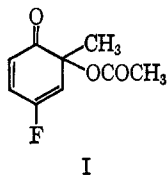


(2)  $J_2$  is slightly negative for both compounds in  $\text{CF}_2\text{Cl}_2$ -dimethyl ether solution and slightly positive in  $\text{CFCl}_3$  solution.<sup>6</sup> Again, because of the bond moments, the dihedral angle in the skew form is expected to be smaller (closer to  $90^\circ$ ) in the more polar solvent. At  $90^\circ$ , the coupling may well be negative.<sup>5</sup>

(3) The corresponding  $^3J_{\text{HF}}$  in the model compound 2-methyl-2-acetoxy-4-fluorocyclohexadien-3,5-one (I)



is<sup>12</sup> 7.06 cps. This compound is probably nearly planar, and the smaller value of  $^3J_{\text{HF}}$  in the butadienes indicates a significant twist about the central C-C single bond.

(4) Variable-temperature infrared<sup>18</sup> studies of these butadienes in  $\text{CS}_2$  solution indicate the presence of two distinguishable conformers, with  $\Delta H = 765$  (dichloro) and 815 (dibromo) cal/mol. This is in excellent agreement with our earlier nmr results in  $\text{CFCl}_3$  solution.<sup>6</sup>

**Acknowledgments.** This work was supported by a grant from the National Science Foundation. We are grateful to Mr. D. Wisnosky for technical assistance and Mr. J. R. Boal for recording the mass spectra.

(13) K. O. Hartman, G. L. Carlson, R. E. Witkowski, and W. G. Fateley, *Spectrochim. Acta*, **24A**, 157 (1968).

## Diazenes. I. Decarboxylation of Phenyl diazenecarboxylic Acid

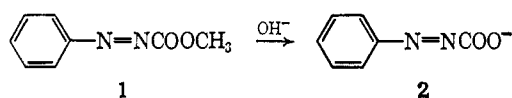
Pih-kuei C. Huang<sup>1</sup> and Edward M. Kosower<sup>2,3</sup>

Contribution from the Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11790. Received November 2, 1967

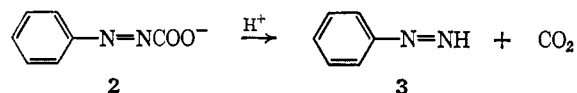
**Abstract:** The synthesis of several aryldiazene-carboxylic acid<sup>4</sup> esters and their conversion to the corresponding salts,  $\text{XArN}=\text{NCOO}^-\text{M}^+$ , are described. The rate constant for hydrolysis of  $\text{C}_6\text{H}_5\text{N}=\text{NCOOCH}_3$  (1) at  $4^\circ$  is  $\sim 2.0 \times 10^2$  l. mole<sup>-1</sup> sec<sup>-1</sup>,  $10^4$  faster than that of the homomorphic ester,  $\text{C}_6\text{H}_5\text{CH}=\text{CHCOOCH}_3$ . The rate constant for the reaction of 1 with sodium methoxide in anhydrous methanol is  $\sim 3 \times 10^{-3}$  l. mole<sup>-1</sup> sec<sup>-1</sup> at  $25^\circ$ , and the  $\text{pK}_a$  of phenyldiazene (3),  $\text{C}_6\text{H}_5\text{N}=\text{NH}$ , is estimated as no more than 27 from a comparison of the rate constants for reaction with hydroxide ion and methoxide ion. Spectroscopic data (ultraviolet-visible, infrared, and nuclear magnetic resonance) are reported for many of the diazene derivatives. A technique for following the decarboxylation of phenyldiazene-carboxylate anion,  $\text{C}_6\text{H}_5\text{N}=\text{NCOO}^-$  (2), in the absence of oxygen has been developed. The rate of decarboxylation varies linearly with hydrogen ion concentration over the pH range 10.4–11.9. Arguments in favor of a mechanism proceeding *via* carbon dioxide loss from the zwitterion  $\text{C}_6\text{H}_5\text{N}=\text{NH}^+\text{COO}^-$  are presented.

Aryldiazene-carboxylic (aryldiazoformic) acids and their derivatives<sup>4</sup> have an old, but rather neglected, place in the chemical literature. The propensity of phenyldiazene-carboxylic acid (2) for decarboxylation was discovered by Widman<sup>6</sup> and Thiele.<sup>7</sup> However, the only previous mechanistic study of the process is that of King<sup>8,9</sup> for the rate of nitrogen evolution from diazenedicarboxylic acid ("azodicarboxylic acid"<sup>11</sup>),  $\text{HOOCN}=\text{NCOOH}$ , over the pH range 11.8–12.8.

Our interest in diazenecarboxylic acid esters (azo esters) was originally aroused by the finding that  $\alpha$ -chymotrypsin catalyzed the hydrolysis of methyl phenyldiazene-carboxylate (1).<sup>10</sup> We found that an under-



standing of the decarboxylation process was vital to further work on the hydrolysis rates of 1. A study of the decarboxylation of 2 is the primary subject of this paper. Discussion of the product of decarboxylation, phenyldiazene (3), is too extensive to be included but may be found in the following papers.<sup>5</sup>



### Results

The preparation of diazenecarboxylic esters and their properties, the hydrolysis of the ester 1, the reaction of 1 with methoxide ion in methanol, the isolation of the diazenecarboxylic acid salts, the spectroscopic properties of the diazenecarboxylic acid derivatives, and the decarboxylation of the anion 2 are described in this section.

**Esters.** Syntheses of the methyl esters of aryldiazene-carboxylic acids of the general formula  $\text{XC}_6\text{H}_4\text{N}=\text{NCOOCH}_3$

(1) (a) This work is abstracted in part from the Ph.D. Thesis of P. C. Huang, State University of New York at Stony Brook, Oct 1966; (b) Predoctoral Fellow of the National Institutes of Health, 1964–1966.

(2) Support from the National Science Foundation, the Army Research Office (Durham), and the National Institutes of Health is gratefully acknowledged.

(3) Alfred P. Sloan Fellow, 1960–1964.

(4) See part II of this series<sup>5</sup> for a discussion of nomenclature.

(5) P. C. Huang and E. M. Kosower, *J. Am. Chem. Soc.*, **90**, 2362, 2367 (1968).

(6) O. Widman, *Ber.*, **28**, 1925 (1895).

(7) J. Thiele, *ibid.*, **28**, 2599 (1895).

(8) C. V. King, *J. Am. Chem. Soc.*, **62**, 379 (1940).

(9) C. V. King and J. J. Josephs, *ibid.*, **66**, 767 (1944).

(10) B. M. Goldschmidt, unpublished results.

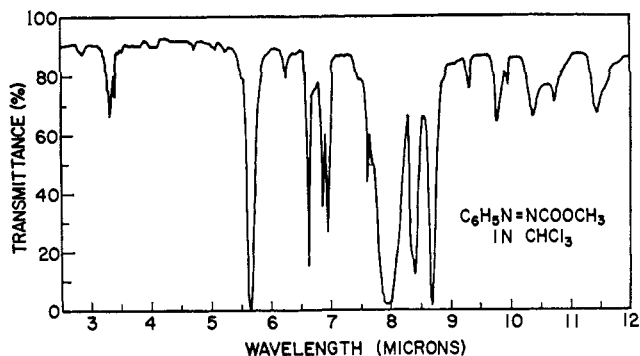
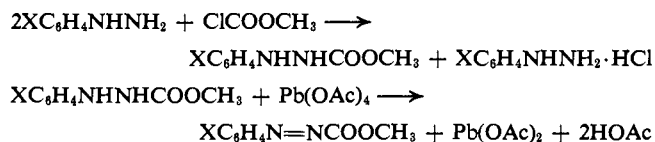


Figure 1. Infrared absorption spectrum of methyl phenyldiazene-carboxylate ( $\sim 5\%$  in chloroform).

NCOOCH<sub>3</sub> are accomplished by condensation of the appropriate aryldiazine with methyl chloroformate followed by oxidation of the hydrazo esters. Lead tetraacetate was found to be satisfactory for the latter process (Clement<sup>11</sup>). An oxidation procedure using N-bromosuccinimide has been reported by Bock and coworkers.<sup>12</sup>

#### Scheme I



Methyl esters of phenyl-, *p*-nitrophenyl-, *p*-bromophenyl-, *p*-methoxyphenyl-, *o*-bromophenyl-, and *o*-tolyldiazene-carboxylic acids are prepared in good yields according to Scheme I. They are either high-boiling red oils or orange crystals and all exhibit infrared carbonyl absorption at 1754–1773 cm<sup>-1</sup> in chloroform. (Carpino, *et al.*,<sup>13</sup> report 1748–1770 cm<sup>-1</sup> for a number of diazenecarboxylic esters.) The  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions will be discussed below. The infrared absorption spectrum of methyl phenyldiazene-carboxylate is shown in Figure 1. The nuclear magnetic resonance spectra of the three esters show the correct proton ratios within experimental error, as shown in Table I.

Table I. Nmr Data<sup>a</sup> for Diazene-carboxylic Esters XC<sub>6</sub>H<sub>4</sub>N=NCOOCH<sub>3</sub>

Substituent	Aliphatic H	Aromatic H	H ratio
H <sup>b</sup>	3.94	7.2–8.0	3.1:5.0
<i>o</i> -CH <sub>3</sub> <sup>c</sup>	2.66, 3.97	7.0–8.0	
<i>o</i> -CH <sub>3</sub> <sup>d</sup>	2.56, 3.94	7.0–8.0	3.1:3.2:4.0
<i>p</i> -OCH <sub>3</sub> <sup>d</sup>	3.78, 4.07	6.87, 7.81 7.02, 7.96	2.9:2.8:2.0:2.0

<sup>a</sup> Tetramethylsilane was used as internal standard. All numbers are expressed in parts per million downfield relative to the TMS signal. <sup>b</sup> Carbon tetrachloride (5–10%) was added to dissolve TMS. <sup>c</sup> 20% in carbon tetrachloride. <sup>d</sup> Neat.

**Base-Catalyzed Hydrolysis of Methyl Phenyldiazene-carboxylate.** The hydrolysis of methyl phenyldiazene-carboxylate is base catalyzed. Even when the hy-

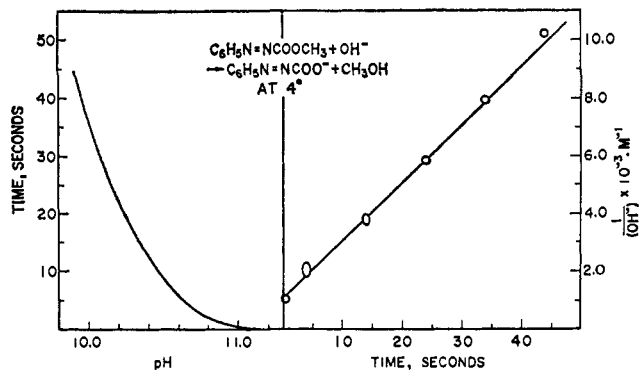


Figure 2. pH vs. time and second-order rate plot for base-catalyzed hydrolysis of methyl phenyldiazene-carboxylate at 4°. Initial concentrations: (ester) = (OH<sup>-</sup>) = 1.0 × 10<sup>-3</sup> M;  $k_2 = 2.0 \times 10^2$  l. mole<sup>-1</sup> sec<sup>-1</sup>.

droxide concentration is kept as low as 1 × 10<sup>-3</sup> M, the reaction is still too rapid to allow precise measurements of the rate by conventional means. Presumably the rate of hydrolysis could have been lowered to a convenient magnitude by a further decrease in the hydroxide ion concentration. However, this strategy is inapplicable due to the decomposition of the hydrolysis product, phenyldiazene-carboxylate anion. The kinetics of this hydrolysis have not yet been pursued in detail.

Rough kinetic data were obtained by hydrolyzing ester 1 at 4° in dilute alkaline solution, with an initial concentration of 1.0 × 10<sup>-3</sup> M in both ester and base. Since the reaction had a half-life on the order of a few seconds, fast mixing of reactants was effected by purging the base solution with nitrogen through a sintered-glass disk while adding the ester solution. The time required for complete mixing was probably less than 1 sec. The change of pH with time was followed by a pH meter attached to a recorder. A reasonably good second-order rate plot, 1/(OH<sup>-</sup>) vs. time, was obtained (Figure 2).

The second-order rate constant and half-life derived therefrom are 2.0 × 10<sup>2</sup> l. mole<sup>-1</sup> sec<sup>-1</sup> and 5 sec, respectively. The results are approximate because of the uncertainty in the time of mixing and the lag in the response (rise time, 0.4 sec for a change of 1 pH unit) of the recorder.

The rate constant for the hydrolysis of methyl phenyldiazene-carboxylate (1) may be compared to those for the hydrolysis of methyl acetate (0.188 l. mole<sup>-1</sup> sec<sup>-1</sup> at 25°<sup>14</sup>) and methyl *trans*-cinnamate (6.04 × 10<sup>-2</sup> l. mole<sup>-1</sup> sec<sup>-1</sup> at 25°<sup>15</sup>). The difference may be understood in terms of a strong electron-withdrawing character for the diazene group. Nucleophilic attack of the hydroxide ion on the carbonyl carbon atom is strongly facilitated by the diazene group.

**Methoxide Ion and Diazene-carboxylic Ester 1.** Hoffmann<sup>16,17</sup> has shown that ethoxide ion reacts with a number of ethyl aryldiazene-carboxylates to produce diethyl carbonate and other compounds *via* an aryl anion. In agreement with the results of Hoffmann, we obtained a substantial yield of dimethyl carbonate (35%) from the reaction of 0.44 M diazenecarboxylic

(11) R. A. Clement, *J. Org. Chem.*, **25**, 1724 (1960); **27**, 1115 (1962).  
 (12) H. Bock, E. Boltin, and J. Kroner, *Ber.*, **99**, 3337 (1966).  
 (13) L. A. Carpino, P. H. Terry, and P. J. Crowley, *J. Org. Chem.*, **26**, 4336 (1961).

(14) E. Anderson and H. B. Pierce, *J. Phys. Chem.*, **22**, 44 (1918).  
 (15) M. L. Bender and B. Zerner, *J. Am. Chem. Soc.*, **84**, 2550 (1962).  
 (16) R. W. Hoffmann, *Angew. Chem.*, **75**, 168 (1963).  
 (17) R. W. Hoffmann, *Ber.*, **97**, 2763 (1964).

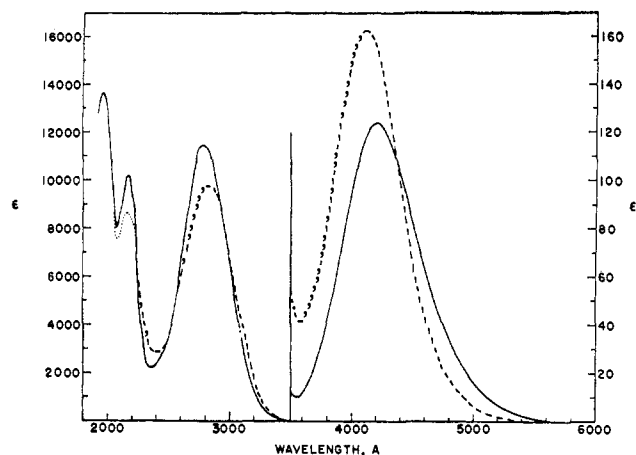
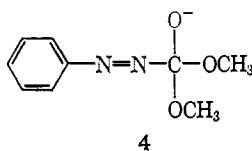


Figure 3. Ultraviolet and visible spectra of methyl phenyldiazene-carboxylate (—) in isooctane based on the spectra of a  $7.73 \times 10^{-3} M$  solution; ultraviolet and visible spectra of phenyldiazene-carboxylate anion (---) in  $1 N$  NaOH, except below  $2250 \text{ \AA}$  (· · · ·) for which the solvent is phosphate buffer,  $0.05 M$ , pH 12, based on the spectra of an  $8.45 \times 10^{-3} M$  solution.

ester **1** and  $0.27 M$  methoxide ion in methanol. We have also found that dimethyl ether is *not* a product of the reaction of methoxide ion with **1** in methanol; displacement of the anion **2** from the methyl ester does not occur.

The decomposition of the diazenecarboxylate in methanol containing methoxide is surprisingly slow, with  $k_2$  at  $25^\circ$  of  $\sim 3 \times 10^{-3} \text{ l. mole}^{-1} \text{ sec}^{-1}$ . In addition, the ultraviolet spectrum of the initial reaction mixture is about the same as that of ester **1** in pure methanol, demonstrating that the tetrahedral intermediate **4** is not present in any significant concentration.



**Phenyldiazene-carboxylic Acid Salts.** The potassium salt of **2** has been prepared by hydrolysis of phenyldiazene-carboxamide at elevated temperatures.<sup>18</sup> Basic hydrolysis of diazenecarboxylic esters is a convenient route to the salts. The sodium salt of **2** is too soluble for facile isolation; the potassium and barium salts precipitate as bright yellow crystals from alkaline solutions. These may be stored as dry solids if small amounts of excess base are present.

**Spectroscopic Data on Electronic Transitions.** All the esters and salts of aryldiazene-carboxylic acids studied exhibit one or two absorption bands in the ultraviolet region and one absorption band in the visible region. The intensities of the absorption bands,  $10^4$  for the molar extinction coefficients of the ultraviolet absorption maxima and  $10^2$  for those of the visible absorption maxima, suggest that they correspond to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions, respectively. The ultraviolet and visible spectra of methyl phenyldiazene-carboxylate are shown in Figure 3.

Spectroscopic data for the esters of aryldiazene-carboxylic acids,  $\text{XC}_6\text{H}_4\text{N}=\text{NCOOCH}_3$ , where X

(18) A. N. Nesmeyanov and O. A. Reutov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 611 (1949); *Chem. Abstr.*, **44**, 7791 (1950).

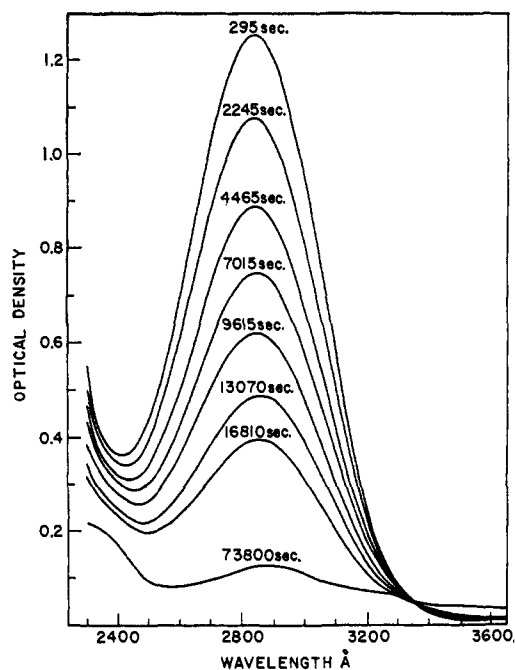


Figure 4. Disappearance of phenyldiazene-carboxylate anion in phosphate buffer, pH 11.56,  $\mu = 0.186$ , at  $25^\circ$ . Initial concentration:  $2.20 \times 10^{-4} M$ .

is H, *p*-NO<sub>2</sub>, *p*-Br, *p*-OCH<sub>3</sub>, *o*-Br, and *o*-CH<sub>3</sub>, are listed in Table II. The solvent sensitivity of the absorptions near  $3000 \text{ \AA}$  for the aryldiazene-carboxylic acid esters is moderate. When the solvent is changed from the nonpolar isooctane ( $Z = 60.1^{19}$ ) to the polar 2,2,3,3-tetrafluoropropanol (TFP,  $Z = 86.3^{19}$ ) for four of the esters, their absorption maxima shift  $130\text{--}190 \text{ \AA}$ . The trend is characteristic of  $\pi \rightarrow \pi^*$  transitions for  $\alpha,\beta$ -unsaturated esters. The solvent effects on the visible bands are interesting but do not warrant detailed discussion. The spectroscopic data for the corresponding carboxylate anions are listed in Table III. The ultraviolet and visible spectra of phenyldiazene-carboxylate anion are also given in Figure 3.

**Decarboxylation of 2.** Acid catalysis of the decomposition of **2** was indicated by preliminary experiments. Carbon dioxide was obtained in 93% yield from the reaction of the barium salt of **2** with aqueous sulfuric acid.

Initial studies of the kinetics of the decarboxylation of **2** were attempted by following the disappearance of the anion spectroscopically. After considerable effort, we concluded that the intermediate phenyldiazene (**3**) was sensitive to oxygen and yielded other compounds with strong light absorption. An arduous technique was thus required for the kinetic studies, involving the preparation of degassed buffer, mixing of the buffer with methyl phenyldiazene-carboxylate (**1**) under vacuum, filling with argon, and withdrawing samples with a hypodermic inserted through a septum. The reaction solution was quenched with strong base and extracted with *n*-heptane. The amount of unreacted **2** was then measured spectroscopically.

Figure 4 shows the disappearance of phenyldiazene-carboxylate anion in a typical run. Rates of decarboxylation were measured at  $25^\circ$  with the same initial phenyldiazene-carboxylate anion concentration in five buffers

(19) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

**Table II.** Ultraviolet and Visible Absorption of Methyl Esters of Aryldiazene-carboxylic Acids

		$\lambda_{\max}, \text{\AA}^a (\epsilon_{\max})^b$ in solvent				
Isooctane	CH <sub>2</sub> Cl <sub>2</sub>	CH <sub>3</sub> CN	CH <sub>3</sub> OH	TFP <sup>c</sup>	H <sub>2</sub> O	
Methyl Phenylidiazene-carboxylate						
1970 <sup>d</sup> (13,600)						
2170 <sup>d</sup> (10,200)		2150 <sup>d</sup> (8800)	2150 <sup>d</sup> (15,200)	2200 <sup>d</sup> (7300)	2220 <sup>d</sup>	
2800 (11,400)		2888 (13,300)	2870 <sup>f</sup> (11,000)	2985 (11,000)	3030 <sup>d</sup>	
4222 (144)		4217 (132)	4203 <sup>g</sup> (141)	4258 (151)		
Methyl <i>p</i> -Nitrophenylidiazene-carboxylate						
		2840 <sup>d</sup> (15,700)				
		4300 <sup>d</sup> (185)				
Methyl <i>p</i> -Bromophenylidiazene-carboxylate						
2260 <sup>d</sup> (9410)		2270 <sup>d</sup> (8870)	2280 <sup>d</sup> (8120)	2270 <sup>d</sup> (7690)		
2950 <sup>d</sup> (14,750)		3020 <sup>d</sup> (14,900)	3020 <sup>d</sup> (13,400)	3120 <sup>d</sup> (14,000)		
4320 (164)		4225 (185)	4200 <sup>d</sup> (196)	4251 (207)		
Methyl <i>p</i> -Methoxyphenylidiazene-carboxylate						
2350 <sup>d</sup> (7400)	2410 <sup>d</sup>					
~3125 <sup>e</sup> (~10,000)	3360 <sup>h</sup>					
~3275 <sup>e</sup> (~10,000)	4250 (sh)					
4140 <sup>d</sup> (200)						
Methyl <i>o</i> -Bromophenylidiazene-carboxylate						
2080 <sup>d</sup> (14,400)		2060 <sup>d</sup> (13,900)		2040 <sup>d</sup> (14,500)		
2290 <sup>d</sup> (8420)		2300 <sup>d</sup> (6480)		2302 (6130)		
2828 (8300)		2896 (8500)		2957 (7950)		
4336 (126)		4320 (142)		4320 (163)		
Methyl <i>o</i> -Tolylidiazene-carboxylate						
2029 (13,900)		2033 (13,500)		2022 (12,800)		
2223 (7900)		2233 (7100)		2233 (6170)		
2881 (10,400)		2952 (10,200)		3040 (9790)		
4289 (145)		4287 (172)		4320 (222)		

<sup>a</sup>  $\pm 5$  Å unless specified otherwise. <sup>b</sup>  $\pm 5\%$ . <sup>c</sup> 2,2,3,3-Tetrafluoropropanol. <sup>d</sup>  $\pm 10$  Å. <sup>e</sup> Estimated maxima resolved from experimental curve. <sup>f</sup> Reported<sup>12</sup> as 2869 Å ( $\epsilon$  10,000) in dioxane. <sup>g</sup> Reported as 4202 Å ( $\epsilon$  131) in dioxane. <sup>h</sup> Broad peak; not possible to resolve as in footnote *e*.

**Table III.** Ultraviolet and Visible Absorption of Aryldiazene-carboxylate Anions (XC<sub>6</sub>H<sub>4</sub>N=NCOO<sup>-</sup>) in Sodium Hydroxide (1 *N*)<sup>a</sup>

X	$\lambda_{\max}, \text{\AA}^b (\epsilon_{\max})^c$ for	
	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$
H	2830 (9800)	4120 (162)
<i>p</i> -NO <sub>2</sub>	2910 (13,800)	4280 (230)
<i>p</i> -Br	2955 (13,000)	4140 (108)
<i>p</i> -OCH <sub>3</sub>	3190 (13,800)	~4000 <sup>d</sup>
<i>o</i> -Br	2845 (7230)	4190 (143)
<i>o</i> -CH <sub>3</sub>	2880 (7320)	4150 (215)

<sup>a</sup> Anion solutions were prepared by dissolving weighed amounts of ester in basic solutions. <sup>b</sup>  $\pm 10$  Å. <sup>c</sup>  $\pm 5\%$ . Quantitative conversion of the ester to the anion is assumed. <sup>d</sup> As a shoulder ( $\epsilon$  400).

(phosphate and carbonate buffers) with pH values between 10.4 and 11.9 and of the same ionic strength. Rates of decarboxylation were also measured in solutions of higher phenylidiazene-carboxylate anion concentration and in buffers of higher ionic strength. A good first-order rate plot,  $\log(D - D_{\infty})$  at 2830 Å *vs.* time, was obtained for each case. A typical rate plot appears in Figure 5. The rate constants of decarboxylation in different buffers are listed in Table IV. The logarithm of the rate constant is plotted against the pH of the medium in Figure 6.

The rate constant for decarboxylation is almost independent of the initial concentration of phenylidiazene-carboxylate anion (compare expt 5 and 6). Changing the medium from phosphate buffer to carbonate buffer of the same pH does not result in a sig-

**Table IV.** Rate Constants for Decarboxylation of Phenylidiazene-carboxylate Anion at 25°

Expt	Buffer <sup>a</sup>	$\mu$	pH	(H <sup>+</sup> ) $\times 10^{12}, M$	C <sub>0</sub> $\times 10^4, M$	k <sup>b</sup> $\times 10^4, \text{sec}^{-1}$
1	Carbonate	0.186	10.43	37.15	2.22	8.07
2	Phosphate	0.189	10.93	11.75	2.23	2.77
3	Phosphate	0.188	11.24	5.754	2.34	1.54
4	Carbonate	0.188	11.24	5.574	2.33	1.72
5	Phosphate	4.91	11.25	5.623	2.57	1.09
6	Phosphate	4.91	11.25	5.623	206.0	1.02
7	Phosphate	0.454	11.26	5.495	2.40	1.33
8	Phosphate	0.186	11.56	2.754	2.20	0.87
9	Phosphate	0.186	11.89	1.288	2.22	0.40

<sup>a</sup> See Table VII for buffer composition. <sup>b</sup>  $\pm 6\%$ .

nificant change in the rate of decarboxylation (compare expt 3 and 4), indicating that a reversible equilibrium involving carbon dioxide does not occur to an appreciable extent. Increasing the buffer concentration results in a slight decrease of the decarboxylation rate (compare expt 3, 5, and 7).

## Discussion

We might have surmised that phenylidiazene is a weak acid on the basis of the large difference in the rate of hydrolysis of methyl phenylidiazene-carboxylate (**1**  $\rightarrow$  **2**) and the rate of loss of the ester **1** in the reaction with methoxide ion. Assuming that the ratio of the rate constants represents a comparison of the rates of the two processes shown in eq 1 and 2, and that the Brønsted

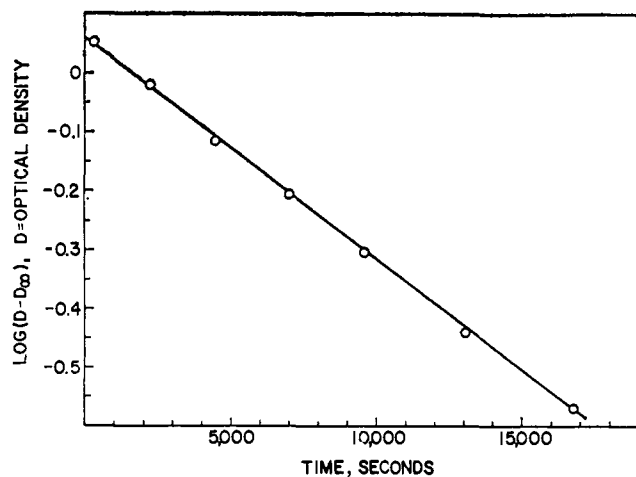
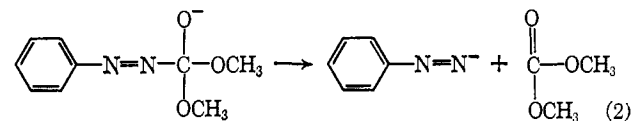
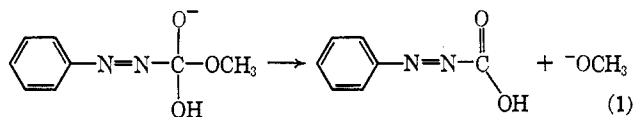


Figure 5. First-order rate plot for decarboxylation of phenyldiazene-carboxylate anion in phosphate buffer, pH 11.56,  $\mu = 0.186$ , at 25°. Kinetics followed at 2830 Å;  $k = 8.72 \times 10^{-5} \text{ sec}^{-1}$ .

“coefficient” for the comparison is 0.5,<sup>20</sup> we may estimate that the  $pK_a$  of phenyldiazene is 11  $pK_a$  units greater than the  $pK_a$  of methanol. If the  $pK_a$  of methanol is 16,<sup>22</sup> the  $pK_a$  of phenyldiazene is 27, considerably smaller than that of ethylene ( $pK_a = 42$ <sup>21</sup>). The value of 27 is clearly a maximum in view of the assumptions used.

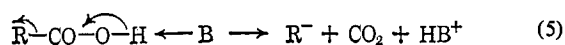
The acidity of phenyldiazene will be considered further in a following article.<sup>5</sup>



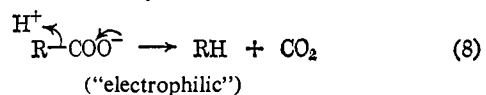
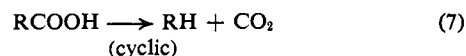
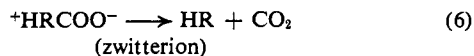
$$2 \log \frac{k_1}{k_2} = 2 \log \frac{8 \times 10^2 \text{ l. mole}^{-1} \text{ sec}^{-1}}{3 \times 10^{-8} \text{ l. mole}^{-1} \text{ sec}^{-1}} \cong 11 \quad (3)$$

The mechanisms of decarboxylation have been summarized by Kosower<sup>23</sup> and those relevant to the present case can be briefly described as in eq 6–8.

Anion formation



Formation of uncharged product



(20) A comparison of ester hydrolysis rates and alcohol acidities suggests that 0.5 is a suitable approximation. The Brønsted coefficient for tritium exchange vs.  $pK_a$  in weak hydrocarbon acids is 0.58: A. Streitwieser, private communication, quoted in ref 21.

(21) E. M. Kosower, “Introduction to Physical Organic Chemistry,” John Wiley and Sons, Inc., New York, N. Y., 1968.

(22) D. J. Cram, “Fundamentals of Carbanion Chemistry,” Academic Press Inc., New York, N. Y., 1965.

(23) E. M. Kosower, “Molecular Biochemistry,” Section 2.2, McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

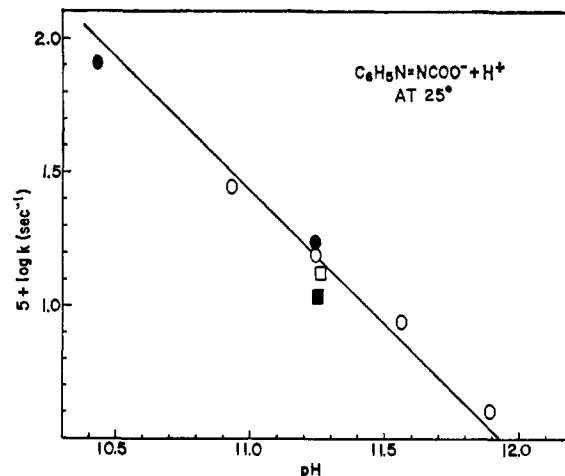
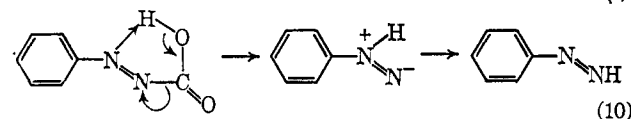
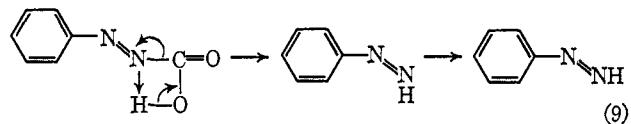


Figure 6. Log  $k$  vs. pH for decarboxylation of phenyldiazene-carboxylate anion at 25°: (○) phosphate buffer,  $\mu = 0.18-0.20$ , ( $\text{C}_6\text{H}_5\text{N}=\text{NCOO}^-$ ) =  $2.2-2.4 \times 10^{-4} \text{ M}$ ; (●) carbonate buffer,  $\mu = 0.18-0.20$ , ( $\text{C}_6\text{H}_5\text{N}=\text{NCOO}^-$ ) =  $2.2-2.4 \times 10^{-4} \text{ M}$ ; (□) phosphate buffer,  $\mu = 0.454$ , ( $\text{C}_6\text{H}_5\text{N}=\text{NCOO}^-$ ) =  $2.4 \times 10^{-4} \text{ M}$ ; (■) phosphate buffer,  $\mu = 4.91$ , ( $\text{C}_6\text{H}_5\text{N}=\text{NCOO}^-$ ) =  $2.6 \times 10^{-4}$  and  $2.1 \times 10^{-2} \text{ M}$ ; straight line was drawn so that  $(d \log k)/(d \text{ pH}) = -1$ .

The decarboxylation of phenyldiazene-carboxylate anion,  $\text{C}_6\text{H}_5\text{N}=\text{NCOO}^-$  (2), is catalyzed by acid (Figure 6), excluding simple transformation of 2 into the anion of phenyldiazene as the pathway for decarboxylation (eq 4).

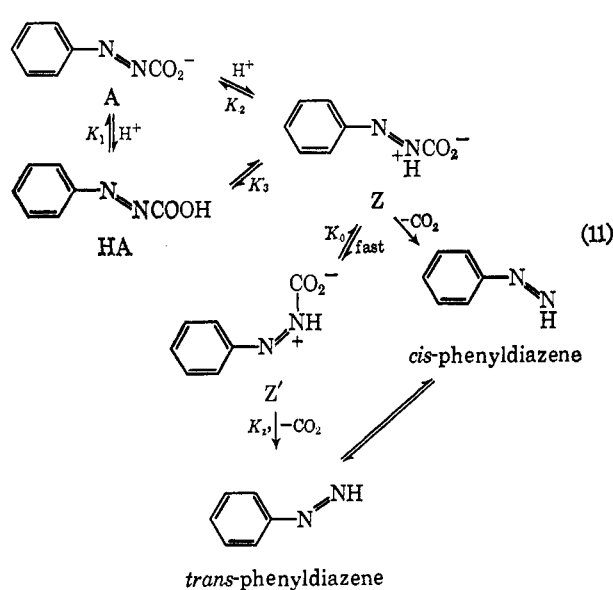
Formation of an anion through the reaction of a base with the undissociated acid is unlikely, as shown by the fact that an increase in buffer concentration actually decreases the rate (eq 5). The “electrophilic” process is excluded on the basis of the implausibility of the concerted mechanism required (eq 8). Replacement of the phosphate buffer by carbonate buffer had little effect on the rate, nullifying the possibility that carbon dioxide loss is reversible.

The cyclic mechanism (eq 9) which produces phenyldiazene directly is not likely on the grounds of the four-membered ring required in the transition state. We cannot ignore the possibility that a cyclic transition state which forms the 1-phenyl-1H-diazene is the pathway by which decarboxylation occurs (eq 10). It is, however, difficult to identify the driving force causing the decarboxylation to be a facile reaction.



The mechanism of decarboxylation which we prefer is that which proceeds via a zwitterion (eq 11; see paper III of this series<sup>5</sup> for a discussion of the equilibrium *cis*-phenyldiazene  $\rightleftharpoons$  *trans*-phenyldiazene).

The dissociation constant  $K_1$  for phenyldiazene-carboxylic acid may be estimated as follows. The ratio of the hydrolysis rates of methyl phenyldiazene-carboxyl-



ate (1)<sup>24</sup> and methyl *trans*-cinnamate<sup>25</sup> is assumed to be the same as the ratio of the dissociation constants of the corresponding acids. The dissociation constant for *trans*-cinnamic acid at 25° is  $3.6 \times 10^{-5}$ ,<sup>26</sup> and the  $K_1$  thus derived for phenyldiazene-carboxylic acid is 0.5.

The equilibrium constant  $K_2$  is estimated as  $\sim 0.32$  from the  $pK_a$  of azobenzene ( $-2.5$  in aqueous sulfuric acid<sup>27</sup>) as corrected for the proximity of the positive charge by 3  $pK_a$  units. (The  $pK_a$  values of acetic acid and protonated betaine,  $(CH_3)_3N^+CH_2COOH$ , are 4.76 and 1.84, respectively).<sup>28</sup> The  $pK_a$  for  $C_6H_5N=NCOOH$  is 0.3, that for  $C_6H_5N=NH^+COO^-$  is 0.5. (Differences between Z and Z' are ignored in this discussion.) Thus, the basicities of the oxygen in the carboxylate group and the  $\alpha$ -nitrogen of the azo group are similar.

The kinetic expression for the decarboxylation reaction is given by eq 12. The equation for zwitterion

$$-d(A)/dt = -d(\text{anion } 2)/dt = k_A(H^+)(A) \quad (12)$$

loss is given by eq 13.

$$-d(Z')/dt = k_{Z'}(Z') = k_{Z'}K_0[(A)(H^+)/K_2] \quad (13)$$

Since  $-d(Z')/dt = -d(A)/dt$ ,  $k_{Z'} = k_A K_2 / K_0$ . The second-order rate constant,  $k_A$ , is  $2.67 \times 10^7$  l. mole<sup>-1</sup> sec<sup>-1</sup> from the data in Table IV. Given the estimate of 0.32 for  $K_2$  and an assumed value of  $10^{-3}$  for  $K_0$ , an estimate of  $10^{10}$  sec<sup>-1</sup> for  $k_{Z'}$  is obtained.

The second-order constant found by King for the acid-catalyzed decomposition of diazenedicarboxylate dianion was  $1.07 \times 10^8$  l. mole<sup>-1</sup> sec<sup>-1</sup>.<sup>8</sup> An estimate for the corresponding reaction of carbamate ion gave  $3 \times 10^8$  l. mole<sup>-1</sup> sec<sup>-1</sup> at 18° as the rate constant for the acid-catalyzed reaction.<sup>29</sup>

(24) At 25°, as extrapolated from 4°:  $8 \times 10^2$  l. mole<sup>-1</sup> sec<sup>-1</sup> with an activation energy of 11 kcal/mole.

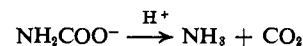
(25) At 25°,  $6 \times 10^{-2}$  l. mole<sup>-1</sup> sec<sup>-1</sup>, according to M. L. Bender and B. Zerner, *J. Am. Chem. Soc.*, **84**, 2550 (1962).

(26) W. A. Roth and R. Stoermer, *Ber.*, **46**, 270 (1913).

(27) I. M. Klotz, H. A. Fless, J. Y. Chen Ho, and M. Mellody, *J. Am. Chem. Soc.*, **76**, 5136 (1954).


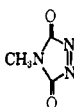
(28) C. Long, Ed., "Biochemists' Handbook," D. Van Nostrand Co., New York, N. Y., 1961, p 46.

(29) C. Faurholt (*Z. Anorg. Allgem. Chem.*, **120**, 84 (1921)) found that a 0.05 M solution of ammonium carbamate in 0.1 N sodium hydroxide was completely decomposed in 3 days at 18°. A half-life of 0.3 day was used to estimate the constant given.



On the basis of the absorption coefficient of the  $n \rightarrow \pi^*$  transition of phenyldiazene, the product observed<sup>5</sup> is *trans*, like the anion from which it is derived (Table V). Conversion of *cis*-azo compounds into

Table V. Absorption Coefficients for Diazene Derivatives,  $n \rightarrow \pi^*$  Transition

	$\lambda_{max}, \text{\AA}$ ( $\epsilon_{max}$ )	Ref
<i>cis</i> Derivatives		
$CH_3N=NCH_3$	3530 (240)	a
$C_6H_5N=NC_6H_5$	4360 (1230)	b
	3150 (446)	c
	5380 (152)	d
<i>trans</i> Derivatives		
$CH_3N=NCH_3$	3430 (25)	a
$C_6H_5N=NC_6H_5$	4450 (420)	b
$CH_3CH_2OOCN=NCOOCH_2CH_3$	4040 (39)	e

<sup>a</sup> R. F. Hutton and C. Steel, *J. Am. Chem. Soc.*, **86**, 745 (1964).

<sup>b</sup> G. Zimmerman, L.-Y. Chow, and U. J. Paik, *ibid.*, **80**, 3528 (1958). <sup>c</sup> R. J. Crawford, A. Mishra, and R. J. Dummel, *ibid.*, **88**, 3959 (1966). <sup>d</sup> J. C. Stickler and W. H. Pirkle, *J. Org. Chem.*, **31**, 3444 (1966). <sup>e</sup> Unpublished results of P. C. Huang.

*trans* derivatives may occur by a unimolecular<sup>30</sup> or bimolecular<sup>31</sup> mechanism. This subject is considered in detail in paper III of this series.<sup>5</sup> Although no close analogy for the interconversion of the isomeric zwitterions (Z and Z') exists, we might cite the rapid isomerization of *cis*-azoxybenzenes into the *trans* isomers as an example.<sup>32</sup>

Our conclusions concerning the mechanism of decomposition of *trans*-phenyldiazene suggest that the decarboxylation to *trans*-phenyldiazene proceeds via the zwitterion Z' and not by way of *cis*-phenyldiazene.<sup>10</sup> It is reasonable that an "unstable" zwitterion (Z') should decompose to a "stable" diazene much more rapidly than a stable zwitterion (Z) would decompose to an "unstable" diazene.

Our studies have demonstrated the facility with which diazenedicarboxylic acids lose carbon dioxide. We have tried to indicate in our discussion some of the complexities in interpreting the results.

## Experimental Section

All melting points and boiling points are uncorrected. All ultraviolet and visible spectra were measured using spectrograde solvents with a Cary Model 14 recording spectrophotometer. The nmr spectra were measured with an A-60 analytical nmr spectrometer (Varian). Infrared spectra were determined on a Perkin-Elmer Infracord. Elementary analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Calculations of rate constants using the method of least squares were performed with the help of a small computer (LOCI-2a, Wang Laboratories, Inc., Tewksbury, Mass.).

(30) D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *J. Am. Chem. Soc.*, **88**, 2775 (1966).

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

(32) D. L. Webb and H. H. Jaffé, *ibid.*, **86**, 2419 (1964).

**Methyl Phenylidiazene-carboxylate.** Methyl phenylhydrazoformate was prepared<sup>33</sup> by condensation of phenylhydrazine with methyl chloroformate in 83% yield. Oxidation of the hydrazo ester was carried out with lead tetraacetate (*cf.* Clement<sup>11</sup>). To a stirred, ice-cooled solution of 5.6 g (0.034 mole) of recrystallized methyl phenylhydrazoformate in 80 ml of methylene chloride in an Erlenmeyer flask was added 16.5 g (0.037 mole) of lead tetraacetate (91% pure) all at once. The red color of the diazene compound appeared immediately. The mixture in the stoppered flask was stirred for 20 min while cooling was maintained. After separation from the solid lead acetate by filtration, the red solution was washed with 1 *N* hydrochloric acid and then with water and dried over anhydrous sodium sulfate. Evaporation of the methylene chloride in a Rinco evaporator left 5.3 g (96% yield) of a red oil. The oil was distilled *in vacuo* under nitrogen, yielding 3.1 g of the product as a red oil, bp 60–61° (0.1 mm) (lit.<sup>12</sup> bp 54° (0.1 mm)). The fore- and after-fractions, 1 g each, contained the same compound in high purity.

*Anal.* Calcd for C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>: C, 58.53; H, 4.91; N, 17.07. Found: C, 58.29; H, 5.10; N, 17.30.

**Methyl *p*-Methoxyphenylidiazene-carboxylate.** Methyl *p*-methoxyphenylidiazene-carboxylate was prepared from *p*-anisidine. *p*-Anisidine (32.0 g, 0.26 mole; Matheson Coleman and Bell) was converted to *p*-methoxyphenylhydrazine after the method of Blaikie and Perkin.<sup>34</sup>

The crude, wet hydrazine was extracted with 1.5 l. of cold ether. The ethereal solution was dried over sodium sulfate and evaporated (temperature kept under 10°) in a Rinco evaporator. Light yellow, shimmering plates separated during evaporation. The process of evaporation was continued until ~16 ml of liquid, now moderately thick and red, was left. The yellow crystals were then filtered on a cold sintered-glass funnel and washed with 4 to 5 ml of cold ether. The yellow crystals weighed 15.2 g (42% yield).

The crude *p*-methoxyphenylhydrazine (15.2 g, 0.11 mole) was dissolved in cold pyridine–water (35:22 ml) to give a red solution. To that solution methyl chloroformate (10 g, 0.106 mole) was added dropwise with cooling and stirring over 20 min. A yellow precipitate was formed. To isolate the product 20 ml of cooled water was added and the precipitate filtered. After shaking the wet precipitate with 150 ml of ether, the undissolved, light yellow solid (3.6 g when dry) and the red ether layer were separated from the aqueous layer. The ether layer was then evaporated until 10–12 ml of red liquid remained. Some large colorless crystals formed from the red liquid after it had been kept in the refrigerator for several hours. After filtering, washing with ether, and drying, the crystals (3.0 g) were combined with the undissolved light yellow solid (total weight, 6.6 g, 31% yield).

The combined crude hydrazo ester (6.6 g, 0.034 mole) was oxidized with 16.5 g (0.034 mole) of lead tetraacetate (91% pure) in methylene chloride in the usual manner. The orange reaction solution, after washing with water (four–five times) until no more brown fluffy precipitate (lead compound) was formed on contact with water, was dried over sodium sulfate and evaporated to yield 5.65 g (86% yield) of the diazene-carboxylic ester as a red oil. The crude oil was distilled twice through a short-path still *in vacuo* to yield 2.3 g of pure methyl *p*-methoxyphenylidiazene-carboxylate, bp 108° (0.09 mm). The structure was established by nmr spectra (see Table I).

*Anal.* Calcd for C<sub>9</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>: C, 55.66; H, 5.19; N, 14.43. Found: C, 55.63; H, 5.23; N, 14.64.

Other methyl aryldiazene-carboxylates were prepared by procedures similar to that used for methyl phenylidiazene-carboxylate. These included: methyl *o*-tolylidiazene-carboxylate, bp 69–70° (0.14 mm) (*Anal.* Calcd for C<sub>9</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>: C, 60.66; H, 5.66; N, 15.72. Found: C, 60.87; H, 5.78; N, 15.87); methyl *o*-bromophenylidiazene-carboxylate, mp 43–45° (*Anal.* Calcd for C<sub>8</sub>H<sub>7</sub>N<sub>2</sub>O<sub>2</sub>Br: C, 39.53; H, 2.90; N, 11.53; Br, 32.88. Found: C, 39.47; H, 2.88; N, 11.62; Br, 32.69); methyl *p*-bromophenylidiazene-carboxylate, sublimed, mp 71–72° (lit.<sup>35</sup> 75–76°) methyl *p*-nitrophenylidiazene-carboxylate, mp 86.8–87.6° (lit.<sup>36</sup> 84–85°).

**Kinetics of Base-Catalyzed Hydrolysis of Methyl Phenylidiazene-carboxylate.** The pH measuring unit consisted of two small electrodes (Beckman glass electrode 39024 and reference electrode 39025), a Sargent pH recording adapter (E. H. Sargent & Co.), and a recorder (Honeywell, pen rise time, 2-sec full span). The span

was adjusted to 1 in./0.5 pH unit across the chart paper with standard buffers (Beckman, pH 6.50 and 7.00).

The electrodes were immersed in 50 ml of 0.0020 *N* sodium hydroxide solution maintained at 4° in a 150-ml beaker with an ice-water bath. A stream of nitrogen was admitted through a sintered-glass disk for mixing. Before carrying out the reaction, the recorder was turned on, with a chart speed of 1 in./10 sec. A solution of 50 ml of freshly prepared 0.0020 *M* methyl phenylidiazene-carboxylate in water at 4° was added to the alkaline solution in as short a time as possible (less than 1 sec). The flow of nitrogen was stopped immediately after the addition of the ester solution. The change of pH with time was recorded by the recorder and is shown in Figure 2. The kinetic data obtained from the pH vs. time plot are listed in Table VI from which the second-order rate plot shown in Figure 2 was made.

**Table VI.** Kinetic Readings for Base-Catalyzed Hydrolysis of Methyl Phenylidiazene-carboxylate at 4°

Time, sec	pH <sup>a</sup>	(OH <sup>-</sup> ) × 10 <sup>4</sup> , <i>M</i>	(1 × 10 <sup>-3</sup> )/(OH <sup>-</sup> ), <i>M</i> <sup>-1</sup>
0	11.00	10.00	1.00
4	10.69	4.90	2.04
14	10.42	2.63	3.80
24	10.23	1.70	5.88
34	10.10	1.26	7.94
44	9.99	0.98	10.20

<sup>a</sup> At 25°.

**Product Studies for the Reaction of Methyl Phenylidiazene-carboxylate with Methoxide Ion.** Anhydrous methanol was prepared<sup>36</sup> by distillation from calcium sulfate. To 1 ml of a cold (2°) solution of 0.27 *N* sodium methoxide in methanol in a flask was added five drops of methyl phenylidiazene-carboxylate (0.0764 g, 4.66 × 10<sup>-4</sup> mole). The solution was allowed to reach room temperature in 10 min. The solution was then evaporated at 30° in a closed apparatus which had been evacuated to 0.2 mm. Colorless distillate (0.7 ml) was collected through cooling with liquid nitrogen and was analyzed by vpc. In addition to the solvent peak, benzene and dimethyl carbonate peaks were observed when the distillate was injected on a 5-ft silicone oil column maintained at 160°. The concentration of dimethyl carbonate in the distillate was estimated to be 0.22 ± 0.04 *M* by comparing its peak height to that from the methanolic solution of authentic dimethyl carbonate (0.15 *M*). Incomplete resolution of the dimethyl carbonate peak from those of the other two components in the distillate enlarged the error limits. The concentration of benzene in the distillate was determined to be 0.0978 *M* spectroscopically.

Control experiments had shown that about 5% of dimethyl carbonate and no benzene would be left behind in the residue under the conditions used for isolation of the products. After correction had been made for the incomplete recovery of dimethyl carbonate, yields of dimethyl carbonate and benzene were calculated to be 36 ± 6 and 15 ± 1%, respectively, based on the amount of ester used.

The distillate was also injected on the silicone oil column maintained at room temperature. No trace of dimethyl ether could be detected from the chromatogram of the distillate when compared with that of authentic dimethyl ether (prepared from the reaction of sodium methoxide with methyl iodide in methanol) in methanol.

**Reaction of Methyl Phenylidiazene-carboxylate with Methoxide Ion.** A 8.4 × 10<sup>-2</sup> *M* solution of methyl phenylidiazene-carboxylate in 0.128 *N* methanolic sodium methoxide was prepared by mixing 0.0690 g of the ester with 5 ml of the methoxide ion solution. The ultraviolet and visible spectra of the solution, in a 0.012-mm cell constructed by putting a 0.012-mm Teflon spacer between two quartz plates (Limit Research Corp., demountable cell, type UV 10) and a 1-mm cell, were taken intermittently. The optical density at 4200 Å changed from 1.0 at the beginning of the reaction to 0.73 after 25 min (one half-life) and 0.46 after 15 hr (reaction completed). The π → π\* absorption maximum was shifted to 2812, 2788, and 2750 Å at 11 min, 35 min, and 15 hr after the reaction had started.

(33) A. Heller, *Ann.*, **263**, 279 (1894).

(34) K. G. Blaikie and W. H. Perkin, Jr., *J. Chem. Soc.*, 313 (1924).

(35) G. Longo, *Gazz. Chim. Ital.*, **63**, 463 (1933).

(36) A. Weissburger, Ed., "Technique of Organic Chemistry," Vol. VII, 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1955, p 335.

The pseudo-first-order rate constant,  $k$ , was calculated as  $4 \times 10^{-4} \text{ sec}^{-1}$  from the half-life of the reaction. The second-order rate constant was obtained from that  $k$  by dividing by the concentration of methoxide ion.

**Preparation of Potassium Phenylidiazene-carboxylate.** To a solution of 8 drops ( $\sim 110 \text{ mg}$ ) of methyl phenylidiazene-carboxylate in 10 drops of acetonitrile were added 20 drops of 4  $N$  sodium hydroxide solution. An orange solution of sodium phenylidiazene-carboxylate was formed after shaking the mixture vigorously for a few minutes. To this solution were added 18 drops of 50% potassium hydroxide solution. The orange precipitate of potassium phenylidiazene-carboxylate was separated from the reaction solution by filtration, washed once with 1  $N$  potassium hydroxide solution, and dried in a vacuum desiccator. The precipitate weighed 60 mg when it was dry. The purity of the potassium salt was determined to be 85% from the spectrum of its solution in 1  $N$  sodium hydroxide ( $\epsilon$  9800 at 2830 Å).

**Preparation of Barium Phenylidiazene-carboxylate.** Fifteen drops ( $\sim 210 \text{ mg}$ ,  $1.3 \times 10^{-3}$  mole) of methyl phenylidiazene-carboxylate was shaken with 2 ml of chilled 2  $N$  sodium hydroxide solution until it dissolved. Solid barium nitrate (0.2 g,  $0.75 \times 10^{-3}$  mole) was added to the solution and the mixture was vibrated vigorously for 10 min. After thorough crushing and mixing of the precipitate with the solution, the yellow barium phenylidiazene-carboxylate was separated, washed with 1  $N$  sodium hydroxide solution, and dried. The yield of the barium salt was  $\sim 70\%$ .

**Quantitative Determination of Carbon Dioxide for the Acid Decarboxylation of Barium Phenylidiazene-carboxylate.** The apparatus for determination of carbon dioxide consisted of a 50-ml, three-necked, round-bottomed flask equipped with a nitrogen inlet capillary tube, a dropping funnel, a concentrated sulfuric acid trap, and a train of three U tubes containing Drierite, Ascarite, and Drierite + Ascarite.

After the system had been flushed with nitrogen for 0.5 hr, 20 ml of 1  $N$  sulfuric acid was introduced through the dropping funnel. The system was flushed with nitrogen for another 10 min. The wet barium phenylidiazene-carboxylate, which had been freshly prepared from 210 mg of methyl phenylidiazene-carboxylate, was dissolved in 10 ml of 1  $N$  sodium hydroxide solution; a small amount of undissolved white solid (presumably barium carbonate) was filtered. Through the dropping funnel, 9.8671 g of the  $\text{CO}_2$ -free solution of barium phenylidiazene-carboxylate, which was found to contain  $8.93 \times 10^{-4}$  mole of phenylidiazene-carboxylate anion by spectroscopic means, was introduced to the stirred sulfuric acid in 5 min. After the reaction mixture had been further purged with nitrogen for 30 min, the increase of weight of the  $\text{CO}_2$ -absorbing tube was determined to be  $36.3 \pm 1 \text{ mg}$ . No increase of weight was found on further purging the system with nitrogen. The yield of carbon dioxide was  $93 \pm 3\%$ .

**pH Measurements of Buffers.** The pH of buffers was measured with a glass electrode (type G 200B, Radiometer) and a Calomel electrode with a pH meter (Model pH 4, Radiometer, Copenhagen, Denmark). The pH of the buffers used as media in rate determinations for decarboxylation of phenylidiazene-carboxylate anion was measured consecutively within 2 hr.

Freshly prepared 0.05  $M$  borax solution was used as standard in pH measurements. The buffers were allowed to reach thermal equilibrium with the room temperature of the laboratory ( $25.0^\circ$ ) prior to measurements. The average of three readings for each buffer was taken. Sodium ion corrections were made for buffers with high concentrations of sodium ion. The uncertainty involved in the measurements of pH was  $\pm 0.02$  pH unit.

**Rate Measurements for Decarboxylation of Phenylidiazene-carboxylate Anion.** Rate measurements were made in eight buffers which are listed in Table VII, and the results are listed in Table IV. The procedures used for the measurements are presented in detail in the following sections.

**A. Start of Reaction.** The apparatus for rate measurements of decarboxylation is shown in Figure 7. In a typical run, 33 ml of buffer was transferred to flask A with a 50-ml hypodermic syringe. The apparatus was then connected through the high-vacuum stopcock to a straight three-way stopcock with its two arms connected to an argon tank (Matheson, purity 99.998% minimum) and an oil pump, respectively. After flask A had been flushed with argon five times by connecting it with the oil pump and argon source alternately through the stopcocks (while the buffer was being cooled by a Dry Ice-acetone bath), the buffer was degassed three times by repeating the cycle of freezing, evacuating, filling with argon, evacuating, and melting. Control experiments showed that loss of weight from degassing was negligible (0.02 g).

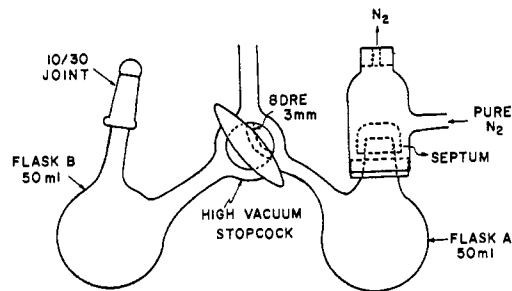


Figure 7. Apparatus for study of kinetics of decarboxylation of phenylidiazene-carboxylate anion.

Flask B, into which 0.250 ml of methyl phenylidiazene-carboxylate in acetonitrile ( $2.0 \times 10^{-2} M$ ) had been introduced, was evacuated with the oil pump for 2.5 min to remove acetonitrile while it was cooled with an ice-water bath. The ester was then degassed three times in the same manner as the buffer solution.

After flasks A and B had reached thermal equilibrium in a thermostated  $25^\circ$  bath, the ester was mixed with the buffer by pouring all the buffer into flask B while the contents of flask B was being swirled. The solution was finally poured back to flask A. The mixing process took  $\sim 80$  sec. Flask A was then connected to the argon source. The time at which the buffer first reached the ester was taken as  $t_0$  for the reaction.

Table VII. Composition<sup>a</sup> of Buffers<sup>b</sup> at  $25^\circ$

Expt <sup>c</sup>	Buffer			
	$\text{Na}_2\text{CO}_3$	$\text{NaHCO}_3$	$\text{Na}_3\text{PO}_4$	$\text{Na}_2\text{HPO}_4$
1 <sup>d</sup>	0.0564	0.0165		
2			0.00819	0.0472
3			0.00135	0.0369
4 <sup>d</sup>	0.0633			
5, 6			0.617	0.403
7			0.0808	0.126
8			0.0208	0.0229
9			0.0306	0.00652

<sup>a</sup> Concentrations are expressed in molarity. <sup>b</sup> Buffers were prepared with distilled,  $\text{CO}_2$ -free water unless specified otherwise. <sup>c</sup> See Table IV. <sup>d</sup> Buffers were prepared with distilled water not  $\text{CO}_2$  free.

**B. Sampling.** Aliquot sampling was performed with a 5-ml hypodermic syringe whose plunger had been coated with a thin layer of Apiezon grease to ensure air tightness. To eliminate the air in the needle, the hypodermic syringe was flushed with nitrogen passing over the septum (Aloe, St. Louis, Mo.) before piercing the septum. About 3.1 ml of the reaction solution was drawn out each time and immediately quenched by ejecting the liquid into 2.00 ml of 1.5  $N$  sodium hydroxide solution in a 5-ml volumetric flask, with the top of the needle kept under the liquid surface, until the mark was reached. The drawing of sample and the quenching process required 40 and 20 sec, respectively. The time 10 sec after quenching had been started was taken as the time when reaction was stopped. The quenching of the first sample was accomplished, in most cases, 200–400 sec after the reaction had started. Eight to ten aliquots were taken at suitable intervals so that the decreases in concentration of the reactant between successive aliquots were roughly the same. The last sampling was made after the reaction had been completed (between 10 and 20 half-lives).

**C. Analyses of Aliquots.** The quenched solution was extracted with 3.5 ml of *n*-heptane (spectrograde) in a 10-ml volumetric flask by vigorous shaking. After centrifuging, the ultraviolet spectrum of the aqueous solution was taken in a 1-cm cell. The spectra for a typical run are shown in Figure 4.

Modified procedures in treating the quenched reaction solutions were used for the reactions in which concentrated buffer was used as the media. Thus in expt 5 (see Table IV) 1.00 ml of 0.6  $N$  sodium hydroxide solution was added to the just quenched solution to avoid the crystallization of sodium phosphate. In expt 6 (see Table IV) 1.00 ml of the quenched solution was diluted 50-fold with 0.6  $N$  sodium hydroxide solution. Five milliliters of this diluted solution was then extracted with *n*-heptane as above.



