temperature of 80 °C. The NMR spectrum of the distillate showed that THF-*3,4*-d_2 comprised 68% of the sample and that the remainder was mainly 2,5-dihydrofuran.

The mixture of THF-d_2 and 2,5-dihydrofuran (~1.5 mL) was dissolved in 10 mL of octane and 1 mL of pyridine. This mixture was brominated at 0 °C by the dropwise addition of 12 mL of a 20% solution of Br_2 in octane. The THF-d_2 was then separated from the 3,4-dibromotetrahydrofuran by vacuum transfer. Distillation of the THF-d_2 through a 6-in. Vigreux column followed by vacuum distillation from −40 to −196 °C gave a material shown to be pure THF by its NMR spectrum. The NMR showed this THF to be 78% deuterated at the 3,4 positions.

Photolysis of Carbon Suboxide and THF. The appropriate quantities of reagents were vacuum transferred to a 499-mL photolysis flask and irradiated at ambient temperature with Vycor-filtered light from a Hanovia 200-W medium-pressure mercury arc.

After photolysis, the flask was cooled to −196 °C and the carbon monoxide pumped into an activated charcoal trap at −196 °C. The CO was then quantitated by GC on a 12-ft 13X molecular sieves column at room temperature. The remaining products were then pumped through a 2 ft × 0.25 in. column containing 20% $AgNO_3$/ethylene glycol on 40/60 firebrick at 0 °C (this removes THF and C_3O_2) and analyzed for ethylene and cyclobutane by GC on a 20-ft dimethylsulfolane (DMS) column at room temperature.

In runs where cyclopentanone was analyzed, cyclohexanone was added as an internal standard immediately after photolysis. The reaction mixture was passed, under vacuum, into a trap at −115 °C. The material not volatile at this temperature was analyzed by gas chromatography on an SE-30 column. The GC was interfaced with a mass spectrometer and cyclopentanone was identified by comparison of its mass spectrum with that of an authentic sample. Although 3,4-dihydropyran and 4-pentenal could be separated from other products by gas chromatography, neither was detected in the reaction mixture. The 3,4-dihydropyran was found to be stable to photolysis under the conditions of the reaction. The 4-pentenal, however, was photolabile under the reaction conditions and would not have been detected if formed in quantities of less than 2×10^{-3} mmol.

In addition to the experiments summarized in Table I, the effect of pressure on the cyclobutane:ethylene ratio over a range of 0.05-0.1 atm was measured. In this pressure range, the cyclobutane:ethylene ratio was given by eq 5 where $a = 9.3 \times 10^{-3}$ atm and $b = 0.288$.

Photolysis of Carbon Suboxide and THF-*3,4*-d_2. This reaction was carried out as described for the undeuterated compound using 1.22 mmol of THF-*3,4*-d_2 and 4.5×10^{-1} mmol of C_3O_2 in an 8-h photolysis. The fraction containing the ethylene was separated as described above and analyzed by mass spectrometry. The mass spectrum showed a large peak for C_2H_3D at *m/e* 29 but no $C_2H_2D_2$ at *m/e* 30.

Photolysis of Cyclopentanone and THF. This photolysis was carried out under identical conditions with those described for THF and C_3O_2. The ethylene and cyclobutane were analyzed as described above. The results of several experiments are listed in Table I. An investigation of the effect of total pressure over the range 0.05-0.1 atm showed that the cyclobutane:ethylene ratio was given by eq 5 where $a = 6.5 \times 10^{-3}$ atm and $b = 0.376$.

Photolysis of Carbon Suboxide and 3. This photolysis was carried out as described above. Products were distilled from −115 to −196 °C under vacuum. The products volatile at 115 °C were analyzed for ketene and ethylene by IR and for propylene and cyclopropane by GC on a 20-ft DMS column. The material not volatile at −115 °C was analyzed for cyclobutanone by GC-mass spectrometry as described above.

Acknowledgment. Financial support by the National Science Foundation through Grant MPS 75-05405 is gratefully acknowledged.

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A CIDNP Study of the Decomposition of Aryldiazenes

William T. Evanochko and Philip B. Shevlin*

Contribution from the Department of Chemistry, Auburn University, Auburn, Alabama 36830.
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Abstract: Phenyldiazene (**1a**) and *p*-nitrophenyldiazene (**1b**) have been prepared by sodium borohydride reduction of the corresponding aryldiazonium salts, by decarboxylation of aryldiazenecarboxylic acids, and by a new method involving hydride transfer from cycloheptatriene to diazonium ions. The decompositions of **1a** and **1b** are accompanied by nuclear polarization (CIDNP). An analysis of the CIDNP signals indicates that spin selection occurs in an aryl radical-arylhydrazyl singlet radical pair. The precursor to this radical pair is postulated to be a pair consisting of an aryldiazenyl radical and an arylhydrazyl radical formed by hydrogen atom transfer between two molecules of aryldiazene.

Aryldiazenes (ArN=NH, **1**) are interesting labile intermediates which have recently been prepared by a number of techniques. Methods of synthesizing **1** include the decarboxylation of aryldiazenecarboxylic acids,[1] sodium borohydride reduction of diazonium ions,[2] oxidation of hydrazines,[3] displacement from metal complexes,[4] and base-induced decom-

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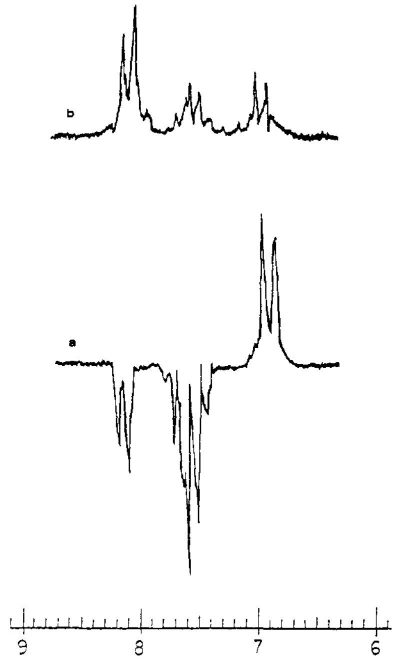


Figure 1. (a) ^{1}H NMR spectrum recorded during the decomposition of *p*-nitrobenzenediazonium tetrafluoroborate (**2b**) in CH_3CN showing emissions due to nitrobenzene and enhanced absorption due to bis-*p*-nitrohydrazobenzene; (b) after completion of reaction.

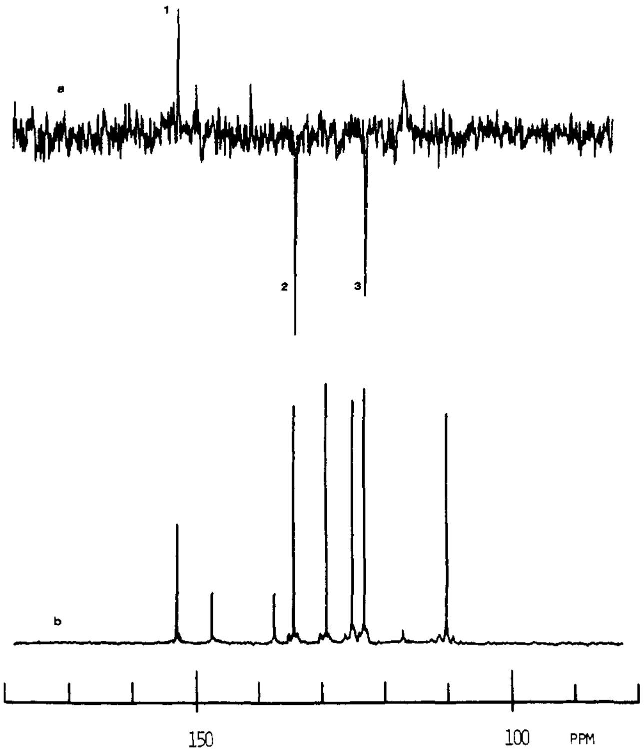


Figure 2. (a) Carbon-13 spectrum recorded during the reduction of *p*-nitrobenzenediazonium tetrafluoroborate (**2b**) in CH_3CN. Assignments: peak 1 is C-1 of bis-*p*-nitrohydrazobenzene (**3b**); peaks 2 and 3 are the para and ortho carbons of nitrobenzene. (b) Carbon-13 spectrum of a mixture of nitrobenzene and **3b** in CH_3CN.

position of *N*-aryl-*N'*-tosylhydrazides.[5]

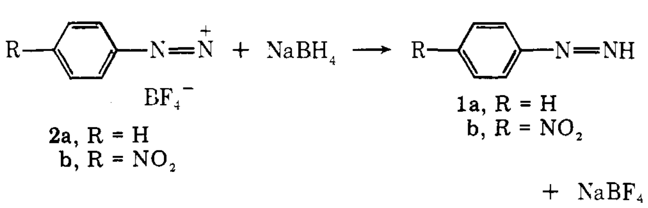
A detailed study of the bimolecular decomposition of diazenes has been presented by Huang and Kosower.[6a-d] The relative insensitivity of the reaction to solvent polarity and to the effect of substituents led these workers to propose a mechanism involving triplet radical pairs.[1] The NMR spectra of several decomposing diazenes exhibited no polarized signals[1] (CIDNP) of the type often associated with reactions involving radical pairs.[7] However, the absence of CIDNP signals is not strong evidence against radical pair formation. Polarized signals are often difficult to detect and their observation is dependent on many factors such as reaction rates and relaxation times.

In fact, there have been a number of reports of CIDNP signals in reductions of diazonium ions, in which aryldiazenes may be intermediates.[8a-c,9] A major product of the second-order decomposition of **1** and of diazonium ion reductions is invariably the arene, ArH.[1] Many of the published CIDNP investigations report only the polarization of this product which likely is a result of diffusion of aryl radicals from a caged pair and subsequent hydrogen abstraction. In the absence of polarization from a cage recombination product, it has not been possible to identify the radical pair and assign its multiplicity.

It is the purpose of this work to present a CIDNP investigation of the mechanism of decomposition of phenyldiazene (**1a**) and *p*-nitrophenyldiazene (**1b**). In order to do this, we generate the aryldiazenes by three different methods and observe similarly polarized CIDNP signals. In the course of this investigation, we have developed a novel method of aryldiazene production involving reduction of diazonium ions with cycloheptatriene.

Results and Discussion

The first goal of this study was to identify the cage recombination product in systems in which the aryldiazene is a likely intermediate and CIDNP signals are observed. In order to do this, we first reacted benzenediazonium fluoroborate (**2a**) and *p*-nitrobenzenediazonium fluoroborate (**2b**) with sodium borohydride. Traylor and McKenna have shown that this reaction is a convenient way of generating **1a** and **1b**.[2] When an aqueous acetonitrile solution of either **2a** or **2b** was reacted with $NaBH_4$, emission for benzene in the case of **2a** and nitrobenzene in the case of **2b** is observed in the ^{1}H NMR spectrum. Emissions from the arene have been reported when diazonium salts are reduced with $NaBH_4$ and reacted with various other nucleophiles.[8f] The ^{13}C NMR also showed emission for the carbons of benzene and for the ortho and para carbons of nitrobenzene upon reduction of **2a** and **2b** with $NaBH_4$.



2a, R = H
b, R = NO_2

1a, R = H
b, R = NO_2

When the reduction of **2b** was carried out in pure acetonitrile rather than acetonitrile-water, a new enhanced absorption appeared as a doublet at δ 6.9 ppm in the ^{1}H spectrum which is shown in Figure 1. This enhanced absorption is also observed in the ^{13}C NMR spectrum at 154.5 ppm (Figure 2). This new peak was identified as bis-*p*-nitrohydrazobenzene (**3b**) by comparison of its ^{1}H and ^{13}C chemical shifts with those of a known sample. Kosower, Haung, and Tsuji reported that **3b** is a major product in the decomposition of **1b**.[6d] The corresponding enhanced absorption of hydrazobenzene (**3a**) was not observed in the reduction of **2a** nor was **3a** reported to be a significant product of the decomposition of **1a**.[6d]

We now feel that we have determined the fate of both partners in the initial radical pair of a reaction in which diazene intermediacy is implicated. However, as is the case with many CIDNP studies, it is possible that the polarized signals arise from a process that is not the major reaction pathway. Kosower and co-workers[6c,d] have shown that diazene decompositions

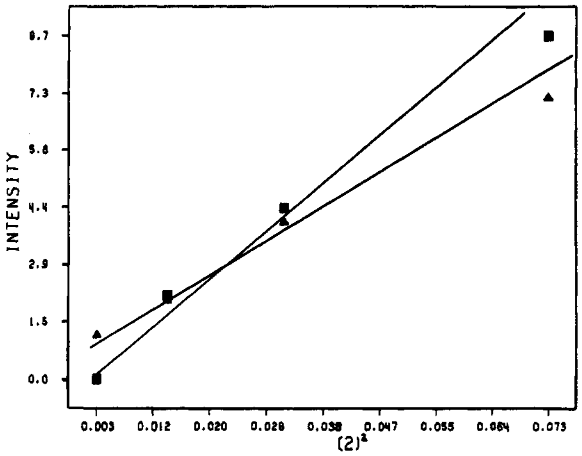
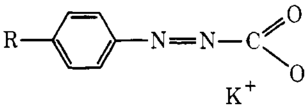


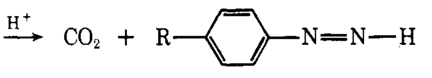
Figure 3. Plot of intensity of signal as a function of square of the concentration for the reduction of diazonium salts by $NaBH_4$: ■, benzenediazonium tetrafluoroborate (**2a**); ▲, *p*-nitrobenzenediazonium tetrafluoroborate (**2b**).

follow second-order kinetics. Hence, if CIDNP signals result from diazene decomposition in the rate-determining step, the initial intensity of the polarized signal should be proportional to the square of the diazonium ion concentration. Figure 3 demonstrates that the intensity of arene emission, measured as soon as possible after mixing diazonium ion and an excess of $NaBH_4$, is indeed proportional to the square of the concentration of **2a** and **2b.** Since oxygen has been reported to react with **1a,**[6a] a reduction was carried out on a degassed solution of **2a.** These conditions resulted in CIDNP signals which were identical with those observed in the presence of oxygen.

In order to ensure that the observed polarizations arise from decomposition of **1a** and **1b,** we also prepared these diazenes by the decarboxylation of aryldiazenecarboxylic acids (eq 1).[6a]



4a, R = H
b, R = NO_2



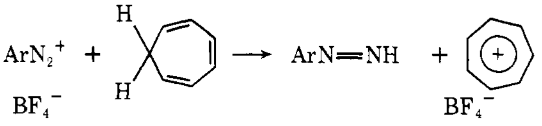
(1)

1a, R = H
b, R = NO_2

When this reaction was carried out on **4a** and **4b** using acetic acid or dimethylamine hydrochloride as the proton source, the ^1H spectrum revealed emission for benzene and nitrobenzene, respectively. Heesing and Kaiser[9] have previously reported a similar emission for the benzene protons when **4a** is treated with HCl. In the present work, signals for the hydrazo compounds (**3a** and **3b**) were observed but they simply grew in intensity as the reaction proceeded and could not be assigned as enhanced absorptions.

However, generation of **1b** in the probe of a ^{13}C spectrometer by reaction of **4b** with acetic acid results in an enhanced absorption for carbon 1 of **3b.** The ^{13}C experiments also reveal emission signals for the ortho and para carbons of nitrobenzene. Hence, preparation of the aryldiazenes by the reaction in eq 1 gives nuclear polarizations similar to those observed when the diazenes are prepared by borohydride reduction of diazonium ions.

The above experiments strongly implicate aryldiazenes in the reaction sequence that leads to nuclear polarization. In order to further establish that the observe CIDNP is due to diazene decomposition, we have developed a new method of synthesizing aryldiazenes. This synthetic method involves hydride transfer from cycloheptatriene (CHT) to diazonium ions (eq 2). When equimolar amounts of CHT and aryldiazonium fluoroborates are mixed in acetonitrile solution, hydride transfer is indicated by the appearance of a signal for tropylium ion at δ 9.3 in the ^1H NMR. CHT has previously been observed to function as a hydride donor in the preparation of tropyliums salts by hydride transfer to the trityl cation.[10] The thermodynamic driving force for the reaction shown in eq 2 is undoubtedly the formation of the stable aromatic tropylium cation.



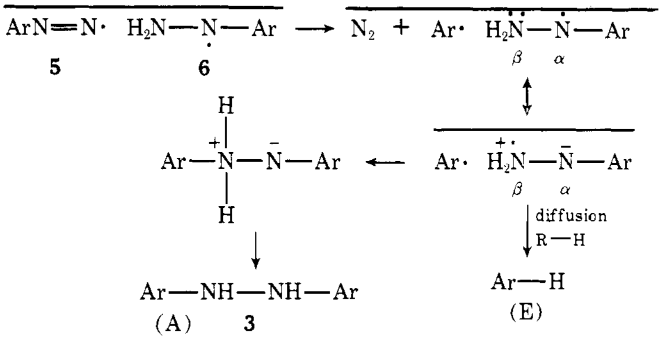
(2)

When either **2a** or **2b** was reacted with CHT, the appearance of the tropylium ion was accompanied by ^1H NMR signals corresponding to benzene and nitrobenzene, respectively. These experiments establish that hydride transfer and concurrent reduction of the diazonium ions occur but they do not prove that aryldiazenes are intermediates.

This latter fact was established by a UV study in which **1b** was detected by the appearance of a peak at 274 nm. This UV absorption has been reported when **1b** is generated by decarboxylation of **4b**[6a] and upon reduction of **2b** with sodium borohydride.[2]

Although we have observed tropylium ion when a variety of diazonium ions are reacted with CHT, the reaction is generally too slow for the observation of CIDNP. However, when **2b** and CHT are heated to 80 °C in acetonitrile solution, an emission for the ortho and meta protons of nitrobenzene is observed in the ^1H NMR. Hence, nuclear polarization also attends the decomposition of aryldiazenes produced by this method.

The fact that the products of aryldiazene decomposition show nuclear polarization when the diazene is generated by three independent methods and that the polarization is the result of a second-order reaction is good evidence that polarization attends diazene decomposition and is not the result of an unrelated reaction. Having determined the identity of both escape and cage recombination products in this system, we may use the radical pair theory[7] of CIDNP to construct a reasonable mechanism for diazene decomposition. We postulate that the reaction proceeds via a radical pair consisting of the aryl diazenyl radical **5**[11] and the 1-arylhydrazyl radical **6.** This radical pair then loses nitrogen to generate a pair consisting of an aryl radical and **6** in which the spin selection leading to polarization occurs.



Kaptein[13] has presented a simple rule that allows one to predict the direction of net nuclear polarization on the basis of the initial multiplicity of the radical pair (μ), the mode of product formation (ε), the sign of the hyperfine coupling constants (*a*), and the difference in *g* values between each partner in the radical pair (Δg). Although the g values of 1-arylhydrazyl radicals have not been reported, 1-alkylhydrazyl radicals, 1-benzylhydrazyl, and triarylhydrazyl radicals all show higher g values than that for phenyl radical.[12a-c] Thus we may assume that g (**6**) > g (Ar·). The values of the hyperfine couplings to both ^{1}H ($a_{H_o} = +17.5$, $a_{H_m} = +6.1$, $a_{H_p} = +1.9$ G)[14a] and ^{13}C ($a_{C_1} = +151.2$, $a_{C_3} = +10.7$ G)[14b] enable us to use Kaptein's rules ($\Gamma_n = \Delta g A \mu \epsilon < 0$) to predict that the protons and ortho and para carbons of arenes, produced by diffusion from the cage and subsequent hydrogen abstraction, will show emission. Likewise, attack of Ar· on the β nitrogen of **6** followed by a rapid proton shift is expected ($\Gamma_n > 0$) to generate hydrazobenzenes showing enhanced absorption for the aryl protons and carbon 1. The above predictions are for a singlet radical pair and confirm that this is the multiplicity of the initial radical pair in this decomposition.

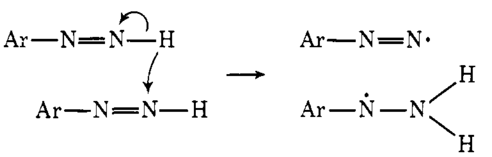
An alternate mechanism involving an aryl radical and a 2-arylhydrazyl radical, **7**, is considered unlikely as **6** is expected

$$\text{Ar}\cdot\ \ \cdot\overset{\text{H}}{\text{N}}-\overset{\text{H}}{\text{N}}-\text{Ar} \longrightarrow \text{Ar}-\overset{\text{H}}{\text{N}}-\overset{\text{H}}{\text{N}}-\text{Ar}$$

7 **3**

to be more stable than **7**. In this connection, note that the electron-withdrawing nitro group in **6b** is expected to increase the spin density on N_β and favor coupling at this position. In accord with this reasoning, decomposition of **1b** gives a higher yield of hydrazobenzene than does decomposition of **1a**.[6d]

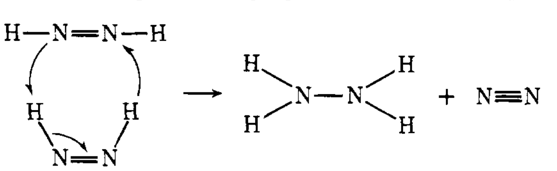
The fact that the decomposition of **1** has been shown to be second order is consistent with a mechanism involving the production of **5** and **6** from two molecules of **1**. Radical pair $\overline{\mathbf{5}+\mathbf{6}}$ is formally derived from hydrogen atom transfer between two aryldiazenes. This transfer can occur in one step as shown in eq 3 or by a variety of two-step mechanisms involving ionic



(3)

or radical-ionic intermediates. However, Kosower has observed only a small increase in the rate of diazene decomposition with increasing solvent polarity.[1] This fact favors a one-step hydrogen atom transfer rather than a mechanism involving the development of formal charges.

The parent compound in the diazene system, N_2H_2, undergoes rapid second-order reaction to produce nitrogen and hydrazine in what is thought to be a concerted $_\sigma2_s + _\pi2_s + _\sigma2_s$ cycloaddition (eq 4).[15] We propose that the first step of this

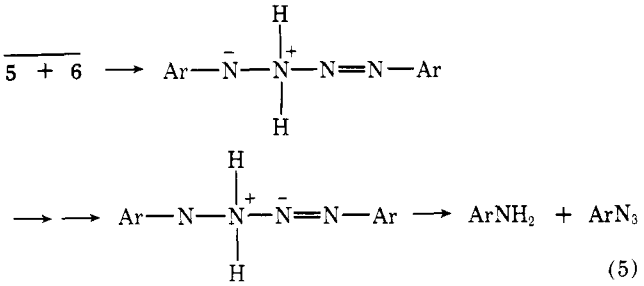


(4)

reaction is nonconcerted in the case of aryldiazenes and generates the initial radical pair directly as shown in eq 3. The preference for nonconcerted reaction in the case of aryldiazenes may be ascribed to stabilization of radical pair $\overline{\mathbf{5}+\mathbf{6}}$ by delocalization of the unpaired electrons. Extensive delocalization is not possible in the hypothetical radical pair produced in two-step diimide self-addition.

An analysis of the products of the borohydride reduction of **2b** using high-pressure liquid chromatography reveals, in addition to nitrobenzene and **3b**, which exhibit polarization, p-nitrophenylhydrazine, p-nitroaniline, and p-nitrophenyl azide. The p-nitrophenylhydrazine undoubtedly arises from hydrogen abstraction by radical **6** after diffusion from the cage. Since most of the unpaired spin is on the nitrogens of **6**, CIDNP signals are not observed for the aryl carbons or hydrogens of the hydrazine.

The p-nitroaniline and the p-nitrophenyl azide are likely formed by coupling of **5** and **6** followed by hydrogen migrations and cleavage (eq 5). The formation of aryl amines, azides, and



$$\overline{5+6} \longrightarrow \text{Ar}-\overset{-}{\text{N}}-\underset{\text{H}}{\overset{\text{H}}{\overset{|+}{\text{N}}}}-\text{N}{=}\text{N}-\text{Ar} \longrightarrow \longrightarrow \text{Ar}-\text{N}-\underset{\text{H}}{\overset{\text{H}}{\overset{|+}{\text{N}}}}-\overset{-}{\text{N}}{=}\text{N}-\text{Ar} \longrightarrow \text{ArNH}_2 + \text{ArN}_3 \quad (5)$$

hydrazines in the borohydride reductions of diazonium ion in aqueous solution has been reported.[16]

A reaction mechanism involving radical pair $\overline{\mathbf{5}+\mathbf{6}}$ can rationalize many of the experimental facts that have been reported for the decomposition of aryldiazenes. The intermediacy of this radical pair is consistent with the observed second-order kinetics as well as with the deuterium isotope effect reported in the decomposition of N-deuteriodiazenes ($k_H/k_D \simeq 5$).[6c]

Conclusion

These CIDNP results indicate that spin selection in aryldiazene decomposition occurs in an aryl radical-arylhydrazyl singlet radical pair. A logical precursor to this radical pair is a pair consisting of $\overline{\mathbf{5}+\mathbf{6}}$ formed by hydrogen atom transfer between two diazenes. This mechanism provides a useful framework in which to consider the reactions of aryldiazenes.

Experimental Section

Materials. Commercial grade cycloheptatriene (Aldrich) and sodium borohydride (Alfa) were used without further purification. Aryldiazonium salts were prepared by standard methods[17] employing sodium nitrite for benzenediazonium fluoroborate (**2a**) and isoamyl nitrite for p-nitrobenzenediazonium tetrafluoroborate (**2b**). The fluoroborate salts were precipitated by the addition of 40% HBF_4. Tropylium fluoroborate was prepared by the method of Dauben, Hannen, and Harmon.[10] Diazenecarboxylates were prepared according to the procedure given by Huang and Kosower.[6a] Bis-p-nitrohydrazobenzene (**3b**) was prepared by reduction of the corresponding azo compound with an aqueous ammonia solution saturated with hydrogen sulfide.[18]

Sodium Borohydride Reduction of Aryldiazonium Salts. For ^{1}H NMR spectra, **2a** (60 mg, 0.31 mmol) or **2b** (60 mg, 0.25 mmol) were dissolved in 0.4 mL of acetonitrile in a 5-mm NMR tube. A suspension of sodium borohydride (30 mg, 0.79 mmol) in 0.3 mL of acetonitrile was added and the spectra were quickly recorded on a Varian EM 390 spectrometer.

Carbon-13 CIDNP was obtained by adding a suspension of $NaBH_4$ (50 mg, 1.32 mmol) in 0.3 mL of CH_3CN to **2a** (200 mg, 1.04 mmol) or **2b** (200 mg, 0.84 mmol) dissolved in 2.0 mL of CH_3CN in a 10-mm NMR tube. The spectra were then recorded on a Varian CFT-20 spectrometer. In typical runs, one 20-μs pulse gave satisfactory signal to noise. Fourteen consecutive free induction decays (FIDs) were stored on a Sykes flexible disc recorder. The FIDs were Fourier transformed at the conclusion of the reaction and the spectra plotted. Each experiment was approximately 2 min in length.

The anaerobic reduction of **2a** was conducted by placing **2a** (60 mg, 0.31 mmol) and $NaBH_4$ (30 mg, 0.79 mmol) in an NMR tube. The tube was evacuated and cooled to −196 °C, and 0.7 mL of degassed acetonitrile was distilled in and frozen just above the solid reactants. When the tube was sealed and allowed to warm up in the probe of an NMR spectrometer, CIDNP emissions for benzene were observed.

A product analysis of the reaction mixture obtained from the borohydride reduction of **2b** (0.25 mmol), under the conditions of the

CIDNP experiment, was carried out on a Waters Associates high-pressure liquid chromatograph equipped with a μBONDAPAK C-18 column using 50% CH_3CN–H_2O eluent at a flow rate of 1 mL min^{-1}. This analysis revealed nitrobenzene (0.066 mmol, 26.2%), **3b** (0.015 mmol, 11.6%), *p*-nitrophenyl azide (0.023 mmol, 9.1%), *p*-nitroaniline (0.026 mmol, 10.3%), and *p*-nitrophenylhydrazine (0.043 mmol, 16.9%).

Effect of Aryldiazonium Salt Concentration on ^{1}H CIDNP Intensity. Four solutions of **2a** or **2b** (0.056, 0.12, 0.18, and 0.27 M in CH_3CN) were prepared. A suspension of $NaBH_4$ (30 mg, 0.790 mmol) in 0.3 mL of CH_3CN was added. The spectra of each solution was recorded as soon as possible after mixing and the intensity of the strongest emission peak measured. The emission intensity in centimeters plotted as a function of the square of concentration of **2a** or **2b** is shown in Figure 3.

Decarboxylation of Aryldiazenecarboxylates. Potassium *p*-nitrophenyldiazenecarboxylate (**4b,** 60 mg, 0.26 mmol) and 0.4 mL of CH_3CN were placed in an NMR tube. Glacial acetic acid (0.3 mL, 5.25 mmol) was added and the ^{1}H NMR spectra immediately recorded. Emissions for the protons of nitrobenzene were observed (δ 7.57, 8.20 ppm). For ^{13}C studies, 200 mg (0.86 mmol) of **4b** in 1.0 mL of CH_3CN and 1.0 mL of glacial acetic acid (17.5 mmol) were employed. Emissions for the ortho and para carbons of nitrobenzene (δ 123.7, 134.3 ppm, Figure 2) and an enhanced absorption for C_1 (δ 154.5 ppm, Figure 2) of **4b** were observed.

The decarboxylation of phenyldiazenecarboxylate (**4a**) was investigated by mixing 50 mg (0.27 mmol) of the salt with 21 mg (0.26 mmol) of dimethylamine hydrochloride in 0.5 mL of Me_2SO and recording the ^{1}H NMR spectrum at 90 °C. These conditions resulted in an emission for the protons of benzene (δ 7.23 ppm).

Reduction of 2a and 2b with Cycloheptatriene. This reaction was initially investigated by preparing solutions containing equimolar amounts of **2a** or **2b** and cycloheptatriene. The ^{1}H NMR spectrum indicated that reduction was taking place as evidenced by the appearance of signals for tropylium ion (δ 9.3 ppm) and for the arene. When an acetonitrile solution of **2b** and cycloheptatriene was placed in the probe at 80 °C, emission for the ortho and meta protons of nitrobenzene was observed.

UV Spectrum of *p*-Nitrophenyldiazene (1b). A solution containing equimolar quantities of **2b** and cycloheptatriene in CH_3CN (1.3×10^{-4} M) was prepared. The UV spectrum of this solution, recorded 24 h after preparation on a Cary 17 spectrometer, showed a peak at 274 nm attributed to **1b**.

A similar experiment was conducted using excess sodium borohydride in place of cycloheptatriene. Identical peaks for **1b** were observed at 274 nm in both studies.

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Oxygenation of 3-Aryl-2-hydroxyacrylic Acids. The Question of Linear Fragmentation vs. Cyclization and Cleavage of Intermediates

Charles W. Jefford,* Willy Knöpfel, and Peter A. Cadby

Contribution from the Department of Organic Chemistry, University of Geneva, 1211 Geneva 4, Switzerland. *Received December 20, 1977*

Abstract: Radical-initiated autoxidation of the enolic tautomer of 4-hydroxyphenylpyruvic acid (**6**) gives the β-hydroperoxy-α-ketocarboxylic acid **9**, which decomposes in inert solvents producing 4-hydroxybenzaldehyde (**8**), carbon monoxide, and carbon dioxide. Base-promoted decomposition of **9** depends on the base used. Nucleophilic bases such as methoxide ion add to the ketone function of **9** creating a tetrahedral intermediate which cleaves to **8** and monomethyl oxalate. *tert*-Butoxide ion, a bulky base, generates the peroxide ion of **9,** which cyclizes onto the ketone function giving the 1,2-dioxetane **7**, which spontaneously cleaves to **8** and oxalic acid. In the absence of base, **9** does not cyclize to **7.** Dye-sensitized photooxygenation of **6** in inert solvents gives oxalic acid and carbon monoxide and dioxide. Quenching studies reveal that oxalic acid results from addition of singlet oxygen to give **7,** whereas "ene" reaction of singlet oxygen and free-radical, type I processes lead to **9,** which collapses to the oxides of carbon. The ratio of the two pathways is dye dependent. Mechanisms are discussed together with their relevance to bioluminescent processes and the cleavage of phenols by dioxygenases.

Whether or not α-hydroperoxycarbonyl compounds cyclize to dioxetanes is of crucial importance in understanding the mechanisms of phenol cleavage by dioxygenases[1] and certain bioluminescent processes.[2] Depending on the nature of the terminal carbonyl substituent (X), cyclization can occur with or without the loss of acid (HX). Subsequently, the

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