THERMAL DECOMPOSITION OF (PRESUMED) BISMETHYLENE DIAZENE

Thesis by

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For Carla

Abstract

Thermal high temperature and base induced low temperature decomposition of 1-sulfonamido-2,3-dimethylaziridines (2, 3) and low temperature oxidation of 1-amino-2,3-dimethylaziridines (4) gives 2-butenes as the major hydrocarbon products (70-99%). The stereochemistry of the products is consistent with a stepwise pathway for decomposition of the presumed intermediate bismethylene diazenes (1).

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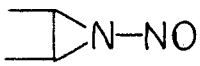
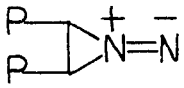
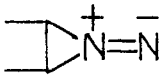
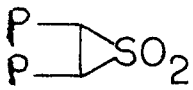
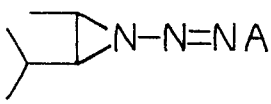
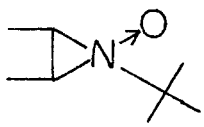
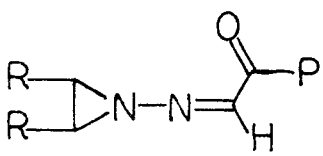
Introduction

N-nitrenes[1] (1,1-diazenes) have been proposed as intermediates in certain reactions of 1,1-disubstituted hydrazines, although none have ever been isolated or observed directly. Cyclic 1,1-diazines have been implicated as intermediates for the generation of presumed diradicals: tetramethylene[2] and trimethylene[3] diazenes for tetramethylene and trimethylene diradicals, respectively. In these cases hydrocarbon products have been found to be very similar to the products resulting from decomposition of the corresponding cyclic azo-compounds (1,2-diazenes). Reported attempts to generate the smallest homologue in this series, bismethylene diazene, have met with some success. Deamination of 2,3-dimethylaziridines by difluoramine at 0° affords 2-butenes with at least 96% retention of configuration[4]. Oxidation of 1-amino-2,3-diphenylaziridines with activated manganese dioxide reportedly[5] gives only retention in the trans case, and predominant (85:15) inversion in the cis case. Lead tetraacetate[6] gives predominant retention (99.0% in the cis, 98.5% in the trans case). In order to determine the effects of mode of generation, temperature, phase, and substitution on the behavior of bismethylene-1,1-diazene thermal decompositions, we sought to further study the dimethyl substituted 1,1-diazene by α-elimination at high and low temperatures, and oxidation at low temperatures.

Similar three membered ring fragmentations proceed in some cases with retained, and in at least one case, mixed stereochemistry (see Table I). The possibility of concerted fragmentations in 1,1-diazene decompositions was stressed by Freeman[4]. According to the Woodward and Hoffman[7] rules of orbital symmetry, non-linear chelotropic extrusion is allowed, and the linear pathway is forbidden. However, stereospecific diradical

Table I: Three Membered Ring Fragmentations.

Compound[a]	r/i[b](%)	T	Conditions	References
	99.0/1.0	-23°to 25°	solution	9
	trans 99/1 cis 97.5/2.5	0°	solution	6
	96/4	0°	neat	4
	99/1	60°	melting	10
	99/1	25°	solution	11
	cis 90/10 trans 60/40	300°	injection port	8
	99.5/0.5	φH reflux	solution	12
	trans[c] 100/0	-20°	solution	13
	R=Me 99/1 R=Ph 98.5/1.5	CH_2Cl_2 reflux	solution	6

(a) These results are for both cis and trans isomers, except as entered; P = C_6H_5, A = p-$NO_2C_6H_4$.

(b) Retention/inversion = r/i.

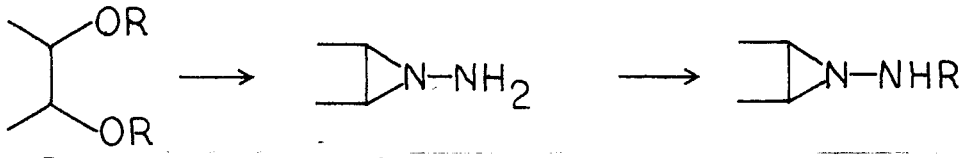
(c) The cis isomer undergoes exclusive 2,3-cycloelimination.

intermediates remain a possibility. A temperature effect might be expected, so examination at both high and low temperatures would be informative. The sulfur monoxide[8] extrusion is the only case so far for which a concerted mechanism can be clearly ruled out, but in this case other reactions interfere at low temperatures.

Results and Discussion

The preparation of the substrates involved in this are outlined in Scheme 1 below.

Scheme 1: Preparation of Substrates



5, 6 — 4 — 2, 3

	R = H	Ms[a]			R =	Ms	Ts[b]
erythro	6a	5a	cis	4a		3a	2a
threo	6b	5b	trans	4b		3b	2b

a) Ms = SO_2CH_3 ; b) Ts = $SO_2C_7H_7$

The commercially available diols, 6, were converted to the crystalline dimethanesulfonates[6], 5, in good yield by treatment with methanesulfonyl chloride in pyridine. Reaction of the dimethanesulfonates with hydrazine gave 30-50% yields of the substituted aziridines[6], 4, which upon treatment with p-toluenesulfonyl chloride (for 2) or methanesulfonyl chloride (for 3) gave the sulfonamidoaziridines[14]. The aminoaziridines, 4, were also available by an independent route, via hydrazinolysis of the phthalimidoaziridines, 7. These were prepared by oxidation of N-aminophthalimide in the presence of cis- or trans-2-butene. The aminoaziridines prepared by the first route exhibited properties identical to those prepared by the second method. Satisfactory infrared, nuclear magnetic resonance, and mass spectral data could be obtained for 1-sulfonamido-cis-2,3-dimethylaziridine, 3a, but elemental analysis (C, H, N) was low (compound

decomposes to volatile products). The unstable trans isomer, 3b, suffered decomposition in the NMR probe (ca 40°, $t_{1/2} \approx 1$ hour) and attempts to obtain a solid sample of this material failed. The crystalline p-toluenesulfonyl derivatives, 2, were somewhat more stable, and could be purified by preparative thin-layer chromatography on silica gel. The spectral data were satisfactory, but the cis isomer showed only decomposition in the inlet of the mass spectrometer.

Thermolyses of the toluenesulfonamido-aziridines, 2, and methanesulfonamido-aziridines, 3, in benzene solution were carried out in a heated tube (305-330°, 30 seconds). Volatile products were trapped at 77K, distilled, and analyzed by analytical vapor phase chromatography. The products of these decompositions can be found in Table II.

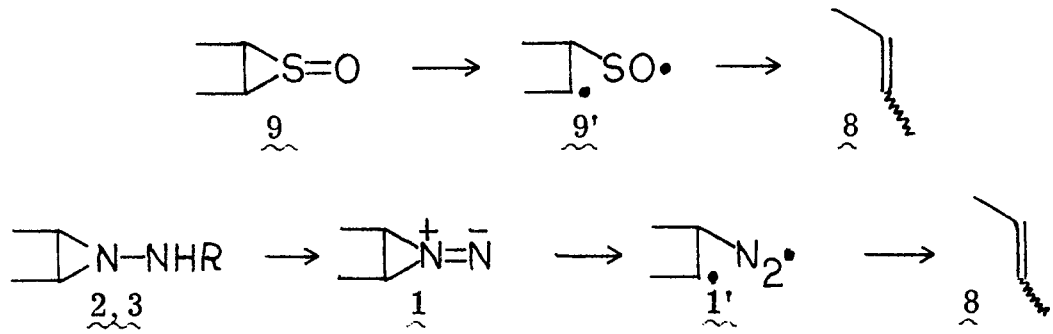
A combined gas chromatography-mass spectroscopy experiment performed on the products of decomposition of 2a identified the bulk of the minor products (components $\gtrsim 0.5\%$) as ethane, propene, and C_5H_{10} isomers (see experimental).

A benzene solution of methanesulfinic acid[16] was found to isomerize cis-butene in the hot tube (as well as in solution), giving rise to suspicion that product distributions might be due to isomerization by that by-product. As a test, cis-3-hexene was copyrolysed with 1-methanesulfonamido-cis-2,3-dimethylaziridine, and cis-2-butene was copyrolysed with 1-methanesulfonamido-cis-2,5-dimethylpyrolidine. These experiments showed little (1.5% for cis-2-butene at 306°, 3.5% at 439°) or no (less than 0.5%) isomerization of the olefins, analyzed by gas chromatography. The ratio of cis and trans butenes produced under these conditions (305-330, some data at 419°) does not show a significant temperature dependence.

The close correspondence of product ratios (of 2-butenes) from 2 or

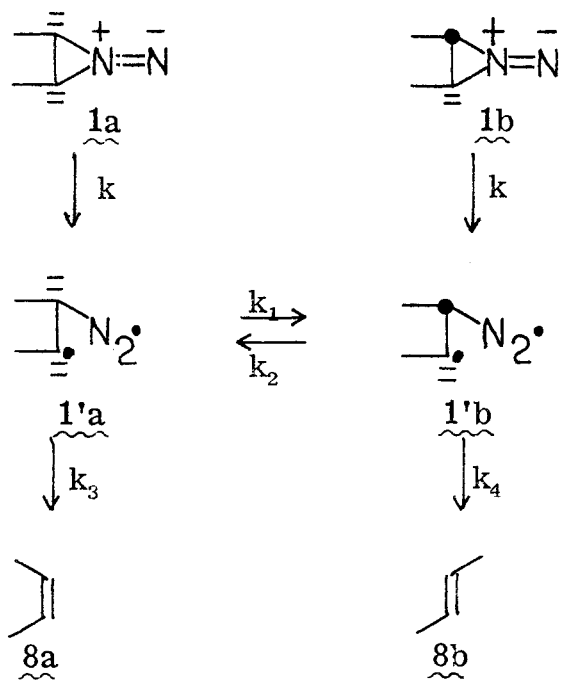
3 and the related episulfoxides[8] supports the hypothesis that the mechanisms may be similar. It was proposed that the episulfoxides fragment in stepwise fashion, perhaps via 9' (Scheme 2). The intermediate diazenyl radical, 1', analogous to 9', could rotate about the C_2-C_3 bond, then lose

Scheme 2



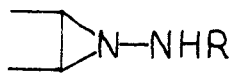
nitrogen to give olefin of the opposite stereochemistry. A kinetic scheme linking the decomposition of each isomer can be written (Scheme 3).

Scheme 3



Assuming back reactions to 1,1-diazenes to be negligible, a steady state analysis of the system yields relative rates of cleavage and rotation for

Table II: Chamber pyrolyses[a].



2, 3

	R = Ts	R = Ms
cis	2a	3a
trans	2b	3b

Compound	T	n-butane	1-butene	t-butene[b]	c-butene[b]	other	unident.[e]
2a	308°	-	2.3	14.1	85.9	0.5	0.1
2b	310°	-	1.2	58.7	41.3	0.1	0.1
3a	310°	0.02	2.0	13.1	86.9	4.0	1.0
3a	419°	0.09	1.4	13.8	86.2	10.4	0.5
3b	330°	-	5.3	65.1	34.9	7.5	-
3b	435°	-	6.7	72.3	27.7	28.7	-
3a[c]	330°	-	4.5	17.0	83.0	6.2	-
8a[d]	306°	-	-	1.5	98.5	-	-
8a[d]	439°	-	-	3.5	96.5	-	-

(a) Typical absolute yields of hydrocarbons was 30-60%.

(b) The sum of 2-butenes normalized to 100%.

(c) Cis-3-hexene (98.4% cis) added was recovered 98.0% cis.

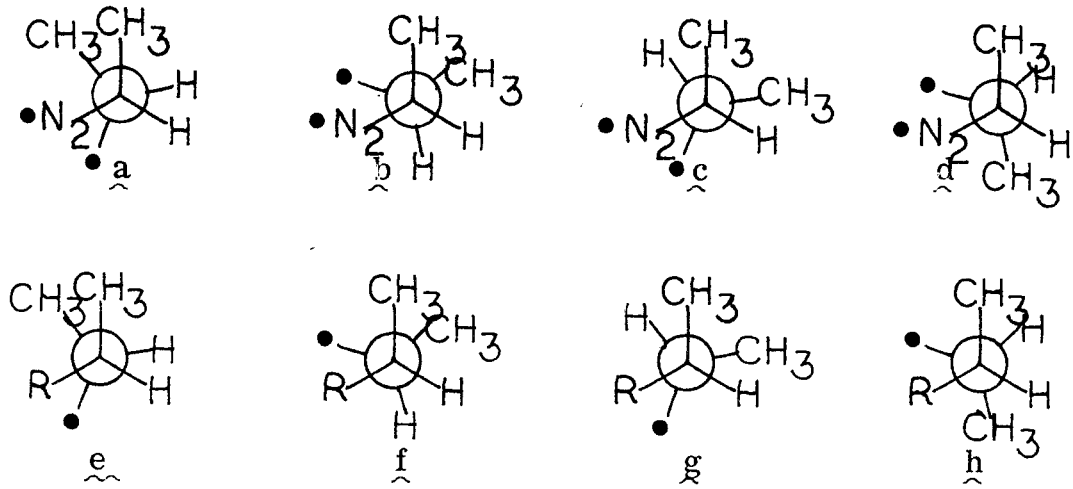
(d) Copyrolysis of cis-2-butene, 8a, and 1-methanesulfonamido-cis-2,5-dimethylpyrrolidine was reported in footnote 9 of reference 2b.

(e) Unidentified hydrocarbons.

each diradical from the product ratios resulting from each isomer. This treatment ignores possible side reactions of the diazenes, diazenyl radicals, and product olefins. The algebraic steps required are detailed in an appendix. Derived relationships and calculated rate ratios are in Table III.

The temptation to use Fischer projections to estimate relative rotational barriers is overwhelming, and is diagrammed in Scheme 4. For the diazene (a, b, c, d, of Scheme 4) and episulfoxide cases, this

Scheme 4: Fischer Projections



approach seems to work. The problem arises, however, with its extension to the case of 1, 2-dimethyl-tetramethylenediyl[2b] (e, f, g, h, of Scheme 4), from which we would expect similar behavior, but observe the reverse. The distribution of steric bulk (Scheme 5) about the terminae of the incipient 2-butene does correspond consistently: cleavage appears to be faster than rotation if the bulky groups are cis (2.6-5.0), while the rates are competitive (1.2-1.5) if the bulky groups are trans. This may be evidence of steric attraction[21].

Table III: Cleavage to Rotation ratios for 1'

1'

Definitions[a]: α = (r/i) cis

β = (r/i) trans

$R_1 = k_3/k_1$

$R_2 = k_4/k_2$

Equations[a]:

$$R_1 = \frac{\alpha\beta - 1}{\beta + 1}$$

$$R_2 = \frac{\alpha\beta - 1}{\alpha + 1}$$

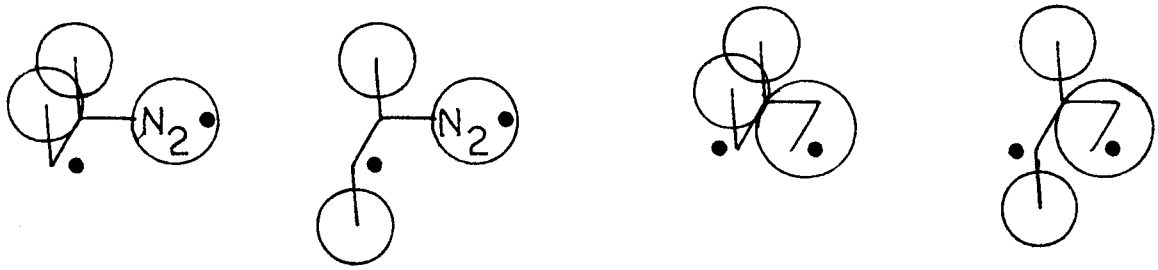
Species	α	β	R_1	R_2
2	6.09	1.42	3.16	1.08
3	6.14	1.86	3.64	1.46
9[b]	9.00	1.50	5.00	1.25
Tetramethylene diradical[c]	-	-	1.2	2.6

(a) See Scheme 3 and Appendix.

(b) Calculated from data in reference 8.

(c) Reference 2b.

Scheme 5

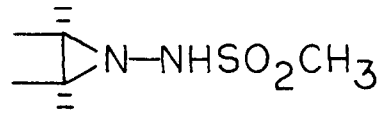


Briefly, the high temperature decomposition of 2 and 3 gives products consistent with diazene intermediates which fragment by a stepwise mechanism. It might therefore be possible to interpret Freeman's diazene experiment[4] in terms of a stereospecific diradical intermediate. There follows a description of attempts to independently generate similar intermediates at lower temperature (0-25°) in order to make a direct comparison with Freeman's diazene[4].

In an early solution phase experiment[14], T. Uyehara of the Dervan Group thermolysed 1-sulfonamido-cis-2,3-dimethyl-aziridine, 3a, in benzene in a sealed tube (see Table IV). The predominant inversion observed could be real, or due to isomerization of the first formed olefins by methanesulfinic acid. A sample of the acid was prepared[16] by the reaction of water with methanesulfinyl chloride, and was found to isomerize cis-2-butene in benzene solution (sealed tube) at 100°. A recent report[17] has confirmed that sulfinic acids are capable of catalytic isomerization of olefins. Further solution phase decompositions were carried out in the presence of at least one equivalent of base.

Base induced decompositions of 3a, 2a, 2b, were carried out in diglyme in sealed tubes under nitrogen atmosphere. The usual base was 2N sodium 2-n-butoxy ethoxide in 2-n-butoxyethanol. Products were

Table IV: Thermolysis[14] of 1-sulfonamido-cis-2,3-dimethylaziridine, 3a .



3a

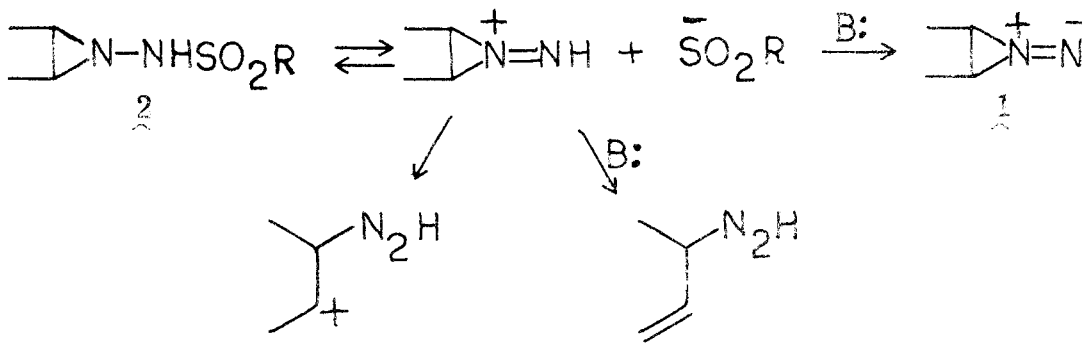
t(min)	T	t-butene	c-butene	yield (%)
15	180°	56	44	51
30	100°	64	36	45

distilled at high vacuum and analyzed by vapor phase chromatography. Results are entered in Table V.

The product olefin ratios from the trans isomer, 2b, show predominant trans stereochemistry. A consistent explanation is that the trans diazene, 1b, is formed, and fragments to olefin with a high degree of retention. This observation fits with Freemans[4] of at least 96% retention.

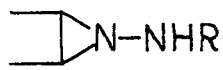
Products from decomposition of the cis isomers are variable. Added olefin was recovered unchanged, hence it seemed unlikely that the products were scrambling under the reaction conditions. In solution, the mechanism of formation of diazenes from sulfonylhydrazines has been proposed to be ionization to the diazenium ion and sulfinate ion, followed by proton transfer to give the diazene (as in Scheme 6). If deprotonation at nitrogen is slow

Scheme 6



compared with the other chemistry available to the diazenium ion, the diazene will be superseded by intermediates whose decomposition products are difficult to precisely predict. The competing pathways probably involve ring cleavage, as indicated, Scheme 5. That proton transfer may in fact be rate limiting is suggested by the base dependence shown in the last two entries of Table V. The stronger base, potassium t-butoxide, gives more retention,

Table V: Base Induced Decomposition Data[a, b]



	R = Ts	R = Ms
cis	2a	3a
trans	2b	3b

2, 3

Compound	T	t[c]	butane	1-butene	t-butene[d]	c-butene[d]	other
3a	25°	2.5h	0.1	0.3	58.0	42.0	4.3
3a[e]	25°	2h	-	2.3	42.0	58.0	7.6
2b	0°	2.5h	0.1	0.1	98.0	2.0	2.0
2b	105°	5m	0.1	-	95.6	4.4	0.4
2a[f]	105°	5m	-	-	60.4	39.6	0.4
2a[g]	105°	5m	-	6.7	32.7	67.3	0.75

(a) Typical absolute hydrocarbon yields were 20-75%.

(b) The base used was 2N sodium 2-(n-butoxy) ethoxide in 2-n-butoxy ethanol, unless otherwise noted.

(c) h=hours, m=minutes.

(d) The sume of 2-butenes was normalized to 100%.

(e) Added cis-3-hexene (98.4 cis) was recovered, 98.6% cis.

(f) Diisopropyl ethylamine was used as the base.

(g) Potassium t-butoxide was used as the base.

but also more 1-butene, presumably via a base-assisted ring cleavage pathway.

It was expected that oxidation of the aminoaziridines, 4 , would proceed without the complications encountered in the base induced fragmentations discussed above. The oxidant primarily studied was activated manganese dioxide. The rate of oxidation with yellow mercuric oxide was inconveniently slow. Results and conditions of oxidation experiments are detailed in Table VI.

The solvent, n-hexane, and aminoaziridine, 4a or 4b , were degassed and distilled onto degassed oxidant. After the reaction time, products were distilled and analysed as before. This route gave almost entirely C_4 hydrocarbons, other products were always less than 1.5%. The appearance of butane in the products deserves some note, as it is not an expected product from the diazene, and occured only negligibly in the hot tube and base induced decompositions. The mechanism of MnO_2 oxidations is not well understood . Oxidation of 1,1-substituted hydroazines is usually explained by invoking diazene intermediates without mention of the mechanism of formation of these intermediates from the hydrazines. A reasonable mechanism (Scheme 7) can be suggested: ring cleavage of the one election oxidation product of 4 would give a radical species which

Scheme 7

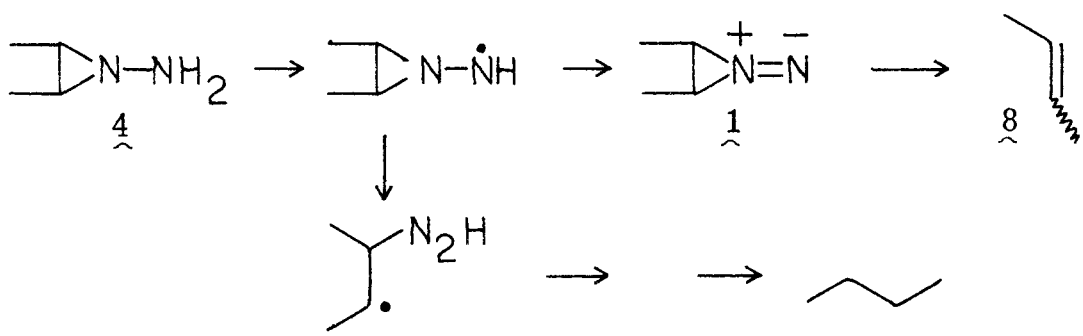
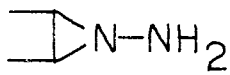


Table VI: Oxidation of 1-Amino-2,3-dimethylaziridines, 4.



4

cis 4a
trans 4b

isomer[a]	t[b]	T	MnO_2[c]	n-butane	1-butene	t butene[d]	c-butene[d]	other
cis	4h	0°	xs	0.1	.06	12.0	88.0	0.1
cis	2h	0°	xs	0.3	0.1	9.8	90.2	0.2
butenes[e]	2h	0°	xs	-	-	9.6	90.4	-
cis	30m	0°	xs	-	-	21.6	73.4	0.1
cis[f]	4m	0°	xs	0.07	-	11.3	88.7	0.2
cis[g,j]	4m	0°	ca 1	-	-	17.0	83.0	0.2
trans	2h	0°	xs	2.5	0.9	89.4	10.6	0.3
trans[k]	40m	0°	xs	10	-	81.9	18.1	-
trans[h]	4m	0°	xs	5.0	1.0	13.0	37.0	0.3
trans[i]	4m	0°	ca 1	29	-	83.0	17.0	1.3

(a) Cis = 4a, trans= 4b, see note (e).

(b) h = hours, m = minutes.

(c) xs = 10-20 equivalents, ca 1 = about equivalent.

(d) The sum of 2-butenes normalized to 100%.

(e) The product from the preceding listing was re-subjected to the reaction conditions.

(f) Cis-2-pentene (98.0% cis) was recovered 97.6% cis.

(g) Added cis-2-pentene (98.0% cis) was recovered 97.7% cis.

(h) Added cis-2-pentene (98.0% cis) was recovered 97.8% cis.

(i) Added cis-2-pentene (98.0% cis) was recovered 97.7% cis.

(j) In this experiment, unreacted starting material (4a) was found to be at least 99% cis.

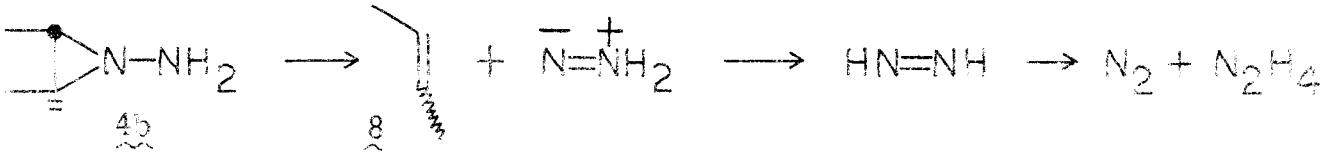
(k) In this experiment, unreacted starting material (4b) was found to be ca 96.6% trans.

could abstract a hydrogen, then lose nitrogen to give n-butane. Cis-2-pentene was recovered essentially unchanged from these oxidations.

Thermal Decomposition of 1-amino-trans-2,3-dimethylaziridine, 4b.

It has been observed during the handling of these and other amino-aziridines, that they are thermally unstable, decomposing to give olefins. In this case, there is evidence for decomposition to cis- and trans-2-butene (injection port, 150-200°, 10-15%), and also for one-bond ring opening (see experimental). Trans-2,3-diphenylaminoaziridine has been reported to evolve trans-stilbene at 25°. It is possible that some N_2H_2 species is intermediate in the production of non-hydrocarbon compounds, and it has been suggested that the parent, aminonitrene, is formed (see Scheme 8). If it was formed, the aminonitrene might be expected to either disproportionate directly to nitrogen and hydrazine, or rearrange to the more stable diimide. The aminonitrene might be directly observable, but diimide[20] would be expected to be. Indeed, hydrazine is observed by gas chromatography during analysis of these compounds, 4, and molecular nitrogen is easily distinguishable in the photelectron spectrum of gaseous 4 passed over a heated filament (ca 400-650°). These facts are consistent with the known disproportionation of diimide.

Scheme 3



Experimental

Melting points were determined on a Thomas-Hoover capillary melting point apparatus, and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer model 257 grating infrared spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian Associates A-60 nuclear magnetic resonance spectrometer operating at 60 MIIz (reported in δ from TMS). Elemental analyses and mass spectra were performed and recorded by the Caltech microanalytical services, under the direction of Dr. Susan Rottschaffer. Analytical vapor phase chromatography equipment employed included a Hewlett-Packard model 5700A gas chromatograph, equipped with a flame ionization detector and a Hewlett-Packard model 3370B electronic integrator.

Preparative vapor phase chromatography was carried out on a Varian aerograph model 920 (thermal conductivity dectector) with a pyrex-lined injection port. Columns utilized were: 10' x $^1/_8$" stainless steel containing Pennwalt 223 amine packing (Applied Science Laboratories, Inc.); 20' x $^1/_8$" stainless steel packed with 10% dibutyltetrachlorophthalate on 100-120 mesh chromosorb P(A/W, DMCS); 20' x $^1/_8$" stainless steel packed with 10% β,β'-oxydipropionitrile on 100-120 mesh chromosorb P(A/W, DMCS); 6' x $^1/_4$", and 10' x $^1/_4$" glass, both packed with Pennwalt 223 amine packing; 10' x $^3/_8$" aluminum, containing 25% β,β'-oxydipropionitrile on 60 80 mesh chromosorb P(A/W, DMCS). For preparative thin layer chromatography, thick silica gel plates (20 x 20cm, Merck) were employed.

Pyrolytic procedures

Vacuum line pyrolyses were carried out in a heated, evacuated,

(10^{-4} - 10^{-5} torr, Hg manometer) cylindrical pyrex chamber, diameter 2.8 cm, length 30 cm, total volume 185 cm^3. Samples to be pyrolysed were introduced via syringe through a small rubber septum sealing the 0.6 cm x 2 cm injector at one end. The other end of the tube could be opened (stopcock) to an evacuated U-shaped trap, with an additional joint, and stopcock for distillation of samples into small tubes for analysis. The chamber was heated by a Hoskins type FD 303A tube furnace, controlled by a temperature controller. Temperature was measured with an iron-constantan thermocouple and potentiometer. In a typical experiment, the system was evacuated, and the stopcocks to the line and to the chamber were then closed. A sample was injected into the chamber, then after a time (usually 5 or 30 seconds, sometimes longer) the pyrolysis tube was opened to the trap, cooled with liquid nitrogen. The sample was removed from the line by distillation into a small tube, which was sealed and removed. The distillate was frozen in the bottom of the tube, broken open, capped with a serum stopper (sometimes additional solvent was added), and on melting, injected into the inlet of an analytical VPC.

The base-induced decompositions were carried out in base-washed, oven-dried pyrex tubes (1.2 x 8.0 cm, joint to $\overline{\$}$ 14/35 male joint, joined to 0.6 x 4.0 cm tube, for degassing and sealing). A solution of the substrate in distilled, degassed diglyme (bubbling nitrogen through the diglyme is not sufficient, but two or three freeze-thaw cycles, preceded by pumping directly on the liquid to remove a trace low-boiling contaminant, is satisfactory) was frozen (77K) under nitrogen in the tube. To this, a solution of the base to be used (usually 2N sodium n-butoxyethoxide in n-butoxyethanol, prepared by stirring n-butoxyethanol, freshly distilled from sodium,

with two equivalents of freshly cut sodium metal for several hours at or below room temperature, 0.1 to 0.2 ml) was added via syringe, and frozen almost immediately. The tube was purged with nitrogen, and sealed with a torch. After the tube was warmed to the desired temperature (and shaken soon after liquification to insure adequate mixing) for a certain time, it was again frozen with liquid nitrogen, the top scored with a triangular file and broken, and volatile products distilled (high vacuum, at room temperature), then distilled again, into a small tube (as before) which was sealed and analy d as described above.

The oxidation experiments were carried out on the vacuum line. A weighed portion of the oxidant (manganese dioxide or mercuric oxide) was carefully degassed (these solids tend to leap out of the tube and contaminate the rest of the line if evacuated too quickly) in a base-washed, oven-dried tube placed on an auxiliary manifold, protected by stopcock. A solution of volatile aminoaziridine in n-hexane (purified by preparative vpc on 20' x $^3/_8$" aluminum column packed with β,β'-oxydipropionitrile) was placed in a tube on the same auxiliary manifold, degassed (freeze-thaw method), and distilled onto the degassed oxidant. The tube was closed off, the liquid nitrogen dewar removed, and either replaced with a dewar filled with ice water, or ambient air for a time, then the reaction tube was opened to the evacuated manifold open to another tube at 77K. The distillate was analy ed by VPC.

Preparation of Meso-2,3-dimethanesulfonyloxy butane[6]

A solution of meso-2,3-butanediol (27.0 g, 0.3 moles, 98% RIC/ROC) in 150 ml dry pyridine was placed in a dry flask under argon equipped with a stirrer. The solution was maintained close to the freezing point of pyridine

(-42°) with a dry ice-acetone bath. Methanesulfonyl chloride (47.5 ml, 0.614 moles, Aldrich, distilled from P_2O_5) was added slowly from a pressure equalizing addition funnel over a period of 1.5 hours. The resulting brownish semi-solid was allowed to warm to room temperature, and stand 0.5 hours. After adding 20 ml distilled water the mixture was poured onto ca. 300 g curshed ice. When the ice had melted the crystals were collected on a coarse glass frit and washed with two 50 ml aqueous sodium chloride, dried ($MgSO_4$), and solvent removed under reduced pressure. One recrystallization from absolute methanol gave 53 g (72%) white crystals, mp 64-7°. NMR($CDCl_3$): 1.25-1.55 (m, 6H, sharp peaks at 1.37, 1.48), 3.08 (s, 6H), 4.65-5.10 (m, 2H); IR(CCl_4); 3035 (w), 2995(w), 2945 (w), 1360 (broad), 1155 (s), 1075 (w), 995 (w), 970 (m), 940 (m), 905 (m).

Preparation of 1-Amino-2,3-cis-dimethylaziridine[6]

In a 100 ml base-washed round-bottomed flask, fitted with serum stopper, reflux condenser, magnetic stirrer and argon inlet, was placed 25.6 g (0.1 mole) meso-2,3-dimethanesulfonyloxybutane. The system was flushed with argon. To this anhydrous hydrazine (21 ml, 0.658 moles, 97% MCB) and hydrazine hydrate (20 ml, 0.412 moles) were added by syringe. The mixture was allowed to stir and maintained at 58-60° (silicone oil bath, preheated to 65°) for four hours. Upon cooling two phases were evident. The reflux condenser was replaced by a short path distillation apparatus (base washed, oven dried). Approximately 20 ml of colorless distillate was collected (to 70° at 125 mm) in a reciever containing a KOH pellet, and cooled by dry ice-acetone. Solid KOH (2.0 g, total) was added portion

wise to the distillate, and this was shaken to effect solution. After standing ca 5 minutes the clear, colorless lighter phase was drawn off (double-ended needle) and stored over a few KOH pellets under inert atmosphere in the freezer while preparative VPC was in progress. The aminoaziridine was prepped on a 5' x $^1/_4$" glass column packed with Pennwalt 223 (Applied Science Laboratories), oven temperature, 110°; injector and detector 160-180°. That slight decomposition to butenes occured under these conditions was confirmed by analytical v.p.c. with the injector off (25-30°). NMR ($CDCl_3$): 1.0-1.2 (dd, J's = 1.5, 4 cps; 6H), 1.4-2.0 (m, 2H), 3.6-3.75 (broad 5, 2H); IR (CCl_4): 3300 (m, b), 3250 (m), 3150 (m), 2990 (heat) (sh, m), 2950 (m), 2920 (m), 2970 (w), 1590 (m, b), 1460 (m), 1405 (s), 1380 (s), 1140, 1070, 1010, 950, 750.

Other components of the distillate could be observed. One, relative retention with respect to 1-amino-cis-2,3-dimethylaziridine of 1.51 on Pennwalt, was isolated and tentatively identified (nmr, ir) as 3-hydrazinobut-1-ene. NMR ($CDCl_3$): 1.14 (d, J = 7, 3H), 2.98 (s, overlapping), 3.0-3.47 (m; J = 7, peaks at 3.10, 3.22, 3.33; overlapping multiplets, total overlapping = 4H); IR (neat): 3255 (b, m), 3175 (w), 3065 (w), 2968 (m), 2917 (m), 2855 (w), 2810 (w), 1625 (w), 1595 (w), 1440 (w), 1405 (m), 1375 (m), 1315 (w), 1250 (w), 1105 (m), 1035 (m), 983 (m), 910 (s), 840 (w).

A different peak, with relative retention (as above) of 1.75 was prepped twice on Pennwalt. NMR and IR (below) suggest that this compound could be cis-3,4-dimethyl-1,2-diazacyclobutane. An NMR experiment was performed which consisted of bubbling O_2 through a solution of this compound in an NMR tube, then measuring its NMR spectrum. A new, strong singlet was observed at 2.13. NMR ($CDCl_3$): 1.00-1.25 (m, sharp peaks at 1.07, 1.17, appearance similar to the cis aminoaziridine methyls

1.93-2.23 (m); IR(neat): 3250-3350 (m), 2960 (s), 2927 (m), 2876 (m), 1610 (w, b), 1560 (m), 1375 (m), 1188 (w), 1150 (w), 1090 (w), 990 (w), 943 (m), 920 (m), 780 (w).

Preparation of 1-Methane sulfonamido-cis-2,3-dimethylaziridine[14]

A solution of 1-amino-cis-2,3-dimethyl aziridine (100 mg, 1.16 mmoles, purified by pvpc on Pennwalt to $\gtrsim$ 99.7% isomeric purity) and triethylamine (120 mg, 1.19 mmoles, distilled from CaH_2, stored over KOH in stoppered flask in a dessicator) in 2 ml methylene chloride (passed through alumina) was stirred in a dry flask under argon at -78°. Methanesulfonyl chloride (85 μl, 1.11 mmoles, distilled from P_2O_5 and stored in a dessicator) was added drop wise from a syringe over 3 minutes. The reaction mixture was allowed to stir 20 minutes at -78°. The bath was removed and stirring continued for 35 minutes. Dilution with 3 ml methylene chloride was followed by washing with 3 ml saturated aqueous $NaHCO_3$, withdrawal of the organic phase by syringe, filtration through $MgSO_4$ and glass wool. The reaction mixture was concentrated under reduced pressure at 25°, to afford 220 mg slightly yellow solid. Recrystallization from low boiling petroleum ether/benzene gave 82 mg product, mp 74-7°, second crop, 18 mg, 68-74°. Total yield 100 mg (52%). An attempt to sublime 22 mg (first crop) at 0.05-0.02 mm and 0-70° onto a cold finger at -78° gave 2 mg white solid, mp 79-80°. NMR ($CDCl_3$): 1.05-1.25 (m, 6H, sharp peaks at 1.0, 1.18), 2.0-2.4 (m, 2H), 3.10 (s, 3H) 5.3-5.9 (broad, 1H); IR (CCl_4): 3295 (w), 3220 (w, b), 3030 (w), 2970 (w), 2935 (w), 1715 (w), 1450 (w), 1410 (w), 1365 (s), 1345 (s), 1320 (s), 1255 (w), 1155 (s), 960 (m), 975 (m); M.S.: 164 (P^+), 85, 79, 70, 65, 55, 56, 42, 41, 39.

Preparation of 1-p-toluenesulfonamido-cis-2,3-dimethylaziridine

To a stirred solution of 1-amino-cis-2,3-dimethylaziridine (100 mg, 1.16 mmoles purified by vpc) and triethylamine (118 mg, 1.17 mmoles) in 2 ml methylene chloride, maintained at -78° (dry ice/acetone) under N_2, was added via syringe a solution of p-toluenesulfonyl chloride (220 mg, 1.15 mmoles; recrystallized from chloroform-petroleum ether (35-60)) in 1.0 ml methylene chloride over a period of five minutes. The reaction mixture was allowed to stir for one hour at -78°, and 1.5 hours at room temperature. The reaction mixture was taken up in 3 ml methylene chloride. This was washed three times with 50 ml aqueous sodium chloride, dried (Na_2SO_4) and concentrated under reduced pressure to afford 60 mg light yellow solid, mp 80-2°. Spectral samples were obtained by preparative t.l.c. (silica gel). NMR ($CDCl_3$): 0.9-1.25 (m, 6H, sharp peaks 0.95, 1.06) 1.9-2.3 (m, 2H), 2.43 (s, 3H), 6.0 (broad, 1H), 7.58 (m, 4H, para substituted aromatic 7.92, 7.78, 7.38, 7.23); IR (CCl_4): 3230 (w), 3190 (w, b), 2950 (sh), 2915 (m), 2864 (m), 1596 (w), 1485 (w), 1446 (w), 1395 (w), 1373 (m), 1341 (m), 1325 (m), 1301 (w), 1286 (w), 1195 (w), 1130 (w), 1167 (s), 1100 (m), 1039 (m), 1015 (w); MS: 273 (from decomposition, $C_7H_7SSO_2C_7H_7$), no peak at 240.

Preparation of D(-)-2,3-dimethanesulfonyloxybutane

A magnetically stirred solution of D(-)-2,3-butanediol (27.0 g, 0.3 moles, Burdick and Jackson, lot 6905) in 225 ml dry pyridine was cooled on a dry ice-acetone bath until freezing was observed on the wall of the flask. Methanesulfonyl chloride (75.0 g, 0.653 moles) distilled from P_2O_5 was added dropwise over an hour with cooling as necessary. Cooling and stirring were continued two hours, then allowed to warm up and stir four hours. The resulting thick white precipitate was filtered on a coarse

glass frit, washed with 50 ml distilled water. Water was removed under aspirator pressure. The crude product was taken up in 800 ml methylene chloride. This was washed with water, dried ($MgSO_4$) and concentrated to afford 64.0 g (86%) colorless crystals, mp 123-5°. NMR ($CDCl_3$): 1.30-1.55 (m, 6H, peaks at 1.41, 1.52), 3.07 (s, 6H), 4.5-4.9 (m, 2H); IR (CCl_4): 3018 (m), 2980 (m), 2926 (w), 1438 (w, b), 1407 (w), 1355 (s), 1340 (s), 1225 (w, b), 1173 (s), 1072 (m), 1020 (m), 968 (s), 934 (s), 904 (s), 854 (m).

Preparation of 1-Amino-trans-2,3-dimethylaziridine[6]

In a 100 ml round-bottomed flask equipped with reflux condenser, magnetic stirbar and nitrogen inlet, was placed 15.0 g (0.061 moles) of d-(-)-2,3-dimethanesulfonyloxybutane. The addition of 15.0 ml (0.47 moles) of anhydrous hydrazine and 15.0 ml (0.31 moles) of hydrazine hydrate was followed by heating for 40 hours at 40°. The reflux condenser was replaced by a short path still head, and distillate collected up to 70° at 110 mm (vacuum pump, controlled nitrogen leak). The distilled material was saturated with KOH (reagent grade), the top layer withdrawn by syringe and distilled again. Distillation at 25° on the vacuum line (10^{-4}-10^{-5} torr) gave 1.0 g product (vpc isomeric purity $\gtrsim$ 99.5%). Attempts to purify this material by preparative vpc on Pennwalt 223 under a variety of conditions were frustrated by the increasing conversion of this material to a compound with relative retention 1.31 to the desired compound.

Retention data suggests that the impurity is the previously isolated 3-hydrazino-but-1-ene. NMR ($CDCl_3$): 1.05-1.80 (m, 8H), overlapping methine and methyl signals peaks at 1.13, 1.18, 1.23, 1.24, 1.36), 3.09 (broad, 2H); IR (CCl_4): 3330 (b), 2930 (s), 2948 (s), 2916 (s), 2860 (m), 1585 (m), 1453 (m), 1380 (m), 1322 (w), 1118 (w), 1083 (w), 1020 (m), 963

(w), 925 (m). MS: 86 (P^+), 71, 59, 56, 55, 44, 42, 41, 34, 32, 29, 28, 27 higher mass peaks (low intensity at 91, 97, 120, 135, 150 (150 may be due to the allylic mesylate).

Attempted preparation of 1-Methanesulfonamido-trans-2,3-dimethylaziridine

To a cooled (-78°), stirred solution of 1-amino-trans-2,3-dimethylaziridine (53 mg, 0.617 mmoles) and triethylamine (62 mg, 0.614 mmoles) in 1.5 ml methylene chloride (passed through Activity grade 1 Alumina), was added methanesulfonyl chloride (67 mg, 0.588 mmoles, distilled from P_2O_5) dropwise. This was allowed to stir 1.5 hours the yellow solution was allowed to warm to 25°. One ml methylene chloride, and one ml saturated $NaHCO_3$ solution were added. The organic phase was drawn off after a few minutes of stirring, concnetrated under reduced pressure at 25°, and the yellow oil taken up in 0.5 ml $CDCl_3$ (passed through alumina) with ca 1% TMS. The nmr spectrum was complicated, but running several spectra showed the products to be unstable to these conditions. The half-life for decomposition (by following the sulfonyl methyl signal at 3.13 δ) was about one hour. The infrared spectra and hot-tube decompositions were run on samples prepared as above, but not subjected to the nmr probe, yields were 35-45%. The material could not be crystallized. IR (neat): 3265 (m), 3217 (m), 2980 (m), 2930 (m), 2870 (w), 1625 (w, b), 1450 (m), 1378 (m), 1322 (s), 1151 (s), 1029 (m), 980 (m), 965 (m), 843 (w), 795 (m), 775 (m).

Preparation of 1-p-Toluenesulfonamido-trans-2,3-dimethylaziridine

A solution of p-toluenesulfonylchloride (203 mg, 1.06 mmoles, recrystallized in 20 ml dry methylene chloride was added over 10 minutes to a stirred solution of 1-amino-trans-2,3-dimethylaziridine (95 mg, 1.10

mmoles) and triethylamine (148 μl, 1.06 mmoles) at 0°. The reaction was stirred 2 hours at 0°, and 1 hour at 25°. This was concentrated under reduced pressure, and the remaining solid extracted with 3 x 5 ml ether. The ether soluble material was redissolved in 20 ml 5:1 ether/methylene chloride, washed with two protions aqueous sodium chloride, dried ($MgSO_4$), and concentrated. Impurities were precipitated from benzene with hexane, and the soluble fraction was recrystallized from benzene to give 60 mg light yellow solid, mp 98-100 (dec, yellow melt). Further purification by thin layer chromatography was achieved, at 50-60% recovery. NMR ($CDCl_3$): 1.00-1.17 (m, 3H, peaks at 1.03, 1.13) 1.46-1.67 (m, 3H peaks at 1.48, 1.59), 1.45 (s, 3H) 3.40 (broad, 2H) 3.87-4.25 (m, 2H), 7.57 (m, 4H, aromatic A_2B_2, $J_1 = 9$, $J_2 = 25$, peaks at 7.85, 7.70, 7.43, 7.28, 7.30); IR (CCl_4): 2720-2990 (w, b), 1595 (w), 1443 (w), 1372 (w), 1350 (m, b), 1300 (w), 1285 (w), 1180 (w), 1164 (s), 1089 (w), 1076 (w), 1014 (w), 840 (w).

Preparation of 1-Phthalimido-trans-2,3-dimethylaziridine[15]

Trans-2-butene (5 ml at -78, K and K) was distilled into a stirred, cooled (-78) suspension of N-aminophthalimide (prepared from hydrazine and phthalimide[19], also available from Aldrich) in 50 ml methylene chloride (distilled from P_2O_5) via a dewar condenser. Lead tetraacetate (4.22 g, 9.53 mmoles, Matheson, Coleman and Bell) was added in four portions over 40 minutes, after which the cold bath was removed and stirring continued. After 1.5 hours the reaction mixture was filtered through celite, then two inches of silica gel. This was concentrated under reduced pressure to give a cloudy yellow oil. Trituration with small volumes of methylene chloride and filtration, followed by solvent removal gave 1.1 g crude product. Column chromatography on 22 g silica gel with diethyl ether/low

boiling petroleum ether (1:9) gave 385 mg (19%) yellow oil, which solidified to a yellow solid, mp 65-7°. NMR ($CDCl_3$): 1.2-1.6 (dd, J = 7, peaks at 1.27, 1.37, 1.38, 1.48), 2.2-3.0 (m, 2H, overlapping multiplets, peaks at 2.25, 2.35, 2.45, 2.53, 2.59, 2.63, 2.78, 2.87, 2.96), 7.77 (s, b, 4H); IR ($CHCl_3$): 3030 (m, sh), 3010 (m, sh), 2975 (m), 2935 (m), 2880 (w), 1781 (m), 1761 (m), 1716 (vs), 1656 (w), 1604 (w), 1461 (m), 1438 (m), 1373 (s), 1356 (m), 1315 (m), 1213 (m, b), 1175 (m), 1133 (m), 1080 (m), 1022 (m), 970 (w), 950 (w), 890 (s), 844 (w).

Preparation of 1-Phthalimido-cis-2,3-dimethylaziridine[15]

Cis-2-butene (10 ml at -78, ca 5-fold excess, K + K Laboratories, Inc.) was distilled into a dry 200 ml round-bottomed flask, containing N-aminophthalimide[3] (5.00 g, 30.8 mmoles) and 100 ml methylene chloride (distilled from CaH_2). The system was flushed with argon, and lead tetra-acetate (13.79 g, 31.2 mmoles) was added over 45 minutes at -78 in small portions every few minutes. The reaction was stirred one hour at -78, 3.0 hours at room temperature, filtered through 1.5 inches of silica gel, then through 1.5 inches of neutral alumina. This was concentrated under reduced pressure. Extraction of the resulting semisolid with ether-petroleum ether 35-60 (1:1) and concentration under reduced pressure gave 2.59 g (39%) of product, sufficiently pure for further synthesis. A portion (400 mg) of this material chromatographed on 11 g silica gel with ether-petroleum ether (1:9) melted at 93-95°. NMR ($CDCl_3$): 1.25-1.55 (m, 6H, peaks at 1.33, 1.37, 1.40, 1.43), 2.4-2.85 (m, 2H), 7.68 (s, 4H); IR ($CHCl_3$): 3125 (m), 2985 (m), 2930 (w), 2870 (w), 1781 (m), 1761 (m), 1726 (s), 1711 (vs), 1604 (w), 1461 (m), 1448 (w), 1431 (w), 1403 (w), 1376 (s), 1356 (m), 1323 (w), 1278 (w), 1210 (w, b), 1175 (m), 1150 (m),

1097 (m), 1080 (m), 1067 (m), 1012 (m), 987 (m), 962 (m), 890 (s), 827 (w).

Preparation of 1-Amino-cis-2,3-dimethylaziridine from 1-Phthalimido-cis-2,3-dimethylaziridine

In a 50 ml base-washed, oven dried, round bottomed flask, fitted with a septum, was placed 1-phthalimido-cis-2,3-dimethylaziridine (2.19 g, 10.1 mmoles, crude-decomposes on chromatography). The flask was flushed with argon. Hydrazine hydrate (15 ml), was added by syringe. The reaction mixture was allowed to stand 1.5 hours, than allowed to stir 0.5 hours at 25°. Then 20 ml diethyl ether (distilled from sodium and benzophenone after refluxing the blue solution under inert atomosphere) was added via syringe. The mixture was allowed to stir a few minutes, and the ether layer was removed. Two more ether extractions (15, 10 ml) and distillation of the solvent from the combined ether layers gave ca 400 mg (about 45%) oil, which was further purified by preparative vpc on Pennwalt 223 (at 110°). Spectral and vpc retention data were identical to material prepared by another method.

Net Stereochemistry of the Preparation of 1-Amino-cis-2,3-dimethylaziridine from cis-2-butene

In this vpc experiment chromatographed samples (ca 50 mg each) of 1-phthalimido-cis-and trans-2,3-dimethylaziridine were each (separately) treated with hydrazine hydrate (0.6 ml) and extracted with 3 ml ether to provide authentic vpc samples. Also, crude 1-phthalimido-cis-2,3-dimethylaziridine (56 g) was treated with hydrazine hydrate (10 ml), and extracted with 20 ml ether. VPC analysis of the extracts on Pennwalt 223 showed that the hydrazinolysis of the crude intermediate gave 1-amino-cis-2,3-dimethylaziridine at least 99% isomerically pure.

Preparation of Methanesulfinylchloride

The procedure followed is essentially that of Douglass[16a]. Methyldisulfide (47.1 g, 0.5 moles, Aldrich) and glacial acetic acid (60.1 g, 1.0 mole) were weighed into a dry 500 ml three-neck round bottom flask, and allowed to stir with cooling (-78°). Chlorine (ca 80 ml at -78, 0.75 moles, Matheson gas products) was distilled from a 100 ml flask via a dewar condenser (-78) into the reaction flask, which was vented via a cold trap (-78), a back-up trap, and an aqueous NaOH bubbler. The reaction vessel was maintained at ca -10 to -15 during the distillation (about 2 hours), cooling was discontinued and stirring continued 1.5 hours. This was then heated to 35-37° with a flameless heat gun. The amber solution was distilled at 1 atm. (100° bath) affording ca 60 ml of distillate (mostly acetyl chloride). Distillation at aspirator pressure gave 60 ml of distillate boiling 40-50°. Redistillation, also at aspirator pressure (20 mm), through a 15 cm glass Vigreaux column gave (after a small fore-run) three fractions: 45-47°, 12 ml, light yellow; 47-48°, 25 ml, yellow; 48-50°, 8 ml, yellow.

Preparation of Methanesulfinic Acid

Methanesulfinic acid has been prepared by Cram and coworkers[16b]. Methanesulfinyl chloride (2.0 g, 20.4 mmoles, bp 45-47° at 20 mm) was allowed to stir in a dry 25 ml flask, with a side arm equipped with a septum, under nitrogen atmosphere. The temperature was maintained below -30°. Distilled water (0.36 ml, 20.0 mmoles) was added dropwise by syringe while nitrogen was bubbled through the solution (to carry off the HCl generated). The addition took only a few minutes and nitrogen bubbling was continued an additional 10 minutes below 0°. The solvent was removed at 0° (2 hours), the flask refilled with nitrogen, and 15 ml ether was added. The two phase

mixture was left to stand in the freezer a few days, whereupon long, thin needles formed. The yellow ethereal solution was removed by syringe, and the crystals washed with three 5 ml portions of pentane. Solvent was further removed under vacuum (0.1 mm) for several hours at 0°. This afforded 0.9 g (55%).

Identification of Minor Products of the Pyrolysis of 1-Methanesulfonamido-cis-2,3-dimethylaziridine by Gas Chromatography-Mass Spectroscopy

The products of the previously described byrolysis of 1-methanesulfonamido-cis-2,3-dimethylaziridine at 310° in the hot tube were analysed by GC-MS for minor components by Mr. M. Keith Murphy of the J. L. Beauchamp research group on GC-MS system assembled by Mr. Jon Burke. Peaks examined and identified are listed in Table 8. Interestingly, when the chromatograph was observed only at m/e 64 a large, tailing peak was observed. The corresponding peak was also observed by monitoring only m/e 48 (64-16). This most likely corresponds to sulfur dioxide, resulting from thermal decomposition of the (presumed) byproduct methanesulfinic acid in the hot tube.

Table 8.

Time	%	rrt	assignment
1:59	4.4	0.196	ethane
2:19	3.5	0.270	propene
3:21	1.4	0.396	1-butene
5:01	0.8	0.618	C_5H_1 (not further identified)
7:26	0.9	0.895	trans-2-pentene
8:11	0.7	1.00	cis-2-pentene

Examination of the Thermal Decomposition of 1-Amino-trans-2,3-dimethylaziridine

This experiment was carried out by Miss Francis Houle of the J. L. Beauchamp research group. The photoelectron spectrometer system has been described. In the gas phase, a degassed sample of 1-amino-trans-2,3-dimethylaziridine was diluted with argon and passed over an electrically heated filament into the photoionization detection system. Products were assigned on the basis of their photoelectron spectra which were recorded at filament temperatures, from 416°-655°C. The major products observed were trans-2-butene (small proprtions of cis-2-butene would not have been distinguishable) and molecular nitrogen. A small (ca 5% with respect to the nitrogen signals) amount of molecular hydrogen was also observable. No hydrazine or ammonia were detected. The fate of the rest of the hydrogen is not known. It was suggested that a piece of tantalum in the detector may have interfered with this experiment.

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Appendix: Derivation for Scheme 3.

Definitions:

$[X]$ = concentration of species X

$A = [1a]$ (i)

$B = [1b]$ (ii)

$C = [1'a]$ (iii)

$D = [1'b]$ (iv)

$E = [8a]$ (v)

$F = [8b]$ (vi)

$\alpha = (r/i)\ cis = (E/F)\ cis$ (vii)

$\beta = (r/i)\ trans = (F/E)\ trans$ (viii)

$R_1 = k_3/k_1$ (ix)

$R_2 = k_4/k_2$ (x)

Equations:

From A (1a):

$$\frac{dD}{dt} = k_1C - k_2D - k_4D = 0 \qquad \text{(steady state)} \tag{1}$$

$$\frac{dC}{dt} = kA + k_2D - k_1C - k_3C \tag{2}$$

from (1)

$$D = \frac{k_1C}{k_2 + k_4} \tag{3}$$

from (2)

$$\frac{dC}{dt} = kA + \left(\frac{k_1k_2}{k_2k_4} - k_1 + k_3\right) C \tag{4}$$

The solution of this differential equation (4) consists of two terms, an exponential part, and a time independent part. For non-zero time the

exponential rapidly approaches zero, and C approaches a steady state value:

$$C = \frac{kA\,(k_2 + k_4)}{(k_1k_4 + k_2k_3 + k_3k_4)} \tag{5}$$

from (3) and (5)

$$D = \frac{k_1kA}{(k_1k_4 + k_2k_3 + k_3k_4)} \tag{6}$$

from (vii), (5) and (6).

$$\alpha = \frac{k_3C}{k_4D} = \frac{k_3}{k_4k_1}(k_2 + k_4) = \frac{k_3}{k_1}\left(\frac{k_2}{k_4} + 1\right) \tag{7}$$

rearranging (7)

$$\alpha = R_1(R_2^{-1} + 1) \tag{8}$$

By a similar sequence for B, from (9) and (10),

$$\frac{dC}{dt} = k_2D - k_1C - k_3C = 0 \tag{9}$$

$$\frac{dD}{dt} = kB + k_1C - k_2D - k_4D \tag{10}$$

equation (11), analogous to (8) is obtained:

$$\beta = \frac{k_4}{k_2}\left(\frac{k_1}{k_3} + 1\right) = R_2(R_1^{-1} + 1) \tag{11}$$

Equations (8) and (11) are simultaneously solved for R_1 and R_2 in terms of and to give equations (12) and (13):

$$R_1 = \frac{\alpha\beta - 1}{\beta + 1} \tag{12}$$

$$R_2 = \frac{\alpha\beta - 1}{\alpha + 1} \tag{13}$$