plete evaporation of the solvent was avoided (otherwise *cis*-stilbene is lost preferentially). Stilbene compositions were determined by glpc (3 ft × $^1/_8$ in. column of 5% Apiezon M on Chromosorb W, ~170°) using an Aerograph Model 600 C Hy-Fi gas chromatograph with recalibrated attenuator circuit resistors.[57] The recorder was a Leeds-Northrup Speedomax W equipped with a Disc integrator. In the case of *tert*-butyl alcohol, azulene concentrations were checked following irradiation, by measuring the absorbance at 577.5 nm. This was necessary because in some samples, for unknown reasons, the azulene was partially consumed during the course of the irradiation. In the case of the benzophenone-sensitized photoisomerization in the presence of Oil Yellow (0.01 *M*), no loss of Oil Yellow was detected by glpc, although there was a 20% decrease in the absorbance of the solution at 380 nm. This decrease may be due to trans → cis photoisomerization of Oil Yellow.[27,28]

Absorption Spectra. Ultraviolet and visible absorption spectra were recorded at room temperature using Cary-14 or -15 spectrophotometers. Spectral features of the $^1S \leftarrow {}^0S$ transition in *trans*-stilbene are: benzene, shoulder at 324.0 nm (ϵ 2.67 × 10^4), maxima at 310.5 (ϵ 2.64 × 10^4) and 298.5 nm (ϵ 2.67 × 10^4); *n*-pentane, shoulder at 320.0 nm (ϵ 1.42 × 10^4), maxima at 306.0 (ϵ 2.45 × 10^4) and 292.0 (ϵ 2.80 × 10^4); *tert*-butyl alcohol, shoulder at 320.0 nm (ϵ 1.57 × 10^4), maxima at 306.3 (ϵ 2.5 × 10^4) and 294.0 nm (ϵ 2.75 × 10^4). Extinction coefficients at 313.0 nm for *trans*- and *cis*-stilbene, respectively, are: benzene, 2.58 × 10^4, 0.354 × 10^4; *n*-pentane, 1.86_2 × 10^4, 0.238 × 10^4; *tert*-butyl alcohol, 1.94_6 × 10^4, 0.259 × 10^4. Extinction coefficients at 366.0 nm in benzene are azulene, 23.7, and benzophenone, 67.

Fluorescence Spectra. Fluorescence spectra were recorded using a Perkin-Elmer-Hitachi MPF-2A spectrophotometer (Phototube, Hitachi R-106). Wavelength calibration of the emission monochromator was achieved using a mercury pen-ray lamp.[58] A calibrated General Electric 30A/T24/7 tungsten ribbon-filament lamp was used to obtain relative emission intensity correction factors.[59,60] Relative fluorescence quantum yields of *trans*-stilbene were determined at 24° using 1-cm square cells. Solution concentrations (~4 × 10^{-5} *M*) were adjusted to the same optical density (1.00 ± 0.02) at the excitation wavelength, 305.0 nm. Fresh solutions were used in duplicate measurements because loss of about 5% of the emission intensity, probably due to trans → cis photoisomerization, occured during the recording of each spectrum. Relative fluorescence quantum yields were determined by cutting and weighing Xerox copies of the corrected fluorescence spectra.

Irradiation Procedures. Samples (3 ml) of solutions containing the desired substrate in the presence or absence of sensitizer and/or quencher were introduced into 13 × 60 mm Pyrex ampoules which were equipped with grease traps and 10/30 female joints. Prior to use, the ampoules were washed once with concentrated NH_4OH, repeatedly with distilled water, and oven-dried. The solutions were degassed in three–four freeze–pump–thaw cycles to about 10^{-6} Torr, and the ampoules were flame sealed at a constriction. The total stilbene concentration was 1.00 × 10^{-2} *M* for all photostationary state measurements. In most cases photostationary states were approached from both sides. In some cases, irradiation times were minimized by using *trans*- and *cis*-stilbene mixtures which bracketed the expected stationary states. Benzophenone-sensitized irradiations and initial isomerization rate experiments were carried out in a merry-go-round apparatus.[61] Fluorenone-sensitized and most direct excitation irradiations were carried out by strapping the ampoules to the outer wall of a Hanovia probe, or to the outer wall of a Pyrex reactor well containing distilled water and the probe and lamp. The latter procedure allows placement of more samples about the lamp. In all cases the samples were immersed in a water bath thermostated at 30.2 ± 0.1°. A 450-W Hanovia 679A "high-pressure" mercury lamp was employed.

Filter Systems. Four filter systems were employed for the above irradiations. (1) The first was a cylindrical uranium glass filter which transmits light of wavelengths longer than 3200 Å. (2) The second system was a combination of Corning CS 7-37 and 0-52 glass filters, transmitting only the group of mercury lines at 366.0 nm. (3) The third system consisted of a water solution containing 0.76 g of $K_2Cr_2O_7$ and 15.38 g of K_2CO_3 per 500 ml. A 1-cm path length (0.9–1.0-cm path lengths were employed) of this solution transmits 0.42 and 10.1% of the mercury lines at 302.5 and 313.0 nm, respectively, as well as light of wavelengths longer than 450.0 nm. (4) The fourth system was identical with the third except for the addition of Corning glass color filters C.S. 7-54. The glass filters do not affect transmission at 302.5 and 313.0 nm, but completely absorb all visible light. It should be noted that information supplied by Hanovia indicates that the relative output of a 450-W lamp at 313.0 and 302.5 nm is 13.2:7.2. Trnasmission spectra of filter systems 1–4 are recorded in ref 60.

Acknowledgment. This research was supported by National Science Foundation Grants GP-7941 and GP-24265.

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[57] We thank M. N. V. McElvar for the calibration.

[58] We thank Dr. R. H. Johnsen for the use of this lamp.

[59] We thank Dr. J. T. Vickers for the use of this lamp.

[60] For details see E. D. Megarity, Ph.D. Thesis, Florida State University, 1969, Tallahassee, Fla. 32306.

[61] F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, 1, 245 (1969).

Origin of the Instability of *N*-Nitrosoaziridines

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Contribution from the Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213. *Received July 19, 1971*

Abstract: *N*-Nitroso-9-azabicyclo[4.2.1]nona-2,4,7-triene (**2**), considered to be a 1,6 adduct of cyclooctatetraene and nitrous oxide, was prepared and found to be thermally stable toward fragmentation. In light of this result the facile cleavage of *N*-nitrosoaziridines to olefins and nitrous oxide is regarded as a consequence of ring strain and associated rehybridization effects which predispose the latter substances toward a particular mode of "nonlinear" cheletropic cycloreversion.

The nitrosation of ethylenimine derivatives and the ensuing facile fragmentation of the intermediate *N*-nitrosoaziridines to olefins and nitrous oxide represents a synthetic sequence of some utility.[1] Mech-

$$\triangleright NH \xrightarrow[(X=Cl,OR,etc.)]{O{=}NX} (\triangleright NNO) \xrightarrow{<0^\circ} \| + N_2O$$

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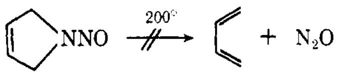
[1] (a) C. L. Bumgardner, K. S. McCallum, and J. P. Freeman, *J. Amer. Chem. Soc.*, **83**, 4417 (1961); (b) W. Rundel and E. Müller, *Chem. Ber.*, **96**, 2528 (1963); (c) R. D. Clark and G. K. Helmkamp, *J. Org. Chem.*, **29**, 1316 (1964). The uses of this reaction for alkene synthesis and cis–trans olefin isomerization have been indicated: (d) R. M. Carlson and S. Y. Lee, *Tetrahedron Lett.*, 4001 (1969).

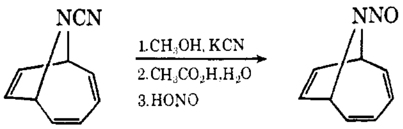
anistically, the cheletropic cycloreversion merits further scrutiny.[2,3] If concerted, this stereospecific[1c] reaction must follow a $[{}_{\pi}2_{s} + {}_{\omega}2_{a}]$ path, of which at least two variants have been conceptualized and designated as *nonlinear* processes.[3] Negative evidence pertaining to nitrous oxide eliminations is found in the stability of the *N*-nitroso-3-pyrroline ring, which apparently fails to undergo fragmentation under forcing conditions.[4] Since the latter heterocycle has potentially available to it a linear $[{}_{\pi}4_{s} + {}_{\omega}2_{s}]$ path, the inference is that either the "nonlinear" mode is uniquely advantageous for N_2O elimination[4] or that some special structural feature(s) of *N*-nitrosoaziridines predisposes them toward fragmentation. We here present evidence that the latter is the case, and offer explanation for the probably more favored "nonlinear" path in these substances.



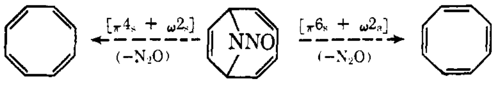
Results

In order to examine the influence of orbital symmetry in N_2O eliminations, we constructed a system in which the $[{}_{\pi}6_{s} + {}_{\omega}2_{a}]$ mode of fragmentation might be observed. The reasoning was based upon the established principle that within a vinylogous series, allowed and disallowed reactions alternate in a fashion which is sufficiently familiar as not to require further elaboration.[3] It is enough to note that symmetry constraints in such an eight-electron system should be similar to the $[{}_{\pi}2_{s} + {}_{\omega}2_{a}]$ four-electron system of *N*-nitrosoaziridines.

A suitable test molecule appeared to be **2**, which was prepared from the cyanonitrene 1,4 (1,6) adduct of cyclooctatetraene[5] (**1**) in several steps without isolation of intermediates. It may be noted that the bicyclic nature of **2** so constrains the system that elimination of N_2O would necessarily be suprafacial with respect to the hydrocarbon component[6] (C_8H_8). In fact, two conceptually distinct fragmentations may be envisioned, both giving the same products. Based upon the precedent of *N*-nitroso-3-pyrroline,[4] the "linear" $[{}_{\pi}4_{s} + {}_{\omega}2_{s}]$ mode was not expected. The molecule **2** was conceived as a test of the "nonlinear" $[{}_{\pi}6_{s} + {}_{\omega}2_{a}]$ cheletropic reaction, in which the only function of the etheno bridge is to ensure that antarafacial cycloreversion with respect to the triene moiety may not be observed.[7,8]



1 **2**



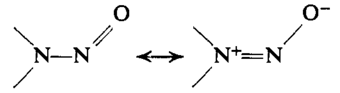
The nitrosamine **2** was found to be a stable substance (mp 47°) which exhibited great renitence toward thermal dissociation to nitrous oxide and cyclooctatetraene. It was recovered unchanged in greater than 50% yield after heating for 30 min at 198° in benzene solution. Eventually at this temperature or at higher temperatures **2** was converted into an intractable black material; negligible evolution of nitrous oxide (or any gas) was observed in the latter case. No further characterization of the products was attempted.

The foregoing should be contrasted with the instability of *N*-nitrosoaziridine and its derivatives; a half-life of 256 min at −15° has been recorded for the ethylene–nitrous oxide adduct.[1c] The thermolysis behavior of **2** is comparable to that of *N*-nitroso-3-pyrroline, which reportedly possesses a half-life of >60 min at 200°,[4] as previously noted.[9]

Discussion

If, then, facile cheletropic fragmentation is unique to three-membered ring nitrosamines, one is led to inquire as to the origin of the special reactivity. An obviously relevant factor is ring strain, which destabilizes the adduct relative to the components in the specific case of *N*-nitrosoaziridines. Whether this is sufficient explanation is debatable.[10] (An artificial and presumptive estimate must be made as to how much residual "ring strain" remains in the transition state.) Furthermore, this supposition alone offers no insight into the orbital symmetry constraints upon fragmentation.

We submit that a plausible interpretation follows from the observation that the nitrosyl group is very likely not coplanar with the three-membered ring in the ground state of *N*-nitrosoaziridines. This may seem unreasonable initially, since in unconstrained nitrosamines (*e.g.*, **2**) there is apparently substantial N–N π bonding resulting in a rotational barrier about that bond of *ca.* 23 kcal/mol. However, comparable delocalization is observed in (isoelectronic) carboxylic amides,[11] yet *N*-(*p*-bromobenzoyl)aziridine was found to possess pyramidal nitrogen in the crystal.[12] This behavior may be conventionally explained as the result of competing hybridization and conjugative effects. The enhanced p character of the carbon–nitrogen (ring) bonds destablizes a potential planar (sp^2) configuration



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(2) "The establishment of a non-least-motion transition state which leaves no stereochemical traces poses to the experimentalist a most fascinating challenge."[3a]

(3) (a) R. Hoffmann and R. B. Woodward, *Science*, **167**, 825 (1970); (b) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969), see especially Section 10.1.

(4) S. D. McGregor and D. M. Lemal, *J. Amer. Chem. Soc.*, **88**, 2858 (1966).

(5) A. G. Anastassiou, *ibid.*, **90**, 1527 (1968).

(6) W. L. Mock, *ibid.*, **92**, 3807 (1970).

(7) W. L. Mock, *ibid.*, **91**, 5682 (1969).

(8) The conclusions of this paper should not be construed as implying that $[{}_{\pi}6_{a} + {}_{\omega}2_{s}]$ fragmentation will not occur under appropriate circumstances with unconstrained nitrosamines; this is a point which should be experimentally examined.

(9) This difference in reactivity represents a $\Delta\Delta G^{\ddagger}$ of >15 kcal/mol. Thermodynamic calculations indicate that dissociation of **2** is likely not prevented by an unfavorable $\Delta H°$; ref 4, footnote 14. It should be recognized that in the case of **2** (and *N*-nitroso-3-pyrroline), fragmentation is not the dominant course of decomposition; therefore, the (hypothetical) cheletropic processes may be of much higher energy.

(10) Parallel studies on episulfone and sulfolenes are not supportive of this premise (unpublished work).

(11) T. H. Siddall and W. E. Stewart, *Progr. Nucl. Magn. Resonance Spectrosc.*, **5**, 33 (1969).

(12) R. P. Shibaeva, L. O. Atovmyan, and R. G. Kostyanovskii, *Dokl. Akad. Nauk SSSR*, **175**, 586 (1967).

of the ring nitrogen more than any energy gain that might be realized from amide type resonance; the result is that normal pyramidal configuration of amine nitrogen more nearly obtains.[13,14] The chemical consequence will be that the conformation depicted with presumed electronic structure should be (if it is not the ground state) relatively accessible to *N*-nitrosoaziridines compared to unconstrained nitrosamines. Such a species is well set up for a concerted $[_{\pi}2_s + {}_{\omega}2_a]$ cycloreversion. The appropriate correlations are given in Chart I for filled orbitals. The pertinent feature is that the antisymmetric combination of σ-bond orbitals is able to correlate with one of the π-allylic molecular orbitals of nitrous oxide, since the N-terminal lone pair of N_2O derives from the electrons in the aziridine nitrogen nonbonding pair.[15]

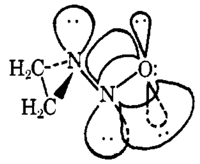
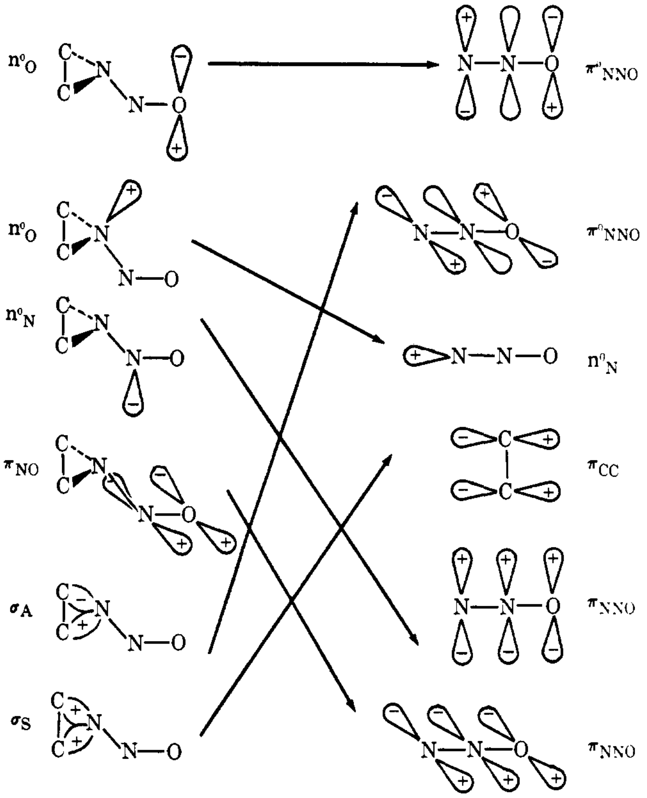


Chart I. Suggested Correlations of Filled Orbitals for *N*-Nitrosoaziridine to Nitrous Oxide Plus Olefin Transformation[a]



[a] Certain alternative linear combinations of the nitrosamine orbitals may be equivalently utilized.

Hence, the instability of *N*-nitrosoaziridines may be ascribed to several related factors. There is the thermodynamic instability (ring strain) which also tends to induce tetrahedral hybridization of the ring nitrogen. One consequence of this is diminution of potential resonance of the nitrosamine functionality. Furthermore, the divergence from regular nitrosamine geometry places the structure in a conformation which leads *with minimal molecular distortion* to a "nonlinear" mode of cheletropic fragmentation. According to this interpretation and the evidence presented earlier, nitrous oxide as a leaving group does not have an inherent propensity for the antarafacial ("nonlinear") process, but rather its departure is promoted by small ring rehybridization effects.[8] This is a principle which may be extendable to other cheletropic reactions,[3,16] and which has further implications for orbital symmetry control in general.

Experimental Section

Synthesis of 2. Advantage was taken of a new, mild procedure[17] for the conversion of cyanamides to secondary amines. A solution of 228 mg (1.6 mmol) of **1**[5] and 150 mg of potassium cyanide in 20 ml of methanol was refluxed for 10 hr. The volume of the solution was then reduced to *ca.* 5 ml by distillation and (after cooling) 25 ml of benzene was added. A flocculent precipitate (KCN) was removed by filtration and solvent was then evaporated under reduced pressure. The oily residue was taken up in 16 ml of acetic acid and 4 ml of water and the resulting solution was refluxed for 22 hr. The solution was cooled and diluted with an equal volume of water, and at 0° a solution of 400 mg of sodium nitrite in 5 ml of water was added. After 5 min the solution was allowed to come to 25° (15 min). Then 50 ml of water was added and solid anhydrous potassium carbonate was cautiously added until near saturation. The resulting solution was extracted with methylene chloride, the extracts were dried (K_2CO_3), and solvent was evaporated under reduced pressure. The residue was taken up in hot hexane, which was concentrated to *ca.* 25 ml and then allowed to stand at 0°. There was collected in several crops 170 mg (72%) of *N*-nitroso-9-azabicyclo[4.2.1]nona-2,4,7-triene (**2**): mp 47–48° (cor); ir (C_2Cl_4) 1441, 1335, and 1321 cm^{-1}; uv max (95% C_2H_5OH) 233 nm (ε 8900) and 356 (62); nmr (CCl_4) δ 5–6.5 ppm (multiplet); mass spectrum (70 eV) *m/e* 148.0632 ($C_8H_8N_2O$ requires 148.0637).

Anal. Calcd for $C_8H_8N_2O$: C, 64.85; H, 5.44; N, 18.91. Found: C, 65.01; H, 5.67; N, 18.77.

Acknowledgment. This work was supported by the National Science Foundation.

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(13) Other factors effecting inversion barriers are lone-pair repulsions, inductive and steric effects, etc.; see A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem., Int. Ed. Engl.*, **9**, 400 (1970).

(14) The spectral data reported in ref 1b and 1c for *N*-nitrosoaziridines (in particular, nmr) are consistent with configurational mobility for the nitrosyl group.

(15) This correlation pattern is one pointed out by Woodward and Hoffmann,[3b] but considered by them as an unlikely process. By our analysis it in fact appears to be the least motion path.[3a] Therefore, its designation as "nonlinear" is given in quotations in the present article. This path was also considered with suspicion by J. P. Freeman and W. H. Graham, *J. Amer. Chem. Soc.*, **89**, 1761 (1967).

(16) R. Huisgen, R. Sustmann, and K. Bunge, *Tetrahedron Lett.*, 3603 (1966); D. Felix, J. Schreiber, K. Piers, U. Horn, and A. Eschenmoser, *Helv. Chim. Acta*, **51**, 1461 (1968); M. H. Akhtar and A. C. Oehschlager, *Tetrahedron*, **26**, 3245 (1970).

(17) A. Donetti, A. Omodei-Sale, and A. Mantegani, *Tetrahedron Lett.*, 3327 (1969).