over sodium carbonate for 1 hr, and filtered. The filtrate was distilled to give 2 g of material, bp 56–61° (19 mm), containing starting dione. A pure sample of **32** was obtained by preparative glpc: ir 5.47, 9.1, and 10.9 μ; nmr δ 4.08 (s, 2) and 1.43 (s, 6).

Reaction of 32 with Acetic Acid.—To an nmr sample of **32** containing methylene chloride as an internal standard, was added 1 equiv of acetic acid. After 63 hr at room temperature, no reaction had occurred. In a similar experiment **32** was treated with excess 40% peracetic acid with the same result.

3-Hydroxy-3-Methylbutanoic Acid β-Lactone (33).—Lactone **33** was prepared as described:[24] ir 5.49, 9.3, and 12.6 μ (doublet); nmr δ 3.18 (s, 2) and 1.53 (s, 6).

Reaction of 33 with Peracetic Acid.—To an nmr sample of **33** in CH_2Cl_2 (containing benzene as an internal standard) was added 4 equiv of 40% peracetic acid. Gas evolution was immediate and in 45 min **33** was completely gone. No new peaks appeared in the spectrum.

Reaction of 36 with Acetic Acid.—A CH_2Cl_2 solution of **36** was treated with 1 equiv of glacial acetic acid at −70°. Glpc analysis showed a single component identified as **30**.

Reaction of 36 with Peracetic Acid.—A CH_2Cl_2 solution of **36** was treated with 2 equiv of 40% peracetic acid at −70°. As the reaction warmed to room temperature, vigorous CO_2 evolution was observed. Ir analysis of the crude product indicated that acetoxy ketone **30** was the predominant product.

Registry No.—**12,** 10008-69-2; **18,** 933-52-8; **19,** 1123-11-1; **23b,** 38202-51-6; **23c,** 38202-52-7; **32,** 1955-45-9; MCPBA, 937-14-4; PNPBA, 943-39-5; tetramethylallene, 1000-87-9; 1,2-dimethylallene, 598-25-4.

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Photochemical Oxidations. VII. Photooxidation of Cyclohexylamine with Oxygen

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The presence of a charge-transfer ultraviolet absorption band for an oxygen-saturated cyclohexylamine solution has been reconfirmed. The absorption of light by this band causes cyclohexanone oxime and *N*-cyclohexylidinecyclohexylamine to be formed in the initial stages of the reaction, *i.e.*, to 0.6% conversion. The oxime is not the precursor of the imine. *N*-Cyclohexyl-1-hydroperoxycyclohexylamine, 1-hydroperoxycyclohexylamine, and the cyclohexylamine–hydrogen peroxide adduct give only the imine under the conditions of the reaction.

The destructive ability of a combination of oxygen and sunlight on organic substances is great and costly. We have been studying the consequences of light on charge-transfer (CT) complexes between various organic materials[1] and oxygen because these are instrumental in a number of degradations. The most dramatic demonstration to date is the fact that saturated hydrocarbons exhibit CT interactions[2a,b,c] with molecular oxygen and the excitation of this uv absorption band causes product formation.[1e–g]

A distinction must be made between those oxidation reactions initiated by sensitization and those by excitation of the CT band though similarities in products and product composition may occur. Among the reports of dye-sensitized oxygenation of amines, Gaffron[3] found that erythrosin photosensitized the oxygenation of *n*-propylamine and chlorophyll photosensitized the oxygenation of *n*-isoamylamine. More recently Schenck[4] reported that the dye-sensitized photooxygenation of primary, secondary, and tertiary amines resulted in the uptake of one, two, or three molecules of oxygen, respectively, indicating that the number of CH groups α to the nitrogen determines the stoichiometry. The products of these reactions were amine hydroperoxides. Others have reported that a variety of reactions occur when amines are irradiated in the presence of dyes and oxygen: α oxidation,[5–9] dehydrogenation,[10,11] and dealkylation.[10] Kinetic studies on the oxygen uptake in the photosensitized oxidation of triethylamine have also been done.[12]

In contrast, no work has been reported concerning the direct photooxidation of amines without sensitizers being present. Evans[2a] has suggested that oxygen charge-transfer complexes could provide a plausible initial stage in these photooxidations. Since it is known that amines also exhibit CT bands with oxygen, we wished to determine the chemical consequences of direct absorption of light by the oxygen–amine charge-transfer band. A number of aliphatic amines, *i.e.*, primary, secondary, and tertiary, were photochemically oxidized with oxygen in the initial studies. All of the aliphatic amines tested reacted; however, since the primary aliphatic amines gave more simple product mixtures than secondary and tertiary amines, these were selected for the initial study. For primary aliphatic amines, our attention was focused on the photooxidation of cyclohexylamine because a procedure for the synthesis of the α hydroperoxide of cyclohexylamine was available.

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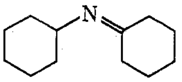
Results and Discussion

The spectral basis for the photooxidation of cyclohexylamine is illustrated in Figure 1. The absorption of oxygen-saturated cyclohexylamine begins at 380 nm and increases towards off scale at 265 nm. Nitrogen-saturated cyclohexylamine is included as a reference. Due to the intense absorption of cyclohexylamine beginning at 265 nm, the correct position of the CT maxima cannot be established. Though amines are known to undergo a slow nonphotochemical oxidation, this enhanced absorption conforms to that of the CT type in that it is reversibly formed, *i.e.*, it can readily be removed by displacing the oxygen by a more inert gas such as nitrogen.

The change transfer occurs with nitrogen as the donor and oxygen the acceptor. Of the three types of liquid phase CT phenomena we have been working with, the amine–oxygen CT absorption is most intense with the ether–oxygen CT band of intermediate strength and the saturated hydrocarbon–oxygen CT band the weakest.[1] This is in agreement with the correlation of increasing CT absorptivity with decreasing ionization potential of various donors.[2c,13a] Neither the presence of a ground state complex between oxygen and the amine nor the extent of its formation can be surmised from these data.

On irradiating the CT band of oxygen-saturated cyclohexylamine, the products, cyclohexanone oxime, *N*-cyclohexylidinecyclohexylamine (**1**), ammonia, and water, are formed. In addition, there are peroxides present in the irradiation solution.

Conceivably, absorption of light by the tail-end absorption of cyclohexylamine and not the CT band could have caused the observed reaction; *cf.* Figure 1. Then the excited state of the amino nitrogen could have entered into the reaction. However the irradiation of nitrogen-saturated cyclohexylamine using a Pyrex filter and a medium-pressure mercury lamp caused no detectable product formation yet these same conditions with oxygen give the observed products. Irradiation using the 350-nm phosphor, low-pressure lamps of the Rayonet reactor also gives the products. Irradiation of the oxygen–cyclohexylamine solution with a tungsten filament lamp did not give any product formation which narrows the wavelengths responsible for product formation to 280–375 nm, the region of the spectrum where the CT band is. Since the amine's absorption is below 280 nm and the direct irradiation of cyclohexylamine is known to give products albeit of a different type,[13b] absorption of light by the extended tail-end absorption of cyclohexylamine did not cause the observed reaction.



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Cyclohexanone oxime is not the precursor of the imine **1** because the reaction rate of the oxime with cyclohexylamine is slow. Under the photochemical reaction conditions, no detectable amount of the imine is formed from the oxime during the time of the irradiation. Cyclohexanone, another possible precursor to the imine **1**, could not be found in the reaction solution.

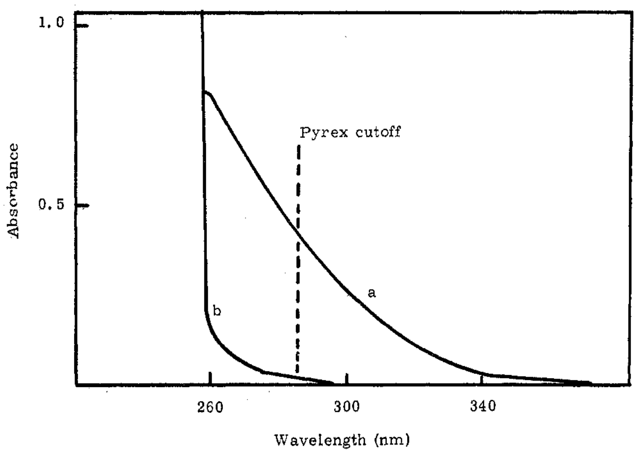


Figure 1.—Ultraviolet spectra of oxygen-saturated cyclohexylamine with nitrogen-saturated cyclohexylamine as a reference (curve a) and nitrogen-saturated cyclohexylamine with an empty cell as reference (curve b).

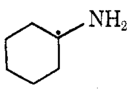
From CT theory the initiation of the product formation can be viewed according to reaction 1 most probably followed by the acid–base reaction 2. With

$$C_6H_{11}NH_2 + O_2 + h\nu \longrightarrow C_6H_{11}\dot{N}H_2^+ + \cdot O_2^- \qquad (1)$$

$$C_6H_{11}\dot{N}H_2^+ + \cdot O_2^- \longrightarrow \underset{\mathbf{2}}{C_6H_{11}\overset{\uparrow}{\dot{N}}H} + \uparrow\cdot O_2H \qquad (2)$$

molecular oxygen being a ground state triplet, both insertion into a CH or NH bond and direct combination of the two radical products of reaction 2 are inhibited. Consequently the amine radical **2** is expected to have a finite lifetime in the reaction solution.

Though the possible presence of **3** in the reaction solution cannot be determined from these data, it has



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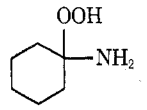

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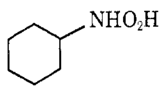

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been postulated to be present for analogous photosensitized reactions and can reasonably be expected to form in this reaction solution as well either by rearrangement of **2** or by reaction of cyclohexylamine with a radical in solution. Noteworthy in this regard is the fact that the dissociation energy of the α-CH bond is slightly larger than that of the NH bond.[14]

With the expected presence of **2** and **3**, the hydroperoxides **4** and **5** are the probable candidates for the peroxides present in the reaction solution. Peroxides were shown to be present in the irradiation solution at 5×10^{-2} *M* by reaction with cobalt(II) acetate and iodometric titration. Treatment of the reaction solution with triphenylphosphine prior to titration proved to be effective in destroying the peroxide concentration. This strongly suggests that the peroxide in solution is there as a hydro- and/or hydrogen peroxide since dialkyl peroxides react only slowly with triphenylphosphine at room temperature whereas hydroperoxides react rapidly.[15]

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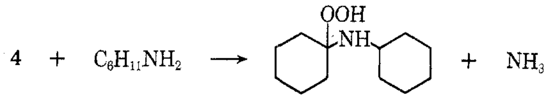
[15] L. Dulog and K. H. Burg, *Z. Anal. Chem.*, **203**, 184 (1964).

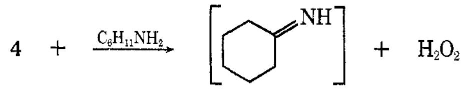
Surprisingly the imine **1** is not formed in so high yield with the triphenylphosphine treatment of the reaction mixture as without. To examine this, the hydroperoxide **4** was synthesized and reacted in cyclohexylamine in the absence of light. *N*-Cyclohexylidinecyclohexylamine was quantitatively formed with no cyclohexanone oxime. Hence **4** can be the precursor of the imine but not the oxime. When **4** is dissolved in cyclohexylamine and immediately treated with triphenylphosphine, cyclohexanone and the imine **1** are formed. The reason for the slight negative influence of triphenylphosphine on the imine yield in the reaction mixture could be due to the partial conversion of the hydroperoxide **4** into cyclohexanone rather than exclusively to the imine **1**. It must be mentioned that, though the hydroperoxide **4** has been isolated from the photosensitized oxidation of cyclohexylamine,[11] we have not been successful in isolating it from these CT-irradiated cyclohexyl-amine–oxygen solutions using the same technique. This is possibly due to its low concentration.

Since the hydroperoxide **4** is known to convert into *N*-cyclohexyl-1-hydroperoxycyclohexylamine, **6**, in cyclohexylamine–benzene, reaction 3,[11] **6** was also prepared to learn of its characteristics in our reaction solution. This peroxide, **6**, is also readily converted into the imine **1** in cyclohexylamine in the absence of light. Analogous to the reaction of **4** with triphenylphosphine, triphenylphosphine transforms **6** into a mixture of cyclohexanone, cyclohexylamine, and the imine **1**.

The mass balance of eq 4 which leads to the probable precursor, **7**, of **1** suggests that hydrogen peroxide is in the reaction solution. Hydrogen peroxide is known to form an adduct **8** with cyclohexylamine according to eq 5.[11] Despite the fact that we were unable to isolate this compound from the reaction solution, **8** was made, dissolved in cyclohexylamine, and irradiated under nitrogen. With these conditions, it was quantitatively converted into the imine **1**. Consequently it can also be a precursor to **1** but cannot be to cyclohexanone oxime.



6 (3)



7 (4)

Reactions which are consistent with available data for the irradiation of oxygen–cyclohexylamine are summarized in reactions 1–10.

$$H_2O_2 + 2C_6H_{11}NH_2 \longrightarrow \underset{\mathbf{8}}{(C_6H_{11}NH_2)_2\cdot H_2O_2} \quad (5)$$

$$2 + R\cdot \longrightarrow 7 + RH \quad (6)$$

$$7 + C_6H_{11}NH_2 \longrightarrow 1 \quad (7)$$

$$6 + C_6H_{11}NH_2 \longrightarrow 1 \quad (8)$$

$$4 + C_6H_{11}NH_2 \longrightarrow 1 + H_2O_2 \quad (9)$$

$$8 + h\nu \longrightarrow 1 \quad (10)$$

We must leave the origin of cyclohexanone oxime as a mystery with the suggestion that the *N*-hydroperoxide may have a role in its formation. Indirect evidence for oxidation on the nitrogen of the amine are (1) *N*-hydroperoxypiperidine found as a product during the radiolysis of piperidine,[16] (2) *N*,*N*-diethylhydroxylamine formed during the thermal oxidation of diethylamine,[17] and (3) triethylamine *N*-oxide formed during the irradiation of an oxygen–triethylamine solution.[18] Hence oxidation of the nitrogen clearly occurs under a variety of conditions. Though *N*-hydroxylcyclohexylamine could not be found in the cyclohexylamine–oxygen irradiation solution, it is converted into cyclohexanone oxime under these conditions.

Experimental Section

Materials.—Cyclohexylamine and cyclohexanone oxime were purchased from Aldrich Chemical Co. Cyclohexylhydroxylamine was synthesized by the method of Borch, *et al.*[19] The hydrogen peroxide–cyclohexylamine adduct and 1-hydroperoxycyclohexylamine were synthesized by the methods of Hawkins.[11,20] Cyclohexylamine (Aldrich Co.) was dried over potassium hydroxide, fractionally distilled from potassium hydroxide and sodium wire under nitrogen, and fractionally redistilled. The purity of the amine was checked by ultraviolet spectroscopy and flame-ionization gas chromatography.

Charge-Transfer Spectrum.—Purified cyclohexylamine was placed in a 1-cm quartz spectrophotometric cell fitted with ground glass stopper, nitrogen bubbled through for 2 min, the stopper put on, and the absorption spectrum recorded using a matched empty cell as a reference. The reference cell was then filled with purified amine and the nitrogen deoxygenating procedure repeated. The resulting spectrum established the base line. Oxygen was then bubbled into the amine in the sample cell for 2 min, the stopper placed on cell, and the spectrum again recorded to obtain the CT spectrum. Afterward, the base line could again be obtained by deoxygenating the sample.

Irradiation of the Oxygen-Saturated Cyclohexylamine Solution, Product Identification.—Oxygen gas was passed into magnetically stirred cyclohexylamine in an immersion well for 30 min prior to irradiation with a Hanovia 450-W medium-pressure lamp. The exit gases were passed first through a salt–ice trap and then a Dry Ice–acetone trap. The cyclohexylamine solution was irradiated for about 3 hr. Aliquots of the reaction mixture were injected into a Beckman GC-5 chromatograph equipped with two 20 ft × $^1/_8$ in., 5% KOH–20% Carbowax–Chromosorb columns[21] and a flame-ionization detector. *N*-Cyclohexylidenecyclohexylamine and cyclohexanone oxime were identified by retention times. The reaction mixture was concentrated by vacuum distillation and divided into two parts. One part was dissolved in absolute ethanol and hydrogenated with an excess 10% Pd/C. The solution was filtered, distilled, and analyzed by glpc. It showed a new peak not present in the original reaction mixture. By comparison of glpc retention time with a known sample and using spiking techniques, the new peak was found to correspond to dicyclohexylamine. Since the imine and oxime peaks were difficult to separate by preparative glpc. the remainder of the concentrated mixture was transferred in a 2 *N* hydrochloric acid solution and extracted with *n*-pentane. After washing with aqueous K_2CO_3 and drying over $MgSO_4$, the pentane solution was separated by preparative glpc into two products, cyclohexanone and cyclohexanone oxime, which were identified by comparing nmr and ir spectra with those of authentic samples.

When the reaction mixture from the photooxidation of cyclohexylamine was reacted with a 0.05 *M* cobalt(II) acetate solution,[22] the pink color of cobalt(II) ion turned to a black precipitate similar to the response of hydrogen peroxide in cyclo-

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hexylamine. The control, prepared by bubbling oxygen into cyclohexylamine for 3 hr in the absence of uv light, turned the pink Co(II) color to greenish brown. The quantity of peroxides in the irradiated oxygen-saturated cyclohexylamine was determined by the method of Vogel.[23] After the irradiated solution was treated with triphenylphosphine, the peroxide content was gone.

Anhydrous copper sulfate turned blue in contact with the oxygen-saturated, irradiated cyclohexylamine solution. By comparison of glpc retention times and spiking procedures using a 8 ft × $^1/_4$ in. Porapak column, water was identified in the reaction mixture.

Ammonia was identified by its characteristic ir spectrum[24] and its glpc retention time using a Porapak column.

Irradiation of Oxygen-Saturated Cyclohexylamine Solution, Filter Studies.—A 1-cm quartz spectrophotometric cell was placed in a holder 2.5 cm from the outside surface of the Pyrex immersion well containing a 450-W lamp. Cyclohexylamine was flushed with oxygen and irradiated for 3 hr. The concentrations of *N*-cyclohexylidenecyclohexylamine and cyclohexanone oxime were 3.81×10^{-2} and 1.12×10^{-2} *M*, respectively, as determined by glpc. Upon repeating the procedure in a Rayonet reactor with the 350-nm phosphor, low-pressure lamps, the amounts of products were reduced to one-third that obtained with Pyrex. With a 100-W tungsten lamp, no products were obtained. Upon repeating the procedure with Pyrex using nitrogen rather than oxygen, no products were observed.

Thermal and Photochemical Reaction of Cyclohexanone Oxime in Cyclohexylamine.—Cyclohexanone oxime (4 g) was dissolved in 25 ml of cyclohexylamine, and 3 ml of this solution was transferred to a 1-cm quartz spectrophotometric cell. After irradiation with a 450-W lamp under nitrogen for 3 hr at a distance of 2.5 cm from the well, no *N*-cyclohexylidenecyclohexylamine was observed. The remaining solution was heated at 45° under nitrogen for 8 hr and a trace amount of *N*-cyclohexylamine was formed.

Oxidation of *N*-Cyclohexylhydroxylamine with Hydrogen Peroxide in Ethanol.—Hydrogen peroxide (30%, 50 ml) was gradually added to a stirred solution of 0.08 *M* *N*-cyclohexylhydroxylamine in ethanol. After being stirred under nitrogen at room temperature for 3 hr, the solution was then saturated with NaCl and extracted with chloroform. The mixture was dried over magnesium sulfate, filtered, concentrated, and poured into a small amount of water to form a white solid. The compound was recrystallized (petroleum ether) and identified as cyclohexanone oxime, mp 85–86° (lit.[25] mp 89–90°) and ir spectrum.

Photolysis of Hydrogen Peroxide–Cyclohexylamine Adduct in Cyclohexylamine.—Cyclohexylamine (3 ml) containing 0.162 mm of the hydrogen peroxide–cyclohexylamine adduct was irradiated in a 1-cm cell with the 450-W lamp in a Pyrex well. After 2.5 hr, 0.165 mm of *N*-cyclohexylidenecyclohexylamine was formed (glpc).

Thermal Decomposition of 1-Hydroperoxycyclohexylamine in Cyclohexylamine.—A 0.0394 *M* cyclohexylamine solution of 1-hydroperoxycyclohexylamine was stirred under nitrogen at 45° for 1 hr. *N*-Cyclohexylidenecyclohexylamine (0.0410 *M*) was produced (glpc).

Decomposition of *N*-Cyclohexyl-1-hydroperoxycyclohexylamine in Cyclohexylamine.—*N*-Cyclohexyl-1-hydroperoxycyclohexylamine (1.0 g) was added to 15 ml of cyclohexylamine, and the solution was stirred under nitrogen for 1 hr. *N*-Cyclohexylidenecyclohexylamine was found and isolated by gas chromatography. The product was identified by glpc retention times and comparing its ir spectrum with an authentic sample.

Registry No.—**1**, 10468-40-3; **4**, 24075-24-9; **6**, 2808-61-9; **8**, 37816-86-7; cyclohexylamine, 108-91-8; cyclohexanone oxime, 100-64-1; cyclohexylamine–oxygen adduct (1:1), 37817-06-4.

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The Effect of Biphenyl Geometry and Substituents on the Multiplicity and Efficiency of the Photocyclization Reactions of 2-Substituted Biphenyls

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The direct and sensitized photochemistry of the unsubstituted, 2′-, 3′-, 4′-, 4-, and 5-methoxy-2-biphenylyl isocyanates are reported. Direct excitation of these compounds yields carbazoles and 6(5*H*)-phenanthridinones. The carbazole arises from decomposition of the isocyanate in its singlet state to a nitrene which undergoes insertion into an aromatic C–H bond. The photocyclization of the isocyanates to 6(5*H*)-phenanthridinones occurs most efficiently *via* acetone sensitization in what is formally a nonoxidative cyclization to an aromatic ring. In contrast to the insensitivity of the singlet state decarbonylation to ring substituent, the photosensitized cyclization process is enhanced by a 4′-, 4-, or 5-methoxy group and dramatically retarded by a 2′- or 3′-methoxy substituent. The related acetone-sensitized photocyclizations of *N*-(2-propylidene)-2-aminobiphenyl and its 2′-, 3′-, and 4′-methoxy derivatives to the corresponding 6,6-dimethyl-5,6-dihydrophenanthridines were also studied. In this series the 3′-methoxy substituent markedly retarded the photocyclization reaction. In contrast to the photocyclization reactions of the isocyanate and imine groups, the imino ether linkage did not undergo the photocyclization reaction. The mechanism of these processes and the low intersystem crossing efficiency in these 2-substituted biphenyls is noted and discussed.

Our interest in the influence of ground- and excited-state geometry on photochemical reactivity[2] led us several years ago to initiate work on the photochemistry of biphenyl systems.[3] Aside from the consequences of markedly different equilibrium geometries of

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[1] (a) Alfred P. Sloan Foundation Fellow, 1971–1973; (b) Camille and Henry Dreyfus Teacher Scholar, 1972–1977.

[2] For a discussion of these factors in diene photochemistry, see J. S. Swenton, J. A. Hyatt, T. J. Walker, and A. L. Crumrine, *J. Amer. Chem. Soc.*, **93**, 4808 (1971); **92**, 1406 (1970).

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