

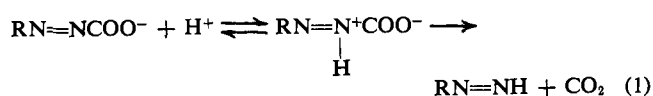
## Diazenes. V. Aryldiazenes

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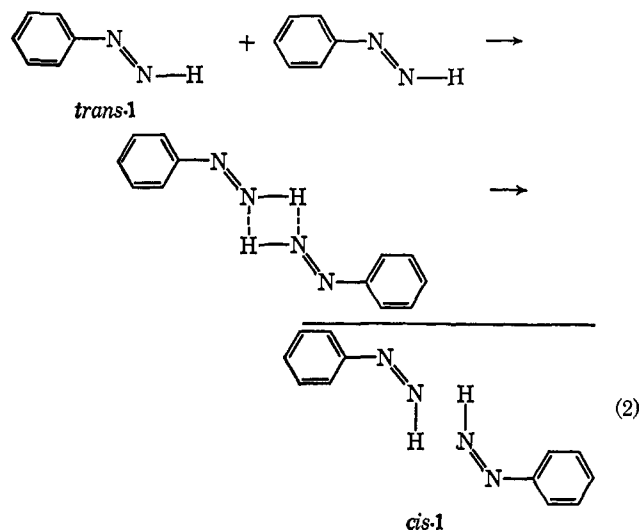
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**Abstract:** New aryldiazenes have been generated from aryldiazene-carboxylic acids by decarboxylation. The aryldiazenes (4-nitrophenyl-, 4-bromophenyl-, 2-bromophenyl-, and 4-methoxyphenyl-) undergo bimolecular decomposition at rates close to that found previously for phenyldiazene ( $k_2$  in  $\text{CH}_3\text{CN}$  at  $25^\circ$ ,  $0.020 \text{ l. mol}^{-1} \text{ sec}^{-1}$ ). The small substituent effect on the bimolecular decomposition ( $\rho < 0.7$ ) is consistent with the proposed rate-limiting step of *trans*-  $\rightarrow$  *cis*-diazene.<sup>1</sup> All aryldiazenes react rapidly with oxygen; however, the rate of the reaction of 4-nitrophenyldiazene with oxygen is slow enough (see text) to be observed. Phenyldiazene reacts rapidly with dithionite ion in water at pH 7.3 but not at all with 1-ethyl-4-carbomethoxy-pyridinyl radical in acetonitrile. The major product of the bimolecular decomposition of aryldiazenes is the corresponding aromatic hydrocarbon (70–79%) except in the case of 4-nitrophenyldiazene, for which the yield of nitrobenzene is only about 30%. The chief product of the bimolecular decomposition of the nitrophenyldiazene has been identified as 4,4'-dinitrohydrazobenzene with the aid of nmr, uv, ir, and mass spectra. The formation of the hydrazine is explained in terms of the previously proposed mechanism.<sup>1</sup>

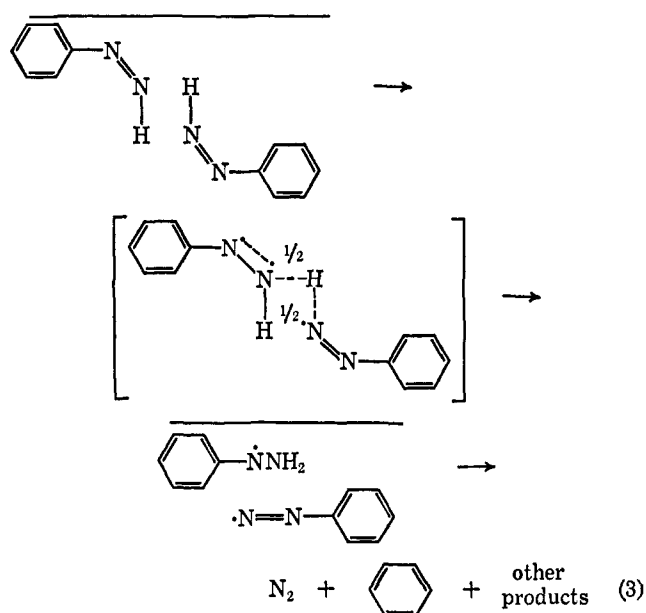
Elusive intermediates no longer, monosubstituted diazenes,  $\text{RN}=\text{NH}$ , may be generated by decarboxylation of the corresponding diazenecarboxylic acids<sup>1</sup> (eq 1). The most interesting property of the monosubstituted diazenes is a bimolecular reaction;



for example, two molecules of phenyldiazene react to form about 80% benzene and nitrogen. The bimolecular reaction is much slower for the deuterated phenyldiazene ( $\text{C}_6\text{H}_5\text{N}=\text{ND}$ ) ( $k_{\text{H}}/k_{\text{D}} \sim 5$ ), exhibits little or no solvent effect, and apparently leads to similar products at low and high initial diazene concentrations. These facts suggest that hydrogen is trans-



ferred in the rate-limiting step, that radicals are involved, and that the products are largely determined within a solvent cage. These conclusions and some additional considerations regarding interconversion of *cis*- and *trans*-diazenes and the accessibility of  ${}^3n, \pi^*$  states of diazenes<sup>1</sup> lead us to a mechanism in which the initial *trans*-monosubstituted diazene is converted into a *cis*-diazene, followed by formation of a pair of radical reaction partners<sup>4</sup> through a twisted triplet transition state (eq 2 and 3).



In order to probe further into the nature of the bimolecular reaction, we have investigated the bimolecular decomposition of a series of substituted aryldiazenes, 4-methoxyphenyldiazene (2), 4-bromophenyldiazene (3), 2-bromophenyldiazene (4), and 4-nitrophenyldiazene (5). The insensitivity of the rate constant for the bimolecular reaction to substituent changes in the aryl moiety and the nature of the unusual major

(1) The previous articles in this series are parts I–III: P.-k. C. Huang and E. M. Kosower, *J. Am. Chem. Soc.*, **90**, 2354, 2362, 2367 (1968), and part IV: D. Severn and E. M. Kosower, *ibid.*, **91**, 1710 (1969).

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

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(4) E. M. Kosower, "An Introduction to Physical Organic Chemistry," Sec. 2.10, John Wiley and Sons, Inc., New York, N. Y., 1968.

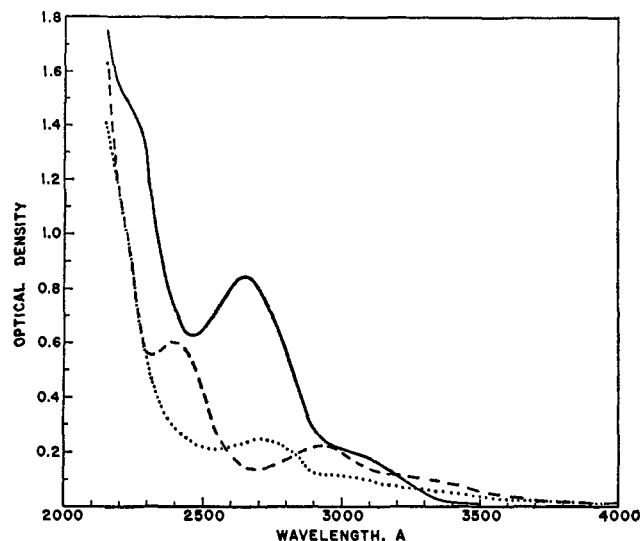


Figure 1. Absorption spectra of 2-bromophenyldiazene (4) — immediately after preparation, - - - - after completion of the bimolecular reaction (4 months), . . . . after exposure of freshly prepared solution to oxygen ( $C_0 = 1.67 \times 10^{-3} M$ ).

product resulting from the decomposition of 5 will be described.

## Results

**Generation of Diazenes.** Diazenecarboxylate esters are readily converted to potassium salts and decarboxylated by means of suitable proton donors, usually amine hydrochlorides, in acetonitrile. We have demonstrated in the case of phenyldiazene<sup>1</sup> that conversion of the carboxylate anion to the salt is quantitative (except for unreacted anion) and we have assumed this to be true for the diazenes described in this paper. Spectroscopic data for the diazenes are summarized in Table I and illustrated for three of the diazenes in Figures 1–3.

Table I. Spectroscopic Properties of Aryldiazenes in Acetonitrile at 25°

Substituent	$\lambda_{\max}, \text{\AA} (\epsilon_{\max})$	
	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$
4-OCH <sub>3</sub> (2)	2280 (9000) 2870 (sh) 2980 (10,300)	... <sup>a</sup>
4-Br (3)	2170 (10,000) 2720 (10,200)	4150 (97)
2-Br (4)	2150 (sh) 2650 (5060)	... <sup>a</sup>
4-NO <sub>2</sub> (5)	2740 (12,300)	... <sup>a</sup>
4-H (1) <sup>b</sup>	2150 (10,400) 2600 (7400)	4175 (~100) <sup>b</sup>

<sup>a</sup> Not determined. <sup>b</sup> Reference 1.

**Bimolecular Disappearance of Diazenes.** Rates of disappearance of the aryldiazenes in acetonitrile solution were followed spectroscopically, yielding the rate constants listed in Table II. At least two initial concentrations of aryldiazene were examined except for the diazene 4.

**Reaction of Diazenes with Oxygen.** A sample of each aryldiazene in acetonitrile solution was exposed to oxygen and ultraviolet and visible spectra were

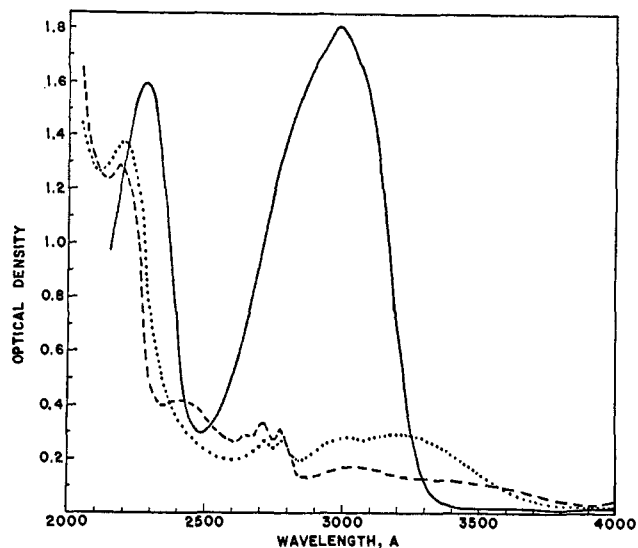


Figure 2. Absorption spectra of 4-methoxyphenyldiazene (2) — immediately after preparation, - - - - after completion of the bimolecular reaction (7 months), . . . . after exposure of freshly prepared solution to oxygen ( $C_0 = 1.83 \times 10^{-3} M$ ).

recorded shortly thereafter. In most cases (2, 3, and 4), the first spectrum taken after reaction with oxygen was identical with all subsequent spectra, demonstrating that complete reaction with oxygen had occurred before the spectrum was recorded (usually less than 30 sec). Compound 5 (4-nitrophenyldiazene) disappeared after mixing with oxygen (concentration of  $5 \times 10^{-3} M$ ) over a period of 200 sec. Several experiments in which the concentration of 5 was monitored at 2850 Å after exposure to oxygen indicated a disappearance rate which increased at the beginning, settled down to

Table II. Rate Data for Bimolecular Disappearance of Aryldiazenes in Acetonitrile at 25°

Substituent	$C_0, M$	$k_2, \text{l. mol}^{-1} \text{sec}^{-1}$
4-OCH <sub>3</sub> (2)	$1.83 \times 10^{-3}$	$5.6 \times 10^{-3}$
	$1.40 \times 10^{-2}$	$7.6 \times 10^{-3}$
4-Br (3)	$0.91 \times 10^{-3}$	$1.09 \times 10^{-2}$
	$1.18 \times 10^{-2}$	$1.27 \times 10^{-2}$
2-Br (4)	$1.67 \times 10^{-3}$	$1.67 \times 10^{-2}$
4-NO <sub>2</sub> (5)	$0.77 \times 10^{-3}$	$2.89 \times 10^{-2}$
	$0.97 \times 10^{-3}$	$2.86 \times 10^{-2}$
	$0.72 \times 10^{-2}$	$2.30 \times 10^{-2}$

an apparently steady rate with zero-order kinetics, and tapered off quickly to a much slower reaction at the end. Complete spectra of the final solutions showed that unstable products continued to change in composition after the diazene 5 had been consumed. To facilitate comparison of the disappearance of diazene caused by oxygen with that due to the bimolecular reaction, the final spectra of three aryldiazene solutions after exposure to oxygen are included in Figures 1–3 and compared with the final spectra obtained for the diazene solutions after completion of the bimolecular reaction as well as the initial spectra.

**Products of Bimolecular Reaction.** Aromatic hydrocarbons are the chief products of the bimolecular reaction of diazenes 2–4. Benzene is formed from phenyldiazene in yields up to 79%, anisole from 2 in 75% yield,

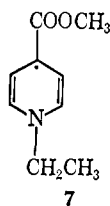
and bromobenzene from the *para* isomer **3** in 71% yield and from the *ortho* isomer **4** in 54% yield. In contrast, nitrobenzene is obtained in only 30–35% yield from **5**, and the major product is a compound with  $\lambda_{\max}$  3680 Å, formed in at least 63% yield.

The major product from the bimolecular decomposition of 4-nitrophenyldiazene was rather difficult to investigate because of apparent instability in the presence of air, but we were able to establish its structure as 4,4'-dinitrohydrazobenzene [1,2-bis(4-nitrophenyl)diazane (**6**)] by means of nmr and mass spectra, comparison with an authentic sample, and oxidation to 4,4'-dinitroazobenzene.



**New Reactions of Diazenes.** Dithionite ion,  $\text{S}_2\text{O}_4^{2-}$ , is a useful reducing agent and is used for the conversion of ferriheme to ferroheme and oxyhemoglobin to deoxyhemoglobin. In connection with our studies of the interaction of phenyldiazene (**1**) with ferroheme and deoxyhemoglobin,<sup>5</sup> we examined the behavior of **1** in the presence of sodium dithionite and can report that rapid loss of **1** occurs in neutral aqueous solution. The spectrum of the product suggests that it might be  $\text{C}_6\text{H}_5\text{NHNHSO}_2^-$  but we have not attempted to confirm this formulation.

The great reactivity of aryldiazenes toward oxygen implied that free radicals might readily react with these compounds. We have been able to demonstrate that the stable free radical, 1-ethyl-4-carbomethoxypyridinyl (**7**),<sup>6</sup> does not catalyze the decomposition of



phenyldiazene.<sup>7</sup> In view of the unreactivity of **7** toward thiols,<sup>8</sup> we can only conclude that “reducing” or donor-free radicals do not abstract hydrogen from phenyldiazene.

## Discussion

The present work extends our knowledge of monosubstituted diazene chemistry. The feeling that high reactivity toward oxygen might be a general property of monosubstituted diazenes is strengthened by our finding that a series of aryldiazenes exhibit such reactivity. The least reactive diazene with respect to oxygen is 4-nitrophenyldiazene; its behavior suggests that 2,4,6-trinitrophenyldiazene might be sufficiently unreactive toward oxygen for a study of the reaction. The “oxygen reaction” is one of the curious and surprising reactions of monosubstituted diazenes; it probably plays a role in oxidation of aryl- and alkylhydrazines through what is often written as  $[\text{RN}=\text{NH}]$ .

(5) P.-k. C. Huang and E. M. Kosower, *Biochim. Biophys. Acta*, **165**, 483 (1968).

(6) See E. M. Kosower and M. Mohammad, *J. Am. Chem. Soc.*, **90**, 3271 (1968), and previous references cited therein.

(7) We thank Dr. M. Mohammad for his help in this experiment.

(8) H. P. Waits, unpublished results.

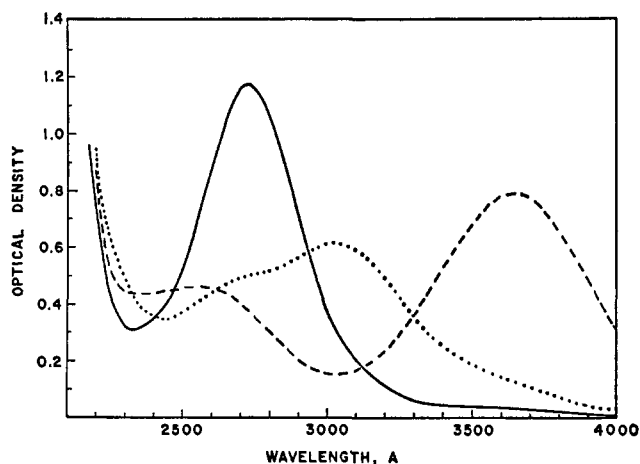
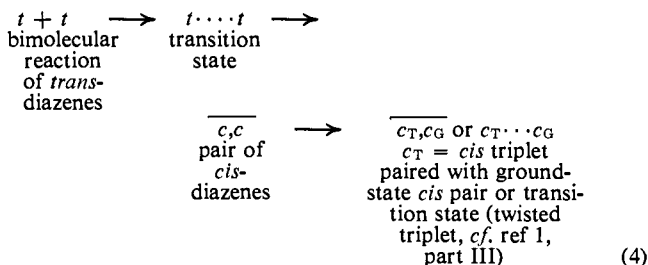


Figure 3. Absorption spectra of 4-nitrophenyldiazene (**5**) — immediately after preparation, ---- after completion of the bimolecular reaction (9 days), . . . . after exposure of freshly prepared solution to oxygen (at least 200 sec were required to obtain a reasonably stable spectrum; see text) ( $C_0 = 0.97 \times 10^{-3} M$ ).

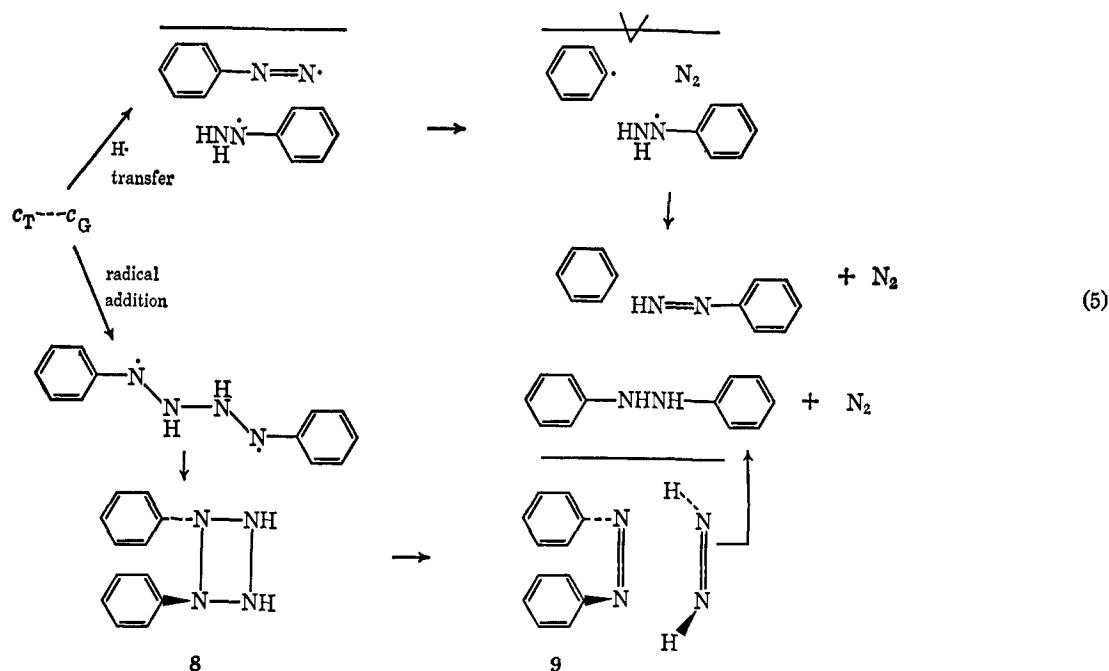
A second surprising reaction of monosubstituted diazenes is the reaction with themselves. The bimolecular disappearance of phenyldiazene has been carefully studied.<sup>1</sup> We have now confirmed that similar reactions occur for a series of aryldiazenes, and that the reaction is almost insensitive to the nature of the substitution on the aromatic ring. The Hammett  $\rho$  value is less than 0.7. The major products of the bimolecular reaction are, in all cases but one, the corresponding aromatic hydrocarbon and small amounts of other compounds with longer wavelength absorption. In the case of 4-nitrophenyldiazene, the principal product is one of the “other compounds” accompanied by a moderate amount of nitrobenzene. We have identified this product as 1,2-bis(4-nitrophenyl)diazane (**6**).

In order to appreciate the significance of **6** as a product of the bimolecular reaction, let us rewrite our proposed mechanism as shown in (eq 4 and 5).



We now ask how the introduction of a nitro group into the 4 position of the phenyl groups of  $c_T, c_G$  might affect the course of the reaction. The effect we seek must occur within the cage since initial concentration has little effect on product composition. Nitro groups are extremely effective for the stabilization of free radicals generated at positions next to a benzene ring, as shown by the example of diphenylpicrylhydrazyl. If the (triplet)  $c_T$  portion of the molecule pair adds to the second diazene rather than abstracting a hydrogen, a 1,4 diradical stabilized at either end would be produced. Such radicals have already been shown to associate through their aromatic  $\pi$  systems,<sup>9</sup> and,

(9) Both 1,3 and 1,4 diradicals have special properties: cf. M. Itoh and E. M. Kosower, *J. Am. Chem. Soc.*, **90**, 1843 (1968).



for this case, a "closed"<sup>9</sup> molecule of this type might well be regarded as the tetraazacyclobutane **8**. The tetraazacyclobutane might decompose in two ways, either to two molecules of starting material or to one molecule of 1,2-bis(4-nitrophenyl)diazene (**9**) and one molecule of diazene (diimide).<sup>10</sup> Since diazene efficiently converts diaryldiazenes into diazanes (hydrazo compounds), the final products isolated would be the diazane and nitrogen. Thus, a simple amplification of our previously proposed mechanism for the bimolecular reaction of diazenes allows us to accommodate the change in product composition caused by the replacement of hydrogen with nitro in the phenyl group (eq 5).

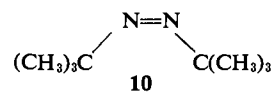
The preferred pathway for the bimolecular reaction of aryldiazenes is H· transfer, as shown by the predominance of hydrocarbon product for the bimolecular reaction of 4-methoxy-, 2-bromo-, 4-bromo-, and unsubstituted phenyldiazenes. Hydrogen transfer leads to a  $\sigma$  and a  $\pi$  radical. If our proposed addition pathway is correct, it follows that the stabilization supplied by a 4-nitro group is sufficient to overcome the energy deficit incurred through the replacement of an N=N bond by an N—N bond to produce two  $\pi$  radicals.

A number of tests of the mechanism might be envisaged (observation of "stable" diradical formation from 2,4,6-trinitrophenyldiazene, effect of deuterium on product distribution (preliminary indications from previous work are in the correct direction<sup>1</sup>), labeling nitrogen next to the ring with N<sup>15</sup>) and might be carried out if circumstances permit.

The low  $\rho$  value found for the bimolecular reaction is consistent with the proposed  $t + t \rightarrow c, c$  conversion as the rate-limiting step, since a four-center reaction involving  $\sigma$  bonds at atoms remote from the ring ought to be insensitive to substitution. The failure of the 2-bromo substituent to affect the rate of the bimolecular reaction also indicates a rate-limiting step involving atoms remote from the ring. (The striking reactivity

of *t*-butyldiazene ( $k_2$  is *ca.* 45 times as great as that for phenyldiazene) indicates that the nature of the bond connecting the R to the diazene group is important.)<sup>11</sup>

We proposed that the  ${}^3n, \pi^*$  state of diazenes would be lowered in energy by some twisting of the ground-state  $\pi$  bond out of a perfectly parallel arrangement.<sup>1</sup> It is of interest, therefore, that *cis*-1,2-bis(*t*-butyl)diazene (**10**) has an  $n \rightarrow \pi^*$  transition at 4470 Å, at much longer wavelengths than the maximum for the *trans* compound at 3675 Å.<sup>12</sup>



We believe that the mechanism outlined in eq 4 and 5 is consistent with the results we have obtained thus far on the properties of monosubstituted diazenes.

### Experimental Section

The esters used to prepare the salts of the aryldiazene carboxylic acids have already been reported.<sup>1</sup> All spectroscopic measurements were made with a Cary Model 14 recording spectrophotometer. All manipulations requiring oxygen-free conditions were carried out with the aid of a vacuum line with normal operating pressure of about  $2 \times 10^{-5}$  mm.<sup>1</sup>

**Generation of Aryldiazenes.** The apparatus shown in Figure 5 of paper II<sup>1</sup> was modified as follows. A flask bearing a vacuum stopcock replaced stopper D, the quartz cell was attached above flask B through two vacuum stopcocks separated by a standard joint, and flask C was removed. These changes permitted several experiments to be carried out on the same preparation of aryldiazene.

For the preparation of 10 ml of  $1 \times 10^{-3}$  M aryldiazene solutions, 2–3 mg of crystalline methyl aryldiazene carboxylate was dissolved in 20  $\mu$ l of acetonitrile (liquids could be added neat) in flask A. Potassium hydroxide solution (1.5 N, 2.0 equiv/equiv of ester) was added and the whole was swirled for 3–4 min. The mixture was evaporated to dryness at room temperature under vacuum. To verify that hydrolysis was complete and to present the salt in a convenient physical form for the next step, 30–40  $\mu$ l of water was added. A clear solution was formed, indicating complete hydrolysis, after which the water was removed under vacuum to leave

(10) The pathway for this reaction can be envisaged as being initiated through a thermal  $n \rightarrow \sigma^*$  transition. The accessibility of  $n, \sigma^*$  states should be remarkably enhanced by the proximity of four filled  $n$  orbitals; *cf.* paper IV in this series.<sup>1</sup> No violation of symmetry limitations is involved.

(11) P.-k. C. Huang and E. M. Kosower, *J. Am. Chem. Soc.*, **89**, 3911 (1967).

(12) We are grateful to Dr. T. Mill, Stanford Research Institute, Menlo Park, Calif., for the information and permission to quote his unpublished results.

the salt as a thin film on the bottom of the flask. This part of the procedure may be carried through in 10 min. Final traces of water were evaporated by pumping on the vacuum line for an additional 7 min. (A tenfold increase in scale did not take much longer and could be used for the preparation of  $1 \times 10^{-2}$  M solutions.) A previously degassed acetonitrile solution (10 ml) of proton source (2.05–2.15 equiv/equiv of ester) (dimethylamine hydrochloride, triethylamine hydrochloride, or imidazole hydrochloride) (in the flask which replaced stopper D) was added to the potassium salt of the aryldiazene-carboxylic acid. The reaction mixture was shaken vigorously for 5 min, following which the yellow aryldiazene solution was filtered from insoluble salts. For kinetic runs, the first spectrum was recorded after the sample solution had reached operating temperature (about 15 min after initial mixing for 25°). The amount of unreacted potassium salt was determined from the spectrum of an alkaline solution of the residual salts, and the molar extinction coefficients of the aryldiazene were based upon the amount of precursor actually consumed.

**Kinetic Measurements of Aryldiazene Disappearance.** The disappearance of aryldiazene was followed by measurements of complete spectra over the region from 4000 to 2000 Å on thermostated samples. Rate constants were derived from optical densities at the maximum for the aryldiazene, with initial concentrations established from the molar extinction coefficients for the aryldiazene (see above). The rate constants were calculated from the slope of a plot of  $1/(D_t - D_\infty)$  vs.  $t$  with the expression

$$k_2 = \text{slope}(D_0 - D_\infty)/C_0$$

**Bimolecular Reaction Products. 4-Methoxyphenyldiazene (2).** Three 50- $\mu$ l aliquots of reaction solution (initial concentration  $1.40 \times 10^{-2}$  M) were injected onto a gc column (Apiezon) and the peaks with the same retention time as anisole were collected and combined. The absorption spectrum of the material was identical with that of anisole ( $\lambda_{\text{max}}$  2770, 2710, 2190 Å); the yield was established on the basis of the spectroscopic absorption coefficients. On long exposure of the reaction solution to air, a broad absorption band at 3460 Å appeared, replacing short-wavelength absorption (below 2600 Å). (4,4'-Dimethoxyazobenzene has an absorption maximum at 3540 Å ( $\epsilon_{\text{max}}$  13,100) in ethanol.<sup>13</sup>)

**4-Bromophenyldiazene (3).** All volatile material was carefully distilled under reduced pressure from a reaction solution of initial concentration  $1.18 \times 10^{-2}$  M by cooling the receiver in liquid nitrogen. The distillate exhibited an ultraviolet spectrum identical with that of bromobenzene ( $\lambda_{\text{max}}$  2110 Å); yield 71%. A broad absorption with  $\lambda_{\text{max}}$  3320 Å appeared in place of one at 2510 Å after the final reaction solution had been exposed to air for 2 days. (4,4'-Dibromoazobenzene has a maximum at 3260 Å ( $\epsilon_{\text{max}}$  24,800) in ethanol.<sup>13</sup>)

**2-Bromophenyldiazene (4).** Distillation of a reaction solution with initial concentration  $1.67 \times 10^{-3}$  M in the manner described for 3 led to a solution with an absorption spectrum identical with that of bromobenzene; yield 54%. A broad absorption with  $\lambda_{\text{max}}$  3220 Å appeared in place of a peak at 2390 Å after the reaction solution had been exposed to air for 4 months.

**4-Nitrophenyldiazene (5).** The bimolecular reaction was allowed to proceed for 11 days with a solution of initial concentration  $0.72 \times 10^{-2}$  M. The final ultraviolet spectrum was very similar to that shown in Figure 3 as "final spectrum." A portion was removed and exposed to air, and the volatile material was removed as described for 3, except that an extra quantity of acetonitrile was added to the residue and the distillation procedure was repeated

to ensure complete removal of nitrobenzene. A spectrum of the distilled solution corresponded to that of nitrobenzene ( $\lambda_{\text{max}}$  2610 Å ( $\epsilon_{\text{max}}$  8350)); yield 30%. The residue from the distillation was chromatographed on thin layer silica gel using chloroform-pentane (3:1) as developer. Eight spots were found. The total combined absorptivity of all these samples after extraction from the chromatogram was far less (ca. 20%) than that of the final reaction solution at 3680 Å, indicating that the major component of the final reaction solution had been destroyed by exposure to air. One of the spots gave a sky blue solution,  $\lambda_{\text{max}}$  5900, 4070 Å, in acetonitrile.

A purification procedure which permitted identification of the major product was carried out as follows. A solution of 5 (90 ml,  $\text{CH}_3\text{CN}$ , initial concentration  $2.0 \times 10^{-2}$  M) was allowed to stand until completion of the bimolecular reaction. Volatile material was removed under vacuum and the reddish brown oily residue dissolved in degassed  $\text{CH}_3\text{CN}$ -ether (100 ml, 1:4). The solution was extracted twice with degassed water (anaerobic conditions), the organic layer was separated and dried (sodium sulfate, then magnesium sulfate), the solution was filtered, and the solvent was removed under vacuum. The dark green residue was extracted with a small amount of  $\text{CH}_3\text{CN}$ , and the extract was concentrated and cooled to about  $-5^\circ$ . The brown precipitate which formed was recrystallized from  $\text{CH}_3\text{CN}$  to yield a brown powder (~60 mg, 24%). The uv, nmr, ir, and mass spectra agreed with those of authentic 1,2-bis(4-nitrophenyl)diazene (6). Air oxidation of the diazene yielded the known diazene, 1,2-bis(4-nitrophenyl)diazene (9).

Spectroscopic properties of the hydrazine 6 may be summarized as follows: uv ( $\text{CH}_3\text{CN}$ ),  $\lambda_{\text{max}}$  ( $\epsilon_{\text{max}}$ ) 3675 Å (27,000), 2225 (13,700), 1940 (34,300); nmr with dimethyl sulfoxide- $d_6$  (TMS reference), 9.33 (singlet), 8.12 (doublet), 6.84 ppm (doublet), ( $J = 10$  cps) (areas 1:2:2); nmr with pyridine- $d_5$ , 10.24 (singlet), 8.25 (doublet), 7.12 ppm (doublet) (areas 1:2:2). Addition of small amounts of  $\text{D}_2\text{O}$  to nmr sample solutions caused the disappearance of the singlet peak.

All samples were handled in the absence of oxygen and all spectra were measured on oxygen-free solutions. Pure 6 derived by synthesis is much less sensitive to oxygen and it must be inferred that an impurity present in the product mixture catalyzed the oxidation of the hydrazine.

**Oxygen Reaction.** Approximately 3–4 ml of aryldiazene solution  $1 \times 10^{-3}$  M in  $\text{CH}_3\text{CN}$  was exposed to oxygen by pouring the solution into a beaker and swirling the contents, then examined in a 1-mm quartz cell after transfer from the beaker. The change in optical density at the wavelength of maximum absorption was followed beginning 14–18 sec after initial exposure to air.

**Reaction of Phenyldiazene (1) with Dithionite Ion.** Phenyldiazene ( $1.1 \times 10^{-4}$  M in aqueous phosphate buffer, pH 7.34, 10 ml)<sup>1</sup> ( $\lambda_{\text{max}}$  2700 Å,  $D_{\text{max}}$  0.80 in 1-cm cell) was transferred through a stopcock into an evacuated flask containing 0.26 mg (Cahn Electrobalance) of sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ , 85% pure,  $1.3 \times 10^{-3}$  mmol). Within 150 sec, the optical density at the maximum for 1 had dropped to 0.48 and fell further to 0.22 in 700 sec. Reaction was apparently complete after 2500 sec. After exposure to air (which destroyed excess dithionite), the solution had a spectrum with maxima at 2730 Å ( $\epsilon$  2500) and 2250 Å ( $\epsilon$  10,000), with absorption coefficients based on quantitative conversion of 1 to product. These maxima are consistent with absorption expected for an aromatic hydrazine derivative like  $\text{C}_6\text{H}_5\text{NHNHSO}_2^-$ .

**Reaction of Phenyldiazene (1) with 1-Ethyl-4-carbomethoxy-pyridinyl (7).** Phenyldiazene solution (4.2 ml,  $1.6 \times 10^{-4}$  M) in acetonitrile<sup>1</sup> was mixed with an acetonitrile solution of 1 (5.0 ml,  $2.7 \times 10^{-4}$  M).<sup>5</sup> No change in the optical density at 3950 Å, a maximum for 7, was observed over a period of several hours.

(13) P. H. Gore and O. H. Wheeler, *J. Org. Chem.*, **26**, 3295 (1961).