Treatment of Data. A first-order rate plot, *i.e.*, log $(D - D_\infty)$ (D denotes optical density at 2830 Å) *vs.* time t, was made for each experiment with all the experimental points except the last one or two. The rate constants were calculated by the method of least squares. The selection of data in this manner was justified since the points used to evaluate the rate constants covered 70–90% of the reaction for all cases. The rate constants are shown in Table IV. The first-order rate plot for a typical run (expt 8) is shown in Figure 5.

The error involved in determination of rate constant of decarboxylation in each buffer is estimated to be ±6%. The uncertainty of the second-order rate constant, therefore, is ±11%, taking into account the uncertainty of ±5% (±0.02 pH unit) involved in determination of the hydrogen ion concentration.

Diazenes. II. Preparation of Phenyldiazene

Pih-kuei C. Huang[1,2] 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: The preparation of phenyldiazene (phenyldiimide), $C_6H_5N{=}NH$ (**3**), by decarboxylation of phenyldiazenecarboxylate anion, $C_6H_5N{=}NCOO^-$ (**2**), is described. All work was carried out in oxygen-free systems because of the sensitivity of **3** to oxygen. The proof of structure of **3** depends upon (1) method of generation, (2) ultraviolet–visible spectra (very similar to that of $C_6H_5N{=}NCH_3$), (3) reduction to phenylhydrazine, and (4) volatility. Phenyldiazene is the first monosubstituted diazene to be directly observed and characterized.

Monosubstituted diazenes (RN=NH) have been postulated as intermediates in many reactions, among which are the preparation of aromatic aldehydes from acyl benzenesulfonylhydrazides,[5] reductive deamination of aliphatic amines,[6] the reduction of ketones with hydrazine,[7] and the oxidation of monosubstituted hydrazines to hydrocarbons.[8] Earliest recognition of the possibility of an aryldiazene as an unstable intermediate was made by Widman[9] for the conversion of 2,4,6-tribromophenyldiazenecarboxylic acid anion into 1,3,5-tribromobenzene upon treatment with acid. Chattaway[10] later explained the formation of benzene and nitrogen from the oxidation of phenylhydrazine as the result of decomposition of phenyldiazene. The preparation of *p*-bromophenyldiazene, claimed by Goldschmidt[11] to result from oxidation of *p*-bromophenylhydrazine with *p*-benzoquinone in ether at −60°, has not yet been confirmed.

In retrospect, the extreme contrast between the instability of diazene (NH=NH) above 120 K[12–14] and the stability of azobenzene (diphenyldiazene, $C_6H_5N{=}NC_6H_5$) up to 600°[15] might have prompted suspicion about the purported behavior of phenyldiazene, $C_6H_5N{=}NH$. It is furthermore surprising that the alacrity with which monosubstituted diazenes apparently lost nitrogen was not viewed with more interest.

$$[RN{=}NH \longrightarrow RH + N_2]$$

We describe in this paper the generation of phenyldiazene in solution.

Results

Aqueous Solution. The necessity for following the kinetics of decarboxylation of the anion **2** (from **1**) under anaerobic conditions[16] suggested that an oxygen-sensitive intermediate was formed in the decomposition

$$\underset{\mathbf{1}}{C_6H_5N{=}NCOOCH_3} \xrightarrow{OH^-} \underset{\mathbf{2}}{C_6H_5N{=}NCOO^-} \qquad (1)$$

of **2**. The obvious possibility was phenyldiazene (**3**). We therefore devised procedures for providing protons to the anion **2** under anaerobic conditions in an apparatus suitable for spectroscopic measurements on the system.

$$\underset{\mathbf{2}}{C_6H_5N{=}NCOO^-} \xrightarrow{H^+} \underset{\mathbf{3}}{C_6H_5N{=}NH} \qquad (2)$$

The linear relationship between the rate of decarboxylation of **2** and the hydrogen ion concentration permits an estimate of the half-life of **2** under neutral conditions as approximately 0.5 sec.[16] The uv absorption curve for anion **2**, λ_{max} 2830 Å (ε 9800, 1 *N* NaOH), is replaced by a new curve, λ_{max} 2700 Å (ε 7400), upon rapid transfer of an alkaline solution of **2** to a phosphate buffer, pH 7.10. The pH of the solution after mixing is 7.34. The new species is phenyldiazene (**3**) on the basis of (1) method of generation (a proton plus phenyldiazenecarboxylate anion) and (2) comparison of the spectrum with that of 1-methyl-2-phenyldiazene, $C_6H_5N{=}NCH_3$ (**4**). The $n \rightarrow \pi^*$ transition may be observed by the use of long light paths. The close correspondence between the spectra of **3** and **4** is illustrated in Table I.

(1) 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.

(2) 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) J. S. McFayden and T. S. Stevens, *J. Chem. Soc.*, 584 (1936).

(6) A. S. Nickon and A. S. Hill, *J. Am. Chem. Soc.*, **86**, 1152 (1964).

(7) H. H. Szmant and M. N. Roman, *ibid.*, **88**, 4034 (1966) (the "Wolff–Kishner reduction").

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

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

(10) F. D. Chattaway, *J. Chem. Soc.*, 1323 (1907).

(11) S. Goldschmidt, *Ber.*, **46**, 1529 (1913).

(12) D. A. Dows, G. C. Pimentel, and E. J. Whittle, *J. Chem. Phys.*, **23**, 1606 (1955).

(13) E. J. Blau, B. F. Hochheimer, and H. J. Unger, *ibid.*, **34**, 1060 (1961).

(14) Kj. Rosengren and G. C. Pimentel, *ibid.*, **43**, 507 (1965).

(15) A. Claus, *Ber.*, **8**, 37 (1875).

(16) P. C. Huang and E. M. Kosower, *J. Am. Chem. Soc.*, **90**, 2354 (1968).

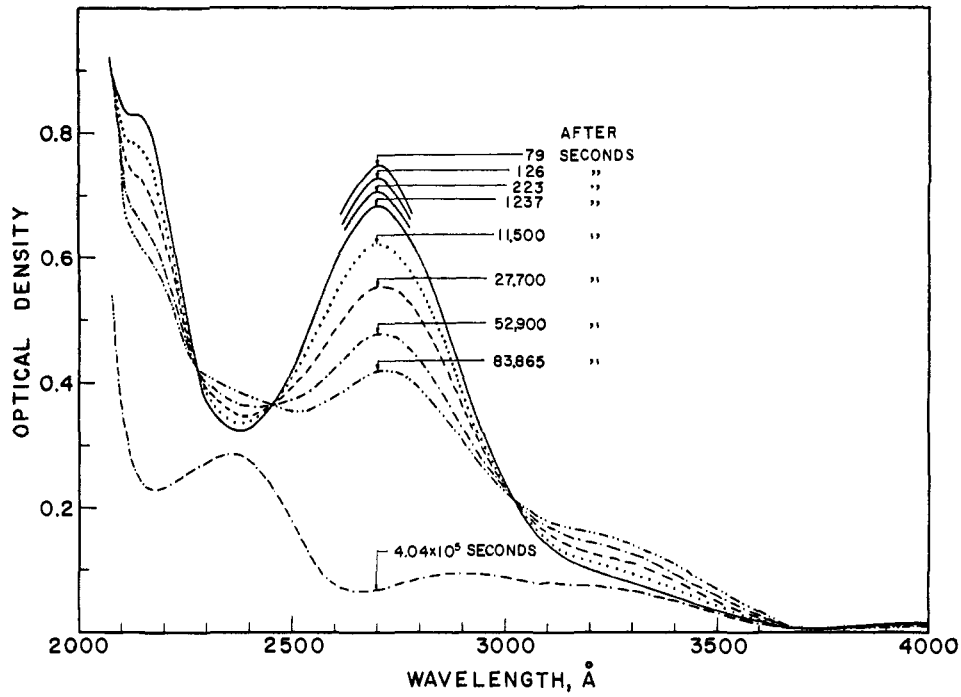


Figure 1. Disappearance of phenyldiazene in phosphate buffer, pH 7.34, μ = 0.167, at 25°. Calculated initial concentration: 1.24×10^{-4} *M* (light path 1 cm).

To our surprise, dilute solutions ($\sim 1 \times 10^{-4}$ *M*) of phenyldiazene in aqueous buffer were moderately stable, the half-life for the disappearance being about 80,000 sec. The course of the disappearance of **3** is illustrated in Figure 1. Both maxima ($\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$) decreased at the same rate and therefore belong to the same species.

Table I. Electronic Transitions of Phenyldiazene (**3**) and 1-Methyl-2-phenyldiazene (**4**)

Compd	Solvent	λ_{max}, Å[a] (ϵ_{max})
3	Acetonitrile	2150 (10,400); 2600 (7400); 4175 (~100)
3	Phosphate buffer[b]–CH_3CN, 4:1 v/v	2130, 2680
3	Phosphate buffer[b]	2140 (10,000); 2700 (7400); 4015 (160)
4	Ethanol	2605[c] (7800)
4	Hexane	3980[d] (120)

[a] ±10 A. [b] pH 7.34, μ = 0.167. [c] P. C. Huang and E. M. Kosower, *J. Am. Chem. Soc.*, **90**, 2367 (1968). [d] E. Haselbach and E. Heilbronner *Helv. Chim. Acta.*, **51**, 16 (1968).

Transfer of the anion **2** to a carbonate buffer, pH 9.13, produced **2** ($\sim 1 \times 10^{-4}$ *M*) which disappeared with a half-life of about 1400 sec, presumably indicating the process in eq 3.[17]

$$C_6H_5N{=}NH + OH^- \longrightarrow [C_6H_5N{=}N]^- \longrightarrow [C_6H_5^-] \longrightarrow C_6H_6 \quad (3)$$

Acetonitrile Solutions. It was deemed likely that the basicity of water contributed to the instability of phenyldiazene in aqueous media. A successful procedure for the preparation of **3** in an anhydrous solvent utilized a carboxylic acid resin, lithium chloride, potassium phenyldiazenecarboxylate, and acetonitrile. After filtration, the phenyldiazene solution was distilled. Benzene and acetonitrile were carefully distilled from the final solution to yield a solution of **3** with a concentration of 1.5×10^{-4} *M*. Solutions with concentrations of **3** up to 10^{-3} *M* could be prepared by this route.

In the course of several experiments designed to evaluate the nucleophilicity of **3**, we discovered that triethylamine had little effect on the stability of **3** in acetonitrile.[18] The use of triethylamine hydrochloride (or another amine hydrochloride) as the proton donor and a tetra-*n*-alkylammonium salt of phenyldiazenecarboxylic acid (eq 4) affords by far the most convenient

$$R_3NH^+Cl^- + C_6H_5N{=}NCOO^- {}^+NR_4' \longrightarrow C_6H_5N{=}NH + R_3N + R_4'N^+Cl^- + CO_2 \quad (4)$$

preparation of monosubstituted diazenes and has been used to prepare solutions as concentrated as 7×10^{-2} *M* phenyldiazene. However, distillation might still be necessary for those experiments in which pure **3** in acetonitrile is desired.

The ultraviolet absorption maxima for **3** appear at shorter wavelengths in acetonitrile than in water. Dilution of the acetonitrile with neutral aqueous buffer (pH 7.34) moves the maxima to positions close to that found for pure aqueous buffer solutions (Table I). A comparison of absorption curves in water and acetonitrile solutions is shown in Figure 2.

Acetonitrile solutions are far more stable than aqueous buffer solutions of the same phenyldiazene concentration (1×10^{-4} *M*). The half-life for the disappearance of **3** at that concentration is about 600,000 sec.

(17) A preliminary account of these experiments was given by E. M. Kosower and P. C. Huang, *J. Am. Chem. Soc.*, 87, 4645 (1965).

(18) Reported by E. M. Kosower and P. C. Huang, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract S-53.

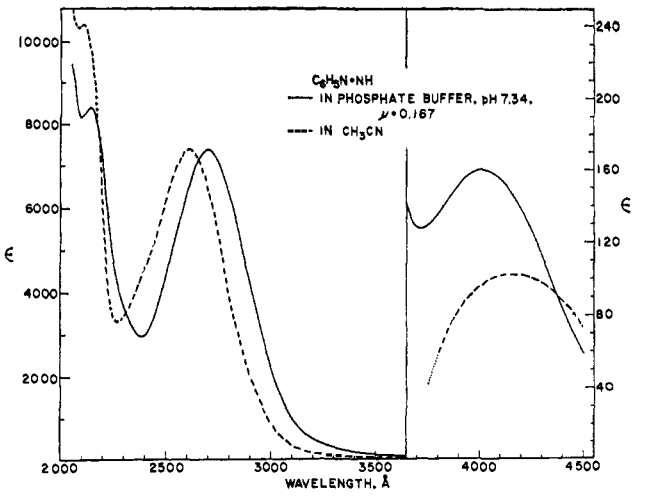


Figure 2. Ultraviolet and visible spectra of phenyldiazene in acetonitrile and in phosphate buffer, pH 7.34, $\mu = 0.167$. The ultraviolet spectrum in phosphate buffer was taken 2500 sec after phenyldiazene had been generated; the visible spectrum was measured within 220 sec after formation. The visible absorption curve in acetonitrile represents an extrapolation to time of mixing.

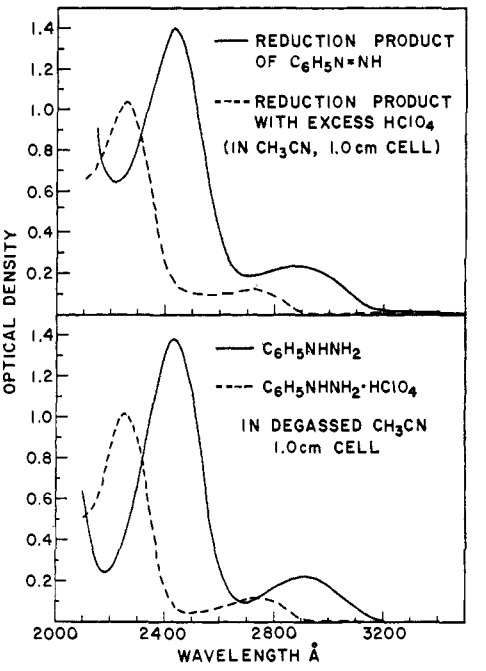


Figure 3. Spectra of phenylhydrazine and the reduction product of phenyldiazene and their perchlorate salts. (1) Reduction product and its perchlorate in the reaction solution with diazene (after removal of absorbing by-product), (2) pure phenylhydrazine and its perchlorate in acetonitrile, in a 1-cm cell.

Reduction. In order to confirm the structure of phenyldiazene, chemical transformation to phenylhydrazine was effected by means of a new diazene-generating system, triethylamine hydrochloride and potassium diazenedicarboxylate (eq 5). (It may be noted that this system is suitable for use in certain anhydrous organic solvents.) The direct formation of phenylhydrazine through reduction of phenyldiazene with diazene was supported by the appearance of isosbestic points in the ultraviolet absorption spectra through which the reaction was followed. The spectrum of the phenylhydrazine formed through reduction was virtually identical with that of authentic phenylhydrazine, and the shift in the absorption spectrum upon addition of acid was the same for the reduction product and the authentic material (Figure 3).

$$2(C_2H_5)_3NH^+Cl^- + K^+\,{}^-OOCN{=}NCOO^-K^+ \longrightarrow 2(C_2H_5)_3N + 2KCl + 2CO_2 + HN{=}NH \quad (5)$$

$$C_6H_5N{=}NH + NH{=}NH \longrightarrow \underset{\mathbf{3}}{C_6H_5NHNH_2} + N_2 \quad (6)$$

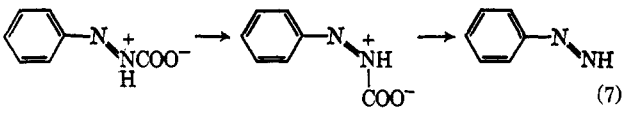
From the known absorption coefficients for phenylhydrazine in acetonitrile, the molar absorption coefficient of **3** was estimated as 7600. (The absorption coefficient in water was at least 7100.) The value of 7400 was adopted as the average absorption coefficient of phenyldiazene. Our present results do not preclude a small solvent effect on the magnitude of the absorption coefficient.

Discussion

Direct examination of a postulated intermediate in a reaction mechanism is always preferred in those cases in which it is possible. Not only can the supposed reactions of the intermediate be evaluated in detail but new and unexpected reactions may be discovered. We shall confirm the validity of this attitude for phenyldiazene in the next paper of this series.[19]

Our interest in phenyldiazene was heightened by its relationship to the active agent (methyl phenyldiazenecarboxylate) in the oxidation of glutathione (a tripeptide thiol) to glutathione disulfide through the generation of free radicals within the red blood cell. The applications of the ester to problems in human genetics[20,21] have been reported elsewhere.

The formation of phenyldiazene through decarboxylation (probably through the zwitterion,[16] eq 7) proceeds with great rapidity even when the proton donor is the



(7)

salt of a strong acid with a base of intermediate strength (triethylamine, dimethylamine, etc.). This circumstance makes practical the preparation of monosubstituted diazenes of less stability than phenyldiazene.[22]

The relative ease with which diazenecarboxylic esters may be prepared from readily available starting materials and the facility with which they may be hydrolyzed to the diazenecarboxylic acid salts suggest that an enormous, new class of reactive compounds, the monosubstituted diazenes, RN=NH, may be generated and studied. Thus far we have not come across any monosubstituted diazenes which may be prepared in pure form at room temperature. However, the methods used for generating these diazenes can certainly be utilized at much lower temperatures, and there seems to be little reason to doubt that certain monosubstituted diazenes may yet be isolated. In addition, the prospect of preparing monosubstituted diazenes which are

(19) See Table I, footnote *c*.

(20) E. R. Rieber, N. S. Kosower, and E. R. Jaffé, *J. Clin. Invest.*, 47, 66 (1968).

(21) N. S. Kosower, G. A. Vanderhoff, and I. M. London, *Blood*, 29, 313 (1967).

(22) *t*-Butyldiazene, for example: P. C. Huang and E. M. Kosower, *J. Am. Chem. Soc.*, 89, 3911 (1967).

Table II. Nomenclature for Dinitrogen Compounds

Formula	Common name	Systematic name
HN=NH	Diimide	Diazene
NH_2NH_2	Hydrazine[a]	Diazane
N≡N	Nitrogen[a]	Diazyne
RN=NH	Alkyldiimide	Alkyldiazene
C_6H_5N=NH	Phenyldiimide	Phenyldiazene
$(CH_3)_2N^+$=N^-	*b*	1,1-Dimethyldiazene
C_6H_5N=NC_6H_5	Azobenzene[a]	Diphenyldiazene
$(CH_3)_2C(CN)N$=$NC(CN)(CH_3)_2$	Azobis(isobutyronitrile)	1,2-Bis(2-cyano-2-propyl)-diazene
C_6H_5N=$NCOO^-K^+$	Potassium phenylazoformate	Potassium phenyldiazenecarboxylate
C_6H_5N=NCN	Phenyldiazocyanide	1-Cyano-2-phenyldiazene
HN=N–	None	Diazenyl group
HN=N·	None	Diazenyl radical
$HN=N^-$	None	Diazenyl anion
$HN=N^+$	Conjugate acid of nitrogen	Diazenyl cation

[a] Preferred on the basis of common usage. [b] *Cf.* W. R. McBride and H. W. Kruse, *J. Am. Chem. Soc.*, **79**, 572 (1957).

stabilized through the use of bulky groups appears inviting, and the knowledge that this type of stabilization has been effective in preparing stable phenoxyl radicals (*e.g.*, 2,4,6-tri-*t*-butylphenoxyl[23]) and stable polyacetylenes (for example, 2,2,17,17-tetramethyl-3,5,7,9,11,13,15-octadecaheptayne[24]) implies that compounds like 2,6-di-*t*-butylphenyldiazene might be stable.

We wish to adopt here and to fortify the nomenclature of polynitrogen compounds as presented by Smith[25] and utilized by Millar and Springall in the latest version of Sidgewick's monograph.[26] Informal acceptance of the polyazane system for dinitrogen compounds will ensure that these compounds can be laid to rest in the literature as carefully as their longer chained brethren. Examples are given in Table II.

The structure of phenyldiazene is based on the following evidence. The method of generation, including the rapid and apparently quantitative conversion of the anion **2** into the diazene **3**, suggests that **3** arises from **2** plus a proton minus carbon dioxide. The two structures which may be written for that stoichiometry are phenyldiazene (**3**) and 1-phenyl-1H-diazene (**5**). We exclude **5** on the basis of the similarity of the n → π^*

C_6H_5N=NH **3** $C_6H_5NH^+$=N^- **5**

and $\pi \rightarrow \pi^*$ transitions of **3** and **4** (1-methyl-2-phenyldiazene). We also believe that the volatility of the product (codistillation with acetonitrile) argues against **5** as the structure. It is, of course, possible that **5** is an intermediate in the formation of **3**. Chemical evidence for the nature of **3** comes from the formation of phenylhydrazine through reduction of **3** with diazene, NH=NH.

The properties of phenyldiazene, including an explanation for our failure to isolate the compound in pure form, are described in the following article of this series.[19]

(23) C. D. Cook, *et al.*, *J. Am. Chem. Soc.*, 78, 2002 (1956); E. Müller and K. Ley, *Ber.*, **88**, 601 (1955).
(24) F. Bohlmann, *ibid.*, **86**, 657 (1953).
(25) P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. 2, W. A. Benjamin, Inc., New York, N. Y., 1966, p 333.
(26) N. V. Sidgewick, "The Organic Chemistry of Nitrogen," revised and rewritten by I. T. Millar and H. D. Springall, Clarendon Press, Oxford, 1966.

Experimental Section

All reactions involving the formation or use of phenyldiazene were carried out in glass apparatus using materials from which oxygen had been removed by degassing through at least three freeze–thaw cycles on a vacuum line, with liquid nitrogen as coolant. (Aqueous solutions and acetonitrile solutions were handled in the same way, although great care must be exercised for the former.) The operating pressure on the line was maintained below 2×10^{-5} mm by a mercury diffusion pump.

Aqueous Solutions. The apparatus used for this purpose is shown in Figure 4. After flushing the apparatus with nitrogen, 5 ml of a buffer (phosphate, pH 7.1, for a final pH of 7.34; carbonate, pH 8.9, for a final pH of 9.13) and 0.050 ml of freshly prepared phenyldiazenecarboxylate anion[16] (0.012–0.02 *M*) in 0.6 *N* sodium hydroxide solution (prepared by dissolving methyl phenyldiazenecarboxylate in the alkaline solution) were introduced into flask A and tube B, respectively, with hypodermic syringes through the constrictions. The apparatus was then sealed off at the constrictions C and D. The aqueous solutions were degassed in about 1.5 hr. Care was taken in melting the solutions to avoid splashing. The rates at which the solutions were frozen and melted were adjusted so that the volume of the solution of phenyldiazenecarboxylate anion remained more or less constant. Constriction F was sealed off after the last degassing.

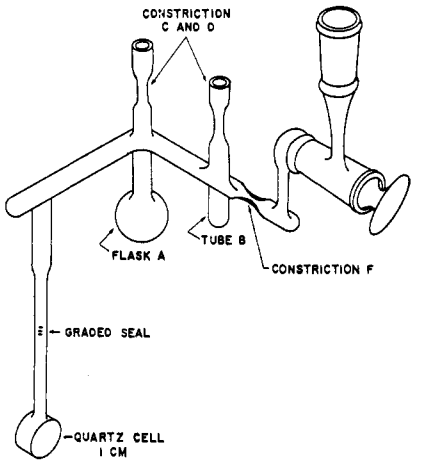


Figure 4. Apparatus for generation of phenyldiazene in aqueous solutions.

After both degassed solutions had been thermostated in a 25° bath for a few minutes, they were mixed quickly by pouring the buffer into tube B. The mixed solution was then poured into the quartz cell. The spectra of the solution were taken while it was thermostated at 25°. The measurement of the first spectrum was

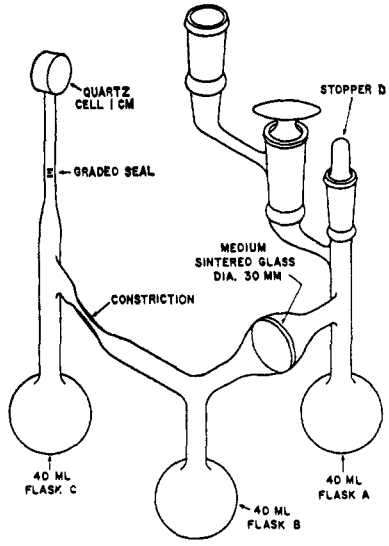


Figure 5. Apparatus for generation of phenyldiazene solutions in acetonitrile.

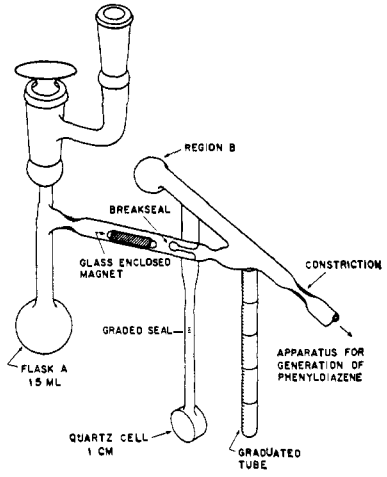


Figure 6. Reaction apparatus A.

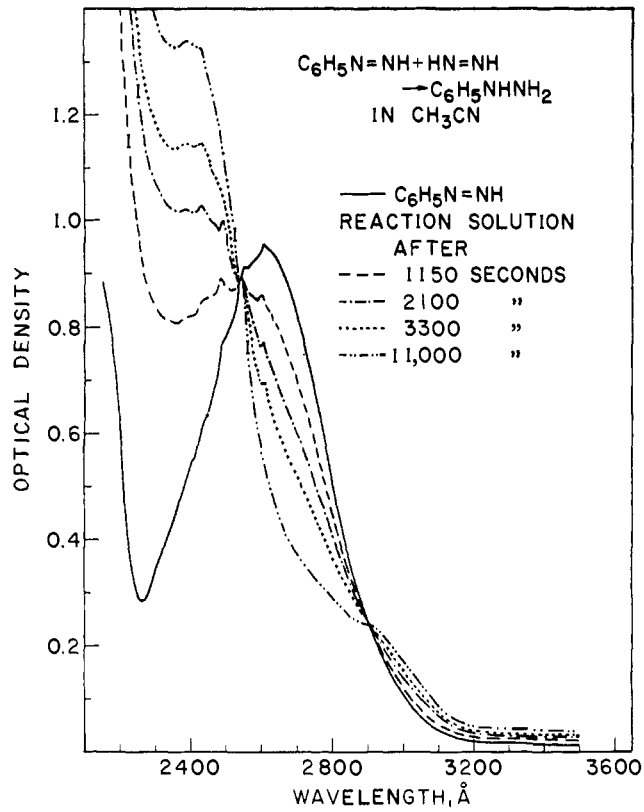


Figure 7. Reaction of phenyldiazene with diazene in acetonitrile at room temperature.

begun within 30–70 sec after mixing. The first few spectra (3000–2500 Å) were taken with fast scan (50 Å/sec) so that the initial changes of the spectra could be observed. Spectra (4000–2000 Å) with normal scan (10 Å/sec) were taken after the reaction had slowed down (~200–500 sec after mixing). The reaction was followed to completion by observation of the $\pi \rightarrow \pi^*$ transition at 2700 Å.

The irreproducibility of the fast initial stages of the reaction (~200–500 sec after mixing) is probably due to the presence of traces of oxygen.

For examination of the low-intensity $n \rightarrow \pi^*$ transition of phenyldiazene ($\sim 1 \times 10^{-4}$ *M*) the apparatus shown in Figure 4 was modified as follows. The 1-cm cell was replaced by a 10-cm cell, a 50-ml flask was used as A, and a 50-ml bulb was placed above the quartz cell to facilitate pouring. The spectra were measured with a slide wire of optical density range 0–0.2.

Some aspects of the rate of disappearance of phenyldiazene in aqueous solutions are taken up in the following article of this series.[19]

Acetonitrile Solutions. Distillation Procedure. The unit in which $\sim 1.5 \times 10^{-4}$ *M* phenyldiazene solutions in acetonitrile were generated is shown in Figure 5. Approximately 20 mg (±1 mg) of potassium phenyldiazenecarboxylate[16] and 20 mg (±1 mg) of lithium chloride (hygroscopic!) were transferred quickly through a long-stemmed funnel into flask A into which 400 mg of previously dried (in a vacuum desiccator), weakly acidic ion-exchange resin (Amberlite IRC-50, Mallinckrodt) and a Teflon-covered magnetic stirring bar had been introduced. The system was evacuated for 15 min for the removal of traces of water. Dry, degassed acetonitrile (15 ml) was distilled into flask A, the mixture was stirred for 15 min at room temperature, then filtered, and the yellow filtrate was collected in flask B which was cooled intermittently to facilitate filtration. The crude phenyldiazene solution in flask B was distilled at room temperature into flask C. Distillation was halted when about 1 ml of liquid remained in flask B.

The faintly yellow distillate which contained $\sim 1.5 \times 10^{-4}$ *M* phenyldiazene along with small amount of benzene ($\sim 1 \times 10^{-4}$ *M*) was satisfactory for carrying out reactions in which the presence of benzene was unimportant. If desired, the removal of benzene, which is more volatile than phenyldiazene, could be effected by slow distillation of a portion of the phenyldiazene solution to flask C.

Amine Hydrochloride Procedure. Phenyldiazene solutions of concentration up to 1×10^{-2} *M* in acetonitrile can be conveniently prepared by using the combination of potassium phenyldiazenecarboxylate and dimethylamine hydrochloride. Methyl phenyldiazenecarboxylate (65 mg, 0.396 mmole) was mixed with potassium hydroxide solutions (1.527 *N*, 0.40 ml) in flask A (see Figure 5) for a few minutes until a homogeneous solution was formed. The solution was then evaporated at room temperature under reduced pressure while flask A was being rotated so that a thin layer of solid potassium salt remained on the bottom. After the system was evacuated on the vacuum line, dry, degassed acetonitrile (30 ml) was distilled into tube A (inserted in place of stopper D) which contained dimethylamine hydrochloride (0.051 g, 0.625 mmole). The amine hydrochloride solution was then shaken with the potassium phenyldiazenecarboxylate for 8 min at room temperature. The resulting yellow solution of phenyldiazene (~0.01 *M*) was separated from a small amount of the unreacted yellow salt by filtration.

Dimethylamine may be removed by cautious distillation of the most volatile material from flask C to flask B followed by freezing and sealing.

In order to prepare phenyldiazene solutions of concentrations greater than 1×10^{-2} *M*, the acetonitrile-soluble tetra-*n*-butylammonium phenyldiazenecarboxylate is required and is prepared by dissolving methyl phenyldiazenecarboxylate (0.333 g, 2.03 mmoles) in tetra-*n*-butylammonium hydroxide solution (1.444 *N*, 2.00 ml) while the mixture is cooled to 18° to minimize decomposition. Essentially dry salt is obtained by evaporation of the solution at room temperature under reduced pressure. Under anaerobic

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 (~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 (~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 (~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]

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

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

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.

(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).