Diazenes. VI. Alkyldiazenes[1]

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Abstract: A series of alkyldiazenes, RN=NH (R = CH_3, CH_3CH_2, $(CH_3)_2CH$, $(CH_3)_3C$, $(CH_3)_3CCH(CH_3)$, c-C_3H_5, and c-C_6H_{11}), has been generated by two different routes, decarboxylation ($RN{=}NCOO^- + H^+$) and elimination ($RN(Ts)NH_2 + OC_2H_5^-$). All alkyldiazenes react rapidly with oxygen and disappear in a bimolecular process, like alkenyldiazenes and aryldiazenes. The rate of the bimolecular reaction varies from 0.015 M^{-1} sec^{-1} for cyclopropyldiazene to 4.5 M^{-1} sec^{-1} for 3,3-dimethyl-2-butyldiazene. The nmr spectrum of methyldiazene in CH_3CN at $-48°$ reveals a quadrupole-broadened band for NH at τ -5.6 ± 0.2 and a doublet for the methyl group at $+6.13$ ($J \sim 2$ Hz). The $n \rightarrow \pi^*$ transition energy for an alkyldiazene falls as the rate of the bimolecular reaction increases. The products of the bimolecular reaction are the corresponding hydrocarbon (RH) (the major product) and the symmetrical hydrazine (RNHNHR). The role of the alkyldiazenes as reaction intermediates is discussed. The pK_a of *tert*-butyldiazene is estimated as 19–21.

For many years, monosubstituted diazenes were regarded as highly unstable intermediates and were warily denoted within brackets. The reduction of ketones by hydrazine presumably proceeded by way of an alkyldiazene.[4] Cram and Bradshaw[5] provided evidence for the alkyldiazene, 2-phenyl-2-butyldiazene, in the form of similar products produced from alkyldiazene generated in different ways. Nickon and Hill postulated the formation of alkyldiazenes for the deamination of amines *via* the tosyl derivative and reaction with nitrene.[6] Other references to monosubstituted diazenes have been previously cited.[7,8]

Hydrazines are of medical importance, and the biological oxidation of alkylhydrazines to hydrocarbons may go by way of alkyldiazenes.[9] The formation of ethylene from 2-hydroxyethylhydrazine may well proceed *via* an alkyldiazene, rather than by the indirect route proposed.[10]

There is clearly interest in obtaining more information about the behavior of alkyldiazenes. Generating known concentrations of monosubstituted diazenes was made possible by the decarboxylation procedure first used for phenyldiazene.[7] Elimination, an alternative approach to alkyldiazenes,[5,6] was used recently by Ackermann and coworkers for the production of methyldiazene.[11]

Properties of intermediates should be observed directly rather than being inferred from the nature of products formed in a particular reaction. Intermediates often exhibit surprising behavior not readily revealed by indirect means. We found this to be true in the case of phenyldiazene.[12]

We describe in this article the generation of a series of alkyldiazenes, most by more than one route, and information on some of their chemical and physical properties. The alkyldiazenes are methyl-, ethyl-, isopropyl-, *tert*-butyl-, cyclohexyl-, cyclopropyl-, and α-methylneopentyldiazenes; the bimolecular rate constant proved to be relatively sensitive to the nature of the alkyl substituent.

Results

Precursors for alkyldiazenes were prepared in straightforward syntheses. Tosylhydrazide ($CH_3C_6H_4SO_2$-$NHNH_2$) was alkylated in dimethyl sulfoxide (eq 1, $CH_3C_6H_4SO_2$ = Ts)

$$\mathrm{TsNHNH_2} \xrightarrow[\mathrm{DMSO}]{\mathrm{LiH}} \mathrm{Li^+TsN^-NH_2} \xrightarrow{\mathrm{RI}} \underset{\mathrm{I}}{\mathrm{RN(Ts)NH_2}} \qquad (1)$$

$$\mathrm{R} = \mathrm{CH_3\ (I\text{-}M),\ CH_3CH_2\ (I\text{-}E),}$$
$$\mathrm{(CH_3)_2CH\ (I\text{-}}i\mathrm{\text{-}P)}$$

Alkyl tosylamides were prepared from the amine (eq 2).

$$\mathrm{RNH_2} \xrightarrow[\mathrm{pyridine}]{\mathrm{TsCl}} \underset{\mathrm{II}}{\mathrm{RNHTs}} \qquad (2)$$

$$\mathrm{R} = \mathrm{CH_3\ (II\text{-}M),\ CH_3CH_2\ (II\text{-}E),}$$
$$\mathrm{(CH_3)CH\ (II\text{-}}i\mathrm{\text{-}P),\ (CH_3)_3C\ (II\text{-}}tert\mathrm{\text{-}B),}$$
$$c\text{-}\mathrm{C_3H_5\ (II\text{-}}c\mathrm{\text{-}P)},\ c\text{-}\mathrm{C_6H_{11}\ (II\text{-}}c\mathrm{\text{-}H)}$$

Most of the alkyldiazanecarboxylate esters were prepared by hydrogenation[13] of carbomethoxyhydrazones (eq 3), or acylation (eq 4).

$$\mathrm{R_1R_2C{=}O + NH_2NHCOOCH_3} \longrightarrow$$
$$\mathrm{R_1R_2C{=}NNHCOOCH_3} \xrightarrow[\text{Raney Ni}]{\mathrm{H_2}} \underset{\mathrm{III}}{\mathrm{R_1R_2CHNHNHCOOCH_3}} \qquad (3)$$

$$\mathrm{R_1 = CH_3,\ R_2 = H\ (III\text{-}E),\ R_1 = R_2 = CH_3\ (III\text{-}}i\mathrm{\text{-}P)}$$
$$\mathrm{R_1, R_2 = {-}(CH_2)_5{-}\ (III\text{-}}c\mathrm{\text{-}H),\ R_1 = (CH_3)_3C,\ R_2 = CH_3\ (III\text{-}M\text{-}}n\mathrm{\text{-}P)}$$

$$\mathrm{CH_3NHNH_2 + (CH_3O)_2C{=}O} \longrightarrow$$
$$\underset{\mathrm{III\text{-}M}}{\mathrm{CH_3NHNHCOOCH_3}} + \mathrm{CH_3N(COOCH_3)NH_2} \qquad (4)$$

Methyl and ethyl cyclopropyldiazanecarboxylates (III-*c*-P and III-*c*-Pe) were prepared from cyclopropyl-

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[1] The preceding article in this series is E. M. Kosower, P.-k. C. Huang, and T. Tsuji, *J. Amer. Chem. Soc.*, **91**, 2325 (1969).

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[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] *Cf.* H. H. Szmant, *Angew. Chem.*, 80, 141 (1968).

[5] D. J. Cram and J. S. Bradshaw, *J. Amer. Chem. Soc.*, **85**, 1108 (1963).

[6] A. Nickon and A. S. Hill, *ibid.*, **86**, 1152 (1964).

[7] P.-k. C. Huang and E. M. Kosower, *ibid.*, **90**, 2362 (1968).

[8] S. G. Cohen and J. Nicholson, *J. Org. Chem.*, **30**, 1162 (1965).

[9] R. A. Prough, J. A. Wittkop, and D. J. Reed, *Arch. Biochem. Biophys.*, **131**, 369 (1966); **140**, 450 (1970).

[10] R. L. Palmer, L. N. Lewis, H. Z. Hield, and J. Kumamoto, *Nature (London)*, **216**, 1216 (1967).

[11] M. N. Ackermann, J. L. Ellenson, and D. H. Robinson, *J. Amer. Chem. Soc.*, **90**, 7173 (1968).

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

[13] M. C. Chaco and N. Rabjohn, *J. Org. Chem.*, **27**, 2765 (1962).

Table I. Properties of Methyl Alkyldiazenecarboxylates

$RN{=}NCOOCH_3$, R =	Bp (mm), °C	Ir,[a] cm^{-1} $\nu_{C=O}$	Ir,[a] cm^{-1} $\nu_{N=N}$	$n^{20}D$
CH_3	42–43 (29)	1770	1560	1.4020
CH_3CH_2	48–50 (18)	1770	1560	1.4080
$(CH_3)_2CH$	36–37 (6)[b]	1765	1550	1.4088
c-C_3H_5[c]	46–48 (0.9)	1760	1545	1.4555
$(CH_3)_3C$[d]	72–75 (69)			1.4107 (25.5°)
$(CH_3)_3CH(CH_3)$	42–43 (0.9)	1770	1550	1.4274
c-C_6H_{11}	37–38 (0.015)[e]	1765	1555	1.4630

[a] In CCl_4. [b] Bp 53–55° (2 mm) for $(CH_3)_2CHNHNHCOOCH_3$. [c] Ethyl ester. [d] Prepared by Dr. D. J. Severn. [e] $C_6H_{11}NHNHCOOCH_3$, solid, mp 63.5–64.5°; bp 99-101° (0.5 mm).

Table II. Nmr Data for Alkyldiazane- and Alkyldiazenecarboxylate Esters

$RNHNHCOOCH_3$, R =	Chemical shift (τ)[a,b] R-N*H*	NHCO	*R*-N			OC*H*$_3$
CH_3	5.95	2.80		7.42 (CH_3)		6.32
CH_3CH_2	6.00	2.60	8.96 (CH_3)		7.16 (CH_2)	6.35
$(CH_3)_2CH$	6.00	2.95	9.05 (CH_3)		6.93 (CH)	6.39
$(CH_3)_3CCH(CH_3)$	6.10	3.30	9.11 (*tert*-Bu)	9.07 (CH_3)	7.32 (CH)	6.35
c-C_6H_{11}	6.20	3.20	8.0–9.0 ($-(CH_2)_5-$)		7.20 (CH)	6.36
c-C_3H_5	5.50	2.80	9.57 ($-CH_2CH_2-$)[d]		7.28 (CH)	5.86 (CH_2) 8.75 (CH_3)[c]
$RN{=}NCOOCH_3$						
CH_3				6.05 (CH_3)[e]		6.12[e]
CH_3CH_2			8.63 (CH_3)		5.94 (CH_2)	6.10
$(CH_3)_2CH$			8.69 (CH_3)		6.12 (CH)	6.10
$(CH_3)_3C$				8.65 (CH_3)		6.15
$(CH_3)_3CCH(CH_3)$			9.02 (*tert*-Bu)	8.85 (CH_3)	6.73 (CH)	6.08
c-C_6H_{11}			7.9–8.8 ($-(CH_2)_5-$)		6.40 (CH)	6.10
c-C_3H_5			8.60 ($-CH_2CH_2-$)[d]		6.36 (CH)	5.69 (CH_2) 8.60 (CH_3)[c]

[a] Chemical shifts in parts per million with tetramethylsilane as τ 10.0. [b] Diazane esters in $CDCl_3$; diazene esters in CCl_4. [c] Ethyl ester· [d] Multiplet centered at the position cited. [e] Assignments might be interchanged.

amine by the elegant nitrene route of Lwowski[14] (eq 5).

$$c\text{-}C_3H_5NH_2 + [:NCOOCH_3] \longrightarrow c\text{-}C_3H_5NHNHCOOCH_3 \quad (5)$$
$$\text{(from } 4\text{-}NO_2C_6H_4SO_2NHCOOCH_3)$$

Oxidation was effected by peracetic acid[15] (eq 6) to the

$$RNHNHCOOCH_3 \xrightarrow[CH_2Cl_2]{CH_3COOOH^*} \underset{\text{IV, 80–90\%}}{RN{=}NCOOCH_3} \quad (6)$$
$$\text{* or } Pb(OAc)_4$$

diazene esters which were in all cases distillable but were difficult to store (rearrangement to the carbomethoxyhydrazones). The least stable ester, methyl methyldiazenecarboxylate (IV-M), dissolved readily in ethanol to give a solution with a maximum at 3765 Å (ε 25). After 2 hr, absorption intensity in the region of the n → π* transition decreased about 5%. Decreases (~4.5% for IV-E and ~2% for IV-*i*-A) were observed in other cases in which a dissociable α-hydrogen was present and, for this reason, fresh solutions of the diazene esters were always used.

Certain properties of the alkyldiazenecarboxylate esters (IV) are presented in Table I. The nmr band positions for both the alkyldiazanecarboxylate (III) and alkyldiazenecarboxylate (IV) esters are given in Table II. The mass spectroscopic patterns for four of the esters (IV-E, IV-*i*-P, IV-*c*-P, and IV-*c*-H) show weak parent peaks and strong peaks for the expected alkyl carbonium ions (*i.e.*, IV-*c*-P → *c*-P$^+$), carbomethoxy groups, and nitrogen. The spectral data are in excellent agreement with the assigned structures.

Diazene esters (IV) are converted to the corresponding anions (V) by treatment with excess sodium or potassium hydroxide at room temperature or below[16] (eq 7). Base-catalyzed isomerization of the diazene-

$$\underset{\text{IV}}{RN{=}NCOOCH_3} \xrightarrow{\text{excess NaOH}} \underset{\text{V (all R)}}{RN{=}NCOO^-} \quad (7)$$

carboxylate ester to the carbomethoxyhydrazone occurs as a side reaction, but, with care, even IV-M can be converted into V-M in yields near 90%. Instability of the ester IV or the anion V required extrapolation of intensity data to zero time. The n → π* transitions for the esters (IV) and the anions (V) are given in Table III.

Table III. Ultraviolet Absorption Bands (n → π* Transition) of Alkyldiazenecarboxylate Esters and Anions

R =	$RN{=}NX$: X = $COOCH_3$ λ_{max} (ϵ_{max})[a]	X = COO^- λ_{max} (ϵ_{max})[b]
CH_3	3765 (25)	3700 (>22)
CH_3CH_2	3785 (25)	3710 (>22)
$(CH_3)_2CH$	3800 (25)	3720 (24)
$(CH_3)_3C$	3830 (26)	3740 (24)
$(CH_3)_3CCH(CH_3)$	3830 (29)	3740 (28)
c-C_6H_{11}	3830 (30)	3730 (28)
c-C_3H_5	3640 (46)[c]	3555 (41)

[a] Å, in ethanol. [b] Å, in ethanol-water (1:1). [c] Ethyl ester.

With these data, absorption coefficients for the alkyldiazenes were obtained. The stability of the isopropyldiazenecarboxylate anion (V-*i*-P) allowed accurate

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(14) W. Lwowski and T. J. Maricich, *J. Amer. Chem. Soc.*, **87**, 3630 (1965).

(15) L. Horder and H. Ferenkess, *Ber.*, **94**, 712 (1961).

(16) Diazenecarboxylate esters are hydrolyzed very readily, with rate constants of hydrolysis perhaps 10^4 greater than those of the homomorphic alkenecarboxylate esters.[17,18]

(17) P.-k. C. Huang and E. M. Kosower, *J. Amer. Chem. Soc.*, **90**, 2354 (1968).

(18) W. Correa, Ph.D. Thesis, State University of New York, Stony Brook, N. Y., 11790 (Jan 1970).

measurement of the absorption coefficient; absorption coefficients for the other anions were either obtained from the quantitative conversion of IV to V, or were assumed equal to that of V-*i*-P.

Formation of Diazenes. Two routes, decarboxylation and elimination, were suitable for the preparation of alkyldiazenes. Decarboxylation of diazenecarboxylate anions can be readily accomplished[17] through the addition of a suitable proton donor to a solution of an anion (eq 8). Although no measurements of the rate

$$\underset{V}{RN{=}NCOO^-} \xrightarrow{BH^+} RN{=}NH^+COO^- \longrightarrow \underset{VI}{RN{=}NH} \qquad (8)$$

of decarboxylation were carried out on alkyldiazenecarboxylic acids, the rates should be higher, if anything, than the rate found for phenyldiazenecarboxylic acid[17] (under our conditions, should be complete within seconds). The advantages of the decarboxylation route to alkyldiazenes are that it is (a) easily done under extremely mild conditions, (b) a quantitative conversion, permitting in most cases the preparation of known concentrations of alkyldiazenes, and (c) accessible from readily available precursors.

Preparation of alkyldiazenes by elimination of *p*-toluenesulfinic acid from 1-alkyl-1-tosyldiazanes (I) was accomplished in two ways, either from I and sodium ethoxide in 30–40% yield (eq 9) or through I

$$\underset{I}{RN(Ts)NH_2} \xrightarrow[EtOH]{Na^+OEt^-} \underset{VI}{RN{=}NH} \qquad (9)$$

$$R = CH_3\ (VI\text{-}M),\ CH_3CH_2\ (VI\text{-}E),\ (CH_3)_2CH\ (VI\text{-}i\text{-}P)$$

from the tosylamide (II) and nitrene (or its equivalent) in 5–35% yield. Higher boiling alkyldiazenes were usually obtained in low yields. A variation on the elimination procedure has been used for the preparation of methyldiazene[11] (eq 10). We have confirmed

$$CH_3NHOH + [:NH]\ (\text{from } NH_2OSO_3H) \xrightarrow[(0.1\ M)]{NaOH} [CH_3N(OH)NH_2] \qquad (10)$$

that this reaction does yield methyldiazene.

Absorption Data for Alkyldiazenes. Known concentrations of alkyldiazenes were generated by decarboxylation of alkyldiazenecarboxylate anions, for which the position and intensity of the absorption maximum for the n → π* transitions were measured. The observed intensities were, in all cases, quite small (ϵ_{max} 17–20, except for VI-*c*-P with ϵ_{max} 28), evidence that the alkyldiazenes are trans in configuration. Values previously reported are for *cis*-1,2-dimethyldiazene (λ_{max} 3530 Å, ϵ_{max} 240) and *trans*-1,2-dimethyldiazene (λ_{max} 3430 Å, ϵ_{max} 25).[19] The instability of the alkyldiazenes toward bimolecular decomposition precluded transfer or isolation in the measurement of the absorption intensities, and the values given are for media which include equimolar amounts of sodium chloride and amine (*cf.* eq 7 and 8). The data are summarized in Table IV.

Nmr Spectrum of Methyldiazene. Successful measurement of nmr spectra for alkenyldiazenes[20a] encouraged like attempts with alkyldiazenes.[20b] Considerable effort was devoted to methyldiazene, the most volatile and the most stable (except for cyclopropyldiazene) of the alkyldiazenes. In two instances, CH_3CN solutions could be prepared by the decarboxylation route. Spectra could not be measured below −48°, and, at this temperature, an extremely broad band appeared at τ −5.6 ± 0.2 along with a doublet at +6.13 ($J \approx 2$ Hz). We assign these to the NH hydrogen and the methyl hydrogens, respectively. The NH band in $CH_3N{=}NH$ is apparently even more broadened by interaction with the ^{14}N-quadrupole than the corresponding NH hydrogen in vinyldiazene or 2-propenyldiazene, but the position (τ −5.6) is not far from that found for the corresponding hydrogen in the alkenyldiazenes (−5.97).[20c] The splitting produced by the NH hydrogen in the methyl hydrogen signal is close to that found for the α-hydrogen of the vinyl group. The ratio of the two signals is not far from the expected 1:3, but the broadness of the NH signal makes this ratio unreliable. Another signal, also broadened, appeared at about τ −2, but could not be assigned on the basis of the information available. (A portion of the spectrum was blanked out by the solvent.)

Table IV. Absorption Data for Alkyldiazenes

RN=NH, R =	λ_{max}, Å (ϵ_{max})[a]	Other solvents λ_{max}, Å (ϵ_{max})
c-C_3H_5	3490 (28)	3500 (CH_3CN)
H		3500[b]
CH_3	3610 (18)	3500 (24) (H_2O)[c] 3620 (CH_3CN)
CH_3CH_2	3670 (18)	
$(CH_3)_2CH$	3680 (20)	
c-C_6H_{11}	3680 (20)	
$(CH_3)_3CCH(CH_3)$	3740 (21)	
$(CH_3)_3C$	3750 (17)	3750 (17) (CH_3CN)

[a] Absorption maxima were measured for distilled ethanol solutions of alkyldiazenes; the absorption coefficients were measured at the maximum indicated by the maxima for pure ethanol solutions in freshly prepared alkyldiazene solutions, which thus contained equimolar amine (usually imidazole), sodium chloride, and a very small amount of water. Since the solvent shifts are negligible, as far as our measurements are concerned, the error introduced by this procedure is very small. The usual concentration of alkyldiazene utilized for these measurements was between 0.005 and 0.01 *M*. [b] A broad, featureless band observed in the condensate from the decomposition of hydrazine in a discharge: A. Trombetti, *Can. J. Phys.*, **46**, 1005 (1968). [c] Reference 11.

Bimolecular Reaction of Alkyldiazenes. All monosubstituted diazenes thus far investigated react with themselves in a reaction which follows bimolecular kinetics. Since almost all of the monosubstituted diazenes disappear so rapidly that it is difficult to study their properties, the rate constant for the bimolecular reaction is an important indication of the chemical behavior of monosubstituted diazenes. We have made measurements of the bimolecular reaction of alkyldiazenes in distilled ethanol solutions; as firm evidence for their presence we have obtained similar rate constants for alkyldiazenes (VI-E, VI-*i*-P, VI-*tert*-B, VI-*c*-H) generated in two independent ways, decarboxylation (eq 8) and elimination (eq 9). Two different approaches to the same elimination process also gave concordant bimolecular rate constants in the case of three of the alkyldiazenes (VI-M, VI-E, VI-*i*-P). The similarity in rate behavior of the rapidly reacting *tert*-butyldiazene generated by two different methods is shown in Figure 1 by a plot of the reciprocal of optical

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(19) R. F. Hutton and C. Steel, *J. Amer. Chem. Soc.*, **86**, 745 (1964).
(20) T. Tsuji and E. M. Kosower, *ibid.*, (a) **91**, 3375 (1969); (b) **92**, 1429 (1970); (c) **93**, 1999 (1970).

Table V. Bimolecular Decomposition Rate Constants of Alkyldiazenes in Ethanol[a]

RN=NH, R =	Preparative method[a] R=NCOO$^-$ + BH$^+$X$^-$	 RNHTs + NH$_2$OSO$_3$H	 RN(Ts)NH$_2$ + OEt$^-$	Rate constant,[d] k_2, M^{-1} sec^{-1}
CH$_3$		0.037, 0.030	0.032	0.030
CH$_3$CH$_2$	0.56, 0.51	0.40	0.52	0.40
(CH$_3$)$_2$CH	0.69, 0.76	0.63	0.57	0.57
(CH$_3$)$_3$C[b]	2.5	2.5, 3.5		2.5
(CH$_3$)$_3$CCH(CH$_3$)	12, 4.5, 4.4, 6.1			4.5
c-C$_6$H$_{11}$	1.3, 1.7, 1.4	0.58		0.58
c-C$_3$H$_5$[c]		0.015		0.015

[a] After the generation of the alkyldiazene in the absence of oxygen by the pathway indicated, the solutions were distilled into a receiver cooled by liquid nitrogen. The apparatus containing the diazene solution was taken off the vacuum line, the alkyldiazene solution brought to 25°, and the rate of disappearance followed spectroscopically. All of the experiments listed in the table were carried out in ethanol at 25°. [b] k_2 in CH$_3$CN at 25°, 0.9 M^{-1} sec^{-1} (P.-k. C. Huang and E. M. Kosower, *J. Amer. Chem. Soc.*, **89**, 3911 (1967) (generated by decarboxylation). [c] k_2 in CH$_3$CN at 25° 0.006 M^{-1} sec^{-1} (generated by decarboxylation). [d] The reproducibility of the rate constants was only fair, as may be seen from the constants listed in the table. We have therefore taken the lowest second-order rate constant for the disappearance of alkyldiazenes as being the most accurate reflection of the intrinsic behavior of alkyldiazenes in the bimolecular reaction.

density *vs.* time. A similar plot for the slowly reacting cyclopropyldiazene is given in Figure 2. A summary of the rate constants obtained for all of the alkyldiazenes is given in Table V.

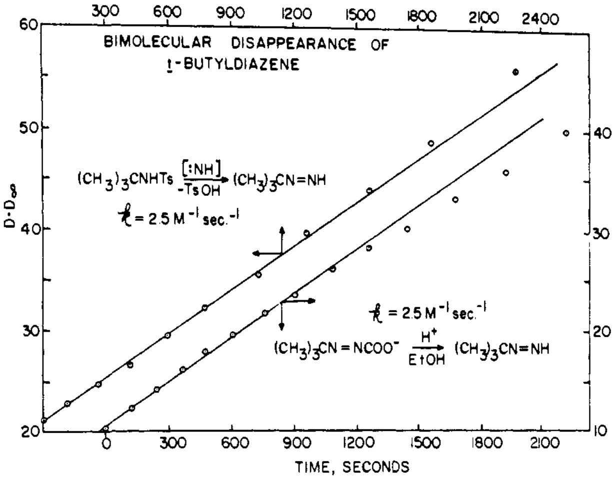
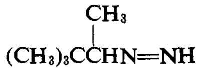


Figure 1. A plot of the reciprocal of optical density *vs.* time for the disappearance of *tert*-butyldiazene. Two different methods of generating the diazene were used. The upper line, which has been displaced for clarity, is for diazene generated by elimination. The lower line shows the behavior of the diazene produced by decarboxylation. In both cases the solvent was ethanol.

Comparisons of the rate constants for *tert*-butyldiazene and cyclopropyldiazene in ethanol and acetonitrile suggest that phenyldiazene would react about three times as rapidly in ethanol as in acetonitrile (estimated rate constant (in ethanol), 0.06 M^{-1} sec^{-1}). Methyldiazene is thus slightly less reactive than phenyldiazene. Ethyldiazene reacts about 13 times as rapidly as methyldiazene, but addition of another methyl group to the alkyl substituent does not materially increase the reactivity, and isopropyldiazene is about 19 times as reactive as methyldiazene. Further substitution does have a marked effect and *tert*-butyldiazene is 83 times as reactive as methyldiazene. Cyclohexyldiazene reacts at almost the same rate as isopropyldiazene and a secondary alkyldiazene with greater steric requirements for the alkyl groups, α-methylneopentyldiazene (VI-M-*n*-P), was almost twice as reactive as *tert*-butyldiazene (VI-*tert*-B) and eight times as reactive as isopropyldiazene. Steric effects are probably important in determining the reactivity of alkyldiazenes in the bimolecular reaction.


$(CH_3)_3C\overset{CH_3}{\overset{|}{C}}HN{=}NH$

VI-M-*n*-P

$(CH_3)_3CN{=}NH$

VI-*tert*-B

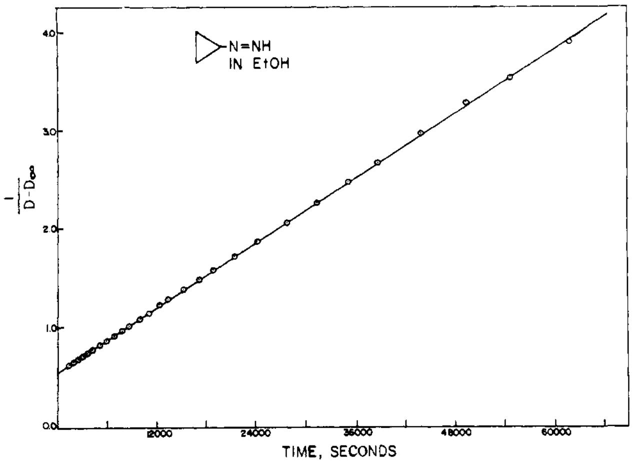


Figure 2. A plot of the reciprocal of optical density *vs.* time for the disappearance of cyclopropyldiazene produced *via* an elimination reaction in ethanol.

Cyclopropyldiazene is one of the most unreactive monosubstituted diazenes we have prepared, with a rate constant about one-half that of methyldiazene.

Products of the Bimolecular Reaction. The alkyldiazenes were generated from the alkyldiazenecarboxylate ion and imidazolium hydrochloride. After a suitable time, the ethanolic solution was frozen, uncondensed gas (N$_2$) pumped off, and volatile material analyzed by infrared spectroscopy except for cyclohexane which was extracted, concentrated, and analyzed by glpc.

In all cases, the product was the alkane corresponding to the alkyldiazene, but the yield was substantially less than quantitative. The only volatile hydrocarbon isolated from cyclopropyldiazene (VI-*c*-P) was cyclopropane in over 50% yield, unaccompanied by any trace of propene. Yields of hydrocarbons in other cases were propane (75%), isobutane (75%), and cyclohexane (82%). The bimolecular reaction is shown in eq 11.

$$2\mathrm{RN{=}NH} \longrightarrow \mathrm{RH} + \text{other products} \qquad (11)$$

We believe that the major part of the "other products" is the symmetrical dialkylhydrazine (1,2-bisdialkyldiazane) (VII) in analogy with the major product formed in the bimolecular reaction of 4-nitrophenyldiazene, that is, 1,2-bis(4-nitrophenyl)diazane (VIII).[1]

RNHNHR VII $\qquad$ $\mathrm{NO_2C_6H_4NHNHC_6H_4NO_2}$ VIII

In the case of cyclohexyldiazene, a substantial quantity of the alkyldiazene was produced, allowed to decompose *via* the bimolecular reaction, and examined for high-boiling product after removal of solvent and cyclohexane. If calculated as 1,2-bis(cyclohexyl)diazane (IX) the yield of high-boiling material was 10%. The nmr spectrum was consistent with this conclusion; oxidation with peracetic acid (which produces the diazene, X) shifts the nmr spectrum downfield, increasing the number of different types of hydrogen observable. The positions of the hydrogens for IX and X are recorded in the Experimental Section.

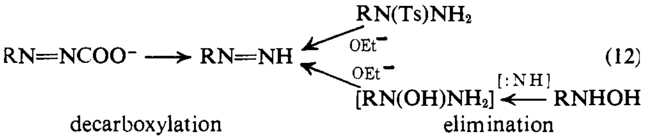
$c\text{-}\mathrm{C_6H_{11}NHNH}\text{-}c\text{-}\mathrm{C_6H_{11}}$ IX $\qquad$ $c\text{-}\mathrm{C_6H_{11}N{=}N}\text{-}c\text{-}\mathrm{C_6H_{11}}$ X

Other Reactions. All of the alkyldiazenes we have examined rapidly disappear after exposure to oxygen. Since aryldiazenes[1,12] and alkenyldiazenes[20] are all sensitive to oxygen (only 4-nitrophenyldiazene reacts with oxygen enough for the disappearance to be observed by rapid loss of light absorption due to the diazene), oxygen sensitivity can be regarded as a property of all monosubstituted diazenes.

Discussion

Proof of Diazene Structure. The structure of the alkyldiazenes described in this work rests on the following points of evidence: (1) multiple origin in straightforward chemical reactions, (2) position of the long wavelength absorption band, (3) volatility consistent with such a structure, and (4) a bimolecular reaction previously found characteristic of other monosubstituted diazenes. Nmr spectral data for methyldiazene are in accord with the structure for this diazene.

We have used two routes to alkyldiazenes: decarboxylation and elimination (eq 12). Cram and Bradshaw also used the "multiple origin criterion" to support their contention that an alkyldiazene was an intermediate in the reactions they studied, relying on the idea that a common set of products would be formed *via* a common intermediate.[5]



$$\begin{tikzcd} & & \mathrm{RN(Ts)NH_2} \arrow[dl, "\mathrm{OEt^-}"'] & \\ \mathrm{RN{=}NCOO^-} \arrow[r] & \mathrm{RN{=}NH} & & \\ & & \mathrm{[RN(OH)NH_2]} \arrow[ul, "\mathrm{OEt^-}"] & \mathrm{RNHOH} \arrow[l, "{[:NH]}"'] \\ \text{decarboxylation} & & \text{elimination} & \end{tikzcd}$$

(12)

There is relatively good agreement for the bimolecular rate constants for the disappearance of given alkyldiazenes generated by different routes (Table V). In addition, the absorption maximum for the alkyldiazenes prepared in different ways agreed (Table IV). Thus, simple chemical reactions, for which the most straightforward result is the formation of alkyldiazene, lead to substances having similar light absorptions and similar kinetic chemical properties. These results validate the application of the "multiple origin criterion" to the question of alkyldiazene structure and constitute strong support for our identification of alkyldiazenes.

The positions of the n → π^* transitions for the alkyldiazenes are compared to the positions of the n → π^* transitions for 1,2-bisdialkyldiazenes in Table VI.

Table VI. Comparison of Absorption Maxima (n → π^* Transitions) for Alkyldiazenes and 1,2-Bisdialkyldiazenes

R =	ΔE_T, kcal/mol	λ_{max}, Å RN=NH	λ_{max}, Å RN=NR[a]	ΔE_T, kcal/mol
$\mathrm{CH_3}$		3610[b]	3430[c]	
	1.2			3.1
$\mathrm{(CH_3)_2CH}$		3680[b]	3560[d]	
	1.5			2.5
$\mathrm{(CH_3)_3C}$		3750[b]	3675[e]	

[a] From ref 21. [b] EtOH. [c] $\mathrm{H_2O}$. [d] Gas. [e] Isooctane.

Three pairs of compounds provide evidence that increasing the size of the alkyl group shifts the position of the n → π^* transition to lower energies. Severn and Kosower[21] have suggested that an inductive effect is the primary cause of the shift. Comparison of the data for the mono- and disubstituted diazenes (Table VI lists the differences in transition energies for changes in alkyl substitution) suggests that the effect is cumulative and might be roughly constant for each methyl group added to the α-carbon. Nevertheless, the n → π^* transition shifts to substantially higher energies on replacement of the alkyl group in RN=NH with R (forming RN=NR). In terms of the usual understanding of the n → π^* transition, we interpret this to mean that the alkyl group decreases the $\mathrm{n_+–n_-}$ splitting. If we assume that the electronic effect of the alkyl group (which causes the decrease in splitting) is constant, we may predict a position for the n → π^* transition of diazene (diimide) as 3840 Å. This is substantially different from the value of 3500 Å reported by Trombetti for NH=NH deposited in an inert matrix.[22]

The intensity of the n → π^* transitions thus far observed for all monosubstituted diazenes is consistent only with a trans structure.

The manner in which we prepare the alkyldiazenes suggests that they are moderately volatile, with RN=NH more volatile than RC≡N but less volatile than $\mathrm{RCH{=}CH_2}$. The alkyldiazenes have "low" molecular weights and there is no substantial solute–solvent interaction. Along the same lines, methyldiazene generated in basic aqueous solution (eq 10) is readily evolved at room temperature, suggesting that methyldiazene is not especially soluble in water.

The most striking characteristic of aryldiazenes and alkenyldiazenes is bimolecular disappearance.[1,12,20] The same behavior for the alkyldiazenes must then be regarded as strong evidence for the assigned structures.

Bimolecular Reaction of Alkyldiazenes. Detailed discussion of the mechanism of the bimolecular reaction[1] will be deferred to a subsequent paper. There are

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(21) D. J. Severn and E. M. Kosower, *J. Amer. Chem. Soc.*, **91**, 1710 (1970).

(22) See Table IV, footnote *b*.

two points worth noting. First, the rate is quite sensitive to the nature of the alkyl group of the alkyldiazene. Although there is a general trend apparent in a plot of the logarithms of the rate constants against either steric substituent constants, E_S, or σ^* constants, no straight line can be drawn. The small solvent effect is inconsistent with a high sensitivity to polar effects of substituents, but is in agreement with the small substituent effect noted for the bimolecular reaction of aryldiazenes.

Second, we should take specific note of the fact that there is a correlation between the n → π* transition energy and the rate of the bimolecular reaction: the lower the energy the faster the reaction.

Implications of Alkyldiazene Behavior. Alkyldiazenes have been proposed as intermediates in a number of reactions. Since their special chemical behavior depends upon concentration, we can divide reactions which proceed through alkyldiazenes as intermediates into two groups: (H) rapid formation of alkyldiazene, high concentration possible, and (L) slow formation of alkyldiazene, low concentration plausible.

Probable members of the H group are the 1,2-elimination reactions (from RNHNHTs and $RN(Ts)NH_2$)[5] and the "nitrene" (or its equivalent) reactions (RNHTs + NH_2OSO_3H,[6] $RNH_2 + NHF_2$[23]). A possible member of this class is the reaction of nitrosotrifluoromethane and ammonia which is claimed to involve trifluoromethyldiazene as an intermediate in forming 70% *N,N*-bistrifluoromethylhydroxylamine.[24]

At high alkyldiazene concentrations, a portion of the hydrocarbon product might be formed *via* the bimolecular reaction route in addition to a base-catalyzed route, for those reactions in which strong base is present. Traces of oxygen or other oxidizing impurities might lead to chain reactions; however, unless molecules able to compete with alkyldiazenes for free radicals are present,[25] the product of the chain reaction is the hydrocarbon (eq 13). The base-catalyzed formation of hydrocarbon proceeds in two steps: (1) reversible formation of the alkyldiazenyl anion (eq 14) and (2) loss of nitrogen from the diazenyl anion followed (or accompanied) by a gain of a proton (eq 15).

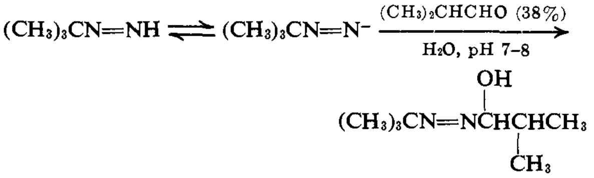
$$\text{RN=NH} + \text{R}\cdot\ (\text{or R}'\cdot) \longrightarrow \text{RH} + \text{RN=N}\cdot \qquad (13)$$

$$\text{RN=N}\cdot \longrightarrow \text{R}\cdot + \text{N}_2$$

$$\text{RN=NH} + \text{B}^- \rightleftharpoons \text{RN=N}^- + \text{BH} \qquad (14)$$

$$\text{RN=N}^- \longrightarrow \text{N}_2 + \text{R}^- \xrightarrow{\text{H}^+} \text{RH} \qquad (15)$$

It is necessary to consider briefly the acidity of alkyldiazenes (eq 14). Although we had previously estimated the pK_a of phenyldiazene as 19–21, results obtained by Hünig and Büttner[26] imply that this estimate should be revised a little downward. In spite of a rapid reaction of all monosubstituted diazenes with oxygen (bimolecular rate constants of $>1\ M^{-1}\ \text{sec}^{-1}$[27]) *tert*-butyldiazenyl anion can be converted into a number of carbonyl addition products (eq 16) with no precautions against the incursion of oxygen.



$$(\text{CH}_3)_3\text{CN=NH} \rightleftharpoons (\text{CH}_3)_3\text{CN=N}^- \xrightarrow[\text{H}_2\text{O, pH 7–8}]{(\text{CH}_3)_2\text{CHCHO (38\%)}} (\text{CH}_3)_3\text{CN=N}\overset{\text{OH}}{\text{C}}\text{H}\underset{\text{CH}_3}{\text{C}}\text{HCH}_3 \qquad (16)$$

Undissociated phenyldiazene is not a nucleophile toward reactive carbonyl compounds,[12] and thus the *tert*-butyldiazenyl anion must be the reactive species in the system used. In the presence of oxygen, we must postulate (a) extremely rapid addition of the anion to the carbonyl compound (concentration about 1 *M*) and (b) sufficient dissociation of the *tert*-butyldiazene to yield an adequate concentration of anion. Assuming an oxygen concentration of 10^{-4} *M*, and an alkyldiazene concentration of 1 *M*,[26] the rate of the oxygen reaction may be estimated (eq 17). The concentration of anion required to produce 38% yield of product and thus the same rate for the carbonyl addition reaction (eq 18), assuming that the anion is in rapid equilibrium with the diazene.

$$-\frac{d(\text{VI-}tert\text{-B})}{dt} = 10^2(1)(10^{-4}) = 10^{-2}\ M\ \text{sec}^{-1} = k_{\text{O}_2}(\text{VI-}tert\text{-B})(\text{O}_2) \qquad (17)$$

$$-\frac{d(\text{anion})}{dt} = 10^9(1)(X) = 10^{-2} = k_{\text{add}}(\text{RCHO})(\text{anion}) \qquad (18)$$

From eq 18, the *tert*-butyldiazenyl anion concentration is estimated as 10^{-11} *M*. From eq 19, at pH 8, the pK_a for *tert*-butyldiazene in water is 20.7, *i.e.*, lying between the values of 19 and 21.

$$K = \frac{(\text{anion})(\text{H}_3\text{O}^+)(\text{OH}^-)}{(\text{diazene})(\text{H}_2\text{O})(\text{OH}^-)} = \frac{(10^{-11})(10^{-15.7})}{(1)(10^{-6})} = 10^{-20.7} \qquad (19)$$

Phenyldiazene should be more acidic than *tert*-butyldiazene (compare benzoic and pivalic acids). The pK_a estimated for phenyldiazene in water is between 17.5 and 19.5, slightly lower than the 19–21 estimated on a completely different basis.

We surmise that phenyldiazenyl anion can return to the diazene as well as lose nitrogen to form the phenyl anion. It should be much harder to generate an alkide ion than a phenyl anion from the diazenyl anion, rapid exchange of the NH in the diazene should be observed, and the diazenyl anion might participate in reactions other than loss of nitrogen. In fact, reversal of the carbonyl addition reaction can be observed through trapping the released diazenyl anion (or diazene) with another carbonyl compound.[26,28] The sodium salt of

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[23] C. L. Baumgardner, K. J. Martin, and J. P. Freeman, *J. Amer. Chem. Soc.*, **85**, 97 (1963).

[24] S. P. Makarov, A. Ya. Yakubovich, S. S. Dubov, and A. N Medvedev, *Dokl. Chem.*, 160, 195 (1965).

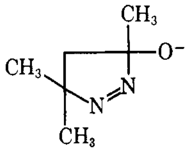
[25] *Cf.*, for example, the reaction of phenylhydrazine with polyhalomethanes reported by E. S. Huyser and R. H. S. Wang, *J. Org. Chem.*, 33, 3901 (1968).

[26] S. Hünig and G. Büttner, *Angew. Chem., Int. Ed. Engl.*, **8**, 451 (1969).

[27] Thorough mixing of a solution of 4-nitrophenyldiazene in acetonitrile (10^{-4} *M*) with air exhibits an initial phase in which the rate of disappearance increases over 15 or 20 sec, followed by a zero-order reaction (second phase) which clearly represents a chain reaction.[1] The initiation step might be a bimolecular reaction with a rate constant closer to 1 M^{-1} sec^{-1} than to 10 M^{-1} sec^{-1}, leading to chain-carrying radicals which cause the apparent rate to increase. *tert*-Butyldiazene might react with oxygen with a rate constant on the order of 10^2 M^{-1} sec^{-1} (*cf.* bimolecular rate constants for 4-nitrophenyldiazene and *tert*-butyldiazene[1]).

[28] Release from a C=N bond is postulated by D. W. Berry, R. W. Bryant, J. K. Smith, and R. G. Landolt, *J. Org. Chem.*, 35, 845 (1970).

another such diazene adduct has been reported as isolable (XI).[29]

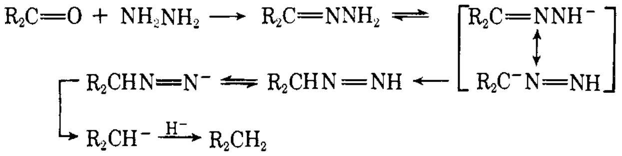


XI

In summary, special characteristics of H-class reactions which might be observed can depend upon (1) the bimolecular reaction of alkyldiazenes with themselves, (2) the free radicals formed from alkyldiazenes *via* reaction with oxygen, and (3) nucleophilic addition of diazenyl anions to appropriate acceptors. Base-catalyzed decomposition of the alkyldiazene to the corresponding hydrocarbon anion can compete, but there is no guarantee that this would be the predominant reaction even under highly basic conditions.

Reactions in which slow formation of an alkyldiazene is to be expected (L-class reactions) include Wolff–Kishner reactions.[4]

The low concentration of alkyldiazene makes the bimolecular reaction unlikely and the reaction with oxygen less likely. Nucleophilic addition by diazenyl anions may occur as well as decomposition of the diazenyl anion to the hydrocarbon anion, followed by formation of the hydrocarbon (eq 20). The rate-limiting step is the formation of the alkyldiazene.[4]



Conclusions. Alkyldiazenes, previously undetected intermediates in a variety of reactions, can be directly examined. Their properties must be understood for a proper appreciation of the reactions in which they participate. Reactions not heretofore considered in analysis of reactions through alkyldiazenes are bimolecular disappearance, reaction with oxygen,[30] and nucleophilic addition of diazenyl anion.[26]

Experimental Section

All melting points are uncorrected. Nmr spectra were measured with a Varian A-60 spectrometer, uv spectra with a Cary Model 14 spectrophotometer, and ir spectra with Perkin-Elmer Model 700 spectrophotometers. Mass spectra were obtained through the cooperation of Dr. A. P. Wolf, Chemistry Department, Brookhaven National Laboratory, with a Hitachi-Perkin-Elmer mass spectrometer. Physical constants are recorded in the tables, if not noted in this section.

1-Alkyl-*p*-toluenesulfonyldiazanes (I). The 1-methyl (I-M), 1-ethyl (I-E), and 1-isopropyl (I-*i*-P) compounds were prepared by reaction of the alkyl iodide with the lithium salt of *p*-toluenesulfonyldiazane (generated with lithium hydride) in dimethyl sulfoxide, dilution with ice-water, extraction with ether, and removal of the solvent. I-M was a solid and was recrystallized from tetrahydrofuran-pentane, mp 75.5–78°. The solid decomposed after several days storage at room temperature. I-E and I-*i*-P were viscous oils.

***N*-Alkyl-*p*-toluenesulfonamides** (II). Alkylamine (RNH_2) was allowed to reacted with *p*-toluenesulfonyl chloride in pyridine. All were known compounds.

Carbomethoxyhydrazones. The carbonyl compound was treated with methyl carbazate ($NH_2NHCOOCH_3$) in methanol containing a small amount of hydrogen chloride at room temperature overnight or at reflux for 1 hr. After removal of the solvent, the residue was recrystallized or distilled: cyclohexanone carbomethoxyhydrazone, bp 135–138° (0.6 mm); pinacolone carbomethoxyhydrazone, mp 65.5–67° (from MeOH-H_2O).

2-Alkyldiazanecarboxylic Acid Methyl Esters (III). The carbomethoxyhydrazone was stirred under a hydrogen atmosphere in methanol or ethanol containing Raney nickel (freshly prepared) until a substantial fraction of the theoretically required hydrogen was absorbed. After filtration and concentration, the residue was distilled. The rate of the reduction varied with structure: III-E, 1.7 hr; III-*i*-P, 10 hr; III-*c*-H, 10 hr; III-M-*n*-P, 25 hr. Hydrogenolysis was considerable in the case of III-E and III-M-*n*-P: III-*i*-P, bp 53–55° (2 mm); III-*c*-H, bp 99–101° (0.5 mm); III-M-*n*-P, bp 82–84° (1.5 mm).

Methyl 2-methyldiazanecarboxylate (III-M) was isolated by the removal through careful distillation (1-ft spinning band column) of the isomeric methyl 1-methyldiazanecarboxylate, bp 49–50° (4.5 mm), contained in the mixture distilled from the reaction of methylhydrazine with twice its weight of dimethyl carbonate at reflux for 1 hr. The crude material crystallized on standing and was recrystallized from ether–cyclohexane.

Ethyl (and methyl) 2-cyclopropyldiazanecarboxylate (III-*c*-P) was prepared by a modification of the procedure of Lwowski[14] as developed by Correa.[31] To cyclopropylamine (Gallard-Schlessinger Chemical Corp.) (19 ml, 0.27 mol) in CH_2Cl_2 (70 ml) held at 0° was added ethyl (or methyl) *N*-4-nitrobenzenesulfonoxycarbamate in portions as a solid or better, in CH_2Cl_2 solution. The solution immediately became cloudy and a solid separated. Additional CH_2Cl_2 (80 ml) was added to permit stirring, which was continued for 2 hr after addition was complete. The product was extracted with ether and the extract washed with water, dried ($MgSO_4$), filtered, and concentrated. The residue was chromatographed through silica gel. Methylene chloride eluted a reddish, tarry oil and ether eluted the desired product. The ethyl ester was obtained in 13% yield. The methyl ester had mp 85.5–86.5° (from cyclohexane after sublimation).

Methyl 2-Alkyldiazenecarboxylates (IV). **With Pb(OAc)$_4$.** A 10% excess of lead tetraacetate was added to the diazane ester (III) in CH_2Cl_2 (50 ml/g of ester) and the mixture stirred for 15 min, filtered, twice washed with ice-cold 0.5 *N* HCl, washed with water, 2.5% $NaHCO_3$, and water, and dried over Na_2SO_4. The solution was concentrated and the residue distilled under reduced pressure.

With Peracetic Acid. A 10% excess of peracetic acid (excess sodium acetate added to neutralize strong acid) was added to diazane ester (III) in CH_2Cl_2 (80 ml/g of ester), allowed to stand for 30 min, washed with 2% $NaHCO_3$ and water, then dried over Na_2SO_4. The diazene ester was distilled under reduced pressure after removal of the solvent.

Alkyldiazenes (VI). ***Via* Decarboxylation.** A typical procedure was that used for isopropyldiazene (VI-*i*-P). Methyl 2-isopropyldiazenecarboxylate (IV-*i*-P) (3.20 mg, 24.6 μmol) was dissolved in an ice-cold mixture of aqueous NaOH (1.403 *N*, 45 μl, 63 μ mol) and ethanol (90 μl). The flask containing the solution was connected to the vacuum line. For measurement of the absorption coefficient of isopropyldiazene, the solution of the isopropyldiazenecarboxylate salt was degassed by three freeze–thaw cycles, mixed with a degassed solution of imidazolium hydrochloride (70 μmol) in ethanol (35 ml) (added through a stopcock), transferred to a 10-cm uv cell, and examined at 3680 Å using a slide wire suitable for the range 0.0–0.2 OD. The optical density was measured as a function of a time, and the initial absorbance obtained from a plot of $1/D - D_\infty$ *vs.* time extrapolated to $t = 0$. The experiment described above yielded a value of 19.6 for the ϵ_{max} of isopropyldiazene. For measurement of the bimolecular rate constant, the aqueous solution of isopropylcarboxylate salt was evaporated before the addition of the imidazolium hydrochloride, and the ethanol solution of the diazene was distilled before transfer to the 10-cm cell for the measurement of the change of the optical density with time.

***Via* Elimination.** A degassed solution of sodium ethoxide in ethanol (35 ml, 0.2 *N*) was added to 1-methyl-1-*p*-toluenesulfonyldiazane (I-M) (96.2 mg, 0.461 mmol) which quickly dissolved. The solution was distilled slowly into a receiver cooled with liquid

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[29] J. P. Freeman and C. P. Rathjen, *Chem. Commun.*, 538 (1969).

[30] Or other oxidizing agents. *Cf.* S. G. Cohen and J. Nicholson, *J. Org. Chem.*, 30, 1162 (1965), and J. B. Aylward, *J. Chem. Soc. C*, 1663 (1969).

[31] W. Correa, Ph.D. Thesis, State University of New York at Stony Brook, Stony Brook, N. Y., 1970.

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^{-6} 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).

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