Monosubstituted Diazenes (Diimides).[1]
Surprising Intermediates

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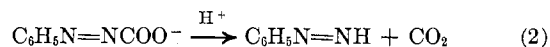*Department of Chemistry, State University of New York, Stony Brook, New York 11790*

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The earliest reference to the possibility of an aryldiazene (aryldiimide,[1] ArN=NH) serving as an unstable intermediate was made by Widman in 1895.[2a] Chattaway explained the formation of benzene and nitrogen from the oxidation of phenylhydrazine as a result of the decomposition of phenyldiazene[2b] (eq 1).

$$C_6H_5NHNH_2 \longrightarrow [C_6H_5N=NH] \longrightarrow C_6H_6 + N_2 \quad (1)$$

Apart from an unconfirmed report about 4-bromophenyldiazene through oxidation of the hydrazine with 1,4-benzoquinone,[3] no chemist had observed a monosubstituted diazene directly up to 1965 even though reactions in which RN=NH had been cited as an intermediate were numerous.

The extreme contrast between the instability of diazene (diimide, HN=NH) above $120°K$[4] and the stability of *trans*-1,2-diphenyldiazene (azobenzene, $C_6H_5N=NC_6H_5$) up to $600°K$[5] might have prompted a search for phenyldiazene ($C_6H_5N=NH$), but did not. Instead, some unexpected light absorption in the spectra of phenyldiazenecarboxylate anion ($C_6H_5N=NC-OO^-$)[6] noted in a study of the decarboxylation reaction at pH 10 led us to try to observe phenyldiazene after reaction at pH 7.4 (eq 2). To our surprise, a new ab-

$$C_6H_5N=NCOO^- \xrightarrow{H^+} C_6H_5N=NH + CO_2 \quad (2)$$

sorption band was produced and remained, disappearing only very slowly.[7] Our success in this simple experi-

ment depended heavily on the previous finding that good kinetics for the decarboxylation *via* spectrophotometric measurements were obtained only in the absence of oxygen. The new absorption was established as that of phenyldiazene, and the long life of this aryldiazene provided the stimulus for a broad investigation into the preparation and properties of monosubstituted diazenes in our laboratory.

Synthesis. Monosubstituted diazenes can be generated by fragmentation, elimination, and oxidation, with examples summarized in Table I. Reduction of aryldiazonium ions might also be useful,[8a] and aryldiazenes are apparently involved in some reactions of these ions.[8b] For quantitative work, decarboxylation seems the most convenient process for aryl- and alkyldiazenes. The precursors are readily prepared, the techniques are simple, and the procedures are adaptable to vacuum line work. Alkenyldiazenes have been prepared only by 1,4 elimination; for these, the discovery of the benzoic acid catalysis of formation of the intermediate hydrazone (eq 3) is the key to good yields.

$$\underset{\overset{|}{OH}}{\overset{\overset{CH_3}{|}}{ClCH_2C}}-NHNH_2 \xrightarrow{C_6H_5COOH} \overset{\overset{CH_3}{|}}{ClCH_2C}=NNH_2 \quad (3)$$

There are hazards and surprises in the syntheses. Monosubstituted diazenes are (1) oxygen sensitive, (2) subject to bimolecular disappearance, and (3) (often) reactive toward base. It is necessary to use the vacuum line or an equivalent method for the exclusion of oxygen in order to maintain solutions of diazenes, dilute solutions must normally be used to avoid the bimolecular disappearance, and the diazene must be distilled when prepared in a highly basic medium. However, certain reactions of alkyldiazenes can sometimes be be carried out without special precautions.[9a,b]

The reactions (*e.g.*, elimination, decarboxylation)

(1) (a) Dinitrogen compounds have, for historical reasons, possessed an interesting variety of common names. In 1968, we proposed that systematic names based on diazene, HN=NH, be adopted in place of the older diimide (Table II, p 2365, ref 1b). This follows the usage by Smith[1c] and clearly complements the standard nomenclature for polynitrogen compounds (triazane, tetrazane, etc.). In addition, 1,1-substituted diazenes are normally listed as 1,1-diaryl-(or alkyl-) diazenium ions and it seems reasonable that 1,2-substituted diazenes should be named according to the same system. (b) P. C. Huang and E. M. Kosower, *J. Amer. Chem. Soc.*, 90, 2362 (1968). (c) P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. I and II, Benjamin, New York, N. Y., 1966.
(2) (a) O. Widman, *Ber.*, 28, 1925 (1895); (b) F. S. Chattaway, *J. Chem. Soc.*, 1323 (1907).
(3) S. Goldschmidt, *Ber.*, 46, 1529 (1913).
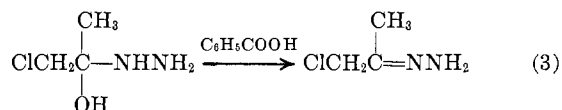(4) K. Rosengren and G. C. Pimentel, *J. Chem. Phys.*, 43, 507 (1965).
(5) A. Claus, *Ber.*, 8, 37 (1875).
(6) P. C. Huang and E. M. Kosower, *J. Amer. Chem. Soc.*, 90, 2354 (1968).
(7) E. M. Kosower and P. C. Huang, *ibid.*, 87, 4645 (1965).

(8) (a) T. G. Traylor, University of California, San Diego, private communication; (b) J. F. Bunnett and H. Takayama, *J. Amer. Chem. Soc.*, 90, 5173 (1968).
(9) (a) M. N. Ackermann, J. L. Ellenson, and D. H. Robison, *ibid.*, 90, 7173 (1968); (b) S. Hünig and G. Büttner, *Angew. Chem., Int. Ed. Engl.*, 8, 451 (1969); *Chem. Ber.*, in press; (c) S. Hünig and J. Crames, *Angew. Chem., Int. Ed. Engl.*, 7, 943 (1968).

Table I
Preparative Methods for Monosubstituted Diazenes, RN=NH

Method	Example	Ref

Method		Ref
Fragmentation		
Decarboxylation	$C_6H_5N=NCOO^- + H^+ \longrightarrow C_6H_5N=NH + CO_2$	a
Deesteration	$C_6H_5N=NC(OCH_3)(C_6H_5)-O^- \xrightarrow{CH_3OH} C_6H_5N=NH + C_6H_5COOCH_3$	b(d), c(d)
Dealdation[e]		f
Elimination		
1,2	$CH_3N(SO_2C_6H_4CH_3)NH_2 + OH^- \longrightarrow CH_3N=NH$	g, h
1,4	$ClCH_2COCH_3 + NH_2NH_2 \xrightarrow{C_6H_5COOH} CH_2=C(CH_3)-N=NH$	i
1,6		j(d)
Oxidation	$-N(H)-N(H)(H) \xrightarrow[\text{or } -2e^-, -2H^+]{-e^-, -e^-, \cdot 2H^+} -N=NH$	k, l(d), m, n(d)
Reduction	$-N^+\equiv N \xrightarrow[\substack{CH_3O^-, \\ (n\text{-}C_4H_9)_3SnH}]{BH_4^-} -N=NH$	o(d), p(d), q(d), r

[a] P. C. Huang and E. M. Kosower, *J. Amer. Chem. Soc.*, **90**, 2354 (1968). [b] R. W. Hoffmann and G. Guhn, *Chem. Ber.*, **100**, 1474 (1967). [c] S. G. Cohen and J. Nicholson, *J. Org. Chem.*, **30**, 1162 (1965). [d] Monosubstituted diazenes not yet directly observed through this route. [e] Loss of aldehyde. This reaction can also occur with the general mechanism shown for deesteration (*cf.* footnote f). [f] S. Hünig, *et al.*, *Chem. Ber.*, in press. [g] T. Tsuji and E. M. Kosower, *J. Amer. Chem. Soc.*, **93**, 1992 (1971). [h] (Probably involving $CH_3N(OH)NH_2$) M. N. Ackerman, J. L. Ellenson, and D. H. Robinson, *ibid.*, **90**, 7173 (1968). [i] T. Tsuji and E. M. Kosower, *ibid.*, **93**, 1999 (1971). [j] D. G. Holland, C. J. Moore, and C. Tamborski, *J. Org. Chem.*, **29**, 3042 (1964). [k] G. Cauquis and M. Genies, *Tetrahedron Lett.*, 3537 (1968). [l] D. Petredis, A. Burke, and A. L. Balch, *J. Amer. Chem. Soc.*, **92**, 428 (1970). [m] F. L. Scott and J. A. Barry, *Tetrahedron Lett.*, 2461 (1968). [n] H. H. Szmant and A. J. Mata, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 15, 1970, Abstract No. ORGN 35. [o] T. Severin, R. Schmitz, J. Loske, and J. Hufnagel, *Chem. Ber.*, **102**, 4152 (1969). [p] J. F. Bunnett and H. Takayama, *J. Amer. Chem. Soc.*, **90**, 5173 (1968). [q] J. Nakagama, M. Yoshida, and O. Simamara, *Tetrahedron*, **26**, 4609 (1970). [r] C. E. McKenna and T. G. Traylor, submitted for publication.

which produce the diazene seem much faster than the corresponding reactions which lead to carbon–carbon double bonds. Except for decarboxylation, these reactions have not been studied kinetically.

Physical Properties. Solutions of monosubstituted diazenes in ethanol and acetonitrile can be easily distilled, suggesting a volatility order $RCH=CH_2 >$ $RN=NH > RCN$ and a lack of specially strong hydrogen bonding by diazenyl NH. The low-intensity (n → π*) transitions) absorption bands of the diazenes vary between 3490 and 3750 Å for unconjugated systems and between 4030 and 4175 Å for conjugated diazenes. The absorption coefficients are very low, between 18 and 100, implying a trans structure for all

of the diazenes. High-intensity bands (π → π* transitions) are similar to those observed for all carbon conjugated systems. These data are summarized in Table II.

Comparison of the n → π* transitions for $CH_3N=NH$ (3610 Å) and *trans*-$CH_3N=NCH_3$ (3430 Å) indicates that alkyl substitution for hydrogen decreases n_+–n-splitting.[10] From the decrease, we estimate the posi-

(10) The long-held belief that there should be little interaction between two filled nonbonding orbitals has been discarded for diazene bonds.[11] The separation ("splitting") of the n_- (bonding) and n_+ (antibonding) levels in *trans*-$CH_3N=NCH_3$ has been determined to be 3.3 ± 0.2 eV by photoelectron spectroscopy.[12]

(11) M. B. Robin, R. R. Hart, and N. A. Keubler, *J. Amer. Chem. Soc.*, **89**, 1564 (1967).

Table II

Absorption Data for Monosubstituted Diazenes

RN=NH, R =	$n \to \pi^*$ transition λ_{max}, mμ (ϵ_{max})	$\pi \to \pi^*$ transition λ_{max}, mμ (ϵ_{max})
Alkyl		
H	3500[a]	
c-C$_3$H$_5$	3490 (28)[b]	
CH$_3$	3610 (18)[b]	
CH$_3$CH$_2$	3670 (18)[b]	
(CH$_3$)$_2$CH	3680 (20)[b]	
c-C$_6$H$_{11}$	3680 (20)[b]	
(CH$_3$)$_3$CCH(CH$_3$)	3740 (21)[b]	
(CH$_3$)$_3$C	3750 (17)[b]	
Alkenyl		
CH$_2$=CH$_2$	4030 (40)[c]	2210 (7200)[c]
CH$_2$=C(CH$_3$)	4100 (41)[c]	2300 (6500)[c]
1-Cyclohexenyl	4010 (54)[c]	2475 (11,000)[c]
Aryl		
C$_6$H$_5$	4175 ($\sim$100)[c]	2600 (7400)[c] 2150 (10,400)[c]
4-BrC$_6$H$_4$	4150 (97)[c]	2720 (10,200)[c] 2170 (10,000)[c]
4-CH$_3$OC$_6$H$_4$	d	2980 (10,300)[c] 2280 (9000)[c]
2-BrC$_6$H$_4$	d	2650 (5060)[c]
4-NO$_2$C$_6$H$_4$	d	2740 (12,300)[c]

[a] A broad, featureless band observed in the condensate from the decomposition of hydrazine in a discharge (A. Trombetti, *Can. J. Phys.*, **46**, 1005 (1968)). [b] In ethanol. [c] In CH$_3$CN. [d] Not determined.

tion of the n $\to$ π^* transition for diazene (diimide, NH=NH) as 3840 Å (Trombetti has reported a weak and broad continuum centered at 3500 Å).[13]

The information available on the structure of diazenes (HN=NH,[13] CH$_3$N=NH,[9a] *trans*-CH$_3$N=NCH$_3$[14]) is consistent with an N–H distance of 1.24–1.25 Å and an NNH angle between 110 and 120°.

The chemical shift of the NH proton in the nmr spectrum of monosubstituted diazenes is surprisingly large, τ −5.6 for methyldiazene[15] and −5.93 for vinyldiazene.[16] At 25° the NH band is very broad but becomes narrower at −60° for vinyldiazene in 1,2-dimethoxyethane. These phenomena are explained by quadrupole broadening, since decoupling the ^{14}N at 25° or at −60° produces an NH band of the same, narrow appearance. From nmr data on CH$_2$=CHCH=NH (=NH, τ −1.22; CH=N, τ 1.95),[17] we might expect the diazenyl NH to appear near τ −4 (CH$_2$=CH$_2$, τ +4.4). The additional shift of the NH proton is still under consideration.

Chemical Properties. Monosubstituted diazenes exhibit a number of expected chemical reactions as well as some surprising chemical properties. It is reasonable that the diazenyl hydrogen should be acidic, and

the pK_a of phenyldiazene is probably about 18 (eq 4).[15,18] The diazenyl anion decomposes, presumably

$$C_6H_5N=NH + OH^- \rightleftharpoons C_6H_5N=N^- + H_2O \qquad (4)$$
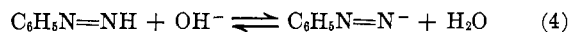
via a carbanion, producing the hydrocarbon by the addition of a proton (eq 5).[19] The diazenyl anion is a

$$C_6H_5N=N^- \longrightarrow N_2 + C_6H_5^- \overset{H^+}{\longrightarrow} C_6H_6 \qquad (5)$$
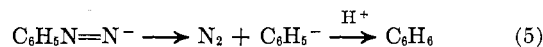
good nucleophile, and addition to a carbonyl group can compete quite successfully with other modes of reaction, as illustrated by the reaction of *tert*-butyldiazenyl anion with formaldehyde[9b,c] (eq 6). This reaction is

$$(CH_3)_3CN=NH + CH_2O \overset{OH^-}{\longrightarrow} (CH_3)_3CN=NCH_2OH \qquad (6)$$
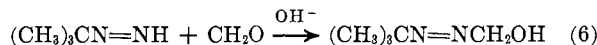
reversible above pH 10, and treatment with RCHO under these conditions leads to (CH$_3$)$_3$CN=NCH-(OH)R[9b] and has interesting consequences if the aldehyde group is attached to the diazenyl group through a carbon chain.[9c] Another obvious reaction is reduction to the hydrazine, which was effected for phenyldiazene using diazene generated from dipotassium 1,2-diazenedicarboxylate and triethylamine hydrochloride in acetonitrile (eq 7).[1b]

$$C_6H_5N=NH \xrightarrow[\substack{(K^+ {}^-O_2CN=NCO_2{}^-K^+) \\ (C_2H_5)_3NH^+Cl^- -CH_3CN}]{HN=NH} C_6H_5NHNH_2 \qquad (7)$$
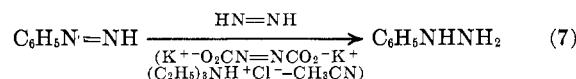
Phenyldiazene is less stable in acid than in neutral solutions, but the course of the reaction in water or with perchloric acid in acetonitrile[18] is obscure. Complexation with metal ions is known for diazene compounds, and a platinum complex of phenyldiazene is easily produced from benzenediazonium ion and *trans*-chlorohydridobis(triethylphosphine)platinum(II).[20] The cuprous complex of phenyldiazene offers a convenient route to phenyldiazene, since it may be formed by the reaction of phenylhydrazine and cupric chloride in water and the resulting complex decomposed with acetonitrile.[21] The composition of the phenyldiazene–copper(I) chloride complex was given as C$_6$H$_5$N=NHCu$_4$Cl$_4$, but others give the initial composition of the somewhat unstable material as C$_6$H$_5$N=NHCu$_2$Cl$_2$.[22] Huang and Kosower[23] showed that phenyldiazene complexed with ferroheme at the iron, but that the complex with hemoglobin probably involved hydrophobic bonding with the protein rather than interaction with the heme iron. The structures of the copper(II) complexes of the monosubstituted diazenes are probably like that found by Brown and Dunitz[24] for the CH$_3$N=NCH$_3$–Cu$_2$Cl$_2$ complex.

The rapidity of the reaction of monosubstituted

(12) E. Haselbach, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Angew. Chem., Int. Ed. Engl.*, **8**, 878 (1969); E. Haselbach and E. Heilbronner, *Helv. Chim. Acta*, **53**, 684 (1970).

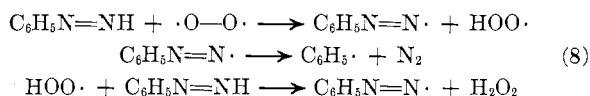(13) A. Trombetti, *Can. J. Phys.*, **46**, 1005 (1968).

(14) C. H. Chang, R. F. Porter, and S. H. Bauer, *J. Amer. Chem. Soc.*, **92**, 5313 (1970).

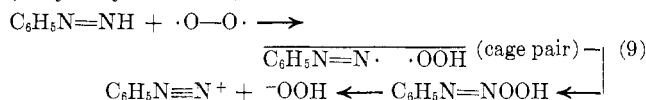(15) T. Tsuji and E. M. Kosower, *ibid.*, **93**, 1992 (1971).

(16) T. Tsuji and E. M. Kosower, *ibid.*, **93**, 1999 (1971).

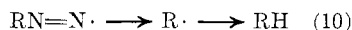(17) B. Bogdanović and M. Velic, *Angew. Chem., Int. Ed. Engl.*, **6**, 803 (1967).

(18) P. C. Huang and E. M. Kosower, *J. Amer. Chem. Soc.*, **90**, 2367 (1968).

(19) D. J. Cram and J. S. Bradshaw, *ibid.*, **85**, 1108 (1963).

(20) G. W. Parshall, *ibid.*, **87**, 2133 (1965); **89**, 1822 (1967).

(21) D. Petredis, A. Burke, and A. L. Balch, *ibid.*, **92**, 428 (1970).

(22) H. H. Szmant and A. J. Mata, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 14–18, 1970.

(23) P. C. Huang and E. M. Kosower, *Biochim. Biophys. Acta*, **165**, 483 (1968); cf. A. Wishnia, *Biochemistry*, **8**, 5064 (1969).

(24) I. D. Brown and J. D. Dunitz, *Acta Crystallogr.*, **13**, 28 (1960).

diazenes with oxygen and other oxidizing agents was unanticipated. · Exposure of a solution of phenyldiazene to air leads to loss of compound faster than can be observed in a simple apparatus. In one case, that of 4-nitrophenyldiazene,[25] a zero-order loss of diazene can be seen after exposure to air. Evidence for phenyl radical formation after exposure of phenyldiazene to air[26] or ferric ion[27] has been given. Benzenediazonium ion can be detected in low yield after exposure of a neutral aqueous solution to air.[28] Two speculative pathways are illustrated in eq 8 and 9. As pointed out

$$C_6H_5N{=}NH + \cdot O{-}O\cdot \longrightarrow C_6H_5N{=}N\cdot + HOO\cdot$$
$$C_6H_5N{=}N\cdot \longrightarrow C_6H_5\cdot + N_2 \qquad (8)$$
$$HOO\cdot + C_6H_5N{=}NH \longrightarrow C_6H_5N{=}N\cdot + H_2O_2$$

(in hydroxylic solvents)

$$C_6H_5N{=}NH + \cdot O{-}O\cdot \longrightarrow$$

$$\overline{C_6H_5N{=}N\cdot \quad \cdot OOH} \text{ (cage pair)} \qquad (9)$$

$$C_6H_5N{\equiv}N^+ + {}^-OOH \longleftarrow C_6H_5N{=}NOOH \longleftarrow$$

by Nicholson and Cohen,[28] the formation of hydrocarbons through oxidation of hydrazines (eq 10) prob-

$$RNHNH_2 \longrightarrow RN{=}NH \longrightarrow$$

$$RN{=}N\cdot \longrightarrow R\cdot \longrightarrow RH \qquad (10)$$

ably proceeds by way of the alkyl or aryl radical formed by oxidation of the monosubstituted diazene.

Bimolecular Reactions. Bimolecular disappearance is the most remarkable reaction of monosubstituted diazenes and is shown, without exception, by every one of the compounds of this class thus far examined. The reaction came to light during an attempt to concentrate dilute solutions of phenyldiazene. Careful distillation of the solvent from the solution raised the concentration of phenyldiazene very little.

The products of the reaction are mainly the corresponding hydrocarbon (usually more than 50%) and some other compounds, of which the chief one is apparently the hydrazine. 4-Nitrophenyldiazene yields the hydrazine as the major product with nitrobenzene formed in 30–35% yield (eq 11).[25]

$$2RN{=}NH \longrightarrow RH + RNHNHR \qquad (11)$$
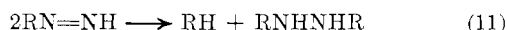
In spite of considerable effort, the mechanism of the reaction is not clear. The scheme which we regard as the best working description of the course of the reaction will be presented after we review some of the evidence concerning this reaction.

The bimolecular character of the reaction is shown by the linearity of a plot of log $t_{1/2}$ vs. the log of the initial concentration (Figure 1). The reaction is not very sensitive to solvent, with a factor of less than 8 between the rate constants for phenyldiazene in water ($Z = 94.6$)[29] and acetonitrile ($Z = 71.3$).[29,30] The lack of

Figure 1. A plot of log $t_{1/2}$ (in seconds) vs. log C_0 (C_0 = initial molar concentration) for the decomposition of phenyldiazene in acetonitrile.

solvent effect indicates that the rate-limiting transition state or any intermediate preceding that state is not significantly different in charge separation from the initial state. The substituent effect on the bimolecular rate constant for aryldiazenes is very small (Hammett ρ value < 0.7), but variation of the alkyl group in alkyldiazenes leads to a substantial change in rate. The bimolecular rate constants are listed in Table III along with the major reaction product. Qualitatively, a steric effect seems to be important in accelerating the reaction. α-Methylneopentyldiazene (MD) reacts more rapidly than *tert*-butyldiazene (BD), although isopropyldiazene is less reactive than *tert*-butyldiazene.

$$\underset{\text{MD}}{(CH_3)_3CCH{-}N{=}NH} \qquad \underset{\text{BD}}{(CH_3)_3CN{=}NH}$$

with the CH$_3$ group shown on the first structure.

Replacement of the diazenyl hydrogen by deuterium led to a marked decrease in the rate of the bimolecular reaction, with k_H/k_D between 4 and 5. Methyldiazene-2-*d* is more stable than the protio compound.[9a]

Small solvent and polar substituent effects exclude (a) electron transfer and (b) hydride transfer as reaction pathways. The isotope effect eliminates an irreversible ene + ene reaction, as found for some alkenes (eq 12).

$$RN{=}NH + RN{=}NH \longrightarrow\!\!\!\!\!/$$

$$R\dot{N}NHNH\dot{N}R \longrightarrow \text{products} \qquad (12)$$

The nmr spectra of vinyldiazene, 2-propenyldiazene, and methyldiazene in acetonitrile or 1,2-dimethoxyethane exhibited no emission lines (CIDNP). Furthermore, mixing pyridinyl radical[31] (Py·) with phenyldiazene did not affect the rate of loss of phenyldiazene,

(25) E. M. Kosower, P. C. Huang, and T. Tsuji, *J. Amer. Chem. Soc.*, **91**, 2325 (1969).

(26) A. Heesing and B. Kaiser, *Tetrahedron Lett.*, 2845 (1970).

(27) J. Nicholson and S. G. Cohen, *J. Amer. Chem. Soc.*, **88**, 2247 (1966).

(28) P. C. Huang, unpublished results.

(29) E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, Section 2.6.

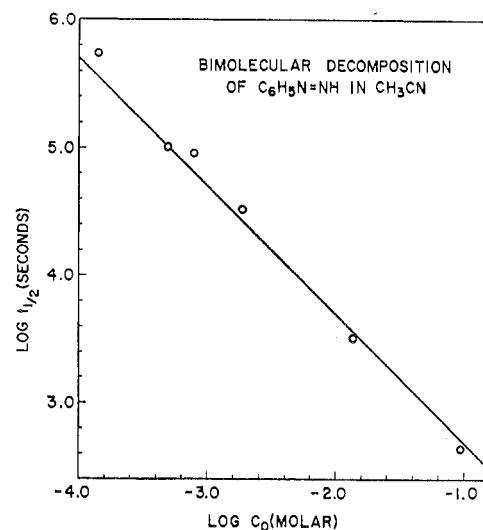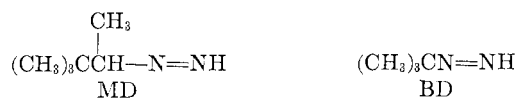(30) Bimolecular disappearance is not well established in water,

presumably because of a contribution to the loss of phenyldiazene from the water-catalyzed conversion to benzene via the diazenyl anion.

(31) E. M. Kosower and E. J. Poziomek, *J. Amer. Chem. Soc.*, **86**, 515 (1964).

Table III

Rates and Products of Bimolecular Reaction of Monosubstituted Diazenes

RN=NH, R =	10^2k, M^{-1} sec^{-1}	Product (% yield)
Aryl[a]		
4-CH$_3$OC$_6$H$_4$	0.66	Anisole (75)
C$_6$H$_5$	2.0	Benzene (70–80)
4-BrC$_6$H$_4$	1.2	Bromobenzene (71)
2-BrC$_6$H$_4$	1.7	Bromobenzene (54)
4-NO$_2$C$_6$H$_4$	2.7	Nitrobenzene (30)[c]
Alkenyl[a]		
CH$_2$=CH	0.17	Ethylene (>70)
CH$_2$=C(CH$_3$)	1.5	Propene (>70)
1-Cyclohexenyl	~0.3	
Alkyl[b]		
CH$_3$	3.0	
CH$_3$CH$_2$	40	
(CH$_3$)$_2$CH	57	Propane (75)
(CH$_3$)$_3$C	250	Isobutane (75)
(CH$_3$)$_3$CCH(CH$_3$)	450	
c-C$_6$H$_{11}$	58	Cyclohexane (82)
c-C$_3$H$_5$	1.5	Cyclopropane (>50)

[a] In CH$_3$CN.   [b] In C$_2$H$_5$OH.   [c] About 60% NO$_2$C$_6$H$_4$NH-NHC$_6$H$_4$NO$_2$ is formed.

Scheme I[a]

[a] Two molecules of *trans*-diazenes interact to form, either directly or via a pair of *cis*-diazenes, a triplet pair. A hydrogen atom is abstracted by either N_1, leading to the hydrazo compound, or by N_2, leading to the hydrocarbon.

but diverted the reaction course to other products.[32] The lack of effect of Py· on the bimolecular reaction rate combined with an interception of an intermediate leads to the following conclusions: (a) the bimolecular reaction is *not* a radical chain reaction, for which a sharp reduction in the rate would have been observed, (b) significant concentrations of radicals are not released in steps in which spin selection can take place (no CIDNP).

The nature of the products is reminiscent of a radical reaction in that no single product is formed and the C$_6$H$_5$D produced from C$_6$H$_5$N=ND contains a substantial amount of C$_6$H$_6$. To reconcile the "radical character" of the reaction with a lack of evidence for *free* free radicals, we believe that the radicals are formed and react within a solvent cage.

Comparison of the data for the n → π* transition of alkyldiazenes with that for the bimolecular reactions shows that there is a good correlation, high rate constants corresponding to low transition energies. This suggests that some excited state may change in energy with substitution in the same way as some intermediate or transition state for the bimolecular reaction.

The bimolecular reaction has a low activation energy, *ca.* 9 kcal/mole, in the case of phenyldiazene.

How can a free-radical reaction be initiated without the introduction of free radicals? Dissociation of diazenes to a diazenyl radical and a hydrogen atom is ruled out on the basis of the low activation energy, there being little chance that a diazenyl radical (RN=N·) would be so stable. Another possibility is thermal conversion of the singlet initial state to a triplet state, stimulated by the interaction of two molecules. There are two lines of argument which
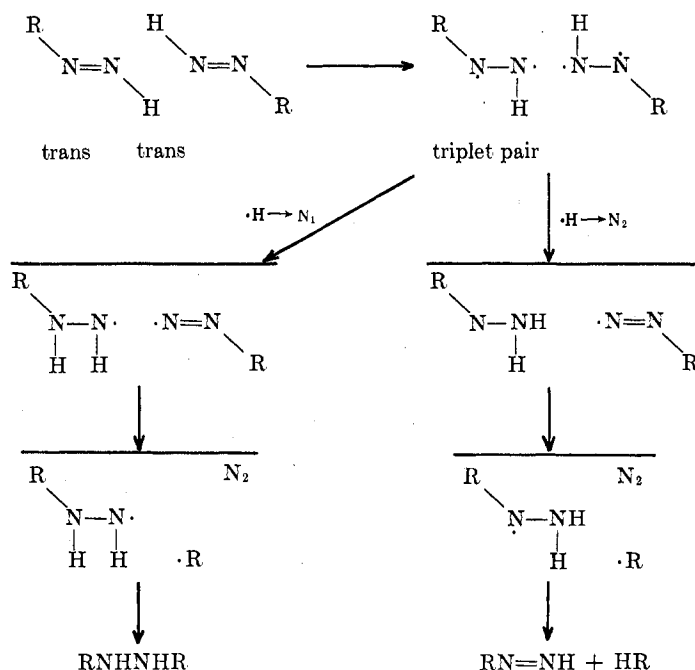
favor the idea that the triplet state could be involved. First, it is likely that the triplet state of diazene itself is not very far above the ground state. An estimate based on a comparison of oxygen and ethylene (Figure 2) suggests a number between 14 and 18 kcal/mol. Second, consideration of the structure of triplet diazene indicates that considerable stabilization might be available through "three-electron bonds." A crude calculation for linear triplet diazene gives 2.2 eV as the energy required to transform the ground state into the triplet form.[33] Presumably the vertical transition energy (^{3}n → π*) would not be very different from that for the thermal conversion. Detailed calculations using Gaussian orbitals yield 2.07 and 3.01 eV for the ^{3}n → π* transition energies of *cis*- and *trans*-NH=NH, respectively.[10,11] Ab initio calculations for *trans*-NH=NH indicate a value of about 2.3 eV for the singlet → triplet vertical transition.[34]

Scheme I omits the possible bimolecular conversion of *trans*- to *cis*-diazenes, followed by rapid thermal formation of a triplet (or pair of triplet) molecule(s). Cis triplets should be lower in energy than trans triplets; bimolecular conversion of imines from one

(32) T. Tsuji and E. M. Kosower, unpublished experiments; Py· = 1-ethyl-4-carbomethoxypyridinyl radical.[31]

(33) The n_+–n_- splitting is 3.3 eV[12] and the π → π* transition energy is about 7.4 eV.[13] The transformation energy is given by the difference between the ground state and the linear triplet state, which we estimate as follows [energy of state × (number of electrons)]: 3.7(2) + 3.3(1/2)(2) − 3.3(1/2)(2) [ground state] less 2.6(4) − 2.6(2) [linear triplet state]. The 3.7 eV for the π state is based on 1/2 × 7.4 (π → π*), and the 3.3 × 1/2 is based on the n_+–n_- splitting. The "three-electron state" is taken as being between the n and π states, *i.e.*, 2.6 eV.

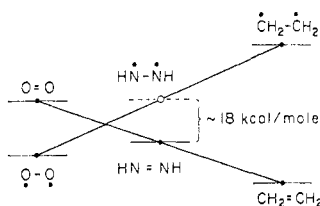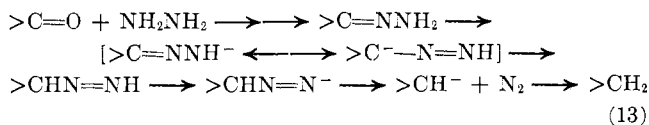(34) Dr. J. Ryan and Professor J. Whitten, personal communication.

Figure 2. Qualitative state diagram for the sequence oxygen, diazene, and ethylene. The triplet–singlet difference for oxygen is 22.5 kcal/mole [R. J. Browne and E. A. Ogryzlo, *Can. J. Chem.*, **43**, 2915 (1965)] and that for ethylene is 57 kcal/mole [A.J. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969)]. The heat of formation of ethylene is 12.5 kcal/mole and that for diazene is estimated from the available values for the relevant heats of formation of the monatomic elements (N, 113 kcal/mole; H, 52.1 kcal/mole) and bond energies (N=N, 109 kcal/mole; N—H, taken as between =C—H, 103 kcal/mole, and ≡C—H, 114 kcal/mole (*cf.* P. S. Skell and J. H. Plonka, *J. Amer. Chem. Soc.*, **92**, 5620 (1970)), or as 107 kcal/mole (S.W. Benson, *J. Chem. Educ.*, **42**, 502 (1965)). An approximately straight line can be drawn between the centers of the three singlet levels. By assuming that a straight line can be drawn between the triplet levels for the same molecules, an estimate of 14–18 kcal/mole can be made for the height of the triplet state of diazene above the singlet state. Lack of good thermodynamic data for NH=NH makes this estimate very rough, but it serves to indicate that one might expect only a relatively small triplet–singlet difference for diazene. It must be emphasized that this treatment is qualitative and that it refers to the most stable forms of these states (*i.e.*, stretched ·NHNH· and perpendicular ·CH$_2$CH$_2$·).

form to another is well known.[35,36] We have indicated only that a triplet pair is formed in Scheme I. Hydrogen transfer can take place to N$_2$ (favored) or to N$_1$ (minor, except in the case of 4-nitrophenyldiazene). Subsequent loss of nitrogen and radical recombination or abstraction of hydrogen within the solvent cage accounts for the products. The mechanism shown is simpler than those previously published,[18,25] but follows the theme of accounting for the reaction through formation of a thermal triplet or triplet pair. Further product and labeling studies will be required to confirm (or invalidate) this scheme.

Chemical Significance of Diazenes. Two reactions in which the intermediacy of monosubstituted diazenes is fairly well accepted are the Wolff–Kishner reduction of ketones to saturated hydrocarbons (eq 13)[37] and the "abnormal" Kishner reduction of α-substituted ketones to alkenes[38] (eq 14). Further discussion has been pub-

$$>C=O + NH_2NH_2 \longrightarrow \longrightarrow >C=NNH_2 \longrightarrow$$
$$[>C=NNH^- \longleftarrow \longrightarrow >C^-\!\!-\!N=NH] \longrightarrow$$
$$>CHN=NH \longrightarrow >CHN=N^- \longrightarrow >CH^- + N_2 \longrightarrow >CH_2 \quad (13)$$

$$XCHC=O + NH_2NH_2 \longrightarrow \longrightarrow XCHC=NNH_2 \longrightarrow$$
$$X^- + CH=C\!\!-\!N=NH \longrightarrow$$
$$CH=C\!\!-\!N=N^- \longrightarrow N_2 + CH=C^- \longrightarrow CH=CH \quad (14)$$

lished elsewhere.[15,16]

Biological Significance of Diazenes. There is considerable feeling that some form of diazene is an intermediate in biological nitrogen fixation, although beyond demonstrations of metal ion complexation[23,39,40] there is little hard evidence. Hydrazines are very important pharmacological agents and may well be oxidized *via* diazenes[41] if, indeed, the diazenes do not represent the biologically active form of the compounds.

An application of diazene chemistry to biological systems lies in the controlled hemolysis of red blood cells (and lysis of other cells) accomplished by (a) consuming the intracellular protective agent, GSH, and (b) generating phenyl radicals from phenyldiazene and oxygen at the cell membrane by loading the cell with carbon monoxide and suspending the cells in oxygenated buffer (eq 15 and 16).[42−44]

2GSH (glutathione) + C$_6$H$_5$N=NCOOCH$_3$ $\longrightarrow$
$$GSSG + C_6H_5NHNHCOOCH_3 \quad (15)$$

$$C_6H_5N=NCOOCH_3 \xrightarrow[-CO_2]{H_2O} C_6H_5N=NH \xrightarrow{O_2}$$

$$C_6H_5\cdot \xrightarrow[\substack{unsaturated \\ lipids}]{O_2 + cell \\ membrane} holes in membrane \quad (16)$$

Conclusions. The chemical potential of monosubstituted diazenes has hardly been explored. They are reactive, accessible intermediates, capable of giving rise to carbonium ions, free radicals, and carbanions. The unique properties of monosubstituted diazenes only recently became apparent. We should see a marked increase in our theoretical and experimental knowledge of these compounds in the next few years.
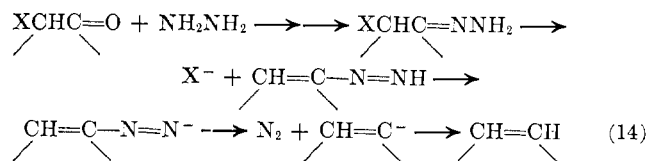
(35) J. B. Lambert, W. L. Oliver, and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 5085 (1965).

(36) See other discussion in ref 18.

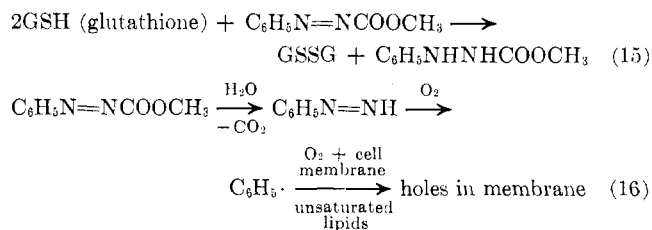(37) H. H. Szmant, *Angew. Chem., Int. Ed. Engl.*, **7**, 120 (1968).

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(44) E. M. Kosower, N. S. Kosower, and E. Gottfried, unpublished results.