4 Hz, 1 H), 4.20 (d, *J* = 6.0 Hz, 1 H), 6.96–7.32 (m, 15 H).

^{13}C NMR: δ = 43.66, 51.38, 62.40, 77.24, 126.92–129.94, 137.09, 140.74, 141.55.

MS: *m*/*z* = 331 (0.1), 196 (13.2), 135 (13.2), 134 (100), 118 (6.9), 91 (47.1), 77 (4.9), 65 (8.0). HRMS: *m*/*z* calcd for $C_{23}H_{27}N_2^+$: 331.2174; found: 331.2152.

Reaction of Aziridine 1a with *N,N*-Ethylmethylmethylene Iminium Chloride 6b

The reaction of aziridine **1a** (0.15 g, 1.0 mmol) and *N,N*-ethylmethylmethylene iminium chloride (**6b**, 0.11 g, 1.0 mmol) generated **7b** (0.15 g, 0.74 mmol, 74% yield), plus a trace amount of an isomeric compound that is believed to be the other regioisomer.

Reaction of Aziridine 1a with *N,N*-Diethylmethylene Iminium Chloride 6c

The reaction of aziridine **1a** (0.15 g, 1.0 mmol) and *N,N*-diethylmethylene iminium chloride (**6c**, 0.12 g, 1.0 mmol) generated **7c** (0.17 g, 0.76 mmol, 76% yield).

Reaction of Aziridine 1a with *N,N*-Benzylmethylmethylene Iminium Chloride 6d

The reaction of aziridine **1a** (0.15 g, 1.0 mmol) and *N,N*-benzylmethylmethylene iminium chloride (**6d**, 0.17 g, 1.0 mmol) generated **7d** (0.25 g, 0.94 mmol, 94% yield).

Reaction of Aziridine 1a with *N,N*-Isopropylmethylmethylene Iminium Chloride 6e

The reaction of aziridine **1a** (0.15 g, 1.0 mmol) and *N,N*-isopropylmethylmethylene iminium chloride (**6e**, 0.12 g, 1.0 mmol) generated **7e** (0.16 g, 0.73 mmol, 73% yield).

Reaction of Aziridine 1a with *N,N*-Diisopropylmethylene Iminium Chloride 6f

The reaction of aziridine **1a** (0.15 g, 1.0 mmol) and *N,N*-diisopropylmethylene iminium chloride (**6f**, 0.15 g, 1.0 mmol) gave **1a** (0.13 g) and a dimer of **1a** in a 5:1 ratio.

Reaction of Aziridine 1a with *N,N*-Piperidylmethylene Iminium Chloride 6g

The reaction of aziridine **1a** (0.15 g, 1.0 mmol) and *N,N*-piperidylmethylene iminium chloride (**6g**, 0.13 g, 1.0 mmol) generated **7g** (0.16 g, 0.70 mmol, 70% yield).

Reaction of Aziridine 1a with Benzyl Methoxymethyl Methylamine

The reaction of aziridine **1a** (0.15 g, 1.0 mmol) and benzyl methoxymethyl methylamine (0.17 g, 1.0 mmol) generated **7d** (0.12 g, 0.45 mmol, 45% yield).

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