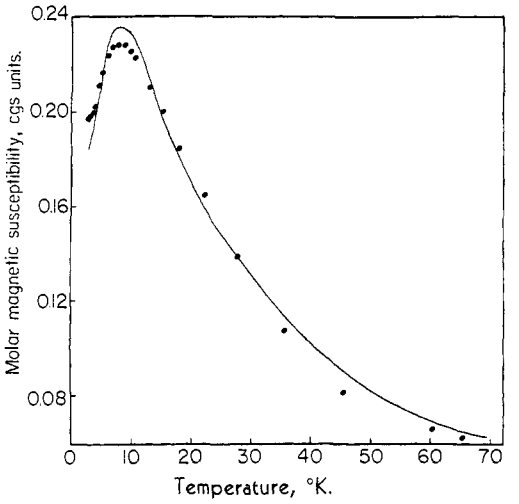

Figure 2. The temperature dependence of the magnetic susceptibility of $[Cu(C_4H_4N_2)(NO_3)_2]_n$. The experimental data (●) are compared to the best fit to the Ising model with $J = -6.0\ cm^{-1}$ and $\langle g \rangle = 2.22$.

where

$$\langle \chi \rangle = \frac{1}{3}\chi_{\parallel} + \frac{2}{3}2\chi_{\perp}$$

The parameters which give the best fit to the experimental data shown in Figure 2 are $\langle g \rangle = 2.22$ and $J = -6.0\ cm^{-1}$.

The best-fit $\langle g \rangle$ value is to be compared with the epr results of Kokoszka and Reimann,[8] who reported $g_z = 2.295$, $g_x = 2.054$, and $g_y = 2.070$ ($\langle g \rangle = 2.133$). They differ by about 0.09 unit. Furthermore, if the presumably more precise epr $\langle g \rangle$ value of 2.133 is used in the calculations, the best-fit J value changes only slightly, to $-5.3\ cm^{-1}$, even though the fit is about four times poorer. This is indicative of the correctness of the calculated J value. The deviation suggests that the Heisenberg model may be more appropriate, since Bonner and Fisher[9] have shown that the susceptibility variation with temperature for this model exhibits more rounded cusps than the Ising model. Measurements on single-crystal samples will permit the selection of the appropriate model.

Additionally, it is important to note that a distinct absorption in the epr spectrum at $g = 3.97$ was observed using an E-3 spectrometer at 9.180 GHz. Although half-field absorptions are sometimes seen for pure powdered samples of copper dimers,[10] such features are rarely observed for polymeric materials.

Owing to the highly unusual structural features of this molecule, the unpaired electron in the σ-antibonding level of the copper ion may interact with the π electrons of the aromatic heterocyclic amine, thus effecting an antiferromagnetic interaction by a superexchange mechanism. Never before have copper ions so far removed from one another been observed to be exchange coupled with an interaction constant of the magnitude of that observed here. Furthermore, these results reflect the importance of the consideration of interactions among the unpaired spins when interpreting magnetic and epr data in systems where the metal ions are far apart.

Acknowledgments. This research was supported by the National Science Foundation through Grant No. GP-22887 and by the Materials Research Center of the University of North Carolina through Contract No. DAHC15 67 C 0223 with ARPA.

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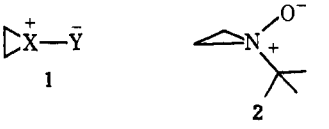
Received May 3, 1971

(8) G. F. Kokoszka and C. W. Reimann, *J. Inorg. Nucl. Chem.*, **32**, 3229 (1970).
(9) J. C. Bonner and M. E. Fisher, *Phys. Rev. A*, **135**, 640 (1964).
(10) See, for example, G. F. Kokoszka and G. Gordon, *Transition Metal Chem.*, **5**, 181 (1969).

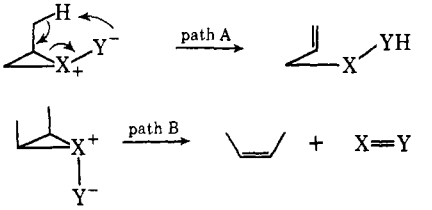
Rearrangement of Strained Dipolar Species, Aziridine *N*-Oxides. II[1]

Sir:

In a study of the chemistry of strained dipoles, exemplified by the general expression **1**, we were recently



able to elucidate the two pathways involved in the decomposition of episulfoxides (**1**, X = S; Y = O), namely a ring opening with concerted hydrogen shift, path A, and a less facile and partially stereospecific ejection of the elements of XY, path B, when the stereo-

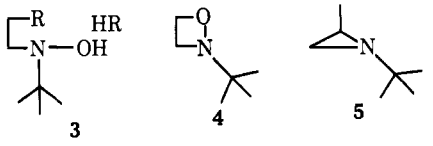


chemistry is not favorable for the hydrogen-transfer reaction. We now report on the aziridine *N*-oxides (**1**, X = NR; Y = O). Although such species have been postulated as intermediates in certain oxidations of aziridines,[2,3] they have until now eluded detection, and our own studies, which have revealed these species for the first time, amply justified the prior intimations of instability.

Ozonolysis of *N*-*tert*-butylaziridine at −75° in methylene chloride (3 g/100 ml) provided a solution of *N*-*tert*-butylaziridine *N*-oxide (**2**)[4] stable up to 0°. Examination of the nmr spectrum[5] of this solution at temperatures up to 0° showed a new *tert*-butyl absorption, δ 1.22 (s, 9 H), and the methylene protons as an A_2B_2 multiplet centered at 2.6 (m, 4 H), significantly shifted downfield from the starting material, 0.80 (s, 9 H), 1.30 (m, 4 H). Above 0° this substance smoothly underwent first-order decomposition into eth-

(1) J. E. Baldwin, S. C. Choi, and G. Höfle, *J. Amer. Chem. Soc.*, **93**, 2810 (1971).
(2) A. Padwa and L. Hamilton, *J. Org. Chem.*, **31**, 1995 (1966).
(3) H. W. Heine, J. D. Meyers, and E. T. Peltzer, *Angew. Chem.*, **82**, 395 (1970); *Angew. Chem., Int. Ed. Engl.*, **8**, 374 (1970).
(4) Previous ozonolyses of *tert*-alkylamines have been reported to lead to *N*-oxides; this area has been reviewed by P. S. Bailey, J. E. Keller, D. A. Mitchard, and H. M. White, *Advan. Chem. Ser.*, No. 77, 58 (1968).
(5) All low-temperature nmr studies were conducted in a Varian HA-100 spectrometer fitted with a variable-temperature probe.

ylene, δ 5.24, trapped as the dibromide, and *tert*-nitrosobutane, δ 1.08 (s), a reaction which was readily apparent from the sudden conversion of the initially water-white solution to the characteristic deep blue of the nitroso compound.[6] The aziridine *N*-oxide **2** was sensitive to acid since addition of 2 equiv of hydrogen bromide in chloroform, at −75°, to the ozonized solution caused complete conversion to the hydrobromide salt **3** (R = Br),[7,8] mp 117–118°. *Anal.* Calcd for $C_6H_{15}NOBr_2$ (mol wt 277): C, 26.01; H, 5.46; N, 5.05; Br, 57.58. Found: C, 26.29; H, 5.48; N, 5.15; Br, 57.58. This substance gave a positive tetrazolium test for the hydroxylamine function. Since it had previously been suggested[2] that aziridine *N*-oxides may convert to 1,2-oxazetidines before dissociation and also to exclude the 1,2-oxazetidine **4** from consideration as a structure for our low-temperature oxidation product we have synthesized **4** by careful treatment of salt **3** (R = Br) with potassium *tert*-butoxide at 0° in tetrahydrofuran. High-vacuum distillation gave 1,2-oxazetidine **4** as an oil, stable up to about 60°,[9] δ 1.15 (s, 9 H), 3.78–5.19 (m, 4 H), reducible with lithium aluminum hydride to *N*-*tert*-butylethanolamine[10] identical with an anthentic sample, and oxidized with *m*-chloroperbenzoic acid to formaldehyde, identified by the 2,4-dinitrophenylhydrazone.[11] Thus, the 1,2-oxazetidine **4** cannot be an intermediate in the conversion of the aziridine oxide **2** into its fragmentation products.



3 **4** **5**

Since the path A noted above for the episulfoxides is precluded by lack of substitution in **2**, we have examined the case of 1-*tert*-butyl-2-methylaziridine (**5**).

(6) To disprove the possibility that our compounds are aziridine–ozone complexes we decomposed the degassed oxide **2**, formed as before at −78°, in a stream of oxygen-free nitrogen allowing the temperature to rise to 25°. The exit gas was passed through the oxygen-sensitive ammoniacal cuprous chloride solution; *cf.* B. B. Bach, *Chem. Ind. (London)*, 1279 (1953). No oxygen was evolved during the formation of ethylene and nitroso compound, as is required for the aziridine–ozone complex. However, the triphenyl phosphite–ozone complex (*cf.* R. W. Murray and M. L. Kaplan, *J. Amer. Chem. Soc.*, **91**, 5358 (1969)) prepared at the same concentration gave a strongly positive test for oxygen at its decomposition point, −20°, in the same system. Therefore the compounds described here cannot be aziridine–ozone complexes.

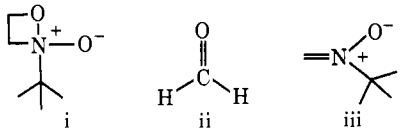
(7) This acid lability of aziridine *N*-oxides was apparent in attempts to oxidize *N*-*tert*-butylaziridine with *m*-chloroperbenzoic acid at −40°, whereby a fair yield of the opened hydroxylamine **3** (R = *m*-chlorobenzoyloxy) as well as nitroso compound was formed. This substance must result from the action of the benzoic acid, resulting from oxidation, upon the aziridine *N*-oxide.

(8) All new compounds have satisfactory spectral data and the crystalline materials yielded correct elemental analyses.

(9) We shall report on the thermal decomposition mode for 1,2-oxazetidines in a future publication.

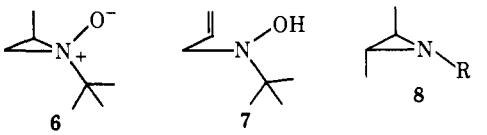
(10) This product was identified by conversion to the hydrochloride salt, mp 154°, identical in mixture melting point and infrared spectrum with an authentic sample; *cf.* A. T. Bottini and J. D. Roberts, *J. Amer. Chem. Soc.*, **80**, 5203 (1958).

(11) Such oxidative cleavages are characteristic of cyclic hydroxylamines (*cf.* N. LeBel, *Trans. N. Y. Acad. Sci.*, 27, 858 (1965)) and in this case presumably proceeds through the oxide i to formaldehyde and nitrone iii.



i ii iii

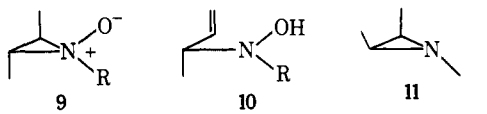
Here a preferred transoid conformer of the precursor (as **5**) might allow oxidation to the oxide **6**, having the required cisoid relationship between the methyl and oxygen atom. This expectation was borne out since ozonolysis of **5** at −75° gave a solution of the oxide **6**, δ (methylene chloride) 1.03 (s, 9 H), 1.21 (d, 3 H), 1.61 (m, 3 H), which on warming to −30° smoothly rearranged to the allylic hydroxylamine **7**, δ ($CDCl_3$) 1.15 (s, 9 H), 3.35 (d, 2 H), 5.20 (m, 2 H), 6.05 (m, 1 H), isolated and characterized as the *p*-nitrobenzoate, mp 81°, ν_{max} 1740 cm^{-1}. As in the previous report[1] the path A appears to be the more facile since measurement of activation energy for the decomposition of **2** and **6** gave values of 22 ± 1 and 15 ± 1 kcal/mol, respectively.[12]



6 **7** **8**

Thus the same mechanistic duality, *i.e.*, ring opening with hydrogen migration (path A), and, in the absence of suitably oriented hydrogen atoms, an olefin forming elimination (path B) are observed here as was found in the episulfoxides.[1]

In the case of 2,3-disubstituted aziridines the presence of inverting species is significant. It appears from our results that the oxygen insertion reaction takes place with retention of configuration at nitrogen in the more stable conformers. Thus ozonolysis of *trans*-1,2,3-trimethylaziridine (**8**, R = Me), as before, could only yield a single oxide **9** (R = Me), and thermal rearrangement took place, on warming up to 0°, cleanly to the hydroxylamine **10** (R = Me): δ ($CDCl_3$) 1.20 (d, 3 H), 2.78 (s, 3 H), 3.52 (m, 1 H), 5.10–6.26 (m, 3 H); *p*-nitrobenzoate mp 218.5–219°. The cis isomer exists largely as conformer **11**, since oxidative transfor-



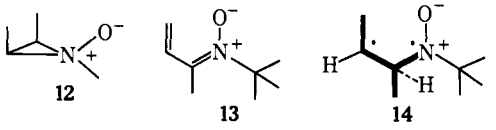
9 **10** **11**

mation occurred to the same hydroxylamine (**10**, R = Me), *via* oxide **12**, whereas the alternative form, with *N*-methyl cis to ring methyls, would be expected to yield fragmentation to olefin and nitroso compound, path B.

In the case of highly substituted and hindered aziridines, however, the two pathways, A and B, converge. Thus, 1-*tert*-butyl-*trans*-2,3-dimethylaziridine (**8**, R = *tert*-butyl), on reaction with ozone (−75°) or with 1 equiv of *m*-chloroperbenzoic acid at −40° converted at −20° to a mixture of *tert*-nitrosobutane, *trans*-2-butene, and the unsaturated nitrone **13** (nmr ($CDCl_3$) δ 1.61 (s, 9 H), 2.20 (s, 3 H), 5.40 (*J* = 6 and 9 Hz, 2 H), 7.59 (*J* = 6 and 9 Hz, 1 H)), the latter probably resulting from further oxidation of the hydroxylamine (**10**, R = *tert*-butyl), which in this case is formed at the temperature of the oxidation due to the instability of the oxide **9** (R = *tert*-butyl). The two paths here seem to be occurring in approximately equal amounts

(12) These measurements were conducted for small extents of decomposition by determination of the disappearance of the nmr signal characteristic of the two oxides **2** and **6** with time. The reactions were essentially first order up to 75% decomposition.

and analysis (glpc) of the olefinic material showed that it was 100% *trans*-2-butene.[13]



12 13 14

In summary, aziridine *N*-oxides behave in the same way as was earlier demonstrated for episulfoxides, showing dual pathways A and B which are stereochemically distinct. The complete stereospecificity of olefin formation for oxide **9** (R = *tert*-butyl) does not militate against the earlier radical interpretation of path B, since the lower temperature required for the aziridine *N*-oxide decompositions would favor retention of stereochemistry in the diradical **14**, a temperature dependence which was also observed in the episulfoxide case.[1] In general, the rearrangement path A seems to be more facile when the stereochemistry is favorable; however, substitution with large hindering groups brings the rate of the two processes together.

Acknowledgment. We wish to thank the U. S. Public Health Service, the National Science Foundation, the Petroleum Research Fund, administered by the American Chemical Society, Eli Lilly and Company, and Hoffman La Roche for support of this research.

(13) Glpc analysis was on a column of 5% silver nitrate saturated tetraethylene glycol, Chromosorb P (10 ft × 1/8 in.) at 0°.
(14) A. P. Sloan Fellow, 1969–1971.

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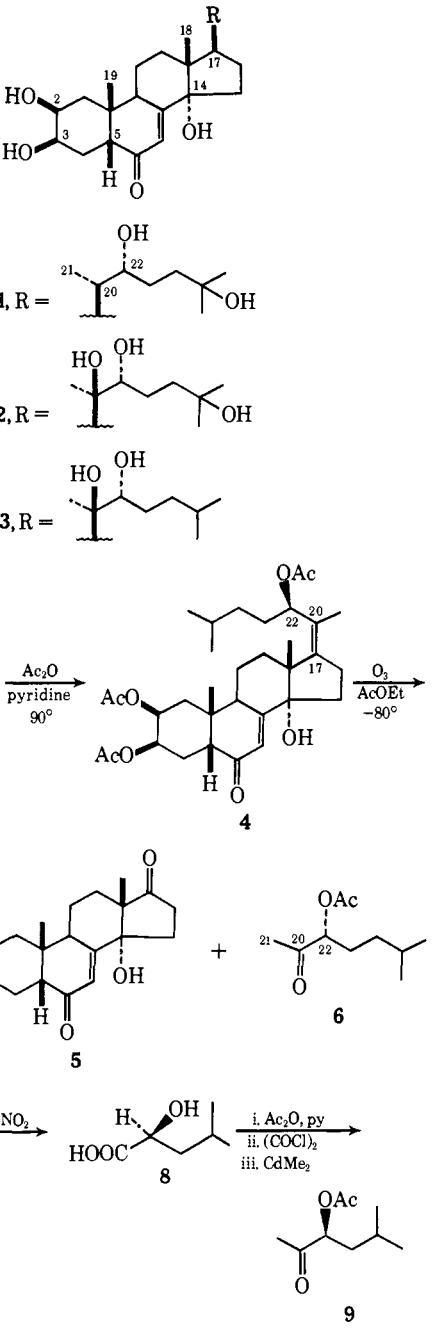
The Absolute Configurations at C-20 and C-22 in Ecdysones

Sir:

Although close to 40 ecdysones have been characterized to date,[1] the full stereochemistry of the side chain has only been elucidated for α-ecdysone (**1**) (X-ray).[2] However, α-ecdysone is the only ecdysone which lacks a 20-hydroxyl group, all other ecdysones having hydroxyl groups at both C-20 and C-22. Hence, nmr comparison of proton signals close to these chiral centers is not applicable in deducing the configurations at C-20 and C-22.

However, the natural ecdysones, excepting α-ecdysone and shidasterone (epimeric at C-20 and/or C-22[3]), have very similar nmr signals originating from the moiety close to C(20)–C(22); thus, the 2,3,22-triacetates all have the following values (data in $CDCl_3$): 1.24 (s, Me, 21-H), 0.85 (s, Me, 18-H), 4.8–4.9 ppm (dd, 22-H, J = 4 and 8 Hz).[1] This clearly suggests that all natural ecdysones excepting the two quoted above have identical configurations at these two centers.

On the other hand, in view of the fact that the biological activity of synthetic ecdysones epimeric at C-20 and/or C-22 is much lower than natural ecdysones,[4]



establishment of configurations at these two centers becomes a problem of prime importance.

The rapid *in vivo* conversion of α-ecdysone to β-ecdysone going through no other detectable intermediate[5–7] suggests that the C-22 configurations are identical in the two ecdysones. Furthermore, the production of both β-ecdysone (**2**) and ponasterone A (**3**) upon catalytic hydrogenation of a 20,22,25-trihydroxy-23-yne side chain[8] furnished direct evidence for the identity of the two respective centers in **2** and **3**. Beyond this there is no chemical evidence which allows one to deduce the C-20 and C-22 configurations. In the following we provide data which establish the configurations as 20*R*,22*R*. These configurations are iden-

(1) K. Nakanishi, *Pure Appl. Chem.*, in press.
(2) R. Huber and W. Hoppe, *Chem. Ber.*, **98**, 2403 (1965).
(3) T. Takemoto, Y. Hikino, T. Okuyama, S. Arihara, and H. Hikino, *Tetrahedron Lett.*, 6095 (1968).
(4) See, *e.g.*, I. T. Harrison, J. B. Siddall, and J. H. Fried, *ibid.*, 3457 (1966).
(5) D. S. King and J. B. Siddall, *Nature (London)*, **221**, 955 (1969).
(6) H. Moriyama, K. Nakanishi, D. S. King, T. Okauchi, J. B. Siddall, and W. Hafferl, *Gen. Comp. Endocrinol.*, **15**, 80 (1970).
(7) L. Cherbas and P. Cherbas, *Biol. Bull.*, **138**, 115 (1970).
(8) G. Hüppi and J. B. Siddall, *Tetrahedron Lett.*, 1113 (1968).