δ 5.29 was assigned to H-2. This signal was split by H-1 and H-3 protons to give a small coupling constant ($J_{2,3}$ = 4.15 Hz), indicating the existence of 1,2- and 2,3-cis orientations. The quartet of H-1 and the triplet of H-2 protons at δ 5.26 and δ 5.29, respectively, collapsed to a pair of doublets by irradiating protons H-3 and 1-NH. The H-4 proton appeared as a quintet by coupling with the neighboring axial protons at C-5 ($J_{4,5a}$ = 8.32 Hz), and the equatorial protons at C-3 and C-5 ($J_{3,4}$ = 3.97 Hz, $J_{4,5e}$ = 4.13 Hz, respectively). These observations indicated that H-4 existed in the axial orientation. The methylene H-5 protons exhibited an eight-line pattern to form the AB portion of an ABX system, and the large $J_{4,5a}$ coupling constant (8.32 Hz) indicated a trans-diaxial arrangement of H-4 and H-5a. The H-5a signal occurred at a lower field (δ 3.94) than that of the H-5e (δ 3.67), proving to be an exception to the rule that an equatorial proton resonates at a field lower than that of a chemically similar but axially oriented proton.[4] This may be the result of the deshielding effect of the axial acetoxy group at C-3. These findings support the *C*1 conformation, and exclude the 1*C* conformation, which would give a smaller $J_{4e,5a}$ coupling constant. The small splitting of the H-1 signal suggested an α-D configuration for structure VII. This was also confirmed by the acetoxy group signals, since one signal was observed at lower field (δ 2.22), indicative of the axial orientation (3-OAc), and the other two signals were observed at higher field (δ 2.10 and δ 2.13), indicating an equatorial orientation (2,4-OAc).[4,24,25]

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Registry No. Ia, 53131-05-8; Ib, 2776-69-4; Ic, 2776-68-3; Id, 2776-85-4; Ie, 84851-65-0; If, 84851-66-1; Ig, 84851-67-2; Ih, 84851-68-3; II (R = Ph), 42891-46-3; III (R = Ph), 42891-47-4; IV (R = *p*-AcC_6H_4), 86336-30-3; V (R = Ph), 86336-31-4; VI (R = Ph), 86363-21-5; VII (R = *p*-AcC_6H_4), 86363-22-6.

Supplementary Material Available: Partial ^1H NMR data for compounds Ih (Figure 5), II (Figure 6), III (Figure 7), IV (Figure 8), V (Figure 9), and VI (Figure 10) (7 pages). Ordering information is given on any current masthead page.

Evolution of Photooxidation Products upon Irradiation of Phenyl Azide in the Presence of Molecular Oxygen

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The reaction of phenylnitrene with oxygen was reinvestigated by irradiating phenyl azide (1) in O_2-saturated acetonitrile solutions. Quantum yields of the disappearance of 1 are calculated from absorption spectral changes, and primary photoproducts are determined by using high-pressure liquid chromatography. The photochemistry of the reaction products (azobenzene, azoxybenzene, nitrobenzene, and nitrosobenzene) are also examined, including measurements of quantum yields and determinations of primary photoproducts and product ratios. A reaction sequence is presented to account for the photooxidation products afforded upon irradiation of 1 in the presence of oxygen. The reaction of phenylnitrene with oxygen is an effective termination step in the autocatalytic chain decomposition of 1.

During our investigation of the photoinitiated autocatalytic chain decomposition (PACD) of phenyl azide[1] (1), azobenzene[2] (2) was the only primary photoproduct when irradiated with 254-nm light in deaerated acetonitrile (CH_3CN) solution.[3] An isosbestic point in the absorption spectra and high-pressure liquid chromatography (LC) verified the two-component system. Upon continued irradiation, the isosbestic point was destroyed as an intractable material was also formed.[4,5] Prolonged irradiation of 1 in aerated solution also afforded azoxybenzene and nitrobenzene.[1]

Abramovitch and Challand[6] have studied the photoreaction of phenyl azide with oxygen in CH_3CN and found nitrobenzene and tars as major photoproducts; trace amounts of azobenzene and aniline were also formed. Upon triplet sensitization, the amount of nitrobenzene was substantially increased; no azobenzene or aniline was formed. Direct excitation of 1 in the presence of the triplet quencher piperylene resulted in negligible amounts of nitrobenzene.[6] Five substituted phenyl azides were also studied,[7] with nitrobenzenes being formed. Corresponding azobenzenes, anilines, and azoxybenzenes were also formed. Azoxybenzene is thought to be formed via reaction of an arylnitrene with its nitrosobenzene;[6,11,12] direct oxidation

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of azobenzene to azoxybenzene is not significant.[13]

Previously, a significant amount of azoxybenzene was formed upon irradiation of **1** in aerated CH_3CN, thus we have reinvestigated the photoreaction of **1** with oxygen. In addition, the photochemistry of azobenzene (**2**), nitrosobenzene (**3**), nitrobenzene (**4**), and azoxybenzene (**5**) and the reaction of **3** and **4** with phenylnitrene are examined. Quantum yields of reaction are calculated from absorption spectral or high-pressure LC measurements and *primary* photoproducts and product ratios determined by using high-pressure LC.

Experimental Section

Materials. Azobenzene (Eastman Organic) was vacuum sublimed; nitrosobenzene (Aldrich) was recrystallized from 95% ethanol; azoxybenzene (Eastman Organic) was recrystallized (2×) from 95% ethanol and then chromatographed to >99% purity; nitrobenzene (Baker) was vacuum distilled; acetonitrile (Spectrograde, Burdick and Jackson), the solvent for all photochemical studies, was used as received. Phenyl azide was prepared according to the procedure of Lindsay and Allen.[14]

Instrumentation. The following instruments were used: Perkin-Elmer Model 575, UV-vis; Perkin-Elmer 580 and Interdata 6/16 minicomputer, IR; Perkin-Elmer R24B, NMR; Bruker WM, 300-MHz NMR; Varian MAT 112 with SS200 data system; Waters ALC/GPC 204 LC with a Spectra-Physics Minigrator.

Photochemistry. All irradiations were performed at room temperature with a 450-W Hg arc and chemical filters[15] or a 1000-W Hg-Xe arc and Schoeffel $^1/_4$-m monochromator. Quantum yields of disappearance were calculated from eq 1 by

$$\phi = NCV\Delta/IFt \qquad (1)$$

measuring absorbance changes, where N = Avogadro's number, C = concentration (mmol/mL), V = volume irradiated (mL), Δ = fraction converted $[(A_0 - A_t)/A_0$; A_0 = absorbance at $t = 0$, A_t = absorbance after time t, t = irradiation time (s)], I = light intensity measured by potassium ferrioxalate[15] prior to and after irradiation, and F = fraction of light absorbed $(1 - 10^{-A_0})$.

For quantum yield determinations, $\Delta < 10\%$ (generally only 2-3%), so that absorption of light by the photoproduct(s) and secondary photochemistry are negligible. Solutions were deaerated by bubbling with N_2 (Grade 0.5, West Penn Laco) for 5 min at 0 °C and oxygenated by bubbling with O_2 (West Penn Laco) for 3 min at 0 °C. All experimentation was performed under red illumination.

Results and Discussion

Phenyl Azide (1). Irradiation of 10^{-4} - 10^{-5} M **1**[16] in deaerated CH_3CN (λ_{max} = 250 nm, $\epsilon_{max} = 1.0 \times 10^4$ M^{-1} cm^{-1}) with 250-nm light results in a decrease of intensity of the 250-nm band maxima and a concomitant increase in intensity in the 270-360-nm region. Continued irradiation reveals a two-component system indicated by an isosbestic point at 271 nm. High-pressure LC verifies the two-component system, phenyl azide and (*E*)-azobenzene (**2**).[17] (*Z*)-Azobenzene *is not a primary photoproduct* of **1**. The quantum yield of disappearance (ϕ_{-1}) is 0.72, a value in good agreement with those of Reiser and coworkers,[18-20] who monitored the production of nitrogen (ϕ_{-N_2}) upon irradiation of **1** in polar ($\phi_{-N_2} = 0.43$)[18,19] and nonpolar ($\phi_{-N_2} = 0.52$)[20] solvents.

Table I. Absorption Spectral Properties[a]

compd	λ_{max}, nm	$10^{-4}\epsilon_{max}$,[b] M^{-1} cm^{-1}
phenyl azide (1)	250	1.00
(*E*)-azobenzene (2)	320	2.29
nitrosobenzene (3)	282	1.01
nitrobenzene (4)	262	1.01
(*E*)-azoxybenzene (5)	321	1.42

[a] Room temperature in CH_3CN. [b] $\epsilon \pm 5\%$.

After prolonged (15 h) irradiation (42.0% conversion) of **1** (1.2×10^{-2} M) in aerated solution, high-pressure LC reveals that azobenzene (5.8%), azoxybenzene (9.6%), nitrobenzene (78.2%), and nitrosobenzene (6.4%) are formed[21] (Table I). This result is not in agreement with that of Abramovitch and Challand,[6] who observed nitrobenzene as the major product.

Upon irradiation of 1.1×10^{-4} M **1** in O_2-saturated CH_3CN, a decrease in intensity of the 250-nm band maxima and a concomitant increase in intensity of the 270-360-nm region are observed. An isosbestic point is present at 262 nm. The position and shape of this absorption differs from that obtained upon irradiation of **1** in deaerated CH_3CN. High-pressure LC confirms the two-component system, and absorption and mass spectral data establish the only stable primary photoproduct as nitrosobenzene (**3**;[17] $\phi_{-1} = 0.69$).

(*E*)-Azobenzene (2). The photochemistry of (*E*)- and (*Z*)-azobenzene has been the subject of considerable interest. Quantum yields of $Z \rightleftarrows E$ photoisomerization were measured upon direct excitation[22-29] and are sensitive to excitation wavelength, solvent, and temperature. Upon irradiation of (*E*)-azobenzene in deaerated CH_3CN, (*Z*)-azobenzene is the only photoproduct ($\phi_{E\to Z} = 0.14$, a value in excellent agreement with that of Bortolus and Monti).[29] In O_2-saturated solutions, (*Z*)-azobenzene is also formed upon irradiation of **2**. Azoxybenzene (**5**) is a primary, minor (less than 1%) photoproduct; however, owing to its low yield,[13] the contribution of **5** via direct oxidation of **2** cannot account for its presence in the photolysis mixture obtained upon irradiation of **1** in an aerated solution.

Nitrosobenzene (3). Azoxybenzene is the photoproduct upon irradiation of N_2-saturated solutions of **3** (ϕ_{-3} = 0.09); however, **2** (4% of the photoproducts at 10% conversions of **3**) is present but is a secondary photoproduct. Azoxybenzene is the major photoproduct when **3** is irradiated in O_2-saturated solution to small conversions (ϕ_{-3} = 0.114); however, continued irradiation reveals that nitrobenzene is also formed. Azoxybenzene is a known

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[16] The quantum yield of disappearance of phenyl azide (ϕ_{-1}) is concentration dependent,[1] thus, photochemical studies were made in dilute solutions.

[17] Upon prolonged irradiation, an intractable material[4,5] is visually observed to be formed, and the isosbestic point of the electronic absorption spectra is destroyed. It is not yet possible to characterize this material, which is insoluble in a wide varieity of organic solvents.

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[21] High-pressure LC peaks correspond to phenyl azide (240 s retention), (*E*)-azobenzene (270 s), nitrosobenzene (290 s), (*E*)-azoxybenzene (330 s), nitrobenzene (375 s), (*Z*)-azobenzene (900 s), and acetonitrile (930 s) on employing a Waters μ-Porasil column (12 × $^1/_4$ in.), 2-3% ether/hexane, 1-2 mL/min flow rate, ca. 1500 psi pressure, and 280-nm absorbance detection.

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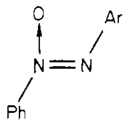
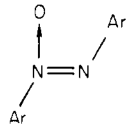
photoproduct of **3** when irradiated in alcoholic solvents,[30-32] dioxane,[33] water,[33] and acidic media.[31]

Alternatively, Pak and Testa[34] report that the photoreduction product, *O*-phenylhydroxylamine (**6**) is the only primary product upon irradiation of **3** with 313-nm light in 2-propanol (ϕ_{-3} = 0.047 in degassed and 0.033 in aerated solution). Coupling of **3** and **6** then affords azoxybenzene.[34] Azoxybenzene is also thought to be the reaction product of phenylnitrene and nitrosobenzene.[6,12]

The reaction of phenylnitrene with **3** was reinvestigated upon 250-nm irradiation of a mixture of 1.14×10^{-4} M **1** and 1.64×10^{-4} M **3** in both N_2- and O_2-saturated CH_3CN. Azobenzene (64%) and azoxybenzene (36%) are the primary photoproducts at 34% conversion in deaerated solution (ϕ_{-1} = 0.54). In O_2-saturated solution ϕ_{-1} = 0.38, with nitrobenzene being formed. However, the amount of **3** *increased* upon prolonged irradiation. Recall that **3** is the only reaction product of phenylnitrene and oxygen. These results agree with those of DeLuca and Renzi,[35] who photolyzed and thermalyzed aryl azides in the presence of **3** and derivatives. Azobenzenes were selectively formed via reaction of two azides or of two nitroso compounds but not from reaction of an azide with the nitroso compound.[35] For example, thermolysis of **1** and 4-methylnitrosobenzene afforded **2** and 4,4′-dimethylazobenzene (**7**). 4-Methylazobenzene was not reported. Azoxybenzenes **8** and **9** are formed as the major products [(**8** + **9**)/(**2** + **7**) ratio of 5/1]. Upon photolysis, **2**, **8**, **9**, and 2-hydroxyazobenzenes (**10**) are formed. 2-Hydroxyazobenzenes are known primary photoisomerization products of the corresponding azoxybenzenes.[32,36-46]



8

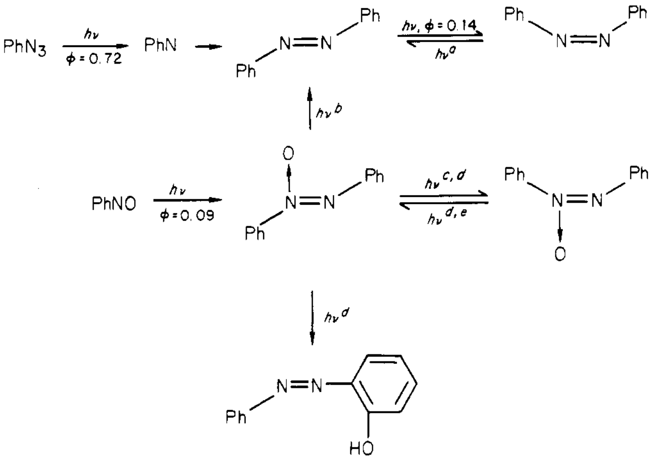


9

Ar = 4-CH_3Ph

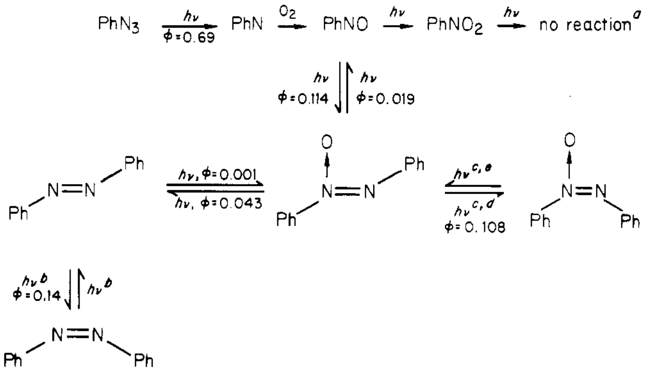
Nitrobenzene (4). Upon irradiation of **4** in deaerated CH_3CN, absorption spectra and high-pressure LC indicate that no photochemical reaction occurred [$\phi_{-4} = 3 \times 10^{-4}$ (upper limit)]. In the presence of **1**, nitrobenzene is also unreactive (ϕ_{-1} = 0.02; probably the result of light absorbed directly by **1** since **2** is the only photoproduct). Hurley and Testa[47] irradiated **4** in 2-propanol with 366-nm light and observed formation of the reduction product *O*-phenylhydroxylamine (**6**; ϕ_{-4} = 0.011) thought oxidized by air to nitrosobenzene which reacts with **6** to form azoxybenzene. Nitrosobenzene and 4-hydroxynitrobenzene are vapor-phase photolysis products of nitrobenzene.[48] The photochemical reduction of aromatic nitro compounds is a general reaction upon irradiation in solvents containing abstractable hydrogen atoms;[31,49-52] however, in CH_3CN we observe no reaction. A variety of products are reported for photolysis of **4** in ether.[53]

Scheme I



[a] Excited singlet-state reaction; $\phi_{Z\to E} = 0.21$.[29] [b] Triplet sensitized; $E_T > 62$ kcal/mol.[40,56] [c] $\phi_{E\to Z}$ = 0.11 in heptane and 0.12 in ethanol.[55] [d] Excited singlet state reaction.[40,41,55] [e] $\phi_{Z\to E}$ = 0.64 in heptane and 0.56 in ethanol.[55]

Scheme II



[a] $\phi_{-4} < 0.0003$ (upper limit). [b] Excited singlet-state reaction; dissolved oxygen has no effect; $\phi_{Z\to E} = 0.21$.[29] [c] Excited singlet state reaction; dissolved oxygen has no effect.[41] [d] $\phi_{E\to Z}$ = 0.12 in heptane and 0.12 in ethanol.[55] [e] $\phi_{Z\to E}$ = 0.67 in heptane and 0.56 in ethanol.[55]

Azoxybenzene (5). The photochemistry of **5** has been extensively studied. 2-Hydroxyazobenzene (**10**) formation,[32,36-46] $E\to Z$ photoisomerization,[40,41,53-55] and triplet-sensitized photoreduction to azobenzene[40,56] have been reported. Since we were concerned with photoreactions

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Table II. Effect of Oxygen on the Quantum Yields of Disappearance of Phenyl Azide[a]

	ϕ_{-1}[c]		
concn,[b] M	N_2[d]	air	O_2[d]
3×10^{-2}	300	10	12
3×10^{-3}	52	2	0.8
3×10^{-4}	3.5	0.7	0.9

[a] 254-nm irradiation. [b] CH_3CN solutions at room temperature. [c] ϕ_{-1} ± 10%. [d] Saturated by bubbling for 5 min with nitrogen or 3 min with oxygen at 0 °C.

of **5** that afford nitrosobenzene or nitrobenzene, its photochemistry was examined in O_2-saturated CH_3CN. At ca. 10% conversions of **5**, azobenzene (25%), nitrosobenzene (11%), and (*Z*)-azoxybenzene (64%) were formed (ϕ_{-5} = 0.17). It is also possible that **10** is a primary photoproduct of **5**; however, high-pressure LC did not ascertain its presence; it may have eluted with solvent. That *E*→*Z* photoisomerization occurred is based upon spectral shifts in absorption spectra; upon irradiation of (*E*)-**5**, a decrease in intensity at its band maxima (326 nm, ϵ = 14 800 M^{-1} cm^{-1})[41] is observed along with a concomitant bathochromic shift in λ_{max} and an increase in intensity at ca. 240 nm. Since (*Z*)-**5** has band maxima at 327 (ϵ = 3900 M^{-1} cm^{-1}) and 239 nm,[54] a decrease in λ_{max} and an increase at ca. 240 nm is expected. Compound **10** has a first band maximum at 327 nm; however, since ϵ = 18,000 M^{-1} cm^{-1}[41] an increase in λ_{max} upon irradiation of **5** would be expected if **10** were a major photoproduct, which was not observed.

General Considerations. We report several new photochemical reactions: (i) In deaerated CH_3CN, irradiation of **1** results in the *exclusive formation of* (*E*)-*azobenzene.* (ii) In the presence of oxygen, *nitrosobenzene is the only primary photoproduct* of **1**. (iii) Upon irradiation of an O_2-saturated solution of nitrosobenzene, nitrobenzene is formed and is unreactive under the experimental conditions. Schemes I and II are summaries of the reactions of phenyl azide in deaerated and O_2-saturated solution, respectively.

These results enable formulation of the reaction sequence upon irradiation of phenyl azide in the presence of oxygen. (i) Irradition of **1** results in the loss of nitrogen[18–20] and formation of phenylnitrene, a ground-state triplet species[8–10] (ϕ_{-1} = 0.7). (ii) Phenylnitrene reacts quantitatively with oxygen to form nitrosobenzene, the only stable primary photoproduct. (iii) Nitrosobenzene then is either photooxidized to nitrobenzene or affords azoxybenzene. (iv) That nitrobenzene is the major photoproduct of the reaction of **1** in the presence of oxygen is a result of the relative photochemical inertness of nitrobenzene under the experimental conditions (ϕ_{-4} = 3×10^{-4}).

Azobenzene can be formed via the direct dimerization of two phenylnitrenes, reaction of phenylnitrene with phenyl azide[2,57,58] or irradiation of azoxybenzene.[40,56] Since ϕ_{-1} is identical in N_2- or O_2-saturated CH_3CN solutions and since only one primary photoproduct results for each solution, (*E*)-azobenzene probably results from nitrene–nitrene dimerization; if a sensitized decomposition of phenyl azide were to occur in dilute solutions, then we might expect ϕ_{-1} to be measurably higher in N_2- vs. O_2-saturated solution, which is not observed.

At $[PhN_3] > 10^{-3}$ M, ϕ_{-1} values significantly greater than unit efficiency have been measured[1] (Table II). In solution phenylnitrene reacts with **1** at a nearly diffusion-controlled rate;[57] however, it is not known whether *two* phenylnitrenes are the direct result of reaction or whether a 1,4-diphenyltetraazadiene[2,58] is formed, which then decomposes into *two* phenylnitrenes. It is clear that reaction of phenylnitrene with oxygen to afford nitrosobenzene effectively quenches the chain decomposition reaction at $[PhN_3] < 3 \times 10^{-3}$ M. For example, at $[PhN_3] = 3 \times 10^{-3}$ M, ϕ_{-1} = 52 for N_2-saturated solution, but ϕ_{-1} = 0.8 for O_2-saturated solution. This latter value indicates essentially a total quenching of the chain reaction. At $[PhN_3] = 3 \times 10^{-2}$ M, oxygen can only partially quench the chain-decomposition reaction, probably due to the fact that its concentration of ca. 5×10^{-3} M is much lower than that of **1**. Similarly, for aerated solutions at $[PhN_3] = 3 \times 10^{-3}$ M oxygen solubility is ca. 10^{-3} M, and incomplete chain quenching is suggested from the measured ϕ_{-1} value. Reaction of phenylnitrene with oxygen thus acts as an effective chain-termination step.

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Registry No. Oxygen, 7782-44-7; phenylnitrene, 2655-25-6; phenyl azide, 622-37-7; (*E*)-azobenzene, 17082-12-1; (*E*)-azoxybenzene, 21650-65-7; nitrobenzene, 98-95-3; nitrosobenzene, 586-96-9.

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