conditions, dry, degassed acetonitrile (4 ml) is introduced into the apparatus by distillation to dissolve the dry salt. The resulting solution is then mixed with acetonitrile (17 ml) containing dimethylamine hydrochloride (0.239 g, 2.93 mmoles) to yield a phenyldiazene solution ($\sim$0.1 *M*).

Reduction of Phenyldiazene with Diazene. Potassium diazenedicarboxylate, a yellow solid (0.436 mg, 2.25×10^{-3} mmole), and 1.218 mg of solid triethylamine hydrochloride (8.9×10^{-3} mmole) were placed in flask A (Figure 6) and the system was evacuated. Phenyldiazene solution (1.27×10^{-4} *M*, 4.6 ml) was introduced through the breakseal. The mixture was shaken in flask A ($\sim$3 hr) until the solid became white; spectra of the supernatant solution were measured intermittently. The spectra are shown in Figure 7. Solvent was evaporated from the reaction solution at room temperature until about 3.0 ml of liquid was left. The spectrum of the residual solution showed absorption maxima at 2420 Å (OD 1.71) and a shoulder at 2900 Å (OD 0.35). The maximum of the high intensity band shifted to 2250 Å (OD 1.15) on the addition of one drop of 70% aqueous perchloric acid to the solution.

In another experiment, 4.7 ml of phenyldiazene solution (OD 1.17) was allowed to react with 1.718 mg of potassium diazenedicarboxylate (8.9×10^{-3} mmole) and 4.860 mg of triethylamine hydrochloride (3.5×10^{-2} mmole). The reaction mixture was shaken continuously (for 45 min) until the yellow solid became white. The spectrum of the reaction solution showed an absorption maximum at 2910 Å (OD 0.270). The absorption below 2470 Å exceeded 2.

Table III. Comparison of Reduction Product of Phenyldiazene with Phenylhydrazine

	Reduction product λ_{max}, Å (OD)	Phenylhydrazine λ_{max}, Å (ϵ_{max})
Free base	2437 (1.378)	2435 (11,020)
	2910 (0.235)	2910 (1820)
$HClO_4$ salt	2259 (1.036)	2256 (9140)
	2727 (0.120)	2730 (948)

After making a correction for the contribution from the high-intensity absorption by extrapolation of the curve for the short-wavelength absorption, the optical density at 2910 was found to be 0.269, which corresponds to 1.48×10^{-4} *M* phenylhydrazine (λ_{max} 2910 Å (ϵ 1820)). Assuming that the reduction was quantitative, the molar extinction coefficient of phenyldiazene was calculated to be 7640.

About 8.5 ml of acetonitrile was distilled into the reaction mixture. The diluted reaction mixture was then evaporated slowly at room temperature (to remove the absorbing volatile impurities) until 3.8 ml of liquid was left. The residue had absorption maxima at 2437 (OD 1.378) and 2910 Å (OD 0.235). The maxima shifted to 2259 (OD 1.036) and 2727 Å (OD 0.12), respectively, after two drops of degassed 7% aqueous perchloric acid was introduced to the residue (see Figure 3). The spectroscopic data are summarized in Table III.

Diazenes. III. Properties of Phenyldiazene[1]

Pih-kuei C. Huang[2a,b] **and Edward M. Kosower**[3,4]

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

Abstract: Phenyldiazene, $C_6H_5N{=}NH$, the first monosubstituted diazene to be observed directly, exhibits unusual chemical properties. The reaction of phenyldiazene with itself is cleanly bimolecular over a concentration range of 650, and its disappearance in this way accounts for the failure to isolate pure phenyldiazene at room temperature. The major products of the bimolecular reaction are benzene (65–80%) and nitrogen (80–84%). Hydrogen transfer is important in the rate-limiting transition state as shown by $k_H/k_D \cong 4$–5. The activation energy for the bimolecular reaction is low ($\sim$9 kcal/mole) and the activation entropy very negative (-23 eu), indicating a highly organized transition state. A mechanism for the bimolecular reaction involving formation of a cage radical pair is suggested. The nitrogens of the diazene group are nonnucleophilic toward methyl chloroformate and benzenesulfonyl chloride, as would be expected for azo compounds. Phenyldiazene is very reactive toward oxygen, reacts with 1,4-benzoquinone, hydroxide ion, and diazene (diimide), and is unreactive toward azobenzene.

Previous work on monosubstituted diazenes (diimides) has suggested the existence of two reaction pathways, one leading to the anion of the substituent (eq 1) and the other producing the radical of the substituent (eq 2).[5,6]

$$\text{precursor} \longrightarrow [RN{=}NH] \longrightarrow [RN{=}N^-] \longrightarrow R^- \qquad (1)$$

$$\text{precursor} \longrightarrow [RN{=}NH] \longrightarrow [RN{=}N\cdot] \longrightarrow R\cdot \qquad (2)$$

Although there is little doubt about the occurrence of a carbanion (**1**) or a radical (**2**) intermediate (or both) in particular cases, great uncertainty about the precise pathways by which the diazene intermediate is converted into carbanions or radicals exists. This uncertainty is underlined by our discovery that phenyldiazene disappears *via* a bimolecular reaction with itself. In addition, phenyldiazene is exceedingly sensitive to oxygen, a circumstance which makes exclusion of radical reactions induced by traces of oxygen even more difficult.

This paper describes our results for some of the reactions of phenyldiazene (**3**), $C_6H_5N{=}NH$, including the bimolecular reaction of phenyldiazene with itself.

Results

We have studied a number of chemical properties of phenyldiazene (**3**). The most extensive series of experiments involve the bimolecular reaction of **3** with itself.

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(1) Article II of this series contains a discussion of nomenclature: P. C. Huang and E. M. Kosower, *J. Am. Chem. Soc.*, **90**, 2362 (1968); paper I: **90**, 2354 (1968).

(2) (a) 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.

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

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

(5) R. W. Hoffmann and G. Guhn, *Ber.*, **100**, 1474 (1967).

(6) S. G. Cohen and J. Nicholson, *J. Org. Chem.*, **30**, 1162 (1965); *cf.* also J. Nicholson and S. G. Cohen, *J. Am. Chem. Soc.*, **88**, 2247 (1966).

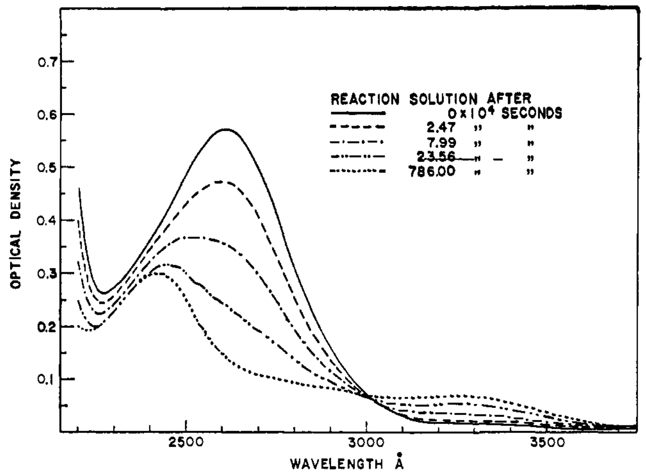

Figure 1. Disappearance of phenyldiazene in acetonitrile at 25°. Initial concentration: 7.74 × 10^{-4} M, observed in a 1-cm cell.

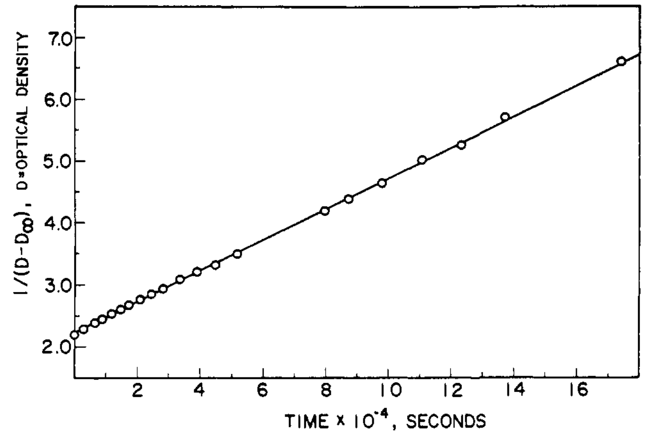

Figure 2. Second-order rate plot for the disappearance of phenyldiazene in acetonitrile at 25°. Initial concentration: 7.74 × 10^{-4} M; kinetics followed at 2610 Å.

Other reactions which have been briefly considered are those with oxidizing agents, reducing agents, and bases. The nucleophilicity of **3** toward several substrates was tested.

The bimolecular disappearance of phenyldiazene prevented its isolation and has thus far precluded investigation of the physical properties of **3** except for those which can be measured for dilute solutions (electronic transitions, vapor pressure).

Bimolecular Reaction. Our early preparations of phenyldiazene in acetonitrile involved the generation of fairly dilute solutions followed by distillation. Attempts to concentrate dilute solutions much beyond 10^{-3} M failed because the rate at which the diazene disappeared increased with concentration. We were able to demonstrate the bimolecular character of the disappearance over a large concentration range by utilizing improved methods for producing high concentrations of phenyldiazene.[1,7]

Rate constants for the disappearance of phenyldiazene in acetonitrile solution at 25° are listed in Table I, and the change in absorption spectrum as the reaction proceeds is illustrated in Figure 1. A plot which demonstrates how well the data conform to expectations

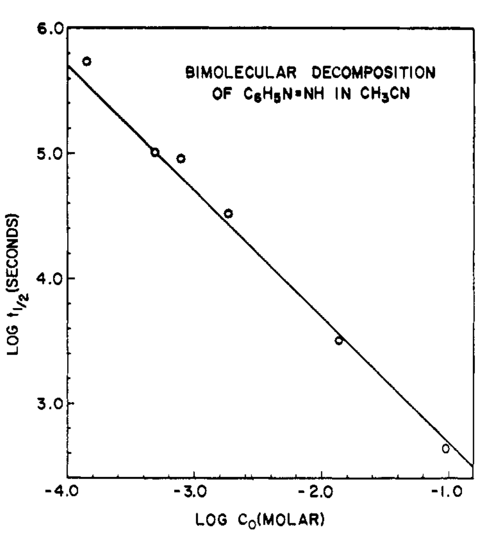

Figure 3. A plot of log $t_{1/2}$ (half-life) against log C_0 (initial concentration) of phenyldiazene in acetonitrile. The straight line is drawn so that the slope is equal to −1. k_2 = antilog (−log C_0 − log $t_{1/2}$) = 0.020 l. mole^{-1} sec^{-1}.

for a second-order reaction is given in Figure 2. Raising the temperature causes a modest increase in rate (corresponding to a small activation energy) but does not change the order of the reaction. Our limited information on reactions at elevated temperature is included in Table I. The character of the reaction of **3** with itself is most clearly demonstrated in a plot of the log of half-lives for the disappearance *vs.* the log of concentration of **3** (Figure 3). The linearity of this plot for a concentration range of 650 establishes the reaction as bimolecular.

Table I. Rate Constants for Bimolecular Disappearance of Phenyldiazene (**3**) and Phenyldiazene-1-*d* (**3**-*d*) in Acetonitrile

C_0, M	Temp, °C	k_2, l. mole^{-1} sec^{-1}	$t_{1/2}$, sec
1.45 × 10^{-4}	25[d]	0.0127	5.43 × 10^{6}
4.84 × 10^{-4}	25[f]	0.0204	1.013 × 10^{5}
7.74 × 10^{-4}	25[d]	0.0146	8.85 × 10^{4}
1.83 × 10^{-3}	25[e]	0.0168	3.25 × 10^{4}
1.35 × 10^{-2}	25[e]	0.0230	3.21 × 10^{3}
9.49 × 10^{-2}	25[g]	0.0248	4.25 × 10^{2}
b	25	0.020[b]	
1.53 × 10^{-4}	40[d]	0.0281[a,c]	4.30 × 10^{6}
	Phenyldiazene-1-*d*		
3.52 × 10^{-4}	25[f]	0.0040	
1.48 × 10^{-3}	25[e]	0.0040	
2.61 × 10^{-2}	25[e]	0.0055	
	$k_H/k_D \cong$ 4–5		

[a] A less accurate experiment at 35° indicated a rate constant of ~0.02 l. mole^{-1} sec^{-1}. [b] Rate constant derived from the plot shown in Figure 3. [c] Corresponds to an activation energy of 8.9 kcal/mole and an entropy of activation of ~ −23 eu (for a standard state of 1 mole/cc). [d] Procedure A for generating **3** (see Experimental Section). [e] Procedure B for generating **3** (see Experimental Section). [f] Procedure C for generating **3** (see Experimental Section). [g] Procedure D for generating **3** (see Experimental Section).

The rate of disappearance of 2-phenyldiazene-1-*d* ($C_6H_5N{=}ND$) is much lower than that of phenyldiazene itself at comparable concentrations, providing unequivocal evidence that hydrogen transfer is associated with the rate-limiting transition state. The isotope effect is imprecise as a result of the problems involved

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(7) P. C. Huang and E. M. Kosower, *J. Am. Chem. Soc.*, **89**, 3910 (1967), contains a preliminary account of the work.

Table II. Products of Bimolecular Reaction of Phenyldiazene[a]

C_0, *M*	Benzene, %	Nitrogen, %	Comments
1.35×10^{-2}	63 ± 10		Spectroscopic changes for product solution after exposure to air indicated 15% yield of hydrazobenzene ($C_6H_5NHNHC_6H_5$) from apparent conversion to azobenzene ($C_6H_5N{=}NC_6H_5$). A 7% yield of the latter was isolated by chromatography.
9.49×10^{-2}	79	~80	
$\sim 2 \times 10^{-1}$	70	82	Hydrazobenzene was isolated from the products immediately after exposure to air. At least nine other compounds were present, including 0.2% diphenyl, on the basis of chromatography.
1.0×10^{-1} (deuterated)	56	>45	$C_6H_5D/(C_6H_5D + C_6H_6) = 73\%$. Product mixture resembled that from the experiment above with at least ten components visible on a thin layer chromatogram.

[a] Generated from a salt and amine hydrochloride in acetonitrile as described in the Experimental Section.

in generating solutions of **3** and **3**-*d* and measuring their rates of disappearance. As illustrated by the rate constants shown in Table I, the k_H/k_D for the bimolecular reaction is between 4 and 5.

The major products of the reaction of **3** with itself are benzene and nitrogen. Some minor products which have been detected are hydrazobenzene and diphenyl. Product data are summarized in Table II. The yield of benzene is apparently diminished in the case of **3**-*d*, and the extent of deuteration is only 73%. Thus, a proportion of the protons acquired in the formation of benzene come either from the solvent, other positions on the benzene ring, or some of the amine derived from the proton source. (Equation 1 describes the process used to form **3**-*d*). Twelve experiments, of the type

$$C_6H_5N{=}NCOO^-K^+ + (C_2H_5)_3ND^+Cl^- \longrightarrow C_6H_5N{=}ND + (C_2H_5)_3N + KCl + CO_2 \quad (3)$$

illustrated in Figure 1, indicate that total light absorption by the reaction solution diminishes considerably as the reaction proceeds, suggesting that all reactions produced large quantities of benzene. (Benzene has a very weak light absorption in the 2500–2700-Å region.) The intensity and shape of the final absorption curve were almost independent of the initial concentration of **3** except for the highest concentration (0.2 *M*), for which an unidentified absorption due to an air-sensitive compound was present at 2700 Å. The latter absorption was noted at intermediate stages in other reactions. The decrease was not so marked (final absorptions were ~45% greater in three experiments) in the case of the deuterated derivative, **3**-*d*, confirming that less benzene arises from **3**-*d* than from **3** itself. The complexity of the product mixture (ten spots were noted in thin layer chromatograms of the products of two runs), the apparent air sensitivity of some of the products, and the relatively small quantities available precluded extensive examination of products of the bimolecular reaction. The bimolecular reaction of phenyldiazene may be written as in eq 4.

$$C_6H_5N{=}NH + C_6H_5N{=}NH \longrightarrow C_6H_6 + N_2 + \text{other products} \quad (4)$$

other products include $C_6H_5NHNHC_6H_5$, $C_6H_5C_6H_5$

Oxidation Reactions. Studies of the decarboxylation of the phenyldiazenecarboxylate ion (paper I of this series[1]) had been made on thoroughly deoxygenated solutions because of the presence of an oxygen-sensitive intermediate. We were able to demonstrate that phenyldiazene was an appropriate choice for that intermediate by finding that phenyldiazene rapidly disappeared upon exposure to air. We were unable to measure any rates for the phenyldiazene and oxygen reaction. Regardless of the initial concentration of **3**, if thorough mixing were ensured, the first spectrum of the solution taken after exposure to oxygen was always the same as the final spectrum. The low intensity of the final spectrum relative to that of the initial **3** as well as some characteristic peaks in the 2600-Å region of the spectrum indicate that benzene is a major product of the oxygen reaction (Figure 4).

Another reaction which might be classed as an oxidation is that of **3** with 1,4-benzoquinone. In preliminary work we have found that phenyldiazene reacts smoothly with the quinone with a stoichiometry of approximately 2:1 **3**:quinone. Thus, for a mixture of 1.2×10^{-4} *M* **3** and equimolar quinone in acetonitrile, spectra indicated that both reactants decreased with time, but about one-half of the original quinone remained unreacted. The spectroscopic changes observed for a reaction solution (1.04×10^{-4} *M* **3** and 0.5×10^{-4} *M* quinone) at room temperature are shown in Figure 5. Under these conditions, the half-life is ~800 sec. The isosbestic point at ~3000 Å indicates that the reaction is a well-defined one. The absorption at 2930 Å may be due to hydroquinone (λ_{max} 2940 Å (ϵ 3500)), corresponding to a yield of 72%. Some additional benzene might have been produced, but no other products are identifiable from the final spectrum.

In dilute acetonitrile solution, the rate of disappearance of **3** was unaffected by equimolar azobenzene.

Reduction Reactions. The reaction of **3** with diazene (HN=NH) produces phenylhydrazine (paper II of this series[1]). Unlike 1-alkylpyridinium ions, phenyldiazene in acetonitrile is unaffected by 3% sodium amalgam.

Reaction with Bases and Acids. Treatment of **3** with 0.1 *N* sodium hydroxide produces benzene in 79 ± 8% yield. The often postulated scheme for the decomposition of diazene intermediates (*e.g.*, in the Wolff–Kishner reaction) is thus confirmed insofar as the pathway for decomposition of the diazene in concerned (eq 5).

$$C_6H_5N{=}NH + OH^- \longrightarrow C_6H_6 + N_2 + H_2O \quad (5)$$

An extensive investigation of the properties of phenyldiazene in aqueous solution was carried out before the examination of acetonitrile solutions. It is virtually certain that the decomposition of **3** in water is, at neutral pH and above, catalyzed by hydroxide ion. The half-life of **3** changes from 1400 sec at pH 9.13 to 80,000 sec at pH 7.34, as would be expected for a reaction de-

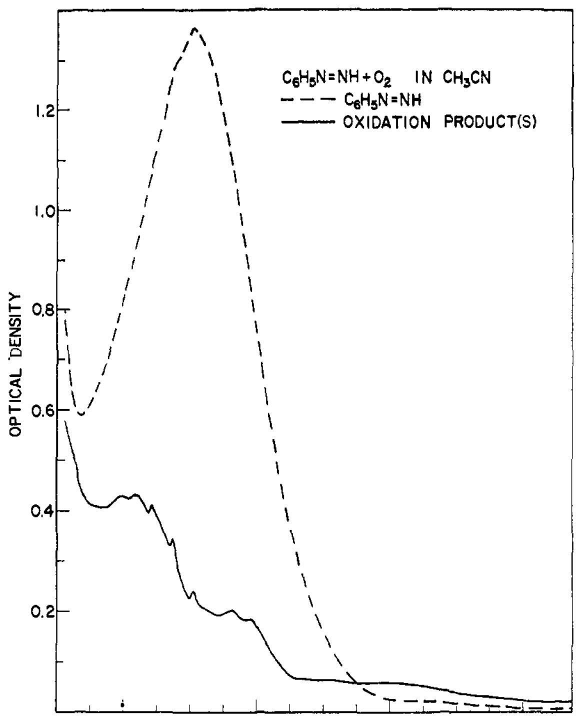


Figure 4. Reaction of phenyldiazene with oxygen in acetonitrile at room temperature. Initial concentration of phenyldiazene: 1.8 × 10^{-4} *M*.

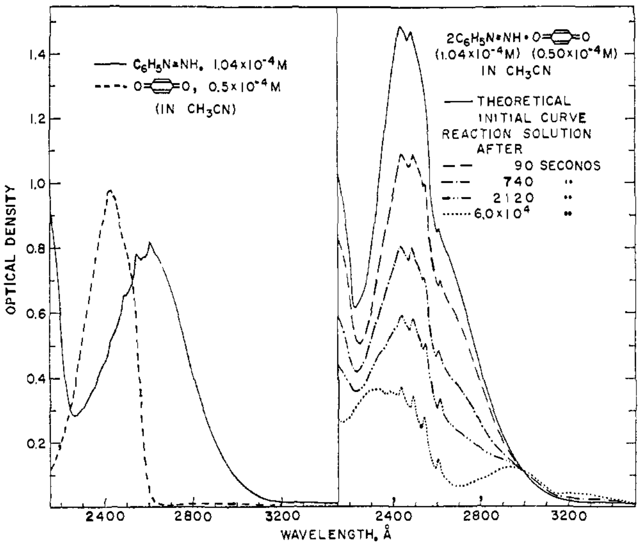


Figure 5. Reaction of phenyldiazene with *p*-benzoquinone in acetonitrile at room temperature. Initial concentrations: phenyldiazene, 1.04 × 10^{-4} *M*; *p*-benzoquinone, 0.50 × 10^{-4} *M*.

pendent upon hydroxide ion (see Figure 1 of paper II[1] for a series of absorption curves depicting the behavior of **3** at pH 7.34).

Acid also catalyzed the disappearance of **3**, the half-life falling to 13,500 sec at pH 3.9 and to 480 sec for 0.01 *N* sulfuric acid. These data are summarized in Table III.

The order of the hydroxide ion catalyzed reaction in water was not easily established. In all runs made in aqueous solution, variable amounts of an initial fast reaction obscured the over-all reaction. We ascribe this somewhat irreproducible phenomenon to traces of oxygen and illustrate it with Figure 6. Although we consider a second-order reaction unlikely on the basis indicated above, our kinetic data could not cover a large range of concentration for a proper demonstration of this conclusion because of the insolubility of most of of the products of phenyldiazene decomposition in water.[8]

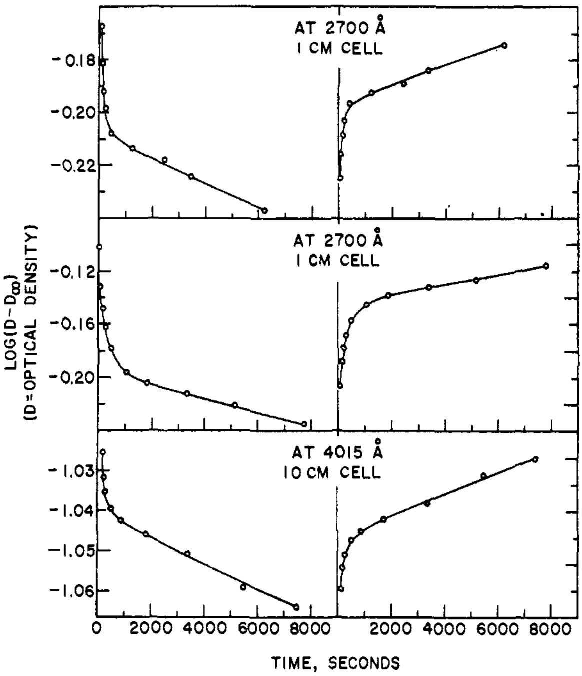


Figure 6. First-order and second-order rate plots for the initial disappearance of phenyldiazene in phosphate buffer, pH 7.34, μ = 0.167, at 25°. Calculated initial concentration (extrapolating back to zero time with inclusion of fast initial reaction; the latter, which varies from case to case, is ascribed to traces of oxygen): (1) 1.24 × 10^{-4} *M*; kinetics followed at 2700 Å; (2) 1.20 × 10^{-4} *M*; kinetics followed at 2700 Å; (3) 0.93 × 10^{-4} *M*; kinetics followed at 4015 Å.

Table III. Stability of Phenyldiazene in Aqueous Solutions at 25°

Expt	Medium	Initial concn × 10^4, *M*	Wave-length,[a] Å	Half-life, sec[f]
1	NaOH, pH 13.8[b]	1	2700	<10
2	Carbonate buffer, pH 9.13[c]	1	2700	1,400
3	Phosphate buffer, pH 7.34[d]	1.3	4015	80,000
4		0.9	4015	70,000
5		1.5	2700	80,000
6		1.2	2700	80,000
7		2.1	2700	52,000
8		1.6	2700	65,000
9	Phosphate buffer,[d] pH 7.34–CH_3CN, 4:1 v/v	2	2680	80,000
10	Acetate buffer,[e] pH 3.9–CH_3CN, 4:1 v/v	1.1	2680	13,500
11	0.01 *N* H_2SO_4–CH_3CN, 4:1 v/v	1.4	2680	480

[a] Reaction followed at the wavelength cited. [b] Na_3PO_4, 0.064 *M*; NaOH, 0.65 *M*. [c] Na_2CO_3, 0.024 *M*; $NaHCO_3$, 0.142 *M*. [d] NaH_2PO_4, 0.0138 *M*; Na_2HPO_4, 0.0513 *M*; μ = 0.167. [e] NaOAc, 0.01 *M*; HOAc, 0.062 *M*. [f] Estimated from first-order plots (linear portion only; see Figure 6).

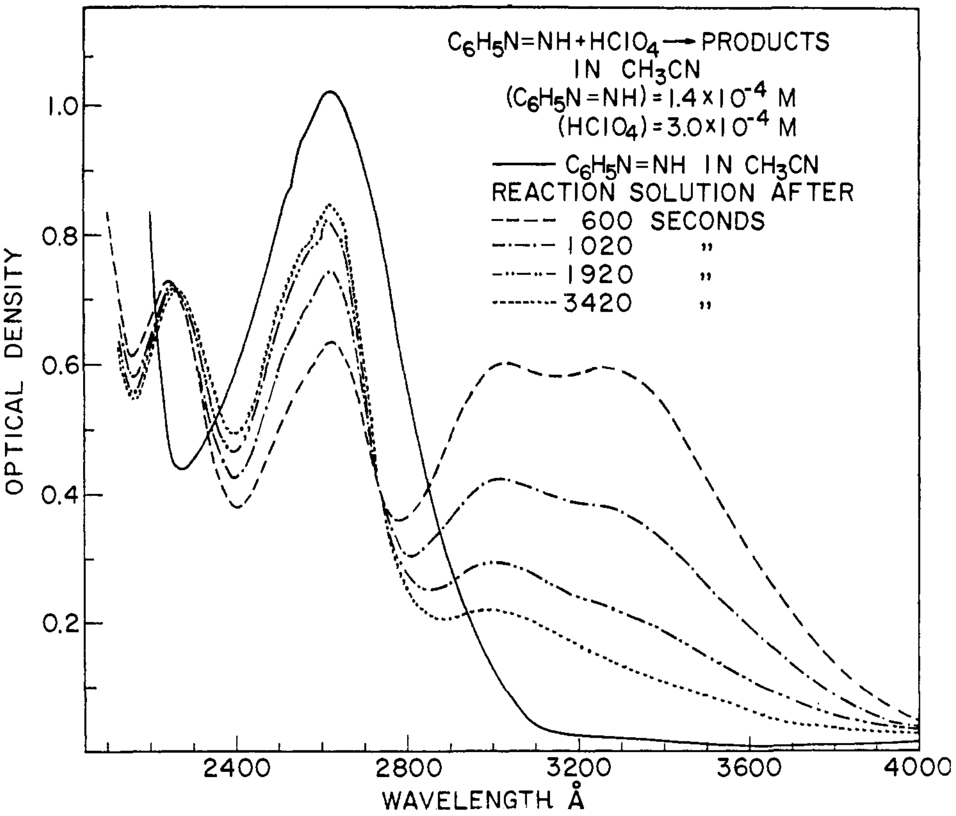


Figure 7. Reaction of phenyldiazene with perchloric acid in acetonitrile at room temperature. Initial concentrations: phenyldiazene, 1.4 $\times 10^{-4}$ *M;* perchloric acid, 3.0 $\times 10^{-4}$ *M.*

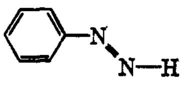
An unusual reaction takes place between **3** and perchloric acid in acetonitrile under oxygen-free conditions (Figure 7). One or more unstable intermediate products are formed very rapidly. It is possible that an oxidation of phenyldiazene has occurred.

In experiments designed to examine the possible nucleophilicity of phenyldiazene toward methyl chloroformate and benzenesulfonyl chloride, triethylamine was added after it was found that the reactions did not proceed. Not only was triethylamine ineffective as a catalyst for the nucleophilic replacements, but it also proved to be completely unreactive toward **3**. (The rate of disappearance of **3** was unchanged by any of these reagents.) This discovery permitted the development of the procedures described in paper II of this series[1] for the generation of **3** using amine hydrochlorides as proton sources.

Physical Properties. At present, the spectroscopic properties reported in paper II[1] are the only definite data on physical properties of phenyldiazene. From the concentration of distilled solutions and the vapor pressure of acetonitrile, we may estimate the vapor pressure of phenyldiazene as about 24 mm at 25°. This compares with the value of 7.5 mm for styrene at the same temperature.[9]

Discussion

The structure assigned to phenyldiazene (**3**) is *trans* on the basis of the low absorption intensity of the longest wavelength absorption band.[10] The accepted assignment for these bands in azo compounds is that of an n → π^* transition. (On the basis of the circular dichroism spectra of optically active azoalkanes[11,12] and theoretical calculations by Robin and coworkers[13] it is possible to narrow the assignment to that of a single electronic transition, $n_+ \rightarrow \pi^*$.)



trans-**3**

Both *cis*- and *trans*-diazenes (diimide) have been detected by infrared measurements on photolyzed matrices of hydrazoic acid in solid nitrogen.[14] No ultraviolet absorption could be found under these conditions past 3000 Å, although Trombetti[15] has noted a weak absorption at 3450 Å thought to be due to diazene in the products of a high-frequency discharge through hydrazine.

Although the *cis* character of the alkene reductions effected by diazene is explicable in terms of the transition state shown in the general eq 6 and it is presumed that *cis*-diazene is the natural precursor of this transition state,[16,17] no evidence has yet been obtained on

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(8) Other monoaryldiazenes undergo bimolecular reaction in acetonitrile at a rate scarcely distinguishable from that of phenyldiazene itself. A monoaryldiazene with an electron-withdrawing group, however decomposes much more rapidly than phenyldiazene in aqueous buffer as would be expected for a hydroxide ion reaction: P. C. Huang, unpublished results.

(9) P. E. Burchfield, *J. Am. Chem. Soc.*, **64**, 2501 (1942).

(10) See paper I of this series.[1]

(11) E. M. Kosower and D. J. Severn, *Tetrahedron Letters*, 3125 (1966).

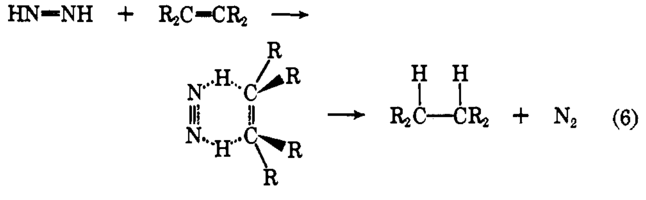
(12) D. J. Severn, unpublished results.

(13) M. B. Robin, R. R. Hart, and N. A. Kuebler, *J. Am. Chem. Soc.*, **89**, 1564 (1967). The originating orbital, n_+, is the antibonding combination of the two nonbonding orbitals on the azo nitrogens.

(14) Kj. Rosengren and G. C. Pimentel, *J. Chem. Phys.*, **43**, 507 (1965).

(15) A. Trombetti, private communication, and Abstracts of the Molecular Spectroscopy Symposium, Columbus, Ohio, Sept 1967.

the geometry of the diazene which participates in this chemical reaction.

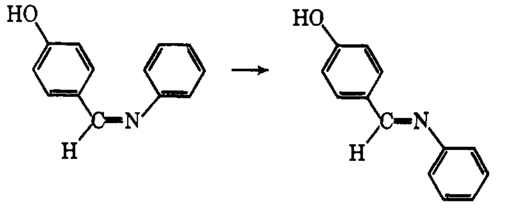


(6)

(presumed transition state)

The possible difference in reactivity of *cis*- and *trans*-diazenes must be considered for the corresponding monosubstituted diazenes, *e.g.*, *cis*-**3** and *trans*-**3**. We must also raise the question (in view of our assignment of the structure of the phenyldiazene which we have observed as *trans*) of the interconversion of the *cis* and *trans* forms of diazene and monosubstituted diazenes.

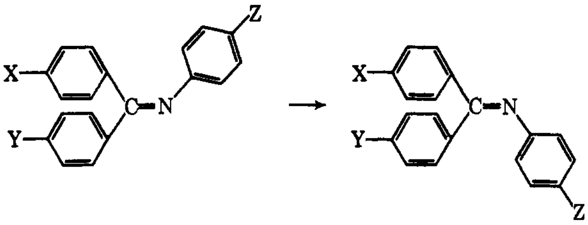
The interconversion of the *cis* and *trans* forms of ketimines varies greatly in rate with the structure of the substrate. The mechanism of the interconversion may be unimolecular[18–20] or bimolecular[21] (eq 7–9).



(7)[19]

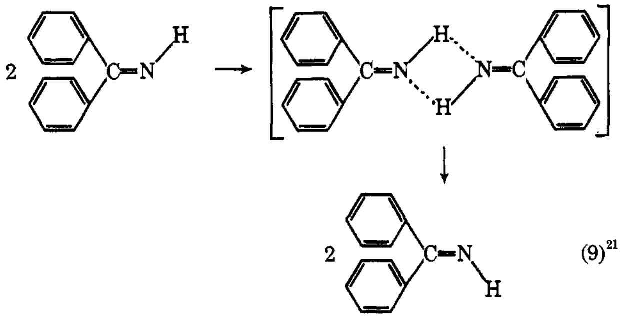
cis *trans*

$k_1^{30°} \sim 7 \times 10^{-1}$ sec^{-1}



(8)[20]

$k_1^{60°} \sim 10^{-1}$ sec^{-1}

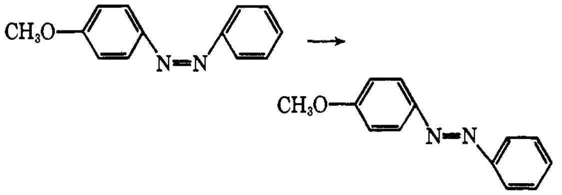


(9)[21]

$k_2^{25°} \sim 10^{3}$ l. mole^{-1} sec^{-1}

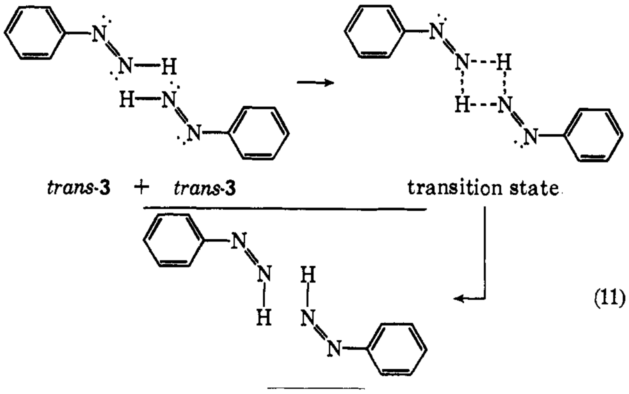
(estimated from data at lower temperatures)

The substitution of a nitrogen for a carbon in the double bond of an aldimine or ketimine diminishes the rate of unimolecular rearrangement by a large factor. Thus, *cis*-4-methoxyazobenzene rearranges to the *trans* compound with a rate constant of about 3 × 10^{-5} sec^{-1} at 40° (eq 10).[22] Depending on whether or not



(10)[22]

the substitution of a nitrogen for a carbon has the same effect or less effect on the rate of the bimolecular rearrangement as on the unimolecular reaction, we may estimate the rate constant for the rearrangement of *trans*-**3** into *cis*-**3** *via* a bimolecular reaction as between 10^{-3} and 10^{-1} l. mole^{-1} sec^{-1}. We assume that the reverse process, *cis*-**3** to *trans*-**3**, if its observation were possible, would be faster by an amount corresponding to the as yet unknown difference in the stabilities of the two isomers. It is striking indeed that the rate constant found for the disappearance of phenyldiazene (**3**) is 2 × 10^{-2} l. mole^{-1} sec^{-1}. This value is well within the range we have estimated for the bimolecular rearrangement of *trans*-**3** to *cis*-**3**, and we shall therefore write this rearrangement as an essential, perhaps the rate-limiting, step in the bimolecular disappearance of phenyldiazene (eq 11).



trans-**3** + *trans*-**3** transition state

(11)

cis-**3**, *cis*-**3**

(line indicates cage pair)[23]

Before we consider the fate of the cage pair of *cis*-phenyldiazenes, let us try to ascertain what kind of a reaction we are studying. The disappearance of phenyldiazene in water is less than ten times as fast as the disappearance of phenyldiazene in acetonitrile. The reaction in water is almost certainly hydroxide ion catalyzed. The bimolecular contribution to the disappearance of **3** in water must then be small and we may conclude that there is little solvent effect on the reaction. Thus, electron transfer or hydride ion transfer, reactions which would proceed through transition states much more polar than the initial states, cannot be the routes by which **3** reacts.

The product composition from the bimolecular disappearance of **3** in acetonitrile does not appear to

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[16] S. Hünig, H. R. Müller, and W. Thier, *Angew. Chem.*, 77, 368 (1965).

[17] C. E. Miller, *J. Chem. Educ.*, **42**, 254 (1965).

[18] D. Y. Curtin and J. W. Hausser, *J. Am. Chem. Soc.*, **83**, 3478 (1961).

[19] D. G. Anderson and G. Wettermark, *ibid.*, **87**, 1433 (1965).

[20] D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *ibid.*, **88**, 2775 (1966); *cf.* also P. H. Ogden and G. V. D. Tiers, *Chem. Commun.*, 527 (1967).

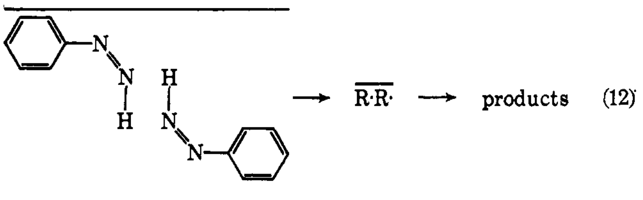
[21] J. B. Lambert, W. L. Oliver, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 5085 (1965).

[22] E. R. Talaty, Ph.D. Thesis, The Ohio State University, 1957; E. R. Talaty and J. C. Fargo, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Abstracts O-203.

[23] E. M. Kosower, "An Introduction to Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1968, Section 2.10.

change very much with the initial concentration of **3**, suggesting that these products are determined by reactions within a solvent cage. The failure of the cage to produce a clean, well-defined set of products suggests a radical reaction, a supposition which is supported by the failure of the reaction of **3**-*d* with itself to give 100% benzene-*d*. The "obvious" choice for a reaction mechanism diradical, $C_6H_5\dot{N}NHNH\dot{N}C_6H_5$, is unequivocally excluded on the basis of the isotope effect as the rate-limiting step and probably excluded as an intermediate after the rate-limiting step because of the absence of evidence for a chain reaction.

We are in this way led to a mechanism (eq 12) in which radicals in a cage are generated from *cis*-phenyldiazene. How can radicals arise from *cis*-**3**?



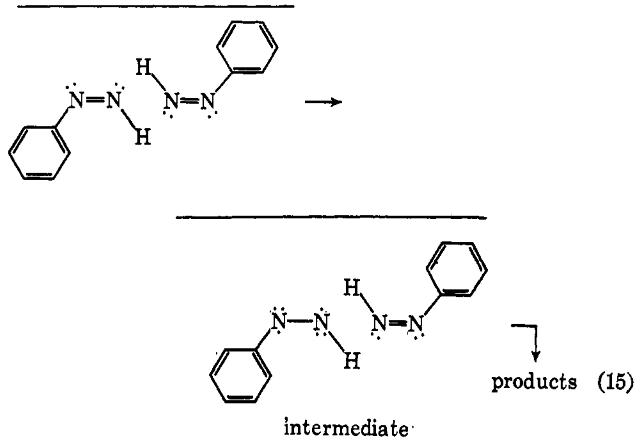
(12)

Although we have not studied the decomposition of *trans*-**3** down to extremely low concentrations, for which unimolecular rearrangement to *cis*-**3** might have been observed, we believe that it is unlikely that unimolecular decomposition of *cis*-**3** should be much faster than that of *trans*-**3**, for which unimolecular decomposition has not been found (eq 13 and 14)

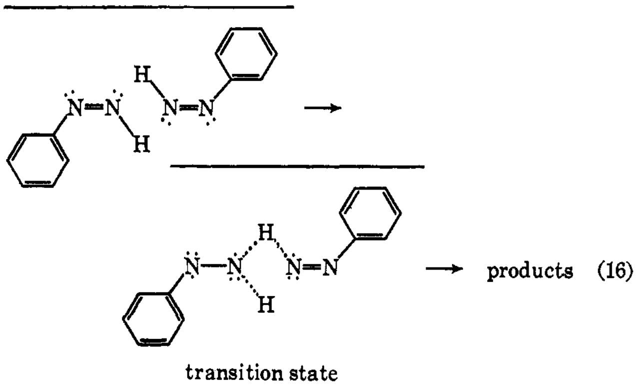
$$C_6H_5N{=}NH \not\rightarrow C_6H_5N{=}N\cdot + H\cdot \quad (13)$$

$$C_6H_5N{=}NH \not\rightarrow C_6H_5\cdot + HN{=}N\cdot \quad (14)$$

We propose that the crucial step in creating radicals from **3** is the conversion of *cis*-**3** to an n,π* triplet or to a transition state for hydrogen transfer in which the triplet contribution to the molecule is significant in permitting the production of radicals. These possibilities are illustrated in eq 15 and 16.



(15)



(16)

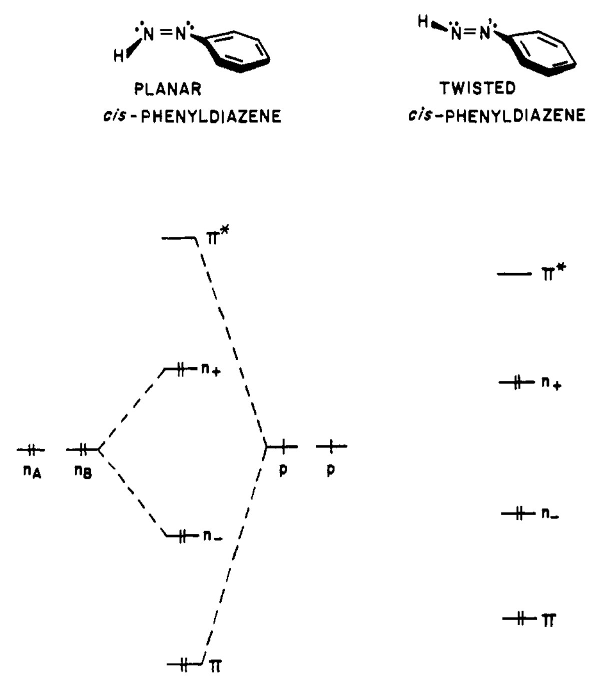


Figure 8. Orbital diagram indicating that twisting the phenyldiazene molecule would lower the π* orbital more than the n_+ orbital, given the assumption that the percentage decrease in overlap is the same for a given angle of twist. Over-all stability declines with increasing angle of twist. It is evident that a twisted triplet might be more stable than a vertical triplet.

Robin and coworkers have calculated the energy required for the $n_+ \rightarrow \pi^*$ triplet transition for *cis*-diazene as 2.07 eV or 47.5 kcal/mole.[13] Assuming that phenyl substitution has the same effect upon the triplet transition as on the singlet $n_+ \rightarrow \pi^*$ transition, we may estimate the $n_+ \rightarrow \pi^*$ triplet transition[24] as 1.30 eV or 30 kcal/mole.

According to the calculations on diazene, and as might be expected, the splitting of the energies of the π and π* orbitals is far greater than the splitting of the orbitals derived by combination of the nonbonding p orbitals. We should thus expect that twisting the NH bond somewhat out of the plane would decrease the overlap but diminish even more the energy of the n,π* triplet with respect to the ground-state energy (Figure 8). We shall assume that this process is sufficient to bring the energy of the n,π* triplet to about 16 kcal/mole above the energy of the *trans*-phenyldiazene, the latter representing the reference state for these estimates. The formation of the triplet would then correspond to eq 15.

Alternatively, the contribution of the triplet to the state of the molecule might be sufficient to aid in the transfer of the hydrogen within the solvent cage from one *cis*-phenyldiazene to the other. The hydrogen

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[24] Diazene has an absorption band, presumably n → π*, at 3450 Å (3.59 eV).[15] Phenyldiazene has an $n_+ \rightarrow \pi^*$ transition at 4175 Å in acetonitrile and 4015 Å in phosphate buffer.[1] We might expect the transition to occur at about 4300 Å in hydrocarbon solvents. A comparison of the absorption maxima for *cis*- and *trans*-azomethanes (see Table V of ref 10) suggests that 4400 Å (2.82 eV) is a fair guess for the position of the singlet $n_+ \rightarrow \pi^*$ transition of *cis*-phenyldiazene.

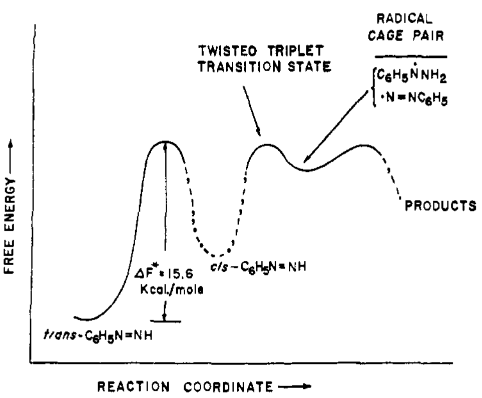
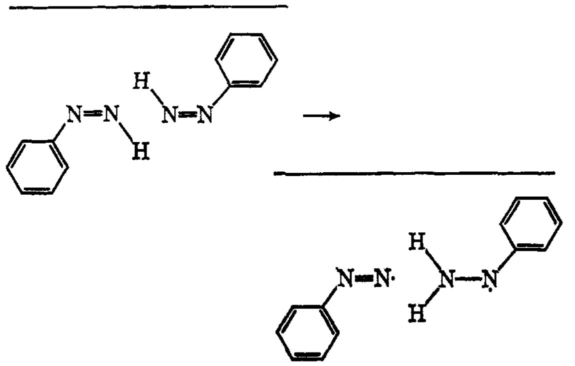


Figure 9. Free energy *vs.* reaction coordinate diagram for the bimolecular reaction of *trans*-phenyldiazene (standard state 1 mole/cc).

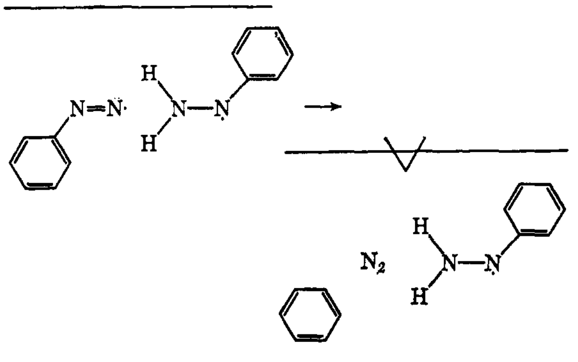
atom transfer would be facilitated by a twisting of the N–H bond of one of the *reaction partners*[23] out of the plane of the system. In the absence of definite information on the *cis*-phenyldiazene triplet we prefer this alternative and can thus write the products of the triplet-stabilized transition state as a phenylazo radical and a phenylhydrazino radical (eq 17).



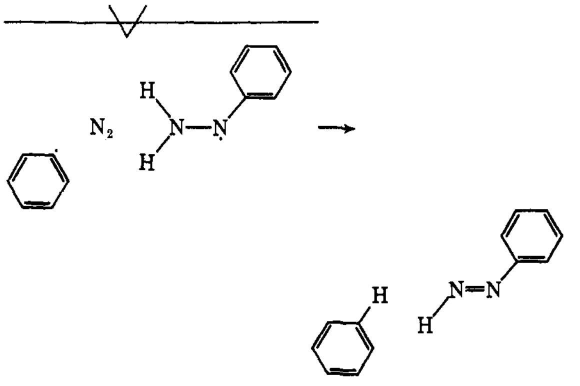
(17)

Neither the phenylhydrazinyl radical nor the phenylazo radical is novel. In fact, the 4-nitrophenylazo radical has been implicated as a reaction partner with the trityl radical within a solvent cage in the decomposition of 4-nitrophenylazotriphenylmethane by Pryor and Smith.[25]

We are now in a position to make some conjectures about the formation of the final products from the reaction partners generated by hydrogen transfer between the pair of *cis*-**3** molecules. Return of the hydrogen from the phenylhydrazino radical to the phenylazo radical can take place in two ways, forming either *cis*-**3** or *trans*-**3**. Dissociation of the phenylazo radical to a phenyl radical and a nitrogen molecule should occur rapidly within the cage, producing the reaction partners, phenylhydrazino radical, phenyl radical, and nitrogen (eq 18). The phenyl radical might abstract hydrogen from the phenylhydrazino radical to produce benzene and either *cis*- or *trans*-phenyldiazene (eq 19). Intracage formation of benzene accounts for the formation of benzene-*d* from **3**-*d*. A small isotope effect upon this reaction (expected because the transition state should resemble the reactants) would cause the yield of benzene to fall in the case of **3**-*d* and increase the yield of other products. We are unable to specify in detail the nature of these other products but might speculate that phenyl radical adds to phenyldiazene to form a 1,2-diphenylhydrazino radical (eq 20). The products from the phenylhydrazino radical are not yet known, although some limited amount of phenylhydrazine formation is not excluded on the basis of the final absorption spectra of reaction mixtures.

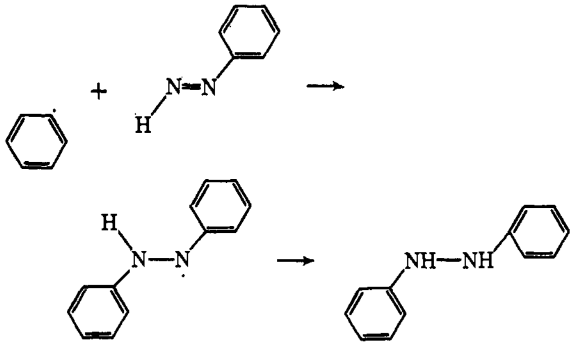


(18)



(19)

trans-**3** (or *cis*-**3**)



(20)

A free-energy *vs.* reaction coordinate diagram (Figure 9) for the bimolecular disappearance of *trans*-phenyldiazene is given for the preferred mechanism: *trans*-**3** → *cis*-**3** → [twisted triplet transition state] → radical cage pair → products. The rate-limiting transition state is shown as the initial *trans* → *cis* rearrangement, a choice supported by the fact that 4-methoxy- and 4-bromophenyldiazenes disappear in a bimolecular reaction at almost the same rate as phenyldiazene.[26]

Acidity of Phenyldiazene. The maximum pK_a for **3** was estimated[10] as 27. Using ammonia as a starting point, a rough calculation of the pK_a, illustrated in Scheme I,[27–30] leads to a value between 19 and 21.

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[25] W. A. Pryor and K. Smith, *J. Am. Chem. Soc.*, **89**, 1741 (1967).

[26] P. C. Huang, unpublished results.

[27] R. P. Bell, "The Proton in Chemistry," Methuen & Co., Ltd., London, 1959, p 88.

Scheme I

Process	ΔpK_a	pK_a
$H_2O + NH_3 \rightleftharpoons NH_2^- + H_3O^+$		35^a
Alkyl substitution ($\rightleftharpoons CH_3NH^-$)	$+1^b$	
Change of hybridization ($\rightleftharpoons CH_2{=}N^-$)	-6^c	
Replacement of CH by N ($\rightleftharpoons HN{=}N^-$)	-6^d	
Replacement of H by C_6H_5 ($\rightleftharpoons C_6H_5N{=}N^-$)	-3 to -5^e	
	$C_6H_5N{=}NH$	19–21

[a] Reference 27. [b] Comparison of pK_a for CH_3CH_3 and that of CH_4 (48 *vs.* 47).[28] [c] Comparison of pK_a for $CH_2{=}CH_2$ and CH_3CH_3.[28] [d] Comparison of the pK_a ($=2.75$) for $4\text{-}ClC_6H_4CH{=}{}^+NHC_6H_5$[28] and that ($-3.47$) for $4\text{-}BrC_6H_4N{=}{}^+NHC_6H_5$.[30] [e] Maximum ΔpK_a derived from a comparison of pK_a for $C_6H_5C{\equiv}CH$ and $HC{\equiv}CH$.[28]

The sensitivity of phenyldiazene toward hydroxide ion even in neutral solution suggests that a pK_a of 19 is reasonable for explaining the rate of disappearance of **3** in water and the solvent isotope effects found by Hoffmann and Guhn (eq 21)

$$\text{in } H_2O \qquad k_{\text{obsd}} \sim 10^{-6}\ \text{sec}^{-1} = k_{3-}K_3 \tag{21}$$

if $K_3 \sim 10^{-19}$, k_{3-} 10^{13} sec^{-1}.

The mechanism for hydroxide ion catalyzed decomposition of **3** is thus

$$C_6H_5N{=}NH \overset{OH^-}{\rightleftharpoons} C_6H_5N{=}N^- \longrightarrow C_6H_5^- + N_2 \longrightarrow C_6H_6 \tag{22}$$

Oxidations. Rapid reaction with oxygen appears to be a characteristic of most of the diazenes we have examined thus far.[26,31] Aldimines are oxidized readily to nitriles in a free-radical chain reaction,[32] and we tentatively propose that oxygen initiates a related set of reactions for phenyldiazene (eq 23–27). Nicholson and Cohen[6] have already shown that phenyl radical can be generated from ferric ion and phenyldiazene.

$$C_6H_5N{=}NH + O_2 \longrightarrow C_6H_5N{=}N\cdot + \cdot O_2H \tag{23}$$

$$C_6H_5N{=}N\cdot \longrightarrow C_6H_5\cdot + N_2 \tag{24}$$

$$C_6H_5\cdot + C_6H_5N{=}NH \longrightarrow C_6H_6 + C_6H_5N{=}N\cdot \tag{25}$$

$$\cdot O_2H + C_6H_5N{=}NH \longrightarrow C_6H_5N{=}N\cdot + H_2O_2 \tag{26}^{33}$$

$$R\cdot + R\cdot \longrightarrow RR \text{ (termination reactions)} \tag{27}$$

Conclusions

Studies of the reactions of monosubstituted diazenes are made difficult by the bimolecular reaction of these compounds with themselves. Nevertheless, diazene and the monosubstituted diazenes occupy a unique niche as important chemical intermediates, and a detailed understanding of their behavior is desirable. If the mechanism proposed for the bimolecular reaction can be confirmed by further work, a rather unusual relationship between the formation of vertical excited state (the n,π^* triplet) and a thermal transition state (the twisted n,π^* triplet) will have been established.

Experimental Section

Phenyldiazene Solutions for Kinetic Measurements. Several variations of the procedures used to generate phenyldiazene have been described.[1] We may classify those used for kinetic measurements as follows. (A) **3** was generated in acetonitrile with acidic ion-exchange resin. Most of the benzene formed as a by-product was removed by distillation. The solution of **3** was distilled and the distillate utilized for kinetic measurements. (B) **3** was generated with an amine hydrochloride. Dimethylamine was removed by distillation and the remainder of the solution of **3** was used. (C) Dilute solutions of **3** were obtained by distillation of more concentrated solutions of **3**. (D) **3** was generated with an amine hydrochloride and tetra-*n*-butylammonium phenyldiazenecarboxylate. (In A, B, and C, the potassium salt of phenyldiazenecarboxylic acid was the source of the phenyldiazene.) In all cases except that using variation D, the solutions of **3** were transferred to a section of the apparatus carrying a quartz cell of suitable path length (0.01, 0.1, or 1 cm), the solution frozen in liquid nitrogen, and the kinetic section sealed off. For variation D, the concentration of **3** produced was high, and the rate of disappearance was too great for many manipulations with the glass. The solution of **3** was transferred to the quartz cell immediately after mixing.

Kinetic Measurements. The disappearance of **3** was followed by measurements of light absorption over the range 4000–2000° ($C_0 < 0.02$ *M*) or 5000–3500 Å ($C_0 > 0.02$ *M*) on thermostated samples. Optical densities were taken for 2600 or 4175 Å, with C_0 established either from the spectroscopic data (ϵ_{2600} 7400) or from the quantity of source material used (*e.g.*, methyl phenyldiazenecarboxylate). The rate constant was evaluated from the slope of a plot of $1/(D_t - D_\infty)$ *vs.* t with the expression: $k_2 = \text{slope}\cdot(D_0 - D_\infty)/C_0$. The slope and intercept were calculated by the method of least squares (using a Wang Laboratories, Inc., LOCI-2A programmable calculator) using experimental points to as much as 80% completion.

Preparation of Solutions of Phenyldiazene-1-*d*. Solutions of phenyldiazene-1-*d* were prepared like those of the protio compound-using $(CH_3)_2ND_2^+Cl^-$ or $(C_2H_5)_3ND^+Cl^-$ as the amine hydro, chlorides (procedure B).

The protio amine hydrochloride (0.4 g) was equilibrated with 2.5 ml of deuterium oxide for 20 min, followed by evaporation of the solution to dryness at room temperature under reduced pressure. The equilibration process was repeated (five times) until no more protons were exchanged as shown by the constancy of the nmr spectrum of the equilibrated amine salt solution. The last equilibration was performed in the reaction apparatus. The part of the reaction apparatus containing the amine salt was separated from the rest of the apparatus by a breakseal.

Potassium deuterioxide, KOD in D_2O, prepared by treating a weighed amount of potassium metal with D_2O in a nitrogen-filled plastic glove bag,[34] was used to hydrolyze methyl phenyldiazenecarboxylate. All transfers were done in the glove bag to minimize contamination by atmospheric moisture.

Products of Bimolecular Decomposition of Phenyldiazene. About 20 ml of 0.2 *M* phenyldiazene solution was prepared from potassium phenyldiazenecarboxylate and triethylamine hydrochloride for product studies. After being kept in the dark at room temperature for 24 hr, the reaction mixture was analyzed.

To determine the nitrogen produced, the reaction solution was removed carefully through a stopcock to an evacuated container until only a very small amount (~0.05 ml) was left, assuring retention of gases. The apparatus which contained the gaseous products was then connected to a manometer through a small trap (cooled with liquid nitrogen) serving the purpose of removing solvent vapor and condensable gases (mainly CO_2). The gases were displaced into the manometer.

The reaction solution was distilled under vacuum to dryness. The distillate was analyzed for benzene by gas chromatography (Packard gas chromatograph, flame detector, 6-ft 20% squalene on a 80–90-mesh Anakrom A column).

The total yield of benzene was determined in the same manner for 20 ml of 0.1 *M* phenyldiazene-1-*d* solution. To determine the C_6H_6/C_6H_5D ratio, about 18 ml of the distillate was extracted with 1.75 ml of CCl_4 in the presence of 21 ml of water. The lower layer, which contained CCl_4, CH_3CN, and benzene, was extracted with 2.6 ml of water eight times to remove the CH_3CN. The final solution, after drying over $MgSO_4$, was put through a gas chroma-

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

(29) E. H. Cordes and W. P. Jencks, *J. Am. Chem. Soc.*, **84**, 835 (1962).

(30) S-J. Yeh and H. H. Jaffé, *ibid.*, **81**, 3274 (1959).

(31) P. C. Huang and E. M. Kosower, *ibid.*, **89**, 3911 (1967).

(32) W. Brackman and P. J. Smit, *Rec. Trav. Chim.*, **82**, 757 (1963).

(33) Hydrogen peroxide does not react with 4-bromophenyldiazene.[26]

(34) Glove bags are polyethylene; supplied by Instrumentation for Industry, Cheltenham, Pa.

tograph (Aerograph, 5-ft 20% Carbowax 20M on a 35–80-mesh Chrom P column). The benzene fraction was collected (~15 mg) and was found to contain 73% C_6H_5D by mass spectrometry.

Isolation of Hydrazobenzene and Diphenyl. Acetonitrile (5 ml) was added to the yellow residue from a (0.2 *M*) phenyldiazene decomposition reaction after distillation to dryness. Thin layer chromatography showed four spots after developing with $CHCl_3$–pentane, 23:19 v/v. The main component (R_f 0.86) was shown to be hydrazobenzene by uv spectrum and formation of benzidine on treatment with 0.1% $HClO_4$ in CH_3CN.

Thick layer chromatography of the solution of the yellow residue gave nine distinct zones after development with $CHCl_3$–pentane, 25:75 v/v. The component with the greatest R_f value (0.63) was colorless and was shown to be diphenyl by its uv spectrum.

Isolation of Azobenzene. The solution from a phenyldiazene decomposition (0.0135*M*) was evaporated to dryness. The residue (in *n*-pentane) was chromatographed on an alumina (acid, Woelm) column (3 mm diameter, 3 cm long). Elution with *n*-pentane saturated with acetonitrile (2 ml) yielded a solution of azobenzene (by uv spectrum).

Reaction with Hydroxide Ion. Distilled phenyldiazene solution in acetonitrile (10.4 ml, (1.97 ± 0.08) × 10^{-4} *M*) was mixed with degassed phosphate buffer (10 ml, pH 7.1, 0.05 *M*) introduced through a breakseal. A spectrum indicated (a) little change in the concentration of **3** and (b) only a trace of benzene. Sodium hydroxide solution (2.5 ml, 1 *M*) was introduced through a second breakseal. Sodium phosphate crystallized as a white solid. A spectrum showed that all of the phenyldiazene had reacted. Benzene was extracted with *n*-pentane (5 ml, two times) after opening to air and adding water (6 ml). The extract was distilled and analyzed by uv spectroscopy. After correcting for incomplete recovery (measured with controls), the yield of benzene was found to be 79 ± 8%.

Reaction with Perchloric Acid. Six milliliters of phenyldiazene solution (1.4 × 10^{-4} *M*) was mixed with 1.5 μl of degassed 70% aqueous perchloric acid (11.8 *N*). Changes in the spectrum of the reaction solution were followed (Figure 7).

Reaction with Benzenesulfonyl Chloride and Methyl Chloroformate. Phenyldiazene solution (1.4 × 10^{-4} *M*, 4.6 ml) was mixed with 0.35 ml of benzenesulfonyl chloride in acetonitrile (1.83 × 10^{-3} *M*). The reaction was followed by spectroscopic means. Degassed triethylamine solution in acetonitrile (5 × 10^{-2} *M*, 0.5 ml) was introduced after 24 hr.

Phenyldiazene solution (1.4 × 10^{-4} *M*, 4.2 ml) was mixed with 0.1 ml of degassed methyl chloroformate solution in acetonitrile (0.59 *M*). After five spectra of the reaction solution had been taken, 5 μl of degassed triethylamine (3.6 × 10^{-2} mmole) was introduced (1 hr after mixing). Other than the normal bimolecular disappearance of **3**, no reaction was observed in either case.

Reaction with Azobenzene. Phenyldiazene solution (1.7 × 10^{-4} *M*, 4.4 ml) was mixed with 0.25 ml of azobenzene solution in acetonitrile (1.34 × 10^{-3} *M*). The reaction was followed for 24 hr. The change in the concentration of **3** was that expected for bimolecular decomposition.

Acknowledgment. The authors are grateful to Dr. Melvin B. Robin, Bell Telephone Laboratories, for some very valuable discussion.

Diels–Alder Reactions of Tetrahalocyclopropenes[1a]

David C. F. Law[1b] and Stephen W. Tobey

Contribution from The Dow Chemical Company, Eastern Research Laboratory, Wayland, Massachusetts 01778. *Received November 20, 1967*

Abstract: Tetrahalocyclopropenes undergo facile 1,4 addition to 1,3-dienes and 2,6 addition to bicyclo[2.2.1]-heptadiene. Certain of the highly strained adducts undergo rearrangement involving stereospecific ionization of labile halide. The relative rate-enhancing effect of halogen substituents in the 3 position on cyclopropene reactivity toward furan is Br > Cl > F. Infrared and H^1 and F^{19} nmr data are reported on all new compounds.

Wiberg and Bartley[2a] have described the high velocity and *endo* stereospecificity of the Diels–Alder reaction between cyclopropene and cyclopentadiene. Battiste[2b] and Closs, *et al.*,[2c] have investigated the reactions of alkyl- and aryl-substituted cyclopropenes with cyclic and open-chain 1,3-dienes and have shown that open-chain dienes react sluggishly, that cyclopropenes monosubstituted in the methylene position give *endo-syn* hydrogen adducts exclusively, and that 3,3-disubstituted cyclopropenes fail totally to form Diels–Alder adducts with *any* diene.[2d] These results have until quite recently[2e] been plausibly ascribed to a strong but unexplained preference for cyclopropene *endo* adduction, along with extreme sensitivity of the *transition state* to the *steric* size of the cyclopropene 3 substituent which must lie *syn* to the diene.[2d]

That such "steric" effects on the transition state *do not* by themselves adequately explain the success or failure of the cyclopropene Diels–Alder reaction is demonstrated by the work reported herein in which we find that *all* tetrahalocyclopropenes[3] undergo facile 1,4 addition to cyclopentadiene, furan, and 1,3-butadiene in spite of the obvious large size of the halogen substituents. Furthermore, competition experiments with furan show clearly that although tetrahalocyclopropenes are less reactive than cyclopropene, tetra*bromo*cyclopropene reacts more readily than tetra*chloro*cyclopropene, and that both these cyclopropenes are more reactive than their counterparts having 3,3-difluoro substituents! Thus, the observed relative rate enhancing effect of halogen substituents in the 3 position on cyclopropene reactivity toward furan is Br > Cl > F, an order directly oppositive to that predicted on steric grounds.

In addition to affecting the rates of Diels–Alder adduct formation, the halogen substituents permit

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[1] (a) Presented at the Symposium International sur la Chimie des Petit Cycles et ses Applications, Louvain, Belgium, Sept 12–15, 1967. (b) Eastern Research Laboratory postdoctoral fellow, 1966–1967.

[2] (a) K. B. Wiberg and W. J. Bartley, *J. Am. Chem. Soc.*, **82**, 6375 (1960); (b) M. A. Battiste, *Tetrahedron Letters*, 3795 (1964); (c) G. L. Closs, L. E. Closs, and W. A. Böll, *J. Am. Chem. Soc.*, **85**, 3796 (1963); (d) G. L. Closs in "Advances in Alicyclic Chemistry," Vol. I, H. Hart and G. J. Karabatsos, Ed., Academic Press Inc., New York, N. Y., 1966, Chapter 2, particularly pp 78–80; (e) W. C. Herndon and L. H. Hall, *Tetrahedron Letters*, 3095 (1967).

[3] (a) S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **88**, 2481 (1966); (b) D. C. F. Law, Ph.D. Thesis, University of Wisconsin, 1967, and Abstracts of Papers, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Paper S52.