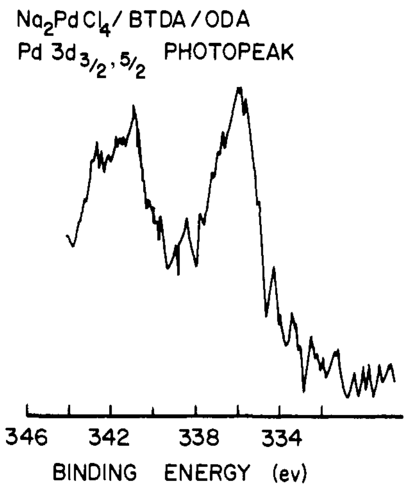

Figure 1. X-ray photoelectron spectrum (Pd $3d_{3/2,5/2}$) of Na_2PdCl_4 containing polyimide film.

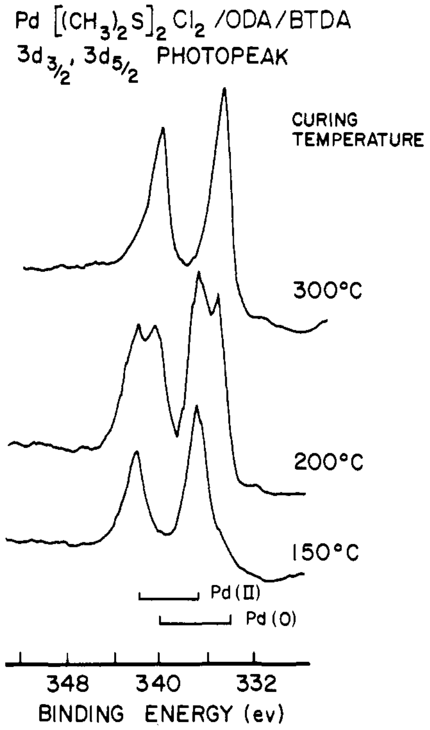

Figure 2. X-ray photoelectron spectrum (Pd $3d_{3/2,5/2}$) of $Pd[S(CH_3)_2]_2Cl_2$ containing polyimide film after curing at various temperatures.

sistivity of Li_2PdCl_4 containing films. After 3-h curing, the XPS spectrum clearly shows evidence for Pd(II) and Pd(0) on the surface. In other words for the higher palladium content complete reduction is not accomplished. Longer heating periods result in more complete reduction but with some polymer degradation.

We have attempted to determine the temperature at which metal reduction takes place within the polyimide-metal complex matrix. We have determined, using infrared spectroscopy, that the BTDA-ODA-polyamic acid "cures" to the polyimide at temperatures below 200 °C. Several samples containing palladium salts which had been "cured" at various temperatures were examined by XPS to determine the oxidation state of the metal. These results clearly indicate that metal reduction takes place above 200 °C in the case of Li_2PdCl_4, and at a somewhat lower temperature in the case of $Pd[S(CH_3)_2]_2Cl_2$ (Figure 2) and apparently has no connection with polyimide formation.

The results described in this preliminary report are unique for palladium at this point. Extension of this study to highly soluble platinum, silver, and gold coordination complexes has not resulted in highly conducting films even though X-ray PES data suggest that reduction to the elemental state has occurred during the curing process. The metal specificity described here regarding the modificiation of polymer film conductivity is reminiscent of the aluminum ion specific enhancement of high temperature adhesive properties of certain polyimides.[11] Certainly other polymer properties should be modifiable with the right choice of metal ion.

Acknowledgment. We thank J. Schaaf and T. Wohlford for technical assistance.

References and Notes

(1) M. M. Labes, P. Love, and T. F. Nicols, *Chem. Rev.*, **79**, 1 (1979).
(2) C. K. Chiang, M. A. Druy, S. C. Gau, A. J. Heeger, E. J. Louis, A. G. MacDiarmid, Y. W. Park, and H. Shirakawa, *J. Am. Chem. Soc.*, **100**, 1013 (1978).
(3) D. M. Ivory, G. G. Miller, J. M. Sowa, L. W. Shacklette, R. R. Chance, and R. H. Baughman, *J. Chem. Phys.*, **71**, 1506 (1979).
(4) D. M. Diggs, *Polym. Eng. Sci.*, 17, 842 (1977).
(5) S. M. Aharoni and A. J. Signorelli, *J. Appl. Polym. Sci.*, **23**, 2653 (1979).
(6) O. Sumita, A. Fukuda, and E. Kuge, *J. Appl. Polym. Sci.*, **23**, 2279 (1979).
(7) M. J. Hannon and K. F. Wissbrun, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 113 (1975).
(8) F. Higashi, C. Su Cho, H. Kakinoki, and O. Sumita, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 2303 (1977).
(9) R. J. Angelo and E. I. du Pont de Nemours & Co., U.S. Patent 3 073 785 (1959).
(10) M. N. Sarboluki, *NASA Tech. Brief*, **3** (2), 36 (1978).
(11) L. T. Taylor, A. K. St. Clair, V. C. Carver, and T. A. Furtsch, *Adv. Chem. Ser.*, in press.
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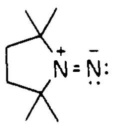
Synthesis and Direct Spectroscopic Observation of *N*-(2,2,5,5-Tetramethylpyrrolidyl)nitrene. Comparison of Five- and Six-Membered Cyclic 1,1-Dialkyldiazenes

Sir:

We report the synthesis, infrared and electronic spectra, and the kinetics of the thermal decomposition of *N*-(2,2,5,5-tetramethylpyrrolidyl)nitrene (**1**). Because the six-membered ring 1,1-diazene **2** has been characterized,[1] these results allow some estimate of the importance of structure on the spectral properties and kinetic behavior of 1,1-dialkyldiazenes.[2] In addition, the first approximate heat of formation of a 1,1-diazene from experiment is provided.



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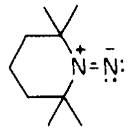

2

Addition of *tert*-butyl hypochlorite (*t*-BuOCl)[3] to a stirred solution of 1-amino-2,2,5,5-tetramethylpyrrolidine (**3**)[4] and triethylamine (Et_3N) in anhydrous diethyl ether at −78 °C

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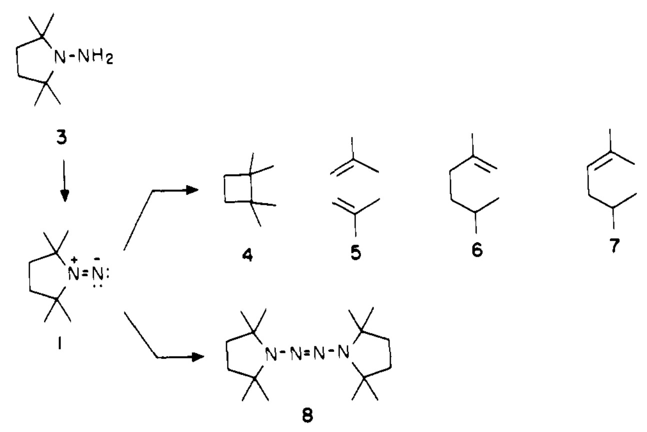
Scheme I



affords, in addition to an insoluble white precipitate (Et_3NHCl), a red solution which is stable for days at −78 °C but decolorizes rapidly at 0 °C, affording hydrocarbon products **4**–**7** and the tetrazene **8**[6] (Scheme I).

Generation of this colored solution at −78 °C followed by filtration at −78 °C gives a clear red solution. This can be further purified by low temperature chromatography (−81 °C) on basic alumina.[8]

Low temperature absorption spectroscopy[9] in the visible region on this solution at −78 °C reveals a structured absorption band with λ_{max} (CH_2Cl_2) at 497 nm, presumably the n-π^* electronic transition. Consistent with this n-π^* assignment, replacement of CH_2Cl_2 with isopropyl alcohol affords a λ_{max} (*i*-PrOH) of 487 nm, a shift of 10 nm to shorter wavelength[11] (Figure 1).

The infrared spectrum (−78 °C) shows a strong absorption at 1638 cm^{-1}, that disappears on warming to 25 °C.[9] This is assigned to the N=N double-bond stretching frequency.[13] To check this assignment, application of Hooke's law allows an approximation of the stretching frequency change for the appropriate $^{14}N{=}^{15}N$ isotopically labeled isomer.[15] The calculated $\nu(^{14}N{=}^{14}N)/\nu(^{14}N{=}^{15}N)$ ratio is 1.0171 or a predicted shift to 1611 cm^{-1}. Synthesis of the corresponding $R_2{}^{14}N{=}^{15}N$ species[16] 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 2).

The chromatographed solution[8] was concentrated (2×10^{-2} M) at low temperature (−78 °C) and inspected by ^1H NMR ($CDCl_3$) revealing absorptions at δ 1.05 and 2.32 which integrate in a 3:1 ratio. Warming this sample results in the disappearance of the 1.04 and 2.32 signals, presumably the 1,1-diazene **1**,[18] while tetrazene signals and absorptions in the region where the C_8 hydrocarbons appear are observed. These NMR results indicate that under some conditions ($\sim 10^{-2}$ M) the unimolecular and bimolecular processes in Scheme I are competitive.

The decay kinetics of **1** were studied in more dilute solution ($\leq 3 \times 10^{-3}$ M) in three different solvents (*n*-hexane, ethyl ether, and tetrahydrofuran), typically in the range of +4 to −21.6 °C by monitoring the optical density of the red solution at 497 nm as a function of time.[9] In dilute solution ($\leq 3 \times 10^{-3}$ M) the disappearance of **1** was strictly first order in Et_2O and THF. In hexane the disappearance of **1** was first order at higher temperatures (−4.8 to −9.0 °C) becoming a combination of first- and higher-order kinetics as the temperature was lowered (−12.8 to −21.4 °C). Plots of ln Abs vs. time at these 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.[1b] The activation parameters are shown in Table I.

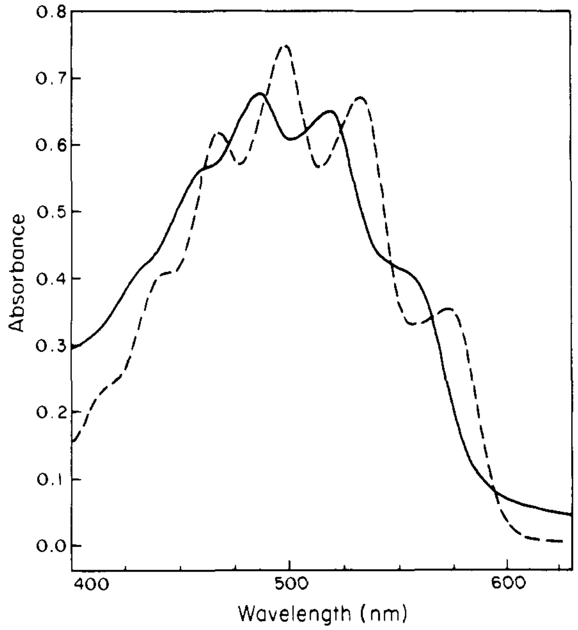


Figure 1. Absorption spectroscopy in CH_2Cl_2: λ_{max} 497 nm (---); in *i*-PrOH, λ_{max} 487 nm (—).

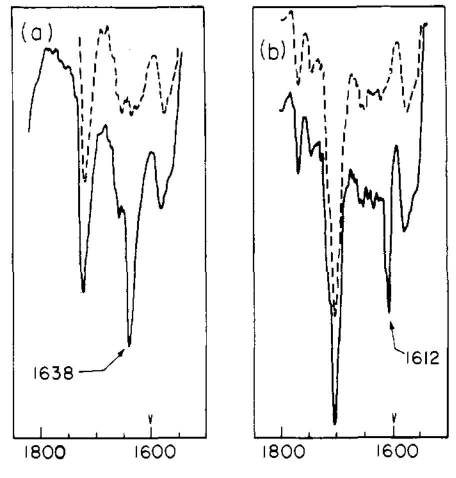


Figure 2. Infrared spectra of (a) $R_2{}^{14}N{=}^{14}N$ and (b) $R_2{}^{14}N{=}^{15}N$ at −78 °C (—) and at −78 °C after warming to 25 °C (---).

We find the rate of decomposition of **1** is sensitive to solvent, the rate increasing with decreasing solvent polarity, k_{rel} = 5.1, 2.4, and 1.0 for *n*-hexane (E_T = 30.9), ethyl ether (E_T = 34.6), and tetrahydrofuran (E_T = 37.4), respectively. The observed rate dependence on solvent polarity is consistent with a polar ground state decomposing by a less polar transition state.

Comparison of the five- and six-membered cyclic 1,1-dialkyldiazenes[1] is shown in Table II. The change from a six-

Table I

solvent	log *A*	E_a, kcal/mol
n-hexane	10.9 ± 0.3	16.8 ± 0.5
ethyl ether	12.4 ± 0.4	19.0 ± 0.6
tetrahydrofuran	12.1 ± 0.3	19.1 ± 0.4

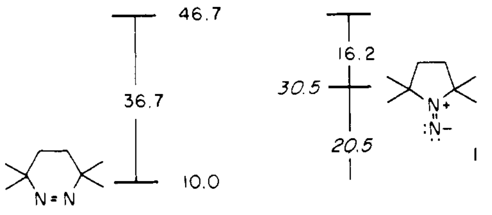
Table II

compd	λ_{max} (CH_2Cl_2), nm	$\nu(^{14}N{=}^{14}N)$, cm^{-1}	log A^a	E_a, kcal/mol^a
1	497	1638	12.4	19.0
2	541^b	1595^b	13.7^c	20.0^c

^{a} In Et_2O. ^{b} Reference 1. ^{c} Reference 19.

membered to a five-membered cyclic 1,1-diazene causes (a) a shift to higher energy for the n-π* transition and a shift to higher wavenumber (cm^{-1}) for the N=N stretching frequency, not unlike that of the isoelectronic counterparts, cyclohexanone → cyclopentanone[19] and (b) similar E_a values for thermal fragmentation. Assuming similar mechanisms are operating in the decomposition of **1** and **2**, we would conclude that the difference in strain energies of these five- and six-membered cyclic 1,1-dialkyldiazenes is small, unlike five- and six-membered cyclic 1,2-diazenes.[20]

Finally, the heat of formation ($\Delta H_f = 10.0 \pm 0.6$ kcal/mol) and the enthalpy of activation ($\Delta H^{\ddagger} = 36.7 \pm 0.5$ kcal/mol) for decomposition of 3,3,6,6-tetramethyltetrahydropyridazine (**9**) are known.[20] The sum of these two values affords a value of 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 **1** and **9**, subtraction of the enthalpy of activation for the decomposition of **1** ($\Delta H^{\ddagger} = 16.2$ kcal/mol, in hexane) affords the first approximate value for the ΔH_f of a 1,1-dialkyldiazene; i.e., $\Delta H_f(\mathbf{1}) = 30.5$ kcal/mol. This value would indicate the 1,1-diazene **1** has a higher heat of formation than the cis 1,2 isomer **9** by 20 kcal/mol.[21]



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References and Notes

(1) (a) Hinsberg, W. D., III; Dervan, P. B. *J. Am. Chem. Soc.* **1978**, *100*, 1608. (b) *Ibid.* **1979**, *101*, 6142.

(2) 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.

(3) Baldwin, J. E.; Brown, J. E.; Hofle, G. *J. Am. Chem. Soc.* **1971**, 93, 788.

(4) Successive treatment of 2,2,5,5-tetramethylpyrrolidine[5] with $NaNO_2$ and lithium aluminum hydride[17] afforded 1-amino-2,2,5,5-tetramethylpyrrolidine (**3**).

(5) For synthesis of 2,2,5,5-tetramethylpyrrolidine see Lunt, E. (May Baker Ltd., Dagenham, Engl.) *Proc. Int. Symp. Nitro Compounds, 1963* **1964**, 291–315.

(6) Hydrocarbons **4–7** are observed in a ratio of 32:31.3:2.3:1, respectively.[7] Tetrazene **8** was isolated and characterized.

(7) Hydrocarbon products were analyzed by analytical VPC (DBT, 60 °C) and compared with authentic samples.

(8) Chromatography on deactivated basic aluminum at −81 °C using dimethyl ether-propane as solvent removed the *tert*-butyl alcohol and unreacted 1-amino-2,2,5,5-tetramethylpyrrolidine resulting in 1,1-diazene with ≤5% tetrazene impurity. Because the 1,1-diazene is sensitive to trace acid, it is important to add triethylamine to the chromatographed solution.

(9) The red solution is introduced via Teflon tubing connected to sample injection ports into a specially designed copper-jacketed quartz cell attached to a cryogenic system[10] maintained at −78 °C.

(10) Air Products Laboratory cryogenic system, Model LC-1-100 liquid nitrogen Dewar assembly, Model WMX-1A optical shroud with injector parts.

(11) Analogous to the solvent effects on the n-π* transition of the carbonyl group.[12]

(12) Calvert, J. G., Pitts, J. N. "Photochemistry"; Wiley: New York, 1966; p 257.

(13) 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 μ) region of the Raman spectrum.[14]

(14) Silverstein, R. M.; Bassler, G. C. "Spectrometric Identification of Organic Compounds"; Wiley: New York, 1967; p 99.

(15) Reference 14, p 66.

(16) Successive treatment of 2,2,5,5-tetramethylpyrrolidine with $Na^{15}NO_2$ (Prochemicals Limited, N.J.), lithium aluminum hydride,[17] and *tert*-BuOCl-Et_3N afforded the ^{15}N-labeled 1,1-diazene **1**.

(17) Roberts, J. R.; Ingold, K. U. *J. Am. Chem. Soc.* **1973**, *95*, 3228.

(18) From the NMR experiment (EM-390), we measured the concentration of **1** against an internal standert (CH_2Cl_2). From this we calculate the extinction coefficient for the n-π* transition of **1**, ε ~20 ± 3.

(19) 2,2,6,6-Tetramethylcyclohexanone: λ_{max} (Et_2O) 305 nm, IR 1690 cm^{-1} (C=O stretch). 2,2,5,5-Tetramethylcyclopentanone: λ_{max} (Et_2O) 296 nm, IR 1730 cm^{-1} (C=O stretch).

(20) Engel, P. S. *J. Am. Chem. Soc.* **1976**, *98*, 1972. Engel, P. S.; Hayes, R. A.; Keifer, L.; Szilagyi, S.; Timberlake, J. W. *Ibid.* **1978**, *100*, 1876, and references cited there.

(21) The 1,2-diazene **9** is not found in the products in the thermal decomposition of the 1,1 isomer **1**.

(22) Alfred P. Sloan Research Fellow, 1977–1979; Camille and Henry Dreyfus Teacher-Scholar, 1978–1983.

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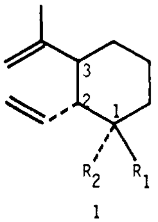
Stereochemical Course of the Cope-Claisen Rearrangement of the Stereoisomeric 2-Vinyl-3-isopropenylcyclohexylvinyl Ethers. A System Having $\Delta G^{\ddagger}_{\text{Claisen}} \gg \Delta G^{\ddagger}_{\text{Cope}}$

Sir:

We have previously demonstrated that the Cope-Claisen rearrangement provides a useful method for driving unfavorable Cope rearrangement equilibria by means of an irreversible Claisen rearrangement.[1] With an interest in constructing chiral germacrane compounds from chiral carvone derivatives, we have investigated the fate of the four diastereomeric vinyl ethers **1a** (TT), **1b** (CT), **2a** (TC), and **2b** (CC)[2] when subjected to thermolysis.



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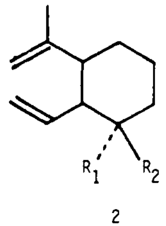
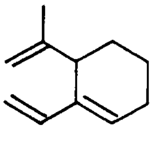


2

a, $R_1 = OCH{=}CH_2$, $R_2 = H$
b, $R_1 = H$, $R_2 = OCH{=}CH_2$



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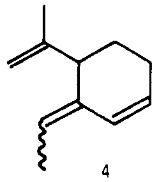

4

Vinyl ethers[3] **1a** (TT) and **1b** (CT) were prepared as outlined in Scheme I, while the preparation of isomer **2a** (TC) has been previously described.[1]

Thermolysis at 312 °C (evacuated sealed tube) of isomers **1** bearing trans-vinylic groups (Table I, entries 1 and 2) provided a nearly identical distribution of products consisting of (*Z,Z*)-8-methyl-2,7-cyclodecadiene-1-acetaldehyde (**10**),[1] a mixture of four major olefins, and an inseparable mixture of two aldehydes, which were shown by 270-MHz NMR not to be any of the geometric endocyclic isomers of **10**. The mass spectra (GC-MS) of the four olefins displayed parent ions (M^+ 148) in agreement with the loss of acetaldehyde from the parent compounds. The 270-MHz NMR spectrum of two of these olefins permitted them to be assigned structures **3** and **4**. In contrast to the isomers **1a** (TT) and **1b** (CT), the product ratio of **10**:(**5** + olefins) is significantly higher as is the absolute

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