THE SYNTHESIS, SPECTROSCOPIC OBSERVATION AND CHEMICAL REACTIVITY OF N-(2,2,6,6-TETRAMETHYLPIPERIDYL)NITRENE

Thesis by

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To My Parents

ACKNOWLEDGEMENTS

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ABSTRACT

1,1-Dialkyldiazenes (aminonitrenes, N-nitrenes) unlike their more stable 1,2-dialkyldiazene isomers (azo compounds) have not yet been isolated or detected by spectroscopic methods, but rather are assumed intermediates based on a substantial body of chemical evidence. The first direct observation of a 1,1-dialkyldiazene is described here. The visible spectrum at -78° of N-(2,2,6,6-tetramethylpiperidyl)nitrene (33) (λ_{max} = 541 nm) provides experimental evidence on (1) the energy required for the $n \rightarrow \pi^*$ electronic transition, and (2) the vibrational spacing of the first electronically excited state. The infrared spectrum at -78° ($^{14}N=^{14}N$ stretch at 1595 cm^{-1}; $^{14}N=^{15}N$ stretch at 1569 cm^{-1}) provides evidence that the 1,1-diazene has considerable N=N double bond character in the ground state.

The first kinetic study of the thermal decomposition of a 1,1-dialkyldiazene is described. The temperature dependence of the unimolecular rate (k_1) of fragmentation of 33 was examined in three different solvents and kinetic evidence for a direct bimolecular pathway for the formation of 1,1'-azo-2,2,6,6-tetra-

methylpiperidine 41 from 33 is provided. The activation parameters for the unimolecular fragmentations are log A = 11.6 ± 0.5, Ea = 16.9 ± 0.7 in n-hexane, log A = 13.7 ± 0.3, Ea = 20.0 ± 0.4 in Et_2O, log A = 13.6 ± 0.3, Ea = 20.1 ± 0.4 kcal/mole in THF. Using computer simulation it is found that the curved portions of the ℓn A vs. time plots may be modelled as competitive unimolecular and bimolecular reactions ($k_{obs} = k_1 + k_2[33]$). In Et_2O at -16°, $k_1 = 5.03 \times 10^{-4}$ sec^{-1} and $k_2 = 5.0 \times 10^{-2}$ liter/mole-sec.

Also reported are proton and carbon-13 nuclear magnetic resonance data for 33, along with the results of a preliminary study of its photoreactivity.

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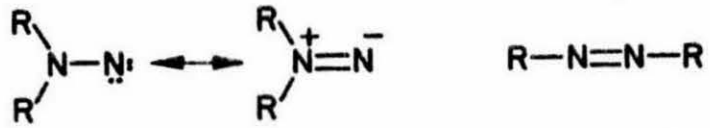
Part I

INTRODUCTION

A fundamental aim of mechanistic organic chemistry is to understand the pathways by which reacting molecules proceed to products. Numerous indirect methods have been used to elucidate reaction pathways.[1,2] Among these are kinetic studies, the use of isotopic tracers, thermochemical measurements, determinations of reaction stereochemistry, and trapping of intermediate species. A more direct method for studying the features of reaction pathways is the spectroscopic observation of reactive intermediates and the study of their chemical behavior. The subject of this thesis is the examination of one such intermediate, the 1,1-dialkyldiazene.

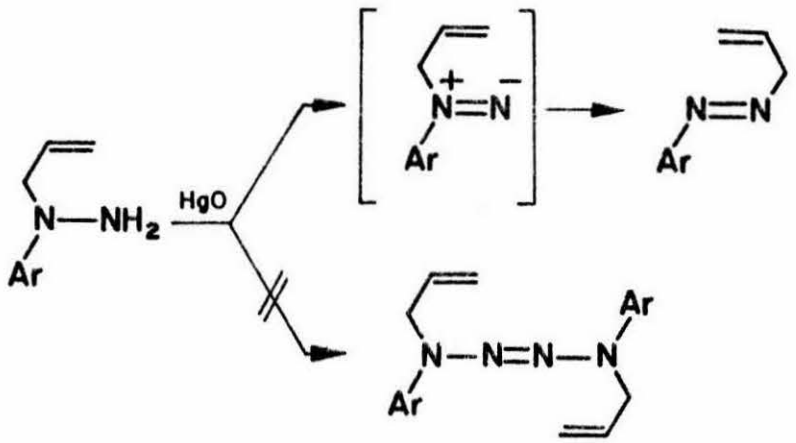
1,1-Dialkyldiazenes[3] (aminonitrenes, N-nitrenes) 1 unlike their more stable 1,2-dialkyldiazene isomers (azo compounds) 2 have not yet been isolated or detected by spectroscopic methods but rather are assumed intermediates based on a substantial body of chemical evidence. The chemical reactions of presumed 1,1-dialkyldiazene intermediates show behavior suggesting that the reacting species is a singlet. For example, they do not exhibit the free



1a 1b 2

radical-like behavior characteristic of triplet nitrenes and they accept a proton on the monovalent nitrogen to yield a fairly stable cation. This is in direct contrast to other nitrenes R-N̈· (3) (eg. alkyl, aryl, carbethoxy and cyano-nitrenes), which are ground state triplets.[4] These results suggest that the 1,1-dialkyldiazene may be represented by the resonance structures 1a and 1b and that the dipolar form 1b contributes importantly to the hybrid.

The existence of 1,1-diazenes was first proposed in 1893 by Michaelis and Luxemburg to explain the formation of 1,2-diazenes rather than the "normal" tetrazene products in the oxidation of 1-allyl-1-aryl hydrazines.[5] In the past



three decades the chemistry of 1,1-diazenes has been investigated extensively;[3] some of the more important results and generalizations concerning 1,1-diazenes are discussed below.

Preparation of 1,1-Diazenes.[3]

There exists a variety of independent methods by which 1,1-diazenes may be generated (see Figure 1). Of these, perhaps the most versatile is the oxidation of 1,1-disubstituted hydrazines (4). A wide variety of oxidants have been used, including mercuric oxide,[6] lead tetraacetate,[7] bromine,[8] manganese dioxide,[9] t-butyl hypochlorite[10] and diethyl azodicarboxylate.[11] The neutralization of 1,1-dialkyldiazenium ions (5) is actually a variation on this method in which a disubstituted hydrazine is oxidized in acidic media and the resulting diazene is trapped as its protonated form; neutralization results in the formation of products characteristic of 1,1-diazenes.[12] The reaction of difluoramine with secondary amines (6) to form 1,1-diazenes[13] has not received much use, presumably due to the explosive nature of the fluorinated reagent. The thermal and photochemical cleavage of N-aminosulfoximines (7) is potentially a useful means of generating 1,1-diazenes.[14] However, the nature of the R-groups is severely restricted by the method of synthesis of 7 (formed by trapping 1,1-diazenes with dimethyl sulfoxide; see below). The decomposition of 1,1-disubstituted-2-sulfonylhydrazines (8) in basic protic media or of the analogous sodium salts in aprotic media are versatile methods for generating 1,1-

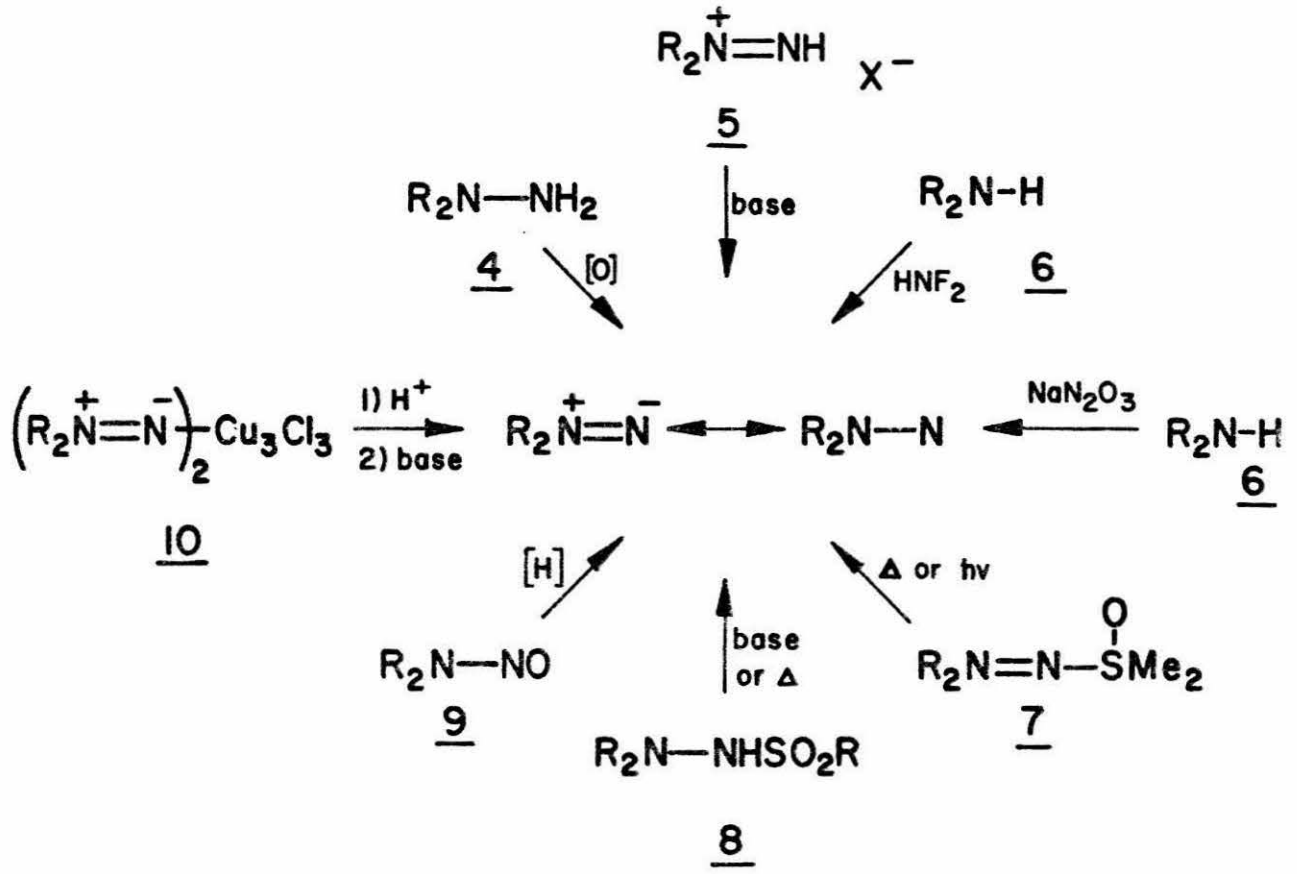


Figure 1. Methods of Preparation of 1,1-Diazenes.

diazenes.[15] The thermolyses of sulfonylhydrazines 8 at 306-439° have recently been shown to yield products consistent with the intermediacy of 1,1-diazenes.[16] The reduction of N-nitrosamines 9 with alkaline sodium dithionite,[17] lithium in liquid ammonia[18] or ethyl diphenylphosphinite[19] in benzene solution has been shown to yield products derived from 1,1-diazenes. The reaction of sodium nitrohydroxamate[20] or N-benzenesulfonylhydroxylamine[21] with secondary amines has been used to generate 1,1-diazenes, apparently proceeding by initial generation of nitroxyl (HN=O) which adds to the secondary amine. Subsequent loss of the elements of water generates the diazene.[3a] Finally, the oxidation of 1,1-dialkylhydrazines with cupric chloride in aqueous solution gave a complex, 10, which released the 1,1-dialkyldiazene upon treatment with acid followed by neutralization.[22]

The Chemistry of 1,1-Diazenes.[3]

1,1-Diazenes exhibit rich and diverse chemistry (see Figure 2); the exact mode of stabilization taken is determined by internal factors (structure and substitution) as well as external factors such as the temperature, the nature of the medium and even the rate of addition of the reactants.[3b] The reactions of 1,1-diazenes may be divided into three types: (1) fragmentations, (2) isomerizations, and (3) bimolecular reactions.

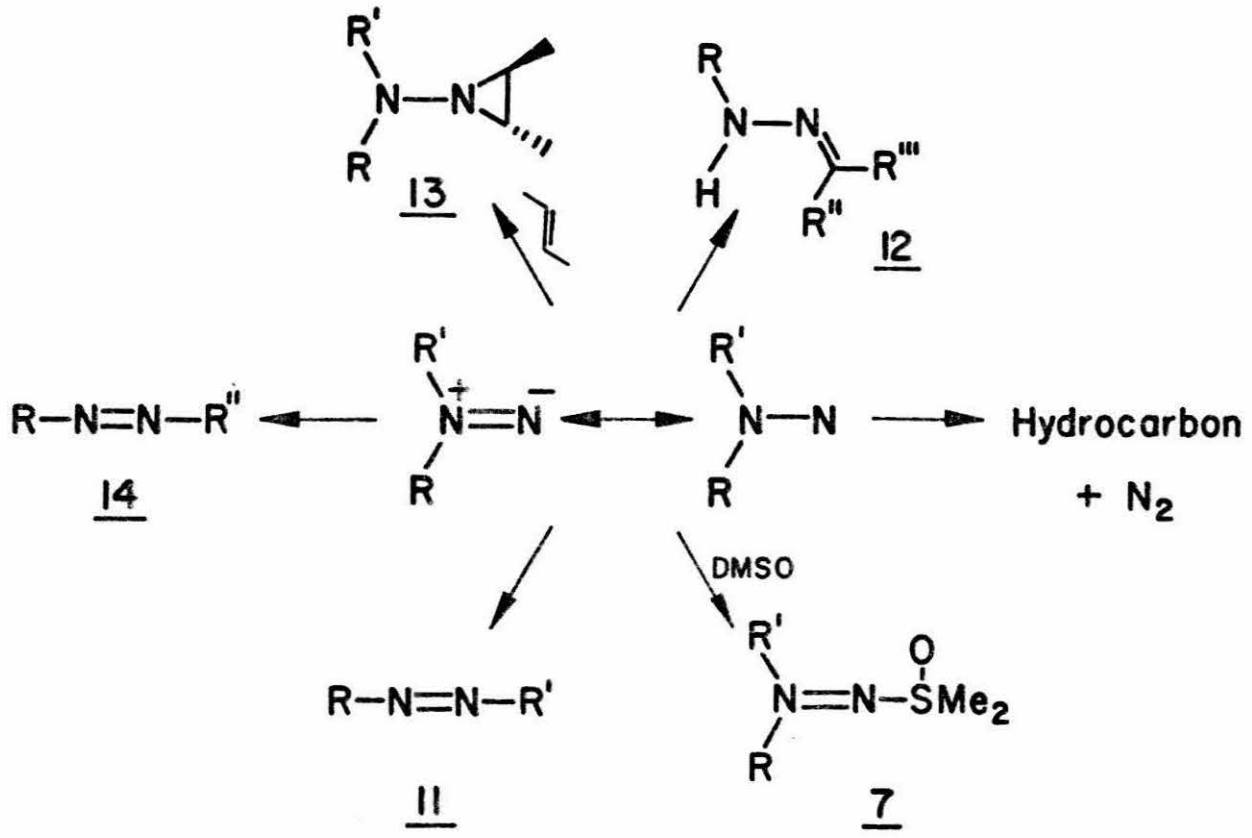
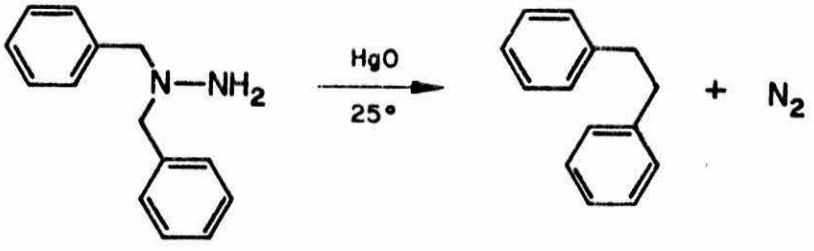
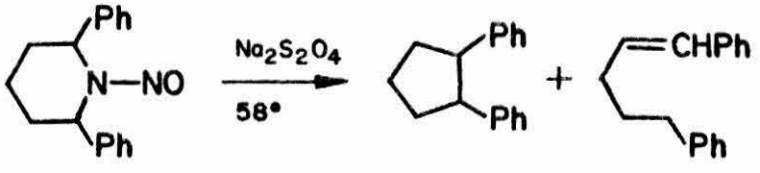


Figure 2. The Reactions of 1,1-Diazenes.

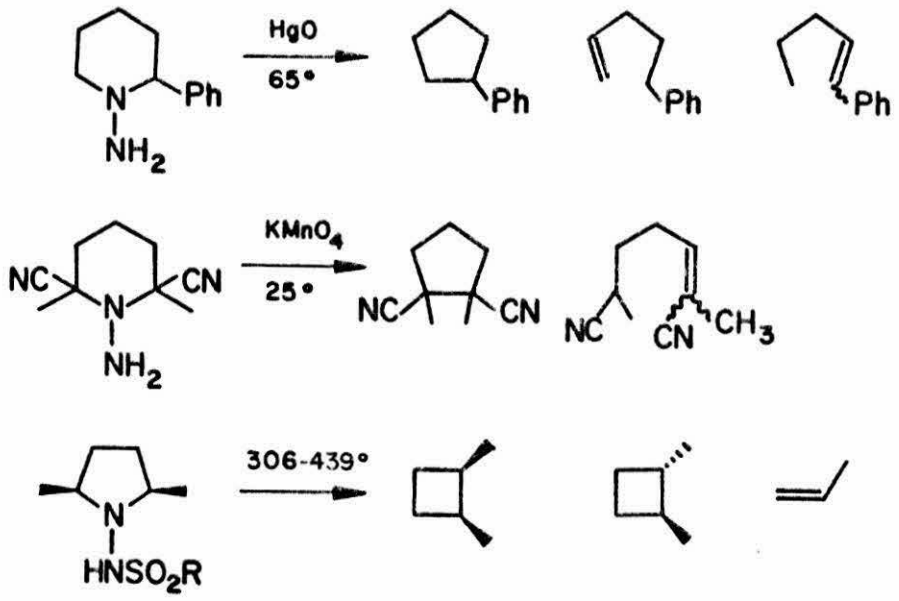
Fragmentation reactions with loss of molecular nitrogen are the decomposition processes of 1,1-diazenes which have been studied in greatest detail. Depending on the structural details of the molecule, substituent-assisted fragmentation, concerted fragmentation or a combination of both may occur. The substituent-assisted process was first observed by Busch and Weiss in 1900:[23]



This mode of fragmentation has also been observed in cyclic cases, with analogous products; for example:[18]

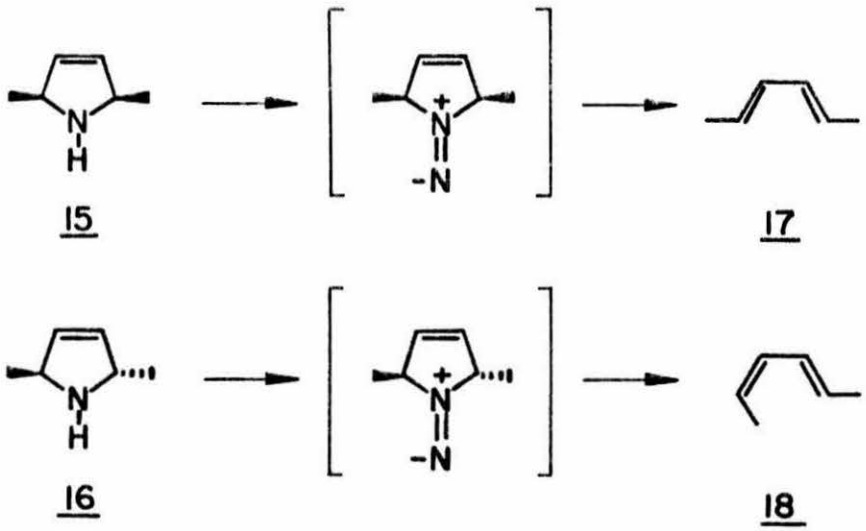


It has been demonstrated that, under appropriate conditions, a variety of substituents and substitution patterns will suffice in making this a dominant decomposition pathway:[16,25,26]



In general, the experimental results are in accord with a mechanism involving radical or biradical species. However, cases are known[16] which may involve competitive biradical and concerted pathways.

Concerted fragmentation of 1,1-diazenes may occur in a number of cases. The stereochemical outcomes of certain decompositions have been in accord with those predicted on the basis of orbital symmetry considerations.[27] For example, McGregor and Lemal found that cis and trans-2,5-dimethyl-3-pyrolline (15 and 16, respectively), when treated with sodium nitrohydroxamate, yielded only the trans-trans and the cis,trans-hexadienes (17 and 18) respectively.



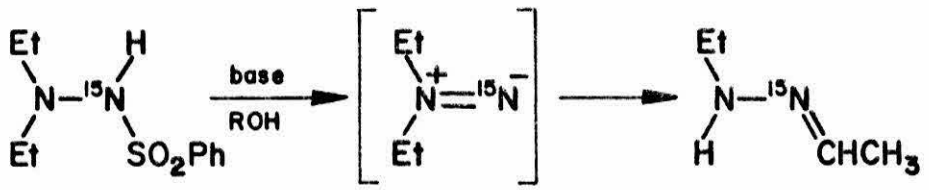
15 17

16 18

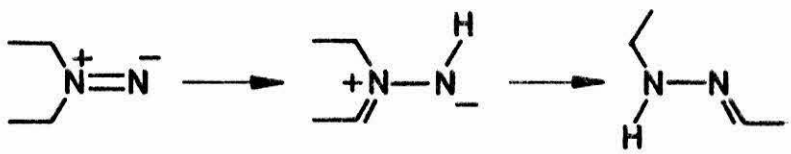
These results are consistent with the disrotatory opening of the intermediate 1,1-diazene.[28] Analogous low-energy concerted pathways have been exploited, for example, in a study of ortho-xylylene ring-closure stereochemistry,[29] and as a mild method for the generation of ortho-benzyne.[30]

Isomerizations of 1,1-diazenes generally take one of two forms: (a) rearrangement of the 1,1-diazene 1 to an isomeric hydrazone 12 or (b) rearrangement to a 1,2-diazene 11 or 14. The formation of hydrazones is a general reaction for all 1,1-diazenes which possess an alkyl C-H bond alpha to the nitrogen functionality.[3] Hydrazones are observed in such cases only when the 1,1-diazene is generated in a protic medium; labelling experiments have demonstrated that the "nitrene" nitrogen ends up as the doubly bonded

nitrogen in the product:[31]



This isomerization has been the subject of intensive research, yet the mechanism remains unknown. 1,2-Diazenes and diaziridines have been ruled out as possible intermediates.[32] At present the reaction is regarded as proceeding through an azomethinimine[3a] 19 which is analogous to the



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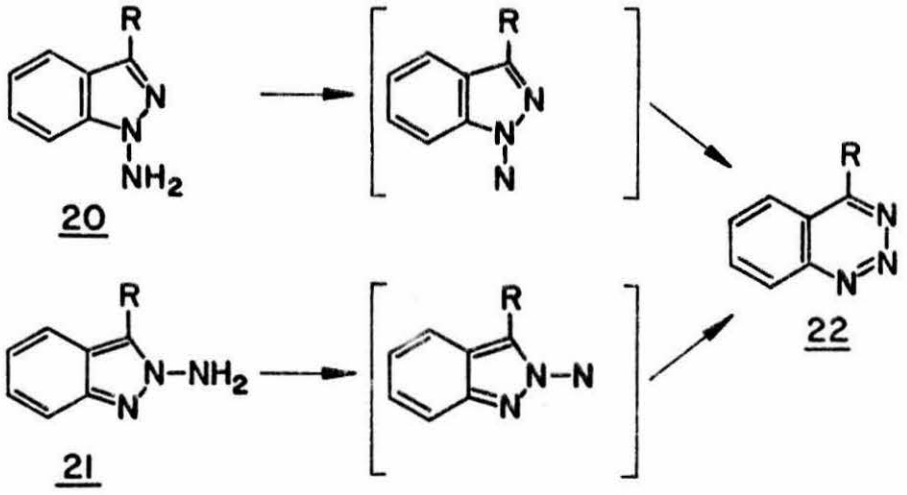
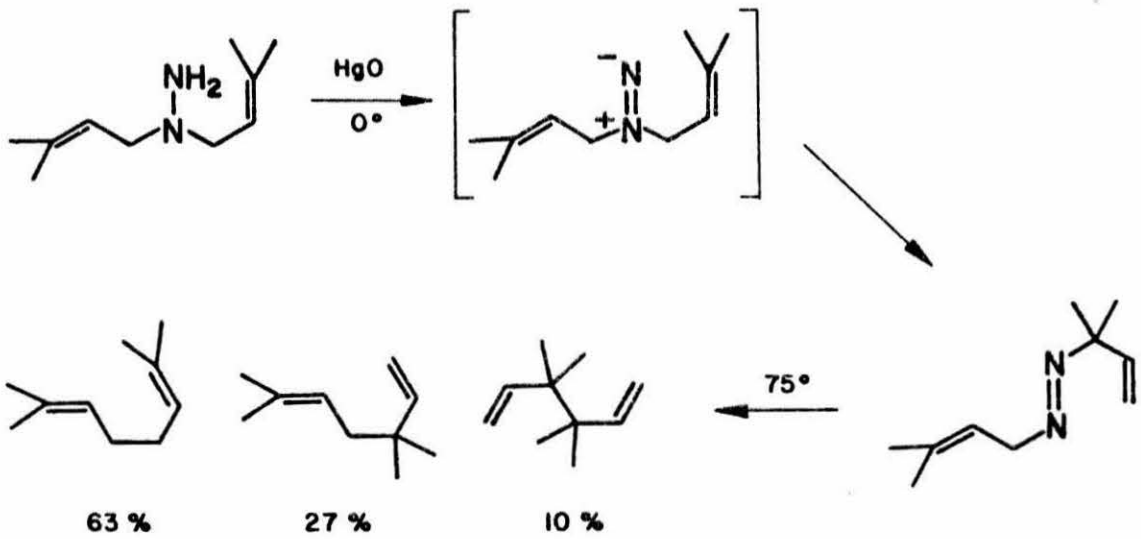
enol form of a ketone. Therefore, the function of the protic solvent may be to facilitate tautomerization of the 1,1-diazene.

Ring expansions of presumed 1,1-diazenes to 1,2-diazenes occur in certain cases where the resulting azo linkage is incorporated in an aromatic system. As an example, Rees and coworkers found that lead tetraacetate oxidation of either 20 or 21 resulted in formation of the

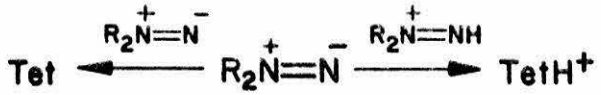
benzotriazine 22.[33]



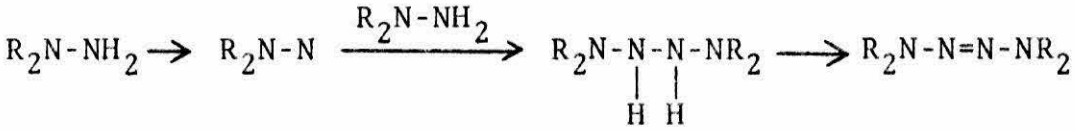
1,2-Diazenes have also been shown to arise from the 2,3-sigmatropic rearrangements of allyl-substituted 1,1-diazenes. The work of Michaelis and Luxemburg[5] provides an example of this (see above). Their early observations have been confirmed and the scope of the reaction broadened by the work of Baldwin and coworkers;[34] they provide evidence that the reaction proceeds in a concerted manner, rather than by a dissociation-recombination route.



The bimolecular chemistry exhibited by 1,1-diazenes includes the formation of tetrazenes 11, addition to π-bonds, and trapping by sulfoxides. The formation of tetrazenes is the most general reaction of 1,1-diazenes. Although tetrazenes are formally the head-to-head dimers of diazenes, it is likely that under most conditions such coupling does not occur and that the tetrazene product arises from some alternative pathway.[3a] For example, the neutralization of solutions of 1,1-dialkyldiazenium ions leads to the formation of tetrazenes[12] probably by reaction of the diazene with a diazenium ion 5. Similarly, in



certain cases the intermediate diazene formed in the oxidation of a 1,1-disubstituted hydrazine might intercept a molecule of starting material yielding a tetrazane 23 which under the reaction conditions reacts further to yield tetrazene. Evidence for this mechanism has been obtained by Rees and coworkers.[35] They have isolated from the lead tetraacetate oxidation of N-aminophthalimide a 90% yield of



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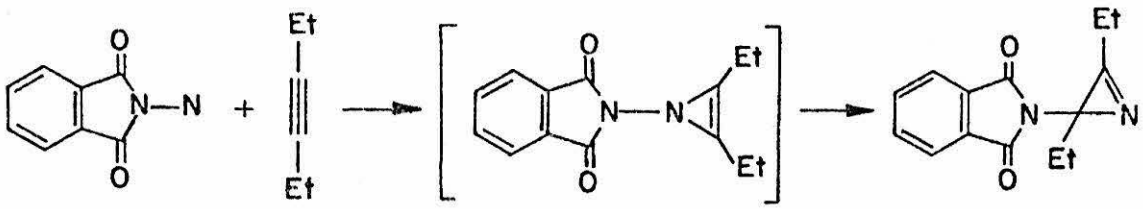
the corresponding tetrazane, which on further oxidation afforded tetrazene. Simple bimolecular dimerization of 1,1-diazenes probably occurs under certain circumstances, for example, in the decomposition of 1,1-dialkyl-2-sulfonylhydrazine salts in aprotic media.[15b]

Simple 1,1-dialkyl diazenes have not been found to undergo addition reactions to π bonds and to dimethyl sulfoxide. Such behavior is exhibited only by diazenes sub-

stituted with electron-withdrawing (e.g., acyl) groups and by diazenes in which the lone pair on the trivalent nitrogen is part of an aromatic system. Such substituents, by delocalization of the amino lone pair electrons, apparently increase the electrophilic character of the "nitrene" nitrogen.[3a] Experimental evidence indicates that the addition of diazenes to alkenes is > 95% stereospecific, even at low alkene concentrations.[36] By analogy to carbene chemistry[37] this is generally taken as evidence that the 1,1-diazene reacts as a singlet and furthermore that the singlet is the ground state. 1,1-Diazenes have been shown to add to both electron-rich and electron-poor olefins.[36b,38] Rees and coworkers have succeeded in adding phthalimidonitrene to acetylenes; the resulting antiaromatic 1-H-azirines 24 undergo a spontaneous rearrangement to 2-H isomers 25:[39]



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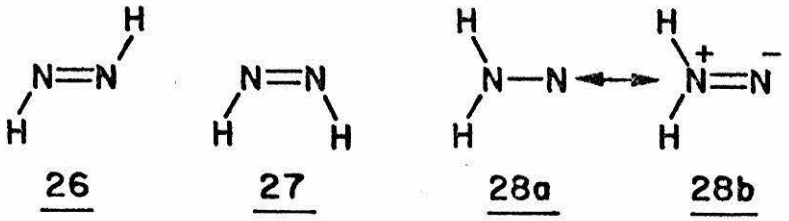
Theoretical Studies of 1,1-Diazenes.

Due to the high reactivity of the systems involved, solid experimental information regarding the properties of the N_2H_2 isomers, 26, 27, and 28 is difficult to obtain.[40] Theoreticians have devoted much time to studies



of the N_2H_2 energy surface,[41-65] investigating the nature of the bonding, the ordering of states, the relative energies of the three isomers, the mechanisms of interconversion of the isomers, the reactions of N_2H_2 species with alkenes, and the energetics of N-H bond cleavage for the isomeric diimides.

The most important question concerning the electronic structure of 1,1-diazene 28 is of the nature of the ground electronic state. Is it a triplet like other nitrenes, or a singlet, as the chemical behavior of 1,1-diazenes implies? Table 1 lists the results of a number of theoretical investigations into this question. It is apparent after an examination of the results that, as the calculational methods become increasingly sophisticated (e.g., by

Table 1

Singlet-Triplet Energy Gap in H_2N-N

Calculational Method	Ground State	S-T Gap*	Reference
STO-3G	T	26.3	49
4-31G	T	11.7	64
HF	T	5.2	54
SCF**	T	2.1	50
4-31G + CI	S	1.6	59
GVB-CI	S	13.8	60

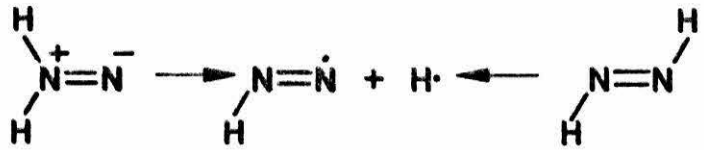
*kcal/mole; both states at equilibrium geometries.
**Restricted open shell - SCF.

employing larger basis sets and extensive configuration interaction), the energy of the triplet increases relative to the singlet. This trend is not unexpected; several of the authors explicitly state that the calculational methods they employed tend to overestimate the stabilities of triplet states.[49,64] The two most recent sets of calculations indicate that the singlet is the ground state.[59,60]

The most recent of these calculations, that of Davis and Goddard,[60] is the most extensive and will be dealt with here in some detail. From their study, the following picture of the parent 1,1-diazene emerges (see Figure 3a). The ground state is a singlet (S_0) of planar geometry, with the dipolar form 28b making a substantial contribution to the electronic structure of the 1,1-diazene. The

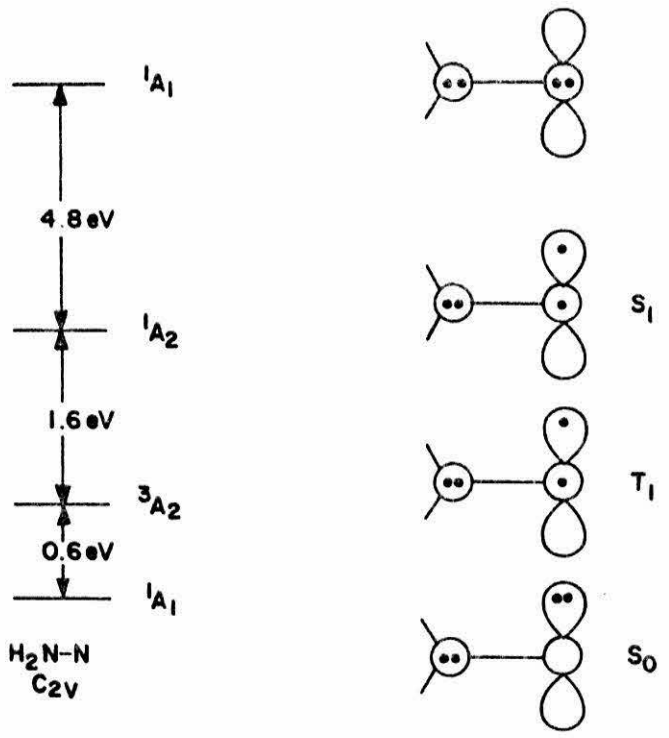
triplet state (T_1) lies 0.6 eV (14 kcal/mole) above the ground state and is also of planar geometry. The first excited singlet (S_1) lies 2.2 eV (51 kcal/mole) above the ground state. The configuration of S_1 corresponds to an n-π^* excited state. Thus the calculations predict that the 1,1-diazene should absorb light at 2.2 eV (560 nm) and hence should be detectable by electronic absorption spectroscopy in the visible region. The N-N bond length calculated for 28 (S_0) is 1.25 Å, identical to the experimental value observed for the 1,2-isomer 26;[66] it is reasonable to expect that 28 will exhibit a N=N stretching vibration in the infrared at a frequency similar to that observed in the Raman spectrum of 26 (1529 cm^{-1}).[67]

Casewit and Goddard have recently performed a set of ab initio calculations investigating the thermochemistry of 26 and 28 (see Figure 3b).[42] Their GVB-CI calculations give a N-H bond energy in the 1,1-isomer 28 of 42.0 kcal/mole and a N-H bond energy in the 1,2-isomer 26 of 71.4



28 26

(a)



(b)

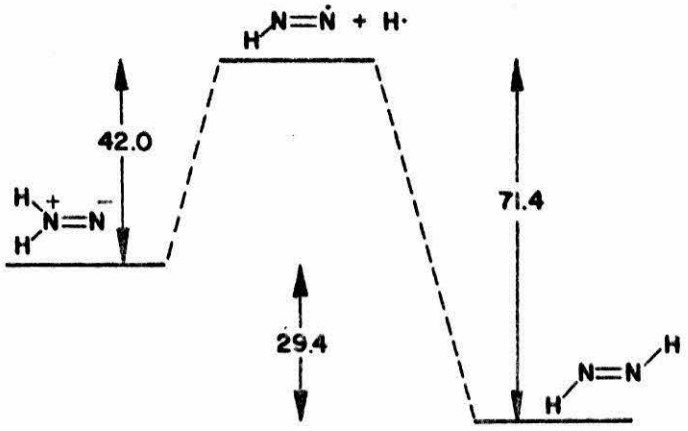
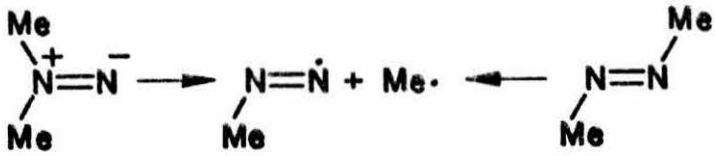


Figure 3 (a) GVB-CI calculations[60] for H_2N-N (C_{2v} symmetry); (b) GVB-CI calculations[42] for the H_2N_2 energy surface and the diazenyl radical H-N=N·.

kcal/mole. Thus the N-H bond in 28 is weaker by ∿ 30 kcal/mole. These calculated bond energies may be used to estimate the C-N bond strengths in alkyl substituted 1,1- and 1,2-diazenes by application of a correction for the difference between a N-CH_3 and a N-H bond (based on D(HMeN-H) - D(HMeN-Me) = 18.5 kcal/mole).[68a] In this manner, Casewit and Goddard estimate the bond energy in 1,1-dimethyldiazene 29 to be 23.5 kcal/mole. Application



29 30

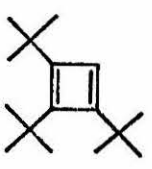
of this correction to the N-H bond energy calculated for 26 leads to a predicted value for the C-N bond strength in 1,2-dimethyldiazene 30 of 52.9 kcal/mole; this is in excellent agreement with the observed activation energy of 52.5 kcal/mole for the thermal decomposition of 30.[68b]

Pasto and Chipman[65] carried out calculations at the STO-3G level on the energetics of the homolytic breakdown of 29. They find the C-N bond energy to be 26.2 kcal/mole, in accord with the estimates of Casewit and Goddard.

Experimental Strategy

The study of reactive intermediates has required the development of many specialized techniques. A number of elegant methods have been applied to the study of such molecules: the use of superacid media for the study of carbonium ions,[69] the use of matrix isolation techniques;[70] flash spectroscopy,[71] and reactant design such that once the intermediate is formed further reaction is slow.[72-74] For the study of 1,1-dialkyl diazenes this last method appears to be the most desirable. It would allow the study of 1,1-diazenes in solution phase by using simple modifications of the spectroscopic techniques commonly employed by organic chemists, such as UV-visible, infrared and nuclear magnetic resonance spectroscopy.

We were encouraged by work in the literature concerning the benefits derived from the synthesis of "persistent" radicals,[72] radicals which may or may not be stabilized by resonance and inductive effects but which are long-lived and therefore subject to spectroscopic inspection because the rate of bimolecular reaction has been drastically slowed down by a steric blockade (see Table 2). The persistent radicals, with a suitable arrangement of bulky groups, have half-lives varying from seconds to years whereas, under similar conditions, transient radicals would have half-lives of less than a millisecond. Since the persistent radicals can easily be prepared in relatively high concentrations, their structural and chemical properties can be examined with an ease and accuracy impossible to attain with transient radicals. The general concept of sterically induced persistence has been exploited in cases involving non-radical intermediates; for example cyclobutadiene and cyclopentadienone, both of which undergo facile dimerization reactions, have been studied in the form of the suitably substituted derivatives 31[73a] and 32.[73b]



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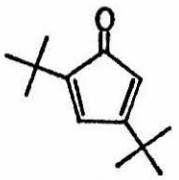

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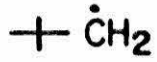
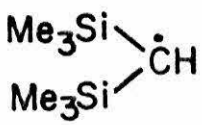
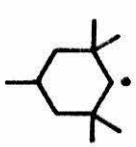
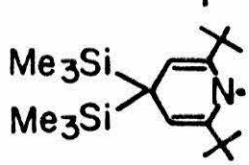
Table 2

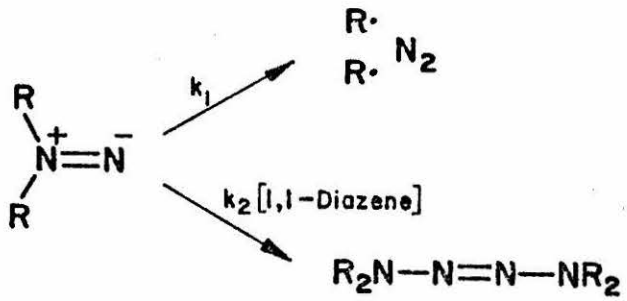
Radical Decay Lifetimes[72]

Not Persistent	$\log t_{1/2}$(sec)*	Decay Kinetics
	- 4.3	second order
	- 3.3	second order

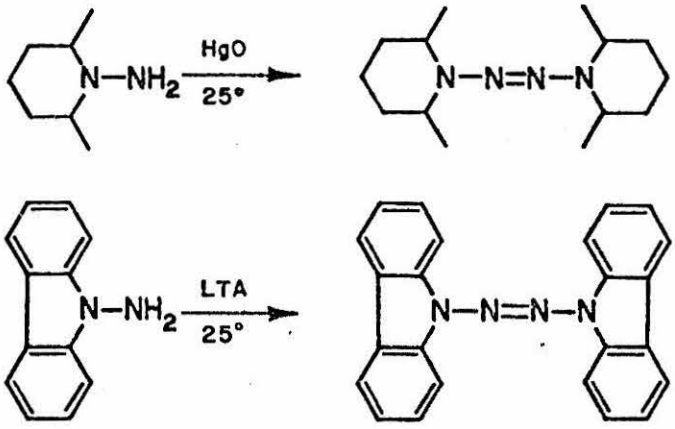
Persistent	$\log t_{1/2}$(sec)*	Decay Kinetics
	2.4	first order
	3.3	first order

*Calculated at 25° and at radical concentrations of 10^{-5}M.

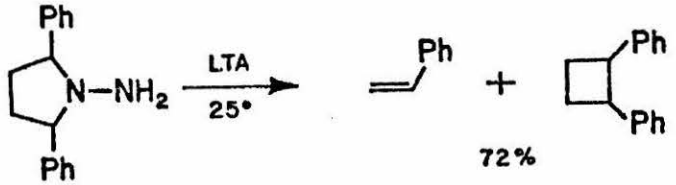
In order to synthesize a "persistent" 1,1-dialkyldiazene two properties must be incorporated in the chosen structure. First, there must be no facile unimolecular fragmentation pathway, and second, there must be a steric blockade to prevent dimerization to tetrazene. The



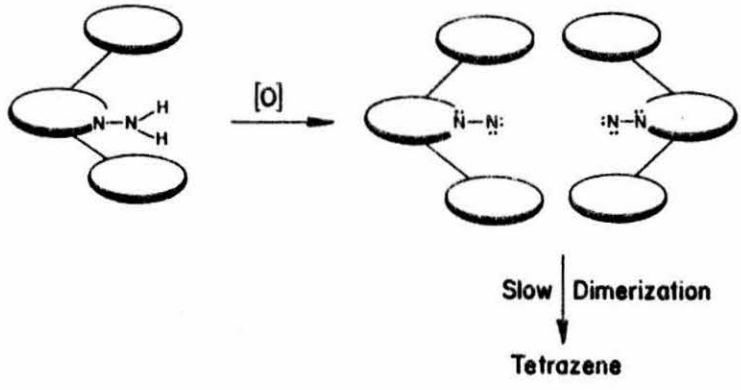
first of these properties may be controlled by appropriate choice of α-substituents. Some cases are known that afford only tetrazene at 25°,[3a,74] whereas others give



high yields of decomposition products:[3a,b,24]



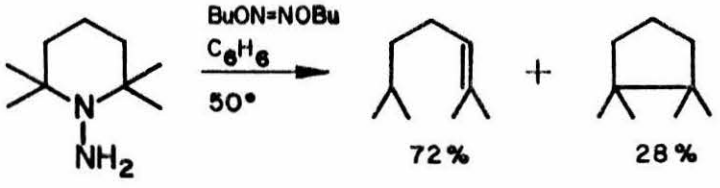
Presumably alkyl and phenyl (but not benzyl) substituted 1,1-diazenes are sufficiently stable to fragmentation at room temperature and below that tetrazene formation occurs. The second property, the steric blockade, may be controlled by the placement of suitably bulky groups such that the dimerization rate to tetrazene is drastically reduced. A simple chemical system which potentially has



the required properties outlined above is that of the tetramethylpiperidylnitrene 33. This system has the

33

added advantage that it lacks α-C-H substitution, thus preventing any 1,1-diazene → hydrazone rearrangement. In an ESR investigation of hydrazyl radicals Ingold and coworkers had cause to investigate the products resulting from the oxidation of the 1,1-hydrazine 36 with t-butyl hyponitrite.[76] They reported the isolation of the hydrocarbons 37 and 38 which are consistent with the intermediacy of the 1,1-diazene 33. The results of our investigations of this model system are discussed below.



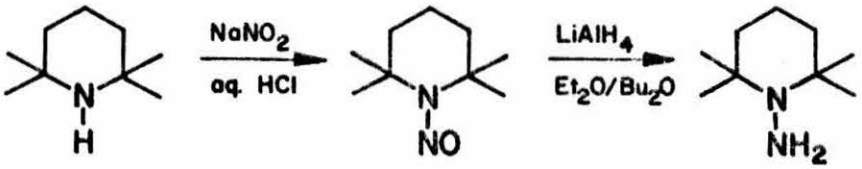
36 37 38

Part II

RESULTS AND DISCUSSION

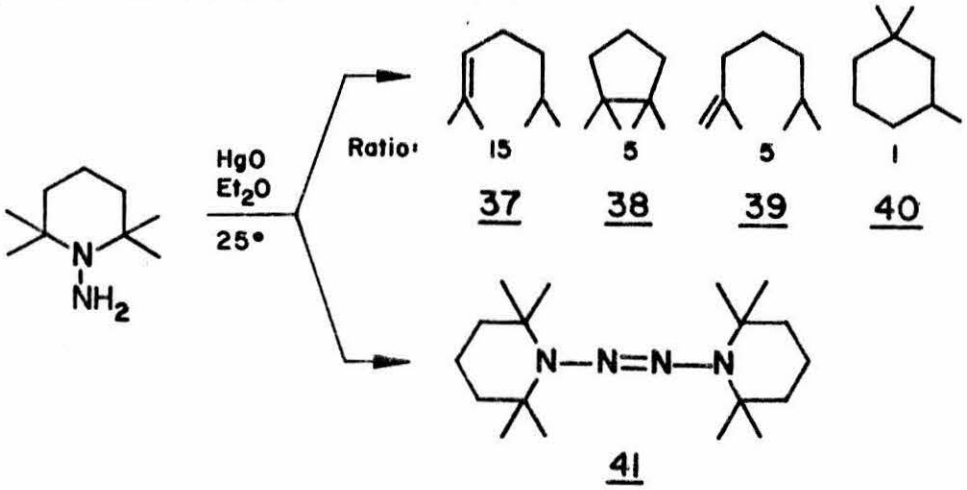
The Synthesis of N-(2,2,6,6-Tetramethylpiperidyl)nitrene (33).

The synthesis of the potential 1,1-diazene precursor 1-amino-2,2,6,6-tetramethylpiperidine (36) is straightforward, employing a standard nitrosation[6] of the commercially available amine 34 followed by lithium aluminum hydride reduction under forcing conditions:[75]



34 35 36

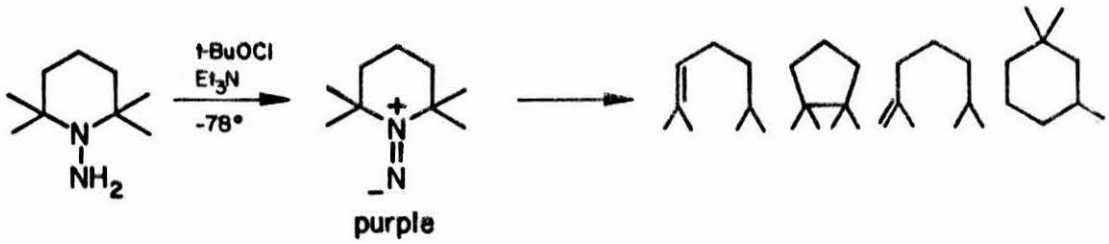
A characterization of the products resulting from the oxidation of 36 was first undertaken. We find that oxidation of 36 in ethyl ether with yellow mercuric oxide at 25° affords, in addition to 37 and 38, small amounts of the isomeric hydrocarbons 39 and 40 in the following approximate ratios:



A typical absolute yield of the C_9 hydrocarbons was 65%. In addition an absolute yield of 20% of the corresponding tetrazene 1,1'-azo-2,2,6,6-tetramethylpiperidine 41 was found by proton NMR examination of the reaction products. These products are, in general, consistent with the formation and subsequent decomposition of the corresponding 1,1-diazene 33. The trimethylcyclohexane 40 is a rather surprising product in that it does not appear to be derived from the expected 1,5-biradical. Possible mechanisms for its formation will be discussed later.

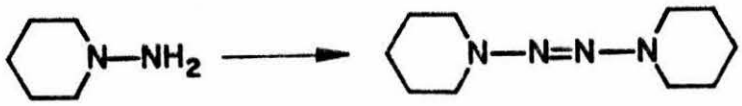
Oxidation studies aimed at generating and detecting the 1,1-diazene were undertaken. The oxidation of 1,1-disubstituted hydrazines with t-butyl hypochlorite in the presence of a tertiary amine is known to proceed readily at low temperatures (-78°) and to yield products consistent with the intermediacy of 1,1-diazenes.[34] We find that the addition of t-butyl hypochlorite to a stirred solution of 36 and triethylamine in anhydrous diethyl ether affords, in addition to an insoluble white precipitate (identified by infrared spectroscopy as triethylamine hydrochloride) an intense purple solution which is stable for hours at -78° but decolorizes in minutes at 0°. Hydrocarbon products 37-40 are observed

in 14-24% yield in a ratio of 24:9.7:2.5:1.0 respectively



36 33 37 38 39 40

by analytical vapor phase chromatography (VPC). Generation of this solution at -78°, followed by filtration at -78° gives a clear, transparent purple solution. Significantly, treatment of the unhindered analogue of 36, 1-aminopiperidine, with t-butyl hypochlorite under identical conditions leads to no such colored solution. After warming, the corresponding tetrazene was detected as a reaction product:



In the following sections the characterization of this colored intermediate and further investigations are described and discussed.

The Electronic Spectrum of N-(2,2,6,6-Tetramethylpiperidyl)-nitrene (33).

The visible absorption spectrum of the colored

ethereal solution described in the previous section was obtained at ∿ -78° using a low-temperature spectroscopic cell. The spectrum reveals a structured absorption band with two maxima at 514 and 543 nm (Figure 4), remarkably close to the $n \rightarrow \pi^*$ electronic transition predicted by Davis and Goddard for the parent system $H_2N\text{-}N$.[60]

The detail in this electronic spectrum appears to be vibrational structure. Although the spectrum is not sufficiently resolved that we can read the wavelengths to any great accuracy, a crude analysis shows the spacings between maxima to be 1040 ± 50 cm^{-1}. Qualitatively the overall appearance of the spectrum is in accord with that expected for a chromophore X-Y whose X-Y separation is slightly larger in the excited state than in the ground state.[77] The energy difference between maxima in the electronic spectrum presumably corresponds to the vibrational level spacing in the excited state of the 1,1-diazene chromophore.

The position of an absorption that involves nonbonding electrons ($n \rightarrow \pi^*$) is particularly sensitive to the polarity and hydrogen bonding capabilities of the solvent. We find that the visible spectrum of the 1,1-diazene 33 is subject to a blue shift with increase in solvent polarity analogous to solvent effects on the

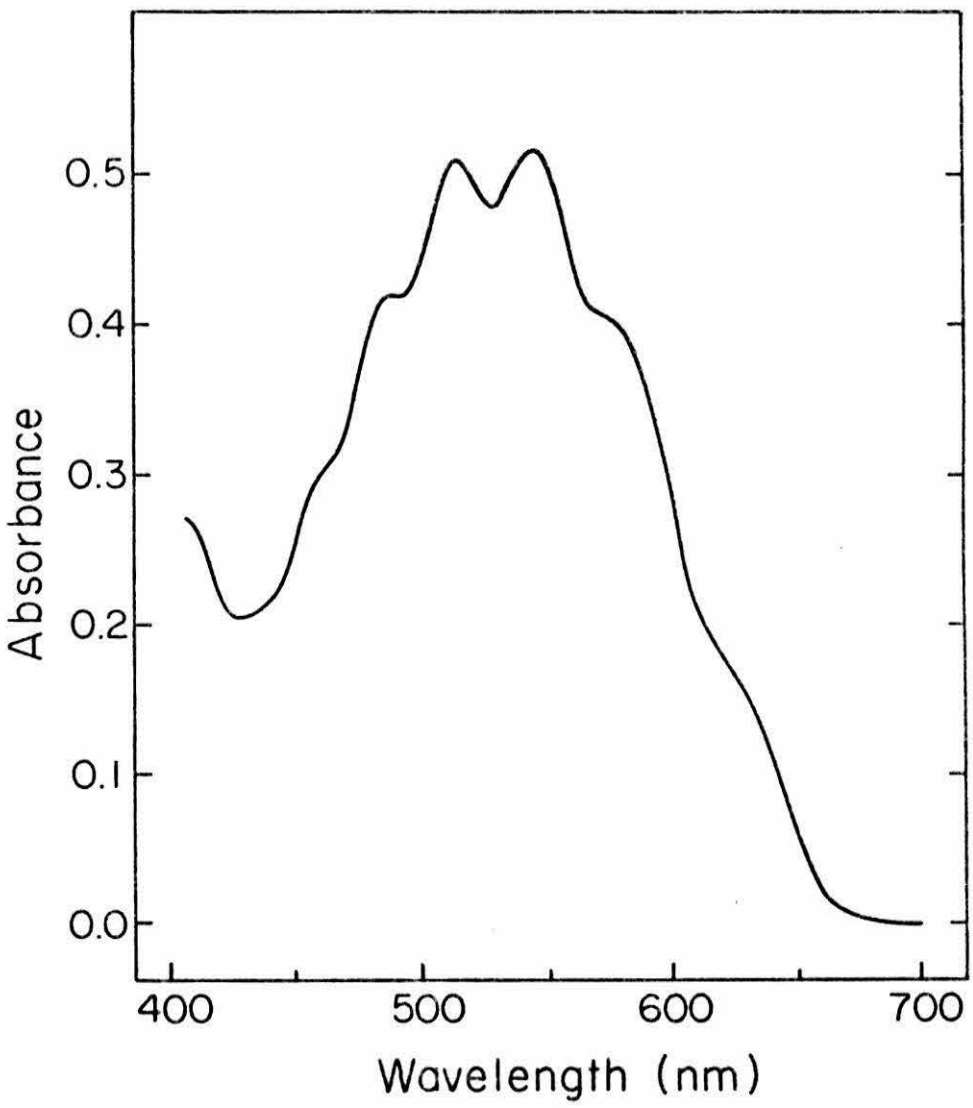


Figure 4. Visible spectrum of 33 at -78° in diethyl ether.

$n \rightarrow \pi^*$ transition of the carbonyl group.[78] When t-butyl hypochlorite is added to 36 in the presence of triethylamine in dimethyl ether at -78°, filtered, concentrated, and diluted with dichloromethane, a λ_{max} at 541 nm is observed. However, if the dimethyl ether is replaced with isopropyl alcohol, a λ_{max} at 526 nm is observed, a shift of 15 nm (1.5 kcal/mole) to shorter wavelength (see Figure 5). An interpretation consistent with this result is that the shift to higher energy for the $n \rightarrow \pi^*$ electronic transition in isopropyl alcohol results from stabilization of the ground state in the more polar solvent. Part of the blue shift could arise from the destabilization of the Franck-Condon excited state in the hydrogen-bonding solvent.[79] For comparison, the $n \rightarrow \pi^*$ transition of acetone shifts from 277 nm in chloroform to 272 nm in ethanol,[78] a shift of 5 nm (1.9 kcal/mole).

Due to the symmetry-forbidden nature of $n \rightarrow \pi^*$ electronic transitions the molar extinction coefficients (ε_{max}) observed are usually quite low. For example, $\varepsilon_{max} \sim 14$ for the acetone $n \rightarrow \pi^*$ transition in the vapor phase.[80] In accord with our assignment of the observed transition as $n \rightarrow \pi^*$, we find that the extinction coefficient of 33 at 543 nm in diethyl ether (ε_{max}) equals

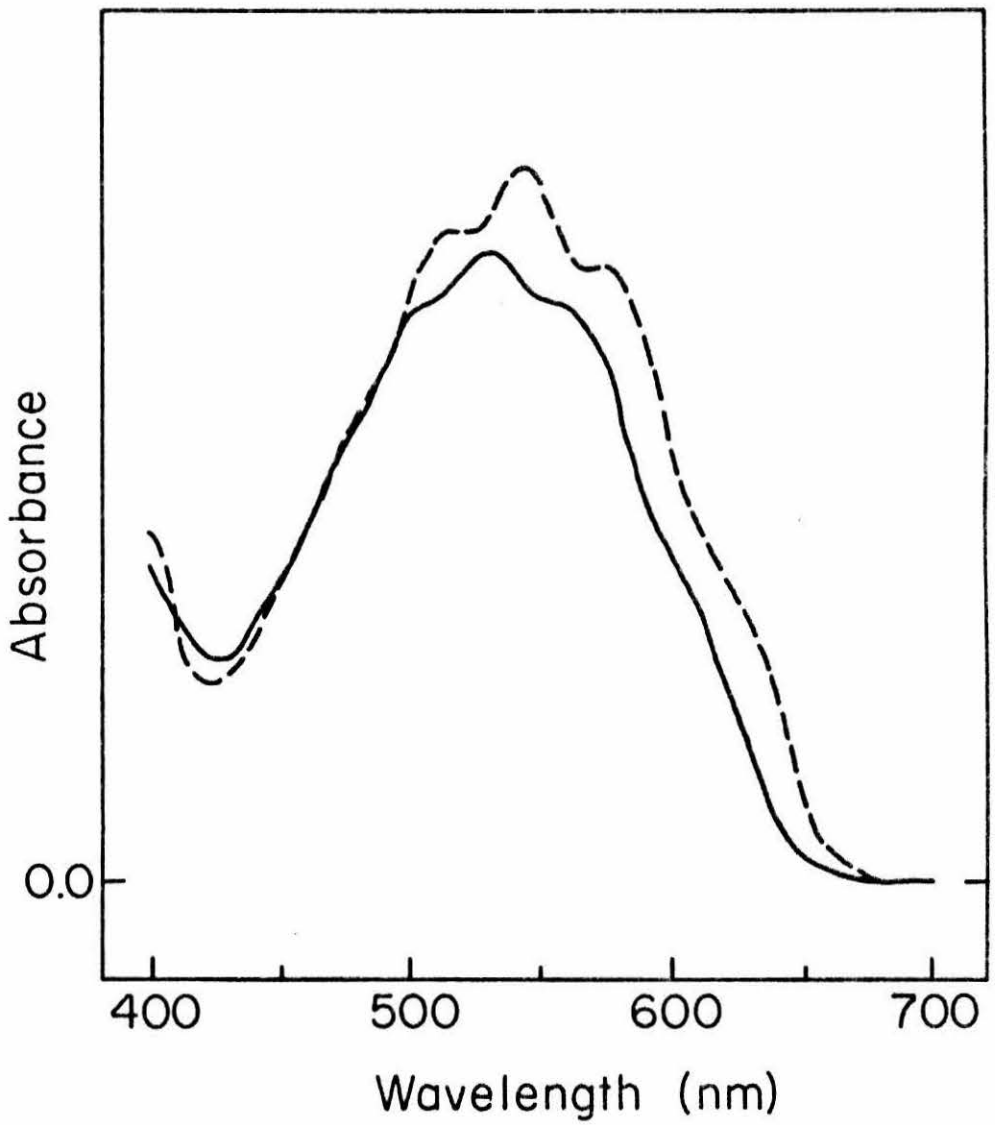
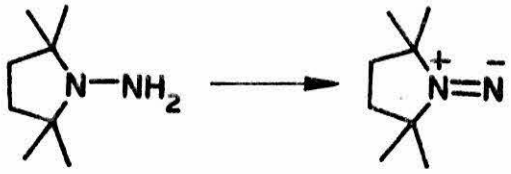


Figure 5. Visible spectrum of 33 at -78° in dichloromethane, λ_{max} 541 nm (---); in isopropyl alcohol, λ_{max} 526 nm (——).

18 ± 3 as measured by a combination of proton NMR and electronic absorption spectroscopy (see Experimental Section).

Recently the electronic spectrum of a second 1,1-dialkyldiazene has been recorded in our laboraties by Schultz.[81] Oxidation of 1-amino-2,2,5,5-tetramethyl-pyrollidine (42) with t-butyl hypochlorite in a manner identical to that described here yields an intense red solution, which is stable for hours at -78° but which decolorizes rapidly at room temperature. Low temperature



42 43

absorption spectroscopy in dichloromethane at -78° reveals a structured absorption band due to 43, quite similar to that observed for 33, but with a λ_{max} at 497 nm; in isopropyl alcohol this band is shifted to λ_{max} 487 nm. For comparison, it is found that the isoelectronic ketones

44 45

similar in structure to the diazenes 33 and 43 (44 and 45, respectively) display a similar change in λ_{max} with change in ring size; in ethyl ether the n → π* absorption of 44 shows a λ_{max} = 305 nm, while that of 45 shows a λ_{max} = 296 nm.

The Infrared Spectrum of N-(2,2,6,6-Tetramethylpiperidyl)-nitrene (33).

When t-butyl hypochlorite is allowed to react with 36 in dimethyl ether in the presence of triethylamine and the reaction mixture is filtered, concentrated, diluted with dichloromethane at -78° and introduced into a low temperature infrared cell at ∿-78° the infrared spectrum shows a strong absorption at 1595 cm^{-1} that disappears when the solution is warmed to 25° (see Figure 6a). This is suggestive of a N=N double-bond stretching frequency (see Table 3). In order to test this assignment, application of Hooke's Law[85] allows an approximation of the stretching frequency change which should be observed upon synthesis of the appropriate $^{14}N{=}^{15}N$ isotopically labelled 1,1-diazene 46. The $\nu(^{14}N{=}^{14}N)/\nu(^{14}N{=}^{15}N)$ ratio calculated in this manner is 1.0171. Thus, the predicted N=N stretching frequency for the labelled 1,1-diazene 46 is 1568 cm^{-1}.

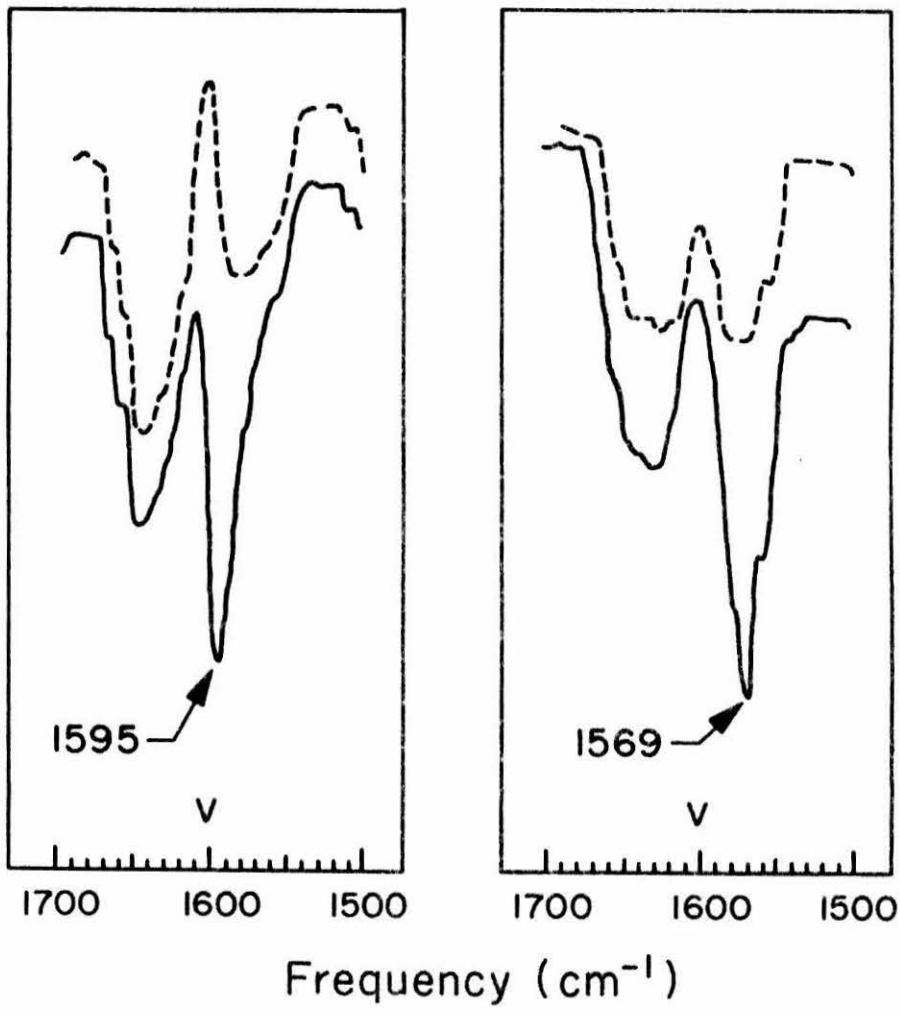
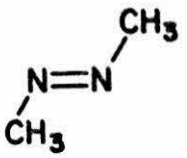
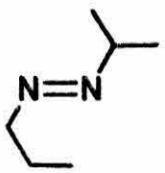
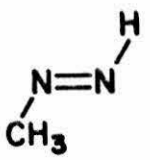


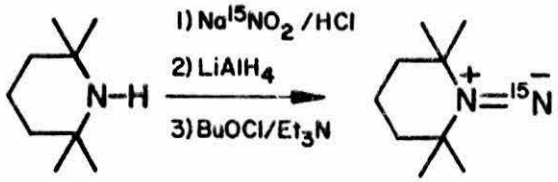
Figure 6. (a) R_2 $^{14}N=^{14}N$; (b) R_2 $^{14}N=^{15}N$. At -78° (——); at -78° after warming to 25° (---).

Table 3

Reported N=N Stretching Frequencies

Compound	ν(N=N) (cm^{-1})	Reference
	1576	82a
	1563	82b
	1545	83
	1575	84

Successive treatment of 2,2,6,6-tetramethylpiperidine 34 with sodium nitrite-^{15}N, lithium aluminum hydride



34 46

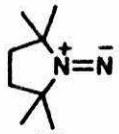
and t-butyl hypochlorite/triethylamine afforded the labelled 1,1-diazene 46, the infrared spectrum of which showed no absorption at 1595 but rather a new absorption at 1569 cm^{-1}, a shift of 26 cm^{-1} consistent with the assignment to a N=N stretch for the 1,1-diazene 33 (see Figure 6b). These results suggest that there is considerable double-bond character in the 1,1-dialkyldiazene N=N bond, remarkably close to a 1,2-diazene isomer. This is in complete accord with the calculations of Davis and Goddard.[60]

A comparison of these IR spectra to similar data recently obtained on the homologous N-(2,2,5,5-tetramethylpyrollidyl)nitrene (43) is instructive.[81] It was found that, in dichloromethane solution at -78°, the diazene 43 exhibits a N=N stretching frequency at 1638 cm^{-1}, and substitution with nitrogen-15 lowers this vibration to

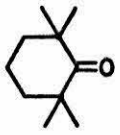
1612 cm^{-1}; thus the effect of 6 → 5 ring contraction is an increase in ν(N=N) of 43 cm^{-1}. Interestingly, we find that in dichloromethane the ketones of similar structure (44 and 45) show shifts of the same magnitude in the C=O stretching frequency:

33

ν(N=N) = 1595 ←Δ = 43 cm^{-1} → ν(N=N) = 1638

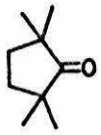


43



44

ν(C=O) = 1690 ←Δ = 40 cm^{-1} → ν(C=O) = 1730



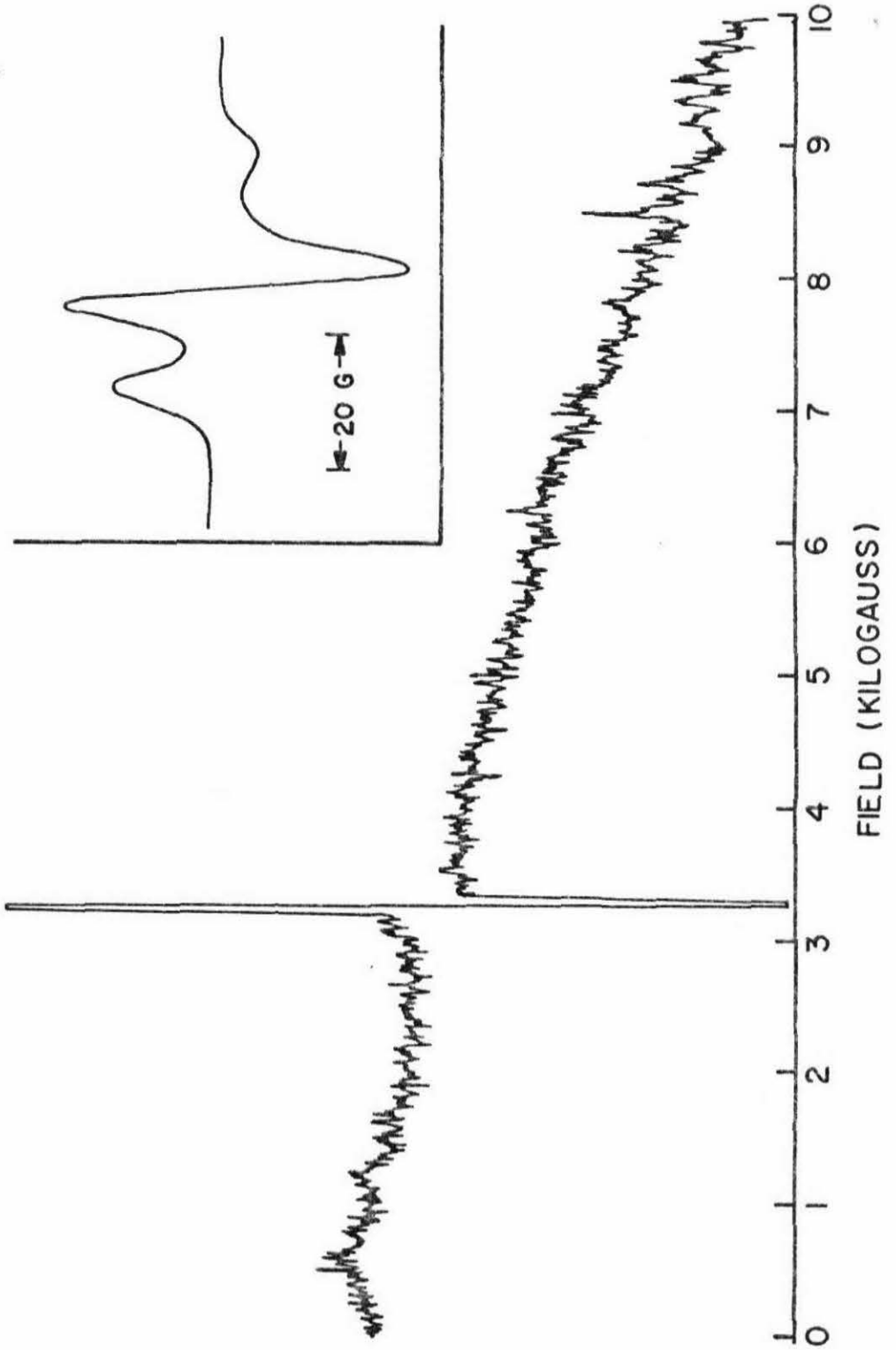
45

A possible explanation of this effect in ketones has been put forward by Coulson.[86] As the C-CO-C bond angle decreases, the carbonyl carbon has greater p-orbital character in the orbitals of the ring with a consequent increase in the s-orbital character of the C-O σ-bond. This in turn increases the force constant of the carbonyl group and causes an increase in the frequency of the carbonyl stretching vibration. Perhaps a similar mechanism is operating in the 1,1-dialkyldiazenes.

Electron Spin Resonance Spectra of N-(2,2,6,6-Tetramethylpiperidyl)nitrene (33).

The multiplicity of the 1,1-diazene ground state and the singlet-triplet gap have been the subjects of a number of theoretical and indirect experimental studies. As was discussed above, both theory and experiment indicate that the ground state should be a singlet. Direct experimental verification of this by electron spin resonance (ESR) studies would be desirable. Based on the known zero-field parameters of alkyl- and arylnitrenes, the first-derivative ESR spectrum of a triplet 1,1-dialkyldiazene would be expected to exhibit a line in the region of 5000-8500 gauss for a microwave frequency of ∿ 9 GHz.[87] A 0.06 molar solution of 1,1-diazene 33 in chloroform was prepared, degassed and frozen at 77°K in the cavity of an ESR spectrometer. We find no features in the spectrum which can be assigned to a triplet 1,1-diazene, even when operating the spectrometer at high sensitivity (see Figure 7). The only feature in the spectrum is an absorption at ∿ 3300 G due to a monoradical species. At 77°K in the solid phase this absorption has the appearance of a distorted triplet (see inset, Figure 7). After warming the sample to 25° and allowing the diazene to decompose, a solution ESR spectrum was recorded at

Figure 7. ESR spectrum of a 0.06 M solution of 33 at 77°K in chloroform, recorded at high sensitivity at 9.234 GHz. Inset: expansion of the region at ∿ 3300 gauss.


20 G
0
1
2
3
4
5
6
7
8
9
10
FIELD (KILOGAUSS)

$\sim$ 270°K. The signal remains in undiminished intensity, being a well-resolved 1:1:1 triplet with a = 16 gauss. This monoradical is most likely 2,2,6,6-tetramethylpiperidyl-N-oxyl, based on a comparison with its published ESR spectrum.[88] The distorted appearance at 77°K is probably due to viscosity effects.[89] The origin of this nitroxide is unclear. A control experiment demonstrated that the starting material 36 contained no paramagnetic impurities.

Nuclear Magnetic Resonance Spectra of N-(2,2,6,6-Tetramethylpiperidyl)nitrene (33).

Proton nuclear magnetic resonance (NMR) spectra of the diazene 33 were obtained in deuterochloroform. The 1,1-diazene was first partially purified by low temperature (-82°) column chromatography on basic alumina. A representative spectrum (shown in Figure 8) indicates the presence of a substantial amount of tetrazene 41 along with absorptions at δ 1.15 and 2.15 ppm which integrate in a 2:1 ratio; these new absorptions are assigned as the methyl protons and the ring protons, respectively, of the 1,1-diazene 33. Warming the sample to 25° results in complete decolorization of the sample and the disappearance of the signals at 1.15 and 2.15 ppm, while the tetrazene signals increase and new signals appear in the

spectral region where the four hydrocarbons 37-40 absorb (Figure 9). These NMR results indicate that under some conditions the unimolecular decomposition of 33 and the bimolecular dimerization to tetrazene 41 are competitive. Since by addition of an internal standard (CH_2Cl_2) the absolute concentration of 1,1-diazene can be measured, a direct determination of its molar extinction coefficient was possible using proton NMR spectroscopy (see above). In addition the absolute yields and mass balance of the hypochlorite oxidation reaction could be determined by the addition of dichloromethane internal standard to the crude reaction mixture. Integration of the NMR spectrum of the mixture then allowed calculation of the yields.

Carbon-13 NMR spectra of 1,1-diazene solutions, obtained in dichloromethane-d_2 at -80°, exhibit four signals which may be attributed to the diazene 33 (Figure 10). Thermolysis of the sample at 25° results in the disappearance of the 1,1-diazene signals and the appearance of new absorptions due to the tetrazene 41 (Figure 11). Identical experiments using hexadeuteroacetone as solvent demonstrate that no absorptions were obscured by the CD_2Cl_2 quintet (see Figures 12 and 13). The carbon-13 chemical shifts of the diazene 33 and assignments are summarized in Figure 14, along with the chemical shifts

Figure 8. Proton NMR spectrum at -55° of 33;
D = 1,1-diazene, T = tetrazene.

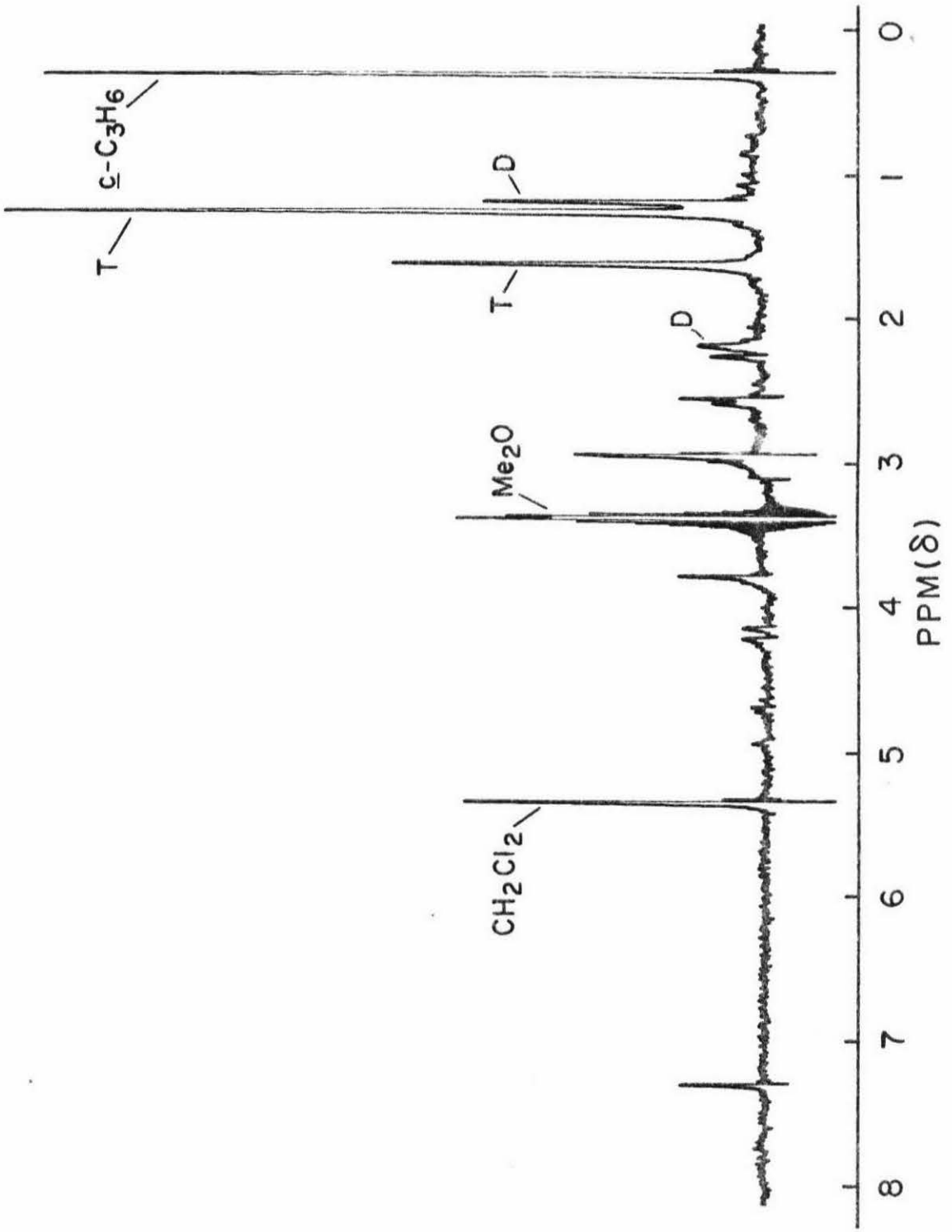

c-C3H6
T
D
T
D
Me2O
CH2Cl2
0
1
2
3
4
5
6
7
8
PPM(δ)

Figure 9. Spectrum after warming sample to 25° (spectrum recorded at -55°); T = tetrazene, H = hydrocarbons.

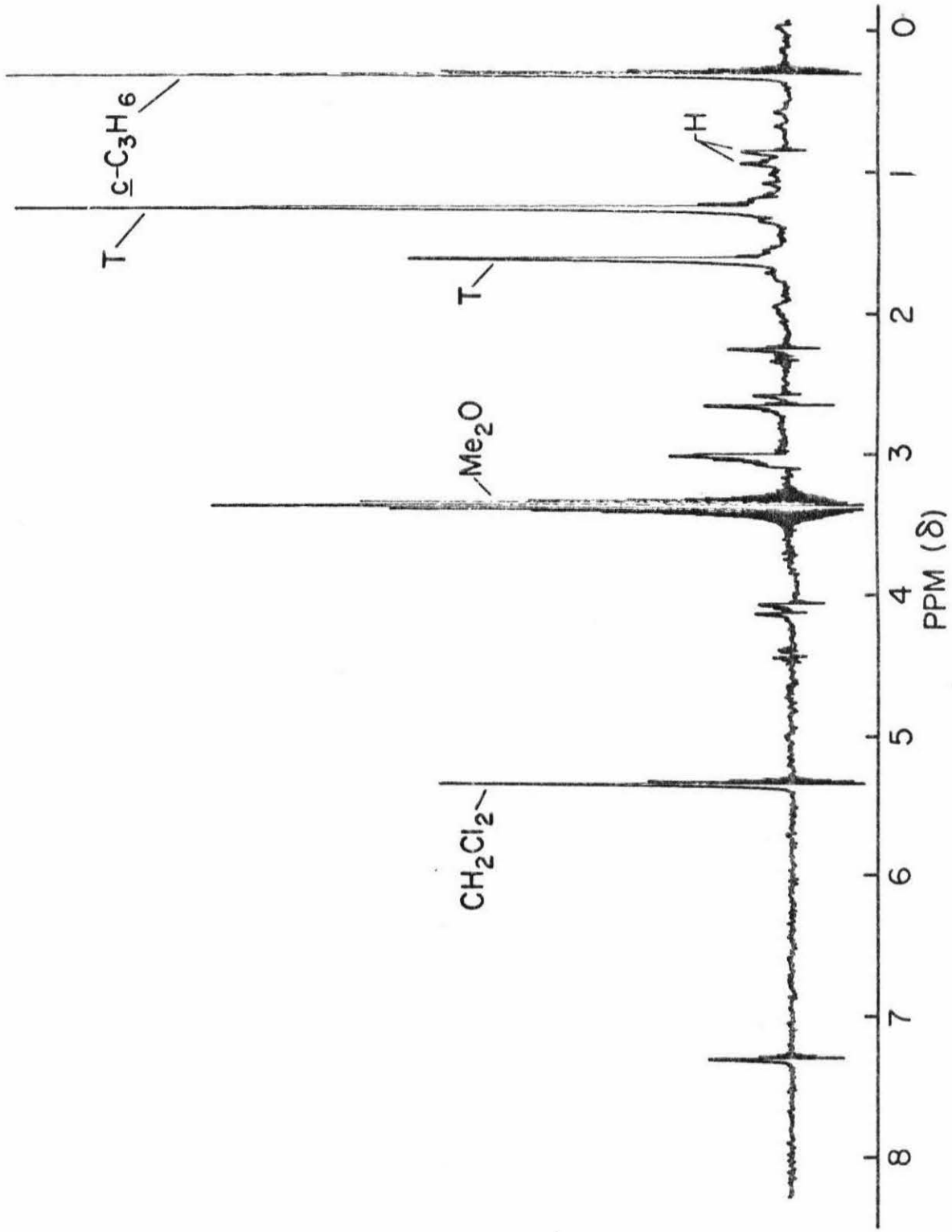

T
c-C3H6
T
H
Me2O
CH2Cl2
0
1
2
3
4
5
6
7
8
PPM (δ)

Figure 10. Carbon-13 NMR spectrum at -80° of a CD_2Cl_2 solution of diazene 33; D = diazene, A = t-butyl alcohol, M = dimethyl ether, N = 1-amino-2,2,6,6-tetramethyl-piperidine, E = triethylamine, T = tetrazene.

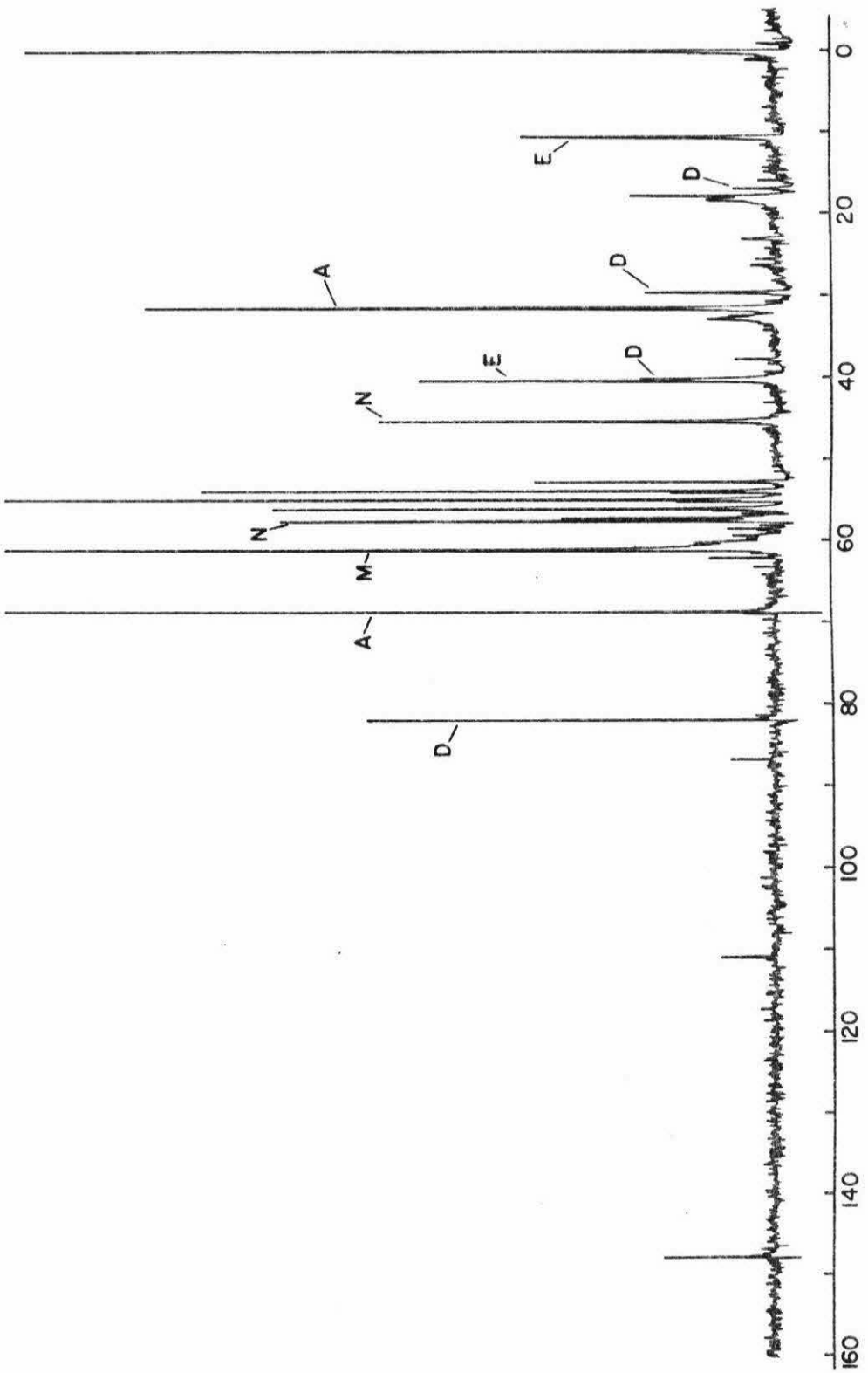

0
20
40
60
80
100
120
140
160
A
D
E
D
D
E
D
N
N
M
A
D

Figure 11. Carbon-13 NMR spectrum at -80° of a CD_2Cl_2 solution of diazene 33 thermolyzed at 25°; see Figure 10 for explanation of symbols.

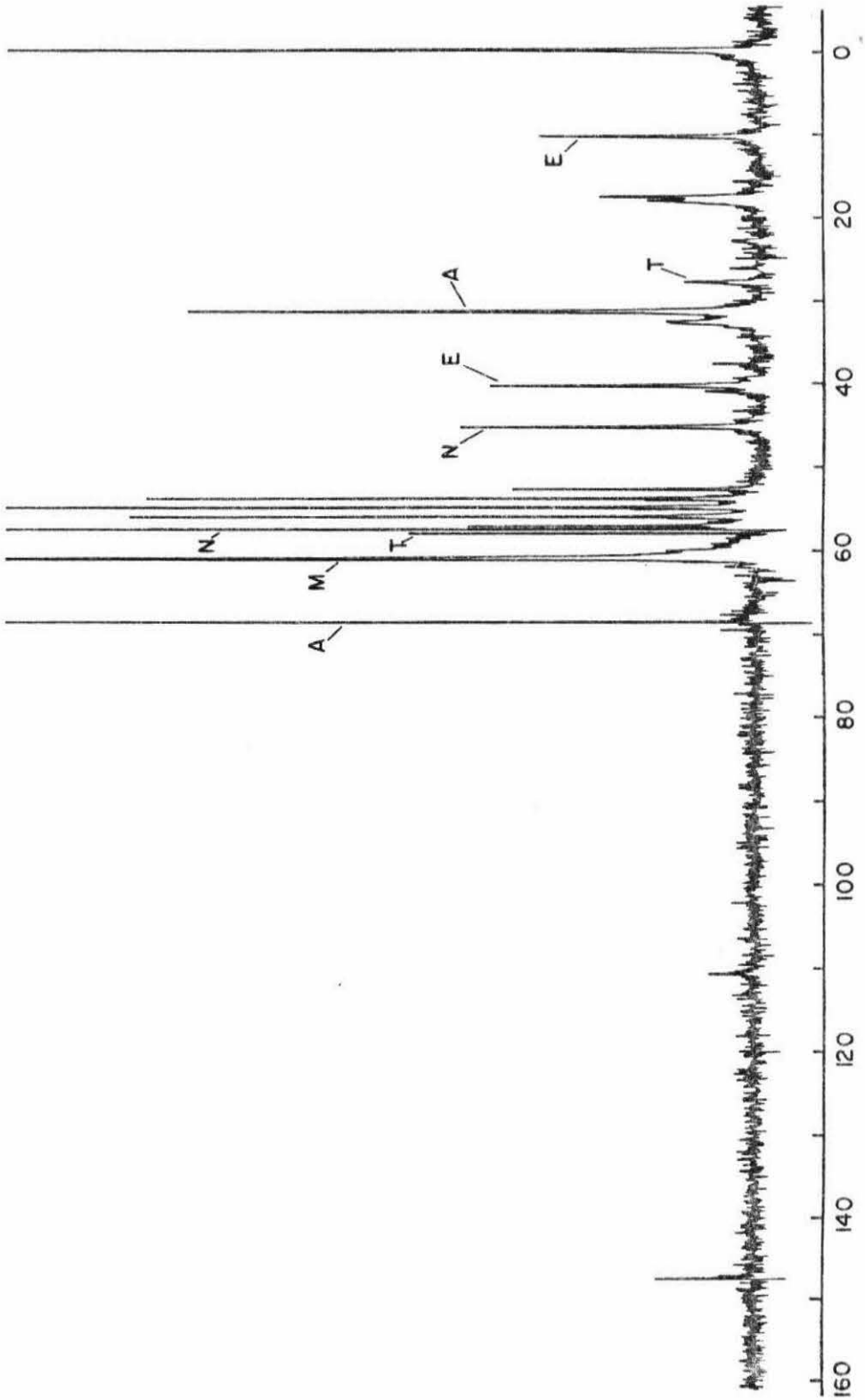

A
M
N
T
N
E
A
T
E
0
20
40
60
80
100
120
140
160

Figure 12. Carbon-13 NMR spectrum at -80° of a hexadeuteroacetone solution of diazene 33; see Figure 10 for explanation of symbols.

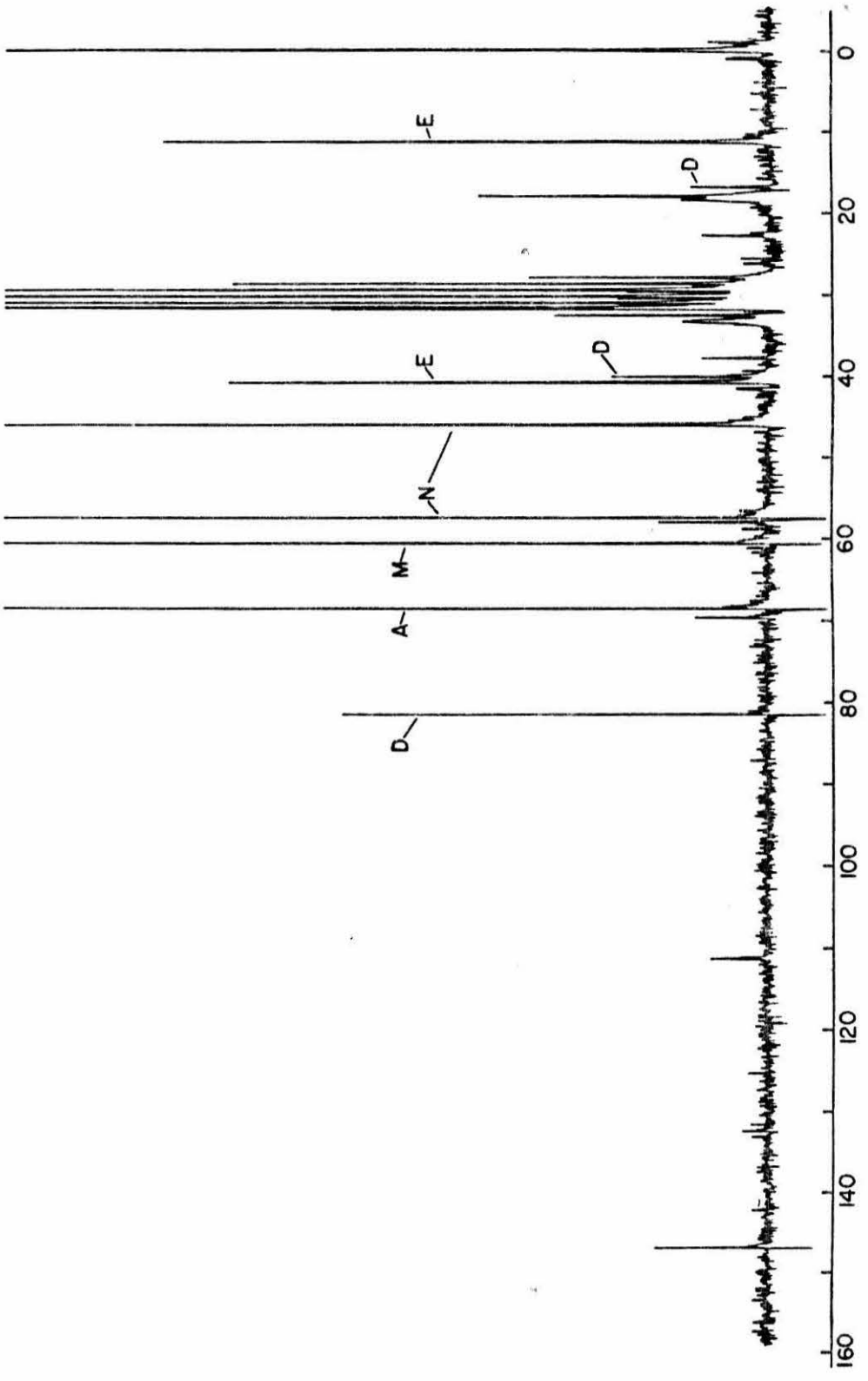
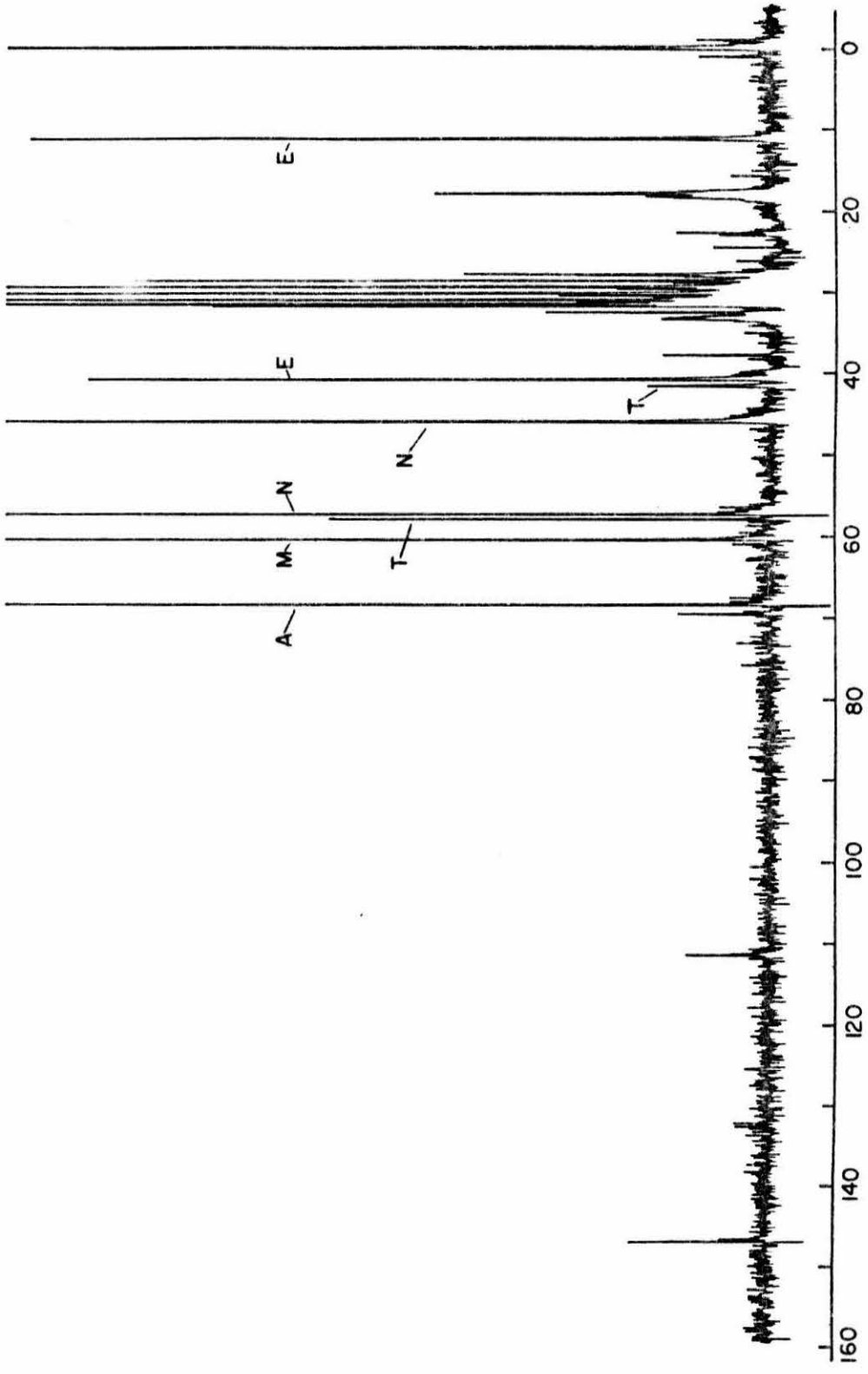
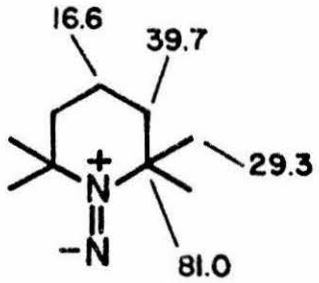
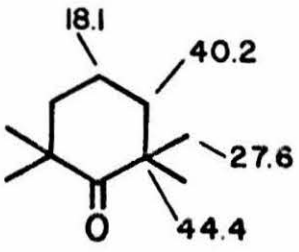

E
D
E
D
N
M
A
D
0
20
40
60
80
100
120
140
160

Figure 13. Carbon-13 NMR spectrum at -80° of a hexadeuteroacetone solution of diazene 33 thermolyzed at 25°; see Figure 10 for explanation of symbols.

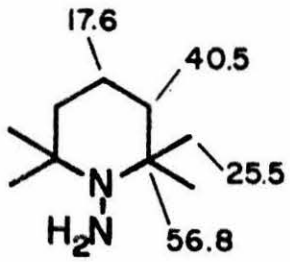

E'
E
T
N
N
M
T
A
0
20
40
60
80
100
120
140
160



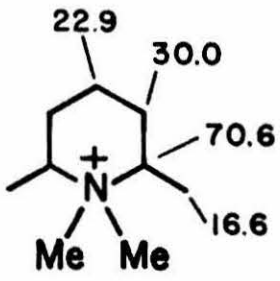
33 in CD_2Cl_2



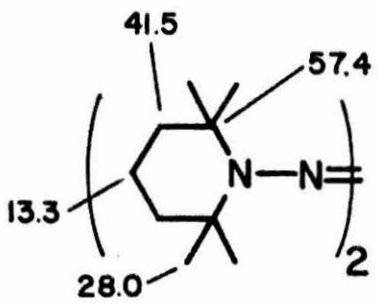
44 in $CDCl_3$



36 in $CDCl_3$



47 in DMSO



41 in $CDCl_3$

Figure 14. Carbon-13 NMR chemical shifts and assignments for diazene 33; shifts are reported as ppm downfield from tetramethylsilane in δ units.

of some model compounds for comparison. The carbon chemical shifts of 33 undoubtedly reflect the contributions of a variety of shielding effects, including substituent inductive effects, steric effects and electric field effects.[90b]

Decomposition Kinetics of N-(2,2,6,6-Tetramethylpiperidyl)-nitrene (33).

To date there is no experimental information concerning the rates and activation parameters of the thermal reactions of 1,1-diazenes. Since such data are important to both theorists and experimentalists, a study of the decomposition kinetics of 1,1-diazene 33 was undertaken.

The diazene used for kinetic studies was purified by column chromatography at -82°, using deactivated basic alumina and dimethyl ether-propane mixtures as the eluting solvent. The chromatography and subsequent addition of excess triethylamine were necessary to obtain reproducible kinetics.

The decay kinetics of 33 were studied in ethyl ether in the temperature range of -1.2° to -21.4° by monitoring the optical density of the purple solution ($\sim 10^{-3}$ moles/liter) at 541 nm as a function of time. The disappearance of 33 was strictly first order at higher temperatures (-1.2° to -11.2°) becoming a combination of first and

higher order kinetics as the temperature was lowered (-13.3° to -21.4°). Plots of $\ell n A$ versus time at the lower temperatures exhibit a curved segment at short times followed by a linear segment at longer times (Figure 15). First order rate constants were taken to be the slopes of the linear portions of these plots; the rate constants from nine kinetic runs in ethyl ether are listed in Table 4.

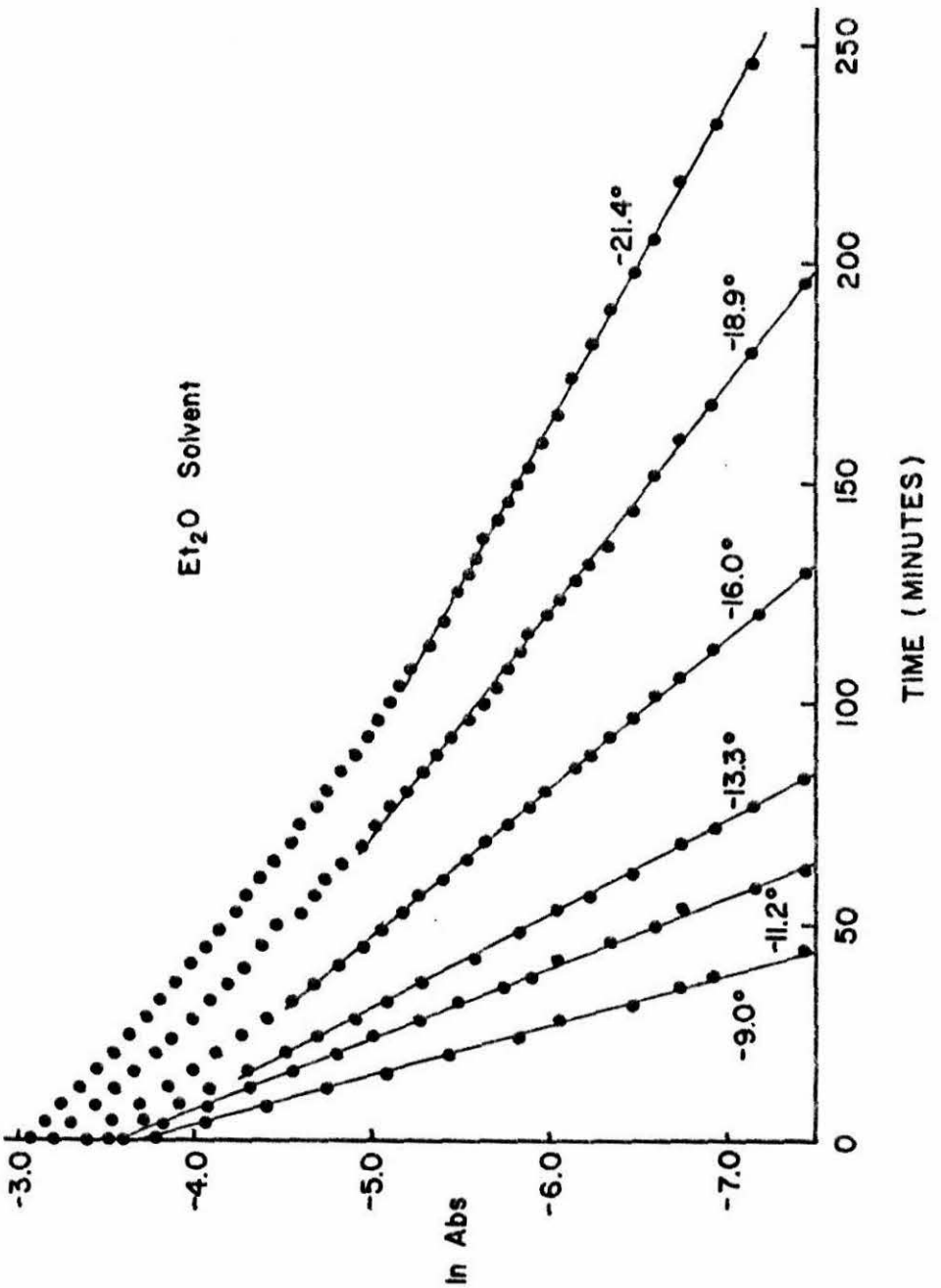
Table 4

First-Order Rate Constants in Ethyl Ether

Temperature (°C)	$k_1 (sec^{-1})$
- 1.2	4.28×10^{-3}
- 3.6	3.14×10^{-3}
- 6.2	2.03×10^{-3}
- 9.0	1.42×10^{-3}
-11.2	1.01×10^{-3}
-13.3	0.763×10^{-3}
-16.0	0.482×10^{-3}
-18.9	0.324×10^{-3}
-21.4	0.226×10^{-3}

These data are plotted in Arrhenius form in Figure 16, yielding the indicated activation parameters. The observed activation energy for the unimolecular thermal decomposition of 1,1-diazene 33 of 20.0 ± 0.4 kcal/mole is substantially lower than that observed in the decomposi-

Figure 15. ℓn A versus time plots for the decomposition of 33 in ethyl ether.


Et2O Solvent
-21.4°
-18.9°
-16.0°
-13.3°
-11.2°
-9.0°
-3.0
-4.0
-5.0
-6.0
-7.0
ln Abs
0
50
100
150
200
250
TIME (MINUTES)

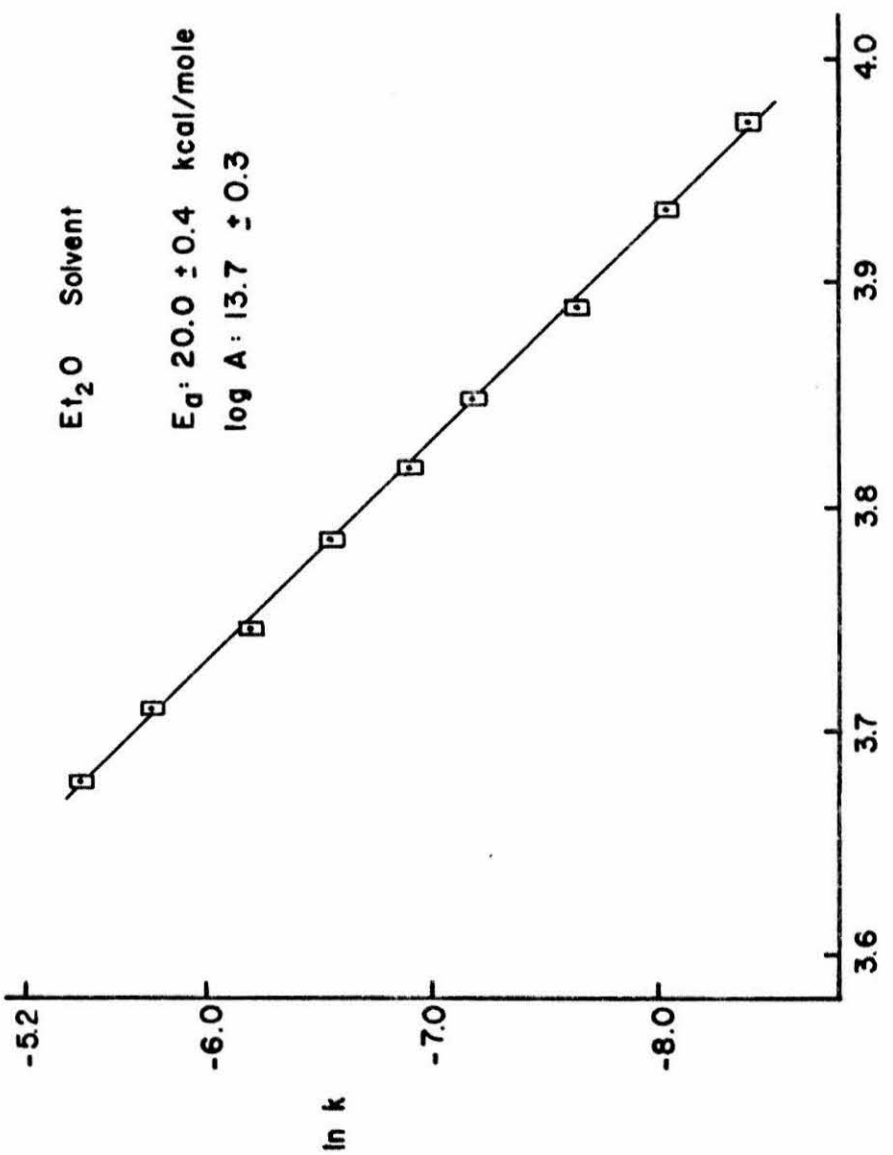
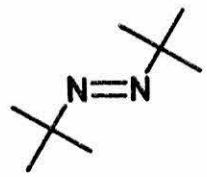


Figure 16. Arrhenius plot of diazene first order decomposition kinetics in ethyl ether (R = 0.999).

tion of similarly substituted 1,2-dialkyldiazenes. For instance, for trans-azo-tert-butane 48 the observed enthalpy of activation is $\Delta H^{\neq}$ = 42.2 ± 0.8 kcal/mole.[91]



48

This is in accord with the theoretical results of Casewit and Goddard[42] and those of Pasto and Chipman.[65]

In order to assess the effect of solvent on the unimolecular decomposition rate of 33, kinetic studies were carried out in n-hexane and in tetrahydrofuran. Analysis of the kinetic data in a manner identical to that employed in the ethyl ether kinetics affords the first order rate constants listed in Table 5 (hexane) and Table 6 (THF). The Arrhenius plots of data are shown in Figure 17 (hexane) and Figure 18 (THF). A comparison of the unimolecular decomposition rates of 33 in the three solvents at the same temperature demonstrates that the rate is sensitive to the nature of the solvent and increases with decreasing solvent polarity (see Table 7). The observed rate dependence on solvent polarity is consistent with a polar

Table 5

First-Order Rate Constants in n-Hexane

Temperature (°C)	k_1 (sec^{-1})
- 8.0	4.34×10^{-3}
-10.4	3.39×10^{-3}
-13.4	2.31×10^{-3}
-16.0	1.69×10^{-3}
-18.9	1.08×10^{-3}
-22.0	0.752×10^{-3}

Table 6

First-Order Rate Constants in Tetrahydrofuran

Temperature (°C)	k_1 (sec^{-1})
+ 4.2	5.24×10^{-3}
+ 2.6	4.25×10^{-3}
- 0.2	2.85×10^{-3}
- 2.6	2.07×10^{-3}
- 5.6	1.36×10^{-3}
- 7.4	1.10×10^{-3}
-10.4	0.683×10^{-3}

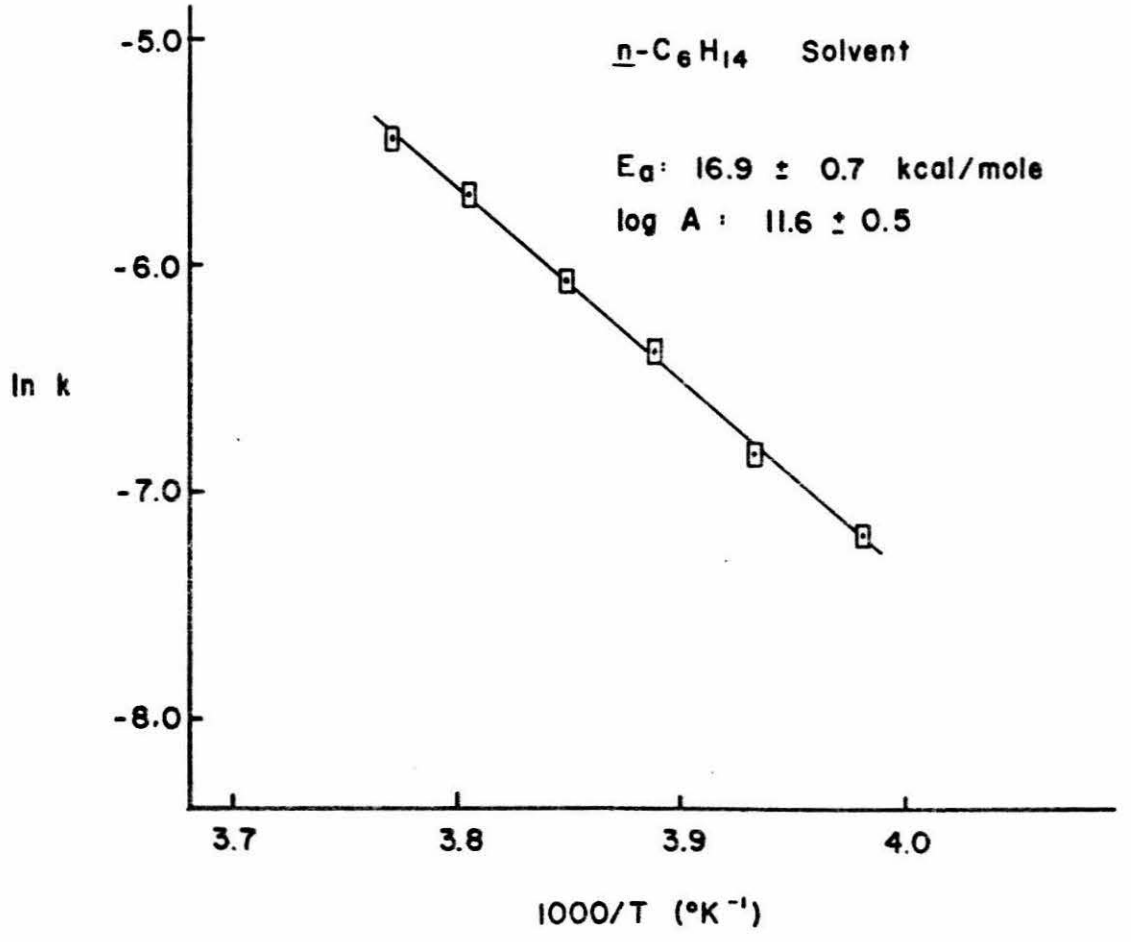


Figure 17. Arrhenius plot of diazene first order decomposition kinetics in n-hexane (R = 0.999).

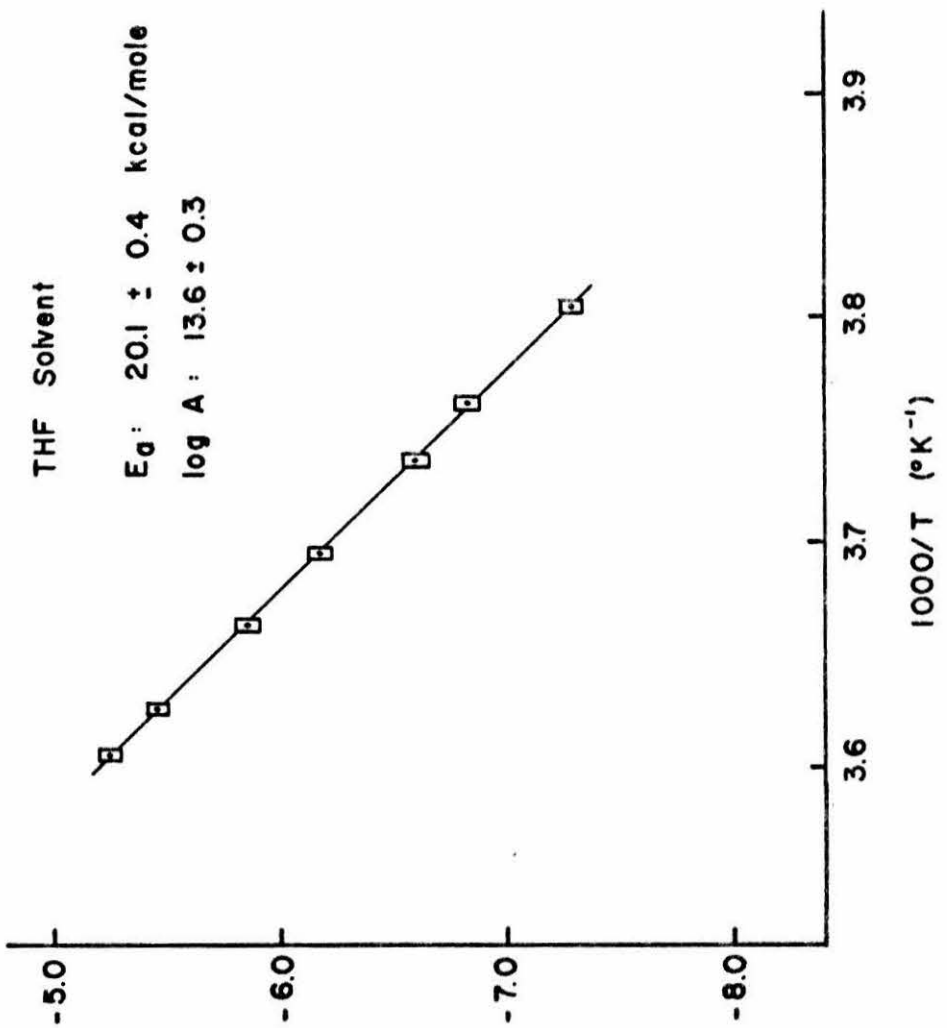


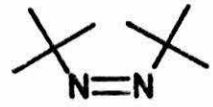
Figure 18. Arrhenius plot of diazene first order decomposition kinetics in tetrahydrofuran (R = 0.999).

Table 7

Solvent Effects on the Decomposition of 33 at -10°C

Solvent	E_t	k_1 (sec^{-1})	k_{rel}	$\Delta G^{\neq}$ (kcal/mole)
n-Hexane	30.9	3.49×10^{-3}	4.8	18.3
Ethyl Ether	34.6	1.23×10^{-3}	1.7	18.9
Tetrahydrofuran	37.4	0.73×10^{-3}	1.0	19.1

ground state decomposing by a less polar transition state. Such an effect has been observed in the decompositions of 1,2-dialkyldiazenes by Rüchardt and coworkers.[92] For the three solvents examined, ℓn k correlates with E_t reasonably well[93] (Figure 19). The indicated line has a slope of 0.24. This is substantially larger than the slopes observed in the azoalkane studies of Rüchardt. For example, they find that the unimolecular decomposition of 49 at -22° gives a linear correlation of ℓn k with E_t with a slope = 0.16.[92a] Presumably this reflects a stronger



49

solvent interaction with the dipolar 1,1-diazene ground state as compared to the relatively non-polar 1,2-diazene ground state.

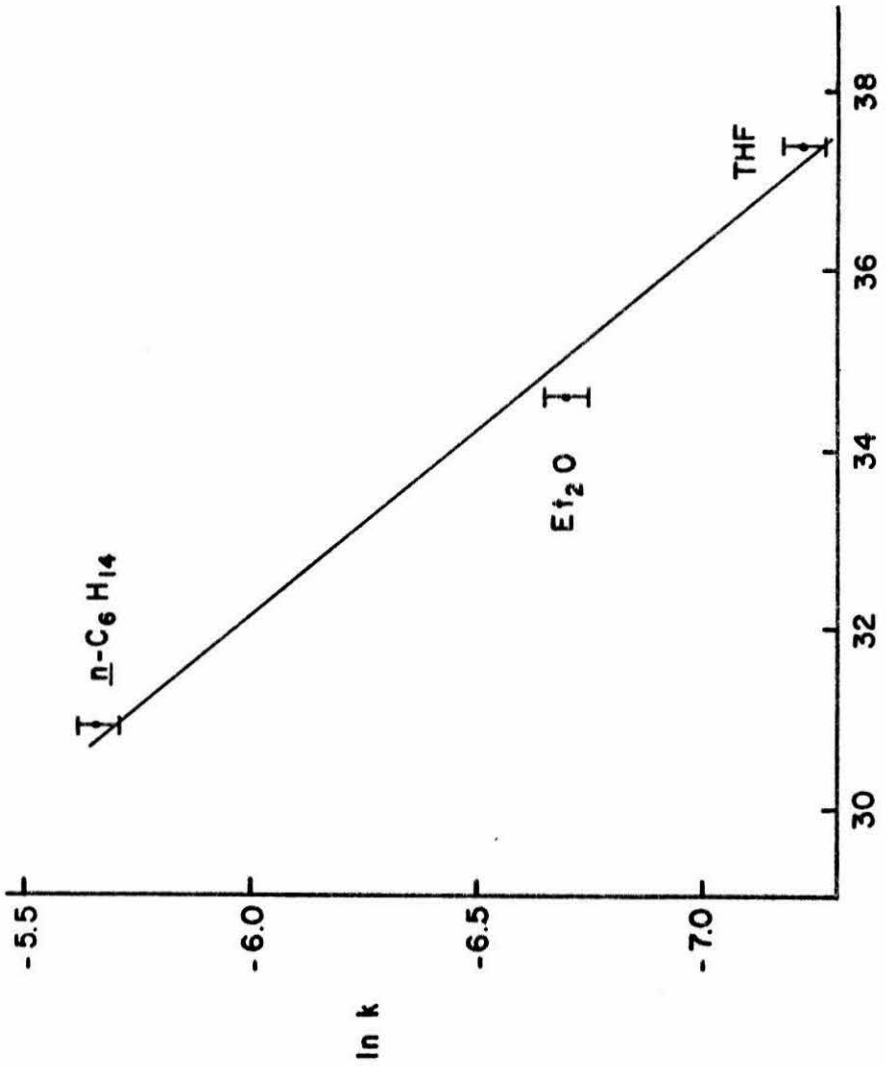


Figure 19. ℓn k versus E_t for the unimolecular decomposition of 33 at -10.0°. The indicated line has a slope of 0.24.

The Arrhenius parameters for the three solvents are summarized in Table 8, along with the calculated enthalpies and entropies of activation.

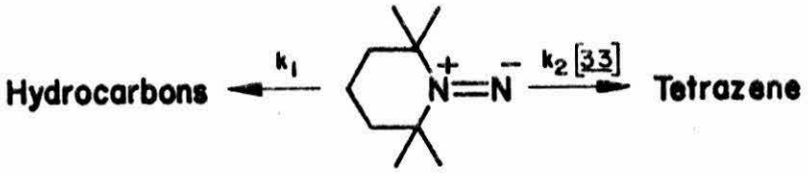
Table 8

Summary of Activation Parameters*

Solvent	log A	E_a (kcal/mole)	$\Delta S^{\neq}$ (kcal/deg-mol)	$\Delta H^{\neq}$ (kcal/mol)
n-Hexane	11.6 ± 0.5	16.9 ± 0.7	-7.3 ± 2.8	16.4 ± 0.7
Ethyl Ether	13.7 ± 0.3	20.0 ± 0.4	+2.3 ± 1.4	19.5 ± 0.4
Tetrahydrofuran	13.6 ± 0.3	20.1 ± 0.4	+1.8 ± 1.4	19.6 ± 0.4

*Error limits represent one standard deviation.

One possible cause for the curvature observed in the ℓn A versus time plots at the lower temperatures studied is a dimerization of the 1,1-diazene 33 in competition with unimolecular decomposition. On the basis of the proton NMR results described above this is a reasonable possibility. Using computer simulation, we find that the curved ℓn A



33

versus time plots of the results in ethyl ether may be modeled as competitive unimolecular and bimolecular re-

actions ($k_{obs} = k_1 + k_2$ [33]).

In the first set of simulations the values of the unimolecular rate constants k_1 were constrained to the experimental values (determined in the manner described above) within experimental error (±5%). The bimolecular rate constants were varied until a satisfactory fit with the experimental data was obtained. We find that an adequate fit may be obtained using the same bimolecular rate constant at all four temperatures that were simulated. The rate constants are given in Table 9 and the fit between experimental and calculated values is illustrated in Figure 20.

Table 9

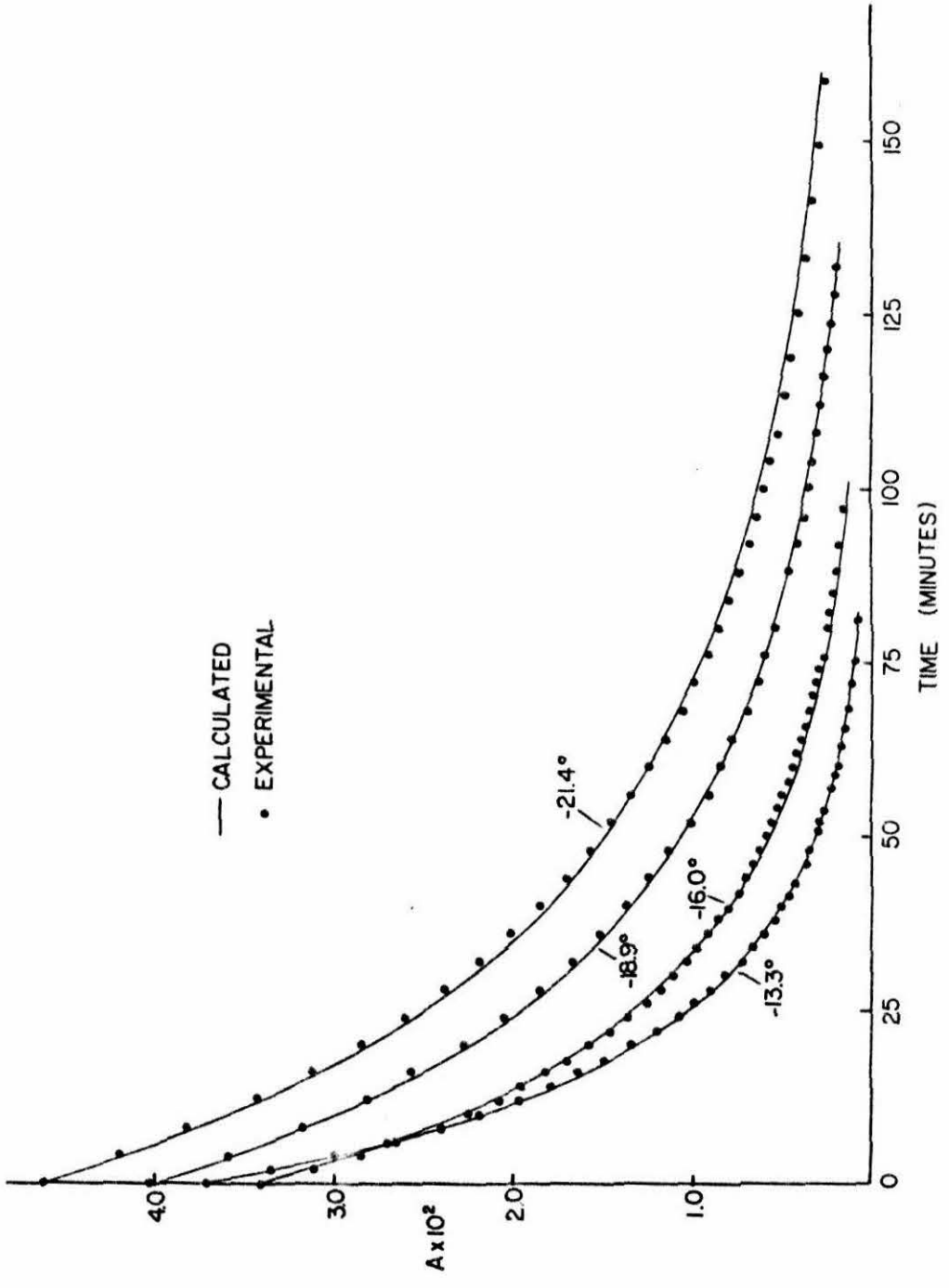
Rate Constants Used in First Simulation;

see Figure 20.

Temperature (°C)	k_1 (sec^{-1})	k_2 (ℓ/mole-sec)
-13.3	7.45×10^{-4}	5.03×10^{-2}
-16.0	5.03×10^{-4}	5.03×10^{-2}
-18.9	3.17×10^{-4}	5.03×10^{-2}
-21.4	2.18×10^{-4}	5.03×10^{-2}

$\log k_1 = 13.7 - 20.0/\theta$

Figure 20. Results of simulation of kinetics in ethyl ether, using the rate constants given in Table 9.


— CALCULATED
• EXPERIMENTAL
-21.4°
-18.9°
-16.0°
-13.3°
A x 10²
4.0
3.0
2.0
1.0
0
25
50
75
100
125
150
TIME (MINUTES)

A second set of simulations was performed, with the only constraint being that the derived rate constants k_1 and k_2 must strictly adhere to an Arrhenius relationship; that is, $\ell n\ k$ must be a linear function of $1/T$. Both k_1 and k_2 were varied until an optimum fit was obtained. The rate constants derived from this simulation are given in Table 10 along with the Arrhenius parameters generated by these rate constants. The fit between the experimental and calculated data is illustrated in Figure 21.

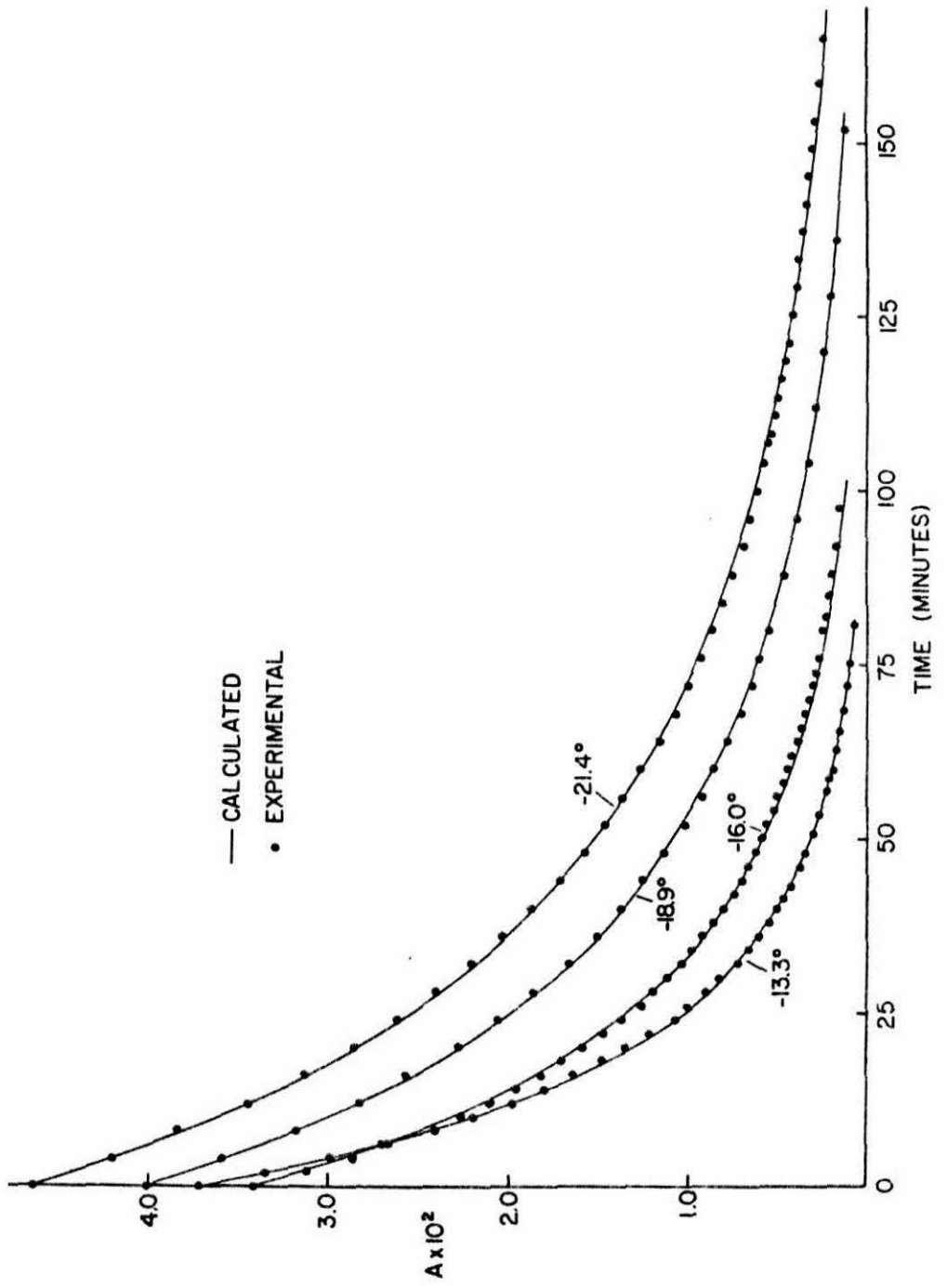
Table 10

Rate Constants Used in Second Simulation;
see Figure 21.

Temperature (°C)	$k_1(sec^{-1})$	$k_2(\ell/mole\text{-}sec)$
-13.3	7.25×10^{-4}	5.95×10^{-2}
-16.0	5.03×10^{-4}	5.16×10^{-2}
-18.9	3.30×10^{-4}	4.43×10^{-2}
-21.4	2.50×10^{-4}	3.89×10^{-2}

$\log k_1 = 11.4 - 17.4/\theta$ $\log k_2 = 4.5 - 6.8/\theta$

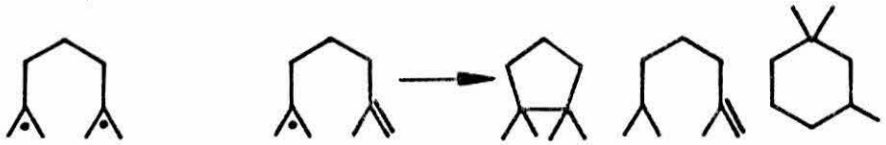
Figure 21. Results of simulation of kinetics in ethyl ether, using the rate constants given in Table 10.


— CALCULATED
• EXPERIMENTAL
-21.4°
-18.9°
-16.0°
-13.3°
A x 10²
4.0
3.0
2.0
1.0
0
25
50
75
100
125
150
TIME (MINUTES)

A number of conclusions may be drawn from the results of these simulations. First, these results demonstrate that the experimental kinetic data are consistent with and thus constitute permissive evidence for competitive unimolecular and bimolecular decomposition pathways. This is the first kinetic evidence for a direct bimolecular pathway for the formation of tetrazenes from 1,1-diazenes, as opposed to the alternative indirect pathways discussed earlier (see Introduction). Second, the results indicate that the temperature dependence of the dimerization rate is small. Although our data are not sufficient to derive accurate Arrhenius parameters, they do allow limits to be placed on the activation energy. The results of the first simulation indicate an $E_a \sim 0$ for the bimolecular process. The second simulation yields an $E_a \sim 7$ kcal/mole. The actual activation energy for the process is probably somewhere between these values. An accurate determination of the E_a for the dimerization reaction will require kinetic studies in temperature and concentration regimes where the unimolecular rate is negligible compared to the bimolecular rate.

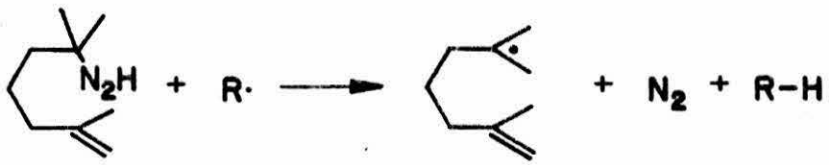
As was mentioned earlier one of the C_9 hydrocarbon products, 1,1,3-trimethylcyclohexane (40), does not appear to be derived from the 1,5-biradical 50. A

likely source of this product is the hexenyl radical 51. Walling and Cioffari have demonstrated[95] that hydrocarbons 38 and 40 may arise from the rearrangement of 51 followed by hydrogen atom abstraction. This raises



50 51 38 39 40

the question of the origin of the radical 51. A possible source is a monosubstituted diazene 52, an isomer of the 1,1-diazene 33. It is believed that reactions of monosubstituted 1,2-diazenes 53 with oxygen proceed by hydrogen atom abstraction followed by deazotization to give



52a (1,1-subst)
b (1,2-subst)

51

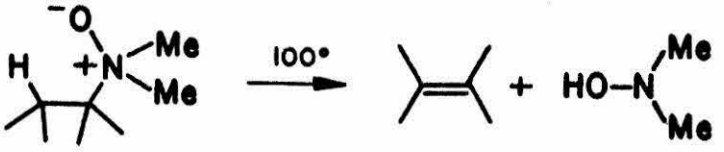
the carbon-centered radical:[96,97]

$$O_2 + R\text{-}N{=}N\text{-}H \longrightarrow R\text{-}N_2\cdot + \cdot O_2H \longrightarrow R\cdot + N_2$$

53

Evidence has been given for the formation of phenyl radical in the exposure of phenyldiazene (53, R = C_6H_5) to air[98] or ferric ion.[97] Presumably the hydrocarbon radical R·, once formed, initiates a chain reaction resulting in the formation of R-H.

The monosubstituted diazene 52 may conceivably arise in two ways: (a) by initial C-N bond cleavage of the 1,1-diazene 33 to the diazenyl biradical 54, followed by hydrogen atom migration to yield 52a or 52b (Figure 22a) or (b) by a direct rearrangement of 33 to 52b (Figure 22b) in a reaction which is similar to the Cope reaction undergone by amine oxides:[99]



To account for the observed products, other competitive pathways leading to the biradical 50 or the radical 56 are required. Conceivably 37 and 38 may arise from 56; 38, 39, and 40 may arise from 51; and 37, 38, and 39 may arise from 50 (see Figure 23).

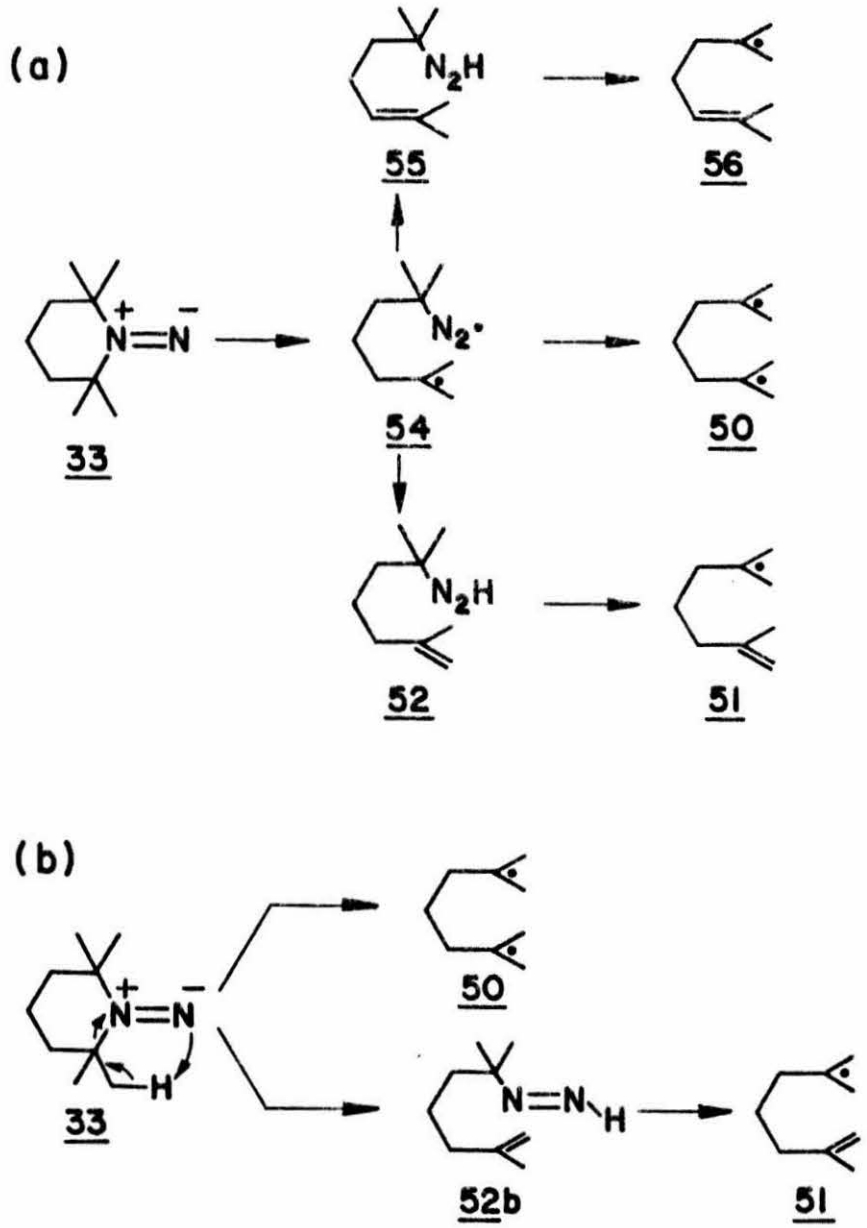


Figure 22. Possible mechanisms for formation of 52; (2) biradical pathway; (b) direct pathway.

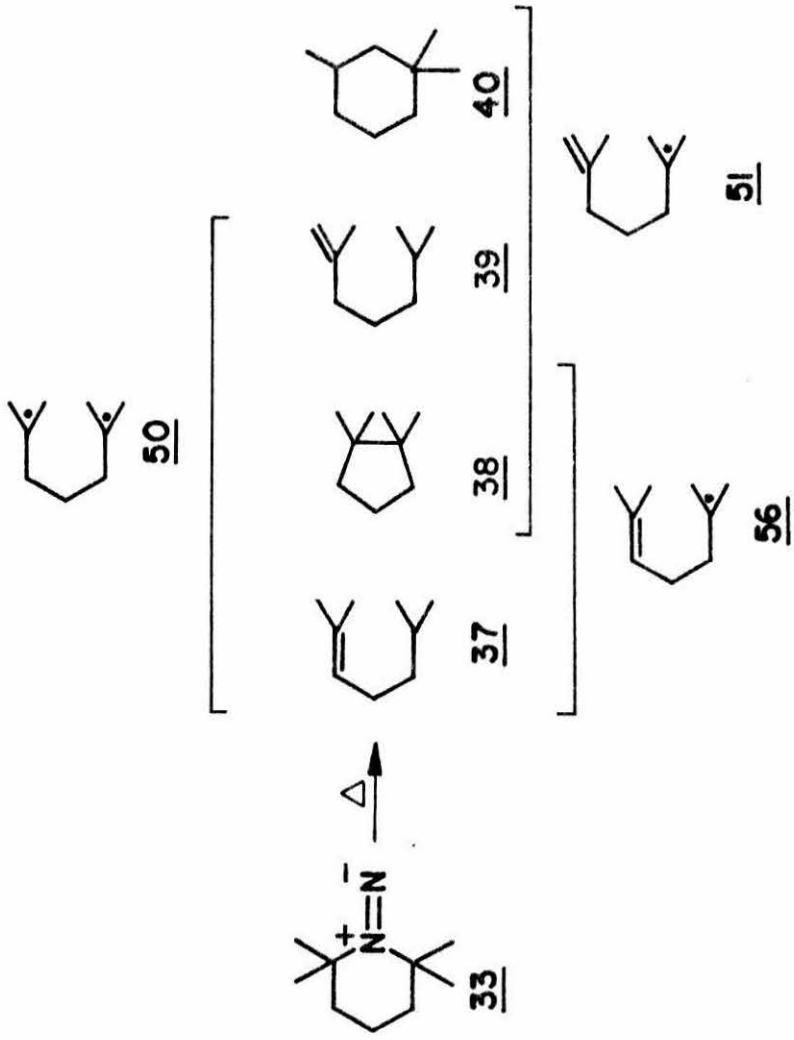


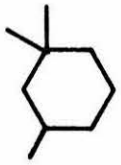
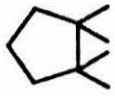
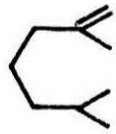
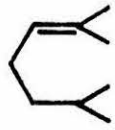
Figure 23. Possible precursors to the observed hydrocarbon products 37-40.

In order to gain information regarding the unimolecular decomposition pathways which the 1,1-diazene 33 follows, a study of the hydrocarbon product ratios as a function of solvent and temperature was undertaken. The 1,1-diazene 33 was generated and purified by column chromatography. Triethylamine and octane were added and the elution solvent was replaced with the solvent of interest (n-hexane, ethyl ether or tetrahydrofuran). Aliquots of the resulting solutions were thermolyzed at 0.0, -10.0, and -20.0° and the hydrocarbon products were analyzed by analytical VPC. The results of this study are given in Table 11.

A quantitative interpretation of these results in terms of the mechanisms illustrated in Figures 22 and 23 will require a knowledge of the behavior of the radicals 51 and 56 in the three solvents of interest in the temperature range -20° to 0°. However, some qualitative conclusions may be drawn from these data. First, it is apparent that, in all three solvents, as the temperature is lowered the absolute yield of hydrocarbon decreases. This is consistent with the existence of a competing decomposition pathway (e.g., tetrazene formation) which becomes increasingly competitive as the temperature is lowered and is in qualitative agreement with our kinetic

Table 11

Hydrocarbon Product Ratios* as a Function of Solvent and Temperature

	 40	 38	 39	 37	Average Relative Yield**
n-Hexane					
0.0°C	2	24	5	68	100%
-10.0°C	2	24	4	69	85%
-20.0°C	1	25	2	72	70%
Ethyl Ether					
0.0°C	5	24	10	61	100%
-10.0"C	5	24	9	62	77%
-20.0°C	4	24	7	65	62%
Tetrahydrofuran					
0.0°C	10	24	11	55	100%
-10.0°C	11	23	12	54	87%
-20.0°C	9	24	9	58	71%

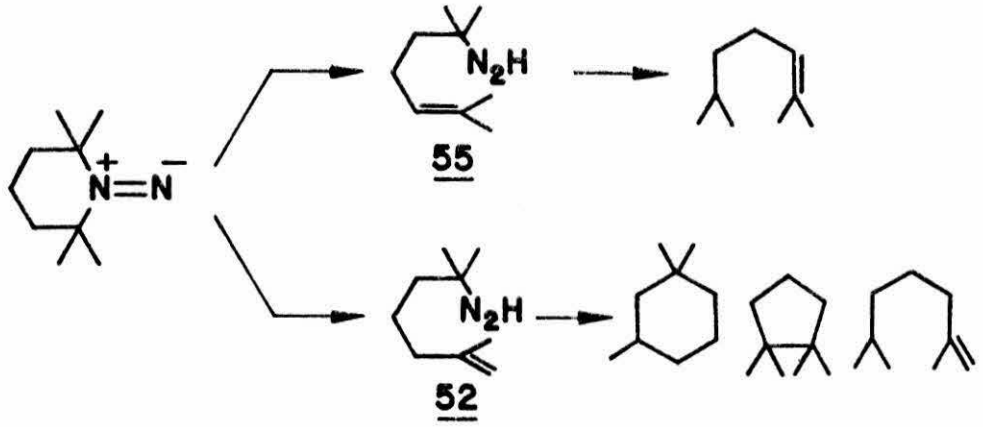
* Values represent averages of duplication determinations.

**Relative to yields at 0.0°C equal to 100%.

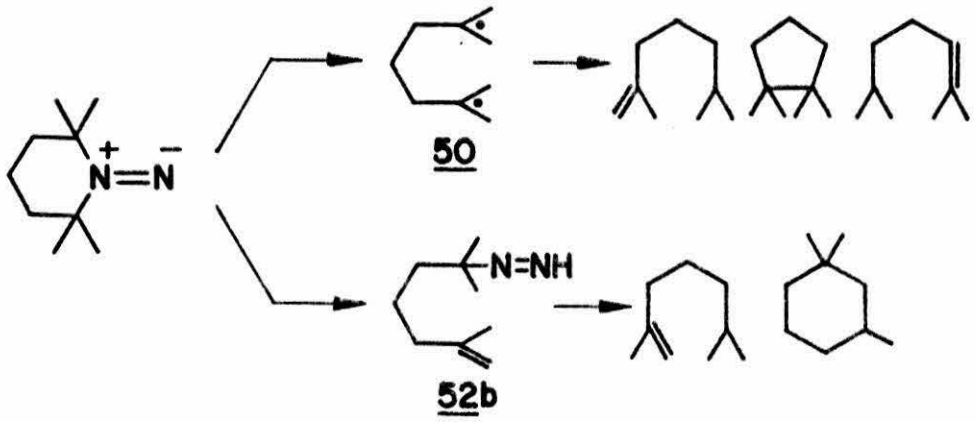
results. Second, it can be seen that as the solvent polarity is increased the relative proportion of trimethylcyclohexane 40 increases. At the same time the relative proportion of olefin 37 decreases. This may simply reflect the variation in the behavior of the radicals 51 and 56 or of the diazenyl biradical 54 as a function of solvent. Alternatively, it may indicate a differential stabilization or destabilization of two alternate decomposition pathways of the diazene 33 with changing polarity of the medium. Finally, the results indicate that the product ratios are not sensitive functions of temperature. In all three solvents a change of 20° in temperature results in variations of 4% or less in the relative proportions of products. In most cases the variations are within experimental error. This lack of temperature sensitivty implies that the competitive pathways leading to the various products 37-40 have very similar activation energies.

As pointed out above, all four products cannot be rationalized with the intermediacy of the biradical 50 alone; nor can they be explained by the intermediacy of monoradical 51 or 56 alone. The unimolecular decomposition of 1,1-diazene 33 must involve a minimum of two

of these intermediates. For example, exclusive competitive formation of diazenes 52 and 55, which in turn lead to the radicals 51 and 56, can account for the observed products. It is not obvious, if this is the

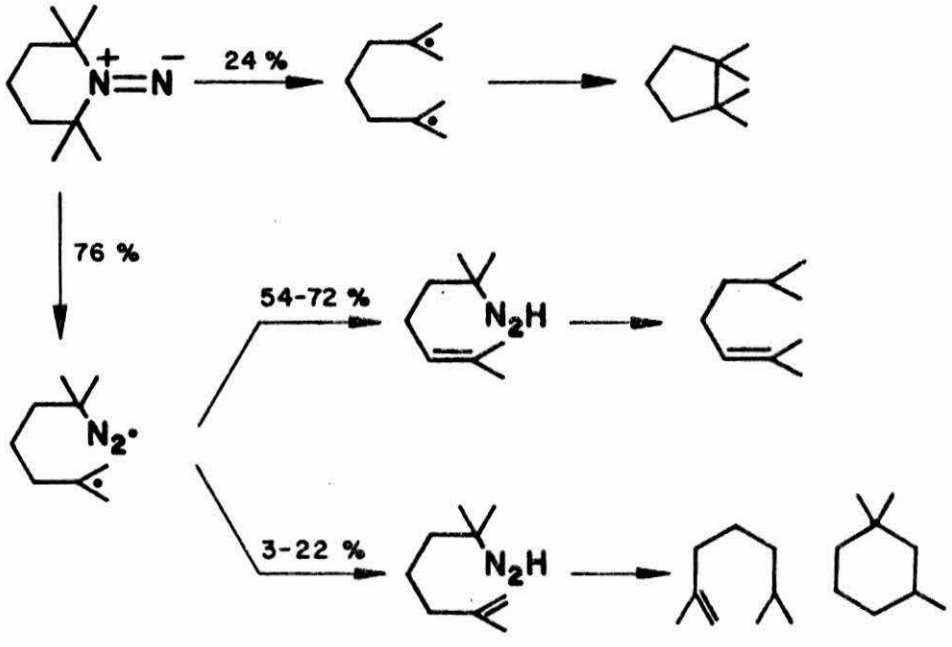


actual mechanism, why the product distributions should vary with solvent and temperature in the observed manner. Alternatively the products may be accounted for by competitive formation of the biradical 50 and the 1,2-diazene 52b:



Again, an explanation for the observed variations in product distribution with solvent and temperature is not obvious.

Inspection of Table 11 reveals that the relative amount of tetramethylcyclopentane 38 is essentially unaffected by solvent and temperature variations, while the amount of olefin 37 is coupled to the amount of 38 and 40. Conceivably this reflects a solvent- and temperature-insensitive bifurcation of 1,1-diazene decomposition pathways. For example, the following scheme is consistent with the product data:



These mechanisms are only speculation, however. Hopefully a better knowledge of the behavior of the radicals 51 and 56 as a function of solvent and temperature will allow more definite conclusions to be reached.

Photoreactivity of N-(2,2,6,6-Tetramethylpiperidyl)-nitrene (33): Preliminary Results.

A preliminary study of the photochemistry of the 1,1-diazene 33 was performed. The photochemistry of 1,1-diazenes might be expected to resemble that of the isoelectronic ketones[100] and the isomeric azo compounds,[101] with σ-bond cleavage leading to radical and biradical species being the predominant mode of photodecomposition. We find that the 1,1-diazene 33 is inert to radiation at 546 nm in ethyl ether in the $n \rightarrow \pi^*$ region. However, broad band irradiation of ethereal solutions of 33 at wavelengths greater than 200 nm brings about ready decomposition of the diazene as evidenced by a rapid bleaching of the solution. VPC analysis of the photolysed solution reveals the formation of the C_9 hydrocarbons 37, 38, and 39 in 97% absolute yield (Figure 24). An upper limit of $\leq$ 0.5% can be placed on the amount of trimethylcyclohexane 40 present.

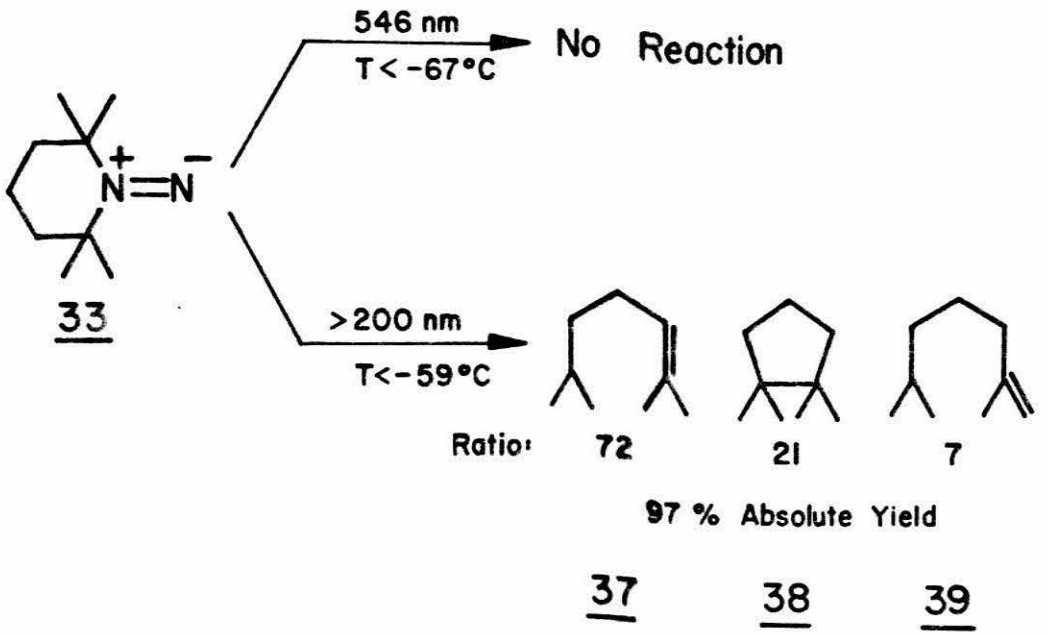


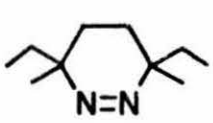
Figure 24. Photochemical behavior of 1,1-diazene 33.

The low photoreactivity of 33 in the n → π* state is rather surprising in view of the thermal lability of the 1,1-diazene. Based on our kinetic studies the n → π* state has sufficient energy for C-N bond cleavage. Apparently other photophysical processes (e.g., internal conversion, intersystem crossing followed by quenching of the triplet state) are more efficient than the photodecomposition process. We cannot rule out the possibility that the 1,1-diazene n → π* singlet state is being quenched by a cosolute.

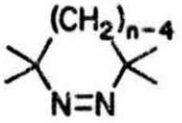
Evidently, irradiation of the 1,1-diazene 33 with ultraviolet light forms an upper excited state of the 1,1-diazene, possibly a π → π* state. Our attempts to detect absorption in the ultraviolet due to the 1,1-diazene 33 have been unsuccessful because of interfering cosolutes which absorb strongly in that region (for example, the tetrazene 41 exhibits a λ_{max} = 252 nm, ε7800 in ethyl ether). The hydrocarbon ratios observed in this photodecomposition (Figure 24) presumably reflect the behavior of the biradical 50 at the temperature of the experiment (-59° to -72°).

Attempted Syntheses of 3,3,7,7-Tetramethyl-1,2-diaza-1-cycloheptene (59).

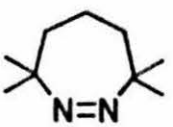
The thermochemistry and the fragmentation reactions of cyclic tertiary substituted 1,2-diazenes have been the subjects of intensive research for over a decade.



57



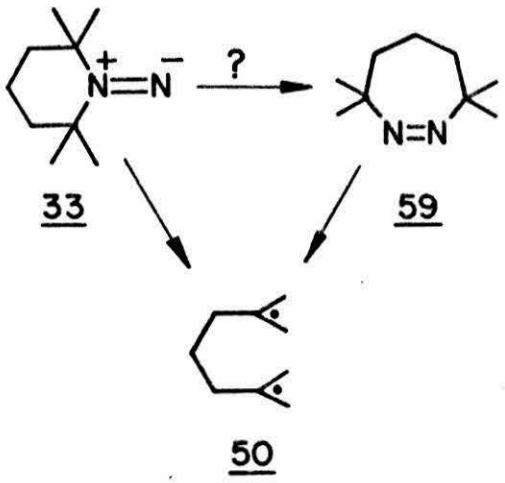
58



59

For example, the thermolysis of compound 57 was employed in an early stereochemical study of 1,4-biradicals.[102] A systematic study of nitrogen extrusion from compounds 58 (n = 4, 5, 6) has led to a better understanding of the ground and excited state energy surfaces of cyclic azo compounds and has revealed interesting thermal and photochemical reactivity patterns.[103] For example 58 (n = 5) photoextrudes nitrogen with almost unit quantum efficiency while the homologous 58 (n = 6) exhibits a quantum yield of 0.008 for nitrogen elimination. The eight-membered ring homologue 58 (n = 8) has recently been synthesized and, interestingly, the isolated compound was the trans-isomer.[92b]

The seven-membered ring 59 in this series of azoalkanes is a desirable compound to have available. A comparison of its reactivity to the other members of the series should prove enlightening. Our interest in this compound derives from the fact that 59 is a possible ring-expansion product resulting from the 1,1-diazene 33.



In addition, since 59 is a precursor for the same biradical species 50 as may result from 1,1-diazene 33 it would be informative to compare thermal and photochemical reactivities and product distributions of the two diazenes. Unfortunately, azoalkane 59 is unknown in the chemical literature. Our attempts to synthesize this compound are described below.

The attempted syntheses of 59 are based on successful syntheses of the lower homologue 58 (n = 6), all of which employ an oxidative coupling of the nitrogen atoms in 2,5-diamino-2,5-dimethylhexane (60). Thus a synthesis of the homologous diamine 61 is required. This compound is readily available using the sequence outlined in Figure 25, where the key step is rearrangement of the diamide 62 to the protected diamine 63.[104]

Our first attempts at ring closure of 61 utilized the method of Greene and Gilbert. These workers were successful in oxidizing 60 to 58 (n = 6) using hydrogen peroxide-sodium tungstate.[105] Application of this reaction to the oxidation of diamine 61 resulted in a complex reaction mixture in which none of the desired azoalkane could be detected by proton NMR and gas chromatography. A variant of this method employs an excess of hydrogen peroxide and the ring-closure product is iso-

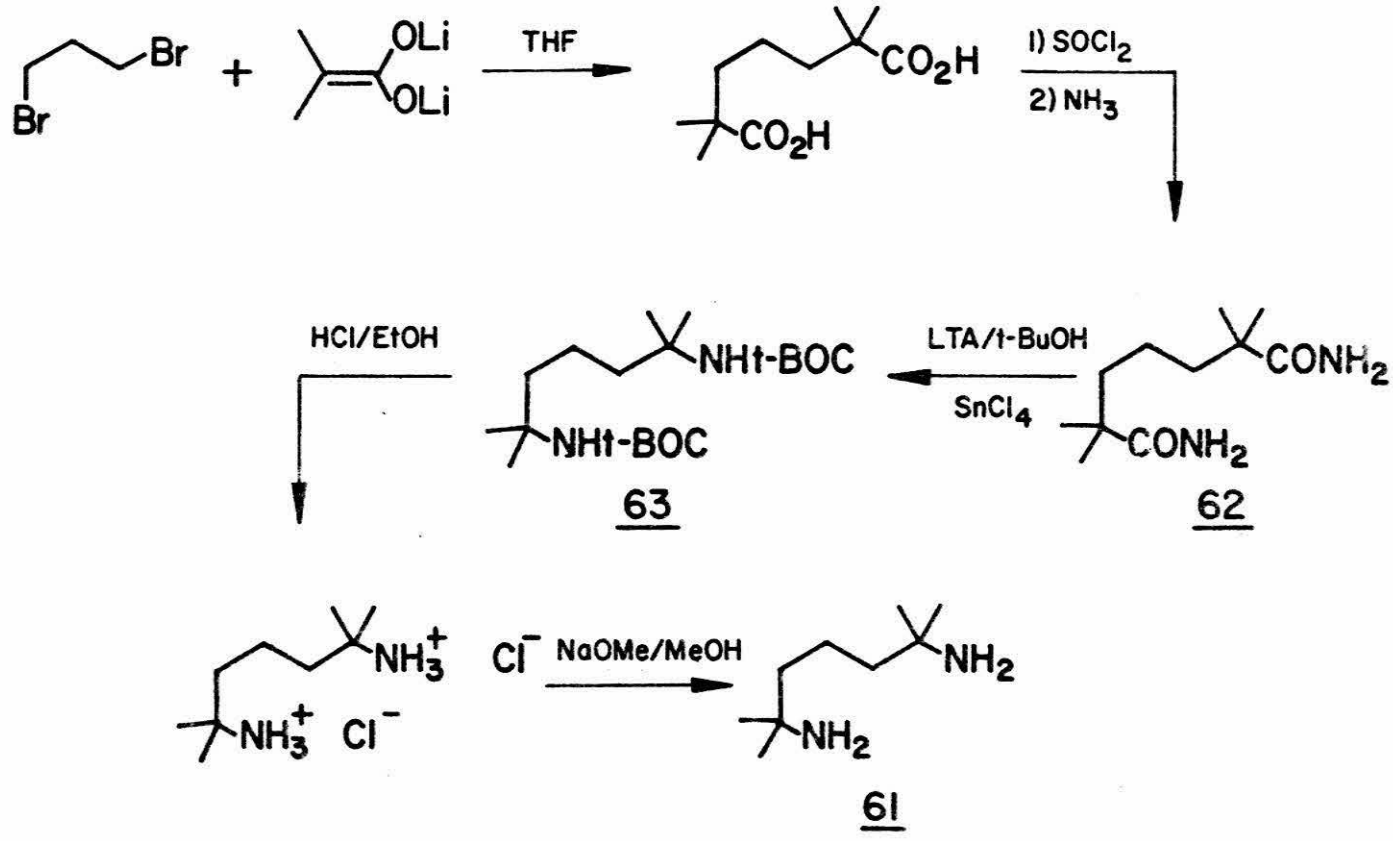
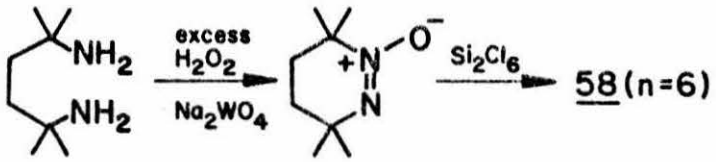


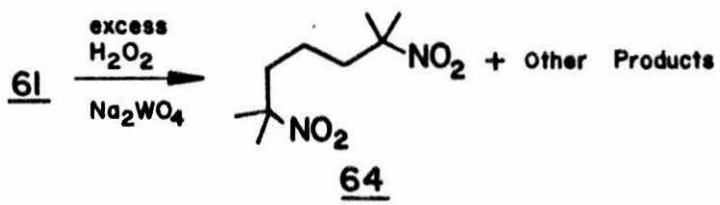
Figure 25. Synthetic route to the diamine 61.

lated as the N-oxide (or the N,N'-dioxide) which is then deoxygenated with hexachlorodisilane.[105] Treatment of



60

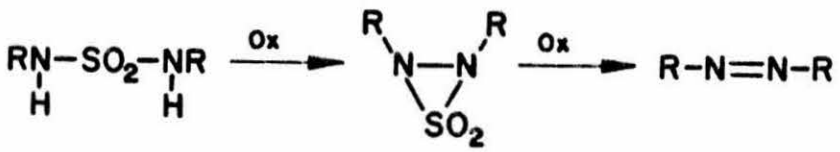
diamine 61 with excess hydrogen peroxide in the presence of sodium tungstate again results in a complex product mixture. Proton NMR examination of this product mixture reveals no absorptions which are consistent with the presence of 59, the corresponding N-oxide or the corresponding N,N'-dioxide. The major component of this mixture was isolated and tentatively identified as the dinitroalkane 64 on the basis of spectral evidence.



64

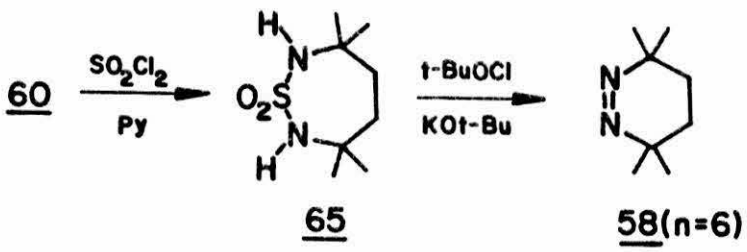
Our second attempt at ring closure of 61 utilized the procedure of Nelsen and Bartlett for the iodine pentafluoride oxidation of amines to azoalkanes.[106] Treatment of the diamine 61 with IF_5 resulted in the formation of a non-volatile product. Examination of the product mixture by proton NMR and gas chromatography did not reveal the presence of the desired azoalkane.

A third approach to 59 was based on the method developed by the groups of Ohme[107] and Timberlake,[108] employing the oxidation of N,N'-dialkyl sulfamides to generate azoalkanes. Such an approach has been success-



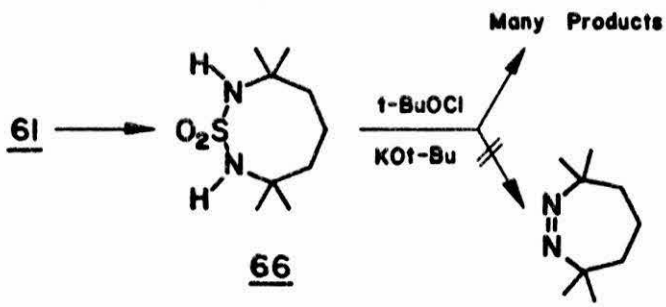
fully employed in the synthesis of a large number of acyclic azoalkanes, but there have been no reports of the formation of cyclic azoalkanes by this method. In order to determine if the synthesis of cyclic azoalkanes was feasible using this method the cyclic sulfamide 65 was synthesized and allowed to react with t-butyl hypochlorite and base. The azoalkane 58 (n = 6) was detected

via gas chromatography to be the sole volatile organic



65 58(n=6)

product. Application of this identical method to 66, the sulfamide derived from diamine 61, results in the formation of a large number of products. Examination of



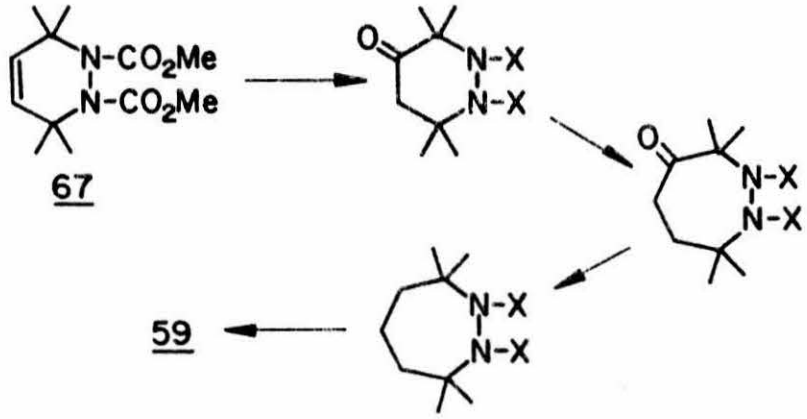
66 59

the product mixture by UV-VIS absorption spectroscopy allows an upper limit of ∿ 0.5% yield of 59 to be estimated.

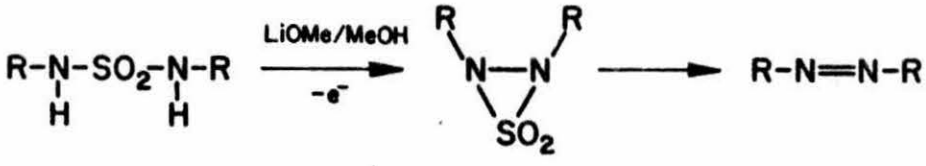
It is rather surprising that the azoalkane 59 so stoutly resists synthesis while the lower and higher homologoues may be readily prepared. An examination of molecular models indicates a possible explanation. The six-membered ring is able to adopt a conformation in which there are no severe steric interactions involving the

four methyl groups. In the seven-membered ring incorporating a cis-azo linkage, such a strain-free conformation is not possible; severe transannular methyl-methyl or methyl-hydrogen interactions are present in all conformations. In the eight-membered ring containing a cis-azo linkage such transannular interactions are so severe that the trans-isomer is apparently the more stable. Although there are no severe steric interactions in the seven-membered ring containing a trans-azo linkage molecular models indicate that such a compound will be highly strained. Thus azoalkane 59 is expected to be a highly strained molecule whether it be cis- or trans-. Presumably this large amount of strain relative to cis-58 (n = 6) and trans-58 (n = 8) is the source of the difficulties experienced in the synthesis of 59.

There are several approaches to 59 which have not yet been tried but which may well prove successful. One possible route is outlined below, starting with the known[92b] diurethane 67. Another approach would involve the electrochemical oxidation of sulfamide 66. Electrochemical methods have been employed to generate strained organic molecules.[109] Bauer and Wendt have recently reported the synthesis of acyclic azoalkanes in high yield by the electrochemical oxidation of the lithium



salts of the corresponding sulfamides.[110] It is possible that employment of electrochemical methods may result in fewer side reactions in the oxidation of 66 than were observed in the chemical oxidation.



Summary

We have been successful in generating and studying the first persistent 1,1-dialkyldiazene. The electronic spectrum of N-(2,2,6,6-tetramethylpiperidyl)nitrene (33) exhibits a structured absorption band in the visible

region (λ_{max} = 541 nm in dichloromethane) assigned as an $n \rightarrow \pi^*$ absorption on the basis of extinction coefficient and solvent shifts. The infrared spectrum of 33 exhibits a strong absorption at 1595 cm^{-1} in dichloromethane which is assigned as a N=N stretch on the basis of isotope shifts. The ESR spectrum of 33 demonstrates that the 1,1-diazene ground state is a singlet. The proton NMR spectrum of 33 in $CDCl_3$ has absorptions at δ 1.15 and 2.15 ppm, assigned to the methyl protons and ring protons, respectively, of the 1,1-diazene. The carbon-13 NMR spectrum of 33 in CD_2Cl_2 shows absorptions at δ 81.0, 39.7, 16.6, and 29.3 ppm, assigned to C-2, C-3, C-4 and CH_3, respectively, of the 1,1-diazene. A study of the decomposition kinetics of 33 in ethyl ether allows the derivation of the following activation parameters: log A = 13.7 ± 0.3, E_a = 20.0 ± 0.4 kcal/mole. Computer modeling of the kinetics in ethyl ether demonstrates that the experimental data are consistent with competitive unimolecular and bimolecular decomposition pathways. The unimolecular decomposition rate of 33 is sensitive to solvent, the rate decreasing with increasing polarity; at -10° k_{rel}(THF) = 1.0, $k_{rel}(Et_2O)$ = 1.7, k_{rel}(n-hexane) = 4.8. A preliminary photochemical study

demonstrates that under our experimental conditions the $n \rightarrow \pi^*$ state of 33 is unreactive. However, broad-band irradiation at $\lambda > 200$ nm results in ready decomposition of 33. A complete photochemical and photophysical study of the 1,1-diazene 33 still remains to be done, including measurements of emission, sensitization experiments and investigations of the nature of the upper excited states of 33.

Part III

EXPERIMENTAL

A) Apparatus: Low-Temperature Spectroscopic Cells and Glassware.

The IR and UV-VIS cells are designed for use in conjunction with an Air Products WMX-1A Vacuum Shroud and LC-1-110 Cyro-Tip Refrigerator.[111] The windows for the vacuum shroud are sodium chloride (purchased from International Crystal Laboratories[112]) for IR spectroscopy and Suprasil I (ground to size from blanks purchased from Amersil, Inc.[113]) for UV-VIS spectroscopy. Samples are introduced into the cells through 18 gauge Teflon tubing (purchased from Alpha Wire Corp.[114]) by applying suction with a syringe.

The cell body of the UV-VIS spectroscopic cell is constructed from OFHC copper, with stainless steel tubing soldered to it. The body is nickel-plated and has a thermocouple well with set screw. The cell windows are Suprasil I and were ground to size from blanks purchased from Amersil, Inc.[113] The seals between the windows and the body are made with Viton O-rings. The cell path length is 10.0 millimeters, the volume is approximately four millimeters.

The cell body of the IR cell is OFHC copper with stainless steel tubing soldered in place. The cell windows are cesium bromide (purchased from International

Crystal Laboratories[112]). Two 0.5 mm lead spacers are used to give a pathlength of 1.0 mm.

The spectroscopic cells were constructed in the Caltech Instrument Shop. The low-temperature filtration funnel and chromatography column were constructed in the Caltech Glassworking Shop.

B) Syntheses and Procedures

Melting points were determined using a Thomas-Hoover Melting Point Apparatus and are uncorrected. Infrared spectra were recorded using a Perkin-Elmer 257 Infrared Spectrophotometer. Proton nuclear magnetic resonance (NMR) spectra were obtained on a Varian Associates A-60A or EM-390 Spectrometer. Chemical shifts are reported as parts per million downfield from tetramethylsilane in δ units and coupling constants are in cycles per second (Hz). Proton NMR data are reported in the order: chemical shift; multiplicity, s = singlet, d = doublet, t = triplet, m = multiplet; number of protons; coupling constant; assignment. Carbon-13 NMR spectra were recorded on a Varian Associates XL-100 Spectrometer; carbon NMR chemical shifts are reported as parts per million downfield from tetramethylsilane in δ units.

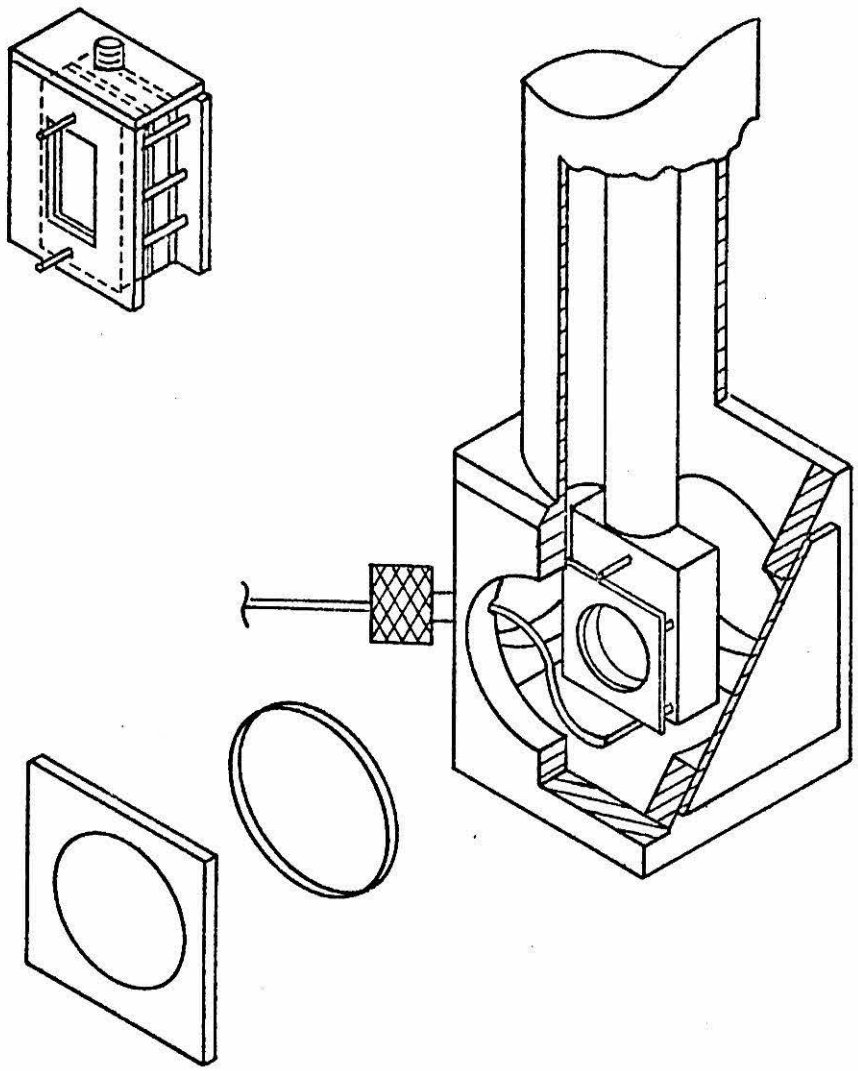
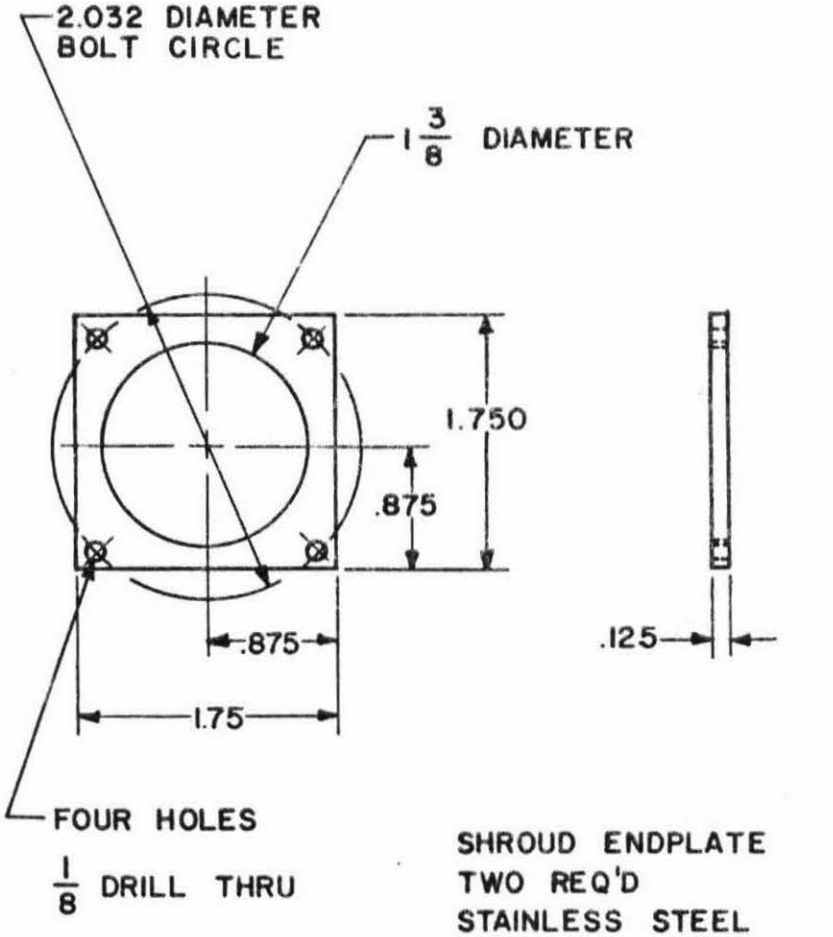
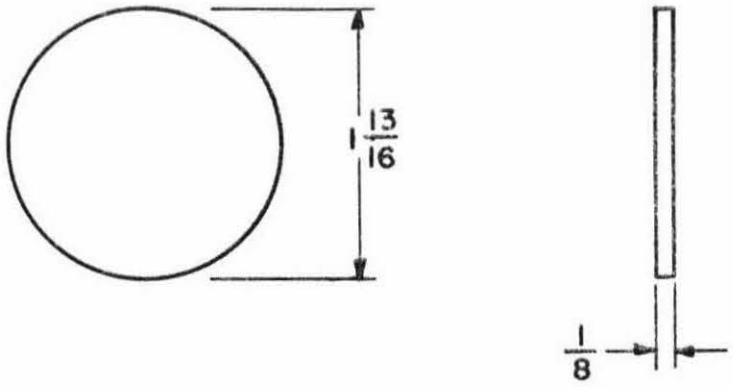


Figure 26. Low temperature spectroscopic cells and shroud.

Figures 27 and 28. Shroud end plate and shroud window.

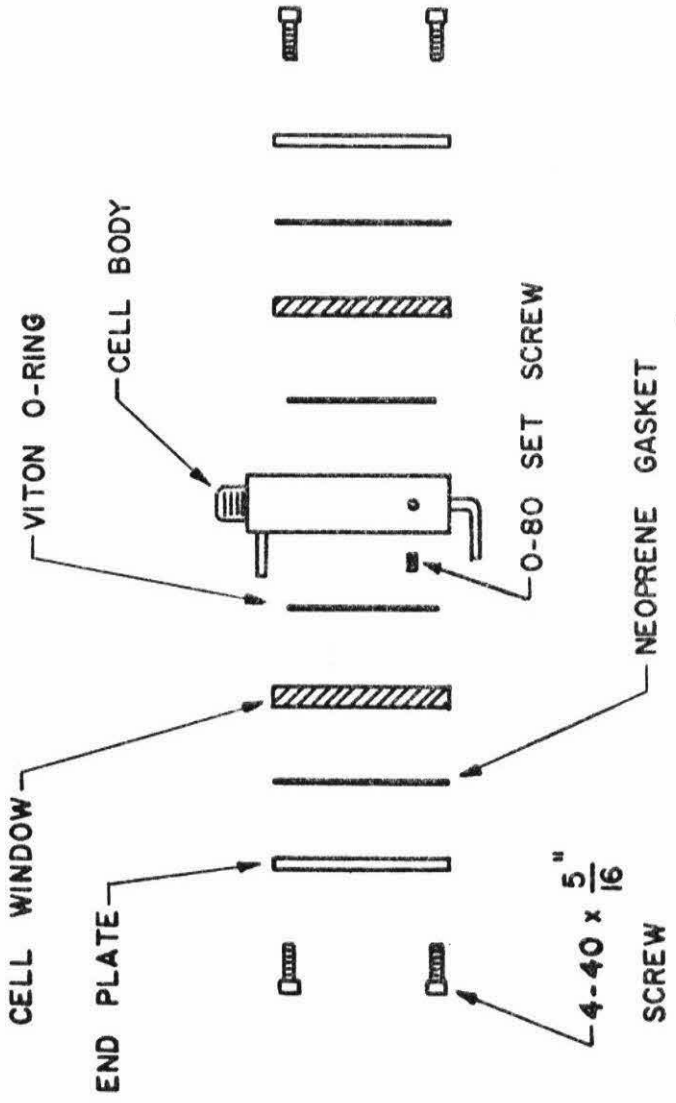


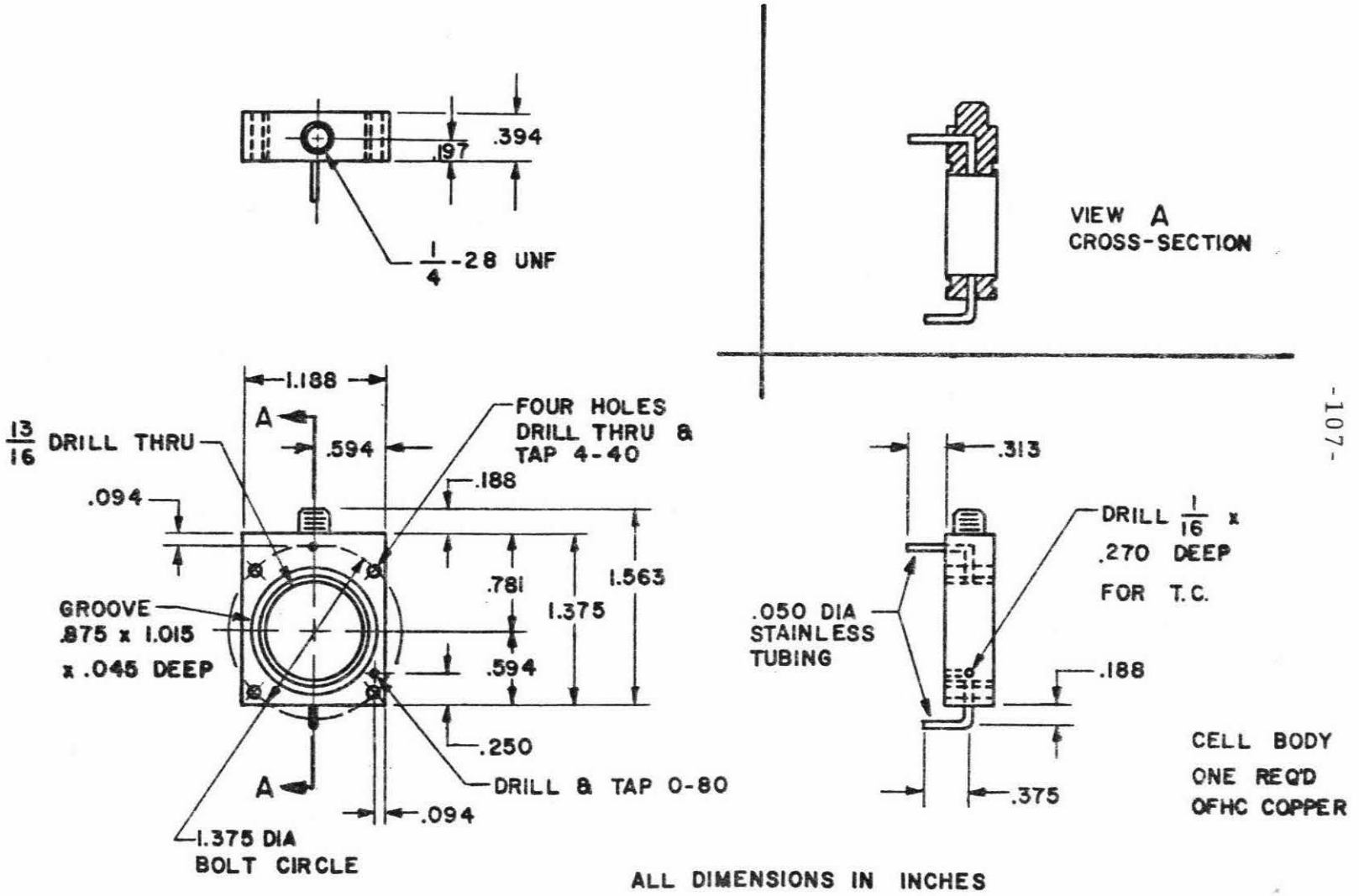
SHROUD ENDPLATE
TWO REQ'D
STAINLESS STEEL
DIMENSIONS IN INCHES



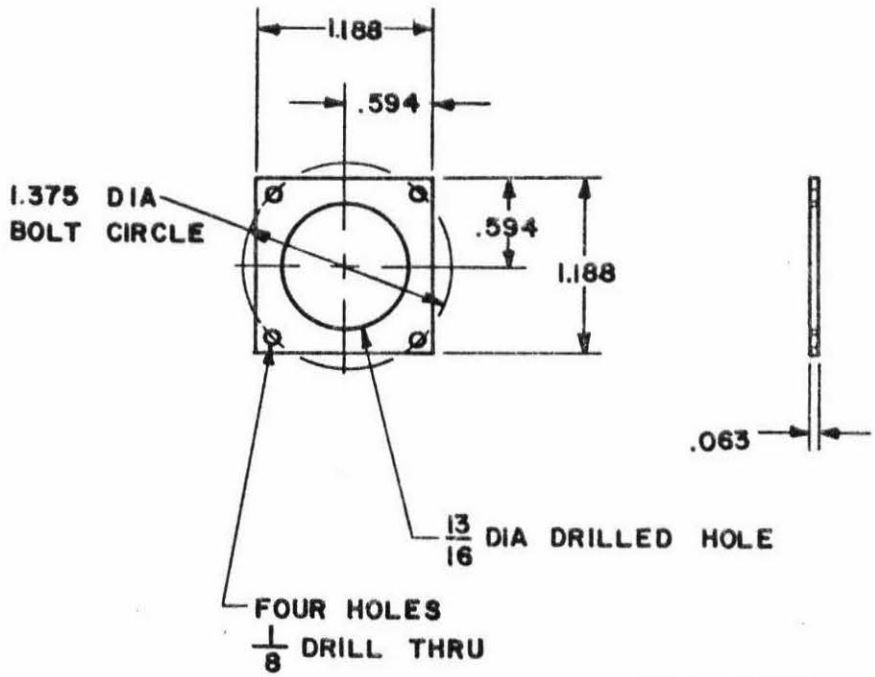
SHROUD WINDOW
TWO REQ'D
SUPRASIL I
DIMENSIONS IN INCHES

Figures 29, 30, 31, and 32. Construction drawings for low temperature UV-VIS spectroscopic cell.


CELL WINDOW
END PLATE
VITON O-RING
CELL BODY
0-80 SET SCREW
NEOPRENE GASKET
4-40 x 5/16"
SCREW



ALL DIMENSIONS IN INCHES

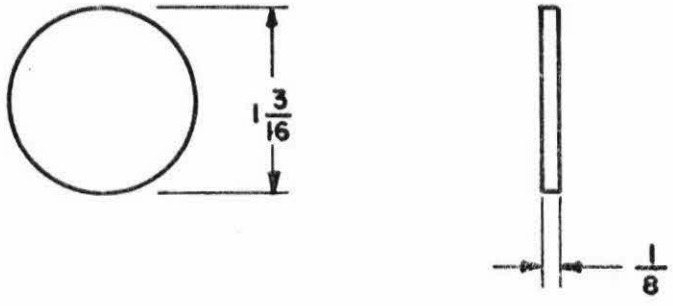


END PLATE

TWO REQ'D

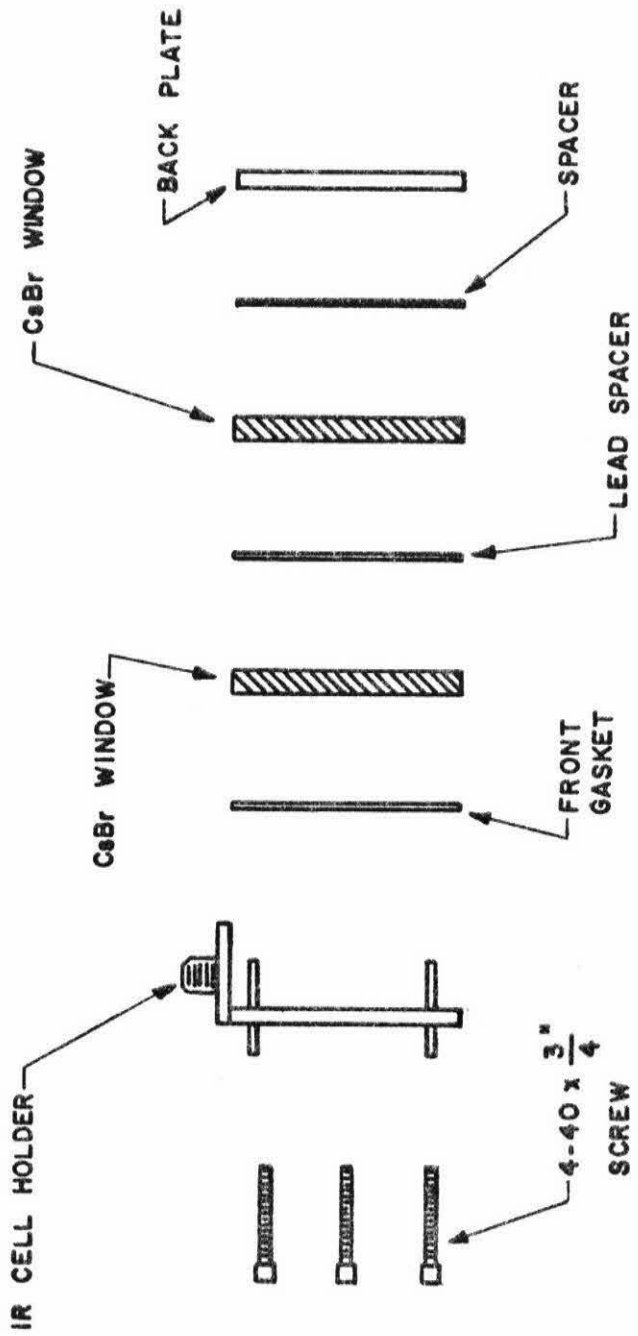
STAINLESS STEEL

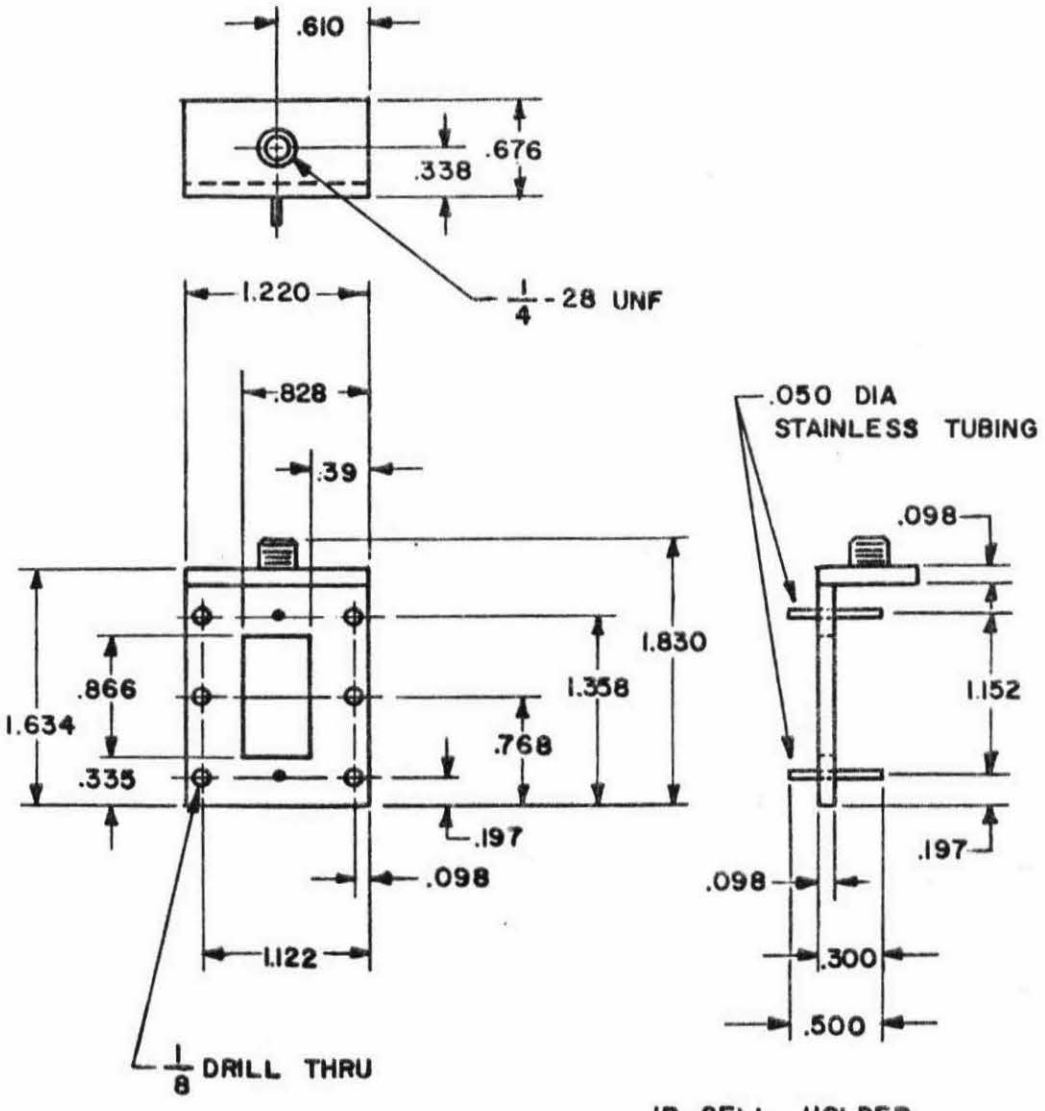
ALL DIMENSIONS IN INCHES



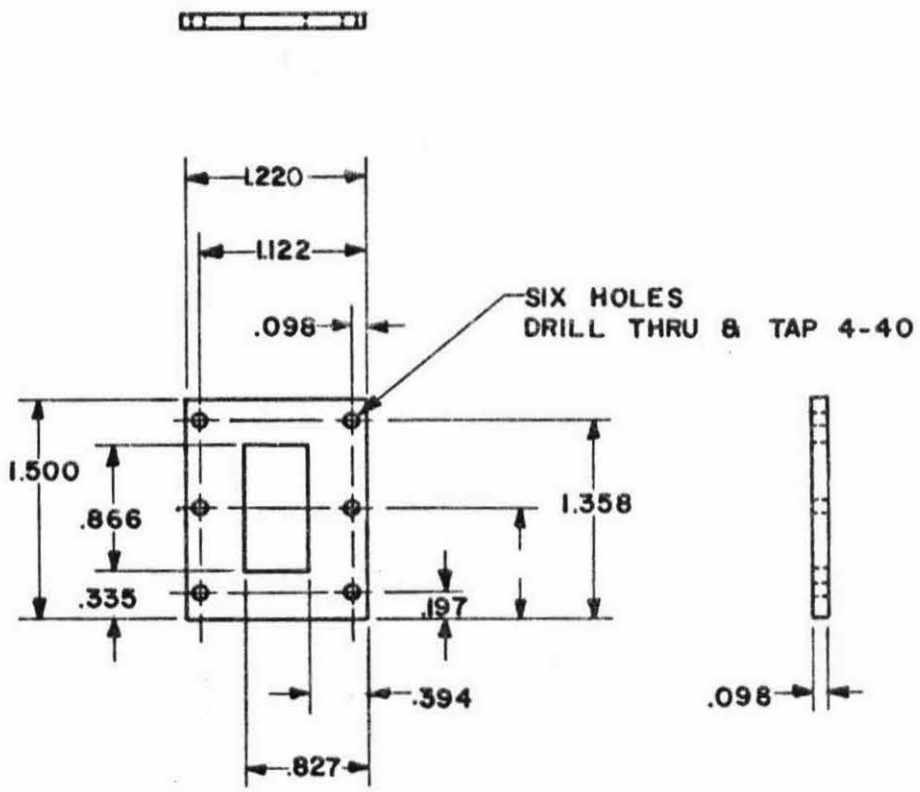
CELL WINDOW
TWO REQ'D
SUPRASIL I

Figure 33, 34, 35, and 36. Construction drawings for low temperature IR spectroscopic cell.

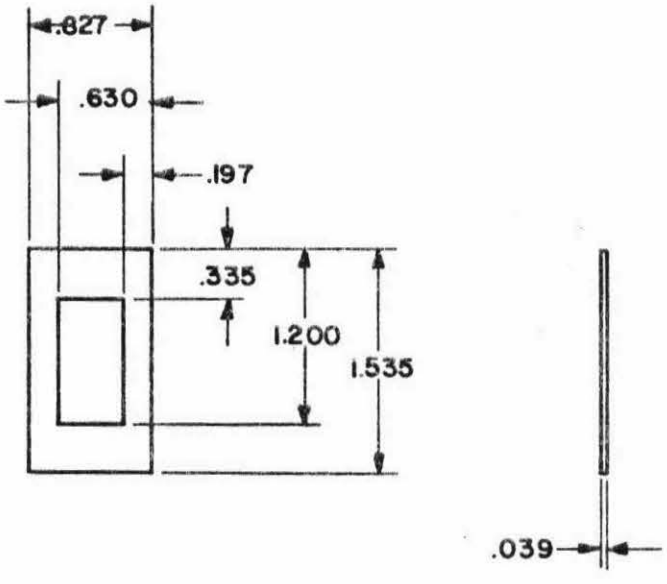

IR CELL HOLDER
4-40 x 3/4"
SCREW
CsBr WINDOW
FRONT
GASKET
CsBr WINDOW
LEAD SPACER
SPACER
BACK PLATE



IR CELL HOLDER
ONE REQ'D
OFHC COPPER

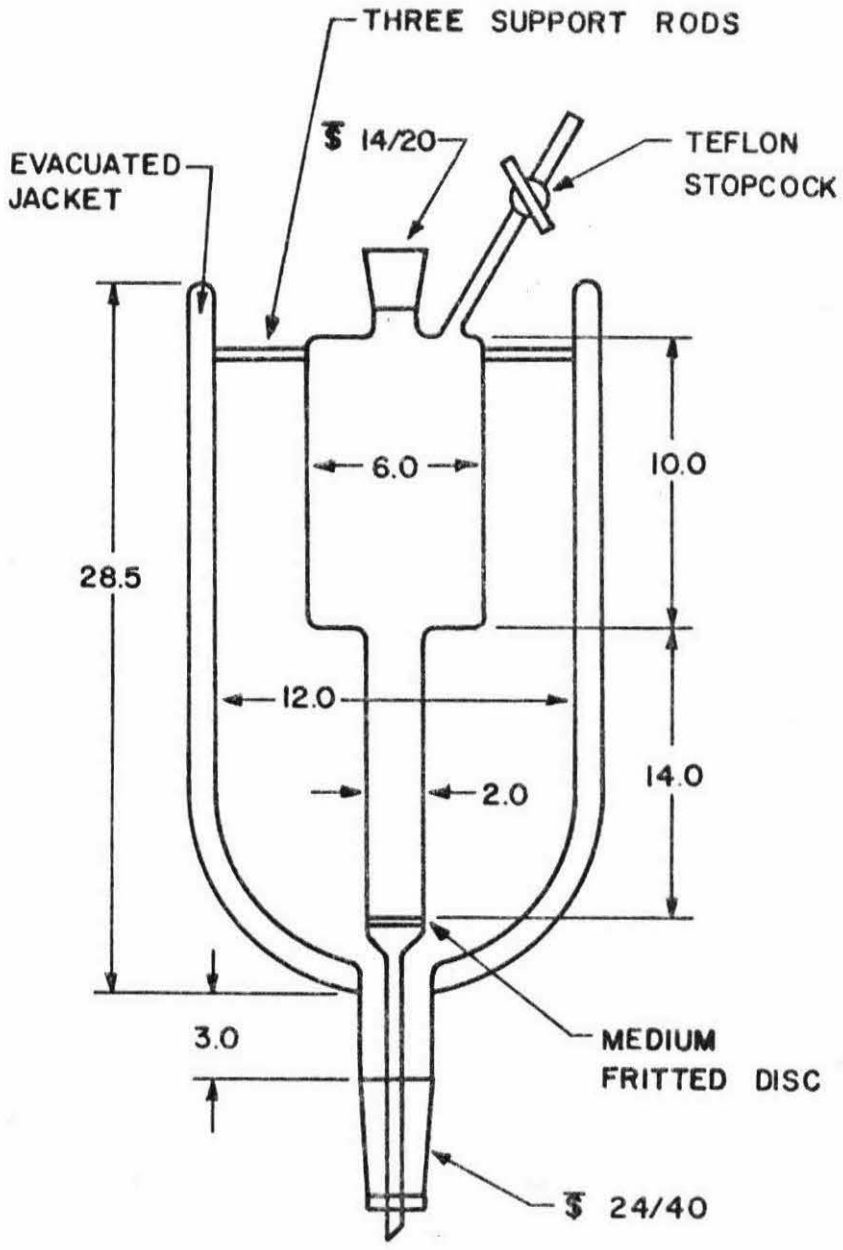


BACK PLATE
ONE REQ'D
OFHC COPPER



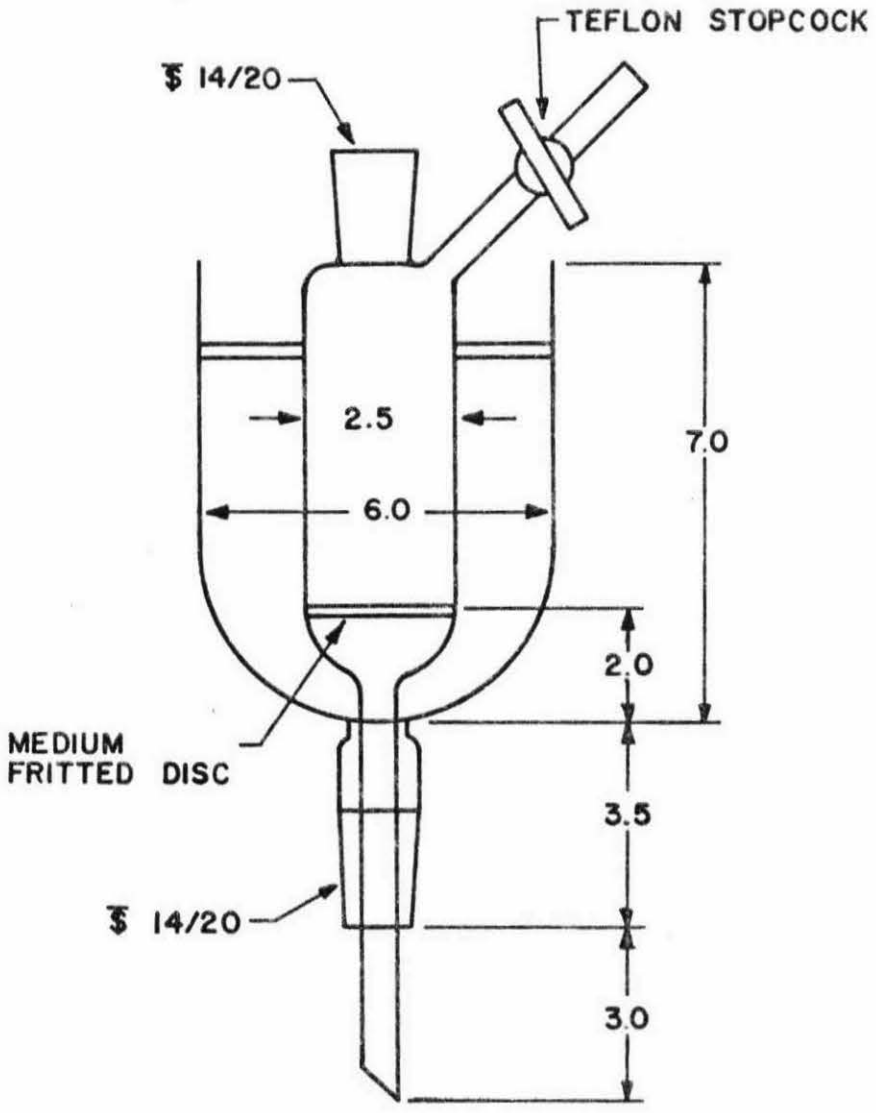
SPACER
ONE REQ'D
LEAD

Figure 37. Low temperature chromatography column.



DIMENSIONS IN CM

Figure 38. Low temperature filtration funnel.



DIMENSIONS IN CM

Analytical vapor phase chromatography (VPC) was performed on a Hewlett-Packard 5700A Gas Chromatograph equipped with flame ionization detector and Hewlett-Packard 3370B Digital Integrator; nitrogen was used as carrier gas. For preparative VPC a Varian Associates 920 Gas Chromatograph was employed using helium as carrier gas. The chromatography columns used in this work are listed in Table 12. Detector response for hydrocarbons was assumed to be 1.00 relative to n-octane. Quantitative analyses of all other compounds were corrected for detector response.

Dibutyl ether was distilled from sodium. Ethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl. Triethylamine, diethylamine and diisopropylamine were distilled from barium oxide. Chloroform was distilled from phosphorous pentoxide. Deuterochloroform used in obtaining diazene NMR spectra was passed through a short column of basic alumina. Acetone-d_6 and methylene chloride-d_2 were dried over 4A molecular sieves. Propane and dimethyl ether used in low-temperature chromatography were dried over 4A molecular sieves. t-Butyl alcohol was distilled from calcium hydride. Pentane and hexane were shaken with concentrated sulfuric acid, saturated

Table 12

VPC Columns

Column Designation	Description
Pennwalt 233	5' x 1/4" glass, 28% Pennwalt 223 on 80/100 Chrom R
Pennwalt 223	10' x 1/8" stainless steel; 28% Pennwalt 223 on 80/100 Chrom R
Carbowax 400	10' x 1/8" stainless steel; 10% Carbowax 400 on 100/120 Chrom P A/W DMCS
β,β	10' x 3/8" aluminum; 25% β,β'-oxydipropionitrile on 60/80 Chrom P
β,β	20' x 1/8" stainless steel; 10% β,β'-oxydipropionitrile on 100/120 chrom P A/W DMCS
UCW-98	10' x 3/8" glass; 25% UCW-98 on 60/80 Chrom W
SF-96	10' x 1/8" stainless steel; 10% SF-96 on 100/120 Chrom P A/W
SF-96	10' x 3/8" aluminum; 25% SF-96 on 45/60 Chrom A

sodium bicarbonate, saturated sodium chloride solution, dried over calcium chloride and distilled from calcium hydride or lithium aluminum hydride. Lead tetraacetate was placed under vacuum for 12 hrs to remove acetic acid. t-Butyl hypochlorite was washed with 10% sodium carbonate, water, dried over calcium chloride and distilled under nitrogen. 1-Amino-2,2,6,6-tetramethylpiperidine was always purified by preparative VPC (Pennwalt 223, 180°) immediately prior to use.

Electron spin resonance (ESR) spectra were obtained using a Varian Associates E-Line Spectrometer. Electronic spectra were obtained using a Cary 14 or 14M Spectrophotometer. Mass spectra were recorded on a Dupont 24-492B Mass Spectrometer. Elemental analyses were performed at the Caltech Microanalytical Laboratory. Unless otherwise indicated, reactions were carried out under a positive pressure of dry nitrogen.

1-Nitroso-2,2,6,6-Tetramethylpiperidine (35).

A modification of the procedure of Overberger and coworkers was used.[6] A solution ~ 0.8 M in HCl was prepared by addition of 14 ml concentrated hydrochloric acid to 200 ml water and placed in a three-necked 1 ℓ round-bottomed flask equipped with magnetic stirrer,

reflux condenser, addition funnel and thermometer. To this was added slowly with cooling 23.7 gm (0.152 mole) of distilled 2,2,6,6-tetramethylpiperidine. After dissolution of the solid the flask was heated to 75° and a solution of 42.1 g (0.61 mole) sodium nitrite in 150 ml water was added over 30 mins. Heating was continued for 96 hrs during which time a yellow oil formed. After cooling to room temperature 100 ml ethyl ether was added to the reaction mixture which was then transferred to a separatory funnel and the layers separated. The aqueous layer was extracted twice with ether. The combined ethereal extracts were washed with 100 ml 10% HCl solution, 100 ml saturated sodium bicarbonate solution, 100 ml of saturated sodium chloride solution. The ethereal extract was dried (Na_2SO_4), concentrated, and distilled giving 25.1 g (89%) of 35: bp 114-117° at 15 torr (lit.[115] 91-92° at 12 torr); IR (CCl_4): 2925 (C-H), 1455 (N=O, CH_2), 1375, 1360 cm^{-1} (gem-dimethyl); NMR ($CDCl_3$) δ 1.90-1.50 (m,6), 1.64 (s,6H, CH_3), 1.40 ppm (s,6H,CH_3); UV (Et_2O) 395 (ε69.5), 238 nm (ε4500) (lit.[115] 397 (ε86), 238 (ε4500).

1-Amino-2,2,6,6-Tetramethylpiperidine (36)

A modification of the procedure of Roberts and Ingold was used.[75] A slurry of 5.0 g (0.13 mole) of lithium aluminum hydride in 150 ml 1:1 ethyl ether/n-

butyl ether was stirred in a 500 ml three-necked round-bottomed flask equipped with addition funnel, magnetic stirrer, thermometer and reflux condenser topped with a still head. To this was added dropwise a solution of 12.5 g (0.071 mole) 1-nitroso-2,2,6,6-tetramethylpiperidine (35) in 25 ml ethyl ether. After stirring for an additional 30 mins solvent was distilled until the internal temperature reached 95°. Heating was continued for four hrs, at which time the reaction mix was cooled to 0° and hydrolyzed by careful addition of a large excess of water. The hydrolyzed mixture was transferred to a separatory funnel and the layers separated. The aqueous layer was extracted (2x75 ml) with ether and the combined organic extracts were extracted (3x100 ml) with 10% HCl solution. The combined acid extracts were made strongly basic with 20% sodium hydroxide solution and were extracted (3x100 ml) with ether. These ethereal extracts were combined and extracted with 100 ml of saturated sodium chloride solution. The ethereal extracts were dried (Na_2SO_4), concentrated and distilled giving 9.1 g (86%) of 36 (95% pure by VPC, Pennwalt 223, 180°): bp 82-85° at 20 torr (lit.[75] 80-83° at 20-21 torr); IR (film) 3350, 3250 (NH_2), 2960, 2925 (C-H), 1370, 1360 cm^{-1} (gem-dimethyl); NMR ($CDCl_3$) δ 2.8

(s,2H,$N\underline{H}_2$), 1.50 (s,6H, ring methylenes), 1.06 ppm (s, 12H,-$C\underline{H}_3$) (lit.[75] 2.8, 1.46, 1.01).

1-Amino(^{15}N)-2,2,6,6-Tetramethylpiperidine (68).

A solution of 0.66 ml concentrated HCl in 6 ml H_2O was prepared and placed in a 25 ml round-bottomed flask, equipped with a serum cap, reflux condenser and magnetic stirrer. To this was added with cooling 1.17 g (8.3 mmol) of 2,2,6,6-tetramethylpiperidine, followed by a solution of 1.00 g $Na^{15}NO_2$ (97.2 atom %, Prochem) in 5 ml of water. The resulting solution was heated to 80° and concentrated HCl was added dropwise with stirring until the solution was slightly acid to pH paper. Heating at 85° was continued for 96 hrs, during which time a yellow oil formed. The mixture was allowed to cool, the organic product was extracted into ether, and the resulting organic layer was washed with 10% HCl solution, saturated sodium bicarbonate solution and saturated sodium chloride solution and dried (Na_2SO_4). This was concentrated affording 1.12 g (79%) of 1-nitroso(^{15}N)-2,2,6,6-tetramethylpiperidine (one spot by TLC [$CHCl_3$, silica gel] with R_f identical to authentic 1-nitroso-2,2,6,6-tetramethylpiperidine). The labelled nitrosamine (1.12 g, 6.55 mmole) was dissolved in 25 ml

of 1:1 ethyl ether/n-butyl ether and combined with 499 mg (13.1 mmol) of lithium aluminum hydride in a 50 ml round-bottomed flask equipped with stir bar, thermometer and reflux condenser topped with a still head. Solvent was distilled from the reaction flask until the internal temperature reached 95°; heating was continued for four hrs. The reaction mixture was cooled and worked up in a manner similar to that used for the unlabelled compound. The crude hydrazine was purified by a high-vacuum distillation (trap-to-trap) at room temperature followed by preparative VPC (Pennwalt 223, 180°) to yield 176 mg (17%) of 68: IR (film) 2960, 2925 (C-H), 1370, 1360 cm^{-1} (gem-dimethyl); MS M^+ = 157 (calc'd. 157); from the relative intensities of the m/e 156 and m/3 157 peaks a 97 ± 2% isotopic purity is calculated.

1,1'-Azo-2,2,6,6-Tetramethylpiperidine (41).

The method of Roberts and Ingold was used.[75] A solution of 638 mg (4.09 mmole) of 1-amino-2,2,6,6-tetramethylpiperidine (36) and 614 mg (8.41 mmole) of diethylamine in 50 ml anhydrous ethyl ether was placed in a 250 ml three-necked round-bottomed flask equipped with dropping funnel and magnetic stirrer. The solution was cooled to 0° and a solution of 2.05 g I_2 (8.1 mmole)

in 100 ml ether was added dropwise with stirring until the iodine color persisted. The reaction mixture was filtered to remove precipitated diethylammonium iodide. The solution was washed three times with 50 ml water, once with 50 ml saturated aqueous sodium chloride and dried (Na_2SO_4). This was concentrated under high vacuum for one hr. The non-volatile residue was dissolved in n-pentane and cooled to -78° which resulted in precipitation of a white solid. The solvent was removed and the compound was recrystallized from pentane at -78° to yield 124 mg (20%) of 41: mp 42-44° (lit.[75] 45-47°); IR ($CHCl_3$) 2925 (C-H), 1460 (CH_2), 1375, 1360 cm^{-1} (gem-dimethyl); NMR ($CDCl_3$) δ 1.60 (s,12H, ring protons), 1.26 ppm (s,24H, CH_3) (lit.[75] 1.57, 1.28); UV (Et_2O) 287 (ε3400), 252 nm (ε7800).

2,6-Dimethyl-2-heptene (37).

A modification of the procedure of Starr and Eastman was used.[116] A solution of 4.31 g (28.0 mmol) of 2,2,6,6-tetramethylcyclohexanone in 400 ml pentane was placed in a quartz photochemical reactor, deoxygenated and cooled to 0°. The solution was photolyzed with a 450 watt Hanovia lamp for 20 hrs. The reaction was followed by analytical VPC (SF-95, 140°). The photolysis mixture was concentrated, distilled under re-

duced pressure. The products were isolated by preparative VPC (β,β, 65°), collecting the two major peaks of relative retention times 3.88 and 5.34 (n-pentane = 1.00). The earlier eluting peak was shown by proton NMR to be 1,1,3-trimethylcyclohexane by comparison with an authentic sample (Chemsampco): NMR ($CDCl_3$) δ 1.8-1.1 (m,9H, ring protons), 0.90 (s,6H,CH_3), 0.80 ppm (d,3H,7Hz,CH-CH_3). The later eluting peak was shown by proton NMR to be identical with 2,6-dimethyl-2-heptene as reported by Starr and Eastman:[116] NMR ($CDCl_3$) δ 5.14 (m,1H, C=C-H), 2.0 (m,2H,C=C-CH_2), 1.70 (s,3H,C=C-CH_3), 1.60 (s,3H,C=C-CH_3), 1.6-1.1 (m,3H), 0.88 ppm (d,6H,6Hz,CH_3-CH-CH_3).

Oxidation of 1-Amino-2,2,6,6-Tetramethylpiperidine 36 with Mercuric Oxide. Characterization of Hydrocarbon Products.

A solution of 1.176 g (7.54 mmol) of 1-amino-2,2,6,6-tetramethylpiperidine (36) in 5 ml anhydrous ethyl ether was added with stirring to a suspension of 6.50 g (30.0 mmol) yellow mercuric oxide in 10 ml ethyl ether at room temperature. After stirring for five hrs the reaction mixture was filtered through Celite and concentrated by distillation. The volatile products were

distilled out under high-vacuum (10^{-5} torr, room temperature) and purified by preparative VPC (β,β, 65°). The four C_9H_{18} isomers eluted in the following order with the retention times relative to ethyl ether = 1.00: 1,1,3-trimethylcyclohexane (1.71), 1,1,2,2-tetramethylcyclopentane (2.03), 2,6-dimethyl-1-heptene and 2,6-dimethyl-2-heptene (2.44). The 1,1,3-trimethylcyclohexane was identified by comparison of its NMR and IR spectra and VPC retention time (ββ, 25°) with those of authentic material (Chemsampco). The 1,1,2,2-tetramethylcyclopentane was identified by its spectral properties: IR ($CHCl_3$) 2950, 2870 (C-H), 1460 (CH_2), 1375, 1365 cm^{-1} (gem-dimethyl); NMR ($CDCl_3$) 1.56, (s,6H,-$C\underline{H}_2$-), 0.85 ppm (s,12H,$C\underline{H}_3$) (lit.[117] δ 1.54, 0.82); MS,M^+ = 126 (calcd. 126). The 2,6-dimethyl-2-heptene was identified by comparison of its NMR and IR spectra and VPC retention time (ββ, 25°) to authentic material: IR (film) 2960, 2920, 2870 (C-H), 1465, 1445 (CH_2), 1380, 1365 cm^{-1} (iso-propyl); NMR (see above). The 2,6-dimethyl-1-heptene was detected as an impurity in the 2,6-dimethyl-2-heptene by its characteristic NMR absorption at δ = 4.70 ppm. The presence of the 1-isomer was confirmed using analytical VPC (ββ, 25°; Carbowax 400, 25°) by coinjection of authentic material

(Chemsampco). In separate experiments, the total absolute yield of the C_9 hydrocarbon products was determined to be 65% by analytical VPC (SF-96, 140°) and the absolute yield of tetrazene 41 was determined to be 20% by proton NMR.

Oxidation of 1-Amino-2,2,6,6-Tetramethylpiperidine 36 with t-Butyl Hypochlorite. General Procedure.[34]

Into a 25 ml round bottomed flask equipped with a magnetic stirrer and cooled to -78° was condensed 12-15 ml of dimethyl ether. To this was added 1-amino-2,2,6,6-tetramethylpiperidine 36 (typically 1-1.5 mmoles; 150-250 mg) by syringe, followed by 1.0 mole-equivalent of triethylamine. With rapid stirring, 1.0 mole-equivalent of t-butyl hypochlorite was added in 10-20 μl portions over a five min period. A pale purple color appeared almost immediately and was fully developed within ten mins. The reaction mixture was stirred at -78° for one hr, then transferred via 10 gauge Teflon tubing to a jacketed filter funnel precooled to -78°. The mixture was filtered under vacuum into a 25 ml three-necked flask precooled to -78° and equipped with magnetic stir bar, serum cap and gas inlet tube. Further manipulations performed on this filtered solution are described below.

Preparation of Solutions of 1,1-Diazene 33 for Visible Absorption Spectroscopy.

Typically, 0.6-1.5 millimole of 1-amino-2,2,6,6-tetramethylpiperidine 36 was oxidized with t-butyl hypochlorite in the manner described above. After filtration the dimethyl ether solution was concentrated to ∿ 2 ml and 4-6 ml of the desired solvent (ethyl ether, n-hexane, dichloromethane or isopropyl alcohol) was chilled to -78° and added to the concentrated solution of 1,1-diazene by means of a stainless steel double-ended needle. After mixing, the solution was drawn into the cooled low-temperature UV-VIS cell and the spectrum recorded.

Preparation of Solutions of 1,1-Diazene 33 for Infrared Spectroscopy.

Approximately 0.8 mmole of 1-amino-2,2,6,6-tetramethylpiperidine (36) was oxidized with t-butyl hypochlorite in the manner described above. After filtration the sample was concentrated to ∿ 2 ml and 4 ml of spectrograde dichloromethane (chilled to -78°) was added via a double-ended stainless steel needle. The flask was again placed under vacuum (∿ 0.03 torr) for 30 mins. Dry nitrogen was admitted to the flask, the sam-

ple was drawn into the low temperature IR cell (pre-cooled to -78°) and the spectrum recorded. The sample was then removed from the cell, allowed to decolorize at 25°, recooled to -78°, drawn into the cell and the spectrum recorded. An identical procedure and scale was used for the N^{15} labelled compound 68.

Oxidation of 1-Amino-2,2,6,6-Tetramethylpiperidine (36) with t-Butyl Hypochlorite. Determination of Hydrocarbon Yields by Analytical VPC.

The general procedure above was used to oxidize 189.9 mg (1.28 mmole) of 1-amino-2,2,6,6-tetramethylpiperidine (36) with t-butyl hypochlorite. Before transferring to the jacketed filter funnel 24.01 mg of n-octane and 27.47 mg of cyclooctane were added to the reaction mixture. After filtration and concentration of the reaction mixture to ∿ 2 ml, 2 ml of dry ethyl ether was added and the resulting solution stirred. The mixture was then allowed to warm to room temperature (decolorize), transferred to another flask and diluted to 3 ml total volume. This mixture was analyzed by analytical VPC (Carbowax 400, 25°). The results of the analysis are tabulated in Table 13. Analysis of the reaction mixture on Pennwalt 223 (170°) revealed that 67 mg (0.43 mmole) of 36 remained unreacted. This gives

Table 13

Compound	Relative Retention Time	Relative Area	Absolute Yield (%)
n-octane	1.00	1.000	---
1,1,3-trimethylcyclohexane (40)	1.55	0.0242	0.4
1,1,3,3-tetramethylcyclopentane (38)	1.65	0.257	3.8
2,6-dimethyl-1-heptene (39)	1.98	0.074	1.1
2,6-dimethyl-2-heptene (37)	2.19	0.637	9.5
		Total Absolute Yield:	14.8%

a total hydrocarbon yield (corrected for unreacted starting material) of 22%.

In another experiment, 236 mg (1.50 mmole) of 36 was oxidized with t-butyl hypochlorite in the manner described above. After filtration and concentration at -78°, 3.6 ml of dry ethyl ether was added, followed by 33.9 mg of cyclooctane. A visible spectrum of the resulting solution was recorded; the solution had an optical density of 1.30 absorbance units at 543 nm. The filtrate weighed 137 mg and was identified as triethylamine hydrochloride (1.0 mmole, 66%) by comparison of its IR spectrum ($CHCl_3$) to authentic material. The ethereal solution was allowed to warm to room temperature (decolorize) and the hydrocarbon yield was determined by analytical VPC (SF-96, 100° and Pennwalt 223, 150°). The results of these analyses show a 24% absolute yield of hydrocarbons, and 0.38 mmoles of 1-amino-2,2,6,6-tetramethylpiperidine remaining. This corresponds to a 32% hydrocarbon yield, corrected for remaining starting material. If it is assumed that the number of moles of hydrocarbon is equal to the number of moles of diazene in the original solution, than an order-of-magnitude estimate of the extinction coefficient can be made:

$$\varepsilon = \frac{A}{\ell c} = \frac{1.30}{(1.00)\ \frac{(0.24)(0.0015)}{0.0036}} \cong 13$$

Oxidation of 1-Amino-2,2,6,6-Tetramethylpiperidine (36) with t-Butyl Hypochlorite. Determination of Absolute Yields by Proton NMR Spectroscopy.

Oxidation of 160 mg (1.03 mmole) of 1-amino-2,2,6,6-tetramethylpiperidine (36) was carried out using the procedure described above. After filtration and concentration, 1.5 ml of deuterochloroform containing 15.0 μℓ dichloromethane was added and the sample was pumped on at ∿ 0.03 torr at -78° for one hr. The sample was then transferred to three 5 mm NMR tubes and stored in liquid nitrogen. Subsequent proton NMR spectroscopy at -70° on this crude reaction mixture resulted in detection of NMR absorptions due to the 1,1-diazene 33: a broad singlet at δ 2.15 and a sharp singlet at δ 1.15 ppm (ratio of areas 1:2 respectively). Integration of the NMR spectrum allowed the calculation of the following approximate absolute yields from the oxidation: t-butyl alcohol, 0.85 mmol (93%); N-(2,2,6,6-tetramethylpiperidyl)nitrene (33), 0.20 mmole (19%); 1,1'-azo-2,2,6,6-tetramethylpiperidine (41), 0.035 mmole (6%). The spectrum also showed 0.58 mmoles of 36 (57%) unreacted.

The estimated concentration of 1,1-diazene 33 is 0.12 moles/liter. The sample was allowed to decolorize by warming to room temperature. The NMR spectrum of this thermolyzed sample indicated that all of the diazene was converted to tetrazene upon warming the sample. (Integration showed the presence of 0.14 mmoles of tetrazene 41).

Preparation of Solutions of 1,1-Diazene 33 for Carbon-13 NMR Spectroscopy.

The oxidation of 300 mg (1.92 mmole) of 1-amino-2,2,6,6-tetramethylpiperidine (36) was carried out using the procedure described above. After filtration at -78°, 5.0 g of dichloromethane-d_2 was added and the sample was placed under vacuum (0.03 torr) for two hrs. The sample was then transferred to a test tube precooled to -78° and containing 150 μl of tetramethylsilane. The sample was placed in a 12 mm NMR tube and the carbon-13 NMR spectrum recorded. Typically, spectra were recorded at -80°, using the following instrument parameters: 5000 Hz spectral width, 0.80 second acquisition time, 5.0 second pulse delay, 55 microsecond pulse width, and accumulating 300 transients. Carbon-13 NMR samples in hexadeuteroacetone were prepared in an identical manner, substituting 3.0 ml of acetone-d_6 for the di-

chloromethane-d_2. After recording the spectrum the sample was allowed to decolorize by warming to room temperature, and a spectrum of the decolorized solution was recorded at -80°.

Preparation of Solutions of 1,1-Diazene 33 for ESR Spectroscopy.

The oxidation of 122 mg (0.78 mmole) of 1-amino-2,2,6,6-tetramethylpiperidine (36) was carried out using the procedure described above. After filtration and concentration at -78°, 1.5 ml of $CHCl_3$ was added and the sample was placed under vacuum (0.03 torr) for two hrs. A portion of this solution was placed in an ESR tube, degassed (four freeze-pump-thaw cycles), placed in the ESR cavity (precooled to 77°K), and the spectrum recorded. The sample was allowed to decolorize at room temperature and a solution ESR spectrum recorded at 270°K. The remainder of the solution of 33 (1.25 ml) was diluted to 4.5 ml with ethyl ether and a visible spectrum showed the optical density of this solution at 543 nm to be A = 0.31. From this the concentration of 1,1-diazene in the ESR experiment can be calculated to be:

$$c = \frac{4.5 \times 0.31}{1.25 \times 18 \times 1.0} \cong 0.06 \text{ moles/liter}$$

A control experiment showed no ESR signal in a solution of 36 in chloroform.

Low-Temperature Column Chromatography. Partial Purification of 1,1-diazene 33.

Deactivated basic alumina was prepared by washing 150 g of Woelm Activity I neutral alumina three times with 150 ml of 12% sodium hydroxide solution and decanting. After washing two times with 150 ml distilled water the alumina was washed three times with anhydrous methanol and dried for seven hours at 215°.

The low-temperature chromatography column was equipped with a 200 ml three-necked round-bottomed flask (equipped with serum cap and gas inlet). A mechanical stirrer was fitted so as to mix the solvent in the jacket surrounding the column. The column was charged with 30 g deactivated basic alumina and capped with a serum cap. The jacket was filled with acetone and cooled to -82° by adding liquid nitrogen and stirring. The column was wetted and rinsed through with 40 ml of liquid propane (cooled to -78°), added by means of a double-ended needle. The concentrated 1,1-diazene solution (prepared by oxidizing ∿ 200 mg 1-amino-2,2,6,6-

tetramethylpiperidine (36) with t-butyl hypochlorite in the manner described above, filtering and concentrating to ∿ 3 ml) was carefully placed on the column via double-ended needle and allowed to percolate onto the adsorbent. Elution was begun with 3:7 dimethyl ether/propane, using a positive pressure of nitrogen at the column head to force the solvent through. When the colored band reached the bottom of the column, elution was halted by releasing the nitrogen pressure at the column head; the forerun was drawn off through a double-ended needle into an evacuated 200 ml flask, cooled to -78°. Elution was resumed until most of the colored band had been collected; this colored solution was drawn off into a 100 ml round bottomed flask equipped with serum cap, magnetic stirrer and nitrogen inlet and precooled to -78°. Approximately three ml of this solution were removed and allowed to warm to room temperature with evaporation of solvent. The residue was dissolved in $CDCl_3$ and examined by proton NMR to determine the degree of purification. By comparison of the volumes and optical densities of the colored solution before and after chromatography it was determined that only ∿ 40% of the 1,1-diazene 33 survives

the chromatography conditions; dimerization to the tetrazene 41 apparently occurs on the alumina surface (see below).

When proton NMR samples of 1,1-diazene 33 were being prepared cyclopropane was substituted for propane, using identical proportions. Proton NMR samples were prepared by adding 1.5 ml of deuterochloroform containing 15 μℓ of dichloromethane to the chromatographed diazene solution and placing the solution under vacuum (0.03 torr) for at least two hrs to remove chromatography solvents. The resulting concentrated solution was placed in 5 mm NMR tubes and the NMR spectra were recorded at -50°. Typically the chromatographed diazene solution contained substantial amounts of triethylamine, tetramethylaminopiperidine (36), tetrazene (41), and 1,1-diazene (33). The chromatography removed t-butyl alcohol, a large portion of unreacted tetramethylaminopiperidine 36, and trace impurities. The extent of purification was not always reproducible; on several occasions the chromatography gave complete separation of the diazene 33 from tetramethylaminopiperidine 36. Triethylamine could be eliminated from the chromatographed diazene by the

use of 0.9 rather than 1.0 equivalents of the tertiary amine in the oxidation reaction. It was possible on occasion to obtain solutions of diazene in which the only contaminant was the tetrazene in a mole ratio of ∿ 2:1 (tetrazene:diazene). Proton NMR spectroscopy on such a solution at -50° indicated that 1,1-diazene 33 was present in a concentration of ∿ 0.03 moles/liter (relative to dichloromethane internal standard present in a concentration of 0.16 moles/liter; see Figure 8). This corresponds to an absolute yield of diazene of ∿ 4%. The sample was warmed to room temperature and allowed to decolorize. Subsequent proton NMR analysis at -50° indicated that ∿ 60% of the 1,1-diazene 33 had extruded nitrogen and formed the hydrocarbons 37-40 while ∿ 30% had dimerized to tetrazene 41, see Figure 9. (There is a large uncertainty associated with these percentages, and these values should be treated as semiquantitative; i.e., the results indicate that, under the conditions of the experiment, the nitrogen extrusion and dimerization pathways are competitive.)

Decomposition Kinetics of 1,1-Diazene 33. Apparatus and Procedures.

Solutions for studying the decomposition kinetics of 1,1-diazene 33 were prepared in the following manner. Typically, ∿ 200 mg of 1-amino-2,2,6,6-tetramethylpiperidine (36) was oxidized with t-butyl hypochlorite and the resulting solution purified by low-temperature column chromatography using the procedure described above. Immediately after the colored band eluted from the column 100 μℓ of dry triethylamine was added to remove any adventitious acid. This was necessary in order to obtain reproducible kinetics. After removal of a 3 ml aliquot of the colored solution for NMR assay of purification, 10-25 ml of the freshly distilled solvent (ethyl ether, n-hexane or tetrahydrofuran), chilled to -78°, was added by means of a double-ended needle, and the resulting solution was placed under vacuum (0.03 torr) for two hours at -78° to remove the chromatography solvents. The solution was then transferred to a 50 ml centrifuge tube and stored in liquid nitrogen until use.

The low-temperature spectroscopic cell was modified in the following ways. The coolant well was capped with a fitting which allowed the circulation of cold liquids through the well (see Figure 39). This fitting consisted

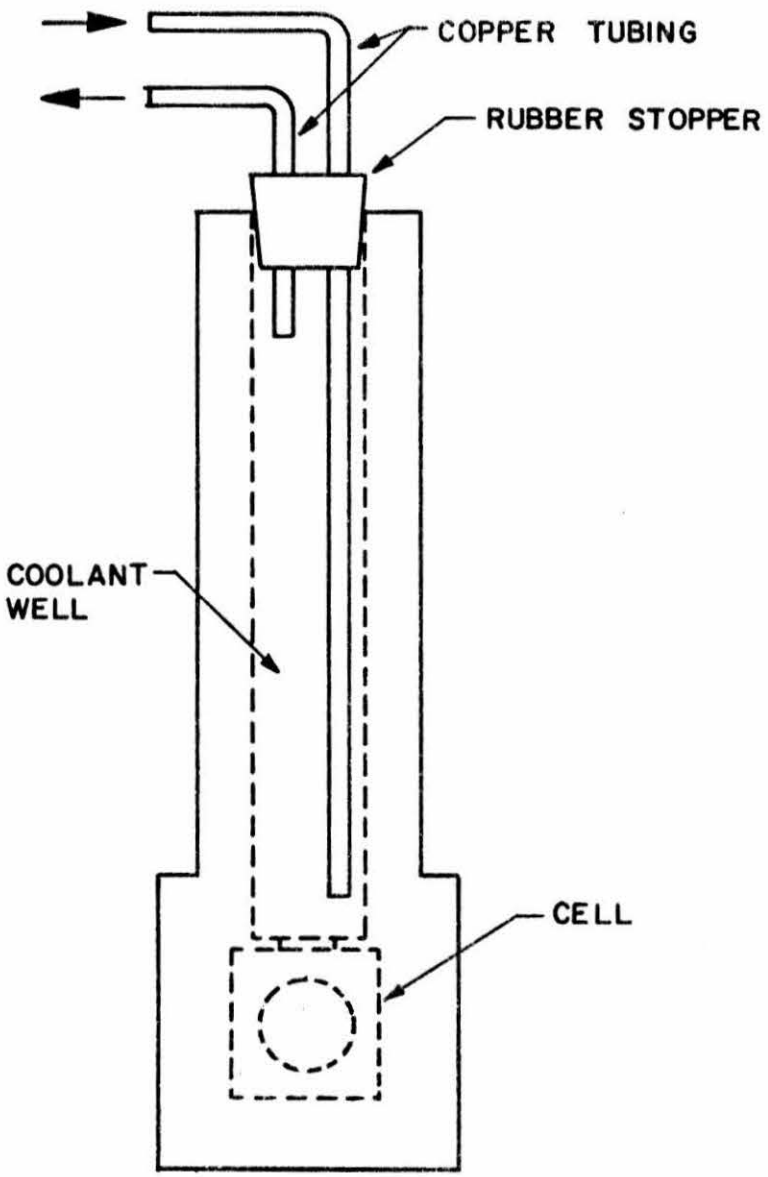


Figure 39. Low temperature spectroscopic cell with modifications for kinetic studies.

of a two-hole rubber stopper and two lengths of 1/4" copper tubing, and was connected via latex tubing to a Little Giant Model 1 immersion pump which provided rapid circulation of cold liquids through the coolant well. The outer cell windows were wrapped with heating tape in order to prevent water condensation during extended kinetic runs.

Two different constant-low temperature baths were used. For kinetic studies above -17°, a Forma Scientific Model 2095 Refrigerated Bath was used, employing ethylene glycol-water as the bath liquid above 0° and methanol as the bath liquid below 0°. For kinetic studies below -17° a constant-low temperature bath constructed in these laboratories (design based on that of Gunn[118]) was employed (see Figure 40). Basically the bath utilizes a reservoir of liquid nitrogen, in thermal contact with the bath liquid, as a refrigerator. Temperature regulation is effected by use of an immersion heater connected to a Yellow Springs Instruments Model 63RC Thermoregulator and Model 633 Probe. Methanol was employed as the bath liquid.

Temperatures were determined by means of an iron-constantan thermocouple imbedded in the body of the spectroscopic cell and connected to a Fluke Model 803B/

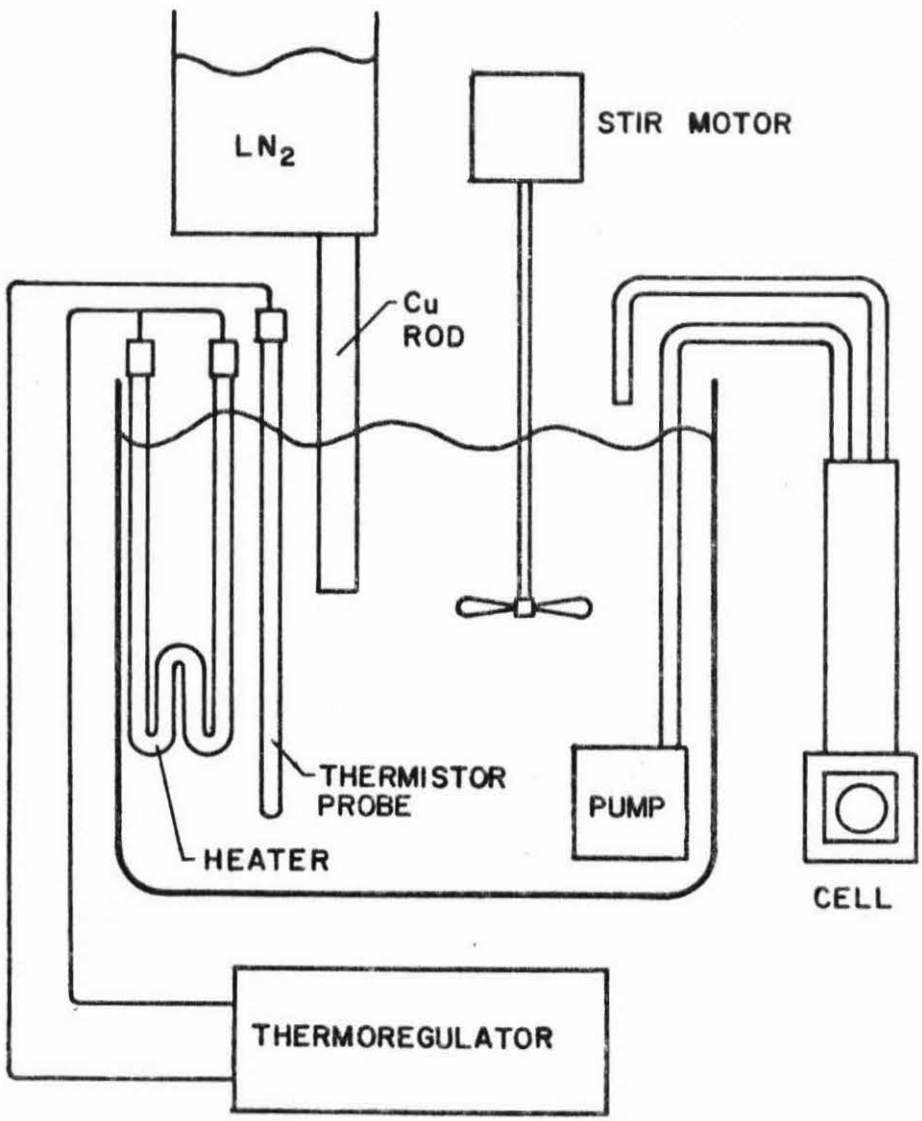


Figure 40. Constant low-temperature circulating bath.

AG differential voltmeter which allowed the determination of temperature to the nearest 0.2°.

A typical kinetics run was carried out in the following manner: the spectroscopic cell was flushed at least four times and filled with freshly distilled solvent. The circulating pump was immersed in the cold constant-temperature bath and the cell allowed to stand until a constant temperature was reached. A 30 ml syringe was filled with dry nitrogen and was used to expel solvent from the cell and flush it with nitrogen. The previously prepared solution of 1,1-diazene 33 was carefully drawn into the cell. The cell was sealed and placed in the spectrophotometer cell compartment and the spectrophotometer was actuated, recording the absorbance at 541 nm as a function of time. The cell temperature was monitored continuously until a constant equilibrium temperature was established (∿ 4 mins) and periodically thereafter. All data obtained prior to temperature equilibration were discarded. Typically the reaction was followed through ten half-lives; the data were analyzed by plotting the logarithm of the absorbance versus time. In cases where spectrophotometer stability was the limiting factor, kinetics were followed over three half-lives and the data were analyzed using the method of Guggenheim.[119a] In all

cases the reported rate constants are derived by conventional linear least-square analysis. The rate constants are estimated to be accurate to ± 5% or better, based on repetitive determinations.

In order to confirm that a truly first-order process was being observed (rather than a pseudo- first-order process) the following control experiment was carried out in each solvent used in this kinetic study: A portion of the stock solution of 1,1-diazene 33 was removed and the rate constant for diazene decomposition was determined. Another portion of the stock solution was removed and diluted with solvent to a volume ∿ 1.5 times the original volume. The rate constant for diazene decomposition was determined for this diluted solution and compared to that for the undiluted solution; in all cases the values were identical within experimental error (± 3% or better).

In each solvent the diazene decomposition kinetics were determined using at least two and usually three independently prepared stock solutions of 1,1-diazene 33. There were no differences observed between the different stock solutions.

Determination of the Extinction Coefficient of 1,1-Diazene 33.

The oxidation of 239 mg (1.53 mmole) of 1-amino-2,2,6,6-tetramethylpiperidine (36) with t-butyl hypochlorite was carried out using the general procedure described above, but substituting trimethylamine for triethylamine. Low-temperature chromatography was carried out as above, using dimethyl ether/cyclopropane as the solvent system. Deuterochloroform (3 ml) was added to the chromatographed diazene solution and the solution was placed under vacuum (0.03 torr) for two hours to remove chromatography solvents. The resulting concentrated solution was transferred to a graduated test tube at -78°. To 2.60 ml of this solution was added 25.4 mg of dichloromethane. Proton NMR analysis of this solution at -50° showed the concentration of 1,1-diazene 33 to be 0.017 ± 0.002 moles/liter. To the remaining 1.40 ml of this solution was added sufficient dry ethyl ether to give a final volume of 4.5 ml. A visible absorption spectrum of this solution gave an absorbance at 543 nm of 0.096 ± 0.005 absorbance units. From this the molar extinction coefficient at 543 nm may be calculated:

$$\varepsilon = \frac{A}{\ell c} = \frac{0.096}{(1.0)(0.017)(\frac{1.40}{4.50})} = 18 \pm 3$$

Photochemical Study of 1,1-Diazene 33.

The oxidation of 1-amino-2,2,6,6-tetramethylpiperidine (36) was carried out as described above and the resulting solution of 1,1-diazene 33 was purified by low-temperature column chromatography. To the solution of chromatographed 1,1-diazene was added 4.2 ml of dry ethyl ether and 8.3 mg of n-octane. An electronic spectrum of the resulting stock solution was recorded, indicating an optical density of 0.38 at 543 nm; this corresponds to a concentration of 1,1-diazene 33 of 2.2×10^{-2} moles/liter. A 2.2 ml portion of the stock solution was diluted to 4.0 ml with ether (O.D. at 543 nm = 0.20) and irradiated with a 1000 watt focused beam xenon arc lamp operating at 760 watts, filtered through a neodymium nitrate/cupric chloride solution filter[120] which passed 31% of the light at 546 nm (filter bandwidth at half-maximum 20 nm); the sample temperature never exceeded -67°. After 180 mins irradiation time the O.D. of the solution at 543 nm was 0.165 (an 18% decrease). The sample was then allowed to stand in the dark at ∿ -72°; after

180 mins the OD at 543 nm was 0.145 (a 12% decrease).

The remaining 2.0 ml of stock solution was irradiated with the same xenon lamp, filtered only through 7.5 cm of distilled water. The sample temperature never exceeded -59°. After 60 mins the sample was completely bleached. The sample was removed and was analyzed by VPC (Carbowax 400, 25°). The results of this analysis are given in Figure 24.

An effort was made to detect by analytical VPC (SF-96, 80°) any 3,3,7,7-tetramethyl-1,2-diaza-1-cycloheptene 59 (the 1,2-diazene isomeric to 1,1-diazene 33) which could have been formed in the photodecomposition. No peaks consistent with the presence of 59 were found, using the retention time of the homologue 58 (n = 6) as an estimated retention time of 59.

Computer Simulation of N-(2,2,6,6-Tetramethylpiperidyl) nitrene (33) Decomposition Kinetics.

The MSIM4 Stochastic Mechanism Simulator developed by Houle and Bunker was used for this simulation.[94] Approximate values of the rate constants were obtained from the experimental kinetic data. These values were refined by trial and error until a satisfactory fit of the simulation to the experimental data was obtained.

Due to the uncertainties in the experimental data, the rate constants derived from these simulations have estimated uncertainties on the order of 20-30%. The results are given in Tables 9 and 10; the fits are shown in Figure 20 and 21.

Thermal Decomposition of 1,1-Diazene 33. Determination of the Effect of Solvent and Temperature on Hydrocarbon Product Ratios.

The oxidation of 1.4-2.1 mmoles of 1-amino-2,2,6,6-tetramethylpiperidine (36) was carried out using the procedure described above. After purification by low-temperature column chromatography, 50 μℓ of triethylamine was added along with 2-3 ml of the solvent of interest (n-hexane, ethyl ether or tetrahydrofuran) and 10.0 μℓ of n-octane as internal standard. The solution of 1,1-diazene 33 was placed under vacuum (0.03 torr) for two hrs to remove chromatography solvents. The resulting solution was placed in six 5 mm x 100 mm base-washed Pyrex tubes (capped with serum caps, thoroughly flushed with dry nitrogen and precooled to -78°). The samples were then thermolyzed at the appropriate temperature (0.0°, -10.0° or -20.0°) using an ice/water or a Forma bath; the samples were

allowed to completely decolorize. After thermolysis the samples were subjected to analytical VPC (ββ, 25°). The results are tabulated in Table 11. These results are the average values resulting from two samples at each temperature. Each sample was analyzed twice to ensure reproducibility.

2,2,6,6-Tetramethylheptanedioic Acid (69).

The method of Creger was used.[104a] In a 1 ℓ three-necked round-bottomed flask equipped with dropping funnel, reflux condenser and magnetic stirrer was placed 310 ml (0.50 moles) of a 1.60 M solution of n-butyllithium in hexane. To this was added with cooling and stirring 50.6 g (0.50 mole) of diisopropylamine in 80 ml dry tetrahydrofuran. The cooling bath was removed and stirring was continued for 30 mins. After recooling to 0°, 22.0 g (0.25 mole) of isobutyric acid was added via syringe with stirring. The mixture was warmed to room temperature and stirred until the solid dissolved. To this was added, with cooling, 25.2 g (0.125 mole) 1,3-dibromopropane. After stirring at room temperature for 20 minutes, an excess of water was added, followed by the addition of 10% HCl until the aqueous layer was strongly acidic. The layers

were separated and the solvent removed under vacuum from the organic layer. The aqueous layer was extracted twice with dichloromethane and these extracts were combined with the residue from the organic layer. The combined extracts were washed three times with 10% sodium hydroxide solution. These basic extracts were acidified with concentrated hydrochloric acid, resulting in the formation of a white precipitate. The solid was extracted into dichloromethane. The solution was washed with saturated sodium chloride solution and dried (Na_2SO_4). The solution was filtered and concentrated. Petroleum ether was added to the residue to precipitate, in three crops, 13.2 g (48%) of 69 as colorless crystals: mp. 167-169° (lit.[121] 168-169.5°); IR ($CHCl_3$) 3600-2300 (C-H,COO-H), 1700 (C=O), 1475 (CH_2), 1408 (C-O-H bend), 1385, 1365 (gem-dimethyl) 935 cm^{-1}(O-H bend); NMR ($CDCl_3$) δ 11.5 (broad,2H,$CO_2\underline{H}$), 1.45 (m,6H,-$C\underline{H}_2$), 1.16 ppm (s,12H,-$C\underline{H}_3$).

2,2,6,6-Tetramethylheptanediamide (62).

Thionyl chloride (50 ml) and 12.20 g (0.056 mole) of 2,2,6,6-heptanedioic acid (69) were combined and heated at reflux for two hrs. The thionyl chloride was removed under aspirator pressure and the crude

diacid chloride was added to 50 ml anhydrous ammonia at -78° dropwise with stirring. The cooling bath was removed and the ammonia allowed to evaporate. The residue was washed twice with 10% sodium hydroxide solution, and the remaining solid was recrystallized from absolute ethanol to yield 9.35 g (78%) of 62 as colorless crystals: mp 194-195° (lit.[121] 193-194°); IR: (nujol) 3395, 3195 (NH_2), 1655 (C=O), 1625 cm^{-1} ($COHN_2$); NMR (CD_3OD) δ 1.45 (m,6H,-CH_2), 1.15 ppm (s, 12H,CH_3).

2,6-Dimethyl-2,6-bis(t-butoxycarbonylamino)heptane (63).

The method of Baumgarten and coworkers was employed.[104b] A 500 ml three-necked round bottomed flask was equipped with a magnetic stirrer and reflux condenser. In it was placed 250 ml of t-butyl alcohol and 9.35 g (0.044 mole) of 2,2,6,6-tetramethylheptanediamide (62). The mixture was heated at reflux until dissolution occurred. The heat was removed and 1.0 ml of tin tetrachloride was added. Lead tetraacetate (39.0 g, 0.088 mole) was added in one portion with stirring. Heating at reflux with stirring was continued for 17 hrs. The t-butyl alcohol was removed under vacuum and the residue was dissolved in ethyl ether,

decanted and washed three times with 10% sodium carbonate solution, once with saturated sodium chloride solution and dried (Na_2SO_4). This was concentrated affording a white solid which was recrystallized from heptane to yield 12.04 g (76%) of 63: IR ($CHCl_3$) 3440 (N-H), 2970 (C-H), 1700 (C=O), 1390, 1365 cm^{-1} (gem-dimethyl); NMR ($CDCl_3$) δ 4.35 (s,2H,N-H), 1.75-1.35 (m,6H,-CH_2-), 1.44 (s,18H,O-C(CH_3)$_3$), 1.25 ppm (s,12H,CH_3).

Anal. Calcd. for $C_{19}H_{38}N_2O_4$: C, 63.65; H, 10.68; N, 7.81. Found: C, 63.60; H, 10.66; N, 7.90.

2,6-Diamino-2,6-Dimethylheptane Dihydrochloride (70).

The procedure of Baumgarten and coworkers was employed.[104b] A solution of 12.04 g (0.0336 mole) of 2,6-dimethyl-2,6-bis(t-butoxycarbonylamino)heptane (63) in 750 ml ethyl alcohol was prepared and cooled to 0°. Hydrogen chloride gas was bubbled through the solution for two hrs. The ethanol was removed under vacuum and the remaining solid was dissolved in the minimum amount of ethanol and precipitated with ethyl ether to yield 6.86 g (88%) of 70 as white crystals: mp > 270°; IR (nujol): 3240 (N-H), 2400, 2240 cm^{-1} (C-NH_3^+); NMR (CD_3OD) δ 1.61 (m,6H,-CH_2), 1.35 ppm (s,12H,-CH_3). An analytical sample was recrystallized from ethanol

acidified with aqueous hydrochloric acid.

Anal. Calcd. for $C_9H_{24}N_2Cl_2 \cdot H_2O$: C, 43.37; H, 10.52; N, 11.24. Found: C, 43.17; H, 10.44; N, 11.25.

2,6-Diamino-2,6-Dimethylheptane (61).

A solution of 992 mg (4.29 mmole) of 2,6-diamino-2,6-dimethylheptane dihydrochloride (70) in 5 ml anhydrous methanol was placed in a 25 ml round bottomed flask equipped with sidearm and magnetic stirrer. To this was added with cooling and stirring 556 mg (10.3 mmole) of sodium methoxide in 10 ml methanol. The methanol was removed under vacuum and the residue was stirred twice with 10 ml portions of dichloromethane. The dichloromethane extracts were filtered under nitrogen and the solvent was removed under vacuum, leaving a yellow oil which was purified by preparative VPC (Pennwalt 223, 175°) to yield 444 mg (66%) of 61 as a colorless oil: IR (film) 3340, 3260 (NH_2) 2950 (C-H), 1595 (N-H), 1465 (CH_2), 1380, 1360 (gem-dimethyl), 1205 (C-N), 855 cm^{-1} (N-H); NMR ($CDCl_3$) δ 1.32 (s,6H,-CH_2), 1.20 (s,4H,NH_2), 1.10 ppm (s,12H,CH_3). Attempted mass spectrometry gave a parent peak at m/e = 159 (calcd. 158), apparently arising from ion-molecule reactions

within the spectrometer. The sample was quite sensitive to exposure to the atmosphere, becoming cloudy within a few minutes of even brief exposure.

Oxidation of 2,6-Diamino-2,6-Dimethylheptane (61) with Hydrogen Peroxide.

The method of Greene and Gilbert was employed.[105] A solution of 6.86 g (0.0297 moles) of 2,6-diamino-2,6-dimethylheptane dihydrochloride (70) was dissolved in 75 ml anhydrous methanol and cooled to 0°. A solution of 3.53 g (0.0653 mole) sodium methoxide in 10 ml methanol was added dropwise with stirring. The methanol was removed and the residue washed twice with ether. The ethereal extracts were filtered under nitrogen and concentrated and the residue was dissolved in 120 ml degassed water. Sodium tungstate dihydrate (0.50 g, 0.0018 mole) was added. To this was added dropwise with stirring 13.6 g (0.12 mole) 30% hydrogen peroxide. Stirring was continued for one hr, during which a blue solid formed. The mixture was extracted with chloroform, the organic layer washed with 10% hydrochloric acid, water and dried ($MgSO_4$). Proton NMR analysis of the residue showed a complex product mixture. None of the absorptions were consistent with the presence of the de-

sired 3,3,7,7-tetramethyl-1,2-diazacycloheptene N-oxide, the N,N'-dioxide or the corresponding azo compound 59 (using the six-membered ring analogues as models).[105] The major product could be isolated (by the addition of heptane to the crude product mixture and filtration) as a solid, mp 65-67°, which was tentatively identified as 2,6-dinitro-2,6-dimethylheptane (64) on the basis of spectral evidence: IR ($CHCl_3$) 2950 (C-H), 1535 (NO_2), 1465, 1395, 1370, 1350 cm^{-1}. NMR ($CDCl_3$) δ 1.88 (m,6H,-CH_2) and 1.55 ppm (s,12H, CH_3).

In another experiment, 372 mg (1.62 mmoles) of 70 was neutralized using sodium methoxide as above. The diamine 61 was dissolved in 3 ml of degassed distilled water containing 50 mg (0.2 mmole) of sodium tungstate dihydrate. A 30% solution of hydrogen peroxide in water (335 μℓ, 3.3 mmoles) was added dropwise over 60 mins. After stirring for another 20 mins the mixture was extracted with dichloromethane and the organic layer was washed with 10% hydrochloric acid, saturated sodium bicarbonate solution, saturated sodium chloride solution, and dried (Na_2SO_4). After filtration and removal of solvent the residue was subjected to high vacuum (10^{-5} torr) distillation at room

temperature. Examination of both the volatile and non-volatile fractions by proton NMR and VPC (UCW-98, 115°) revealed no absorptions or peaks consistent with the presence of the desired azo compound 59.

Oxidation of 2,6-Diamino-2,6-Dimethylheptane (61) with Iodine Pentafluoride.

A modification of the method of Nelsen and Bartlett was used.[106] A solution of 88 μℓ (0.29 g, 1.3 mmole) of iodine pentafluoride and 3.0 ml of dry pyridine in 10 ml dry dichloromethane was prepared in a 25 ml round bottomed flask equipped with magnetic stirrer and addition funnel. To this was added dropwise with stirring at -20° a solution of 229 mg (1.45 mmole) of 2,6-diamino-2,6-dimethylheptane (61) (purified by preparative VPC; Pennwalt 223, 175°) in 4.0 ml dichloromethane. The mixture was stirred for one hr at -20° followed by one hr at 0°. Water was then added, the mixture was transferred to a separatory funnel and the layers separated. The organic layer was washed twice with 10% hydrochloric acid, twice with 10% sodium thiosulfate, once with saturated sodium bicarbonate, once with saturated sodium chloride solution and dried (Na_2SO_4). This was concentrated and distilled (10^{-5} torr) at room temperature. Proton NMR examination of the vola-

tile fraction showed nothing but traces of dichloromethane. Proton NMR examination ($CDCl_3$) of the non-volatile residue showed a multiplet centered at δ 1.55 and three overlapping singlets centered at 1.05 ppm. Examination of the non-volatile residue by VPC (UCW-98, 115°) showed no peaks in the region expected for 3,3,7,7-tetramethyl-1,2-diaza-1-cycloheptene (59) (based on the retention time of the six-membered ring analogue). An infrared spectrum ($CHCl_3$) of the non-volatile residue exhibited absorptions at 2960, 1465, 1375, and 1355 cm^{-1}.

3,3,6,6-Tetramethyl-2,7-Diaza-1-thiacycloheptane-1,1-Dioxide (65).

A modification of the procedure of Ohme and coworkers was employed.[107] A 500 ml three-necked round-bottomed flask was equipped with a reflux condenser, addition funnel and magnetic stirrer and charged with 200 ml of dry chloroform. Sulfuryl chloride (0.29 ml, 3.5 mmole) was added, the flask was cooled to 0° and 1.1 g (14 mmole) of dry pyridine was added dropwise with stirring; the flask was then briefly warmed to room temperature. After cooling to -50°, 0.50 g (3.5

mmole) of 2,5-diamino-2,5-dimethylhexane (60) in 10 ml chloroform was added. The reaction mixture was allowed to slowly warm to room temperature and stirred for 19 hrs. After one hr at reflux the flask was cooled and an excess of water was added. The layers were separated and the organic layer was washed twice with 5% hydrochloric acid, once with saturated sodium bicarbonate solution, once with saturated sodium chloride solution and dried (Na_2SO_4). This was concentrated and chromatographed on 30 g Activity I silica gel, eluting first with 150 ml chloroform, followed by 200 ml anhydrous methanol. The methanol fraction was concentrated and the residue sublimed (85° at 0.02 torr) to yield 0.134 g (19%) of 65 as colorless crystals: mp 189-190°; IR ($CHCl_3$) 3380, 3260 (N-H), 2970, 2920 (C-H), 1415, 1380, 1365 (gem-dimethyl), 1325, 1160, 1130 cm^{-1}(>SO_2); NMR ($CDCl_3$) δ 4.35 (s,2H,N-H), 1.88 (s,4H,-CH_2-), 1.30 ppm (s,12H,CH_3); MS,M^+ = 206 (calcd. 206). An analytical sample was recrystallized from toluene.

Anal. Calcd. for $C_8H_{18}N_2SO_2$: C, 46.58; H, 8.79; N, 13.58. Found: C, 46.90; H, 8.66; N, 13.75.

3,3,6,6-Tetramethyl-1,2-Diaza-1-Cyclohexene (58, n = 6).

The method of Timberlake and coworkers was employed.[108] A solution of 92 mg (0.44 mole) of 3,3,6,6-tetramethyl-2,7-diaza-1-thiacycloheptane-1,1-dioxide (65) in 10 ml dry t-butyl alcohol was placed in a 25 ml round bottomed flask. To this was added 101 mg (0.90 mmol) of potassium t-butoxide, and the mixture was stirred briefly. To this was added 98 mg (0.90 mmole) of t-butyl hypochlorite. The mixture was stirred for 12 hrs at room temperature. After removal of the reaction solvent under vacuum the residue was dissolved in dichloromethane and subjected to a high vacuum (10^{-5} torr) distillation at room temperature. Analysis by VPC (UCW-98, 125°) indicated the 1,2-diazene 58 (n = 6) as the sole volatile organic product.

3,3,7,7-Tetramethyl-2,8-Diaza-1-Thiacyclooctane-1,1-Dioxide (66).

This compound was prepared in a matter identical to that described above for 65. From 930 mg (5.88 mmoles) of 2,6-dimethyl-2,6-diaminoheptane (61) (purified by VPC; Pennwalt 223, 175°) was prepared 213 mg (16.5% yield) of 66 as white crystals: sublimes at 95° at 0.025 torr; mp. 225-226°; IR ($CHCl_3$) 3380, 3270

(N-H), 2950 (C-H), 1450, 1400, 1380, 1365 (gem-dimethyl), 1305, 1135 (>SO_2); NMR ($CDCl_3$) δ 4.40 (s,2H,N-H), 2.0-1.6 (m,6H,-CH_2), 1.30 ppm (s,12H,CH_3); MS,M^+ = 220 (calcd. M^+ = 220).

Anal. Calcd. for $C_9H_{20}N_2SO_2$: C, 49.06; H, 9.15; N, 12.71. Found: C, 48.74; H, 8.89; N, 12.77.

Oxidation of 3,3,7,7-Tetramethyl-2,8-Diaza-1-Thiacyclo-octane-1,1-Dioxide (66) with t-Butyl Hypochlorite.

A solution of 218 mg (1.94 mmoles) of potassium t-butoxide in 15 ml dry t-butyl alcohol was placed in a 50 ml round bottomed flask. To this was added 213 mg (0.97 mmole) of 66 as a suspension in 10 ml t-butyl alcohol. After stirring at 30° for 30 mins, 211 mg (1.94 mmole) of t-butyl hypochlorite was added slowly; stirring at 30° was continued for 23 hrs. This was concentrated at 35°. The residue was subjected to distillation at room temperature (10^{-5} torr). The volatile fraction was examined by VPC (UCW-98, 125°) and was a complex mixture of at least 11 compounds. Examination of the volatile fraction by visible absorption spectroscopy showed no distinctive features in the region around 380 nm (azo n → π* region). Examination by proton NMR showed that the bulk of the non-volatile fraction was unreacted starting material, with

traces of other compounds present.

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