nitrogen, the pressure being maintained at a low enough value to permit a reasonable rate of transfer. Distillation was continued until about 5 ml of viscous residue remained in the reaction flask. The frozen distillate was warmed to 25° and transferred to a 10-cm uv cell. The absorption intensity was followed as a function of time. A similar procedure was followed for the generation of alkyldiazenes from *p*-toluenesulfonamides, with a solution of hydroxylamine-*O*-sulfonic acid (1.12 mmol) in EtOH (18 ml) being added to the amide (1.19 mmol) in sodium ethoxide-ethanol (1 *N*, 18 ml).

Kinetics. Absorption intensity of the alkyldiazene solution was followed as a function of time. It was usually important to allow the reaction to proceed to completion rather than obtaining an absorption intensity at infinite time by exposure of the solution to the air. Apparently small amounts of weakly absorbing products are destroyed along with the residual alkyldiazene in the chain reaction resulting from the reaction of oxygen with the alkyldiazene. A plot of $1/(D_t - D_\infty)$ *vs.* t (in seconds) yields a slope which is multiplied by the appropriate ϵ to yield the rate constant. The rate constants obtained in various experiments are summarized in Table V. The linearity of the plots was reasonable (see Figures 1 and 2) to 60–80% reaction, but it proved to be relatively difficult to reproduce rate constants with high precision. In view of the high reactivity of alkyldiazenes toward oxidizing impurities, it is not surprising that such difficulties would be encountered. It was thus of significance to find that alkyldiazenes generated by different procedures exhibited similar bimolecular rate constants.

Nmr Spectrum of Methyldiazene. The sample of methyldiazene was prepared as follows. Aqueous potassium hydroxide (1.50 *N*, 500 μl, 0.75 mmol) was added with stirring to methyl methyldiazenecarboxylate (100 μl, *ca.* 1 mmol) in CH_3CN (1 ml) cooled to 0°. The mixture was shaken thoroughly (Vortex, Jr. mixer) and the solvent removed under vacuum (1–2 mm until residue was viscous, high vacuum (10^{-5} mm) until dry). The amorphous light yellow solid potassium salt was scraped from the walls and pulverized with a spatula, the flask evacuated and cooled to 77°K, and a CH_3CN solution of $Et_3NH^+Cl^-$ (equivalent to original KOH) added at a rate such that the liquid froze immediately in the flask. The mixture was warmed up with stirring while connected to a receiver cooled to 77°K. The distillate was melted and poured into an nmr tube, and the tube sealed off after freezing the contents. The tube was stored at 77°K until use. The spectrum was measured at −48°.

Products of Bimolecular Decomposition of Alkyldiazenes. Specified quantities of methyl alkyldiazenecarboxylates were hydrolyzed with a 10% excess of KOH in ethanol (0.5 *N* in base), the solutions degassed, and all solvent then removed. Imidazolium hydrochloride (15% excess over KOH) in ethanol (50 ml 1.4 mmol of ester) was added, and the mixture allowed to stand for 6 half-lives (*cf.* Table V) of the bimolecular decomposition of alkyldiazenes. The solution was frozen in liquid nitrogen, uncondensable gas pumped off (N_2), and the highly volatile product collected in a receiver cooled to 77°K along with a small amount of ethanol. The distillate was melted, evaporated into an ir cell, and the ir spectrum measured. The partial pressure of the hydrocarbon within the cell was evaluated by the comparison of the intensity of a suitable line or two in the ir spectrum with that of a standard (a set of curves for known pressures of gas) after measurement of the total pressure. The yield of hydrocarbons obtained in this manner was propane (75%), isobutane (75%), and cyclopropane (48%). No propene was detected in the spectrum of the cyclopropane. It is probable that the stated yield in the case of cyclopropane is too low. Cyclohexyldiazene was prepared as described above, but the reaction mixture was extracted with four volumes of *n*-pentane/volume of ethanol, rather than being distilled. The pentane extract was washed with water, dried, and concentrated slowly through a 1-ft packed column. The residue was analyzed by glpc, with the yield of cyclohexane (82%) being estimated from a standard. For an examination of the high-boiling products from cyclohexyldiazene, the reaction was carried out in the way described above except that the reaction mixture was filtered and concentrated until only 3 ml of ethanol remained of 100 ml initially used. The residue was light yellow, and was extracted with ether, the ether solution washed twice with water and dried over $MgSO_4$. The solution was filtered and the filtrate concentrated. The residual oil (62 mg) was dissolved in $CHCl_3$-*d* and the nmr spectrum measured. Peaks appeared at τ 7.66 and 8.38 with a peak ratio somewhat below 2:1. These peaks would be consistent with the structure 1,2-bis(cyclohexyl)diazane, *c*-$C_6H_{11}NHNH$-*c*-C_6H_{11}. The $CHCl_3$-*d* solution was treated with a small amount of peracetic acid. The important peaks in the spectrum all shifted downfield, the most prominent being those at 6.87, 7.58, and 8.20, roughly in the ratios 1:4:6. These positions, the ratios, and the shifts of the original spectrum after treatment with peracetic acid all point rather strongly to 1,2-bis(cyclohexyl)diazene as the correct structure for the product.

Diazenes. VII. Alkenyldiazenes[1]

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Received July 2, 1970

Abstract: Vinyldiazene ($CH_2{=}CHN{=}NH$) and 2-propenyldiazene, from the appropriate chlorocarbonyl compound and hydrazine under oxygen-free conditions, are characterized by (1) bimolecular disappearance, (2) expected $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, (3) high volatility, and (4) nmr spectra. Vinyldiazene has the lowest bimolecular reaction rate constant of any monosubstituted diazene thus far examined, 0.0017 M^{-1} sec^{-1} in CH_3CN at 25°. Cyclohexenyldiazene has been briefly studied. The position of the NH singlet in the nmr spectrum of alkenyldiazenes is unusually low, at τ −5.95, and broadening with temperature is due to quadrupole broadening (^{14}N-decoupling experiments).

Preparation of aryldiazenes[4–7] led us to seek other monosubstituted diazenes. We have described the preparation and properties of alkyldiazenes,[1,8] and can now report the preparation of alkenyldiazenes.[9]

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[1] The preceding article in this series is T. Tsuji and E. M. Kosower, *J. Amer. Chem. Soc.*, **93**, 1992 (1971).

[2] On leave from the Faculty of Engineering Science, Osaka University, Osaka, Japan.

[3] Support is gratefully acknowledged from the National Institutes of Health, the Army Research Office (Durham), and the Petroleum Research Fund (PRF-3695-A1).

[4] E. M. Kosower and P.-k. C. Huang, *J. Amer. Chem. Soc.*, **87**, 4645 (1965).

[5] P.-k. C. Huang and E. M. Kosower, *ibid.*, **89**, 3910 (1967).

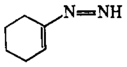
[6] P.-k. C. Huang and E. M. Kosower, *ibid.*, **90**, 2367 (1968).

[7] E. M. Kosower, P.-k. C. Huang, and T. Tsuji, *ibid.*, **91**, 2325 (1969).

[8] P.-k. C. Huang and E. M. Kosower, *ibid.*, **89**, 3911 (1967).

[9] Preliminary communication: T. Tsuji and E. M. Kosower, *ibid.*, **91**, 3375 (1969).

Table I. Light Absorption Data for Alkenyldiazenes

Alkenyldiazene	Solvent	$\pi \rightarrow \pi^*$ transition λ_{max}, Å (ϵ_{max})	$n \rightarrow \pi^*$ transition λ_{max}, Å (ϵ_{max})
$CH_2{=}C(CH_3)N{=}NCH_3$[a]	95% EtOH	2,320 (6,060)	3,860 (55)
$CH_2{=}CHN{=}NCH_3$	CH_3CN	2,215[b]	3,880[b]
$CH_2{=}C(CH_3)N{=}NH$	CH_3CN	2,300 (6,500)	4,100 (41)
	DME[c]		4,140[b]
$CH_2{=}CHN{=}NH$	CH_3CN	2,210 (7,200)	4,030 (40)
	DME[c]		4,085[b]
	CH_3CN	2,475 (11,000)	4,010 (54)

[a] Reference 17. [b] ϵ not measured. [c] 1,2-Dimethoxyethane.

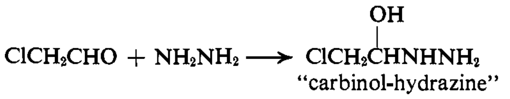
Results

Although 1,4-elimination to α,β-unsaturated diazenes from hydrazone derivatives has been known for a long time[10] (eq 1), it has not been frequently utilized,

$$XCC{=}NNHR \xrightarrow{B} C{=}CN{=}NR + BH^+X^- \quad (1)$$

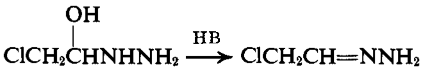
probably because the product is fairly susceptible to further nucleophilic attack. Most of the reported work has been carried out with phenylhydrazones,[11-16] although recently Gillis and Hagarty[17] have prepared 1-methyl-2-alkenyldiazenes by the 1,4-elimination route from methylhydrazine.

Alkenyldiazenes could be synthesized through the reaction of hydrazine with an appropriate chloro derivative of a carbonyl compound. The formation of vinyldiazene from chloroacetaldehyde is illustrated in eq 2-4.



$$ClCH_2CHO + NH_2NH_2 \longrightarrow ClCH_2\overset{OH}{\overset{|}{C}}HNHNH_2 \quad (2)$$

"carbinol-hydrazine"



$$ClCH_2\overset{OH}{\overset{|}{C}}HNHNH_2 \xrightarrow{HB} ClCH_2CH{=}NNH_2 \quad (3)$$

$$ClCH_2CH{=}NNH_2 \xrightarrow{B} CH_2{=}CHN{=}NH + BH^+Cl^- \quad (4)$$

The instability of monosubstituted diazenes required that the synthesis be carried through as quickly as possible. The general acid catalysis[18] necessary for the dehydration of the "carbinol-hydrazine" (eq 3) could be effected with benzoic acid in acetonitrile, because of the low basicity of hydrazine. Hydrazine in a small quantity of degassed acetonitrile is distilled into a mixture of chloroacetaldehyde hemihydrate, magnesium sulfate, and benzoic acid in acetonitrile. After 5 min at 25°, the solution of vinyldiazene is distilled. Solutions in other solvents can also be prepared: hexane, 1,2-dimethoxyethane (DME), and triethylamine.

Vinyldiazene, 2-propenyldiazene, and cyclohexenyldiazene have been prepared, and certain properties of vinyldiazene and 2-propenyldiazene have been examined in detail.

Light Absorption Data for Alkenyldiazenes. Absorption spectra were measured in acetonitrile (Table I). The absorption intensities were determined by measuring the maximum amount of alkenyldiazene formed from carefully weighed quantities of reactants in acetonitrile. The benzoic acid catalyzed reaction was complete within several minutes; filtration of the reaction solution permitted quantitative determination of the absorbance of the alkenyldiazene.

Alkenyldiazenes possess, as expected, two light absorption bands, a weak absorption ($n \rightarrow \pi^*$ transition), and a strong absorption ($\pi \rightarrow \pi^*$ transition). Data for two 1-methyl-2-alkenyldiazenes are included in the table for comparison; the methyl group shifts the long wavelength absorption to shorter wavelengths. A similar effect of the methyl group on the weak absorption band can be noted in the case of alkyldiazenes.[1]

Nmr Spectra of Alkenyldiazenes. Two factors, relative stability and a suitable procedure, made it possible for us to investigate the nmr spectra of alkenyldiazenes. Concentrated solutions were collected as frozen distillates at 77°K, melted and transferred to nmr tubes at low temperatures. The nmr tubes were sealed off after refreezing the contents and could be stored at 77°K.

Nmr spectra of vinyldiazene and 2-propenyldiazene were measured in a number of solvents, but the one which was utilized most was 1,2-dimethoxyethane (glyme, DME). The nmr spectrum (vinyl hydrogen region) for vinyldiazene in DME at $-60°$ is shown in Figure 1. The spectrum is in remarkably good agreement with the assigned structure and constitutes unequivocal evidence that alkenyldiazenes have been generated and distilled. In the case of vinyldiazene, three types of hydrogen can be recognized. At highest field is a multiplet assignable to $CH_2{=}$ (τ 3.2-3.5). At somewhat lower field is a quartet of line pairs ascribed to the single hydrogen of the vinyl group (${=}CH{-}$) (τ 2.4-2.8). The most remarkable feature of the spectrum is a line due to a single hydrogen at τ -5.93 which must be assigned to the hydrogen of the diazene group (${=}NH$). Coupling of the diazenyl hydrogen to the α-hydrogen of the vinyl group (J = 1.6 Hz) is demonstrated by the absence of such coupling when the hydrogen is replaced with a methyl group ($CH_2{=}CHN{=}NCH_3$), as shown in the vinyl hydrogen nmr spectrum in Figure 2.

The rather simple nmr spectrum of 2-propenyldiazene has a three-hydrogen singlet at highest field

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(10) (a) F. D. Chattaway and R. Bennett, *J. Chem. Soc.*, 2850 (1927); (b) F. D. Chattaway and F. G. Duldy, *ibid.*, 2756 (1928); (c) F. D. Chattaway and L. H. Farinholt, *ibid.*, 94 (1930).

(11) L. Caglioti, P. Grasselli, and G. Rosini, *Tetrahedron Lett.*, 4545 (1965).

(12) L. Caglioti, G. Rosini, and F. Rossi, *J. Amer. Chem. Soc.*, **88**, 3865 (1966).

(13) H. Simon and W. Moldenhauer, *Chem. Ber.*, **101**, 2124 (1968).

(14) S. Brodka and H. Simon, *ibid.*, **102**, 3647 (1969).

(15) J. Buckingham and R. D. Guthrie, *J. Chem. Soc. C*, 1939 (1969).

(16) A. Roedig and W. Wenzel, *Justus Liebigs Ann. Chem.*, **728**, 1 (1969).

(17) B. T. Gillis and J. D. Hagarty, *J. Amer. Chem. Soc.*, **87**, 4576 (1965).

(18) W. P. Jencks, *ibid.*, **81**, 475 (1959).

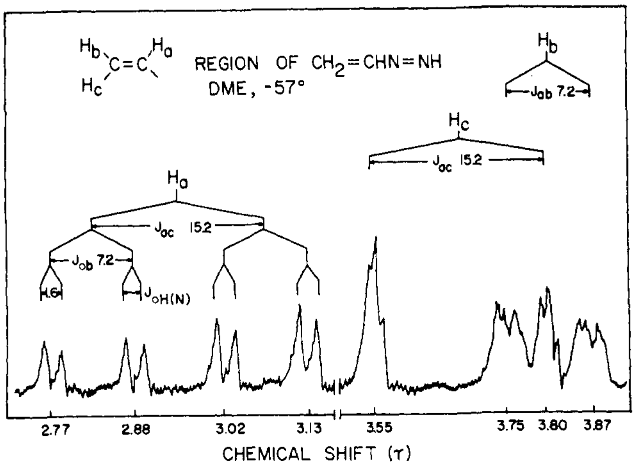


Figure 1. Nmr spectrum in the vinyl hydrogen region of vinyldiazene, $CH_2{=}CHN{=}NH$, taken in 1,2-dimethoxyethane (DME) at −57°. The major splittings are included, with $J_{trans\text{-}HH(ac)} = 15.2$ Hz, $J_{cis\text{-}HH(ab)} = 7.2$ Hz, and a probable $J_{aH(N)} = 1.6$ Hz. Additional splittings in the H_b and H_c regions could possibly be explained by a small J_{bc} coupling along with a $J_{bH(N)}$ coupling, but these are not indicated. Although the interpretation is not final, the spectrum appears much more straightforward than most vinyl hydrogen nmr spectra. Spectra are referred to tetramethylsilane (TMS) with important signals centered at τ 2.77, 2.88, 3.02, 3.13 (H_a), 3.55, 3.75, 3.80, and 3.87 (H_c centered around 3.67, H_b centered around 3.81). Signals measured at the same time but not shown on the chart are those for the diazenyl hydrogen (NH) at −5.93 and for ethylene at 4.60.

(τ 8.22), a two-hydrogen singlet at intermediate field (3.87), and a singlet due to the diazenyl hydrogen at −5.97.

We also investigated the effect of temperature on the NH line. At −60°, the NH line of vinyldiazene is somewhat broadened. As the temperature was raised, the NH line broadened more and more and was scarcely observable at 25°. To distinguish exchange broadening from quadrupole broadening by nitrogen-14, the NH line was examined (with an HA-100) at a number of temperatures with and without irradiation to decouple the nitrogen-14. At all temperatures, decoupling converted the NH line into a single relatively sharp line (width *ca.* 3 Hz). The temperature effect on the NH line of vinyldiazene and the effect of decoupling the nitrogen-14 is shown in Figure 3. Quadrupole broadening is clearly responsible for the behavior of the NH line at different temperatures. The sharp lines observed in the rest of the spectrum at any of the temperatures used represent additional evidence against any exchange processes with rates in certain ranges.

Nmr spectra in several other solvents are similar to those obtained using DME at the same temperature, but the stability of the solutions was lower. No emission lines were observed in any of the nmr spectra.

Bimolecular Reaction of Alkenyldiazenes. The absorbance of solutions of vinyldiazene and 2-propenyldiazene decreases with time, at a rate which indicates a bimolecular reaction between alkenyldiazene molecules. Most of the rate measurements were carried out in acetonitrile, in which the absorption of the diazene decreased smoothly to a very low value. In DME, the rate constant for the bimolecular reaction was slightly lower than that observed in acetonitrile, and an isosbestic point in the absorption curves was present due to the formation of a substance absorbing at shorter wavelengths, λ_{max} 2850 Å, ϵ_{app} 60. The reaction rate was higher in hexane than in acetonitrile but the decrease did not follow good bimolecular kinetics. Failure to observe bimolecular kinetics occurred whenever scrupulous care was not taken to exclude contamination. Pouring a vinyldiazene or 2-propenyldiazene solution in DME through a joint (permitting peroxides or other impurities to be acquired) led to initial rates of disappearance which were those expected. However, the rates of disappearance increased with time, indicating the initiation of free radical chain reactions. Solutions in DME which were transferred by distillation rather than by pouring exhibited good bimolecular kinetics for the disappearance of the n → π^* absorption band.

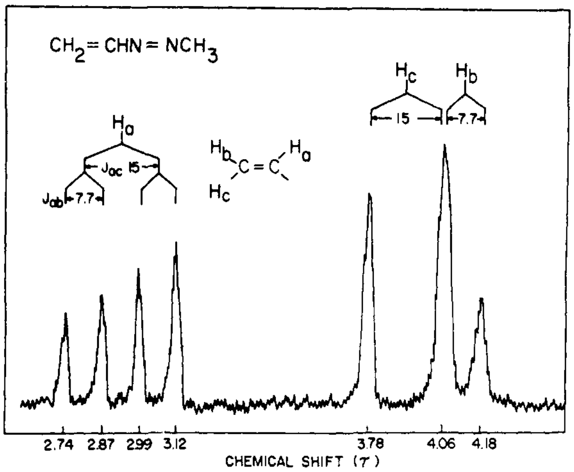


Figure 2. Nmr spectrum in the vinyl hydrogen region of 1-methyl-2-vinyldiazene, $CH_2{=}CHN{=}N{-}CH_3$, in 1,2-dimethoxyethane (DME) at 25°. The major splittings are very similar to those seen in the nmr spectrum of vinyldiazene, with $J_{trans\text{-}HH(ac)} = 15$ Hz and $J_{cis\text{-}HH(ab)} = 7.7$ Hz. Other splittings are apparently small or missing, especially that assigned to $J_{aH(N)}$ in vinyldiazene. The important signals (referred to TMS, τ 10.0) are found at τ 2.74, 2.87, 2.99, and 3.12 (H_a), 3.78, 4.06, and 4.18 (H_b and H_c).

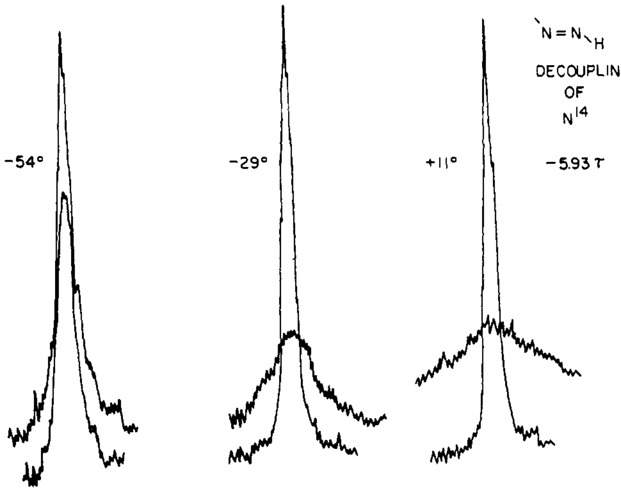
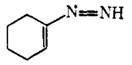


Figure 3. The nmr spectrum in the diazenyl hydrogen region of vinyldiazene in 1,2-dimethoxyethane (DME) at three different temperatures, −54, −29, and +11°. Decoupling of the ^{14}N produced fairly narrow and similar signals at all temperatures, proving that quadrupole broadening was the only significant mechanism responsible for the observed broadening. Spectra were taken with an HA-100.

Several attempts to measure the rate of disappearance of 2-methyl-1-propenyldiazene in acetonitrile were made. The initial rates were low, comparable to those found for vinyldiazene, but branching chain reactions were apparently initiated by impurities in the solutions, leading to rapid disappearance of the alkenyldiazene. Preliminary studies on 1-cyclohexenyldiazene showed it to be somewhat more reactive than vinyldiazene. We had observed the sudden onset of rapid disappearance in the case of alkyldiazene solutions on a few occasions.

The bimolecular rate constants for alkenyldiazenes are listed in Table II. Vinyldiazene disappears at the lowest rate of any of the monosubstituted diazenes thus far encountered, with a rate constant in acetonitrile of 0.0017 M^{-1} sec^{-1}. 2-Propenyldiazene reacts with itself with a rate constant of 0.015 M^{-1} sec^{-1} in acetonitrile, and 1-cyclohexenyldiazene shows a bimolecular rate constant of *ca.* 0.003 M^{-1} sec^{-1}.

Table II. Bimolecular Decomposition Rate Constants for Alkenyldiazenes[a]

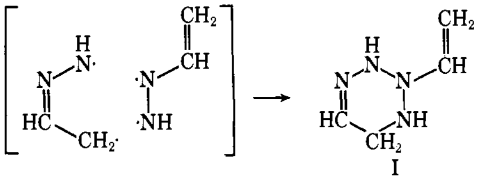
Alkenyldiazene	Solvent	Rate constant, M^{-1} sec^{-1}
$CH_2{=}CHN{=}NH$	CH_3CN	0.0017
	DME[b]	0.0009
	n-Heptane	∼0.002[c]
$CH_2{=}C(CH_3)N{=}NH$	CH_3CN	0.015
	DME[b]	
	CH_3CN	∼0.003[c]

[a] At 25°. [b] 1,2-Dimethoxyethane. [c] Approximate initial rate constant.

Products of the Bimolecular Reaction. After allowing distilled solutions of alkenyldiazenes to stand for 6 half-lives, the volatile alkenes were distilled, trapped in carbon disulfide, and titrated with bromine. The yields of ethylene and propene were similar (about 72 ± 5%). The 1,2-dibromoethane product from the bromine titration was confirmed by glpc.

The nmr spectra of ethylene and propene are quite distinct from those of the alkenyldiazenes. The formation of ethylene and propene could be easily observed in nmr spectra of solutions allowed to stand at room temperature. The ultimate yields of alkenes were high. Unfortunately the nmr spectrum of the solvent did not permit us to detect small amounts of other products.

In DME, vinyldiazene definitely yields a small amount of another product, the material with λ_{max} 2850 Å (ϵ_{app} 60). The product is unstable and slowly changes to other substances with much less absorption in the ultraviolet. A speculation (I) based on our previous work on the formation of 1,2-bis(4-nitrophenyl)diazane from 4-nitrophenyldiazene[7] is shown (eq 5).


I

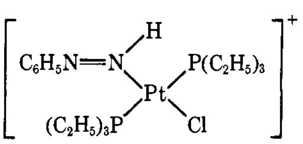
(5)

Discussion

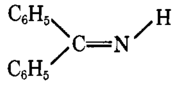
Proof of Structure of Alkenyldiazenes. A summary is (1) nmr spectra, (2) $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the expected positions and intensities (the intensity of the $n \rightarrow \pi^*$ transition is in agreement with a trans structure for the diazene group), (3) method of synthesis, (4) bimolecular reaction, a characteristic shown by all monosubstituted diazenes, (5) high sensitivity toward oxygen, another characteristic exhibited by all monosubstituted diazenes thus far examined, (6) high volatility, and (7) the products of the bimolecular reaction (the corresponding hydrocarbon in less than quantitative yield).

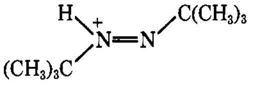
Nmr Spectra. The nmr spectrum of vinyldiazene appears to be typical of that for a vinyl derivative in the region of the vinyl hydrogen shifts. The NH region shows some distinctly unusual features. Broadening of the moderately sharp NH singlet observed at −60° as the temperature is raised could be traced to quadrupole broadening by nitrogen-14. Irradiation at both low and high temperatures produced a sharp singlet. There is no sign of any exchange process with appropriate rates.

The most striking feature of the nmr spectrum of vinyl- and 2-propenyldiazenes is the position of the NH singlet at τ −5.95, not far from the position assigned to the NH hydrogen in $CH_3N{=}NH$ (−5.6).[1] Parshall has reported without comment that the protonated forms of arylazoplatinum complexes (II) show a singlet hydrogen at τ −5.[19] In one case, he also noted that a broadened NH singlet was converted into a sharp doublet (J = 77 Hz) with satellites due to Pt^{195}H coupling (J = 80 Hz) if the nitrogen-14 were replaced with nitrogen-15.[19]


II

The NH hydrogen of diphenylketimine (III) has a broad singlet at τ +0.5 at −40°. The NH hydrogen broadens due to exchange as the temperature is raised.[20] Protonated 1,2-bis(*tert*-butyl)diazene (IV) (azoisobutane) exhibits a singlet NH at −2.82 in 95–97% sulfuric acid at −10°, with the correct intensity ratio between the methyl hydrogen signals and the NH signal.[21] The NH of acraldimine appears at −1.22, and the CH hydrogen (-C*H*=NH) is found at 1.95.[22] If we take these two hydrogens as representative of those α and β to a nitrogen within a double bond, we may estimate the


III


IV

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(19) G. W. Parshall, *J. Amer. Chem. Soc.*, **87**, 2133 (1965); **89**, 1822 (1967).

(20) J. B. Lambert, W. L. Oliver, and J. D. Roberts, *ibid.*, **87**, 5085 (1965).

(21) E. Haselbach and E. Heilbronner, *Tetrahedron Lett.*, 4531 (1967).

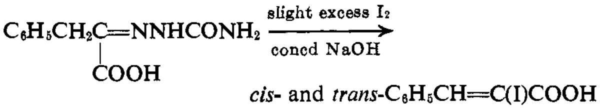
(22) B. Bogdanović and M. Velić, *Angew. Chem., Int. Ed. Engl.*, **6**, 803 (1967).

chemical shift (with respect to ethylene) as −8.4, and a diazenyl hydrogen at about −4.

The position of the NH singlet in the nmr spectrum is an intrinsic property of the diazenyl hydrogen rather than being due to some intermolecular process. We believe that its position reflects some special character for the diazenyl hydrogen bond but will defer discussion of the significance to a later date.

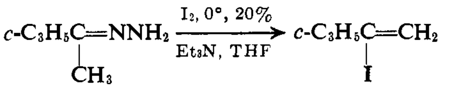
Alkenyldiazenes as Chemical Intermediates. Kishner discovered that reduction of α-substituted ketones with hydrazine led to alkenes.[23] There is general agreement that alkenyldiazenes are intermediates in this[24-28] and related reactions.[29,30]

A reaction discovered by Bougault[31] and independently by Barton and coworkers[32] may involve alkenyldiazenes as intermediates. Treatment of the semicarbazides of certain α-keto acids with halogen and base produces a haloalkene[31] (eq 6). The Barton procedure



$$\underset{\displaystyle \text{COOH}}{\mathrm{C_6H_5CH_2C{=}NNHCONH_2}} \xrightarrow[\text{concd NaOH}]{\text{slight excess } I_2} \textit{cis-}\text{ and }\textit{trans-}\mathrm{C_6H_5CH{=}C(I)COOH} \quad (6)$$

has been applied a number of times to hydrazones of ketones, including camphor hydrazone[33] and methyl cyclopropyl ketone hydrazone.[34] The reaction of the latter is illustrated in eq 7. Two reasonable partial



$$c\text{-}\mathrm{C_3H_5}\underset{\displaystyle \mathrm{CH_3}}{\mathrm{C}}\mathrm{{=}NNH_2} \xrightarrow[\text{Et}_3\text{N, THF}]{\text{I}_2\text{, 0°, 20\%}} c\text{-}\mathrm{C_3H_5}\underset{\displaystyle \mathrm{I}}{\mathrm{C}}\mathrm{{=}CH_2} \quad (7)$$

pathways can be postulated for this reaction: (1) formation of the alkenyldiazene which is converted into a 1-iodo-2-alkenyldiazene (eq 8) or (2) formation of an *N*,*N*-diiodohydrazone which yields the 1-iodo-2-alkenyldiazene (eq 9). Subsequent loss of nitrogen may well proceed through ionization, loss of nitrogen from the diazonium iodide to produce an alkenium ion iodide ion pair, followed by collapse to the observed iodoalkene product (eq 10).

$$\mathrm{CH_3C(R){=}NNH_2} \longrightarrow \mathrm{CH_3C(R){=}NNHI} \longrightarrow \mathrm{CH_2{=}C(R)N{=}NH} \longrightarrow \mathrm{CH_2{=}C(R)N{=}NI} \quad (8)$$

$$\mathrm{CH_3C(R){=}NNH_2} \longrightarrow \mathrm{CH_3C(R){=}NNHI} \longrightarrow \mathrm{CH_3C(R){=}NNI_2} \longrightarrow \mathrm{CH_2{=}C(R)N{=}NI} \quad (9)$$

$$\mathrm{CH_2{=}C(R)N{=}NI} \longrightarrow \mathrm{CH_2{=}C(R)N_2^+I^-} \longrightarrow \mathrm{CH_2{=}C(R)^+I^-} \longrightarrow \mathrm{CH_2{=}C(R)I} \quad (10)$$

We regard a combination of eq 9 (pathway 2) and eq 10 as the most reasonable description of the Bougault–Barton reaction.

Conclusions. Alkenyldiazenes appear to be a reasonably accessible set of chemically reactive substances. The usefulness of the alkenyldiazenes for chemical synthesis awaits further investigation of their properties, as is true for all of the monosubstituted diazenes. Among the possibilities which appear as reasonable goals are (a) formation of hydrocarbon anions with hydride or alkide ion (eq 11), (b) formation of hydrocarbon radicals by the addition of a suitable oxidizing radical in small quantity (eq 12), and (c) correlation of the rate of

$$\mathrm{RN{=}NH + LiH \longrightarrow RN{=}NLi \longrightarrow RLi + N_2} \quad (11)$$

$$\mathrm{RN{=}NH + PhO\cdot \longrightarrow RN{=}N\cdot \longrightarrow R\cdot + N_2} \quad (12a)$$

$$\mathrm{R\cdot + RN{=}NH \longrightarrow RH + RN{=}N\cdot} \quad (12b)$$

$$\mathrm{R\cdot + ZX \longrightarrow RX + Z\cdot} \quad (12c)$$

$$\mathrm{RN{=}NH + Z\cdot \longrightarrow R\cdot + ZH + N_2} \quad (12d)$$

base-catalyzed decomposition with the acidity constants for hydrocarbons estimated in other ways.[35]

The unusual character of monosubstituted diazenes requires further investigation and a deeper explanation.

Experimental Section

All experiments with alkenyldiazenes were carried out on the vacuum line, using purified, dried, and degassed solvents. Drying solvents on the line was usually done with Linde Molecular Sieve 4A, previously heated to 450° under vacuum to remove traces of oxygen. Nmr spectra were taken with an A-60 spectrometer (Varian Associates) except for those taken for the ^{14}N-decoupling measurements, which were done with a Varian HA-100 nmr spectrometer.[36] Uv and visible absorption spectra were measured with a Cary Model 14 spectrophotometer.

Materials. Chloroacetaldehyde semihydrate was prepared from 2-chloroacetaldehyde diethyl acetal (K & K Chemicals) by heating with oxalic acid according to the procedure of Natterer.[37] Chloroacetone was commercial material (Aldrich) purified by distillation before use. 2-Chlorocyclohexanone was prepared by chlorination of cyclohexanone.[38]

Vinyldiazene. A solution of hydrazine (220 µl, 6.85 mmol) in acetonitrile (1 ml) was degassed and distilled into a mixture of chloroacetaldehyde semihydrate (240 mg, 2.74 mmol), benzoic acid (240 mg, 2 mmol), and magnesium sulfate (1 g) in acetonitrile (80 ml). After stirring for 5 min, the solution was distilled into a receiver cooled to 77°K under high vacuum. After melting and bringing to 25°, the distillate had a volume of 74 ml and had an absorbance of 1.00 at 4030 Å, corresponding to a concentration of 0.025 *M* vinyldiazene (68% yield).

Product. The solution was allowed to stand 14 days, volatile material collected in a tube containing CS_2 at 77°K, and the distillate melted (up to 25°) and titrated with 0.193 *M* Br_2–CS_2 at −100° (volume required 6.75 ± 0.25 ml corresponding to 1.3 mmol of alkene). From the rate constant and the concentration initially used, it was estimated that 98% of the alkenyldiazene (6 half-lives) had decomposed *via* the bimolecular reaction. The yield of ethylene was thus 72 ± 5%. Glpc analysis confirmed the identity of the reaction product as 1,2-dibromoethane (Apiezon Grease L column) through retention time and an ir spectrum was identical with that of authentic material.

Other Procedural Variants. High-boiling solvents can be used as reaction media (*e.g.*, diethylene glycol dimethyl ether (diglyme), dimethylformamide (DMF), etc.) for the generation of alkenyldiazenes as can a variety of other solvents (benzene, cyclohexane, triethylamine, etc.). The distilled solution of vinyldiazene in triethylamine was at first clear yellow but soon turned cloudy, and white crystals separated from the solution. Distillation of the

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suspension yielded a clear yellow solution which, however, soon turned cloudy again. The nature of the reaction is unknown but might involve addition of triethylamine to the double bond. Yields of distilled alkenyldiazenes from high-boiling reaction media were low. Solutions in solvents other than CH_3CN and DME were not extensively investigated.

2-Propenyldiazene. Procedures used for the generation and distillation of propenyldiazene were similar to those used for vinyldiazene, except that the carbonyl compound was chloroacetone. Since propenyldiazene was more reactive in the bimolecular reaction, measurements had to be carried out more quickly than for vinyldiazene.

Rate Measurements. The disappearance of the absorption band due to the $n \rightarrow \pi^*$ transition was followed with time using a cell in a thermostatted cell compartment (25°). Rate constants were calculated as previously described.[1]

Nmr Measurements. The major problem in preparing samples of alkenyldiazenes suitable for nmr studies was to attain sufficient concentrations of the alkenyldiazenes in the solvents used. The circumstance that benzoic acid could be used as a catalyst for acclerating hydrazone formation even in solutions which contained hydrazine was very helpful. Up to 0.3 M solutions of vinyldiazene and 2-propenyldiazene in *n*-heptane, DME, and CH_3CN were prepared and examined at various temperatures from -60 to $+25°$. Alkenyldiazenes were collected together with solvent by distillation into a receiver held at 77°K. The solvents were melted at the lowest possible temperature (DME, $-65°$; CH_3CN, $-40°$; *n*-hexane, $-95°$) and the solutions poured quickly through a side arm into an nmr tube sealed onto the apparatus. The solutions were frozen in liquid nitrogen, the nmr tube was sealed off and spectra were taken at various temperatures and times. In most cases, a small amount of tetramethylsilane was distilled into the solution or added to the original reaction medium.

1-Methyl-2-vinyldiazene was prepared in exactly the same manner as vinyldiazene from chloroacetaldehyde semihydrate and methylhydrazine. The nmr spectrum and the uv spectrum were consistent with the assigned structure. The compound was not further characterized. Data are recorded in Table I and in Figure 2.

Nmr Samples of Alkenyldiazenes. Vinyldiazene. Degassed hydrazine (80 μl in 1 ml of solvent) was distilled into a mixture of chloroacetaldehyde semihydrate (150 mg) and benzoic acid (100 mg) in a solvent (CH_3CN, 4 ml; or DME, 4 ml; or CD_3CN, 2 ml). The mixture was warmed to room temperature and stirred for 1.5–2 min, the yellow color of the vinyldiazene appearing rapidly. The mixture was then distilled into a receiver at 77°K, about 1 ml of distillate being collected. The frozen vinyldiazene solution was melted at the lowest possible temperature, the intensely yellow (or orange) solution transferred to an nmr tube, the solution frozen, and the tube sealed off. The nmr sample of **2-propenyldiazene** was prepared in exactly the same manner.

Solvent and Substituent Effects on the Thermal Isomerization of Substituted Azobenzenes. A Flash Spectroscopic Study

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Abstract: Thermal isomerization of some para-donor/para′-acceptor-substituted azobenzenes [for example, 4-(diethylamino)-4′-nitroazobenzene] was studied by observing relaxation to equilibrium following flash photolysis. Several of these dyes show much faster rates of thermal isomerization than those measured for azobenzene and its monosubstituted derivatives. The observation of sizable solvent effects on the rates and activation energies for thermal isomerization suggests that a rotational mechanism might be operative for these azobenzenes.

The thermal and photochemical isomerization of azobenzenes has been the subject of much investigation.[5–12] In contrast to the stilbenes which show sizable activation energies for thermal isomerization and thus exist as discrete, isolable isomers at ordinary temperatures, azobenzenes are readily isomerized (activation energies *ca.* 23 kcal/mol)[6] at room temperature. The mechanism of the facile thermal isomerization of azobenzene is still the subject of investigation. Schulte-Frohlinde suggested that azobenzenes isomerize thermally by rotation about the N=N bond;[8] however, since an N=N bond should have a higher barrier to rotation than a C=C bond[13,14] the explanation is less than satisfactory. Others have suggested that contributions from dipolar structures can lower the barrier to rotation in azobenzenes.[5–7] The lack of major solvent or substituent effects on the rate of isomerization of several azobenzenes has been cited as evidence against the rotational mechanism.[9,15] An alternative mechanism for thermal isomerization of azobenzenes is inversion of one or both of the nitrogens through a linear (sp hybridized) transition state in which the double bond is retained.[9,13] Evidence favoring this path includes the finding that imines, for which this path is possible, have rapid rates of isomerization,[16] but ole-

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[15] Reports that the isomerization rates of substituted azobenzenes follow a Hammett σp relationship[7] have been challenged by Talaty and Fargo,[9] who suggest that the lack of such a relationship argues against involvement of dipolar resonance structures.