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Direct Studies of 1,1-Diazenes. Syntheses, Infrared and Electronic Spectra, and Kinetics of the Thermal Decomposition of *N*-(2,2,6,6-Tetramethylpiperidyl)nitrene and *N*-(2,2,5,5-Tetramethylpyrrolidyl)nitrene[1,2]

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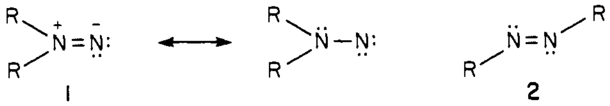
Abstract: The syntheses, direct spectroscopic observation, and kinetics of thermal decomposition of the persistent 1,1-diazenes, *N*-(2,2,6,6-tetramethylpiperidyl)nitrene (**4**) and *N*-(2,2,5,5-tetramethylpyrrolidyl)nitrene (**5**) are reported. The electronic absorption spectrum of **4** at −78 °C reveals a structured absorption for the n,π^* transition: $\lambda_{max} = 543$ nm, $\lambda_{0,0} = 620$ nm, and $\epsilon_{max} = 18 \pm 3$ in Et_2O; $\lambda_{max} = 541$ nm and $\lambda_{0,0} = 610$ nm in CH_2Cl_2; $\lambda_{max} = 526$ nm and $\lambda_{0,0} = 592$ nm in *i*-PrOH. The electronic absorption spectrum of 1,1-diazene **5** at −78 °C reveals a structured absorption band for the n,π^* transition: $\lambda_{max} = 497$ nm and $\lambda_{0,0} = 572$ nm and $\epsilon_{max} = 20 \pm 3$ in CH_2Cl_2; $\lambda_{max} = 487$ nm and $\lambda_{0,0} = 552$ nm in *i*-PrOH. The infrared spectrum of **4** shows a strong absorption at 1595 cm^{-1} ($R_2{}^{14}N{=}{}^{14}N$ stretch) and provides evidence that 1,1-diazene **4** has considerable N=N double-bond character in the ground state. The infrared spectrum of **5** shows a strong absorption at 1638 cm^{-1} ($R_2{}^{14}N{=}{}^{14}N$ stretch). The unimolecular rate of thermal decomposition of **4** is sensitive to solvent, the rate increasing with decreasing solvent polarity ($k_{rel} = 1.0, 1.7, 4.8$ in THF, Et_2O, and hexane, respectively). The activation parameters for the unimolecular fragmentation of 1,1-diazene **4** are as follows: $\log A = 11.6 \pm 0.5$ and $E_a = 16.9 \pm 0.7$ kcal mol^{-1} in hexane; $\log A = 13.7 \pm 0.3$ and $E_a = 20.0 \pm 0.4$ kcal mol^{-1} in Et_2O; $\log A = 13.6 \pm 0.3$ and $E_a = 20.1 \pm 0.4$ kcal mol^{-1} in THF. The activation parameters for the bimolecular dimerization of **4** are $\log A = 3.8 \pm 0.7$ and $E_a = 6.4 \pm 0.9$ kcal mol^{-1} in $CDCl_3$. The unimolecular rate of thermal decomposition of **5** is sensitive to solvent, the rate increasing with decreasing solvent polarity, $k_{rel} = 1.0$, 2.4, and 5.1 for THF, Et_2O, and hexane, respectively. The activation parameters for the unimolecular fragmentation of 1,1-diazene **5** are as follows: $\log A = 10.9 \pm 0.3$ and $E_a = 16.8 \pm 0.5$ kcal mol^{-1} in hexane; $\log A = 12.4 \pm 0.4$ and $E_a = 19.0 \pm 0.6$ kcal mol^{-1} in Et_2O; $\log A = 12.1 \pm 0.3$ and $E_a = 19.1 \pm 0.4$ kcal mol^{-1} in THF. At −41.1 °C the bimolecular rate constant for the dimerization of **5** is 8.5×10^{-5} L/(mol s), 90 times slower than that found for **4**. The change from a six-membered to a five-membered ring 1,1-diazene causes a shift to higher energy for the n,π^* transition and a shift to increased wavenumber (cm^{-1}) for the N=N stretching frequency, not unlike that of the isoelectronic ketones, tetramethylcyclohexanone and tetramethylcyclopentanone. Similar E_a values for the unimolecular thermal fragmentation of **4** and **5** may indicate the strain energy difference between **4** and **5** is also small. An approximate value of 30.5 kcal mol^{-1} for the heat of formation of the 1,1-diazene **5** is estimated, indicating the 1,1-diazene **5** has a higher heat of formation than the *cis*-1,2-diazene isomer by 20 kcal mol^{-1}.

1,1-Diazenes (aminonitrenes, *N*-nitrenes) **1**, unlike their more



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stable 1,2-diazene isomers (azo compounds) **2**, are usually not isolated or detected by spectroscopic methods but rather are assumed intermediates on the basis of a substantial body of chemical evidence.[5] Experimental data on the structure, kinetics of decomposition, thermochemistry, and photochemistry of the 1,1-diazene have been lacking. We describe here the synthesis and characterization of two "persistent" 1,1-diazenes which have allowed the first *direct* studies on this reactive species.[2]

Theory

The nature of the bonding and the relative energies of the states of the parent 1,1-diazene (H_2N–N) have been the subject of several theoretical studies. Early ab initio studies of the 1,1-diazene resulted in a triplet ground state, but more recent calculations employing larger basis sets and configuration interaction find the singlet is the ground state (Table I).[6]

Table I. Singlet-Triplet Energy Gap in H_2N-N

calculational method	ground state	S-T gap[a]	ref[6]
STO-3G	triplet	26.3	Baird, 1973
4-31G	triplet	11.7	Pople, 1974
HF	triplet	5.2	Ahirichs, 1976
SCF	triplet	2.1	Wagniere, 1973
4-31G-CI	singlet	1.6	Baird, 1977
GVB-CI	singlet	13.8	Goddard, 1977

[a] kcal mol^{-1}, both states at equilibrium geometries.

From the recent calculations of Davis and Goddard (GVB-CI) the following theoretical picture of the parent 1,1-diazene emerges.[6f] The ground state is a singlet state ($^1A_1$) with the triplet ($^3A_2$) lying 13.8 kcal/mol higher. The stabilization of the singlet state is due to the large amount of double-bond character in the NN bond ($H_2{}^+N{=}N{:}^-$) as reflected in the short bond length (R_e = 1.25 Å) and the large dipole moment (μ = 4.036 D). In contrast the $^3A_2$ state has R_e = 1.37 Å and μ = 2.35 D. The first excited singlet S_1 corresponds to an n,π^* excited state and lies 50.7 kcal/mol above the ground state. Important to the experimentalist, the calculations predict that the 1,1-diazene should absorb light in the visible region. Due to the strong π-bonding interaction in

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(1) We are grateful to the National Science Foundation for generous support.

(2) For a preliminary report see: (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. *J. Am. Chem. Soc.* **1980**, *102*, 878. (d) *Ibid.* **1981**, *103*, 1563.

(3) National Science Foundation Predoctoral Fellow.

(4) Camille and Henry Dreyfus Teacher-Scholar, 1978–1983.

(5) For reviews of 1,1-diazene behavior 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.

(6) (a) Baird, N. C.; Barr, R. F. *Can. J. Chem.* **1973**, *51*, 3303. (b) Lanthon, W. A.; Curtiss, L. A.; Helve, W. J.; Lisle, J. B.; Pople, J. A. *Prog. Phys. Org. Chem.* **1974**, *11*, 1975. (c) Ahlrichs, R.; Staemmler, V. *Chem. Phys. Lett.* **1976**, *37*, 77. (d) Wagniere, G. *Theor. Chim. Acta* **1973**, *31*, 269. (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*, 711.

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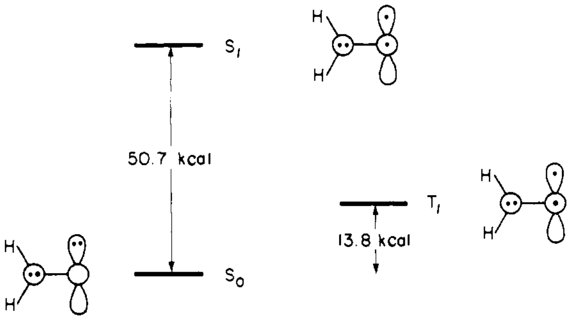
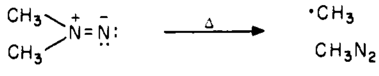
the singlet ground state S_0 is planar whereas S_1 and T_1 have optimum pyramidal geometries with a 21° angle between the H_2N plane and the NN axis and an inversion barrier of 0.2 kcal/mol^{-1}.



Theoretical studies on the C–N bond strengths of the 1,1-diazene find substantially lower values than that of the trans-1,2-isomer.[7] For example, the homolytic decomposition of *N*-(dimethylamino)nitrene (**3**) is calculated to be endothermic by



$$(CH_3)_2\overset{+}{N}{=}\overset{-}{\ddot{N}}: \xrightarrow{\Delta} \begin{matrix}{}^{\bullet}CH_3\\ CH_3N_2{}^{\bullet}\end{matrix}$$

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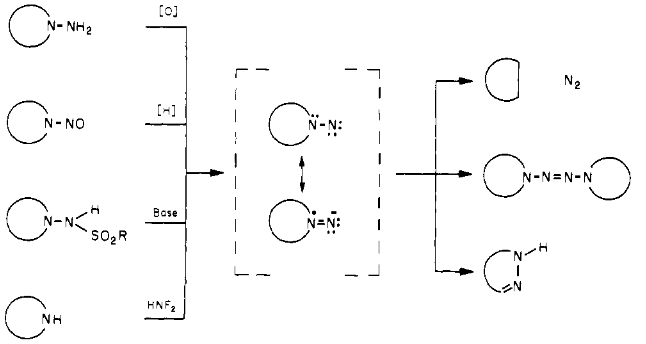
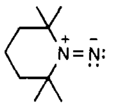
23.5[7a] and 26.2 kcal/mol.[7b] For comparison, *trans*-1,2-dimethyldiazene has an enthalpy of activation $\Delta H^{\ddagger}$ of 52 kcal/mol.[8]

Experiment

There are several methods reported for the generation of presumed 1,1-diazenes, those most versatile being the oxidation of 1,1-disubstituted hydrazines, the reduction of *N*-nitrosamines, and the base-induced decomposition of 1,1-disubstituted 2-sulfonylhydrazines.[5] Though not exclusive, the reactions ascribed to 1,1-diazenes can be divided into three general classes: fragmentation (extrusion of molecular nitrogen), isomerization (e.g., 1,1-diazene → hydrazone rearrangement), and bimolecular reactions (e.g., 1,1-diazene → tetrazene). Apparently the competition among these reaction paths is determined by several factors such as structure, substitution, reaction conditions, and method of generation.[5]



For *direct* studies, the synthetic targets chosen where *N*-(2,2,6,6-tetramethylpiperidyl)nitrene (**4**) and *N*-(2,2,5,5-tetramethylpyrrolidyl)nitrene (**5**). These molecules lack α-C–H substitution, eliminating the 1,1-diazene → hydrazone rearrangement, and, importantly, contain a suitable arrangement of bulky groups that should drastically slow down the dimerization of 1,1-diazene to tetrazene.[9]



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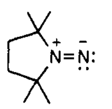

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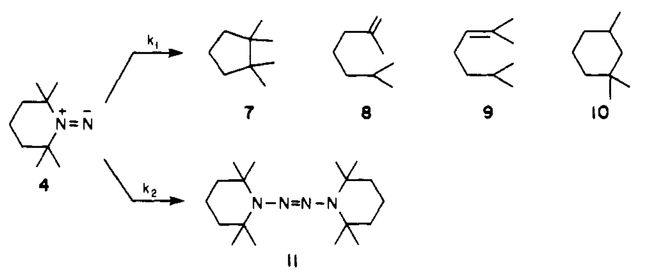
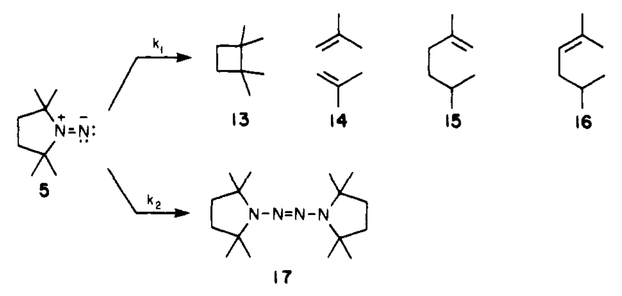
Scheme I



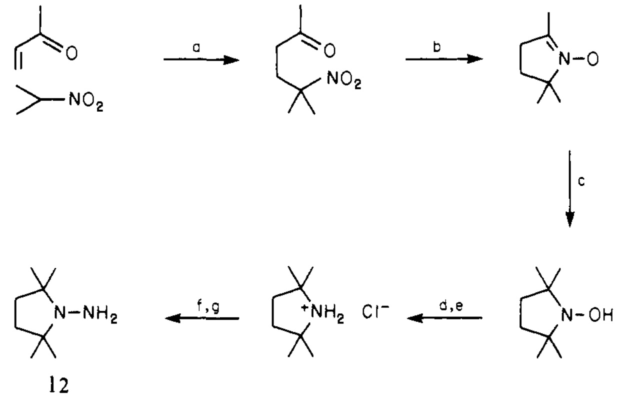
Scheme II



Results

Syntheses of *N*-(2,2,6,6-Tetramethylpiperidyl)nitrene (4) and *N*-(2,2,5,5-Tetramethylpyrrolidyl)nitrene (5). Nitrosation of 2,2,6,6-tetramethylpiperidine followed by reduction with lithium aluminum hydride affords the known compound 1-amino-2,2,6,6-tetramethylpiperidine (**6**).[10] Addition of *tert*-butyl hypochlorite (*t*-BuOCl) to a stirred solution of **6** and triethylamine in anhydrous diethyl ether at –78 °C affords, in addition to an insoluble white precipitate (Et_3NHCl), an intense purple solution which is stable for hours at –78 °C. This purple solution decolorizes rapidly at 0 °C, affording hydrocarbon products **7–10** and tetrazene **11**.

The precursor to the five membered 1,1-diazene (**5**), 1-amino-2,2,5,5-tetramethylpyrrolidine (**12**), was synthesized in six steps from methyl vinyl ketone and 2-nitropropane.[11]



a) Triton-B b) Zn, NH_4Cl c) CH_3MgI d) RaNi/H_2 e) HCl f) $NaNO_2$/85° g) $LiAlH_4$/95°

Oxidation of hydrazine **12** with *tert*-butyl hypochlorite and triethylamine in anhydrous diethyl ether at –78 °C affords a persistent red solution of 1,1-diazene **5** as well as triethylamine hydrochloride. The 1,1-diazene **5** decolorizes at 0 °C affording hydrocarbon products **13–16** and tetrazene **17**.

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(7) (a) Casewit, C. J.; Goddard, W. A. *J. Am. Chem. Soc.* **1980**, *102*, 4057. (b) Pasto, D. J.; Chipman, D. M. *Ibid.* **1979**, *101*, 2290.

(8) (a) Martin, J. C.; Timberlake, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 978. (b) See also: Engel, P. S.; Hayes, R. A.; Keifer, L.; Szilagyi, S.; Timberlake, J. W. *Ibid.* **1978**, *100*, 1876.

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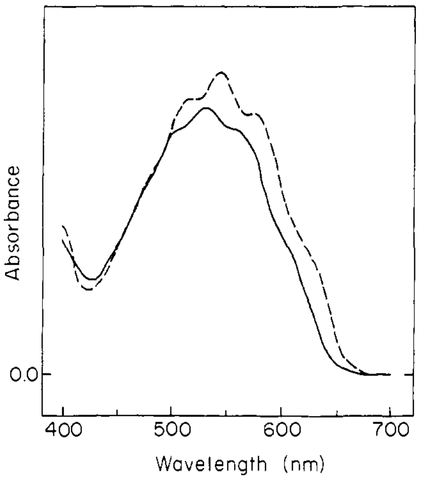

Figure 1. Absorption spectrum of **4** at −78 °C in CH_2Cl_2 (---) and *i*-PrOH (—).

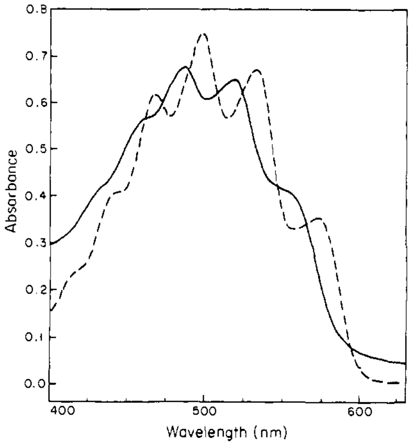

Figure 2. Absorption spectrum of **5** at −78 °C in CH_2Cl_2 (---) and *i*-PrOH (—).

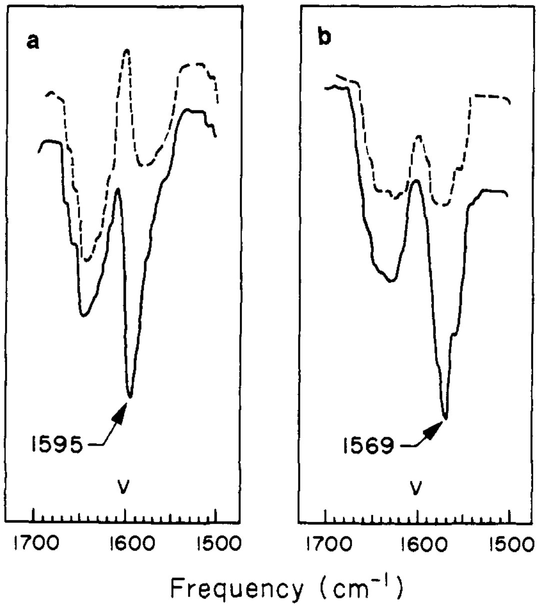

Figure 3. Infrared spectra of **4**: (a) $R_2{}^{14}N{=}{}^{14}N$ and (b) $R_2{}^{14}N{=}{}^{15}N$ at −78 °C (—) and at −78 °C after it was warmed to 25 °C (---).

Electronic Spectra of *N*-(2,2,6,6-Tetramethylpiperidyl)nitrene (4) and *N*-(2,2,5,5-Tetramethylpyrrolidyl)nitrene (5). *tert*-Butyl hypochlorite oxidation of hydrazines **6** and **12** in anhydrous dimethyl ether at −78 °C followed by filtration at −78 °C yields clear solutions of 1,1-diazenes **4** and **5**, respectively. Concentration of the purple solution of **4**, dilution with methylene chloride, and subsequent low-temperature absorption spectroscopy reveal a structured absorption band with λ_{max} = 541 nm and $\lambda_{0,0}$ = 610 nm (46.9 kcal).[2,12] This absorption is close to the n,π^* electronic transition calculated by Goddard for the parent system, H_2N–N.[6f]

The detail in this electronic spectrum appears to be the vibrational spacing of the singlet excited state S_1 of 1,1-diazene **4**. A crude analysis shows the spacings between maxima to be ~1040 cm^{-1}. Qualitatively, the overall appearance of the spectrum is in accord with that expected for a chromophore X-Y whose X-Y separation is larger in the excited state than in the ground state.[13]

The position of an absorption that involves nonbonding electrons (n,π^*) is particularly sensitive to the polarity of the solvent. The 1,1-diazene chromophore is isoelectronic with the carbonyl group. The visible spectrum of the 1,1-diazene is subject to a blue shift with increase in solvent polarity analogous to solvent effects on the n,π^* transition of the carbonyl group.[14] When *t*-BuOCl is added to **6** in the presence of triethylamine in dimethyl ether at −78 °C, filtered, concentrated, and diluted with isopropyl alcohol, a λ_{max} = 526 nm and $\lambda_{0,0}$ = 592 nm is observed, a shift of ~18 nm to shorter wavelength, (0,0 transition) (Figure 1).[12,13] The shift to higher energy for the n,π^* electronic transition in isopropyl alcohol results presumeably from differential solvation of ground and excited states reflecting the different electronic structures of S_0 and S_1.[15] By combination of low-temperature ^1H NMR and electronic absorption spectroscopy, the measured extinction coefficient (ϵ_{max}) for the 1,1-diazene **4** is 18 ± 3 (Et_2O) consistent with an n,π^* symmetry forbidden transition.

The clear red solution of 1,1-diazene **5** was further purified by low-temperature chromatography (−88 °C) prior to low-temperature absorption spectroscopy. 1,1-Diazene **5** has structured absorption spectra similar in appearance to that of **4**. The λ_{max} in dichloromethane is 497 nm and $\lambda_{0,0}$ is 572 nm (50.0 kcal) (ϵ_{max} = 20 ± 3).[2,12] The spacing between the maxima is approximately 1238 cm^{-1}. Replacement of CH_2Cl_2 with isopropyl alcohol affords λ_{max} (*i*-PrOH) of 487 nm and $\lambda_{0,0}$ = 552 nm, a blue shift of 20 nm to shorter wavelength (0,0 transition) (Figure 2).[13]

Infrared Spectra of *N*-(2,2,6,6-Tetramethylpiperidyl)nitrene (4) and *N*-(2,2,5,5-Tetramethylpyrrolidyl)nitrene (5). When *t*-BuOCl is allowed to react with hydrazine **6** in the presence of triethylamine and the reaction mixture is filtered, concentrated, diluted with CH_2Cl_2 at −78 °C, and introduced into a copper-jacketed infrared cell (CsBr) at −78 °C, the infrared spectrum of **4** shows a strong absorption at 1595 cm^{-1} that disappears on warming to 25 °C. This is assigned as an N=N double-bonded stretching frequency.[16] To test this, application of Hooke's law allows an approximation of the stretching frequency for the appropriate $^{14}N{=}{}^{15}N$ isotopically labeled isomer.[17] The calculated $\nu(^{14}N{=}{}^{14}N)/\nu(^{14}N{=}{}^{15}N)$ ratio is 1.0171, giving a predicted shift for the $^{14}N{=}{}^{15}N$ species to 1568 cm^{-1}. Synthesis of the corresponding $R_2{}^{14}N{=}{}^{15}N$ species[18] affords an infrared spectrum with no absorption at 1595 cm^{-1} but rather a new absorption at 1569 cm^{-1}, a shift of 26 cm^{-1}, consistent with the assignment of an N=N stretch for the 1,1-diazene (Figure 3).

The infrared spectra of the 1,1-diazene **5** shows a strong absorption (N=N stretch) at 1638 cm^{-1} that disappears on warming. The calculated $\nu(^{14}N{=}{}^{14}N)/\nu(^{14}N{=}{}^{15}N)$ ratio of 1.0171 predicts a shift to 1611 cm^{-1} for **5**. Synthesis of the corresponding

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(12) Assignments of the first absorption bands as 0,0 are tentative.

(13) Turro, N. J. "Molecular Photochemistry"; W. A. Benjamin: Reading, MA, 1965; p 37.

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(15) For example see: Huberfield, P.; Lux, M. S.; Rosen, D. *J. Am. Chem. Soc.* **1977**, *99*, 6828.

(16) The N=N stretching vibration of a symmetrical trans azo compound is forbidden in the infrared but absorbs in the 1576 cm^{-1} (6.35 μm) region of the Raman spectra.[17]

(17) Silverstein, R. M.; Bassler, G. C. "Spectrometric Identification of Organic Compounds"; Wiley: New York, 1967; p 66.

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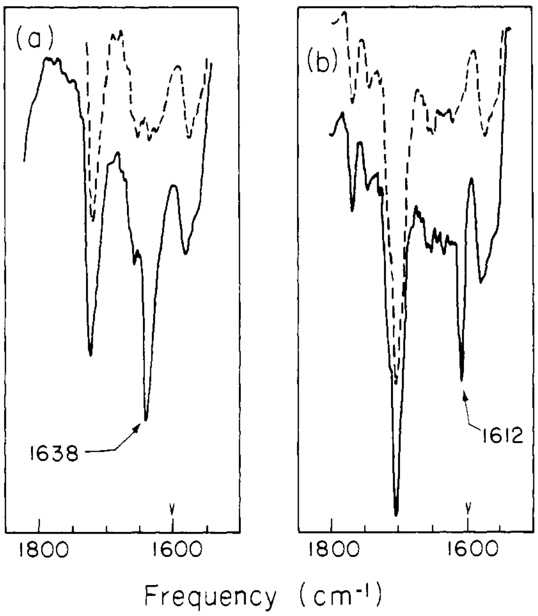

Figure 4. Infrared spectra of **5**: $R_2{}^{14}N{=}{}^{14}N$ and $R_2{}^{14}N{=}{}^{15}N$ at −78 °C (—) and at −78 °C after it was warmed to 25 °C (---).

Table II. Unimolecular Decomposition of 1,1-Diazenes 4 and 5

1,1-diazene	solvent	E_a, kcal mol^{-1}	log A	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
4	hexane	16.9 ± 0.7	11.6 ± 0.5	16.4 ± 0.5	−7.3 ± 2.3
4	THF	20.1 ± 0.4	13.6 ± 0.3	19.6 ± 0.4	1.8 ± 1.4
4	Et_2O	20.0 ± 0.4	13.7 ± 0.3	19.5 ± 0.4	2.3 ± 1.4
5	hexane	16.8 ± 0.5	10.9 ± 0.3	16.2 ± 0.5	−10.7 ± 1.4
5	Et_2O	19.0 ± 0.6	12.4 ± 0.4	18.5 ± 0.4	−5.2 ± 1.4
5	THF	19.1 ± 0.4	12.1 ± 0.3	18.4 ± 0.6	−3.8 ± 1.8

$R_2{}^{14}N{=}{}^{15}N$ species[19] affords an infrared spectrum with no absorption at 1638 cm^{-1} but rather a new absorption at 1612 cm^{-1}, a shift of 26 cm^{-1} (Figure 4). These results confirm that there is considerable double-bond character in the 1,1-diazene N=N bond, remarkably close to a 1,2-diazene isomer.

Kinetics of the Thermal Decomposition of *N*-(2,2,6,6-Tetramethylpiperidyl)nitrene (4) and *N*-(2,2,5,5-Tetramethylpyrrolidyl)nitrene (5). For kinetic studies, the purple and red 1,1-diazenes **4** and **5** were chromatographed (−88 °C) on basic alumina (propane/dimethyl ether elutant). Because the 1,1-diazenes are sensitive to trace acid, excess triethylamine was added. The chromatographed 1,1-diazenes **4** and **5** were concentrated at low temperature (−78 °C) and inspected by ^1H NMR ($CDCl_3$) revealing in addition to their corresponding tetrazenes absorptions at 1.15 and 2.15 δ (2:1 ratio) for 1,1-diazene **4** and 1.05 and 2.32 δ (3:1 ratio) for 1,1-diazene **5**. Warming both samples to 25 °C results in the disappearance of the 1,1-diazene signals while the tetrazene and hydrocarbon product signals grow in. These NMR results indicate that under some conditions the unimolecular and bimolecular reactions in Schemes I and II are competitive.

The unimolecular decay kinetics of 1,1-diazenes **4** and **5** were studied in dilute solution ($\sim 10^{-3}$ M) in three different solvents (hexane, ethyl ether, and tetrahydrofuran). The disappearance of **4** and **5** was followed by monitoring the optical density of the purple and red solutions at 541 and 497 nm, respectively, as a function of time in the temperature range of +4 to −21.6 °C. The rates of disappearance of the 1,1-diazenes were strictly first order at higher temperatures, becoming a combination of first and higher order kinetics as the temperature was lowered. Plots of ln A vs. time at the lower temperatures afforded a curved segment at short times followed by a linear segment at longer times. First-order rate constants were taken to be the slopes of the linear portions of these plots. The observed activation energies for the unimolecular 1,1-diazene decompositions in Et_2O are 20.0 ± 0.4 and 19.0 ± 0.6 kcal/mol for **4** and **5**,, respectively. These are substantially lower energies of activation than those observed for the decomposition of similarly substituted 1,2-dialkyldiazenes.[8] The activation parameters for the unimolecular decomposition of 1,1-diazenes **4** and **5** in three different solvents are shown in Table II.

Table III. Relative Rates of Unimolecular Decomposition of 1,1-Diazenes 4 and 5 at −10.0 °C

1,1-diazene	solvent	E_T	k, s^{-1}	k_{rel}	$\Delta G^{\ddagger}$, kcal mol^{-1}
4	hexane	30.9	3.49×10^{-3}	4.8	18.3 ± 1.3
4	Et_2O	34.6	1.23×10^{-3}	1.7	18.9 ± 0.8
4	THF	37.4	0.73×10^{-3}	1.0	19.1 ± 0.8
5	hexane	30.9	1.1×10^{-3}	5.1	19.0 ± 0.9
5	Et_2O	34.6	5.2×10^{-4}	2.4	19.9 ± 1.0
5	THF	37.4	2.2×10^{-4}	1.0	19.4 ± 0.9

Table IV. Bimolecular Decomposition of 1,1-Diazene 4[a]

temp, °C	k_2, L/(mol s)	temp, °C	k_2, L/(mol s)
−30.6	1.53×10^{-2}	−60.5	2.23×10^{-3}
−41.1	7.36×10^{-3}	−70.2	1.17×10^{-3}
−50.4	3.91×10^{-3}		

[a] 0.1 M in $CDCl_3$.

Table V. Relative Rates of Dimerization of 1,1-Diazenes 4 and 5 at −41.1 °C

1,1-diazene	k_2, L/(mol s)	k_{rel}
4	7.4×10^{-3}	90
5	8.6×10^{-5}	1

Table VI. Electronic Absorption Spectra of 1,1-Diazenes 4 and 5

1,1-diazene	solvent	λ_{max}, nm	$\lambda_{0,0}$,[12] nm	0,0, kcal
4	CH_2Cl_2	541	610	46.9
4	*i*-PrOH	526	592	48.5
5	CH_2Cl_2	497	572	50.2
5	*i*-PrOH	487	552	52.0

We find the rates of decomposition of 1,1-diazenes **4** and **5** are sensitive to solvent, the rate increasing with decreasing sovlent polarity (Table III). The observed rate dependence on solvent polarity is consistent with a polar ground state decomposing by a less polar transition state. Such an effect has been observed in the decompositions of 1,2-dialkyldiazenes by Rüchardt and co-workers.[20] For the three solvents examined ln k_1 correlates with E_T reasonably well.[21]

Our qualitative observations on the dimerization of the 1,1-diazenes indicated that the five-membered species **5** is significantly *more persistent* than the six-membered counterpart **4**. In the temperature range −30 to −90 °C the unimolecular fragmentation of **4** and **5** is slow. Between −30 and −90 °C the dimerization of *N*-(2,2,6,6-tetramethylpiperidyl)nitrene **4** was sufficiently fast to obtain accurate bimolecular rate constants and Arrhenius parameters.

The bimolecular rates of the dimerization, 1,1-diazene to tetrazene, were followed by ^1H NMR. Plotting log k as a function of $1/T$ affords a straight line from which the Arrhenius parameters for 1,1-diazene **4** were determined, E_a = 6.4 ± 0.9 kcal/mol and log A = 3.8 ± 0.7 (ΔH^{*} = 5.8 kcal/mol, ΔS^{*} = −43.2 eu). This is the first experimental determination of the E_a and log A for

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(19) Successive treatment of 2,2,5,5-tetramethylpyrrolidine with $Na^{15}NO_2$ (Prochemicals Limited, NJ), lithium aluminum hydride, and *t*-BuOCl/Et_3N afforded the ^{15}N-labeled 1,1-diazene **5**.

(20) (a) Schulz, A.; Rüchardt, C. *Tetrahedron Lett.* **1976**, 3883. (b) Duismann, W.; Rüchardt, C. *Chem. Ber.* **1978**, *111*, 596.

(21) Reichardt, C. *Angew Chem., Int. Ed. Engl.* **1965**, *4*, 29 and references cited there.

Table VII. Infrared Spectra of 1,1-Diazenes 4 and 5[a]

1,1-diazene	$\nu(R_2{}^{14}N{=}{}^{14}N)$, cm^{-1}	$\nu(R_2{}^{14}N{=}{}^{15}N)$, cm^{-1}
4	1595	1569
5	1638	1612

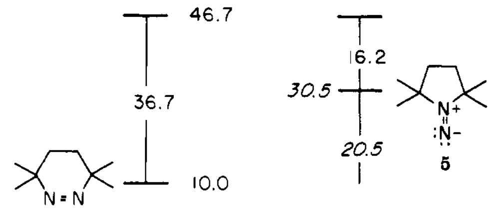
[a] In CH_2Cl_2.

Table VIII. Hydrocarbon Product Ratios from 1,1- and 1,2-Diazenes 5 and 19

compd	conditns	13	14	15	16
5	0 °C[a]	49	47	2.0	1.0
19	140 °C[b]	46	52	1.5	0.5

[a] Et_2O. [b] Benzene.

Scheme III



19

the direct bimolecular dimerization of 1,1-diazenes to form tetrazenes (Table IV).

Due to the slower dimerization of *N*-(2,2,5,5-tetramethylpyrrolidyl)nitrene **5**, accurate bimolecular rate constants could not be obtained at −30 to −90 °C. However, for purposes of comparison with **4**, a rate constant for the dimerization of **5** was obtained at −41.1 °C. At this temperature, the dimerization rate of **5** is found to be 2 orders of magnitude slower than the dimerization of **4** (Table V).

Discussion

Comparisons of the electronic absorption and infrared spectra of the 1,1-diazenes **4** and **5** are shown in Table VI. The change from a six-membered to a five-membered cyclic 1,1-diazene causes a shift to higher energy for the n,π^* transition and a shift to higher energy for the N=N stretching frequency. For comparison to the isoelectronic ketones, 2,2,6,6-tetramethylcyclohexanone has an electronic spectrum with $\lambda_{max}(Et_2O)$ of 305 nm and an infrared absorption (C=O stretch) of 1690 cm^{-1} while 2,2,5,5-tetramethylcyclopentanone has $\lambda_{max}(Et_2O)$ of 296 nm and an IR absorption (C=O stretch) of 1730 cm^{-1}.[22]

1,1-Diazenes **4** and **5** have similar E_a values for unimolecular decomposition. If similar mechanisms are operating in the unimolecular decomposition of **4** and **5**, this suggests that the difference in strain energies of these cyclic diazenes may be small.

The heat of formation of a 1,1-diazene has not been determined and may be a difficult value to obtain due to the lability of 1,1-diazenes. The heat of formation (ΔH_f = 10.0 ± 0.6 kcal/mol) and the enthalpy of activation ($\Delta H^\ddagger$ = 36.7 ± 0.5 kcal/mol) for decomposition of 3,3,6,6-tetramethyltetrahydropyridazine (**19**) are known.[23] The sum of these two values affords a value for the heat of formation of the corresponding transition state, $\Delta H_f^\ddagger$ = 46.7 kcal/mol. If similar intermediates of similar energy intervene in the decomposition of **5** and **19**, subtraction of the enthalpy of activation for the decomposition of **5** ($\Delta H^\ddagger$ = 16.2 kcal/mol in hexane) affords an approximate value for the ΔH_f of the 1,1-diazene **5**; i.e., ΔH_f (**5**) = 30.5 kcal/mol. This *approximate* value would indicate the 1,1-diazene **5** has a higher heat of formation than the cis 1,2-isomer **19** by 20 kcal/mol (Scheme III).

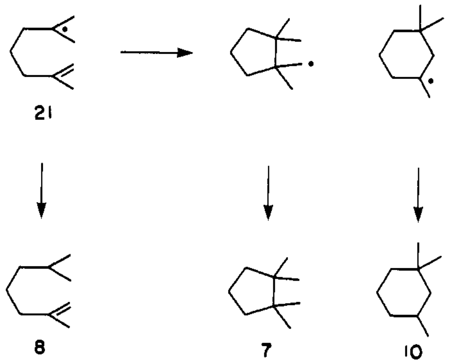
Table IX. Hydrocarbon Product Ratios from 4 at 0 °C

compd	conditns	7	8	9	10
4	hexane	24	5	68	2
4	Et_2O	24	10	61	5
4	THF	24	11	55	10

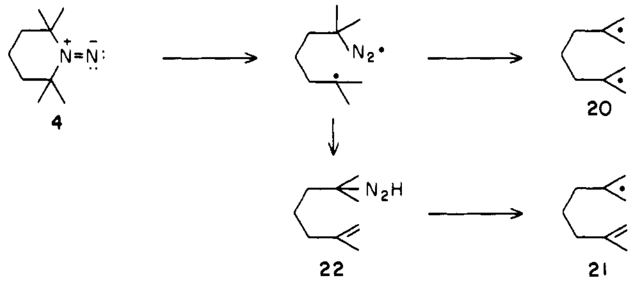
Table X. VPC Columns

designation	description
Pennwalt 223	10 ft × 1/8 in. stainless steel; 28% Pennwalt 223 on 80/100 Chrom R
Pennwalt 223	10 ft × 1/4 in. glass, 28% Pennwalt 223 on 80/100 Chrom R
Carbowax 400	10 ft × 1/8 in. stainless steel; 10% Carbowax 400 on 100/120 Chrom P A/W DMCS
β,β	20 ft × 1/8 in. stainless steel; 10% β,β′-oxydipropionitrile on 100/120 Chrom P A/W DMCS
β,β	10 ft × 3/8 in. aluminum; 25% β,β′-oxydipropionitrile on 60/80 Chrom P
SF-96	10 ft × 3/8 in. aluminum; 25% SF-96 on 45/60 Chrom A.
SF-96	10 ft × 1/8 in. stainless steel; 10% SF-96 on 100/120 Chrom P A/W

Scheme IV



Scheme V



Mechanism of the Decompositions of 1,1-Diazenes 4 and 5. The hydrocarbon products **13**–**16** from the unimolecular thermal decomposition of **5** are consistent with a 1,4-biradical precursor formed from loss of N_2. The product ratios from the 1,1 and 1,2 isomers[24] are similar. We do not have any information on whether C–N bond breaking is occurring simultaneously or stepwise. The 1,1-isomer **5** does not rearrange to the 1,2-diazene **19**.

The hydrocarbon products from the decomposition of 1,1-diazene **4** are more difficult to interpret (Table IX). Hydrocarbons **7**–**9** from the thermal decomposition of **4** are consistent with a 1,5-biradical precursor **20** formed from loss of N_2 (Table IX). However, it is not obvious how the 1,1,3-trimethylcyclohexane (**10**) product could be derived from a 1,5 biradical. A more probable source of this product is the monoradical **21**.

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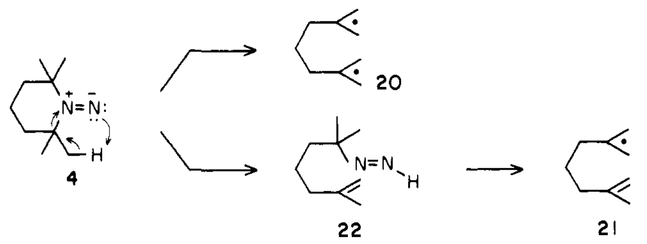
[22] Hinsberg, W. D., III, Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1979.

[23] Engel, P. S. *J. Am. Chem. Soc.* **1976**, *98*, 1972.

[24] For the synthesis of 3,3,6,6-tetramethyl-1,2-diazacyclohexene (**19**) see: Greene, F. D.; Gilbert, K. E. *J. Org. Chem.* **1975**, *40*, 1409.

Scheme VI



Walling and Cioffari[25] have provided evidence that hydrocarbons **7** and **10** may arise from the rearrangement of radical **21** (Scheme IV). One possible source of radical **21** is the 1,2-diazene **22**, an isomer of the 1,1-diazene **4**. 1,2-Diazene **22** would be expected to undergo radical chain decomposition to the hydrocarbon products **7**, **8**, and **10**. The 1,2-diazene **22** may conceivably arise in two ways: (a) by initial one bond C–N cleavage of 1,1-diazene **4** to the diazenyl biradical **23** followed by intramolecular hydrogen atom migration (Scheme V) or (b) by a *direct* rearrangment similar to the elimination reaction of amine oxides (Scheme VI).[26] In summary, the appearance of 1,1,3-trimethylcyclohexane (**10**) may be evidenced for stepwise C–N cleavage (at least in part) or a concerted intramolecular elimination reaction in competition with 1,5-biradical formation.

Summary

The unstable 1,1-diazene had not been characterized by direct methods. The only knowledge of 1,1-diazene structure and bond strengths came from theoretical work. By synthesizing the "persistent" *N*-(2,2,6,6-tetramethylpiperidyl)nitrene (**4**) and *N*-(2,2,5,5-tetramethylpyrrolidyl)nitrene (**5**), we have obtained the electronic and infrared spectra and kinetics of the thermal decomposition of two 1,1-diazenes. The n,π^* absorption of the 1,1-diazene (a) occurs in the visible (~50 kcal/mol), (b) reveals the vibrational spacing in S_1, indicating a longer N–N bond length in S_1 than S_0, (c) has a low extinction coefficient ($\epsilon \approx$ 15–20), and (d) blue shifts in polar solvents. The infrared spectrum of the 1,1-diazene reveals an N=N double bond in ground-state S_0. The unimolecular kinetics of the thermal decomposition indicate bond strengths for these substituted 1,1-diazenes in the range of 20 kcal/mol. The hydrocarbon products can be interpreted as being derived from biradical precursors resulting from loss of N_2. One minor product in the decomposition of **4** raises the issue of either single-bond cleavage to a diazenyl biradical or a concerted elimination reaction of 1,1-diazenes to olefins. The bimolecular kinetics provide direct evidence that tetrazenes, often observed in the oxidation of 1,1-disubstituted hydrazines, can occur from the dimerization of 1,1-diazenes. The dimerization reaction is characterized as a low A, low E_a process. The dimerization rates vary with structure, the five-membered cyclic 1,1-diazene being more persistent. The photochemistry of the 1,1-diazene remains to be explored as well as the experimental determination of the S_0–T_1 energy gap.

Experimental Section

Melting points were determined by using a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 257 infrared spectrophotometer. Proton nuclear magnetic resonance (NMR) spectra were obtained on a Varian Associates A-60A, EM-390 spectrometer or Jeol FX-90. Chemical shifts are reported as parts per million (ppm) downfield from tetramethylsilane in δ units and coupling constants are in hertz (Hz). Electronic spectra were obtained on a Cary 14 Spectrophotometer.

For analytical vapor phase chromatography (VPC) a Hewlett-Packard 5700A gas chomatograph equipped with a flame ionization detector and nitrogen carrier gas was used. The 0.125-in. packed stainless steel columns used in this instrument are listed in Table X. Quantitative VPC analysis was accomplished using a Hewlett-Packard 3370A electronic digital integrator. For preparative VPC a Varian 920 instrument equipped with a thermal conductivity detector and helium carrier gas was used. The 0.375-in. packed aluminum columns used are listed in Table X. Detector response for hydrocarbons was assumed to be 1.00 relative to octane. Quantitative analyses of all other compounds were corrected for detector response.

Dibutyl ether was distilled from sodium. Ethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl. Triethylamine was distilled from barium oxide. Chloroform and fluorotrichloromethane were distilled from phosphorous pentoxide and passed through a short column of basic alumina. Deuteriochloroform used for obtaining 1,1-diazene NMR spectra was passed through a short column of basic alumina. Propane and dimethyl ether used in low-temperature chromatography were dried over 4A molecular sieves. Hexane was washed with concentrated sulfuric acid, saturated sodium bicarbonate, and saturated sodium chloride solution, dried ($CaCl_2$), and distilled from calcium hydride or lithium aluminum hydride. *tert*-Butyl hypochlorite was washed with 10% sodium carbonate and water, dried ($CaCl_2$), and distilled under nitrogen. 1-Amino-2,2,6,6-tetramethylpiperidine and 1-amino-2,2,5,5-tetramethylpyrrolidine were always purified by preparative VPC (Pennwalt 223, 180 and 160 °C, respectively) immediately prior to use.

Mass spectra were recorded on a DuPont 24-492B mass spectrometer. Elemental analyses were performed at the Caltech Microanalytical Laboratory and Galbraith Laboratories, Knoxville, TN. Unless otherwise indicated, reactions were carried out under a positive pressure of dry nitrogen.

Low-Temperature Spectroscopic Cells. The IR and UV-visible cells are designed for use in conjunction with an Air Products WMX-1A vacuum shroud and LC-1-110 Cryo-Tip refrigerator. The windows for the vacuum shroud are sodium chloride (International Crystal Laboratories) for IR spectroscopy and Suprasil I, ground to size from blanks (Amersil, Inc.), for UV-visible spectroscopy. Samples were introduced into the cells through 18 gauge Teflon tubing (Alpha Wire Corp.) by applying suction with a syringe. The cell body of the UV-visible spectroscopic cell is constructed from OFHC copper, with stainless steel tubing soldered to it. The body is nickel-plated and has a thermocouple well with set screw. The cell windows are Suprasil I and were ground to size from blanks (Amersil, Inc.). The seals between the windows and the body were made with Viton O-rings. The cell path length is 10.0 mm, and the volume is approximately 4 mL. The cell body of the IR cell is OFHC copper with stainless steel tubing soldered in place. The cell windows are cesium bromide (International Crystal Laboratories). Two 0.5-mm lead spacers are used to give a pathlength of 1.0 mm. The spectroscopic cells were constructed in the Chemistry Division/Caltech Instrument Shop.[22]

1-Nitroso-2,2,6,6-tetramethylpiperidine (23). A modification of the procedure of Overberger and co-workers was used.[27] A solution ~0.8 M in HCl was prepared by addition of 14 mL of concentrated hydrochloric acid to 200 mL of water and placed in a three-necked 1-L round-bottom flask equipped with magnetic stirrer, reflux condenser, addition funnel, and thermometer. To this was added slowly with cooling 23.7 g (0.152 mol) of distilled 2,2,6,6-tetramethylpiperidine. The reaction mixture was heated to 75 °C, and a solution of 42.1 g (0.61 mol) of sodium nitrite in 150 mL of water was added over 30 min. Heating was continued for 96 h during which time a yellow oil formed. After the mixture was cooled to room temperature, 100 mL of ethyl ether was added to the reaction mixture and the layers were separated. The aqueous layer was extracted twice with ether. The combined ethereal extracts were washed with 100 mL of 10% HCl solution, 100 mL of saturated sodium bicarbonate solution, and 100 mL of saturated sodium chloride solution. The ethereal extracts were dried (Na_2SO_4), concentrated, and distilled, giving 25.1 g (89%) of 1-nitroso-2,2,6,6-tetramethylpiperidine (**23**): bp 114–117 °C (15 torr) (lit.[28] 91–92 °C (12 torr)); IR (CCl_4) 2925, ,1455, 1375, 1360 cm^{-1}; NMR ($CDCl_3$) δ 1.90–1.50 (m, 6 H), 1.64 (s, 6 H), 1.40 (s, 6 H); UV (Et_2O) 395 nm (ϵ 69.5), 238 (4500) (lit.[28] 397 nm (ϵ 86), 238 (4500)).

1-Amino-2,2,6,6-tetramethylpiperidine (6). A modification of the procedure of Roberts and Ingold was used.[29] A slurry of 5.0 g (0.13 mol) of lithium aluminum hydride in 150 mL of 1:1 ethyl ether/*n*-butyl ether was stirred in a 500-mL three-necked round-bottomed flask equipped with addition funnel, magnetic stirrer, thermometer, and reflux condenser fitted with a still head. To this was added dropwise a solution of 12.5 g (0.071 mol) of 1-nitroso-2,2,6,6-tetramethylpiperidine (**23**) in 25 mL of ethyl ether. After the solution was stirred for an additional 30 min, solvent was distilled until the internal temperature reached 95 °C. Heating was continued for 4 h, at which time the reaction mixture was

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[25] Walling, C.; Cioffari, A. *J. Am. Chem. Soc.* **1972**, *94*, 6059.

[26] DePuy, C. H.; King, R. W. *Chem. Rev.* **1960**, *60*, 431.

[27] Overberger, C. G.; Lombardino, J. G.; Hiskey, R. G. *J. Am. Chem. Soc.* **1957**, *79*, 6430.

[28] McKay, D.; Waters, W. A. *J. Chem. Soc. C* **1966**, 813.

[29] Roberts, J. R.; Ingold, K. U. *J. Am. Chem. Soc.* **1973**, *95*, 3228.

cooled to 0 °C and hydrolyzed by careful addition of a large excess of water. The layers were separated, and the aqueous layer was extracted with ether. The combined organic extracts were extracted with 10% HCl solution. The combined acid extracts were made strongly basic with 20% sodium hydroxide solution and were extracted with ether. These ethereal extracts were combined and washed with 100 mL of saturated sodium chloride solution. The ethereal extracts were dried (Na_2SO_4), concentrated, and distilled affording 9.1 g (86%) of **6** (95% pure by VPC, Pennwalt 223, 180 °C): bp 82–85 °C (20 torr) (lit.[29] 80–83 °C (20–21 torr)); IR (film) 3350, 3250, 2960, 2925, 1370, 1360 cm^{-1}; NMR ($CDCl_3$) δ 2.8 (s, 2 H), 1.50 (s, 6 H), 1.06 (s, 12 H).

1-Nitroso-2,2,5,5-tetramethylpyrrolidine (24). To a solution of 8 g (0.05 mol) of 2,2,5,5-tetramethylpyrrolidine hydrochloride in 100 mL of water at 85 °C was added slowly with stirring 15.3 g (0.22 mol) of sodium nitrite in 50 mL of water. The reaction temperature was maintained at 85 °C for 72 h during which time a yellow oil formed. After the solution was cooled to room temperature, 30 mL of ethyl ether was added to the reaction mixture and the layers were separated. The aqueous layer was extracted twice with ether. The combined ethereal extracts were washed with 30 mL of 10% HCl solution, 100 mL of saturated sodium bicarbonate solution, and 100 mL of saturated sodium chloride solution. The ethereal extract was dried (Na_2SO_4) and concentrated, affording 6.9 g (90%) of 1-nitroso-2,2,5,5-tetramethylpyrrolidine (**24**). This was further purified by preparative VPC (Pennwalt 223, 200 °C): mp 51–52 °C; IR (CCl_4) 2930, 1460,, 1375, 1365 cm^{-1}; NMR ($CDCl_3$) δ 1.90 (t, 4 H, $J = 3.5$ Hz), 1.6 (s, 6 H), 1.45 (s, 6 H). Anal. Calcd for $C_8H_{16}N_2O$: C, 61.15; H, 10.32; N, 17.93. Found: C, 61.37; H, 10.50; N, 17.69.

1-Amino-2,2,5,5-tetramethylpyrrolidine (12). A slurry of 2.2 g (0.05 mol) of lithium aluminum hydride in 70 mL of 6:1 *n*-butyl ether/diethyl ether under N_2 was heated with distillation of solvent until the internal temperature reached 100 °C. A solution of 5 g (0.032 mol) of 1-nitroso-2,2,5,5-tetramethylpyrrolidine in 20 mL of *n*-butyl ether was then added cautiously over 1 h, never allowing the temperature to rise above 105 °C. Heating was continued for 4 h; the reaction mixture was cooled to 0 °C and hydrolyzed by careful addition of a large excess of water. The hydrolyzed mixture was transferred to a separatory funnel, and the layers were separated. The aqueous layer was extracted twice with ether, and the combined organic extracts were extracted three times with 10% HCl solution. The combined acid extracts were made strongly basic with 20% sodium hydroxide solution and were extracted three times with ether. The ethereal extracts were combined and washed with 100 mL of saturated sodium chloride solution. The ethereal extracts were dried (Na_2SO_4) and concentrated, affording a colorless oil. This oil was further purified by a distillation under reduced pressure at 25 °C followed by preparative VPC (Pennwalt 223, 160 °C), affording 2.5 g (34%) of 1-amino-2,2,5,5-tetramethylpyrrolidine (**12**): IR (film) 3350, 3220, 2950, 2930, 1370, 1355 cm^{-1}; NMR ($CDCl_3$) δ 2.8 (s, 2 H), 1.6 (s, 4 H), 1.03 (s, 12 H). This hydrazine compound is air sensitive. Anal. Calcd for benzamide ($C_{15}H_{22}N_2O$): C, 73.13; H, 9.00; N, 11.37. Found: C, 73.07; H, 9.03; N, 11.14.

1,1-Azo-2,2,5,5-tetramethylpyrrolidine (17). A 250-mg (1.75-mmol) sample of 1-amino-2,2,5,5-tetramethylpyrrolidine (**12**) was stirred under an oxygen atmosphere for 24 h. The resulting white crystalline solid was further purified by heating to 50 °C (0.05 torr) for 3 h, to yield 191 mg (78%) of **17**: mp 62–63.5 °C; IR ($CHCl_3$) 1940, 1460, 1375, 1360 cm^{-1}; NMR ($CDCl_3$) δ 1.7 (s, 8 H), 1.3 (s, 24 H); UV (2,2,5-trimethylpentane) 300 nm (ϵ 8600), 254 (3300). Anal. Calcd for $C_{16}H_{32}N_4$: C, 68.52; H, 11.50; N, 19.97. Found: C, 68.30; H, 11.35; N, 19.88.

General Procedure for Synthesis and Purification of 1,1-Diazenes 4 and 5. Into an argon-purged 25-mL flask was placed 1.75 mmol of hydrazine **6** or **12**. The flask was cooled to −78 °C; 12–15 mL of dry methyl ether was added followed by 1.50 mmol of triethylamine. With rapid stirring 1.60 mmol of *tert*-butyl hypochlorite was added dropwise over a 15-min period. A purple or pink color appeared almost immediately and was fully developed within 10 min. The reaction mixture was stirred at −78 °C for 1 h and then transferred under positive argon pressure via 18 gauge Teflon tubing to a argon-purged jacketed filter funnel precooled to −78 °C. The mixture was filtered under vacuum into a 25-mL three-neck flask precooled to −78 °C and equipped with serum cap and gas inlet tube. The solution was then concentrated to 2–3 mL for chromatography.

Deactivated basic alumina was prepared by washing 150 g of Woelm Activity I neutral alumina three times with 150 mL of 20% sodium hydroxide solution and decanting. After being washed three times with 150 mL distilled water, the alumina was washed three times with anhydrous methanol and dried 12 h at 350 °C.

A jacketed low-temperature chromatography column was equipped with a 200-mL three-neck round-bottomed flask (equipped with serum cap and gas inlet). The column was charged with 30 g of deactivated basic alumina and capped. After being purged the column with argon, the jacket was filled with acetone and cooled to −88 °C by adding liquid nitrogen and stirring vigorously. The column was wetted and rinsed through with 40 mL of dry liquid propane (cooled to −78 °C), added by means of a double-ended needle. The concentrated 1,1-diazene solution was carefully placed on the column via a double-ended needle and allowed to percolate onto the adsorbent. Elution was begun with 2:3 dimethyl ether/propane by using a positive pressure of argon at the column head to force the solvent through. When the colored band reached the bottom of the column head, the forerun was drawn off through a double-ended needle into an evacuated 200-mL flask, cooled to −78 °C. Elution was resumed until two-thirds of the colored band had been collected. This colored solution was drawn off into a 100-mL round-bottom flask equipped with serum cap, argon inlet, and several milliliters of appropriate solvent such as hexane, THF, or diethyl ether, precooled to −78 °C. A 50-μl sample of triethylamine was added, and the propane/methyl ether was then removed under reduced pressure, leaving a concentrated 1,1-diazene solution. Low temperature chromatography afforded 1,1-diazene **4** and tetrazene **11** (2:1 ratio, respectively) and small amounts of 1-amino-2,2,6,6-tetramethylpiperidine (**12**). Low-temperature chromatography afforded 1,1-diazene **5** with ≤5% tetrazene **17**. *Both 1,1-diazenes 4 and 5 are sensitive to trace acid.*

Spectroscopy. Visible Absorption Spectroscopy. Typically 0.6–1.5 mmol of the appropriate hydrazine **6** or **12** was oxidized with *tert*-butyl hypochlorite in the manner described above. The solution was filtered at −78 °C through a jacketed frit into 4–6 mL of the desired precooled solvent and concentrated. Dry argon was admitted to the flask, and 1,1-diazene solution was drawn into a low temperature UV–visible cell (−78 °C) and the spectrum recorded at −78 °C.

Infrared Spectroscopy. Typically 0.6–1.5 mmol of the appropriate hydrazine compound **6** or **12** was oxidized with *tert*-butyl hypochlorite as described above. The resulting solution was filtered at −78 °C through a jacketed frit and then concentrated into 2 mL of spectrograde dichloromethane which had been previously passed through a short column of basic alumina. Dry argon was admitted to the flask, the sample was drawn into a low temperature IR cell (−78 °C), and the spectrum was recorded at −78 °C. The sample was then removed from the cell, allowed to decolorize at 25 °C, recooled to −78 °C, and drawn into the cell and the spectrum recorded.

Determination of the Extinction Coefficient. Approximately 1.5 mmol of the appropriate hydrazine **6** or **12** was oxidized and purified by low-temperature chromatography. The resulting solution was concentrated in 3 mL of deuteriochloroform. The flask was flushed with dry argon and the solution transferred via Teflon tubing to a graduated test tube at −78 °C. To 1.6 mL of this solution was added 25.4 mg of dichloromethane. The concentration of 1,1-diazene was determined by proton NMR analysis at −78 °C. To the remaining 1.4 mL of this solution was added sufficient dry ethyl ether or dichloromethane to give a volume of 4.5 mL. The visible absorption spectrum of this solution then allowed calculation of the molar extinction coefficient.

Nuclear Magnetic Resonance Spectroscopy. Approximately 1.5 mmol of the appropriate hydrazine **6** or **12** was oxidized and the resulting solution purified by low-temperature chromatography and concentrated into 5 mL of deuteriochloroform which had previously been passed through a short column of basic alumina. Dry argon was admitted to the flask and the 1,1-diazene solution transferred to a capped graduated test tube at −78 °C. Dichloromethane was then added to this solution as an internal standard. The 1,1-diazene solutions were frozen in liquid N_2 until use, at which time approximately 0.3 mL of the thawed solutions were transferred via 18 gauge Teflon tubing under positive argon pressure into 5-mm NMR tubes (−78 °C) equipped with serum caps. Spectra were recorded on either a Varian EM-390 or Jeol FX-90 NMR spectrometer at −60 °C.

Unimolecular Decomposition Kinetics. Solutions for studying the decomposition kinetics of 1,1-diazenes **4** and **5** were prepared in the following manner. Typically ~200 mg of the hydrazine **6** or **12** was oxidized and the resulting solution purified by low temperature chromatography and concentrated in 25–50 mL of freshly distilled ethyl ether, hexane, or tetrahydrofuran chilled to −78 °C and containing 50 μL of triethylamine. Kinetic measurements were done in a low-temperature spectroscopic cell and cooled by a circulating bath liquid and temperature was determined to the nearest 0.2 °C by means of an iron constantan thermocouple embedded in the cell body.[22] A typical kinetics run was carried out in the following manner: the spectroscopic cell was flushed four times and filled with freshly distilled solvent. The cell was cooled to the desired temperature, solvent expelled with an argon filled syringe, and the chromatographed 1,1-diazene then drawn into the cell. The absorbance of **4** and **5** was monitored at 541 and 497 nm, respectively, as a function of time. All data prior to temperature equilibration were discarded. Typically the reaction was followed through 10 half-lives, and the reported rate constants are derived by conventional linear least-squares analysis. In order to confirm a first-order process, rate constants for 1,1-diazene decompositions were determined for two different concentrations, and in all cases the values were identical within experimental error.

Bimolecular Decomposition Kinetics. Solutions for studying the bimolecular kinetics were prepared in the following manner. A 500-mg sample of the hydrazine **6** or **12** was oxidized and purified by low-temperature chromatography and concentrated in approximately 2.5 mL of deuteriochloroform which had been passed through a short column of basic alumina. The concentrated solution was transferred via 18 gauge Teflon tubing to a graduated test tube at −78 °C. A 25-mg sample of triethylamine and 25 mg of dichloromethane were added as an internal standard. Approximately 0.3 mL of the 1,1-diazene solution transferred into a base-washed argon-purged NMR tube at −78 °C. The tube was then transferred to a precooled JEOL FX-90 NMR probe, and after a 5-min equilibration period data collection was begun. Disappearance of 1,1-diazenes **4** and **5** was monitored by integrating the δ 2.15 and 2.32 peaks, respectively, relative to the methylene protons of triethylamine at discrete time intervals preprogrammed into a kinetic program on the JEOL FX-90 NMR spectrometer. The triethylamine concentration could be calculated and agreed with an independent measurement relative to the second dichloromethane standard. The reported rate constants are derived by conventional linear least-squares analysis. Temperatures were calibrated by measuring methanol chemical shift vs. temperature.

Products from the Oxidation of 1-Amino-2,2,6,6-tetramethylpiperidine (6). Approximately 1 mmol of 1-amino-2,2,6,6-tetramethylpiperidine (**6**) was oxidized with *tert*-butyl hypochlorite and filtered through a jacketed frit. The solution was transferred via a double-ended needle into a test tube capped with a rubber septum. The purple solution was warmed to room temperature and analyzed by VPC (β,β, 65 °C). The four C_9H_{18} isomers eluted in the following order with the retention times relative to ethyl ether (1.00): 1,1,3-trimethylcyclohexane (**10**) (1.71), 1,1,2,2-tetramethylcyclopentane (**7**) (2.03), 2,6-dimethyl-1-heptene (**8**) and 2,6-dimethyl-2-heptene (**9**) (2.44). The 2,6-dimethyl-1-heptene (**8**), 2,6-dimethyl-2-heptene (**9**), and 1,1,3-trimethylcyclohexane (**10**) were identified by comparison of NMR and IR spectra and VPC retention times (β,β, 25 °C) with those of authentic material. The 1,1,2,2-tetramethylcyclopentane (**7**) was identified by its spectral properties: IR ($CHCl_3$) 2950, 2870, 1460, 1375, 1365 cm^{-1}; NMR ($CDCl_3$) δ 1.56 (s, 6 H), 0.85 (s, 12 H);[30] mass spectrum, $M^+ = 126$ (calcd 126). Tetrazene product was identified as 1,1-azo-2,2,6,6-tetramethylpiperidine (**11**). Authentic material for comparison was synthesized according to the method of Roberts and Ingold.[29]

2,6-Dimethyl-2-heptene (9). A modification of the procedure of Starr and Eastman was used.[31] A solution of 4.31 g (28.0 mmol) of 2,2,6,6-tetramethylcyclohexanone in 400 mL of pentane was placed in a quartz photochemical reactor, deoxygenated, and cooled to 0 °C. The solution was photolyzed with a 450-W Hanovia lamp for 20 h. The reaction was followed by analytical VPC (SF-96, 140 °C). The photolysis mixture was concentrated and distilled under reduced pressure. The products were isolated by preparative VPC (β,β, 65 °C), collection the two major peaks of relative retention times 3.88 and 5.34 (pentane = 1.00). The first eluting peak was shown by proton NMR to be 1,1,3-trimethylcyclohexane (**10**) by comparison with an authentic sample (Chemsampco): NMR ($CDCl_3$) δ 1.8–1.1 (m, 9 H), 0.90 (s, 6 H), 0.80 (d, 3 H, 7 Hz). The later eluting peak was shown by proton NMR to be identical with that of 2,6-dimethyl-2-heptene as reported by Starr and Eastman:[31] NMR ($CDCl_3$) δ 5.14 (m, 1 H), 2.0 (m, 2 H), 1.70 (s, 3 H), 1.60 (s, 3 H), 1.6–1.1 (m, 3 H), 0.88 (d, 6 H, 6 Hz).

Products from the Oxidation of 1-Amino-2,2,5,5-tetramethylpyrrolidine (12). Approximately 1 mmol of 1-amino-2,2,5,5-tetramethylpyrrolidine (**12**) was oxidized with *tert*-butyl hypochlorite and filtered through a jacketed frit. The solution was transferred via a double-ended needle into a test tube capped with a rubber septum. The red solution was warmed to room temperature and analyzed by VPC (Carbowax 400, 25 °C). All peaks were identified by coinjection of authentic materials. 2-Methylpropene (**14**) was obtained from Matheson, 2,5-dimethyl-1-hexene (**15**), 2,5-dimethyl-2-hexene (**16**), and 1,1,3-trimethylcyclopentane (not present) were obtained from Chemsampco, and 1,1,2,2-tetramethylcyclobutane (**13**) was synthesized by the method of Porter.[32]

Hydrocarbon Yields. The appropriate hydrazine (1.5 mm) was oxidized with *tert*-butyl hypochlorite, filtered, chromatographed, and concentrated in 3 mL of solvent containing 50 μl of $CHCl_3$. The solution was then transferred via a double-ended needle to a graduated test tube sealed with a serum cap. Approximately 0.3 mL of this solution was transferred to an NMR tube (−78 °C) containing 50 μl of CD_2Cl_2. The concentration of 1,1-diazene was determined by low-temperature ^{1}H NMR (0.01–0.05 M). The sample was then warmed at 0, −10, or −20 °C, recooled, and analyzed by ^{1}H NMR. The relative yields of tetrazene were typically 60–80% and are dependent on temperature and concentration. The only other thermolysis products were hydrocarbons. Aliquots (150 μL) of the remaining stock solution were placed in 5 mm × 100 mm base-washed Pyrex tubes (capped with serum caps, thoroughly flushed with dry nitrogen, and precooled to −78 °C). The samples were pyrolyzed at the appropriate temperature until completely decolorized, cooled to −78 °C, and analyzed by VPC with a precooled syringe. Assignment of the product peaks was carried out by coinjection techniques using authentic samples. Relative retention times for *N*-(2,2,6,6-tetramethylpiperidyl)nitrene decomposition products are (Carbowax 400, 25 °C) as follows: 1,1,3-trimethylcyclohexane (**10**) (1.0), 1,1,3,3-tetramethylcyclopentane (**7**) (1.06), 2,6-dimethyl-1-heptene (**8**) (1.28), and 2,6-dimethyl-2-heptene (**9**) (1.41). Typical yields were 20–30%. Relative retention times for *N*-(2,2,5,5-tetramethylpyrrolidyl)nitrene decomposition products are (Carbowax 400, 25 °C) as follows: 2-methylpropene (**14**) (1.0), 1,1,2,2-tetramethylcyclobutane (**13**) (3.0), 2,5-dimethyl-1-hexene (**15**) (4.71), and 2,5-dimethyl-2-hexene (**16**) (4.85). Typical yields were 20–30%. The 1,2-diazene **19** was shown to be absent (<1%) by comparison with authentic **19** (SF-96, 110 °C).

Registry No. 4, 66337-86-8; **5**, 73331-62-1; **6**, 6130-92-3; **7**, 52688-89-8; **8**, 3074-78-0; **9**, 5557-98-2; **10**, 3073-66-3; **11**, 42053-22-5; **12**, 73331-61-0; **13**, 52897-98-0; **14**, 115-11-7; **15**, 6975-92-4; **16**, 3404-78-2; **17**, 73331-63-2; **19**, 19403-24-8; **23**, 6130-93-4; **24**, 4567-13-9; 2,2,6,6-tetramethylpiperidine, 768-66-1; 2,2,5,5-tetramethylpyrrolidine HCl, 4567-23-1.

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