Articles

Iron Carbonyl Promoted Conversion of an Aziridine and an Amine Oxide to a 1,2-Diamine

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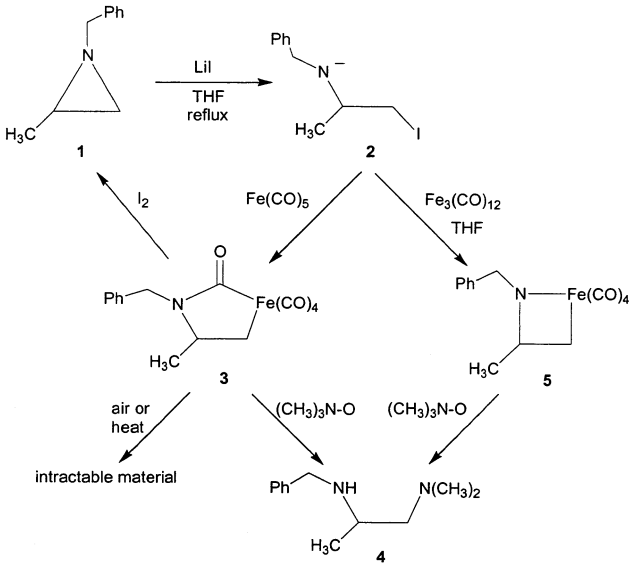
The conversion of an aziridine to a 1,2-diamine using an iron carbonyl complex and an amine oxide is studied. We have found that when the aziridine is substituted by only alkyl groups, it is the less substituted carbon−nitrogen bond that is broken, whereas, when the aziridine is substituted by a phenyl group at either the nitrogen or the carbon, it is the more substituted carbon−nitrogen bond that is broken. With a 2,3-disubstituted aziridine, the reaction proceeds with net retention of stereochemistry. Because the nitrogen in the amine oxide is trisubstituted and the same nitrogen in the product is disubstituted, various amine oxides have been tried to determine the preference for which group will be removed. We have shown that the intermediate iron complex will react with an iminium salt to give the exact same product as is obtained from the corresponding amine oxide.

As is evident from a recent, comprehensive review article,[1] 1,2-diamines or, as they are referred to in that paper, vicinal diamines are biologically and medically important compounds. In addition, they are important in organic synthesis as starting materials, as chiral auxiliaries, and as chiral ligands to a variety of metal complexes.[2−4]

Although there are known conversions of aziridines to 1,2-diamines, the number is rather small.[1,5−7] In addition, most require electron-withdrawing groups on the nitrogen and a strong nucleophile, such as azide, to open the ring. Alternatively, the aziridine can be converted to an aziridinium ion, which can then be ring-opened with a large variety of nucleophiles.[8,9]

A number of years ago, we discovered a novel three-step/one-pot conversion of an aziridine to a 1,2-diamine, shown in Scheme 1.[10] The first two steps of the reaction are (a) the reaction of LiI with aziridine **1** in refluxing THF to give the ring-opened compound **2** and (b) the reaction of **2** with $Fe(CO)_5$ to generate the ring-closed compound **3**. Our initial goal was to force complex **3** to undergo a reductive-elimination reaction to generate a β-lactam. However, unlike reductive-elimination reactions of nickel to form carbon−nitrogen bonds,[11,12] with iron complex **3** using heat or oxidants such as air and Ce(IV) only generated intractable material. When I_2 was used as the oxidant, aziridine **1** was regenerated. When the carbonyl removing agent[13] $(CH_3)_3N-O$ was used, diamine **4** was generated in 45% yield. Although the yield is moderate, the crude product is very clean and requires little purification.

Scheme 1



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(1) Lucet, D.; LeGall, T.; Mioskowski, C. *Angew. Chem., Int. Ed.* **1998**, *37*, 2581.
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Scheme 2

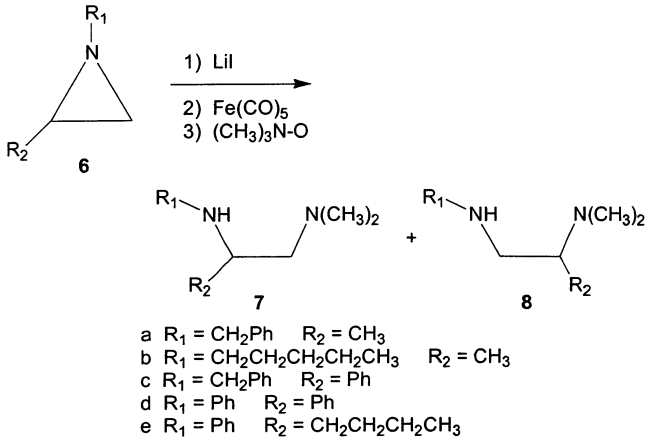


Table 1. Products from the Reaction of Various Aziridines with Trimethylamine Oxide

aziridine	product	yield, %	aziridine	product	yield, %
1 = **6a**	**4** = **7a**	45	**6d**	**8d**	13
6b	**7b**	40	**6e**	**8e**	47
6c	**8c**	46			

Because the final product does not contain a carbonyl, we next tried $Fe(CO)_4(THF)$, which is easily generated from $Fe_3(CO)_{12}$ and THF, as the iron source. Upon reaction of $Fe(CO)_4(THF)$ with **2**, metallacycle **5** was generated. Diamine **4** was again the only product from the reaction of **5** with $(CH_3)_3N-O$.

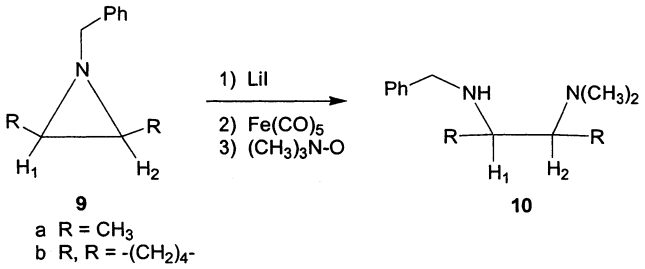
We next discovered that the conversion of **1** to **4** does not have to be done in three separate steps. It can be done in one step by simply stirring aziridine **1**, $Fe_3(CO)_{12}$, $(CH_3)_3N-O$, and LiI in THF overnight at room temperature in an open Erlenmeyer flask; i.e., the reaction is totally air stable!

In this paper, we have extended the scope of this reaction to include a variety of aziridines, amine oxides, and metal carbonyl sources. In addition, we have determined which bond of the aziridine is broken, we have determined the relative stereochemistry of the aziridine and the product diamine, and we have determined which group on the amine oxide is most likely to be lost. Finally, we have shown that the intermediate iron complex will react with an iminium salt to give the exact same product as is obtained from the corresponding amine oxide.

Results and Discussion

Variations in the Aziridine. In this section, we used $(CH_3)_3N-O$ as the amine oxide and varied the substituent on the aziridine. In each case, $Fe(CO)_5$ was used as the metal and the reaction was done in three separate steps. These conditions were chosen because they are the most general. As shown in Scheme 2 and Table 1, for compounds **6a** (this is equivalent to compound **1**) and **6b**, when the nitrogen and a carbon are both substituted by alkyl groups, it is the less substituted carbon−nitrogen bond which is broken to give products **7a** (this is equivalent to compound **4**) and **7b**, respectively. Neither of the regioisomers **8a** or **8b** can be detected by ^1H NMR spectroscopy or gas chromatography/mass spectrometry. (We estimate that we are getting at least a 25:1 ratio of **7** to **8**.)

Scheme 3



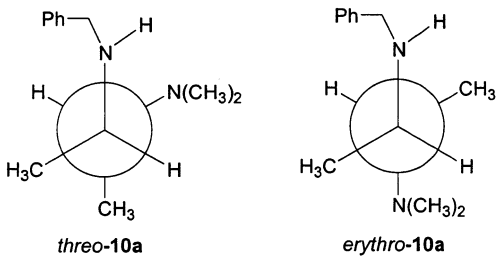
When carbon-2 is substituted by a phenyl group as in **6c**, it is the more substituted carbon−nitrogen bond that is broken exclusively to give **8c**. This change in regiochemistry has been observed previously for similar types of ring-opening reactions;[6−8] i.e., with alkyls it is the less substituted C−N bond and with aryls it is the more substituted C−N bond that is broken. With **6d** (the diphenyl case), the more substituted carbon−nitrogen bond also is broken to give **8d** as the only isolated product. Unfortunately, here the isolated yield is very low and we obtain a large amount of intractable material.

The one case that is surprising to us is **6e**, in which the nitrogen is substituted by a phenyl and the carbon by an alkyl. Here it is the more substituted carbon−nitrogen bond that is broken to give **8e**. No **7e** was observed. (As above, we estimate on the basis of baseline noise that we are getting at least a 25:1 ratio of the product observed to the product not observed.)

For 1-benzyl-2,3-dimethylaziridine (**9a**) 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 (Scheme 3). This was determined by the differences in the chemical shifts of the two products. (The product from *cis*-**9a** has its methyl groups at 1.09 and 1.14 ppm and H_1 and H_2 at 2.3 and 2.9 ppm. The product from *trans*-**9a** has its methyl groups at 0.8 and 1.0 ppm and H_1 and H_2 at 2.2 and 2.3 ppm.)

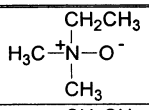
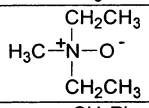
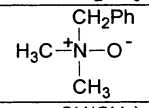
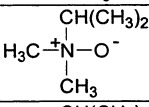
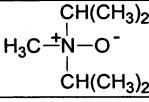
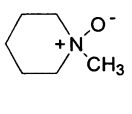
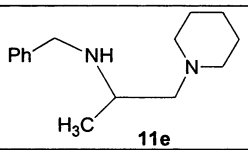
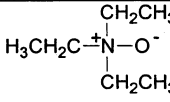
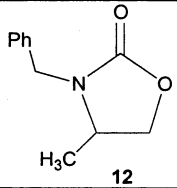
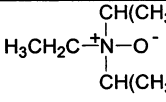
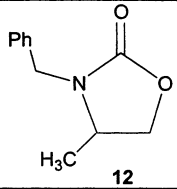
To determine the stereochemistry of each product, we attempted to use the H−H coupling constant between H_1 and H_2; however, this proved unsuccessful. First of all, the exact J value between H_1 and H_2 was hard to determine because each proton also is split by a methyl group. An approximate J value of 6 Hz could be obtained and was the same for each of the two isomers of product **10a**.

In an attempt to understand this result, we performed molecular mechanics calculations using the MMFF94 force filed package from SpartanPro. The lowest energy conformations of *threo*-**10a** and *erythro*-**10a** are



In the threo isomer, the two amino groups have a small

Table 2. Products from the Reaction of Aziridine 1 with Various Amine Oxides

Entry	Amine Oxide	Product(s) and Ratio	Overall Yield
1		**4** 29% **11a** 71%	70%
2		**11a** 67% **11b** 33%	48%
3		**4** 76% **11c** 24%	69%
4		**11d**	41%
5		**11d**	23%
6		 **11e**	31%
7		 **12**	45%
8		 **12**	25%

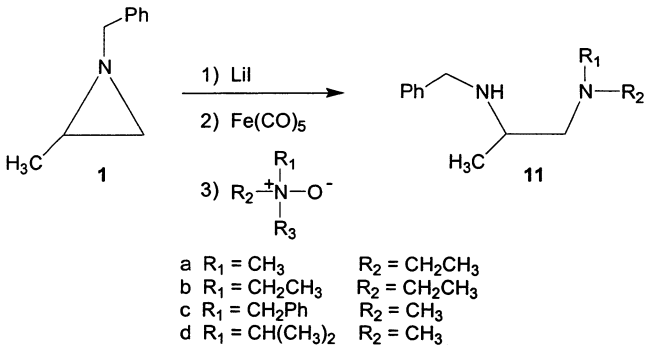
dihedral angle of 50° to allow hydrogen bonding, and the two hydrogens have a dihedral angle of 172°. In contrast, for the erythro isomer, the two amino groups have a very large dihedral angle of 175°, which causes the dihedral angle for the two hydrogens to be 177°. Because the H−C−C−H dihedral angle for the two isomers is approximately the same, it is now not surprising that the *J* values are so similar.

To eliminate the possibility of free rotation, we next tried aziridine **9b**, which gives 1,2-diaminocyclohexane **10b** as the product. If the two amine groups are trans, we should observe a large diaxial coupling between H_1 and H_2. In contrast, if the two amines are cis, the *J* value will be small. A *J* value of 2.4 Hz was obtained, which indicates that the two amino groups are cis. Thus, this transformation proceeds with net retention of stereochemistry.

Variations in the Amine Oxide. In this section, as shown in Scheme 4, we used 1-benzyl-2-methylaziridine (**1**) and varied the amine oxide. As above, $Fe(CO)_5$ was used as the metal source in the three-step procedure. These reactions were done to determine the ease of losing different groups from the starting trialkylamine oxide.

On the basis of entries 1 and 2 of Table 2, there is little difference between the loss of a methyl group and

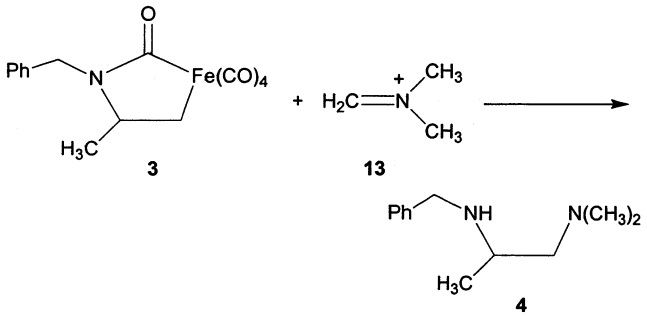
Scheme 4



the loss of an ethyl group. In entry 1, the observed ratio of products (29:71) is not much different from the statistical ratio of 33:67. In entry 2, the observed and statistical ratios are both 67:33. These results are inconsistent with the alkyl group being lost only by an S_N2 reaction, because in a classic S_N2 reaction, the methyl should be lost 1 or 2 orders of magnitude faster than the ethyl group.[14] It is possible that the methyl is lost in an S_N2 reaction and the ethyl in an E2 reaction, but we do not know this for certain.

(14) See for example: Smith, M. B. *Organic Synthesis*; McGraw-Hill: New York, 2002; p 105.

Scheme 5



For entry 3, we observe an approximate 6:1 ratio for loss of benzyl vs loss of methyl. This is close to the ratio expected for an S_N2 reaction. For entries 4 and 6, only the methyl group is lost and none of the isopropyl group or ring. Again, these results are consistent with an S_N2 reaction for loss of the third group from the amine. However, for entry 5, which has two isopropyl groups and one methyl group, it is strictly the isopropyl that is lost, albeit in lower yield. Our first thought was that the methyldiisopropylamine oxide was contaminated by dimethylisopropylamine oxide and, thus, entries 4 and 5 were actually the exactly the same. However, on the basis of ^{1}H NMR spectroscopy, the methyldiisopropylamine oxide is not contaminated by dimethylisopropylamine oxide.

A very surprising result is in entries 7 and 8, in which a diamine is not generated but rather an oxazolidinone. Oxazolidinone **12** can be obtained directly from the oxidation of intermediate **3** or, probably more likely, from the oxidation of an isomer of intermediate **3** in which the oxygen and iron are reversed. The obvious question is, if an ethyl and methyl group are lost equally well in entries 1 and 2, why is an ethyl group not lost in either entry **7** or **8**? We are not sure of the answer but suggest that the size of the amine oxide may play a role in whether it acts as a nitrogen source to generate the diamine or as an oxidant to generate the oxazolidinone.

Next we wanted to determine that, if an amine oxide and a free amine are both added to the reaction mixture, which one will be incorporated into the product diamine. For example, if we use a mixture of trimethylamine oxide and an excess of diethylmethylamine, would we get compound **4**, **11a**, or **11b**? When we ran this reaction, it gave only diamine **4**, i.e., the same product as if no free amine was added. We then decided to use an amine oxide, such as pyridinium oxide, which could not be incorporated into the diamine. Using a mixture of pyridinium oxide and triethylamine gave back an almost quantitative yield of the starting aziridine **1**. We have found no example of a free amine being incorporated into the product diamine. In other words, iron complex **3** does not act as an electrophile.

Therefore, we decide to investigate if complex **3** would act as a nucleophile. As shown in Scheme 5, the reaction of **3** with iminium salt **13** generates diamine **4** in the same yield as the reaction of **3** with trimethylamine oxide. We next tried the reaction of the iron complex derived from cyclohexane derivative **9b** with iminium **13** and again obtained the exact same product (**10b**) as we did using trimethylamine oxide. Because iron complexes are known to convert amine oxides to amines and iminium salts,[13,15−17] we speculate that the amine oxide is converted to the iminium group before it reacts with complex **3**.

Because the conversion of aziridine **1** to iron complex **3** most likely involves two S_N2 reactions leading to net retention of stereochemistry, and because we know the conversion of **1** to **4** involves net retention of stereochemistry, we speculate that the conversion shown in Scheme 5 must proceed with retention.

Variations in the Metal Complex. In this section, we used 1-benzyl-2-methylaziridine (**1**) and trimethylamine oxide and varied the metal complex. Any of the three iron carbonyl complexes $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ work equally well, giving about a 45% isolated yield of product, either by the three-step reaction or by mixing all the species together. Other metal carbonyl complexes do not work in this reaction. For example, $V(CO)_6$, $Cr(CO)_6$, and $W(CO)_6$ give very low yields (about 10%). The metal complexes $Co_2(CO)_8$ and $Mn_2(CO)_{10}$ do not generate any diamine. They give compound **1** and a six-membered-ring dimer of compound **1**.

Conclusion

The conversion of an aziridine to a 1,2-diamine using an iron carbonyl complex and an amine oxide was studied. We have 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. With a 2,3-disubstituted aziridine, the reaction proceeds with net retention of stereochemistry. Because the nitrogen in the amine oxide is trisubstituted and the same nitrogen in the product is disubstituted, various amine oxides were tried to determine the preference for which group will be removed. Unfortunately, some of these results are confusing. Finally, we have shown that iron complex **3** will react with an iminium salt to give the exact same product as is obtained from the corresponding amine oxide. Thus, we think the amine oxide is converted to an iminium salt before it reacts.

Experimental Section

General Considerations. All reactions were carried out using oven-dried glassware that was cooled under an argon atmosphere or in a desiccator. All reactions were carried out under an argon atmosphere unless otherwise noted.

Tetrahydrofuran was freshly distilled from potassium benzophenone ketyl. Benzyl bromide was distilled prior to use. Triethylamine was distilled from barium oxide. All other chemicals were purchased from Aldrich or Strem and used with no further purification unless otherwise noted. The syntheses and spectral data for compounds **1**, **4**, **6d**, **6e**, *cis*- and *trans*-**9a**, **9b**, and **12** have been reported previously.[10,12,18−20]

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(19) De Parrodi, C. A.; Vazquez, V.; Quintero, L.; Juaristi, E. *Synth. Commun.* **2001**, *31*, 3295.
(20) Callier-Dublanchet, A.; Quiclet Sire, B.; Zard, S. Z. *Tetrahedron Lett.* **1995**, *36*, 8791.

Appropriate precautions were taken because 2-methylaziridine, according to Aldrich, is highly toxic and a cancer suspect agent.

Instrumentation. All NMR spectra were recorded on a Bruker 250 MHz NMR spectrometer in $CDCl_3$ with chemical shifts referenced to tetramethylsilane at 0.00 ppm. All GC/mass spectra were recorded on a Hewlett-Packard 6890, equipped with an SPB-1 capillary column. The initial injection temperature was 70 °C; the temperature was then raised to 315 °C at 10 °C/min and then held at 320 °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 $CDCl_3$ unless otherwise noted. High-resolution mass spectra were obtained on an Ion Spec FT-ICR using electrospray ionization.

2-Methyl-1-pentylaziridine (6b). To 2-Methylaziridine (2.3 mL, 33 mmol) in 250 mL of THF at −78 °C was slowly added 1.5 M *n*-butyllithium in hexane (22.0 mL, 33.0 mmol) over a period of 15 min. The solution was then stirred at 0 °C for an additional 30 min. 1-Bromopentane (4.50 g, 30.0 mmol) was slowly added over a period of 5 min at −78 °C, and the solution was stirred at 0 °C for 1 h. After workup by the addition of saturated ammonium chloride solution (20 mL), the product was extracted into ether (250 mL) and the extract dried with anhydrous potassium carbonate. Evaporation of the solvent gave 2-methyl-1-pentylaziridine **(6b)**: yield 3.43 g (27.0 mmol, 90%); ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J = 6.6 Hz, 3 H), 1.17 (d, J = 5.2 Hz, 3 H), 1.26−1.34 (m, 6 H), 1.45−1.58 (m, 3 H), 2.16−2.24 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.13, 18.47, 22.82, 29.76, 34.55, 34.76, 61.59; IR ($CDCl_3$) 2960 (m), 2930 (m), 2861 (m), 2191 (w), 1456 (m), 1401 (w), 1367 (w), 1064 (w) cm^{-1}; MS *m/e* 127 (4.0), 126 (4.1), 113 (8.7), 112 (96.1), 98 (15.2), 85 (9.6), 84 (29.1), 72 (19.7), 71 (96.4), 70 (67.3), 69 (7.0), 68 (6.1), 58 (22.2), 57 (66.4), 56 (100); high-resolution MS found 128.1434, calculated for $C_8H_{18}N^+$ 128.1434.

1-Benzyl-2-phenylaziridine (6c). A mixture of styrene oxide (4.80 g, 40.0 mmol) and benzylamine (4.28 g, 40.0 mmol) was stirred at room temperature for 72 h. The crude product, 2-(benzylamino)-1-phenylethanol, was washed with boiling hexane to remove impurities to give 6.45 g of the product (28.4 mmol, 71% yield): ^{1}H NMR ($CDCl_3$) δ 2.75 (dd, J = 8.6, 12.2 Hz, 1 H), 2.94 (dd, J = 3.6, 12.2 Hz, 1 H), 3.80 (d, J = 13.5 Hz, 1 H), 3.86 (d, J = 13.5 Hz, 1 H), 4.72 (dd, J = 3.6, 8.7 Hz, 1 H), 7.25−7.35 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 53.53, 56.61, 71.93, 125.89−128.47, 139.77, 142.94; IR ($CDCl_3$) 3609 (m), 3423 (br m), 3155 (m), 3087 (w), 3066 (m), 3030 (m), 2901 (m), 2843 (m), 2253 (s), 1495 (w), 1454 (m), 1383 (w), 1201 (w), 1096 (m), 1060 (w), 1028 (w) cm^{-1}; MS *m/e* 227 (1.5), 120 (64.2), 91 (100), 77 (21.4), 65 (18.6); high-resolution MS found 228.1384, calculated for $C_{15}H_{18}ON^+$ 228.1383.

To an ice-cold solution of triphenylphosphine (5.26 g, 20.0 mmol) in 30 mL of acetonitrile was added, drop by drop, an ice-cold solution of bromine (3.20 g, 20.0 mmol) in 12 mL of acetonitrile. To the mixture was slowly added the crude 2-(benzylamino)-1-phenylethanol (4.54 g, 20.0 mmol), followed by drop by drop addition of triethylamine (6.06 g, 60.0 mmol) in 12 mL of acetonitrile at 0 °C. The reaction mixture was stirred at room temperature for 30 min, triethylamine hydrobromide was filtered off, and the solution was concentrated by rotary evaporation. The residue was treated with hexane (2 × 20 mL), concentrated to 10 mL, and filtered to remove triphenylphosphine oxide; then the solution was evaporated to give 2.30 g (33.0 mmol, 55% yield) of 1-benzyl-2-phenylaziridine (**6c**): ^{1}H NMR ($CDCl_3$) δ 1.82 (d, J = 6.2 Hz, 1 H), 1.97 (d, J = 3.3 Hz, 1 H), 2.46−2.50 (m, 1 H), 3.58 (d, J = 13.8 Hz, 1 H), 3.67 (d, J = 13.8 Hz, 1 H), 7.25−7.37 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 37.85, 41.43, 64.68, 125.43−128.43, 139.06, 140.07; IR ($CDCl_3$) 3087 (w), 3065 (m), 3032 (m), 2983 (w), 2929 (w), 2831 (m), 2248 (m), 1702 (m), 1603 (w), 1496 (m), 1453 (m), 1356 (w), 1203 (w), 1087 (w), 1028 (m); MS *m/e* 209 (2.1), 208 (10.5), 118 (45.2), 91 (100), 65 (18.1); high-resolution MS found 210.1275, calculated for $C_{15}H_{16}N^+$ 210.1283.

General Procedure for the Conversion of an Aziridine to a Diamine. A mixture of the aziridine (1.0 mmol) and lithium iodide (0.20 g, 1.5 mmol) in 30 mL of THF was refluxed for 15 min. This reaction mixture was cooled to room temperature. Then $Fe(CO)_5$ (0.15 mL, 1.2 mmol) was added and the solution was again heated to reflux for 3 h. The reaction mixture was cooled to room temperature. Then the amine oxide was added and the solution was stirred at room temperature. After at least 20 h, the reaction mixture was added to 50 mL of ether. Then the mixture was treated with 100 mL of water 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 150 mL of ether, in three portions. The ether solutions were mixed together, dried with anhydrous K_2CO_3, and evaporated to dryness. The remaining oil was easily purified by using a short alumina column in a disposable pipet, with methylene chloride and ethyl acetate as eluent, to give the corresponding 1,2-diamine.

Aziridine 6b with Trimethylamine Oxide. Aziridine **6b** (0.13 g, 1.0 mmol) was used with 0.55 g (5.0 mmol) of trimethylamine oxide to give 0.07 g (0.4 mmol, 40% yield) of **7b**: ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J = 3.7 Hz, 3 H), 1.25−1.38 (m, 6 H), 1.43 (d, J = 6.5 Hz, 3 H), 1.80−1.83 (m, 2 H), 2.32 (s, 6 H), 2.78−2.87 (m, 2 H), 3.07−3.15 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.96, 14.50, 22.27, 26.36, 28.94, 44.76, 45.64, 51.85, 61.81; IR ($CDCl_3$) 2960 (m), 2945 (m), 2843 (w), 2253 (w), 2217 (m), 1460 (m), 1320 (w), 919 (s), 732 (s) cm^{-1}; MS *m/e* 172 (0.3), 171 (0.3), 170 (0.3), 169 (1.0), 114 (100), 71 (6.7), 59 (21.6), 58 (91); high-resolution MS found 173.2018, calculated for $C_{14}H_{25}N_2^+$ 173.2017.

Aziridine 6c with Trimethylamine Oxide. Aziridine **6c** (0.21 g, 1.0 mmol) was used with 0.55 g (5.0 mmol) of trimethylamine oxide to give 0.12 g (0.46 mmol, 46% yield) of **8c**: ^{1}H NMR ($CDCl_3$) δ 2.14 (s, 6 H), 2.84 (dd, J = 6.7, 11.6 Hz, 1 H), 3.09 (dd, J = 7.3, 11.1 Hz, 1 H), 3.50 (t, J = 6.8 Hz, 1 H), 3.78 (s, 2 H), 7.20−7.32 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 41.43, 49.15, 52.99, 127.08−128.20, 128.53, 130.46; IR ($CDCl_3$) 3040 (w), 3005 (w), 2942 (m), 2252 (m), 2204 (w), 1666 (m), 1495 (w), 1455 (m), 915 (s), 750 (s) cm^{-1}; MS *m/e* 251 (0.1), 135 (13.01), 134 (100), 91 (28.6), 65 (8.1); high-resolution MS found 255.1854, calculated for $C_{17}H_{23}N_2^+$ 255.1861.

Aziridine 6d with Trimethylamine Oxide. Aziridine **6d** (0.20 g, 1.0 mmol) was used with 0.55 g (5.0 mmol) of trimethylamine oxide to give 0.030 g (0.13 mmol, 13% yield) of **8d**: ^{1}H NMR ($CDCl_3$) δ 2.20 (s, 6 H), 3.28−3.35 (m, 1 H), 3.48−3.65 (m, 2 H), 4.20 (br s, 1 H), 6.59−6.71 (m, 3 H), 7.12−7.68 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 41.98, 45.52, 68.43, 113.10, 117.37, 127.75−132.26, 137.54, 148.51; IR ($CDCl_3$) 3383 (w), 3155 (m), 3032 (m), 3028 (m), 2939 (m), 2865 (m), 2829 (m), 2785 (m), 2253 (m), 1794 (w), 1603 (m), 1505 (m), 1479 (m), 1454 (m), 1437 (m), 1382 (m), 1314 (w), 1262 (w), 1180 (m), 1120 (m), 1097 (m), 904 (s), 720 (s) cm^{-1}; MS *m/e* 240 (0.5), 194 (0.8), 135 (10.4), 134 (100), 118 (7.1), 91 (8.2), 77 (9.9), 65 (2.7), 51 (3.8); high-resolution MS found 241.1699, calculated for $C_{16}H_{21}N_2^+$ 241.1699.

Aziridine 6e with Trimethylamine Oxide. Aziridine **6e** (0.18 g, 1.0 mmol) was used with 0.55 g (5.0 mmol) of trimethylamine oxide to give 0.10 g (0.47 mmol, 47% yield) of **8e**: ^{1}H NMR ($CDCl_3$) δ 0.92 (t, J = 6.1 Hz, 3 H), 1.17−1.65 (m, 6 H), 2.25 (s, 6 H), 2.60−2.69 (m, 1 H), 2.80 (t, J = 10.5 Hz, 1 H), 3.16 (dd, J = 3.9, 11.2 Hz, 1 H), 6.62−6.70 (m, 3 H), 7.17 (t, J = 7.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.17, 23.16, 24.97, 29.70, 40.20, 44.42, 62.90, 113.02, 117.04, 129.27, 148.92; IR ($CDCl_3$) 3362 (w), 3040 (w), 3030 (w), 2960 (m), 2932 (m), 2861 (m), 2828 (m), 2788 (w), 2246 (w), 1603 (m), 1505 (m), 1482 (m), 1426 (w), 1380 (w), 1318 (w), 1260 (w), 1180 (w), 1040 (w), 916 (s), 720 (s) cm^{-1}; MS *m/e* 220 (1.0), 115 (18.5),

114 (100), 106 (13.6), 77 (18.8), 71 (14.7), 58 (25.5); high-resolution MS found 221.2012, calculated for $C_{14}H_{25}N_2^+$ 221.2012.

***cis*-Aziridine 9a with Trimethylamine Oxide.** *cis*-Aziridine **9a** (0.16 g, 1.0 mmol) was used with 0.55 g (5.0 mmol) of trimethylamine oxide to give 0.090 g (0.45 mmol, 45% yield) of **10a**: ^{1}H NMR ($CDCl_3$) δ 1.09 (d, J = 6.6 Hz, 3 H), 1.14 (d, J = 6.6 Hz, 3 H), 2.28−2.37 (m, 7 H), 2.94−2.98 (m, 1 H), 3.70 (d, J = 13.2 Hz, 1 H), 3.97 (d, J = 13.2 Hz, 1 H), 7.24−7.34 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 9.79, 12.62, 38.56, 42.24, 51.18, 52.78, 64.43, 126.37−127.93, 140.46; IR ($CDCl_3$) 3069 (w), 3065 (w), 3030 (m), 2967 (m), 2930 (m), 2870 (m), 2824 (m), 2781 (m), 2246 (w), 2203 (m), 1660 (m), 1495 (w), 1454 (m), 1382 (w), 1358 (w), 1261 (w), 1162 (w), 1097 (w), 1028 (w), 928 (s), 720 (s); MS *m*/*e* 206 (0.3), 134 (5.2), 91 (27.8), 73 (7.2), 72 (100), 65 (6.7), 56 (5.2); high-resolution MS found 207.1856, calculated for $C_{13}H_{23}N_2^+$ 207.1856.

***trans*-Aziridine 9a with Trimethylamine Oxide.** *trans*-Aziridine **9a** (0.16 g, 1.0 mmol) was used with 0.55 g (5.0 mmol) of trimethylamine oxide to give 0.13 g (0.62 mmol, 62% yield) of an isomeric **10a**: ^{1}H NMR ($CDCl_3$) δ 0.82 (d, J = 6.1 Hz, 3 H), 1.01 (d, J = 5.5 Hz, 3 H), 2.06 (s, 6 H), 2.20−2.22 (m, 1 H), 2.33−2.38 (m, 1 H), 3.61 (d, J = 13.3 Hz, 1 H), 3.92 (d, J = 13.3 Hz, 1 H), 7.26−7.31 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 6.97, 16.75, 39.87, 51.35, 54.09, 63.55, 126.66−128.27, 140.67; IR ($CDCl_3$) 3068 (w), 3040 (w), 3029 (m), 2973 (m), 2938 (m), 2828 (m), 2786 (w), 2253 (m), 1658 (w), 1454 (m), 1381 (m), 1265 (w), 1097 (w), 906 (s), 734 (s); MS *m*/*e* 206 (0.3), 134 (5.2), 91 (27.8), 73 (7.2), 72 (100), 65 (6.7), 56 (5.2); high-resolution MS found 207.1856, calculated for $C_{13}H_{23}N_2^+$ 207.1856.

Aziridine 9b with Trimethylamine Oxide. Aziridine **9b** (0.09 g, 0.5 mmol) was used with 0.28 g (2.5 mol) of trimethylamine oxide to give 0.030 g (0.13 mmol, 26% yield) of *N*-benzyl-*N*′,*N*′-dimethylcyclohexane-1,2-diamine (**10b**): ^{1}H NMR ($CDCl_3$) δ 1.10−1.33 (m, 3 H), 1.40−1.82 (m, 5 H), 2.00 (br s, 1 H), 2.11 (s, 6 H), 2.95 (d, J = 2.4 Hz, 1 H), 3.59 (d, J = 13.4 Hz, 1 H), 3.87 (d, J = 13.3 Hz, 1 H), 7.20−7.34 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 19.11, 25.22, 25.69, 28.00, 43.11, 51.55, 52.14, 67.54, 126.86, 128.09, 128.26, 128.38, 128.55, 141.29; IR ($CDCl_3$) 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); MS *m*/*e* 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); high-resolution MS found 233.2055, calculated for $C_{15}H_{25}N_2^+$ 233.2018.

Aziridine 1 with Ethyldimethylamine Oxide. Ethyldimethylamine oxide (0.45 g, 5.0 mmol) was used to give 0.040 g (0.21 mmol, 21% yield) of **4** and 0.10 g (0.49 mmol, 49% yield) of **11a**: ^{1}H NMR ($CDCl_3$) δ 0.96−1.02 (m, 6 H), 2.05−2.12 (m, 4 H), 2.22−2.47 (m, 3 H), 2.52 (br s, 1 H), 2.68−2.76 (m, 1 H), 3.68 (d, J = 13.4 Hz, 1 H), 3.93 (d, J = 13.4 Hz, 1 H), 7.20−7.32 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 12.44, 18.47, 41.93, 49.10, 51.51, 51.80, 63.95, 126.77−128.43, 141.00; IR ($CDCl_3$) 3276 (w), 3065 (w), 3030 (w), 2971 (m), 2840 (m), 2799 (m), 2252 (m), 2185 (w), 1495 (w), 1454 (m), 1375 (m), 1225 (w), 1140 (w), 1049 (w), 1045 (w), 915 (s), 741 (s) cm^{-1}; MS *m*/*e* 207 (0.5), 206 (0.6), 135 (8.2), 134 (70.9), 92 (10.7), 91 (100), 73 (17.6), 72 (72.0), 65 (16.5), 58 (20.3); high-resolution MS found 207.1856, calculated for $C_{13}H_{23}N_2^+$ 207.1856.

Aziridine 1 with Diethylmethylamine Oxide. Diethylmethylamine oxide (0.52 g, 5.0 mmol) was used to give 0.070 g (0.34 mmol, 34% yield) of **11a** and 0.030 g (0.14 mmol, 14% yield) of **11b**: ^{1}H NMR ($CDCl_3$) δ 0.96 (t, J = 7.2 Hz, 6 H), 1.10 (d, J = 6.1 Hz, 3 H), 2.27−2.58 (m, 6 H), 2.71−2.80 (m, 1 H), 3.73 (d, J = 13.4 Hz, 1 H), 4.03 (d, J = 13.4 Hz, 1 H), 7.25−7.34 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 11.72, 17.42, 18.35, 47.04, 49.36, 50.71, 59.36, 64.71, 126.95−128.59, 139.02; IR ($CDCl_3$) 3276 (w), 3065 (w), 3030 (w), 2971 (m), 2933 (m), 2874 (w), 2818 (m), 2252 (w), 2213 (m), 1495 (w), 1454, (m),1375 (m), 1202 (w), 1140 (w), 1063 (m), 915 (s), 728 (s) cm^{-1}; MS *m*/*e* 220 (0.6), 135 (7.3), 134 (64.7), 92 (10.1), 91 (100), 87 (25.5), 86 (100), 72 (34.8), 65 (17.6), 58 (17.4); high-resolution MS found 221.2012, calculated for $C_{14}H_{25}N_2^+$ 221.2012.

Aziridine 1 with Benzyldimethylamine Oxide. Benzyldimethylamine oxide (0.76 g, 5.0 mmol) was used to give 0.080 g (0.42 mmol, 42% yield) of **4** and 0.070 g (0.27 mmol, 27% yield) of **11c**: ^{1}H NMR ($CDCl_3$) δ 1.06 (d, J = 6.1 Hz, 3 H), 2.07 (s, 3 H), 2.13−2.25 (m, 1 H), 2.48 (t, J = 12.3, 1 H), 2.74−2.90 (m, 1 H), 3.37 (d, J = 13.1 Hz, 1 H), 3.52 (d, J = 13.1 Hz, 1 H), 3.72 (d, J = 13.3 Hz, 1 H), 3.96 (d, J = 13.3 Hz, 1 H), 7.23−7.33 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 18.01, 42.44, 49.44, 51.24, 62.68, 64.00, 127−129.01, 139.18, 140.15; IR ($CDCl_3$) 3030 (w), 3000 (w), 2936 (m), 2932 (m), 2800 (m), 2253 (m), 1664 (m), 1495 (w), 1454 (m), 1375 (w), 1027 (w), 911 (s) 747 (s) cm^{-1}; MS *m*/*e* 269 (1.1), 265 (2.1), 135 (17.0), 134 (54.3), 91 (100), 65 (11.7); high-resolution MS found 269.2034, calculated for $C_{18}H_{25}N_2^+$ 269.2018.

Aziridine 1 with Isopropyldimethylamine Oxide. Isopropyldimethylamine oxide (0.52 g, 5.0 mmol) was used to give 0.090 g (0.41 mmol, 41% yield) of **11d**: ^{1}H NMR ($CDCl_3$) δ 0.92−1.05 (m, 9 H), 2.06 (s, 3 H), 2.15−2.34 (m, 2 H), 2.61−2.84 (m, 3 H), 3.68 (d, J = 13.5 Hz, 1 H), 3.93 (d, J = 13.5 Hz, 1 H), 7.22−7.33 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 17.59, 18.31, 18.77, 37.12, 49.49, 51.52, 54.39, 59.83, 127.42−128.90, 140.46; IR ($CDCl_3$) 3276 (w), 3065 (w), 3028 (m), 2968 (s), 2932 (m), 2847 (m), 2802 (m), 2247 (w), 2183 (m), 1602 (w), 1495 (m), 1455 (m), 1376 (m), 1363 (m), 1224 (w), 1159 (w), 1119 (w), 1062 (w), 1000 (w), 935 (w), 917 (s), 741 (s) cm^{-1}; MS *m*/*e* 219 (0.2), 217 (4.1), 134 (43.3), 92 (11.3), 91 (100), 87 (26.3), 86 (73.2), 72 (28.9), 65 (8.2), 56 (5.2); high-resolution MS found 221.2023, calculated for $C_{14}H_{25}N_2^+$ 221.2018.

Aziridine 1 with *N*-Methylpiperidine Oxide. *N*-Methylpiperidine oxide (0.58 g, 5.0 mmol) was used to give 0.070 g (0.31 mmol, 31% yield) of **11e**: ^{1}H NMR ($CDCl_3$) δ 1.00 (d, J = 6.1 Hz, 3 H), 1.41−1.52 (m, 6 H), 2.05−2.35 (m, 6 H), 2.68−2.76 (m, 1 H), 3.67 (d, J = 13.5 Hz, 1 H), 3.94 (d, J = 13.5 Hz, 1 H), 7.23−7.32 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 18.04, 24.51, 26.15, 48.05, 51.00, 54.79, 65.11, 126.99−128.47, 140.28; IR ($CDCl_3$) 3030 (m), 2939 (m), 2855 (m), 2806 (m), 1454 (m), 1376 (w), 1354 (w), 1157 (w), 1054 (w), 903 (s), 733 (s) cm^{-1}; MS *m*/*e* 232 (0.6), 229 (0.8), 134 (28.3), 99 (27.7), 98 (100), 91 (76.6), 65 (14.7), 58 (12.0); high-resolution MS found 233.2013, calculated for $C_{15}H_{25}N_2^+$ 233.2012.

Aziridine 1 with Diisopropylmethylamine Oxide. Diisopropylmethylamine oxide (0.66 g, 5.0 mmol) was used to give 0.050 g (0.23 mmol, 23% yield) of **11d**.

Aziridine 1 with Ethyldiisopropylamine Oxide. Ethyldiisopropylamine oxide (0.73 g, 5.0 mmol) was used to give 0.050 g (0.25 mmol, 25% yield) of oxazolidinone **12**.

Aziridine 1 with Triethylamine Oxide. Triethylamine oxide (0.59 g, 5.0 mmol) was used to give 0.090 g (0.45 mmol, 45% yield) of oxazolidinone **12**.

Aziridine 1 with Trimethylamine Oxide with Added Diethylmethylamine. Starting with 0.15 g (1.0 mmol) of aziridine **1**, a mixture of trimethylamine oxide (0.05 g, 0.5 mmol) and diethylmethylamine (0.9 g, 10 mmol) was used in place of the amine oxide. After the short alumina column, 0.080 g (0.42 mmol, 42% yield) diamine **4** was obtained.

Aziridine 1 with Pyridine Oxide with Added Triethylamine. Starting with 0.15 g (1.0 mmol) of aziridine **1**, a mixture of pyridine oxide (0.50 g, 5.0 mmol) and triethylamine (0.3 g, 5 mmol) was used. The crude product (0.14 g) consisted of 92% starting aziridine **1** and 4% dimer of **1**, as determined by GC/MS.

Aziridine 1 with *N*,*N*-Dimethylmethyleneammonium Chloride. The reaction was run as in the general procedure, except the trimethylamine oxide was replaced by *N*,*N*-dimethylmethyleneammonium chloride (0.47 g, 5.0 mmol) to give 0.086 g (0.45 mmol, 45% yield) of **4**.

Aziridine 9b with *N*,*N*-Dimethylmethyleneammonium Chloride. The reaction was run as in the general procedure,

except the trimethylamine oxide was replaced by *N*,*N*-dimethylmethyleneammonium chloride (0.47 g, 5.0 mmol) to give 0.194 g (0.83 mmol, 83% yield) of **10b**.

Aziridine 1 with Trimethylamine Oxide with Various Metal Complexes. The usual general procedure was used, except the metal complex was changed.

Iron nonacarbonyl: 0.44 g (1.2 mmol) was used to give 0.090 g (0.46 mmol, 46% yield) of **4**.

Iron dodecacarbonyl: 0.60 g (1.2 mmol) was used to give 0.080 (0.42 mmol, 42% yield) of **4**.

Vanadium hexacarbonyl: 0.26 g (1.2 mmol) was used to give 0.020 (0.10 mmol, 10% yield) of **4**.

Chromium hexacarbonyl: 0.26 g (1.2 mmol) was used to give 0.020 (0.11 mmol, 11% yield) of **4**.

Dicobalt octacarbonyl: 0.41 g (1.2 mmol) was used to give a mixture of starting aziridine **1** and a dimer of **1**.

Manganese carbonyl: 0.47 g (1.2 mmol) was used to give a mixture of starting aziridine **1** and a dimer of **1**.

Tungsten hexacarbonyl: 0.42 g (1.2 mmol) was used to give 0.01 g (0.05 mmol, 5% yield) of **4**.

Acknowledgment. We thank Prof. S. Z. Zard for a copy of the NMR spectrum of compound **12**.

Supporting Information Available: ^{1}H NMR spectra for compound **10a** generated from *cis*-**9a**, compound **10a** generated from *trans*-**9a**, and compound **10b** and ball and stick drawings of the lowest energy conformation of *erythro*-**10a** and *threo*-**10a** from the molecular mechanics calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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