SYNTHESIS AND CHARACTERIZATION OF 1,1-DI-*TERT*-BUTYLDIAZENE

Thesis by

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To My Parents

and to Sue

Acknowledgements

I would like to thank my research advisor, Peter Dervan, for his enthusiasm and support throughout this work. I would also like to thank the members of the Dervan group for contributing to a friendly, cohesive atmosphere which isn't always found in a research group. This especially applies to Dan Duan and Mark Mitchell whom I've had the pleasure of knowing from start to finish. Special thanks go to Bill Hinsberg for all his help in my first year here and for laying the ground work in the study of persistent 1,1-diazenes. I am indebted to Jan Owen and Debbie Chester for getting this thesis typed during a busy time. Thanks also go to the staff of the Caltech Chemistry Department for their frequent assistance. Bill Croasmun's conscientious efforts in obtaining 500 MHz spectra at -120°C are greatly appreciated. Financial support of this research from the National Science Foundation is also acknowledged. Final thanks go to Sue for her love and support which made it all easier.

Abstract

The synthesis and direct observation of 1,1-di-tert-butyldiazene (**16**) at -127°C is described. The absorption spectrum of a red solution of 1,1-diazene **16** reveals a structured absorption band with λ_{max} at 506 nm (Me_2O, -125°C). The vibrational spacing in S_1 is about 1200 cm^{-1}. The excited state of **16** emits weakly with a single maximum at 715 nm observed in the fluorescence spectrum (Me_2O:CD_2Cl_2, -196°C). The proton NMR spectrum of **16** occurs as a singlet at 1.41 ppm. Monitoring this NMR absorption at $-94^0 \pm 2$°C shows that 1,1-diazene **16** decomposes with a first-order rate of 1.8×10^{-3} sec^{-1} to form isobutane, isobutylene and hexamethylethane. This rate is 10^8 and 10^{34} times faster than the thermal decomposition of the corresponding cis and trans 1,2-di-tert-butyldiazene isomers. The free energy of activation for decomposition of 1,1-diazene **16** is found to be 12.5 $\pm$ 0.2 kcal/mol at -94°C which is much lower than the values of 19.1 and 19.4 kcal/lmole calculated at -94°C for N-(2,2,6,6-tetramethylpiperidyl)nitrene (**3**) and N-(2,2,5,5-tetramethylpyrrolidyl)nitrene (**4**), respectively. This difference between **16** and the cyclic-1,1-diazenes **3** and **4** can be attributed to a large steric interaction between the tert-butyl groups in 1,1-diazene **16**.

In order to investigate the nature of the singlet-triplet gap in 1,1-diazenes, 2,5-di-tert-butyl-N-pyrrolynitrene (**22**) was generated but was found to be too reactive towards dimerization to be persistent. In the presence of dimethylsulfoxide, however, N-pyrrolynitrene (**22**) can be trapped as N-(2,5-di-tert-butyl-N'-pyrrolyl)dimethylsulfoximine (**38**). N-(2,5-di-tert-

butyl-N'-pyrrolyl)-d^6-dimethylsulfoximine (**38**-d^6) exchanges with free dimethylsulfoxide at 50°C in solution, presumably by generation and retrapping of pyrrolylnitrene **22**.

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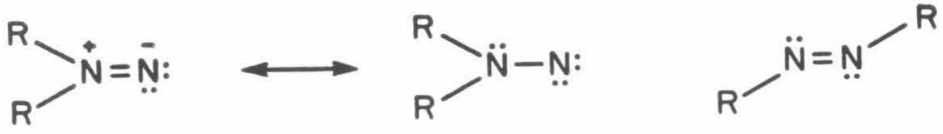
INTRODUCTION

1,1-Diazenes (aminonitrenes, N-nitrenes) **1**,[1] unlike their more stable 1,2-diazene isomers (azo compounds) **2**,[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.[1] The 1,1-diazene can be represented



1a **1b** **2**

by two different resonance structures, **1a** and **1b**, and the relative importance of each is dependent on the substituents R. 1,1-Dialkyldiazenes, best represented by structure **1a**, are isoelectronic to ketones. However, when the internal nitrogen lone pair is delocalized onto the substituents the diazene is less able to form the dipolar resonance structure **1a** and is more correctly described by structure **1b**. Such electron deficient 1,1-diazenes should exhibit nitrene-like behavior.

Theoretical Studies

The nature of the bonding and the relative energies of the states for the parent 1,1-diazene (H_2N-N) have been the subject of several theoretical studies.[3] Recent GVB-CI calculations by Davis and Goddard[3e] indicate that structure **1** is an accurate picture for the ground state. The electron configurations for the three lowest

valence states are shown in Figure 1 with the calculated relative energies.

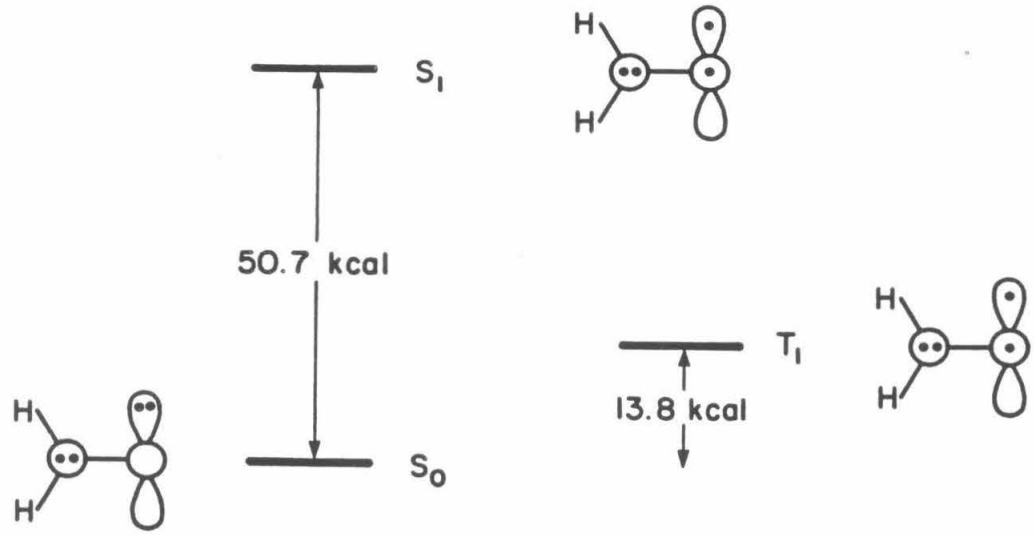


Figure 1. GVB-CI calculations[3e] for H_2N-N.

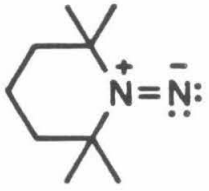
The singlet ground state (S_0) is planar with a large degree of delocalization of the internal nitrogen lone pair onto the terminal nitrogen. The GVB π orbitals are similar to those for a double bond and the calculated N-N bond length of 1.25 Å is equal to the value observed for diimide. The calculated dipole moment of 4.0 D also indicates substantial double bond character.

The S_1 and T_1 states have electron configuration similar to the lowest singlet and triplet states of nitrene (H-N). Interaction of the amino nitrogen lone pair with the nitrene π electron is equivalent in both spin states so the 37 kcal separation corresponds to the singlet-triplet gap for nitrene. The S_1 excited state can be reached by a $n \rightarrow \pi^*$ transition from S_0. A visible absorption near 560 nm is predicted from the energy spacing between these states. The most

favorable geometry for both the S_1 and T_1 states is pyramidal due to antibonding character in the π bond.

Persistent Cyclic 1,1-Diazenes.

Direct experimental studies of the 1,1-diazene functional group became available recently with the preparation, by Hinsberg, Schultz and Dervan, of the persistent cyclic 1,1-diazenes 3[4] and 4[5]. Both molecules



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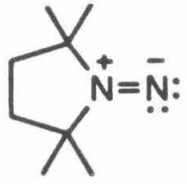

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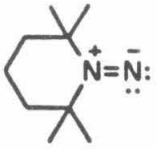
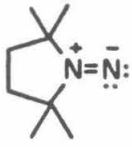
are made from oxidation of the corresponding N-amino compounds by tert-butyl hypochlorite at -78°C. These diazenes owe their persistance to their synthesis at low temperature where the loss of nitrogen does not occur and to their steric bulk which retards dimerization to form 2-tetrazenes.

As expected from the theoretical studies, 1,1-diazenes 3 and 4 are colored compounds giving purple and red solutions, respectively. Absorption and emission spectra are shown in Figures 2 and 3.[6] The absorptions are $n \rightarrow \pi^*$ transitions which show a blue shift in isopropanol and have an extinction coefficient of 20. The emission occurs from S_1 with a fluorescence quantum yield of 7×10^{-3}.[7] The lifetime of the excited state S_1 is about 23 nanoseconds with internal conversion being the primary mode of decay.[7]

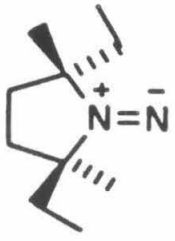
Infrared absorptions are observed at 1595 cm^{-1} for the 6 membered ring diazene and at 1638 cm^{-1} for the 5 membered ring.[6] These absorptions were characterized as the N=N stretch by measuring the shift produced when the diazene is labeled with ^{15}N at the terminal nitrogen. The similarity of these values to the 1576 cm^{-1} Raman active N-N stretch observed for trans 1,2-diazenes further stresses that the 1,1-diazene contains a large amount of double bond character.

	electronic (nm)		infrared (cm^{-1})	
	$\lambda_{max}(CH_2Cl_2)$	$\lambda_{max}(iPrOH)$	$^{14}N{=}^{14}N$	$^{14}N{=}^{15}N$
	543	526	1595	1568
	497	487	1638	1612

Warming the 1,1-diazene solutions to 0°C leads to the decomposition products shown in Figure 4.[6] Bimolecular decomposition (k_2) is a low A-low E_a process (E_a=6.4±0.9 kcal/mole and Log A=3.8±0.7 for dimerization of **3**) which predominates at temperatures below -30°C. At higher temperatures the unimolecular loss of nitrogen becomes dominant. The Arrhenius parameters determined for the unimolecular 1,1-diazene decompositions in ether are E_a = 20.0 ± 0.4 kcal/mol and log A = 13.7 ± 0.3 for 1,1,-diazene **3** and E_a = 19.0 ± 0.6 kcal/mol and log A = 12.4 ± 0.4, for 1,1-diazene **4**.

The direct and triplet sensitized photolyses of **4** yield tetrazene **14** and the four hydrocarbons **10-13** in 4:1 and 9:1 ratios,

respectively.[8] A spin correlation effect is observed for the hydrocarbon products resulting from direct and triplet sensitized decomposition of d,l-**15**.[7]



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In addition, the 1,1-diazenes **3** and **4** have been studied by ^{1}H, ^{13}C and ^{15}N NMR spectroscopy.[6,9,10]

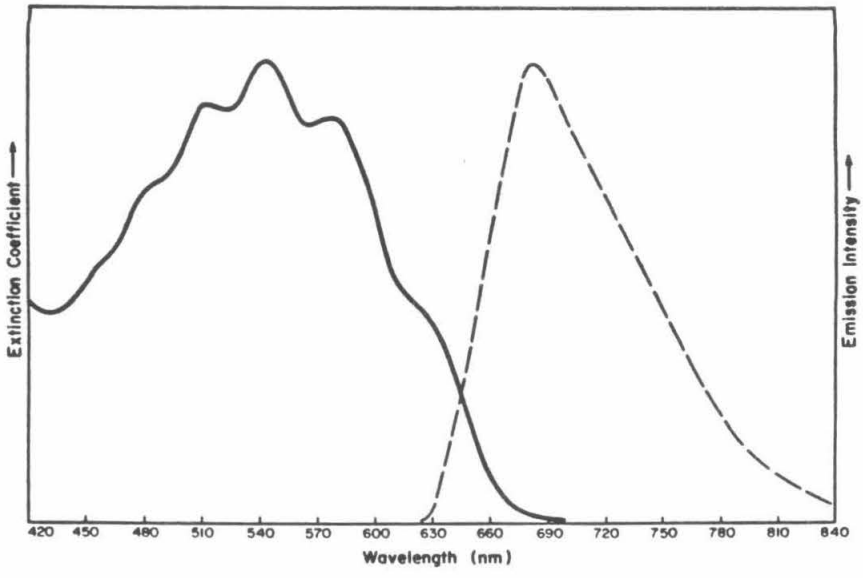

Figure 2. Absorption (——) and fluorescence (- - -) spectra of **3** in $CFCl_3$ at -78°C and -196°C, respectively.[7]

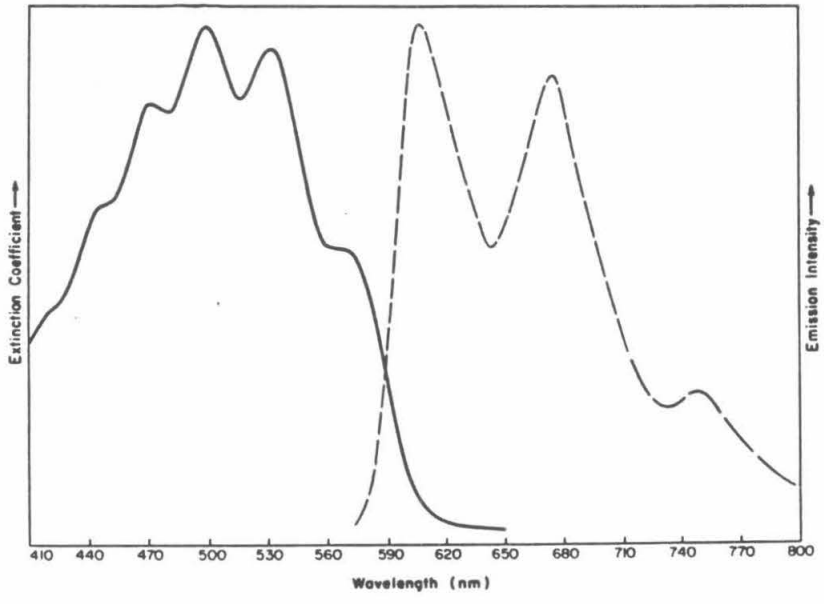

Figure 3. Absorption (——) and fluorescence (- - -) spectra of **4** in $CFCl_3$ at -78°C and -196°C, respectively.[7]

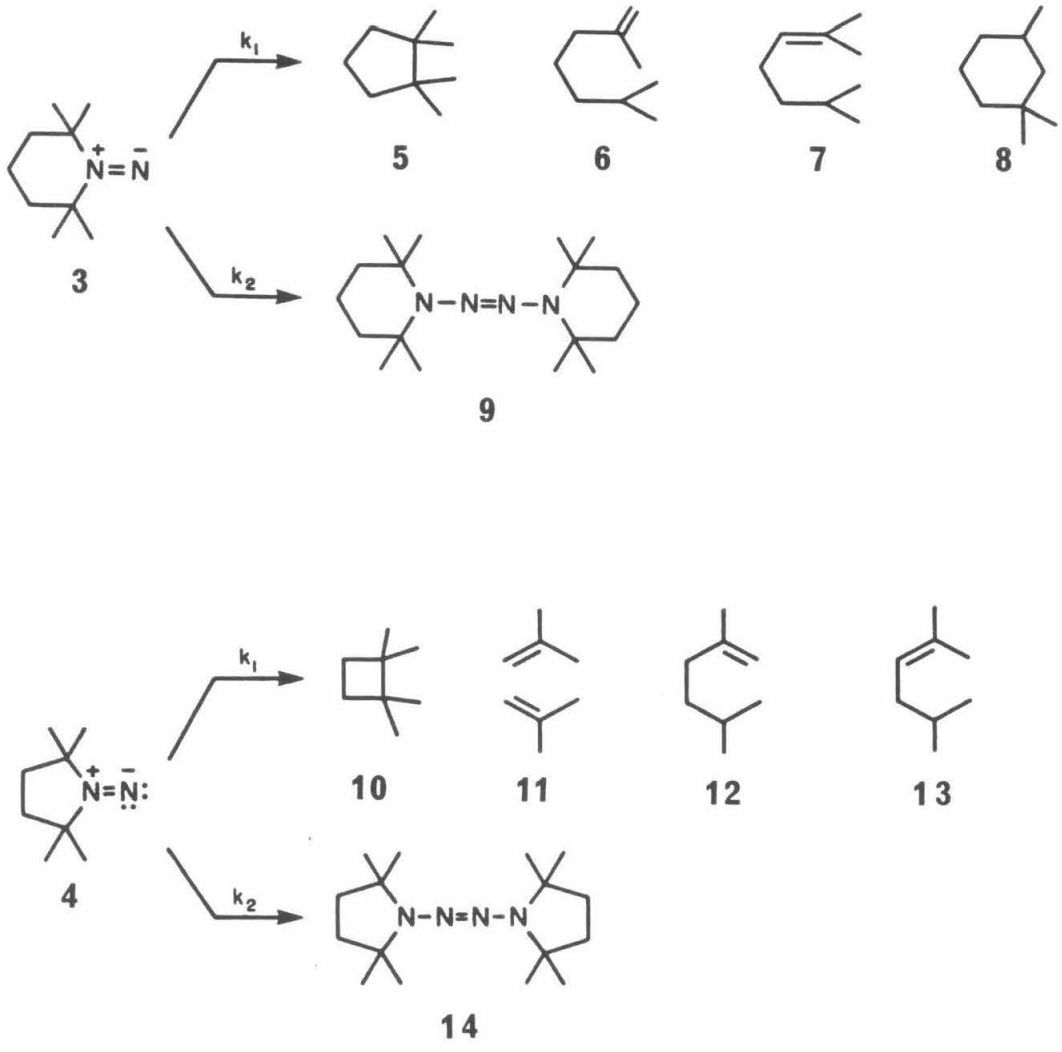

Figure 4. Unimolecular and Bimolecular decomposition products for **3** and **4**.[6]

Acyclic 1,1-Diazenes

Direct observation of an acyclic 1,1-diazene has not been reported. The requirement for steric protection in persistent 1,1-diazenes suggests 1,1-di-tert-butyldiazene **16**, 1,1-di-(1-adamantyl)diazene **17**, and 1,1-di(1-norbornyl)diazene **18** as synthetic targets. These three 1,1-diazenes are an interesting series because of their relationship to the bridgehead substituted 1,2-diazene isomers.[11,12]

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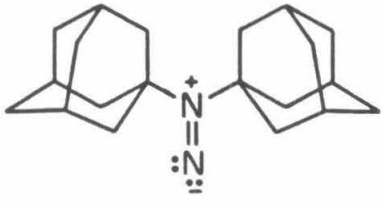

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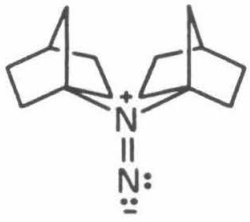

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Bridgehead substitution in trans-1,2-diazenes greatly increases stability towards fragmentation. Relative rates for extrusion of nitrogen from the symmetrical tert-butyl, 1-adamantyl and 1-norbornyl trans-1,2-diazenes are listed in Figure 5.[11] This stabilization effect is also observed in the cis-1,2-diazenes produced by irradiation of the trans isomers.[12]

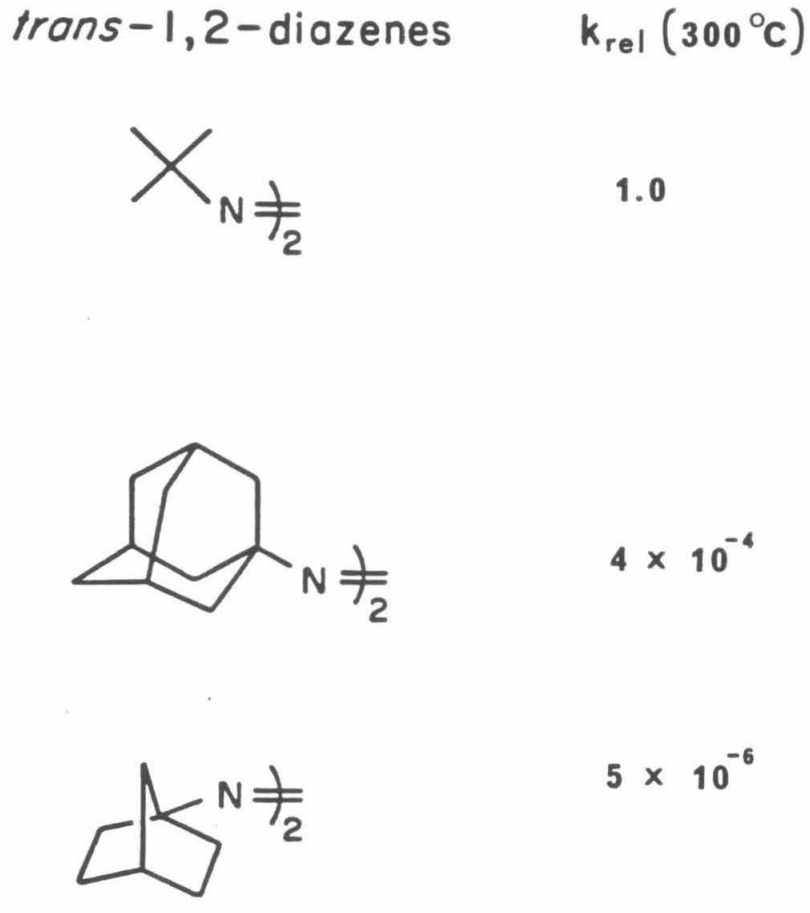


Figure 5. Relative decomposition rates for bridgehead substituted trans 1,2-diazenes.[11]

The steric interaction of the tert-butyl groups becomes quite severe in cis-1,2-di-tert-butyldiazene. The enthalpy of activation for decomposition of the cis isomer is 18.6 kcal/mole[13] compared to 43.1 kcal/mole[14] for the trans isomer. Only part, probably about half, of the 24 kcal of strain energy in cis-1,2-di-tert-butyldiazene comes from the tert-butyl steric interaction with the remainder due to electronic repulsion of the cis- nitrogen lone pairs. The severity of the lone pair interaction in the crowded cis-1,2-tert-butyldiazene is indicated by the λ_{max} at 447 nm which is 4000 cm^{-1} lower in energy than the λ_{max} (380 nm) for cis-1,2-di-isopropyldiazene.[12a]

The bridgehead cis-1,2-diazenes also have large steric interactions between the tertiary groups. Because bridgehead substitution slows down fragmentation, however, isomerization to the trans isomer is competitive with loss of nitrogen for cis-1,2-di-(1-adamantyl)diazene and is the sole decomposition process for cis-1,2-di(1-norbornyl)diazene.[12]

The bridgehead stabilization effect on 1,2-diazenes is apparently not entirely due to the instability of the bridgehead radicals which are formed on decomposition. Several measures of radical stability agree that stability of adamantane-1-yl is nearly normal for a tertiary radical,[15] yet trans-1,2-di(1-adamantyl)diazene decomposes about 3500 times slower than the tert-butyl analog.[11] This peculiarity in the azo decompositions has been attributed to a requirement for planarity in the transition state which is even greater than demanded by the developing radical center.[16,11] It would be interesting to know if 1,1-di(1-adamantyl)diazene **17** is stabilized

in a similar way.

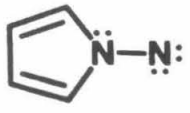
Acyclic 1,1-diazenes containing tertiary substituents are expected to have destabilizing steric interactions as do the cis-1,2-diazenes. Bridgehead substitution, however, should counter the destabilizing steric interaction by increasing C-N bond strengths. A diazene such as 1,1-di(1-norbonyl)diazene (**18**) might even be stable at room temperature if the steric protection is sufficient to prevent dimerization. Chapter 1 of this thesis describes the synthesis and characterization of 1,1-di-tert-butyldiazene (**16**) along with studies directed towards the preparation of 1,1-di(1-adamantyl)diazene (**17**).

The Singlet-Triplet Gap and N-Pyrrolylnitrene

The lowest triplet state (T_1) for 1,1-diazene (H_2N_2) is predicted from theoretical studies to be about 14 kcal/mole higher in energy than the singlet ground state (S_0).[3e] The isoelectronic carbonyl functional group, on the other hand, has a small energy gap between T_1 and the first excited singlet state (S_1) which makes T_1 easily accessible photochemically. Reducing the availability of the amino lone pair for delocalization onto the univalent nitrogen in a 1,1-diazene should destabilize the ground state singlet and could conceivably raise S_0 to be nearly degenerate with or even higher in energy than the lowest triplet state. The triplet state of a properly designed aminonitrene, then, might be accessible as the ground state.

N-pyrrolylnitrene (**19**) has a destabilized singlet state because the amino lone pair is delocalized into a pyrrole ring which has a resonance energy of about 21 kcal/mole.[17] The high energy nature of this molecule relative to 1,1-dialkyl diazenes is evidenced by the

stability of the sulfonylhydrazine sodium salt **20** which is stable at 225°C[18] while the dialkyl sulfonyl hydrazine salts **21** decompose to diazene products at 110°C.[1b]



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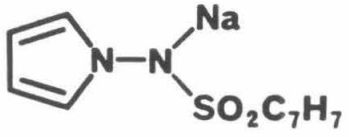

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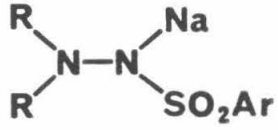

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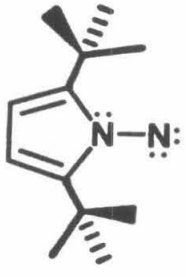
The N-pyrrolylnitrene chosen for this study is 2,5-di-tert-butyl-N-pyrrolylnitrene (**22**). The tert-butyl substituents are designed to provide steric bulk to protect **22** from dimerization in solution and from attack at the reactive α positions of the pyrrole ring. Although some electron deficient 1,1-diazenes have been trapped with olefins and sulfoxides, trapping of a pyrrolylnitrene has never been reported.[1] The generation of **22** and trapping of this species with dimethylsulfoxide is described in Chapter 2.



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RESULTS AND DISCUSSION

Chapter 1

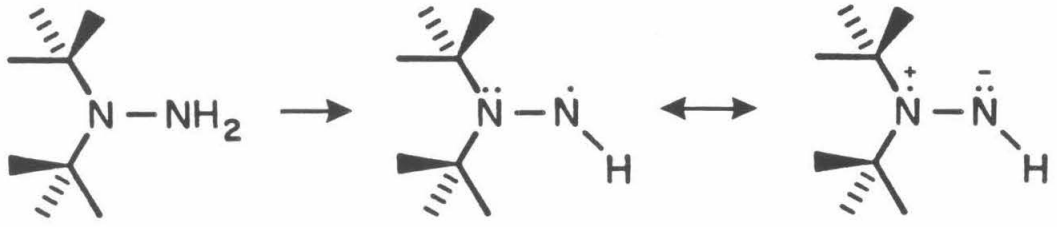
Acyclic 1,1-Diazenes

Synthesis of 1,1-Di-tert-butyldiazene (16).

Synthesis of 1,1-di-tert-butylhydrazine (**24**) is the first step towards generation of 1,1-di-tert-butyldiazene (**16**). The synthesis of 1,1-di-tert-butylnitrosamine (**23**) (Figure 6) is known in the literature although reduction of this compound by standard methods to the hydrazine was reported to be unsuccessful.[19] We find, however, that reduction of 1,1-di-tert-butylnitrosamine (**23**) with sodium in refluxing ethanol under an inert atmosphere produces hydrazine **24** in 55% yield.

23 **24**

Hydrazine **24** is extremely air sensitive and must be purified immediately before use by preparative VPC with collection under an argon atmosphere.[20] We presume that steric interaction between the tert-butyl groups causes this sensitivity to oxygen. Abstraction of a hydrogen atom would afford a stabilized hydrazyl radical **25**, with



24 **25**

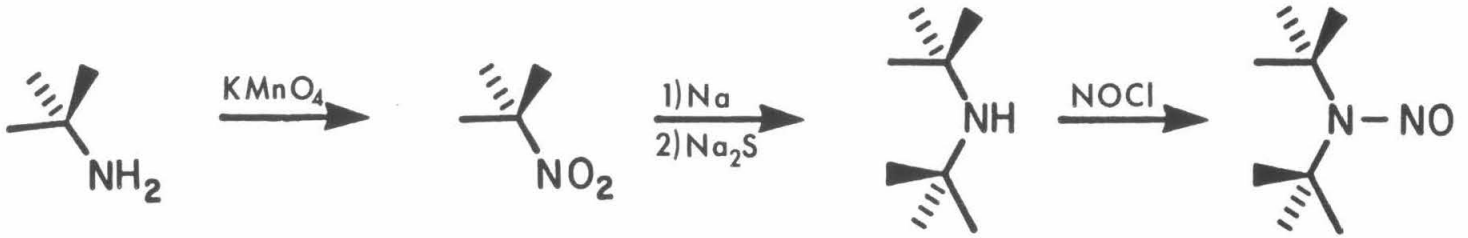
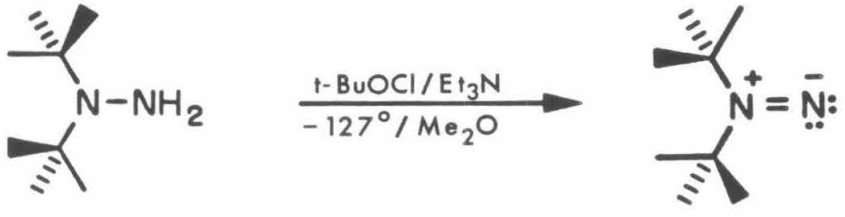


Figure 6. Synthesis of 1,1-Di-<u>tert</u>-butylnitrosamine (**23**).[19]

delocalization to form a 3 electron bond, increasing the angle between the tert-butyl groups. Moreover, relief of steric interaction should also occur when hydrazine **24** is oxidized to the 1,1-diazene **16.**

Addition of tert-butylhypochlorite to a dimethylether solution of 1,1-di-tert-butylhydrazine (**24**) and triethylamine at -78°C produces a white precipitate without the appearance of color indicative of a persistent 1,1-diazene. However, when the oxidation is performed at -127°C using a n-propanol/liquid nitrogen bath a red solution which decolorizes rapidly at -90°C is obtained in addition to the white precipitate. Darker solutions are formed when a precooled solution (-127°C) of tert-butylhypochlorite in chlorotrifluoromethane is added in portions to the rapidly stirred dimethylether solution of 1,1-di-tert-butylhydrazine (**24**) and triethylamine. Filtration of this colored solution at -127°C to remove triethylamine hydrochloride gives a clear red solution of 1,1-diazene **16** for spectroscopic analysis. The bulk of the chlorotrifluoromethane is removed under vacuum to increase the concentration of the solution.



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Electronic Absorption and Emission Spectra of 1,1-Di-tert-butyldiazene (16).

The 1,1-diazene functional group is isoelectronic to a carbonyl and exhibits a n → π^* electronic transition in the visible. The

visible absorption spectrum of 1,1-di-tert-butyldiazene (**16**) in dimethylether was obtained using a low temperature spectroscopic cell kept at -125°C with frequent additions of liquid nitrogen and is shown in Figure 7. The λ_{max} at 506 nm for 1,1-di-tert-butyldiazene (**16**) falls between the λ_{max} of the cyclic diazenes as does the corresponding ketone series shown in Table 1. As expected for a $n \rightarrow \pi^*$ transition where the ground state is more polar than S_1, the use of a more polar solvent, dimethylether: n-propanol (1:1), shifts the spectrum 730 cm^{-1} to higher energy.

The fine structure observed in the absorption spectrum shows vibrational spacings of about 1200 cm^{-1}. This corresponds to the stretching frequency for the nitrogen-nitrogen bond in S_1 which has been weakened by antibonding character. The nitrogen-nitrogen double bond in the ground state of 1,1-di-tert-butyldiazene (**16**) should have a stretching frequency of about 1600 cm^{-1} based on stretching frequencies observed for the cyclic diazenes **3** and **4**.[22]

The excited state of 1,1-di-tert-butyldiazene (**16**) emits weakly at -196°C with a λ_{max} at 715 nm as shown in Figure 8. The width of the emission band is large enough to contain up to three unresolved vibrational spacings of 1600 cm^{-1} for the ground state. The absorption and fluorescence λ_{max} are separated by 209 nm indicating that the equilibrium geometries of S_0 and S_1 states of 1,1-diazene **16** differ substantially.

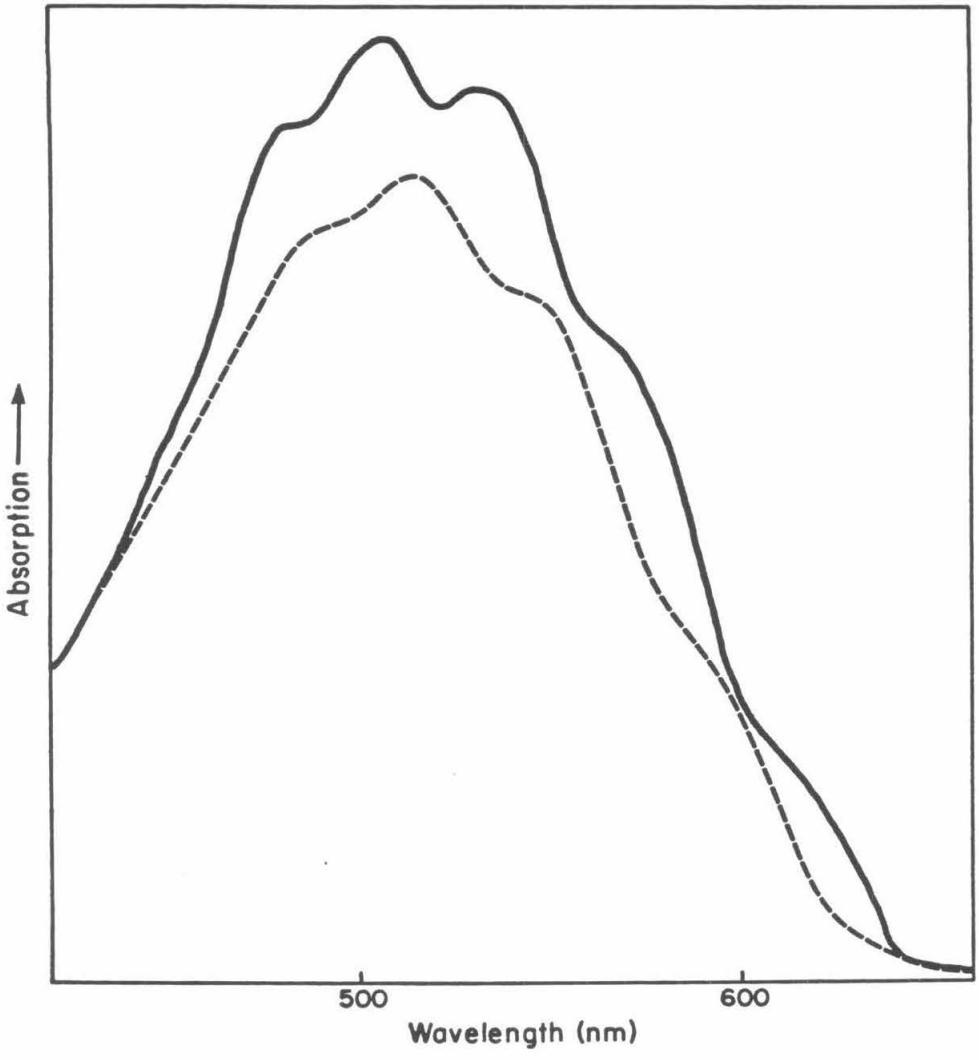


Figure 7. Absorption spectrum of **16** at -125°C in Me_2O (——) and n-PrOH:Me_2O (1:1) (- - -).

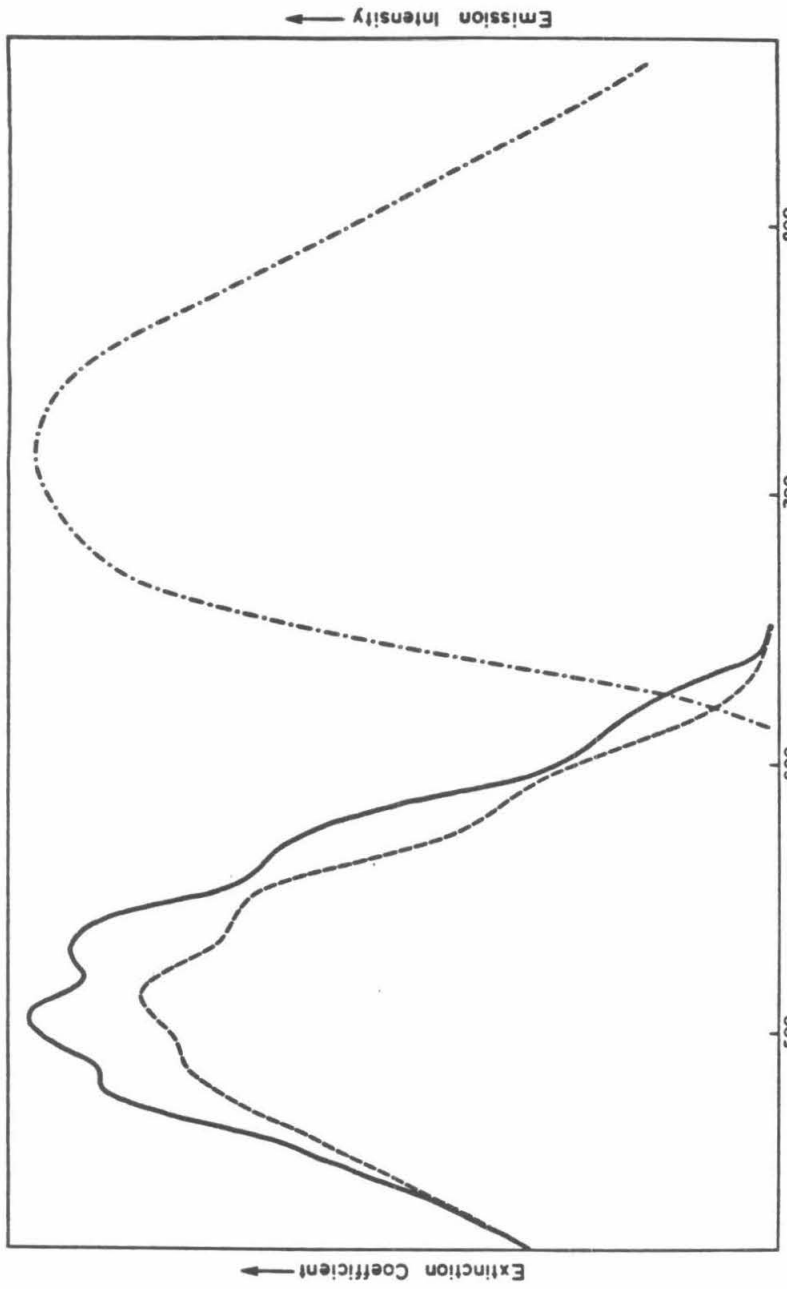
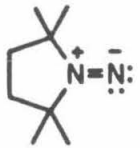
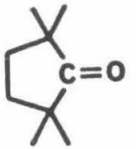
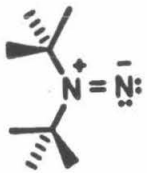
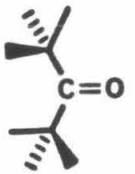
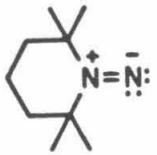
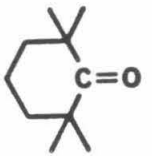


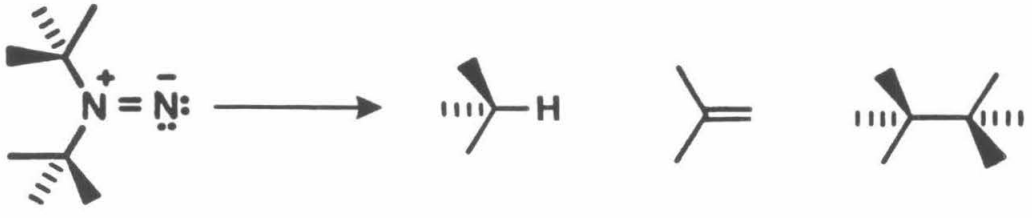
Figure 8. Absorption spectrum of **16** at -125°C in Me_2O (——) and n-PrOH-Me_2O (- - -). Emission spectrum of **16** at 77°K in Me_2O-CD_2Cl_2 glass (-·-·-).

TABLE I. Comparison of Absorption Maxima for 1,1-Diazenes 3, 4, and 16 and Their Corresponding Ketones.

	$\lambda_{max}(Me_2O)$	$E(cm^{-1})$	$E(cm^{-1})$	λ_{max}(hexane)	
	497 nm	20120	33725	296 nm	
	506 nm	19763	33650	297 nm	
	543 nm	18416	32830	305 nm	

Proton NMR Spectroscopy of 1,1-Di-tert-butyldiazene (16).

Proton NMR spectra of 1,1-diazene **16** were obtained at -120°C using dimethylether: deuteriodichloromethane (4:1) as solvent.[23] Separate oxidations produced nearly identical solutions with a representative spectrum shown in Figure 9. The singlet at 1.41 ppm is assigned to 1,1-di-tert-butyldiazene (**16**) and disappears along with the red color when the sample is warmed to -80°C. The remaining absorptions in the spectra are acetone as internal reference (s, 2.1 ppm), isobutylene (s, 1.68), tert-butylchloride (s, 1.58), triethylamine (t, 0.97), isobutane (d, 0.87) and hexamethylethane (s, 0.84). The peak at 1.16 ppm is composed of unreacted hydrazine **24**, tert-butanol and possibly 1,1,4,4-tetra-tert-butyl-2-tetrazene. One of these, probably tert-butanol, shows a temperature dependence for chemical shift which causes the 1.16 ppm absorption to split at -80°C.



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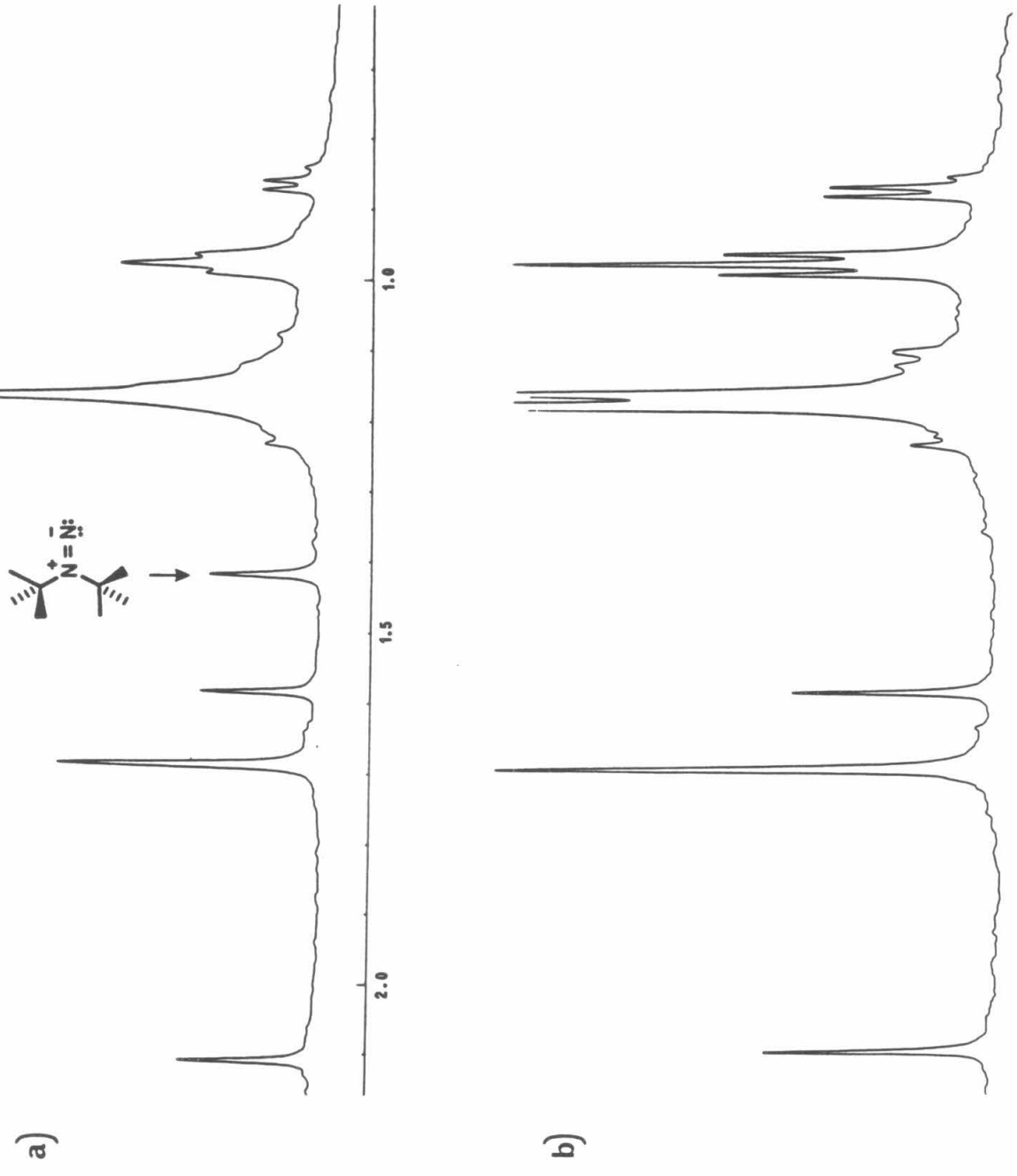
As the 1,1-diazene signal at 1.41 ppm disappears, increases in the hydrocarbon absorptions can be observed by cut and weigh integration. Results for several sets of spectra indicate that the

Figure 9. Low temperature proton NMR spectra a) of a red 1,1-di-tert-butyldiazene (**16**) solution at -120°C and b) after warming the solution at -80°C.


a)
2.0
1.5
1.0
b)

increases in the three hydrocarbon products account for the amount of diazene decomposed and that isobutylene and isobutane are formed in a ratio of approximately 1:1. The tert-butylchloride and large amount of isobutylene present in the -120°C spectra apparently arise by a pathway other than 1,1-diazene decomposition and will be discussed later.

Decomposition Kinetics of 1,1-Di-tert-butyldiazene (16).

The decay kinetics of 1,1-diazene **16** were studied by monitoring the disappearance of its NMR absorption at four temperatures between -94°C and -107°C (Figure 10). The samples used for kinetics were the same as those described for NMR spectroscopy. Since only one of the four temperatures falls on the methanol temperature calibration curve[24], temperature calibration was a problem. Calibration of the 10°C range above -94°C was assumed to hold for the region -94°C to -105°C and error in temperature measurement was estimated to be within ±2°C.[25]

Disappearance of 1,1-diazene **16** is first order with no evidence of curvature through as many as four halflives in the plots of ln A versus time shown in Figure 11. The rates for each temperature are listed in Table 2 and were determined by least squares analysis. Free energy of activation ($\Delta G^{\ddagger}$) was calculated for each temperature,[26] but the errors involved do not permit accurate determination of the Arrhenius parameters. An E_a of 9.7 ±4.3 kcal/mol[27] and a log A of 9.1 ± 5.5 are obtained from least squares analysis of the ln k versus 1/T plot for the four rates.[28]

Since the activation parameters for the 1,2-diazene isomers are

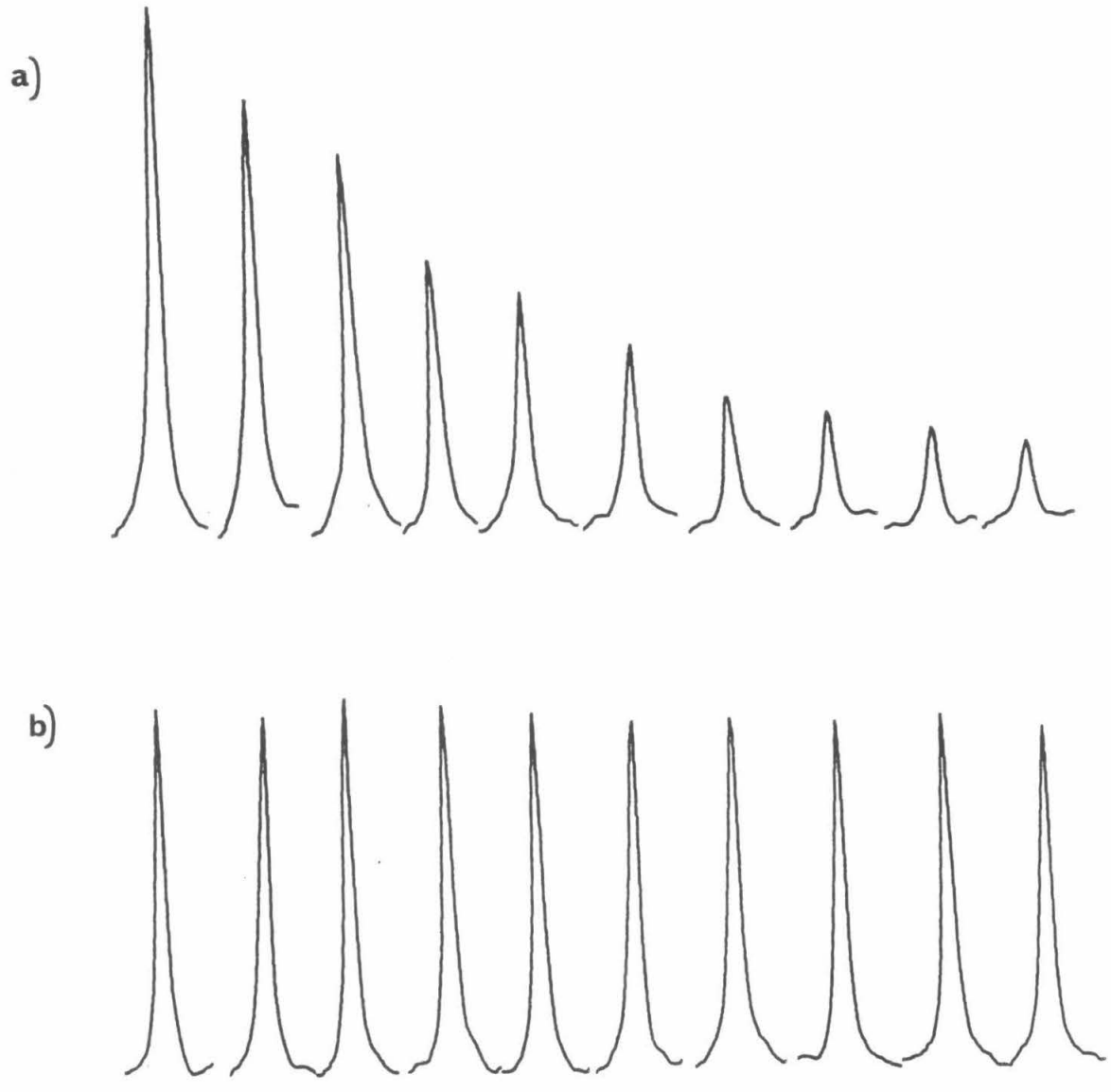


Figure 10. Proton NMR absorptions at -94°C for a) 1,1-di-tert-butyldiazene (**16**) and b) tert-butylchloride measured every 114 seconds.

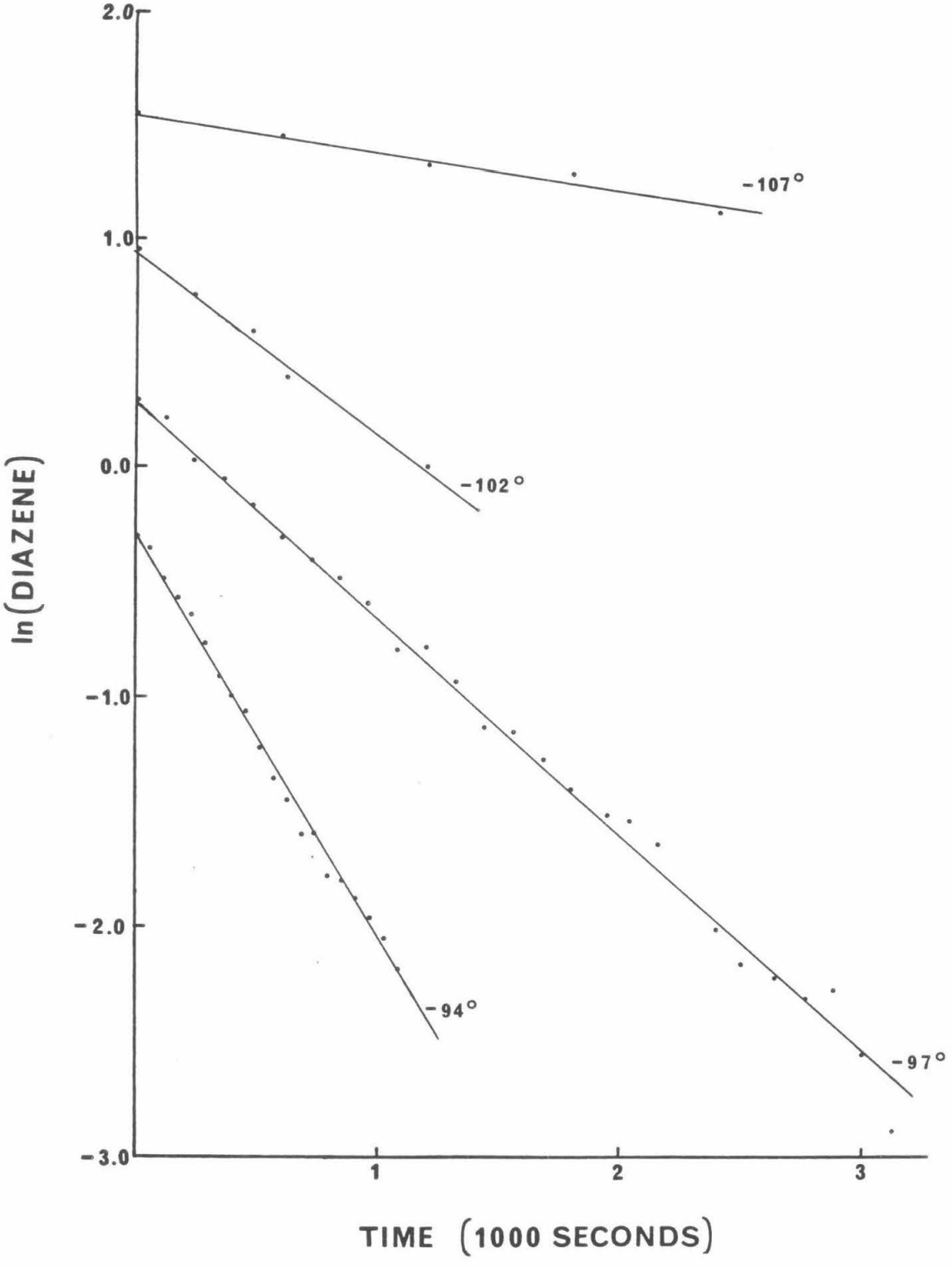


Figure 11. Ln A versus time plots for decomposition of **16** in dimethylether.

known, relative rates for thermal decomposition can be calculated for comparison with 1,1-diazene **16** at -94°C (Table 3). The gap between the relative rates of the cis and trans isomers is very large because the cis molecule is destabilized by a steric interaction between the tert-butyl groups and severe electron repulsion in the n_ lone pair molecular orbital. The 1,1-isomer **16**, which should be inherently less stable in the strainfree case, is further destabilized by the tert-butyl steric interaction.[29]

The differences in the free energies of activation ($\Delta G^{\ddagger}$) for the 1,1-diazene decompositions can be interpreted as relative strain energies if the 1,1-diazenes are decomposing by similar mechanisms with similar entropies of activation ($\Delta S^{\ddagger}$) and if most of the strain is relieved in the transition state. On this basis, 1,1-di-tert-butyldiazene (**16**) has about 7 kcal/mole more strain energy than do the cyclic 1,1-diazenes **3** and **4** which have nearly equal amounts of strain. The strain energy for 1,1-di-tert-butyldiazene (**16**), then, is 7 kcal/mole plus whatever strain energy exists in the cyclic diazenes. Since the strain energy in the cyclic diazene[3] is expected to be small, the strain in 1,1-di-tert-butyldiazene (**16**) appears to be consistent with the strain energy of 12 kcal/mole calculated for the tert-butyl interaction in 1,1-di-tert-butylethylene.[25]

Table 2. First Order Rate Constants for Decomposition of **16**.

Temperature (°C)	No. of spectra	time interval (sec)	k_1 (sec^{-1})
-94	20	57	1.77×10^{-3}
-97	26	120	0.95×10^{-3}
-102	5	240	0.79×10^{-3}
-107	5	600	0.17×10^{-3}

Table 3. Relative Rates for Decomposition of Di-tert-butyldiazene Isomers at -94°C.

Diazene	Solvent	$\Delta G^{\ddagger}$(-94°C)	k_{rel}
trans-1,2-di-tert-butyl	hexadecane	40.2[a]	2×10^{-34}
cis-1,2-di-tert-butyl	pentane	17.7[b]	5×10^{-7}
1,1-di-tert-butyl (**16**)	dimethylether	12.5	1

a) Ref. 14; b) Ref. 13.

Table 4. Relative Rates and $\Delta G^{\ddagger}$'s for 1,1-Diazene Decompositions at -94°C

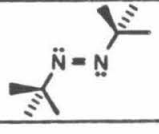
Diazene	$\Delta G^{\ddagger}$ (kcal/mol)	k_{rel}
3	19.1[a]	4×10^{-9}
4	19.4[a]	10^{-8}
16	12.5	1

9) Ref. 6.

Analysis of Products from 1,1-Di-tert-butylhydrazine (24) Oxidations.

Products obtained from the reaction of 1,1-di-tert-butylhydrazine (**24**) with two different oxidants, tert-butylhypochlorite and nickel peroxide, were analyzed by analytical VPC (Table 5). Both reactions were carried out at -78°C. 1,1-Diazene **16** is not stable at this temperature.

Table 5. Product Ratios From Oxidation of 1,1-di-tert-butylhydrazine (**24**).[a]

Oxidant					
tert-Butylhypochlorite	1.0	2.6	0.1	0.5	0.03
Nickel Peroxide	1.0	1.6	0.2	—	—

[a]Molar ratios determined by VPC.

The three hydrocarbon products, isobutane, isobutylene and hexamethylethane, are produced in molar ratios of 1.0:2.6:0.1 from the hypochlorite oxidation with a total yield of 38% based on C_4 groups. A 5% yield of tert-butylchloride and a very small component (0.3%), which may be 1,2-di-tert-butyldiazene by VPC, were also observed from this oxidation.

Oxidation with nickel peroxide, however, quantitatively produces only the hydrocarbon products. The molar ratios found for isobutane, isobutylene and hexamethylethane are 1.0:1.6:0.2. The 1,2-diazene isomer is not observed from this oxidation.

Monitoring the appearance of the three hydrocarbon products by NMR while diazene **16** decomposes shows that the increases in the hydrocarbon absorptions account for the amount of diazene lost. Dimerization of 1,1- diazene **16** to form tetra-tert-butyl-2-tetrazene (**28**) is therefore not a significant pathway for diazene decomposition. The hydrocarbon products are formed in an approximate molar ratio of 1.0:1.0:0.05 (isobutane:isobutylene:hexamethylethane) which is consistent with molar ratios obtained from VPC analysis of the bulk oxidation products if excess isobutylene is explained as arising from other oxidative processes which will be discussed below.

A reasonable mechanism for decomposition of 1,1-di-tert-butyldiazene (**16**) involves loss of nitrogen by either one or two bond cleavage to give tert-butyl radicals which disproportionate or combine to give isobutane, isobutylene and hexamethylethane. Thermal and photochemical decomposition of the

1,2-di-tert-butyldiazene isomers and di-tert-butylketone give isobutane, isobutylene, and hexamethylethane in the amounts shown in Table 6 consistent with the behavior of tert butyl radicals. The product ratios observed for 1,1-diazene **16** by NMR are similar to the ratios reported for decomposition of cis-1,2-di-tert-butyldiazene at -23°C.

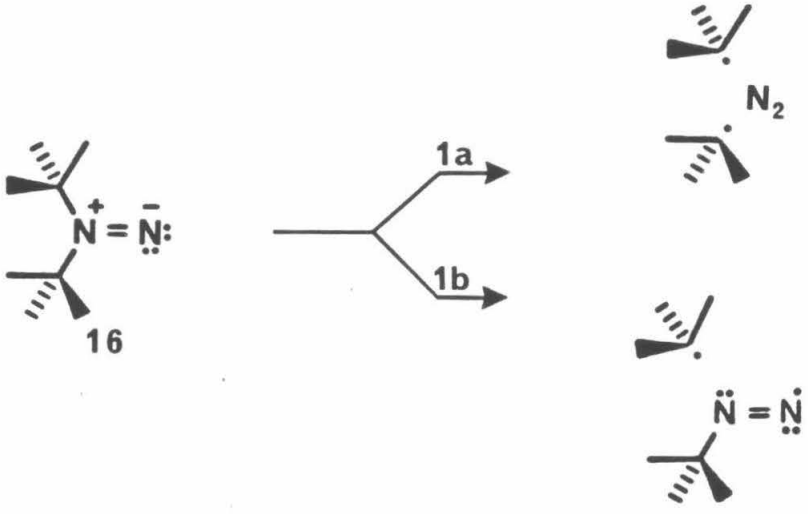


Figure 12a. Radical mechanism for decomposition of 1,1-diazene **16**.

Table 6. Molar Product Ratios for Some Related Decompositions

Compound	Decomposition			
cis-1,2-Di-tert-butyldiazene[a]	MeOH, -23°C	1.0	1.0	0.1
trans-1,2-Di-tert-butyldiazene[b]	hν , 30°C	1.0	0.92	0.12
trans-1,2-Di-tert-butyldiazene[c]	9 torr, 260°C	1.0	1.0	0.36
Di-tert-butylketone[b]	hν , 30°C	1.0	0.87	0.15

a) Ref. 30, b) Ref. 31, c) Ref. 32.

A second possible mechanism for decomposition of 1,1-diazene **16** is concerted elimination of isobutylene. The tert-butyldiimide which would be formed in this mechanism can decompose by either a bimolecular or a radical

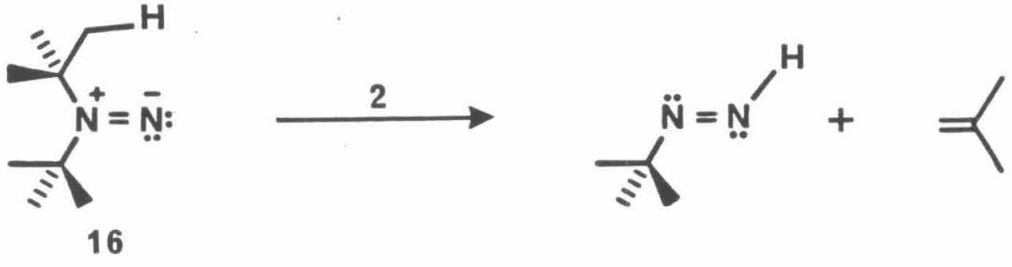


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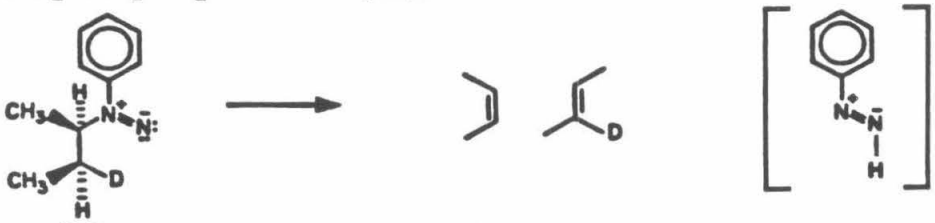
Figure 12b. Concerted mechanism for decomposition of 1,1—diazene (**16**).

chain pathway to give isobutane.[34] The major products expected from a concerted decomposition of 1,1-diazene **16** are, then, isobutylene and isobutane. Evidence for such a mechanism has been found in the stereospecific elimination of 2-butene from 1-sec-butyl-1-phenyldiazene (**26**).



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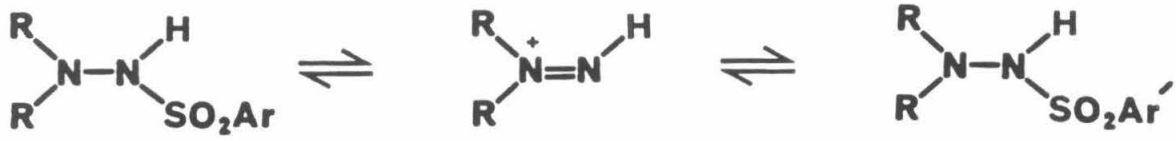
Although the concerted mechanism cannot be ruled out for **16**, the formation of hexamethylethane appears to indicate that loss of nitrogen to give tert-butyl radicals is a decomposition pathway for 1,1-di-tert-butyldiazene (**16**).

As mentioned before, tert-butylchloride and a large amount of the isobutylene formed in the hypochlorite oxidation apparently arise from some oxidative pathway other than decomposition of the 1,1-diazene. These two products suggest the intermediacy of tert-butyl cation and can be explained by the mechanistic scheme shown in Figure 13. Formation of the diazenium ion from 1,1-hydrazines having a good leaving group in the 2 position is precedented by the exchange of sulfonate groups in 1,1-dialkyl-2-sulfonylhydrazines. Cleavage of tert-butyl cation from



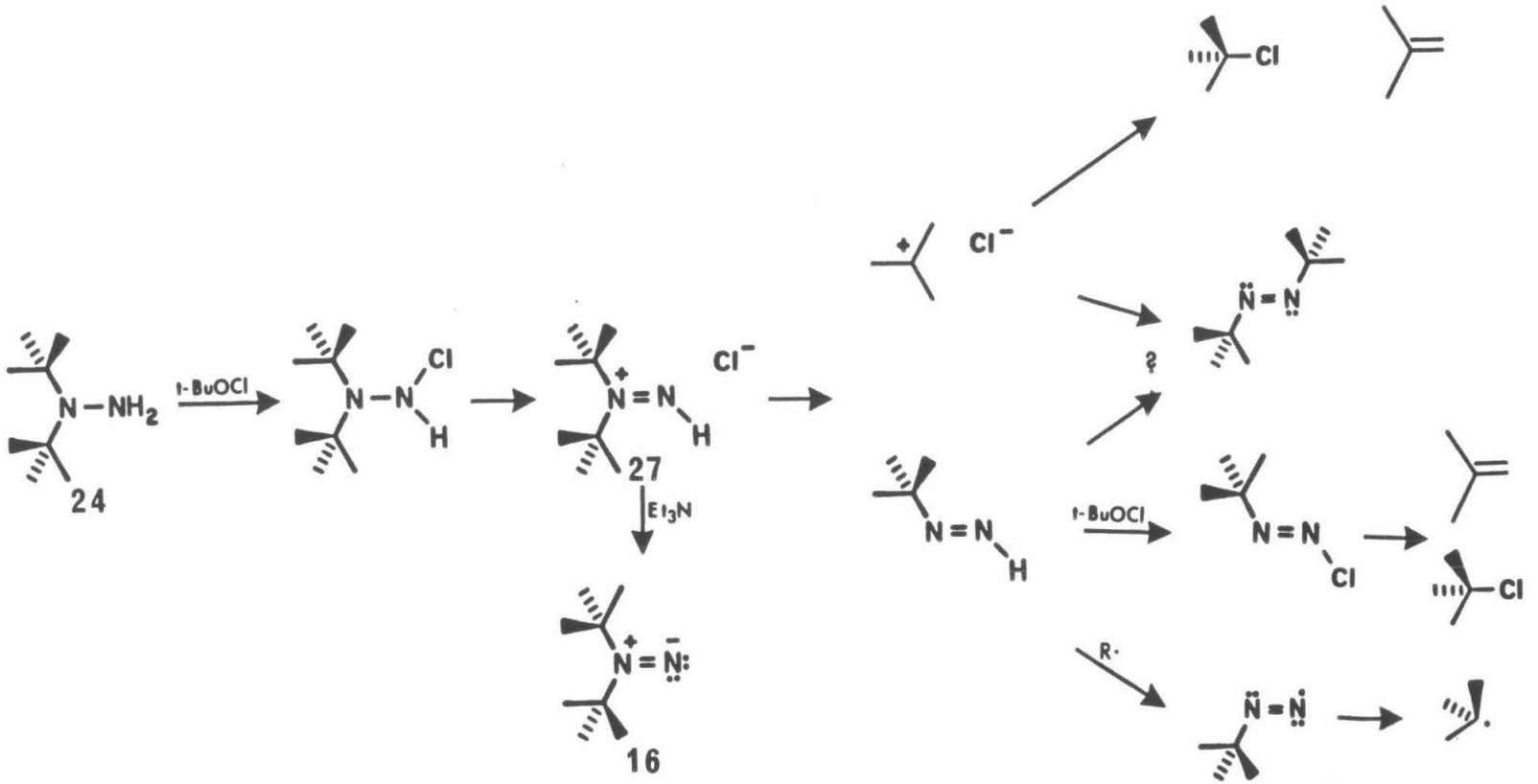


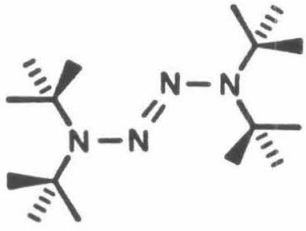
Figure 13. Mechanistic scheme for tert-butylhypochlorite oxidation of 1,1-di-tert-butylhydrazine (**24**).

1,1-di-tert-butyldiazenium ion (27) relieves the steric interaction between the tert-butyl groups. The tert-butyl cation can either combine with chloride ion to give tert-butylchloride or lose a proton to triethylamine to form isobutylene. tert-Butyldiimide is very susceptible to radical induced chain decomposition and should also react with tert-butylhypochlorite. The trans-1,2-di-tert-butyldiazene which appears to be a product of the oxidation could be formed by capture of tert-butyl cation by tert-butyldiimide followed by deprotonation.

Nickel peroxide is a cleaner oxidant which unfortunately reacts too slowly at -127°C to generate concentrated solutions of 1,1-diazene. The high ratio of isobutylene to isobutane (1.6:1) may arise from reaction of tert-butyl radical with the excess of nickel peroxide used. The ratio of products observed is what would be expected from 77% cage disproportionation-combination with complete scavenging of out of cage radicals by nickel peroxide to form isobutylene. Tanner, et al., find 50-90% cage reaction, depending on solvent viscosity, for thermal decomposition of cis-1,2-di-tert-butyldiazene generated at 30°C from photolysis of the trans isomer.[31]

Synthesis and Irradiation of 1,1,4,4-Tetra-tert-butyl-2-tetrazene (28).

Bimolecular reaction to form 2-tetrazenes has been observed for the cyclic 1,1-diazenes but is too slow to compete with the increased rate of unimolecular decomposition in 1,1-di-tert-butyldiazene (**16**). 1,1,4,4-tetra-tert-butyl-2-tetrazene (**28**) can be made, however, by stirring neat 1,1-di-tert-butylhydrazine (**24**) at 0°C under an atmosphere of oxygen. Hydrazyl radical **25** and 1,1,4,4-tetra-tert-butyltetrazane (**29**), shown in Figure 14, are the probable intermediates in this reaction. White needles are produced which give correct elemental analysis and are very similar to those obtained for 1,1'-azo-2,2,5,5-tetramethylpyrrolidine (**14**).[6]



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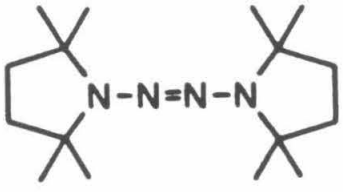

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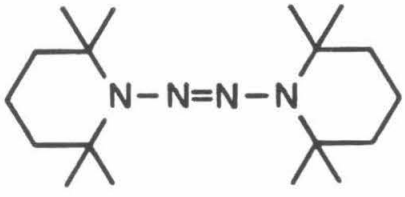

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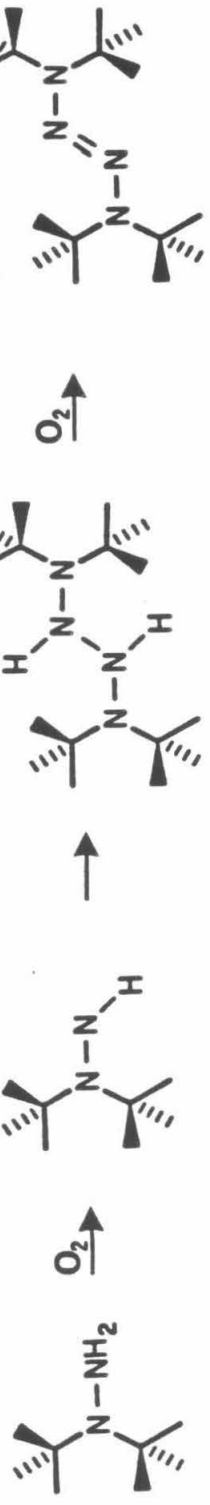


Figure 14. Mechanism for formation of tetrazene **28.**

Unlike tetrazene **14**, however, 1,1,4,4-tetra-tert-butyl-2-tetrazene (**28**) is labile in solution at room temperature and even solid samples sometimes decompose on standing at room temperature. A deuteriobenzene solution of tetrazene **28** sealed in a NMR tube decomposes over a few days at room temperature to form di-tert-butylamine and the tert-butyl radical products, isobutane, isobutylene and hexamethylethane. The mechanism for formation of these products is unknown but may be related to attack of dialkylamino radical on the 2-tetrazene which has been reported for 1,1'-azo-2,2,6,6-tetramethylpiperidine (**9**).[35] Radical induced chain decomposition could explain the variable stability of solid samples of tetrazene **28**.

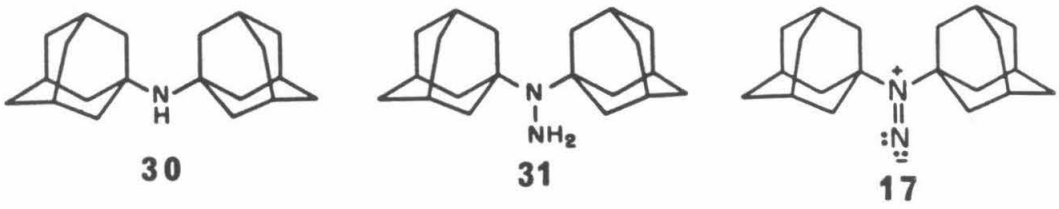
The UV spectrum of tetrazene **28** has a single absorption at 230 nm (ϵ1500) in diethylether which is in sharp contrast to the double maxima at 254 nm and 300 nm observed for tetrazene **14**. Dimethylether-dichloromethane and 2-methyltetrahydrofuran solutions of tetrazene **28**, saturated at 0°C, can be quickly frozen at -196°C to give clear glasses without precipitation of tetrazene. When these glasses are irradiated with UV light a red color is produced within 15 minutes but continued irradiation does not produce an observable increase in intensity. When the red glass is thawed at -127°C (n-propanol/liquid nitrogen) bubbling occurs and tetrazene **28** precipitates from solution while the red color persists. Further warming above -80°C destroys the red color with gas evolution and the resulting colorless solution can be refrozen and irradiated to reform the red coloration. Attempts to obtain clear red solutions free of precipitate for optical and NMR spectroscopy failed and the red

compound was never characterized.

From these observations, the red substance appears to be a photolabile intermediate which is generated at a steady state concentration determined by the concentration of tetrazene **28**. The appearance and stability of the red color are similar to what is observed for 1,1-di-tert-butyldiazene (**16**) although cleavage of the tetrazene into its diazene monomers is considered unlikely. Another possible intermediate is the cis isomer of tetrazene **28**. Ingold, et. al.,[36] have reported the observation of a photolabile intermediate in the photolysis of 1,1,4,4-tetra-isopropyl-2-tetrazene which they suggest is cis-1,1,4,4-tetra-isopropyl-2-tetrazene. This intermediate forms diisopropylamino radicals either photochemically or thermally with an E_a of about 24 kcal/mole. Based on these observations, it is conceivable that cis-tetra-tert-butyl-2-tetrazene, like 1,1-diazene **16**, could be a red compound which is thermally labile at -80°C.

Approaches to the Synthesis of 1,1-Di(1-adamantyl)diazene (17).

The possibility of stabilizing acyclic 1,1-diazenes with bridgehead substitution makes 1,1-di(1-adamantyl)diazene (**17**) an attractive synthetic target. 1-Adamantyl is the only bridgehead group for which the synthesis of the disubstituted secondary amine has been reported.[37] Di(1-adamantyl)amine (**30**) is needed to make the diazene precursor, 1,1-di(1-adamantyl)hydrazine (**31**).



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The overall yield of the secondary amine in this synthesis (Figure 15), however, is only 5% and a more efficient route was desired.

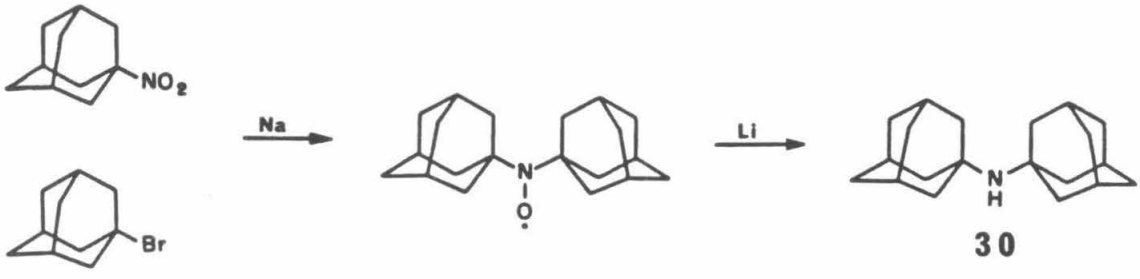

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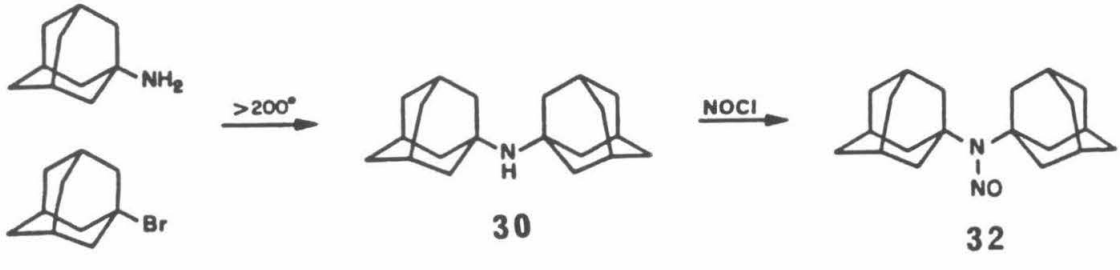
Figure 15. Literature route to di(1-adamantyl)amine.[37]

We found that heating two equivalents of 1-adamantylamine with 1-adamantylbromide at 220°C produced di-1-adamantylamine (**30**) in 80% isolated yield. Nitrosation of this amine with nitrosylchloride in pyridine gives 1,1-di(1-adamantyl)nitrosamine (**32**). This nitrosamine, like 1,1-di-tert-butylnitrosamine (**23**), is acid sensitive and partial decomposition to give 1-adamantanol and di-1-adamantylether is observed on silica gel.



30 32

Reduction of nitrosamine **32** to give 1,1-di(1-adamantyl)-hydrazine (**31**) is difficult because of steric hindrance and sensitivity to rearrangement. Several basic reducing conditions were attempted under an inert atmosphere and amine products were collected by precipitation as hydrochlorides. In every case the only amine product found was the overreduced di(1-adamantyl)amine (**30**). Lithium in liquid ammonia gave a small amount of secondary amine with the rest of nitrosamine **32** left unreacted. Aluminum amalgam in refluxing diethylether,sodium in refluxing ethanol and lithium aluminum hydride in di-n-butylether at 100°C all produced 1-adamantanol and di-1-adamantylether along with the overreduced secondary amine. The lithium aluminum hydride reaction also yielded some adamantane and 1,1'-biadamantane. These radical products may result from decomposition of a reduction intermediate or from oxidation of the desired hydrazine. The amine fraction from this reaction however shows no sign of either hydrazine **31** or the hydrocarbons which would be formed from its decomposition.

From the results of this work with 1-adamantyl substitution it is concluded that the best approach for synthesizing a bridgehead substituted 1,1-dialkyldiazene is to use a smaller group such as 1-bicyclo[2.2.2] or 1-bicyclo[2.2.1](1-norbornyl). Both of these tertiary bridgehead groups show a large stabilization effect in the 1,2-diazenes.[11] The smaller size will lessen strain due to steric interactions in the 1,1-diazene and should make the nitrosamine easier

to reduce. The difficulty in these two systems, however, will be synthesizing the secondary amines. There is some reason to believe that the bicyclo[2.2.2] group can be used in a similar condensation reaction as was used to make di-1-adamantylamine.[38]

Di-1-norbornylamine may be approached by reaction of 1-norbornyl lithium with 1-nitronorbornane followed by hydrolysis to give di-1-norbornylnitroxide which could be easily reduced to the amine.[39]

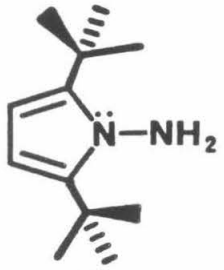
RESULTS AND DISCUSSION

Chapter 2

Generation and Trapping of 2,5-Di-tert-butyl-N-pyrrolylnitrene (22).

Synthesis of N-Amino-2,5-di-tert-butylpyrrole (33).

N-Amino-2,5—di-tert-butylpyrrole (33) was desired as a precursor to 2,5-di-tert-butyl-N-pyrrolylnitrene (22). The appropriately substituted pyrrole ring can be made by the



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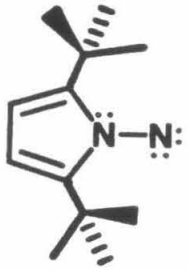

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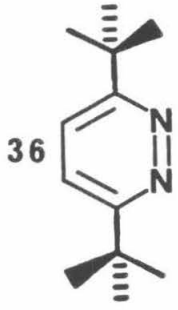
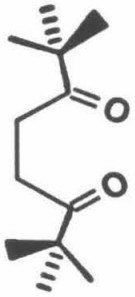


condensation reaction of 2,2,7,7-tetramethylocta-3,6-dione(34) with ammonia.[40] The dione 34 is available from oxidative coupling of the enolate of pinnacolone using cupric chloride.[41] The N-aminopyrrole 33 then, can conceivably be synthesized either from direct condensation



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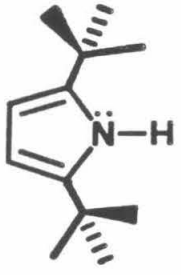
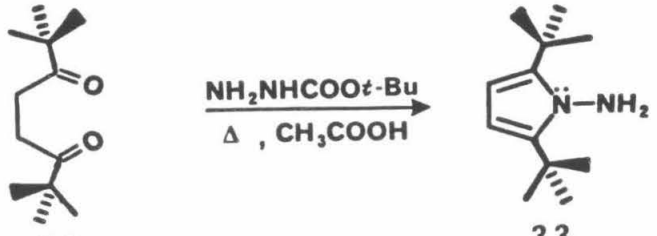


35

of 34 with a hydrazine or by amination of pyrrole 35.

Condensation of dione 34 with hydrazine gives 3,6-di-tert-butylpyridazine (36) as the isolated product after air oxidation. This is a convenient route for preparation of the ring expanded isomer of aminonitrene 22. Use of the blocked hydrazine, tert-butylcarbazate, gave condensation to form the 5 membered ring after a reflux period of 30 hours in glacial acetic acid. Hydrolysis of the carbazate occurred under the reaction conditions resulting in a

mixture of pyrrole and pyridazine products. N-amino-2,5-di-tert-butylpyrrole (33) was isolated by chromatography and recrystallization in 40% yield.

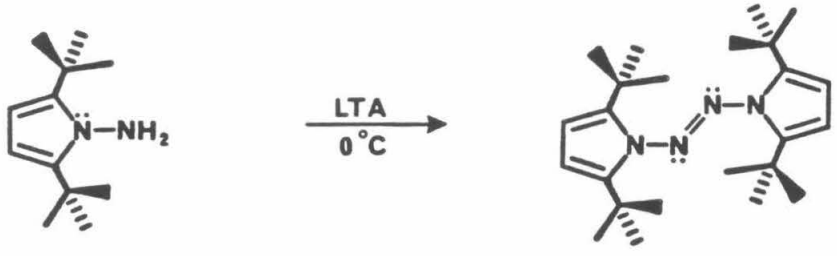


34 33

Generation and Trapping of 2,5-Di-tert-butyl-N-pyrrolylnitrene (22).

N-Aminopyrrole **33** is quite resistant to oxidation at the aminonitrogen due to the reduced availability of the nitrogen lone pair in the pyrrole ring. For example, **33** is indefinitely stable in air, in sharp contrast to 1,1-di-tert-butylhydrazine (**24**) which decomposes in minutes on exposure to air. Oxidants such as mercuric oxide, manganese dioxide and photochemically generated tert-butoxy radicals all gave no reaction with **33** at room temperature while halogenated oxidants such as iodine and tert-butylhypochlorite attacked the pyrrole ring. Lead tetraacetate was the only reagent found to be suitable for oxidizing the amino group in **33**.

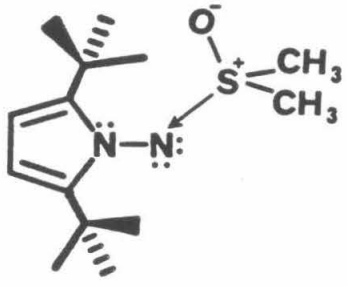
Reaction of N-amino-2,5-di-tert-butylpyrrole (33) with lead tetraacetate at 0°C affords 1,1'-azo-2,5-di-tert-butylpyrrolyle (37) as the only major product. This reaction is very slow at -78°C



33 37

producing a low yield of **37** after several hours with most of the aminopyrrole remaining unreacted. It appears from this oxidation that pyrrolylnitrene **22** is being formed but is too reactive to be stable towards dimerization, even at -78°C.

When the oxidation of **33** is performed in the presence of dimethylsulfoxide, pyrrolylnitrene **22** is efficiently trapped as N-(2,5-di-tert-butyl-N'-pyrrolyl)dimethylsulfoximine (**38**). Dimethylsulfoxide is a nucleophillic trap which adds to electron



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deficient aminonitrenes. The thermal behavior of this adduct will be discussed in the following section. Attempts to trap aminonitrene **22** with ethylene, tetramethylethylene and diethylfumarate were unsuccessful with dimerization of **22** to form tetrazene **37** observed instead of olefin addition.

A photochemical precursor to 1,1-diazenes would be very useful for making especially reactive molecules in inert environments such as low temperature glasses. Preparation of stable N-azides has been attempted[42] but the synthesis of dimethylaminoazide is the only successful example reported.[43] Photoextrusion of nitrogen from N-azido-2,5-di-tert- butylpyrrole (**39**) would be a convenient way to

generate pyrrolylnitrene **22** in rigid glasses or in a solution free of lead or acid contaminants. The synthesis of **39** was attempted using the diazo transfer reaction shown in Figure 16. A stable N-azide was never isolated but observation of tetrazene **37** as a product along with bubbling during the reaction were taken as evidence of an unstable N-azide **39**.

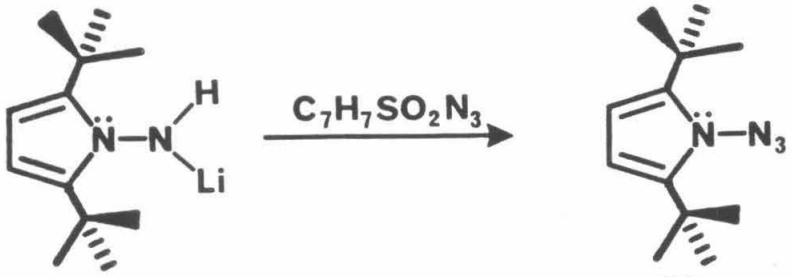

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Figure 16. Attempted diazo transfer reaction from tosylazide to the lithium salt of aminopyrrole **22**.

Thermal Chemistry of N-(2,5-Di-tert-butyl-N'pyrrolyl) -dimethylsulfoximine (38).

N-Pyrrolylsulfoximine **38** forms white crystals which are quite stable until heated near their melting point at 111°C. In solution, however, N-pyrrolylsulfoximine **38** is labile at room temperature. Heating **38** in tetrahydrofuran at 50°C produced 15% decomposition to tetrazene **37** and free dimethylsulfoxide in less than four hours. Further decomposition at this temperature is apparently inhibited by the free dimethylsulfoxide formed.

To study this effect, N-(2,5-di-tert-butyl-N'-pyrrolyl)-d_6-dimethyl-sulfoximine (**38-d_6**) was prepared by lead tetraacetate oxidation of N-aminopyrrole **33** in the presence of d_6-dimethylsulfoxide. When deuterated sulfoximine **38-d_6** is heated with three equivalents of dimethylsulfoxide at 50°C in carbon

tetrachloride rapid exchange of the sulfoxide groups is observed. Analysis of the solution by NMR shows that the protonated

dimethylsulfoxide is 89% equilibrated between adduct and free dimethylsulfoxide after 3 1/2 hours and equilibration is complete after 12 hours at 50°C. This exchange process apparently occurs by thermal generation of N-pyrrolylnitrene **22** followed by rapid retrapping with dimethylsulfoxide. The fact that dimerization occurs to form tetrazene **37** in the absence of dimethylsulfoxide supports this mechanism and rules out direct bimolecular substitution of sulfoxide groups.

Synthesis of N-pyrrolylnitrene **22** from N-pyrrolyl sulfoximine **38** was attempted using flash thermolysis with condensation of products at 77°K. Heating **38** to sublime it into a quartz tube at 450°C produced decomposition in the sublimation tube with condensation of 2,5-di- tert-butylpyrrole **35** and dimethylsulfoxide. Pyrrole **35** is probably formed from decomposition of tetrazene **37** which was collected along with pyrrole **35** and unreacted sulfoximine **38** when a solution of **38** was slowly dropped through a vertical quartz tube at 360°C under vacuum. No evidence for pyrrolylnitrene **22** at 77°K was observed from either of these pyrolyses.

Experimental Section

Melting points were determined using a Thomas-Hoover Melting Point Apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 257 or a Beckman IR 4210 spectrometer. Proton nuclear magnetic resonance (NMR) spectra were obtained on a Varian Associates EM-390 or a Jeol FX-90 spectrometer. Low temperature proton spectra were obtained using a Bruker WM500 500 MHz spectrometer. Chemical shifts are reported as parts per million downfield from tetramethylsilane (δ units) and multiplicity is given as s=singlet, d=doublet, t=triplet, m=multiplet and b=broad.

Electronic spectra were recorded using a Cary 219 or a Beckman Model 25 spectrophotometer. A UV-visible cell designed[44] for use in conjunction with an Air Products WMX-1A Vacuum Shroud and LC-1-110 Cryo-tip Refrigerator,[45] shown in Figure 17, was used to obtain electronic spectra at low temperatures. The windows for the vacuum shroud and the cell are Suprasil I, ground to size from blanks (Amersil, Inc.[46]). Samples were introduced into the cell through precooled 18 gauge teflon tubing (Alpha Wire Corp.[47]) by applying suction with a syringe. The cell body 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 seals between the windows and body were made with Viton O-Rings. The cell path length is 10 mm and the volume is approximately 4 ml. The cell was constructed in the Chemistry Division/Caltech Instrument Shop.

Filtrations at low temperatures were performed using a medium frit filter disc built into a vacuum jacketed cooling bath. This apparatus was constructed in the Caltech Glass Working Shop and is

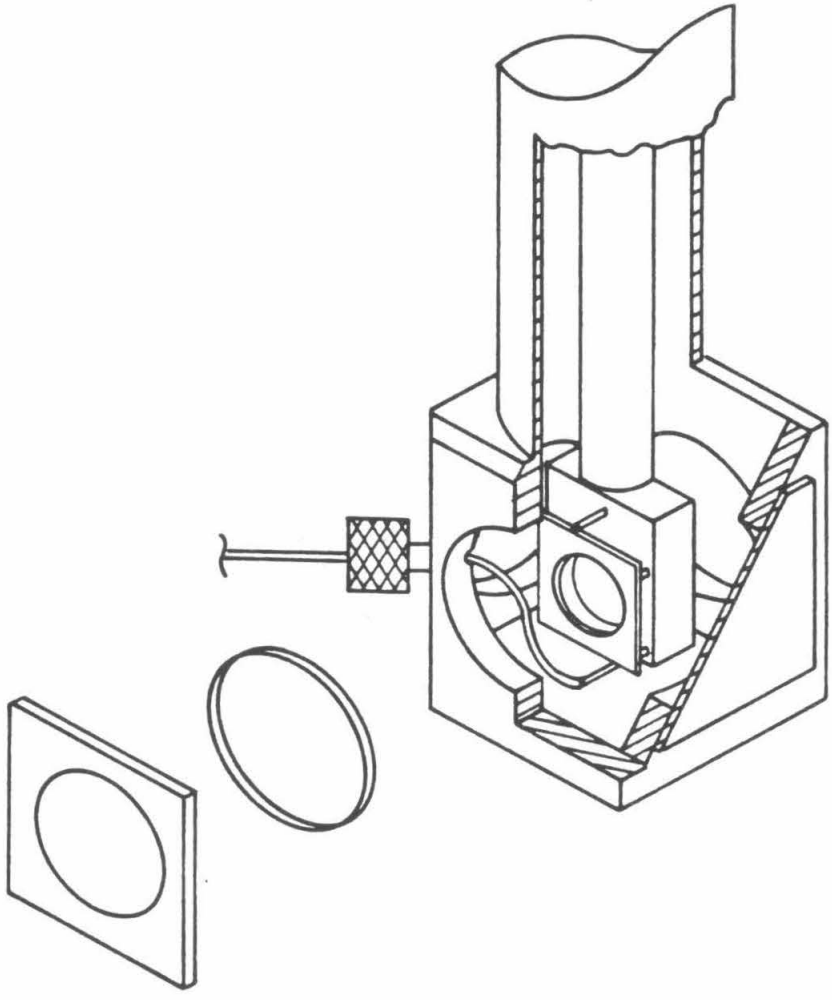

Figure 17. Low temperature spectroscopic cell[44] and shroud.

shown in Figure 18. A dry ice/acetone slush bath was used to cool to -78°C and a liquid nitrogen/n-propanol slurry was used at -127°C.

1,2-Dimethoxyethane (glyme) was distilled from lithium aluminum hydride. Ethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl. Pyridine was dried over 4A molecular sieves. Chlorotrifluoromethane and dimethylether were used directly as they were condensed from gas cylinders. Deuteriodichloromethane was passed through a short column of basic alumina before use. Dichloromethane was distilled from calcium hydride. Dimethylsulfoxide was distilled from lithium aluminum hydride. Lead tetraacetate was recrystallized from acetic acid and pumped dry. tert-Butylhypochlorite was washed with 10% sodium carbonate solution and water, dried ($CaCl_2$), and distilled under reduced pressure. Triethylamine was distilled from KOH pellets. 1,1-Di-tert-butylhydrazine (**24**) was always purified by preparative VPC (Pennwalt 223, 130°) and collected under argon atmosphere immediately prior to use.

A Hewlett-Packard 5700 A gas chromatograph equipped with a Hewlett-Packard 1870 A inlet splitter and a flame ionization detector was used for capillary vapor phase chromatography (VPC). Hydrogen was employed as the carrier gas and the makeup gas was nitrogen. Packed column analytical VPC was done using a Hewlett-Packard 5720 A gas chromatograph equipped with a flame ionization detector and nitrogen carrier gas. This instrument was used with 0.125 in. packed stainless steel columns. Quantitative VPC analysis with both instruments was accomplished using a Hewlett-Packard 3390 A electronic integrator. Detector response for hydrocarbons was assumed to be 1.0 relative to pentane. A Varian 920 instrument, equipped with a thermal

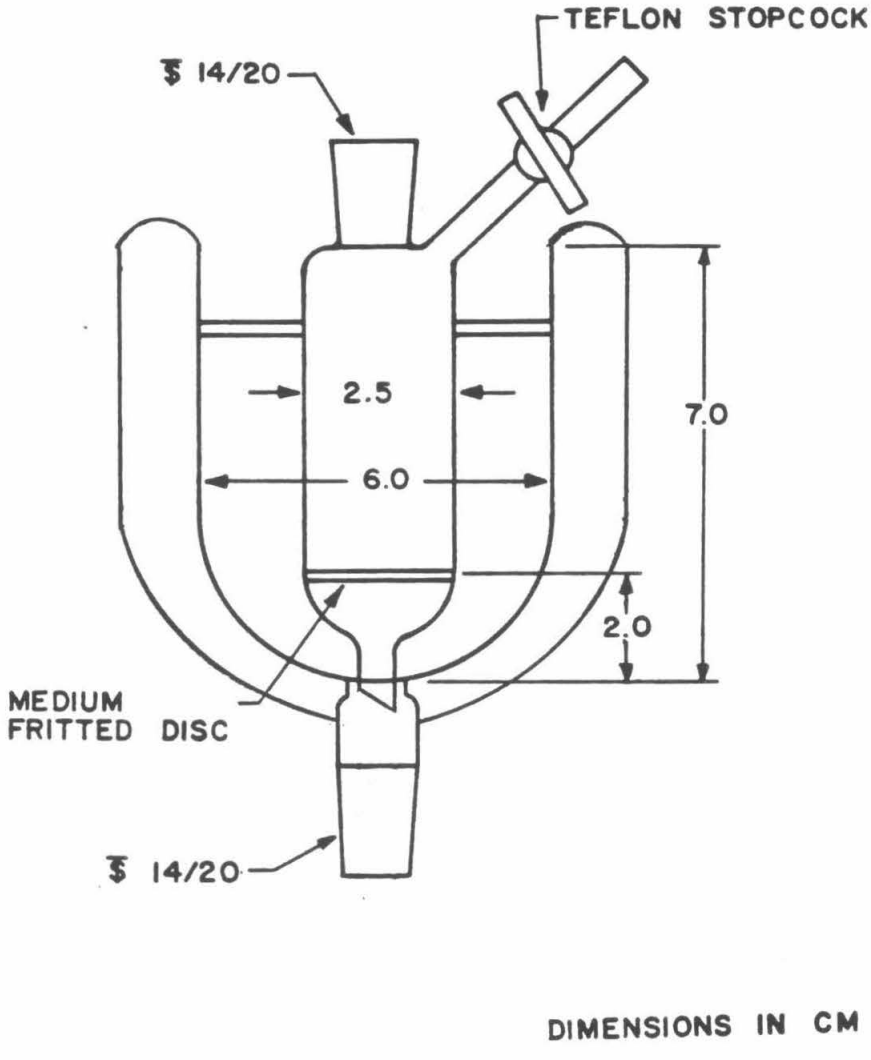

Figure 18. Vacuum jacketed low temperature filtration funnel.

conductivity detector, helium carrier gas and 0.375 inch packed aluminum columns, was used for preparative VPC. The analytical and preparative columns used are described in Table 7.

Mass spectra were recorded on a DuPont 24-492B Mass Spectrometer. Elemental analyses were performed at Spang Microanalytical Laboratory, Eagle Harbor, Michigan, and at Galbraith Laboratories, Knoxville, Tennessee. Reactions were carried out under a positive pressure of dry argon. All low temperature solution transfers were performed using teflon tubing and a rapid stream of argon.

2-Methyl-2-nitropropane.

The procedure of Kornblum was followed.[48] To a stirred solution of 650 gm (4.11 mole) potassium permanganate in 3 liters of distilled water was added 100 gm (1.37 mole) of tert-butyl amine. This mixture was stirred for 8 hours at room temperature followed by heating to 55°C for an additional 8 hours. The product was removed from the reaction mixture by steam distillation at 90°C. The organic phase was washed with 10% HCl solution and saturated sodium chloride solution, dried ($MgSO_4$), and distilled at 127°C to give 115 gm (80%) of a colorless liquid which solidified at room temperature, 2-methyl-2-nitropropane: IR (film) 3000, 2950, 1545, 1375, 1350, 860 cm^{-1}; NMR ($CDCl_3$) δ 1.6 (s).

Table 7

VPC Columns

Column Designation	Description
Pennwalt-223	3'xl/4"glass, 28% Pennwalt 223 on 80/100 Chrom R.
Pennwalt-223	4'xl/8" stainless steel, 28% Pennwalt 223 on 80/100 Chrom R.
Pennwalt-223	5'xl/4" glass, 28% Pennwalt 223 on 80/100 Chrom R.
DBT	20'xl/8" stainless steel, 10% Dibutylytetrachlorophthalate on 100/120 Chrom P AW-DMCS.
Carbowax 400	10'xl/8" stainless steel, 10% Carbowax 400 on 100/120 Chrom P AW-DMCS
SE-54	15 meter 0.31 mm ID fused silica SE-54 capillary.
SF-96	1'xl/8" stainless steel, 10% SF-96 on 100/120 Chrom W AW-DMCS.
SF-96	10'xl/8" stainless steel, 10% SF-96 on 100/120 Chrom P AW-DMCS.

Di-tert-butylamine.

Di-tert-butylamine was prepared from 2-methyl-2-nitropropane by a modification of the procedure of Back and Barton.[19] To a 1 liter flask fitted with an overhead stirrer and containing 400 ml of freshly distilled glyme (LAH) was added 93 gm (0.90 mole) of 2-methyl-2-nitropropane. Addition of 21 gm (0.90 mole) of sodium cut into small pieces caused the surface of the metal to turn bright gold and the pale lavender color of the 2-methyl-2-nitropropane radical anion formed in solution. The suspension was stirred, as a white precipitate formed, for 4 days until the lavender color was no longer present. The white slurry was then added to a 5 liter flask containing 600 gm of crushed sodium sulfide nonahydrate and 12 gm (2.5 mole) of sulfur stirred from above in 900 ml of dimethylformamide. The dark green mixture was illuminated from below with a 100 watt light bulb for 75 minutes. The reaction mixture was divided into two halves and each half was poured into 1 liter of a saturated potassium carbonate solution and extracted (4x250 ml) with pentane. The combined pentane extracts from both halves were washed (2x200 ml) with water and dried (Na_2SO_4). Gaseous HCl was bubbled into the pentane solution to precipitate the amine products. The white precipitate was collected by filtration and washed with ether to give 49.2 gm of amine hydrochlorides. Shaking this solid with 20% NaOH solution liberated the amines and the organic layer was separated and distilled (60°–67°C at 130 mm) to give 26 gm (45%) of di-tert- butylamine (98% pure by analytical VPC, 15' Pennwalt-223,130°): IR (film) 2980, 1475, 1385, 1365, 1230 cm^{-1}; NMR ($CDCl_3$) δ 1.17 (s).

Di-tert-butylnitrosamine (23).

A modification of the procedure of Back and Barton was used.[19] A solution of 25 gm (0.19 mole) of di-tert-butylamine in 100 ml dry pyridine was cooled with an ice-methanol bath. Nitrosyl chloride was passed into this solution until a red color persisted. The cold mixture was added to 400 ml water and extracted (1x400 ml, 2x200 ml) with ether. The sensitivity of nitrosamine **23** to acid requires removal of pyridine by repeated washing of a pentane solution with water. The ether was removed under reduced pressure and the resulting orange oil was taken up with 400 ml pentane and 400ml water. The aqueous layer was separated and extracted (2x200 ml) with pentane. The combined pentane fractions were washed (4x300 ml) with water, dried (Na_2SO_4) and concentrated under reduced pressure to give 26 gm (85%) of a yellow oil which solidified at room temperature, di-tert-butylnitrosamine (**23**): IR (film) 2970, 1435, 1390, 1370, 1265, 1190, 1120, 1015 cm^{-1}; NMR ($CDCl_3$) δ 1.67 (s, 9H), 1.52 (s, 9H); UV (Et_2O) 385 nm (ϵ 44), 236 (5300).

1,1-Di-tert-butylhydrazine (24).

Nitrosamine **23** was warmed until melted and 0.5 gm (3.2 mole) of the yellow oil was dissolved in 4 ml absolute ethanol. This solution was added to a 25 ml flask fitted with a reflux condenser under argon. As the flask was lowered into a preheated oil bath small pieces of sodium were added under argon flow. Additional pieces of sodium were added to maintain a molten globule of sodium in the refluxing ethanol for 20 minutes. During this time the yellow color had completely faded and a white solid had formed. The mixture was then cooled in an

ice bath before 20 ml of deoxygenated water was added to quench the excess sodium and dissolve the sodium ethoxide. The resulting cloudy solution was extracted (2x5 ml) with ether in a separatory funnel which had been flushed with argon. The combined ether extracts were then concentrated to about 2 ml under a stream of argon and dried (Na_2SO_4). Preparative VPC (3' Pennwalt-223, 130°) with collection under an argon atmosphere yielded 250 mg (55%) of 1,1-di-tert-butylhydrazine (**24**) (99% pure by analytical VPC, SE-54): IR (film) 3380, 3240, 2980, 1485, 1390, 1370, 1205, 860 cm^{-1}; NMR ($CDCl_3$) δ 2.80 (b, 2H), 1.24 (s, 18H).

2-Benzamido-1,1-Di-tert-butylhydrazine.

To a suspension of 240 mg (1.67 mmol) of freshly prepared 1,1-di-tert-butylhydrazine (**24**) in 2 ml of 10% sodium hydroxide solution at 0°C was added 400 μl (3.5 mmol) of benzoylchloride. The mixture was stirred overnight to allow excess benzoylchloride to hydrolyze. The white solid which had formed was extracted into ether, dried (Na_2SO_4), and concentrated to dryness. This solid was chromatographed on silica gel using first dichloromethane followed by diethyl ether as eluting solvents. The product (R_f c.a. .35, Et_2O/silica) was collected in 2 fractions which were free of impurities: M.P. 153-155°C; IR (CH_2Cl_2) 2980, 1690, 1515, 1490, 1395, 1370, 1200 cm^{-1}; NMR ($CDCl_3$) δ 7.8 (m, 2H), 7.5 (m, 3H) 6.95 (b, 1H), 1.31 (s, 18H); Anal. Calcd. for $C_{15}H_{24}N_2O$: C, 72.54; H, 9.74; N, 11.28. Found: C, 72.40; H, 9.69; N, 11.11.

1,1,4,4-Tetra-tert-butyl-2-tetrazene (37).

To a 10 ml flask fitted with a balloon filled with oxygen was added 420 mg (2.9 mmol) of 1,1-di-tert-butylhydrazine (**24**). Hydrazine **24** was stirred under oxygen at 0°C for 2 hours as the clear oil became a white paste. The flask was then evacuated at room temperature to give a dry white solid. This solid was transferred to a vial and was evacuated in a vacuum desicator for 30 min. to give 156 mg (37%) of fine white needles which were sufficiently pure for elemental analysis: M.P. 49-50°C; IR (mull) 2990, 1620, 1485, 1395, 1375, 1305, 1200, 1155, 930 cm^{-1}; NMR ($CDCl_3$) δ 1.27 (s); UV (Et_2O), 230 nm (ϵ 1500); Anal. Calcd. for $C_{16}H_{36}N_4$: C, 67.55; H, 12.76; N, 19.69. Found: C, 67.29; H, 12.63; N, 19.44.

Oxidation of 1,1-Di-tert-butylhydrazine (24) with tert-Butylhypochlorite. Preparation of Solutions of 1,1-Diazene 16 for Visible Absorption Spectroscopy.

A 50 ml roundbottom flask was purged with argon and cooled to -127°C (n-propanol/liquid nitrogen bath). To this flask was added 5 ml of dimethyl ether, 150 mg (1.05 mmole) of freshly prepped 1,1-di-tert-butylhydrazine (**24**) and 134 mg (1.3 mmole) of triethylamine. To a second cooled flask (-127°C) was added 5 ml chlorotrifluoromethane (Freon-13), 0.5 ml dimethyl ether and 115 mg (1.05 mmole) tert-butylhypochlorite. The pale yellow hypochlorite solution was added in small portions over 15 minutes to the rapidly stirred solution of hydrazine **24** causing a red color and white precipitate to form. The solution was stirred at -127°C for 45 minutes while a jacketed filter funnel with a 0.5 in. pad of celite

was cooled to -127°C. The red solution was quickly forced through teflon tubing into the cold filter funnel and a clear red solution was pulled through the frit into a flask at -127°C under vacuum. After stirring under vacuum to remove chlorotrifluoromethane, this solution was drawn into a low temperature UV-visible absorption cell which was maintained at -125°C to -130°C using liquid nitrogen. The visible spectrum was recorded at -125°C ± 1°C.

Preparation of 1,1-Di-tert-butyldiazene (16) Solutions for Proton NMR Spectroscopy.

To prepare solutions of 1,1-diazene **16** for proton NMR spectroscopy, only 2 ml of dimethyl ether was used to dissolve the amines in the oxidation procedure described for visible spectroscopy. The red solution is then filtered into a cold flask (-127°C) containing 500 μl of deuteriodichloromethane which had previously been passed through a short column of basic alumina. After removal of chlorotrifluoromethane under vacuum, dry argon was admitted to the flask and 0.3 ml portions of the diazene solution were transferred, via 18 gauge teflon tubing under positive argon pressure, into 5 mm NMR tubes (-127°C) which were equipped with serum caps. Proton spectra were recorded at -120°C using a Bruker 500 MHz NMR spectrometer.

Emission Spectroscopy of 1,1-Diazene 16.

The dimethyl ether:deuteriodichloromethane (4:1) solutions of 1,1-diazene **16** in 5mm NMR tubes, prepared as described above for NMR spectroscopy, formed a clear glass when quickly frozen to -196°C.

Emission spectra were recorded using a non-commercial spectrophotometer in Professor H.B. Gray's group at Caltech. The 510 nm line of a 200 W mercury-xenon lamp was used for excitation. The emission spectrum was monitored through a Corning 3-67 filter with a Hamatsu R406 PMT. Response factors for the R406 PMT are 0.719 (549 nm), 0.534 (600), 0.392 (651), 0.306 (699), 0.207 (750), 0.134 (801), 0.094 (849) and 0.066 (900). Warming the sample to -78°C to decompose 1,1-diazene **16** followed by refreezing the glass at -196°C causes complete loss of the emission signal.

Decomposition Kinetics for 1,1-Diazene 16.

Decomposition of 1,1-diazene **16** was monitored by NMR spectroscopy. Acetone was added as an internal reference to solutions prepared for NMR spectroscopy as described above. The samples were placed in the probe of a Bruker 500 MHz spectrometer at the desired temperature and allowed to equilibrate for at least 5 minutes. The temperature measured by a thermocouple within the probe was calibrated at -92°C using the chemical shifts of methanol. The actual temperature was found to be about 2°C colder than the thermocouple indicated. Spectra were taken at regular time intervals by fourier transforming 32 pulses which were accumulated in 55 seconds. Time intervals and the number of spectra taken are summarized with the rate data in Table 8. Integrations were measured by cutting and weighing the diazene and acetone absorptions and by measuring the peak heights of these two singlets. Both methods gave the same rate, however measuring peak heights was less sensitive to poor shimming and would typically give less scatter. All plots were first order with no

TABLE 8. Errors in First Order Rate Constants for Decompositions of 16.

Temperature (°C)	No. of Spectra	$k_1(sec^{-1})(x10^3)$	$s^a(x10^3)$	$ts^b(x10^3)$
- 94	20	1.77	0.03	0.06
- 97	26	0.95	0.016	0.032
-102	5	0.79	0.016	0.05
-107	5	0.17	0.017	0.05

(a) Standard deviation of the slope. (b) Error in k_1 at 95% confidence limit.

evidence of curvature observable. Rates were determined by least squares analysis and are shown in Table 8 with error limits representing one standard deviation.

Oxidation of 1,1-Di-tert-butylhydrazine (24) with tert-Butylhypochlorite. Product Yields by Analytical VPC.

To a chilled solution(-78°C) of 179 mg (1.24 mmole) of 1,1-di-tert-butylhydrazine (**24**) and 126 mg (1.24 mmol) of triethylamine in 5 ml of diethyl ether were added 66 mg of n-pentane and 70 mg of n-octane as internal standards. Hydrazine **24** was oxidized by slow addition of a cold solution (-78°C) of one equivalent of tert-butylhypochlorite in 5 ml diethyl ether. A white precipitate was formed during the addition but the red color of 1,1-diazene **16** was never observed.

This mixture was stirred for 30 minutes and analyzed by analytical VPC (Dibutyl tetrachlorophthalate, 25°C; Carbowax 400, 25°C; SE-54, 25°C and 55°C). The hydrocarbon products, isobutane, isobutylene and hexamethylethane, were observed in 10%, 26% and 2% yields, respectively, for a combined absolute yield of 38%. The yields are calculated as the number of mmoles of C_4 groups for each product divided by twice the number of mmoles of 1,1-di-tert-butylhydrazine (**24**) (based on C_4 groups). The amount of unreacted hydrazine **24** was found to be 39%. The three hydrocarbon products were then formed in a combined yield of 62%, based on the amount of hydrazine **24** which had reacted. Two additional products were observed. tert-Butylchloride was found in 5% yield and had also been observed in NMR experiments. The second product was present in

approximately 0.3% yield and coinjected with authentic trans-1,2-di-tert-butyldiazene. The assignment of this small component as trans-1,2-di-tert-butyldiazene cannot be made unambiguously, however. The yield and column used for each product is summarized in Table 9.

Oxidation of 1,1-Di-tert-butylhydrazine (24) with Nickel Peroxide. Determination of Hydrocarbon Product Ratios by Analytical VPC.

A solution containing 205 mg (1.42 mmole) of 1,1-di-tert-butylhydrazine (**24**), 124 mg n-octane and 94.5 mg n-pentane in 10 ml of diethyl ether was prepared and cooled to -78°C. A ten-fold excess (3 gm, 13 mmol available 0) of dry nickel peroxide[49] was added to this solution through a solid addition funnel. The suspension was stirred for 90 minutes and then was filtered at -78°C using a jacketed frit. Analysis of the filtered solution by analytical VPC (SE-54, 25°C, 55°C; Dibutyltetrachlorophthalate, 25°C) showed that hydrazine **24** had totally reacted. The only products observed from the reaction were the 3 hydrocarbons, isobutane, isobutylene and hexamethylethane. They were formed quantitatively in the ratio 35:59:6 for isobutane:isobutylene:hexamethylethane. Significantly, none (<0.1%) of the rearranged product, 1,2-di-tert-butyldiazene, was observed.

Irradiation of 1,1,4,4-Tetra-tert-butyl-2-tetrazene (37) in a glass at-196°C.

A solution of 68 mg tetrazene **37** and 40 μ l triethylamine in 1.1 ml of dimethyl ether:deuteriodichloromethane (8:3) was placed into 5

TABLE 9. Product Yields from tert-Butylhypochlorite.

Oxidation of Hydrazine 24.

Compound	VPC Column (^{o}C)	Yield (%)
Isobutylene	DBT, 25^{o}	26
Isobutane	DBT, 25^{o}	10
Hexamethylethane	SE-54, 25^{o}	2
1,1-Di-tert-butylhydrazine (24)	SE-54, 55^{o}	39
tert-Butylchloride	Carbowax 400, 25^{o}	5
trans-1,2-Di-tertbutyldiazene	Carbowax 400, 25^{o}	0.3

mm NMR tubes and frozen at -196°C in a quartz finger dewar to form a clear glass. Irradiation of these samples with a 1000 W Xe arc lamp filtered through a visible absorbing-UV transmitting filter (Corning 7-54) produced a red color which reached a steady intensity within 15 minutes. Gas bubbles are released when the glass is thawed at -127°C but the red color persists until warmed to -78°C. The red solution is quite viscous with a cloudy precipitate which prevents examination by NMR. The samples were removed from the NMR tubes with partial decomposition and mixed with 2 ml of chlorotrifluoromethane at -127°C. The red color remained in a thin layer floating on the freon with the precipitate. Filtration at -127°C passed a clear solution while the red color and precipitate remained on the frit.

A similar red color was produced when a 2-methyl tetrahydrofuran glass containing tetrazene was used and when neat crystals of tetrazene **37** were irradiated at -196°C. A steady intensity for the red coloration was quickly reached in the 2-methyltetrahydrofuran glass. Warming the sample to -80°C until colorless followed by refreezing and further illumination regenerated the red color.

Di(1-adamantyl)amine (30).

A heavy walled glass tube was filled with 3.15 gm (0.015 mol) 1-adamantylbromide and 4.5 gm (0.03 mol) 1-adamantylamine and sealed under vacuum. After heating the tube at 220°C for 40 hours the solidified product was crushed and shaken in a separatory funnel containing 100 ml of 20% NaOH solution and 250 ml ethyl ether until the solid dissolved. When 10% aqueous HCl solution was added to the organic phase, di(1-adamantyl)amine hydrochloride precipitated as a

white solid. The product was filtered and shaken with 20% NaOH solution and diethyl ether to regenerate the secondary amine. Most of the excess monoadamantylamine was washed into the aqueous HCl solution as checked by TLC. The ether layer was dried (Na_2SO_4) and concentrated under reduced pressure to give a white solid which was further purified by column chromatography (neutral alumina/ether) to give 3.4 gm (80%) of di(1-adamantyl)amine: M.P. 196-197°C; IR (CCl_4) 2930, 2860, 1490, 1455, 1355, 1310, 1165, 1100 cm^{-1}; NMR ($CDCl_3$) δ 2.0 (b, 6H), 1.78 (m, 12H), 1.64 (m, 12H).

1,1-Di(1-adamantyl)nitrosamine (32).

A 1 liter flask containing 11.0gm (0.039 mol) of di(1-adamantylamine (**30**) and 12.5 ml dry pyridine stirred in 200ml dry diethyl ether was cooled with an ice/methanol bath to -20°C. To this solution was slowly added 7.0 ml of nitrosyl chloride which had been condensed into a graduated centrifuge tube, dissolved in cold ether, and transferred to a cooled jacketed addition funnel. The reaction was allowed to warm to room temperature and stirred overnight. After adding the suspension to water, additional ether was needed to dissolve the product. The ether layer was washed with water and saturated $NaHCO_3$ and dried (Na_2SO_4). Removal of ether gave a yellow orange solid which smelled of pyridine. The product was redissolved in ether and passed through a column of neutral alumina which removed the orange color and the pyridine. The resulting yellow solid was recrystallized from ether/pentane and was pure by TLC (ether/silica): M.P. 187-188°C; IR (CCl_4) 2905, 2850, 1445, 1350, 1300, 1195, 1115, 1080, 970 cm^{-1}; NMR ($CDCl_3$) δ 2.38 (m, 12H), 2.14 (b, 6H), 1.73 (m,

12H); Anal. Calcd. for $C_{20}H_{30}H_2O$: C, 76.39; H, 9.62; N, 8.91. Found: C, 76.24; H, 9.83; N, 8.82.

N-Amino-2,5-di-tert-butylpyrrole (33).

A solution of 23.78 gm (0.12 moles) 2,2,7,7-tetramethylocta-3,6-dione[41] and 31.7 gm (0.24 moles) tert-butylcarbazate in 70 ml glacial acetic acid was refluxed for 28 hours under nitrogen. After cooling, the reaction mixture was added to 100 ml of water and the resulting suspension was extracted with 2x150 ml of ether. The ether layer was washed with 5x100 ml 10 N HCl, 3x100 ml saturated sodium bicarbonate, 100 ml saturated sodium chloride and dried ($MgSO_4$). Concentration of this solution gave a light yellow solid which was chromatographed (400 gm silica/methylene chloride) and 9.4 gm (40%) of N-aminopyrrole **33** was collected as the first elutant. The white solid (95% pure by analytical VPC, 4' Pennwalt-223, 200°C) was further purified by preparative VPC (5' Pennwalt 223, 190°C) or by recrystallization from hexane to give fine white needles: M.P. 66-67°C; IR (CCl_4) 3380, 3300, 3103, 2960, 1476, 1460, 1389, 1360, 1250, 950, 870 cm^{-1}; NMR ($CDCl_3$) δ 5.38 (s, 2H), 4.23 (b, 2H), 1.35 (s, 18H); mass spectrum, m/z (rel. intensity) 194 (14), 179 (19), 137 (3), 123 (25), 57 (15); Anal. Calcd. for $C_{12}H_{22}N_2$: C, 74.17; H, 11.41; N, 14.42. Found: C, 74.21; H, 11.49; N, 14.31.

3,6-Di-tert-butylpyridazine (36).

A solution of 1.5 gm (7.6 mmoles) 2,2,7,7-tetramethylocta-3,6-dione (**34**) and 0.49 gm (15.2 mmoles) hydrazine in 3.5 ml glacial acetic acid was refluxed under nitrogen for two hours. The mixture

was cooled, made basic with a saturated solution of potassium carbonate and extracted 3x25 ml with ethyl ether. The ether extracts were washed with 10 ml of water, dried ($MgSO_4$) and concentrated to a white solid. Recrystallization from ether/pentane gave 0.55 gm of fine white needles (35%): M.P. 170-175°C [lit. M.P. 175-177°C];[50] IR (Nujol) 3035, 1585, 1475, 1428, 1360, 1148, 865 cm^{-1}; NMR ($CDCl_3$) δ 7.40 (s, 2H), 1.44 (s, 18H).

1,1'Azo-2,5-di-tert-butylpyrrole (37).

Using a solid addition funnel, 460 mg (1.1 equiv.) of lead tetraacetate was slowly added to a solution of 200 mg (1.0 mmole) of N-amino-2,5-di-tert-butylpyrrole (**33**) in 10 ml dry methylene chloride cooled to 0°C under nitrogen. The solution first turned yellow and then reddish brown. After an hour of stirring at 0°C the reaction mixture was washed with water, saturated sodium bicarbonate, dried ($MgSO_4$) and concentrated. The reddish residue was chromatographed (silica/methylene chloride) to give 50 mg (25%) of light yellow tetrazene **37**: M.P. 102-103°C; IR (CH_2Cl_2) 3105, 2990, 1460, 1397, 1366, 1200, 1100, 1018 cm^{-1}; NMR ($CDCl_3$) δ 6.0 (s, 4H), 1.30 (s, 36H); exact mass calcd. for $C_{24}H_{40}N_4$ 384.325, found 384.326.

N-(2,5-Di-tert-butyl-N'-pyrrolyl)dimethylsulfoximine (38).

Using a solid addition funnel, 0.34 gm (0.77 mmole) lead tetraacetate was added over an hour to a solution of 150 mg (0.77 mmol) of N-amino-2,5-di-tert-butyl pyrrole (**33**) in 4 ml each of methylene chloride and dimethyl sulfoxide at 0°C. After stirring for an additional one and one-half hours the mixture was taken up in more

methylene chloride and washed with water, saturated sodium bicarbonate and saturated sodium chloride. After drying ($MgSO_4$) the solvent was removed to give a reddish solid which was recrystallized (chloroform/hexane) to give 70 mg (34%) of near white crystals: M.P. 111-112°C (decomp.); IR (CH_2Cl_2) 3110, 2985, 1396, 1363, 1307, 1205, 1058, 1023, 944 cm^{-1}; NMR ($CDCl_3$) δ 5.80 (s, 2H), 3.03 (s, 6H), 1.36 (s, 18H); Anal. Calcd. for $C_{14}H_{46}N_2OS$: C, 62.18; H, 9.69; N, 10.36. Found: C. 62.18; H, 9.89; N, 10.28.

N-(2,5-Di-tert-butyl-N'-pyrrolyl)-d_6-dimethylsulfoximine (38-d^6).

The deuterated dimethylsulfoxide adduct was prepared using dimethylsulfoxide-d^6 in the same procedure used to make **38**: IR (CH_2Cl_2) 3105, 2970, 2260, 2140, 1393, 1361, 1210, 1058, 1020, 959 cm^{-1}; NMR ($CDCl_3$) δ 5.80 (s, 2H), 1.38 (s, 18H).

Solution Thermolysis of N-(2,5-Di-tert-butyl-N'-pyrrolyl) dimethylsulfoximine (38) at 50°C.

A pyrolysis tube containing 300 μl of a 0.059 M tetrahydrofuran solution of sulfoximine **38** was sealed under vacuum and placed in an oil bath at 50°C. After 4 hours the tube was opened and the THF was removed under reduced pressure. Analysis of the products by NMR showed that 15% of the dimethylsulfoxide adduct had decomposed cleanly to give tetrazene **37** and free dimethylsulfoxide.

Solution Thermolysis of N-(2,5-Di-tert-butyl-N'-pyrrolyl)-d^6-dimethylsulfoximine (38-d^6) in the Presence of Dimethylsulfoxide.

A solution of 5.06 mg (0.0184 mmoles) deuterated adduct (**38-d^6**)

and 4.3 mg (3 equivalents) dimethylsulfoxide in 0.5 ml of carbon tetrachloride was placed in a 5 mm NMR tube, degassed and sealed under vacuum. The NMR spectrum of this solution shows that the dimethylsulfoxide adduct is completely deuterated before thermolysis. After heating the tubes at 50°C for 3-1/2 hours the dimethylsulfoxide adduct was 33% deuterated at the sulfoximine methyls which corresponds to 89% equilibration of d^6-dimethylsulfoxide between the dimethylsulfoxide adduct and free dimethylsulfoxide. After 12-1/2 hours of thermolysis dimethyl sulfoxide was 97% equilibrated. Although the solution had become slightly brown, tetrazene **37** or any other product were not observed in the NMR spectrum.

Attempted Flash Pyrolysis of Dimethylsulfoximine (38).

Dimethylsulfoximine **38** was placed in a sublimation tube near the inlet of a quartz tube heated to 450°C with a Hodgkin's furnace. A liquid nitrogen cooled finger was placed at the outlet of the heated tube and the system was evacuated to 0.2 torr. Sublimation did not occur until the sublimation tube was heated to 90-100°C and the white crystals began to yellow. The yellow condensate on the cold finger did not change color when thawed and NMR analysis showed this material to be composed of dimethylsulfoxide and 2,5-di-tert-butylpyrrole (**35**). The residue in the sublimation tube contained both tetrazene **37** and pyrrole **35** but neither dimethylsulfoximine **38** or dimethylsulfoxide were present.

Dropping of a solution of dimethylsulfoximine **38** directly into the pyrolysis tube was also attempted. A solution of 15.7 gm of the dimethylsulfoximine in 25 ml of decalin was added dropwise into a

vertical quartz tube heated at 360°C under vacuum. A golden brown solid was condensed at the bottom of the hot tube in a 50 ml flask at -196°C. After removal of most of the decalin under vacuum at 34°C the residue was found to contain 82% unreacted dimethylsulfoximine **38** and 18% tetrazene **37**.

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(27) The errors are reported as the 95% confidence limits instead of single standard deviations because of the small number of points in the analysis.

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