The most satisfactory approach to the introduction of the required C-7 hydroxyl group involved a three-step sequence.[14] Ketalization (ethylene glycol, PhH, TsOH, 80 °C) of **13** afforded the C-13 ketal [mp 258–260 °C; IR ($CDCl_3$) (Nujol) 1665, 1625, 1095, 1015] in quantitative yield, which when hydroxylated (1.3 equiv of Br_2/AIBN/CCl_4–$CHCl_3$–H_2O/70 °C) led to a 2:1 mixture (the desired isomer predominating) of the epimeric C-7 alcohols (65%), mp 95–100 °C; NMR δ 1.42 (s, 3 H), 4.06 (s, 7 H), 5.29, 5.84 (s, 1 H), 7.17–8.07 (m, 4 H), 13.61, 13.75 (s, 1 H); IR ($CDCl_3$) (Nujol) 3675, 1675, 1630; MS *m/e* 426 (M^+), 321, 87. Subsequent deketalization (80% CF_3CO_2H/0 °C) of this mixture then gave quantitatively racemic **14**, mp 210–213 °C, NMR δ 2.41 ($COCH_3$), 4.08 (OCH_3), 7.18–8.00 (ArH), 13.66 (ArOH); MS *m/e* 382 (M^+), 321, 293, 44, 43; UV (max) (MeOH) 415, 258, 228 mm; TLC R_f = 0.3 (silica) in CH_3OH:CH_2Cl_2::1:20. This material proved to be identical in all of these characteristics with a sample of the natural product[15] having mp 210–213 °C, mmp 210–213 °C.

The application of the above approach to related anthracyclinones is being investigated.

Acknowledgment. We thank Dr. C. Iden for mass spectra and Mr. M. Kendrick for assistance with high-performance LC. We are indebted to the National Institutes of Health for a grant (CA20197) in aid of this research and Farmitalia/Carlo Erba Spa. (Milano, Italy) for generous financial support.

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[14] F. Arcamone, L. Bernardi, B. Patelli, P. Giardino, A. DiMarco, A. M. Casazza, C. Soranzo, and G. Pratesi, *Experientia*, **34**, 1255 (1978).

[15] We are grateful to Dr. F. Arcamone for a generous donation of samples of 11-deoxydaunomycin and 11-deoxydaunomycinone.

Photochemistry of a 1,1-Diazene, *N*-(2,2,5,5-Tetramethylpyrrolidinyl)nitrene

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The photochemistry of the 1,1-diazene has never been examined due to its transient nature. Several theoretical groups have calculated the order of the electronic states of the 1,1-diazene (aminonitrene, *N*-nitrene) during the past decade.[1,2] Goddard's GVB–CI calculations of the parent H_2N–N suggest a ground-state singlet with low-lying n,π^* singlet (50.7 kcal) and triplet states (13.8 kcal) (Figure 1).[1f] The 1,1-diazene is isoelectronic with the carbonyl, a functional group whose photochemistry is well documented. The recent synthesis and characterization of persistent 1,1-diazenes[3] allows an investigation of the photochemical reactivity of this species. We report the direct and sensitized irradiation of N-(2,2,5,5-tetramethylpyrrolidinyl)nitrene **1** in the visible region (n,π^* transition) which reveal both unimolecular and bimolecular photoreactivity. In addition, the fluorescence spectrum of a 1,1-diazene has been obtained.

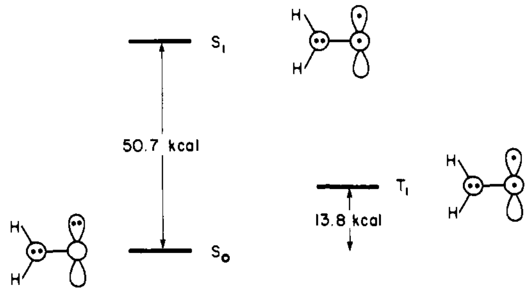

Figure 1.

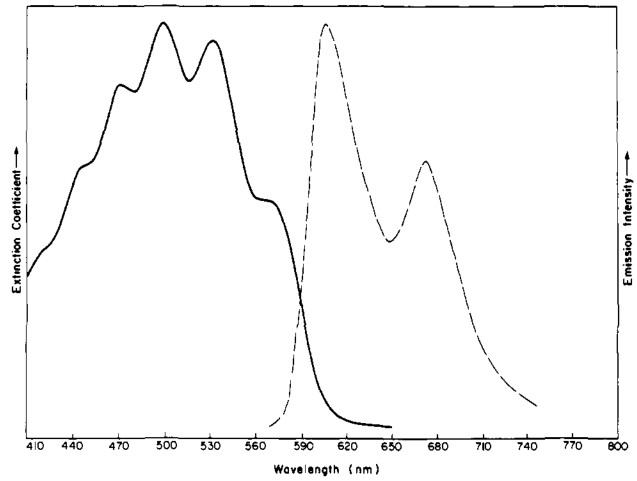

Figure 2. Absorption spectrum of **1** at −78 °C (—). Fluorescence spectrum of **1** at −196 °C (---).

Addition of *tert*-butyl hypochlorite to a stirred solution of 1-amino-2,2,5,5-tetramethylpyrrolidine and triethylamine in anhydrous dimethyl ether at −78 °C affords, in addition to an insoluble white precipitate (Et_3NHCl), a red solution (λ_{max} 497 nm, ϵ 20, Et_2O) of the 1,1-diazene **1** which is stable for days at −78 °C.[3c] This solution is filtered at −78 °C, further purified by low-temperature chromatography (−85 °C) on basic alumina (propane/dimethyl ether eluant), and concentrated in $CFCl_3$. Low-temperature ^1H NMR spectrscopy (−60 °C, $CFCl_3$) reveals 98% 1,1-diazene, 2% tetrazene, and small amounts of dimethyl ether. The absorption and fluorescence spectra of 1,1-diazene **1** in $CFCl_3$ are shown in Figure 2. The absorption spectrum of **1** (λ_{max} 497; 0–0 band, 565 nm; $CFCl_3$)[4] is sufficiently resolved to give the vibrational spacing of S_1, 1238 cm^{-1} (N–N stretch). For the fluorescence spectrum,[5] the 0–0 band at 607 nm is the maximum. The spacing between the peaks at 607 and 672 nm corresponds to 4.6 kcal, consistent with the 1638-cm^{-1} (4.7 kcal) N=N stretch of S_0 obtained from the infrared spectrum of **1**.[3c] The fact that the shape of the absorption and fluorescence spectra[6] are so different suggests that the thermally equilibrated S_0 and S_1 states of the 1,1-diazene **1** have *different geometries*. Goddard's calculations find that the thermally equilibrated S_0 and S_1 states of the 1,1-diazene are planar and pyramidal, respectively.[1f] The absorption and fluorescence spectra are separated by 42 nm, a Stokes shift probably due at least in part to differential solvation of S_0 and S_1.[4] A rough estimate of the fluorescence quantum yield (ϕ_F) is $\sim 10^{-3}$.[7] The value for k_f determined from the integrated

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† National Science Foundation Predoctoral Fellow.

‡ Camille and Henry Dreyfus Teacher-Scholar, 1978–83.

[1] (a) Hayes, L. J.; Billingsley, R. P.; Trindle, C. *J. Org. Chem.* **1972**, *37*, 3924. (b) Baird, N. C.; Barr, R. F. *Can. J. Chem.* **1973**, *51*, 3303. (c) Lathon, W. A.; Curtiss, L. A.; Hehre, W. J.; Lisle, J. B.; Pople, J. A. *Prog. Phys. Org. Chem.* **1974**, *1*, 175. (d) Ahlrichs, R.; Staemmler, V. *Chem. Phys. Lett.* **1976**, *37*, 77. (e) Baird, N. C.; Wernette, D. A. *Can. J. Chem.* **1977**, *55*, 350. (f) Davis, J. H.; Goddard, W. A. *J. Am. Chem. Soc.* **1977**, *99*, 7111. (g) Casewit, C. J.; Goddard, W. A. *J. Am. Chem. Soc.* **1980**, *102*, 4057.

[2] For reviews see: (a) Lemal, D. M. In "Nitrenes"; Lwowski, W., Ed.; Interscience: New York, 1970; Chapter 10. (b) Ioffe, B. V.; Kuznetsov, M. H. *Russ. Chem. Rev.* (*Engl. Transl.*) **1972**, *41*, 131.

[3] (a) Hinsberg, W. D., III; Dervan, P. B. *J. Am. Chem. Soc.* **1978**, *100*, 1608. (b) *Ibid.* **1979**, *101*, 6142. (c) Schultz, P. G.; Dervan, P. B. *Ibid.* **1980**, *102*, 878. (d) Dervan, P. B.; Squillacote, M.; Lahti, P. M.; Sylwester, A.; Roberts, J. D. *Ibid.*, in press.

[4] In CH_2Cl_2, 1,1-diazene **1** has a λ_{max} of 497 nm and 0–0 band of 572 nm. The λ_{max} and 0–0 band both blue shift in isopropanol to 487 and 552 nm, respectively.[3c]

[5] Fluorescence spectra were recorded with exciting wavelength 450 nm and Corning 3-71 emission filter and are corrected. Emission intensity goes to zero on warming.

[6] For a recent report on the spectroscopy and photochemistry of cyclic 1,2-diazenes, see: Mirbach, M. J.; Liu, K-C; Mirbach, M. F.; Cherry, W. R.; Turro, N. J.; Engel, P. S. *J. Am. Chem. Soc.* **1978**, *100*, 5122.

[7] Spectrum was corrected (Hamamatsu R955 PMT) and measured relative to rubrene $\Phi_f = 1$, exciting wavelength 480 nm.

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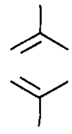
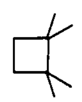
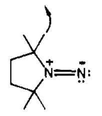
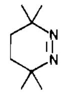
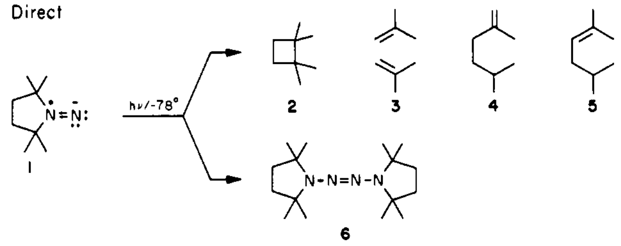
Table I

compd	conditions			hexenes
	0 °C, thermal[a]	47	49	4.0
	−10 °C, thermal[a]	53	44	3.5
	−20 °C, thermal[a]	59	39	2.0
	−78 °C, $h\nu$ (direct)[a]	54	44	2.0
1	−78 °C, $h\nu$ (sens)[a]	74	24	2.0
	140 °C, thermal[b]	52	46	2.0
	−78 °C, $h\nu$ (direct)[a]	56	42	2.0
7	−78 °C, $h\nu$ (sens)[c]	72	26	2.0

[a] $CFCl_3$. [b] Benzene. [c] CH_2Cl_2.

absorption spectrum is 1.3×10^5 s^{-1}.[8]

For photochemical studies, the degassed chromatographed solution of **1** (~0.03 M in $CFCl_3$) was irradiated at 466–610 nm at −78 °C.[9] After 12 h of irradiation at −78 °C the red color had completely disappeared. Vapor-phase chromatography[10] and ^1H NMR spectroscopy reveal four hydrocarbon products **2–5** and tetrazene **6** in a 1:4 ratio. Controls show that 0.03 M solutions of the 1,1-diazene in $CFCl_3$ at −78 °C are stable.



The four hydrocarbon products **2–5** appear to be products from the photochemical extrusion of molecular nitrogen from **1**. The details of the mechanism for the loss of nitrogen are as yet unknown, but the products are the same as found in the thermal decomposition of **1**. The tetrazene **6**, an unexpected photoproduct, probably results from the bimolecular reaction of S_1 and/or T_1 with S_0.

Triplet sensitization experiments were carried out at longer wavelengths at −78 °C. Irradiation of degassed chromatographed solutions of **1** (0.03 M in $CFCl_3$) at >608 nm[11] in the presence of 0.02–0.05 M azulene sensitizer (E_T = 31 kcal),[12] where the 1,1-diazene was shown to be unreactive on direct irradiation, affords four hydrocarbon products **2–5** and tetrazene **6** in a 1:9 ratio. The product compositions from the thermal, direct irradiation and sensitized decompositions of **1** and the 1,2-diazene isomer **7**[13,15] are summarized in Table I.

The 2-methylpropene/tetramethylcyclobutane ratios for the direct and sensitized photodecomposition of the 1,1-diazene **1** are 1.14 and 3.08, respectively. Importantly, the 2-methylpropene/tetramethylcyclobutane ratios are the *same* from the 1,1- and 1,2-diazene isomers in the direct and sensitized photolyses. Common singlet and triplet 1,4-biradicals formed from loss of nitrogen from S_1 and T_1, respectively, from **1** and **7** would be sufficient to explain these results. Bartlett and Porter have shown a spin correlation effect on the product ratios in the direct and triplet sensitized photodecomposition of cyclic 1,2-diazenes similar to **7**.[17,18] Because the hydrocarbon product ratios from **1** are different for direct vs. sensitized photolyses, but in agreement with the product ratios from the 1,2-diazene isomer **7**, this may indicate a spin correlation effect in the 1,1-diazene case. This apparent lack of significant intersystem crossing would be consistent with the large calcualted S_1–T_1 gap in the 1,1-diazene.[1f] Control experiments show that the 1,1-diazene **1** does not rearrange (<1%) to the more stable 1,2-isomer **7** under direct or sensitized photolysis.[19]

In summary, evidence has been provided that S_1 of the 1,1-diazene **1** is deactivated at least in part by fluorescence, loss of nitrogen, and tetrazene formation. Similarly, T_1 is deactivated in part by loss of nitrogen and tetrazene formation. The appearance of tetrazene **6** on direct irradiation is significant because, in the absence of $S_1 \rightarrow T_1$ intersystem crossing, one can estimate an *upper limit* of $\leq 7 \times 10^7$ s^{-1} [20] on the unimolecular rate for loss of N_2 from S_1. Issues that are currently under investigation include a direct measurement of the lifetime of S_1, a stereochemical test to quantitate the apparent spin correlation effect and a search for triplet emission which would locate the S_0–T_1 gap in the 1,1-diazene.

Acknowledgment. We are grateful to the National Science Foundation (CHE80-06495) for support of this research.

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[8] Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA, 1978.

[9] Irradiation with 1000-W xenon lamp, Corning filters CS3-70, and CS4-96.

[10] Hydrocarbon products were analyzed by analytical VPC (Carbowax 400, 25 °C) and compared with authentic samples. Tetrazene/hydrocarbon ratios were determined by NMR spectroscopy.

[11] Irradiated with 1000-W xenon lamp, Corning filter CS-2-59.

[12] Murov, S. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973.

[13] 3,3,6,6-Tetramethyl-1,2-diazacyclohexene (**7**) was synthesized by the method of Greene.[14]

[14] Greene, F. D.; Gilbert, K. E. *J. Org. Chem.* **1975**, *40*, 1409

[15] Direct and triplet irradiation with 1000-W xenon lamp, Schott filter WG-335. The 1,2-diazene **7** has been shown to be effectively triplet sensitized by thioxanthone.[16]

[16] Porter, N. A. Ph.D. Thesis, Harvad University, Cambridge, MA 1969.

[17] Bartlett, P. D.; Porter, N. A. *J. Am. Chem. Soc.* **1968**, 90, 5317.

[18] For an excellent discussion and review of spin correlation effects in 1,2-diazenes, see: Engel, P. S. *Chem. Rev.* **1980**, *80*, 99.

[19] However, we cannot rule out that photoexcited **1** rearranges to photoexcited **7** which then undergoes reaction.

[20] Assuming $k(S_1 + S_0) \leq 9.3 \times 10^9$ M^{-1} s^{-1}, concentration of $S_0 \leq 0.03$ M, and ratio of hydrocarbons/tetrazene products = 0.25.

Secondary Ion Mass Spectrometry of Molecular Solids: A Source of Cluster Ions

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Secondary ion mass spectrometry (SIMS) shows considerable promise as a method for characterization of nonvolatile molecular solids.[1] The observed molecular ions and fragment ions are often accompanied by cluster ions. In the case of solid hydrocarbons (methane,[2] cyclohexane,[3] benzene[3]), a rich variety of cluster ions is formed, but no repeating solvating unit is readily detected. On the other hand, several solids composed of small molecules yield cluster ions of regular composition [$H^+(H_2O)_n$ from ice,[3] $(N_2)_n^+$ and $N(N_2)_n^+$ from solid nitrogen,[2,4] $C^+(CO)_n$, $C_2^+(CO)_n$, and $(CO)_n^+$ from solid CO,[4] $C^+(CO_2)_n$ and $(CO_2)_n^+$ from solid CO_2[5]],

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[1] R. J. Day, S. E. Unger, and R. G. Cooks, *Anal. Chem.*, **52**, 557–72A (1980); B. L. Garrison, *J. Am. Chem. Soc.*, **102**, 6553–6555 (1980); N. Winograd and B. L. Garrison, *Acc. Chem. Res.*, **13**, 406–412 (1980).

[2] H. T. Jonkman and J. Michl, *Springer Ser. Chem. Phys.*, **9**, 292–294 (1979).

[3] G. M. Lancaster, F. Honda, Y. Fukuda, and J. W. Rabalais, *J. Am. Chem. Soc.*, **101**, 1951–1958 (1979).

[4] H. T. Jonkman and J. Michl, *J. Am. Chem. Soc.*, **103**, 733–737 (1981).

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