

Rearrangement of 1,2-Diazene *N*-Oxides. 3.* Photochemical Isomerization of Bicyclic *cis*-1,2-Diazene *N*-Oxides to Oxadiaziridines

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The photochemical behaviour of four bicyclic and one monocyclic aliphatic *cis*-1,2-diazene *N*-oxide was studied by means of UV- and NMR spectroscopy at low temperature. All bicyclic compounds photolyze to labile transients assigned as *cis*-oxadiaziridines. When samples of these compounds in poly(vinyl chloride) or methanol are slowly heated, 60–100% of the starting materials are reformed. First order time dependence is

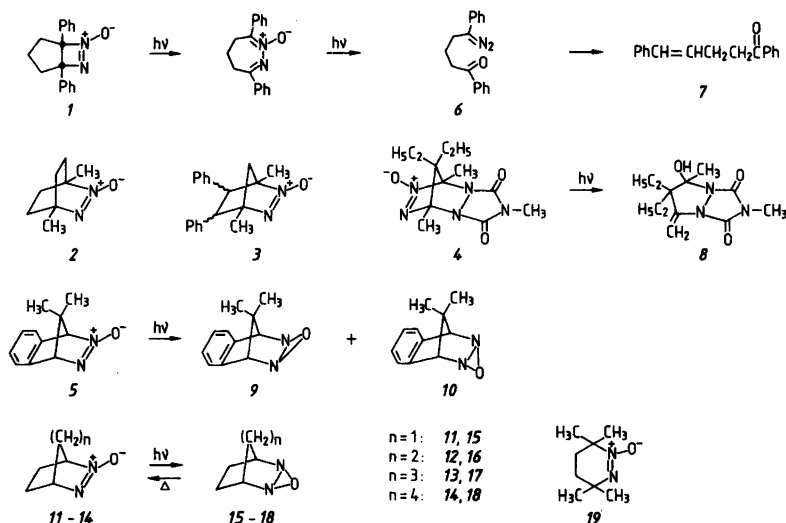
observed for these thermal reversions. The kinetic stabilities of *cis* and *trans* oxadiaziridines are compared and discussed.

The photochemical behaviour of aliphatic *trans*-1,2-diazene *N*-oxides has previously been the subject of several studies.^{2–8} Irradiation with ultraviolet light may lead to any of four unimolecular reactions: (1) Elimination of dinitrogen oxide,² (2) *cis*–*trans* isomerization,³ (3) deoxygenation,⁴ and (4) formation of oxadiaziridines.^{5–8} The *cis*-1,2-diazene *N*-oxides may share some of the properties of the *trans* compounds but they have not attracted much

* Part 1 and 2. See Ref. 1.

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Scheme 1.

attention. Irradiation of compound 1 (Scheme 1) results in the formation of 7, which was proposed to arise from decomposition of the diazoketone, 6.⁹ On the other hand, compounds 2, 3 (Ref. 10) and 11 (Ref. 6) polymerize upon irradiation at room temperature whereas 4 is transformed into 8, probably via a diazenoxyl diradical.¹⁰ Recently^{11,12} it was reported that dimethylisoidene may be generated by irradiation of compound 5 in frozen solution at 77 K. However, irradiation in liquid solution at 193 K produces oxadiaziridines 9 and 10. At 253 K starting material was reformed from these after several hours.

In order to obtain further insight into the photochemistry of *cis*-diazene *N*-oxides compounds 11–14 (Ref. 13) and 19 (Ref. 14) were prepared and their photochemical behaviour was studied.

RESULTS

Photolysis of compounds 11, 12, 14, and 19 in poly(vinyl chloride) (PVC) at 77 K. UV spectra. Solutions (~0.05 M) in thin PVC films (see Experimental) of these compounds were irradiated (Table 1) and absorption spectra were recorded

during the course of irradiation. In all cases, the absorption bands (Table 1) due to the starting materials gradually decreased in intensity with no concomitant formation of product absorptions above 200 nm. Irradiations were discontinued after 40–75% of conversion, and the films were slowly heated to room temperature. During the warm-up the absorption bands due to the starting materials increased in intensity.* The degrees of reversibility are given in Table 1.

Photolysis of compounds 11–14 in methanol at 193 K. UV spectra. Solutions ($\sim 2.5 \times 10^{-4}$ M) of these compounds were irradiated as described above (Table 1). The same spectroscopic behaviour was observed. After partial photolysis solutions were slowly warmed up. When the UV absorption due to the starting materials began to increase in intensity, the temperature was fixed (Table 2) and the absorbances of the signals at their respective λ_{\max} values were recorded as a function of time. By plotting $\log(A_{\infty} - A_t)$ vs. time straight lines were obtained, i.e. first order time dependence is observed

* K. E. Gilbert (private communication) has studied the photolysis of 19 and has observed formation of dienes and amines.

Table 1. Photolysis of diazene *N*-oxides 11–14 and 19 in methanol at 193 K and in PVC at 77 K.

Compound	λ_{\max}/nm	Excitation wavelength/nm	Degree of conversion/%	Reversibility/%
11 ^a	225	250(15)	70	80
11 ^b	229	275(20)	60	70
12 ^a	227	250(20)	70	100
12 ^b	230	260(20)	75	100
13 ^a	232	250(20)	50	100
14 ^a	234	>200	70	60
14 ^b	237	250(15)	45	65
19 ^b	234	250(20)	40	~2

^a Methanol as solvent. ^b PVC as solvent.

Table 2. Kinetic data for the oxadiaziridine→diazene *N*-oxide isomerizations in methanol.

Compound	Temp./K	$t_{1/2}/\text{min.}$	$k/10^4 \text{ s}^{-1}$	Correlation coefficient	$\Delta G^\ddagger/(\text{kJ/mol})^a$
15	223(1)	32	3.6	0.994	68.6
16	249(2)	30	3.9	0.988	77.0
17	255(1)	41	2.8	0.998	79.5
18	268(1)	38	3.0	0.998	83.3

^a ΔG^\ddagger was calculated from the expression $k = kT/h \exp(-\Delta G^\ddagger/RT)$.

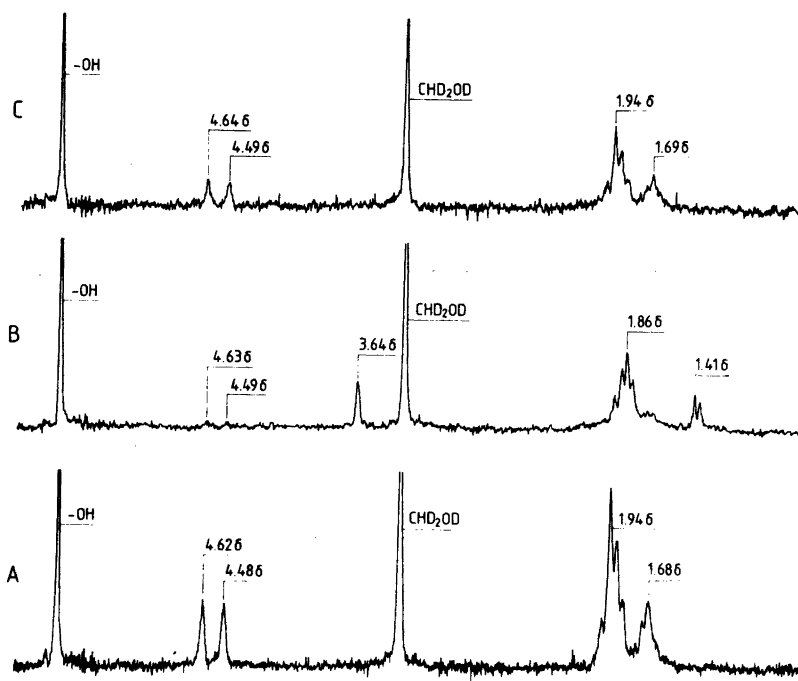


Fig. 1. 270 MHz ^1H NMR spectra of compound **12** in CD_3OD at 213 K. Spectrum A, before photolysis, spectrum B, after photolysis ($\lambda > 200$ nm) at 193 K, spectrum C, after heating the photolyzed sample to room temperature and recooling to 213 K.

for the thermal reversions. Least squares calculations of rate constants and ΔG^\ddagger values are given in Table 2.

Photolysis of compounds 12 and 13 in methanol- d_4 at 193 K. ^1H -NMR spectra. The UV experiments above showed that starting materials **12** and **13** were reformed quantitatively when photolyzed samples were heated to room temperature. The photolysis of these compounds (0.1 M in CD_3OD) was therefore followed by ^1H NMR spectroscopy.

The 270 MHz spectrum of compound **12** is shown in Fig. 1. The two bridgehead protons absorb at $\delta = 4.62$ and 4.48 (at 60 MHz in CDCl_3 these protons appear as a broad singlet, see Ref. 13). Upon photolysis ($\lambda > 200$ nm) the spectrum of compound **12** gradually disappeared and new resonance lines were observed at $\delta = 3.64$ (singlet) and $\delta = 1.86$ and 1.41 (multiplets). The temperature of the sample was now fixed at 248 K. This caused the signals of the intermediate to disappear with simultaneous enhancement of absorptions due to the starting material. The half-life of the intermediate was estimated from the peak areas to be approximately $\frac{1}{2}$

h. The same half-life was estimated by UV spectroscopy (Table 2) indicating that the same photolysis product had been formed at these widely different concentrations of the starting material.

NMR spectra (90 MHz) recorded during photolysis of compound **13** (Fig. 2, bridgehead protons at $\delta = 4.44$, decoupling experiments revealed a small chemical shift difference (0.09 ppm) showed the development of absorption at $\delta = 4.18$, 3.76 (ratio of areas $\sim 1:3$), and at $\delta = 1.83$ and 1.78. After heating to room temperature only signals corresponding to the starting material were observed.

DISCUSSION

The thermally unstable photoproducts formed by photolysis of compounds **11–14** may *a priori* be assigned any of the structures **15–18** and **20–22** (Scheme 2). Some of these candidates may, however, be ruled out since the photoproducts must possess the following chemical and spectroscopic properties: (i) Fast isomerization to starting material below

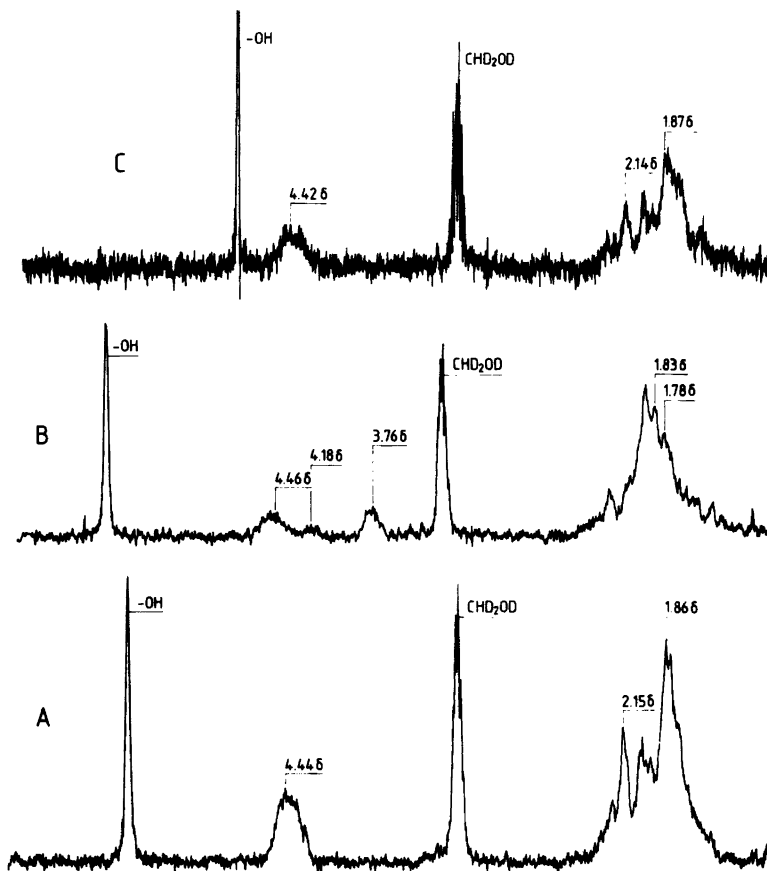
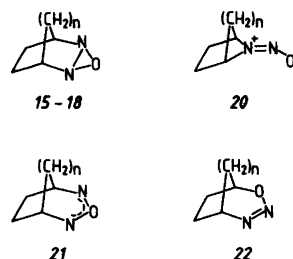


Fig. 2. 90 MHz ^1H NMR spectra of compound 13 in CD_3OD at 221 K. Spectrum A, before photolysis, spectrum B, after photolysis ($\lambda > 200$ nm) at 193 K, spectrum C, after heating the photolyzed sample to room temperature.

0°C (Table 2). (ii) The photoproduct from compound 12 (Fig. 1, and probably also the photoproduct from compound 13, Fig. 2) possesses two bridgehead protons which are chemically equivalent ($\Delta\delta < 0.02$ ppm). The resonance line of these protons is found at higher magnetic field (0.9 ppm) relative to the bridgehead protons of the starting material (0.7 ppm for the photoproduct from compound 13). (iii) Candidates for the assignment of structure must not possess intense absorptions above 200 nm in the electronic spectrum.

The *N*-nitroso amine 20 does not obey any of these criteria since the bridgehead protons of 20 would not be expected to be chemically equivalent.¹⁵ *N*-Nitroso amines also possess intense



Scheme 2.

$\pi-\pi^*$ transitions around 230 nm¹⁶ and rearrangements into diazene *N*-oxides have not been described.^{17,18} The reverse thermal isomerization, *i.e.* diazene *N*-oxide \rightarrow *N*-nitroso amine has

recently been observed at higher temperatures.¹ The heteroallylic system **21** would be expected to absorb intensely above 200 nm and the bridgehead protons in **22** would probably be non-equivalent. Only the *cis*-oxadiaziridine system **15–18** is expected to obey the three criteria found experimentally. Thus, the *cis*-oxadiaziridines **9** and **10** isomerize rather fast at 253 K^{11,12} and *trans*-oxadiaziridines (Table 3) all isomerize into diazene *N*-oxides at room temperature.^{5–8} The protons α to nitrogen in *trans*-oxadiaziridines absorb at higher magnetic field relative to the same protons in the corresponding *cis*- and *trans*-diazene *N*-oxides¹⁰ (e.g. $\delta = 3.37$ and 4.17 in *trans*-azoxybutane, $\delta = 2.63$ in *trans*-dibutyloxadiaziridine⁶). Furthermore, *trans*-oxadiaziridines do not absorb above 200 nm.⁶

Photolysis of the diazene *N*-oxide **5** was previously reported to yield an *exo* and *endo* oxadiaziridine in the approximate ratio of 2.5:1^{11,12} (bridgehead protons at $\delta = 4.64$ in the major product and $\delta = 4.81$ in the minor). Unfortunately, our data (Fig. 2) does not permit any conclusion about the presence of both an *exo* and an *endo* isomer of compound **17**. The difference in chemical shift values between the bridgehead protons of *exo*- and *endo*-**17** is expected to be small (see above). It is uncertain whether the peak at $\delta = 4.18$ (Fig. 2) can be assigned to compound **17**.

Besides compound **17**, compounds **15** and **18** may also be photochemically generated in both *endo* and *exo* isomers. When such mixtures decay thermally, the UV absorptions of the parent *N*-oxides may both reappear in first order reactions. However, since first order kinetics is observed (Table 2), we conclude that either one of the isomers predominate or the

endo and *exo* isomers decay with nearly identical rate constants or, fast equilibrium exists between the isomers at the temperature of thermal reversion.

The most labile *cis*-oxadiaziridine is compound **15** which isomerizes to the parent *N*-oxide with $\Delta G^\ddagger = 68.6$ kJ/mol. By enlargement of the bridge ΔG^\ddagger increases gradually (83:3 kJ/mol for compound **18**, see Table 3). Intuitively, this order of reactivity is expected since the strain energy of the tricyclic *cis*-oxadiaziridines should decrease from compound **15** to compound **18**.¹⁹ *trans*-Oxadiaziridines are generally less labile. *trans*-Di-*tert*-butyloxadiaziridine thus isomerizes 1200 times slower relative to compound **18** ($\Delta \Delta G^\ddagger = 17.5$ kJ/mol). This difference in reactivity between *cis* compounds and between *cis* and *trans* compounds might either be due to higher ground state energies or, it might be a transition state effect. Both effects could also be operative.

Similar differences in reactivity between *cis* and *trans* substituted three-membered heterocyclic rings have been described in the literature. Diaziridinones decompose thermally to carbon monoxide and the corresponding diazenes.²⁰ *trans*-Di-*tert*-butyldiaziridinone decomposes with $\Delta G^\ddagger \sim 146$ kJ/mol while 2,2,5,5-tetramethyl-1,6-diazabicyclo[4.1.0]heptan-7-one (*cis* stereochemistry) decomposes with $\Delta G^\ddagger \sim 105$ kJ/mol. It was proposed that the difference in reactivity was due to differences in ground state stabilization.²⁰

EXPERIMENTAL

Compounds. **11–14** were prepared according to Ref. 13, **19** according to Ref. 14.

Table 3. Rate constants for the oxadiaziridine \rightarrow diazene *N*-oxide isomerizations.

Compound	Solvent	Temp./K	ΔG^\ddagger / kJ/mol	k/s^{-1} at 298 K ^a	k_{rel} at 298 K
15	CH ₃ OH	223	68.6	5.8	450000
16	CH ₃ OH	249	77.0	9.8×10^{-2}	7500
17	CH ₃ OH	255	79.5	7.2×10^{-2}	5500
18	CH ₃ OH	268	83.3	1.6×10^{-2}	1200
<i>b</i>	CD ₃ OD	298	96.2	8.4×10^{-5}	6.5
<i>c</i>	CD ₃ OD	295	98.7	3.0×10^{-5}	2.3
<i>d</i>	CCl ₄	301	98.7	3.0×10^{-5}	2.3
<i>e</i>	CH ₃ OH	301	100.8	1.3×10^{-5}	1.0

^a k was calculated from the expression $k = kT/h \exp(-\Delta G^\ddagger/RT)$. ^b *trans*-2-Cyclohexyl-3-methyloxadiaziridine, Ref. 8. ^c *trans*-2,3-Diisopropylloxadiaziridine, Ref. 7. ^d *trans*-2,3-Dibutyloxadiaziridine, Ref. 6. ^e *trans*-2,3-Di-*tert*-butyloxadiaziridine, Ref. 6.

Polymer films. Poly(vinyl chloride) (PVC), Corvic D 60/13, was used without further purification. Films (approx. 25 μm and approx. 0.05 M in *N*-oxide) were prepared using the solvent casting technique.²¹ Purified tetrahydrofuran was used as solvent.

Photolyses. Irradiations were carried out using a Bausch and Lomb SP-200 mercury point source with or without monochromator. The light beam was focussed using quartz lenses.

UV spectra were recorded on a Cary 14 instrument. The low temperature UV cell, cooled with liquid nitrogen, is described in Ref. 22. Temperatures higher than 77 K were fixed using a temperature control unit. Experiments in liquid solution were carried out using approx. 2.5×10^{-4} M solutions of compounds in methanol of Uvasol quality.

¹H NMR spectra were recorded using a Bruker HX-90 E (continuous wave mode) and a Bruker HX-270 (Fourier transform mode) instrument. 0.1 M solutions of compounds 12 and 13 in CD₃OD (Me₄Si as internal standard) were photolyzed ($\lambda > 200$ nm) in quartz NMR tubes in a quartz dewar, cooled with dry ice. After 8 and 3 h, respectively, tubes were quickly transferred to the pre-cooled NMR apparatus.

Acknowledgement. We are indebted to the Danish Natural Science Research Council for financial support.

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Received March 3, 1982.