

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 Br₂ 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 13× molecular sieves column at room temperature. The remaining products were then pumped through a 2 ft × 0.25 in. column containing 20% AgNO₃/ethylene glycol on 40/60 firebrick at 0 °C (this removes THF and C₃O₂) 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-pentalen 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-pentalen, 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 C₃O₂ 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 C₂H₃D at *m/e* 29 but no C₂H₂D₂ at *m/e* 30.

Photolysis of Cyclopentanone and THF. This photolysis was carried out under identical conditions with those described for THF and C₃O₂.

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.

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A CIDNP Study of the Decomposition of Aryldiazenes

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Abstract: Phenyl diazene (**1a**) and *p*-nitrophenyl diazene (**1b**) have been prepared by sodium borohydride reduction of the corresponding aryldiazonium salts, by decarboxylation of aryldiazene carboxylic 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 aryldiazanyl 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 decarbox-

ylation of aryldiazene carboxylic acids,¹ sodium borohydride reduction of diazonium ions,² oxidation of hydrazines,³ displacement from metal complexes,⁴ and base-induced decom-

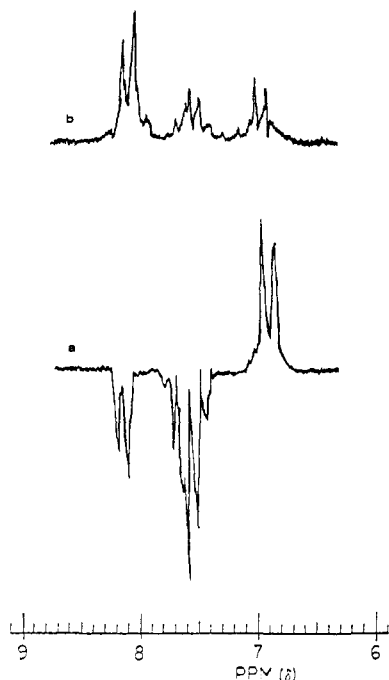


Figure 1. (a) ^1H NMR spectrum recorded during the decomposition of *p*-nitrobenzenediazonium tetrafluoroborate (**2b**) in CH_3CN showing emissions due to nitrobenzene and enhanced absorption due to bis-*p*-nitrohydrazobenzene; (b) after completion of reaction.

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

A detailed study of the bimolecular decomposition of diazenes has been presented by Huang and Kosover.^{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 signals¹ (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 bo-

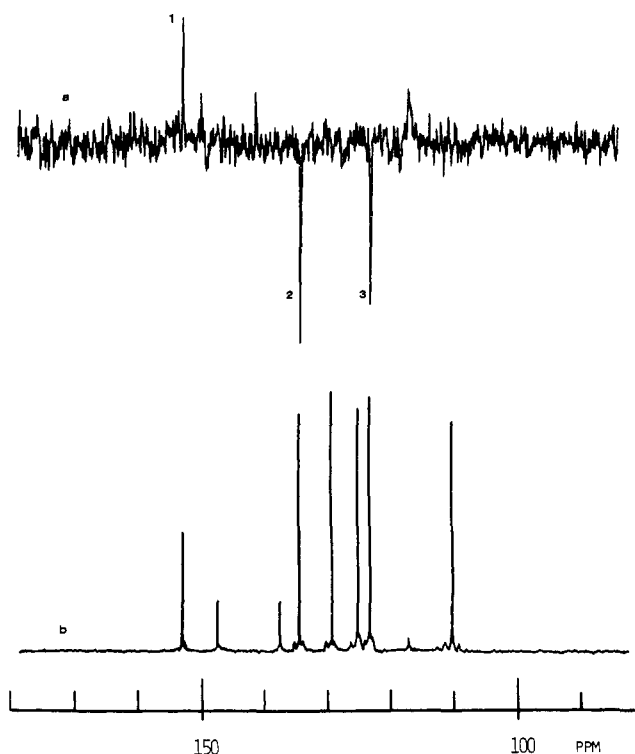
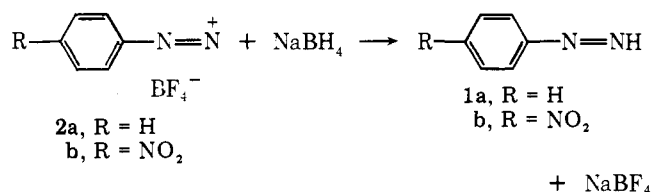


Figure 2. (a) Carbon-13 spectrum recorded during the reduction of *p*-nitrobenzenediazonium tetrafluoroborate (**2b**) in CH_3CN . Assignments: peak 1 is C-1 of bis-*p*-nitrohydrazobenzene (**3b**); peaks 2 and 3 are the para and ortho carbons of nitrobenzene. (b) Carbon-13 spectrum of a mixture of nitrobenzene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

rohydride. 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 ^1H 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 .

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 ^1H 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 ^1H and ^{13}C chemical shifts with those of a known sample. Kosover, 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. Kosover and co-workers^{6c,d} have shown that diazene decompositions

CIDNP experiment, was carried out on a Waters Associates high-pressure liquid chromatograph equipped with a μ BONDAPAK 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 ^1H 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 Aryldiazene-carboxylates. Potassium *p*-nitrophenyldiazene-carboxylate (**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 ^1H 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 phenyldiazene-carboxylate (**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 ^1H 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 ^1H 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

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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 dioxygenases¹ 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