Unusual Photochemistry of 4-Chlorobiphenyl in Water

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The photochemistry of 4-chlorobiphenyl in deoxygenated, doubly distilled water has been studied. When the reaction is carried to completion, equimolar amounts of 3- and 4-hydroxybiphenyl are produced; no biphenyl is formed, however. Experiments proved that arenium ions, arynes, and addition–elimination mechanisms are not involved in the formation of 3-hydroxybiphenyl. A plausible alternative is that 4-chlorobiphenyl isomerizes to the 3-isomer which then undergoes photohydrolysis. This was shown to be the case by capillary gas chromatography. The unique properties of water appear to be responsible for the unusual behavior of 4-chlorobiphenyl in water.

The photochemistry of chloroaromatic compounds has been studied extensively,[1-3] in part because of its relevance to the degradation of pollutants such as PCBs and dioxin by sunlight in the aquatic environment.[4-7] When the compounds are photolyzed in hydrocarbon[2b,c,f,g,3c] and mixed water organic solvents,[7i] the chemistry is initiated by homolytic cleavage of the carbon–chlorine bond to generate an aryl radical which then abstracts a hydrogen atom from the organic component of the solvent, whereas in alcohols, both the homolytic reaction and ionic/heterolytic processess—to generate aryl ethers—compete (eq 1).[3d,g,i,j]

$$\mathrm{ArH} + \mathrm{ArOR} \xleftarrow[\mathrm{ROH}]{h\nu} \mathrm{ArCl} \overset{h\nu}{\rightleftharpoons} \mathrm{Cl}\cdot + \mathrm{Ar}\cdot \xrightarrow{\mathrm{RH}} \mathrm{ArH} \qquad (1)$$

Even though aryl chlorides are soluble in alcohols, alkanes, and CH_3CN/H_2O, these solvents are not good models for water. Water, in addition to its nucleophilic character and large dielect constant, has a very large hydrogen–oxygen bond strength.[8] This means that the abstraction of a hydrogen atom from water by an aryl radical will be inefficient. The reaction of the phenyl radical with H_2O, for example, to form benzene and a hydroxyl radical is endothermic in the gas phase (eq 2).[9] As a result of this,

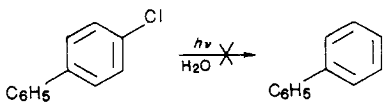
$$C_6H_5\cdot + H_2O \rightarrow C_6H_6 + HO\cdot \qquad (2)$$

ionic/heterolytic and other reactions will then become competitive or dominant. Nonetheless, water is not an ideal solvent for hydrophobic compounds but, with the advent of sensitive analytical methodology, the study of the photochemistry of poorly soluble chloroaromatics at very low concentration in water becomes feasible. We wish to report that indeed the photochemistry of 4-chlorobiphenyl is significantly altered when performed in water.

Results

Because HCl is generated during the photolysis of 4-chlorobiphenyl (1), a model for PCBs, in H_2O, it was possible to monitor the reaction by in situ pH measurements using the device shown in Figure 1. This device insured that the solution was continually circulated and exposed to both the light and glass electrode but that the electrode was not exposed to the ultraviolet radiation or otherwise aberrant pH readings were obtained. Apparently a thin film of 1 is formed on the electrode. When the electrode is exposed to light, the film yields high local concentrations of HCl on the electrode surface.

Photolysis of 10^{-5}–10^{-6} M 4-chlorobiphenyl (1) in deoxygenated, doubly distilled water at λ >300 nm (Pyrex filter) was approximately first order in 1 as expected for a dilute solution.[10] If the reaction were run long enough, about 1 equiv of HCl was produced. The reaction also yielded what appeared to be 4-hydroxybiphenyl (2), exclusively, by HPLC analysis; no biphenyl (3) was detected (eq 3). That no biphenyl is produced in this reaction was



1 3

(3)

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(8) *Handbook of Chemistry and Physics*, 63rd ed.; Weust, R. C., Ed.; CRC Press: Boca Raton, FL, 1982; p F-197.

(9) Benson, S. W. *Thermochemical Calculations*, 2nd ed.; Wiley: New York, 1976.

(10) For the photolysis of a substrate (S) at ordinary concentrations the disappearance of S is zero order in substrate and first order in the rate at which the light is adsorbed by the substrate (Ia). When [S] is very low, Ia ∝ [S]. Thus the rate of disappearance of S is first order in S. See ref 4.

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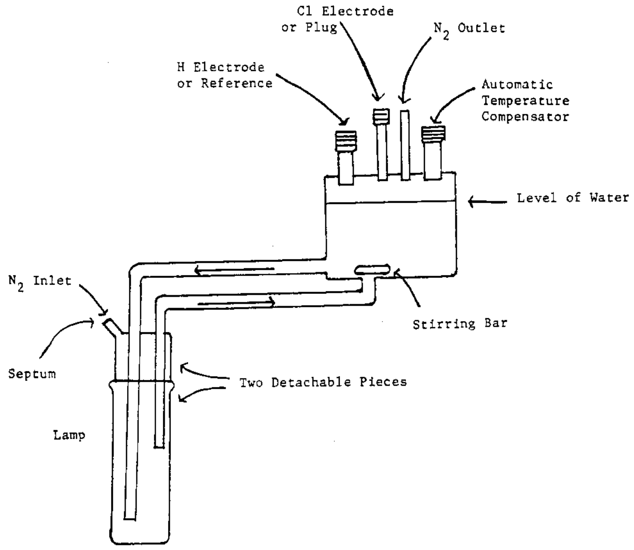
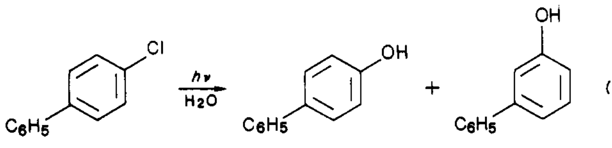


Figure 1. Apparatus used to measure pH during the photolysis of 4-chlorobiphenyl in water. After filling with water, the lower left vessel did not leak. The arrows indicate the direction of flow when the solution in the upper right vessel is stirred.

demonstrated further by photolysis of ^{14}C-labeled 4-chlorobiphenyl, isolation of any labeled biphenyl by either (1) isotopic dilution with unlabeled biphenyl and recrystallization[11] or (2) collection of the appropriate fractions off the HPLC column, and analysis of both by liquid scintillation counting. Had one biphenyl molecule been generated for every 1 000 000 molecules of 4-chlorobiphenyl that reacted, it would have been detected in these experiments.

Surprisingly, the photoproduct turned out not to be 4-hydroxybiphenyl but an inseparable 1:1 mixture of 3- (4) and 4-hydroxybiphenyl (2), (eq 4). This was proven in

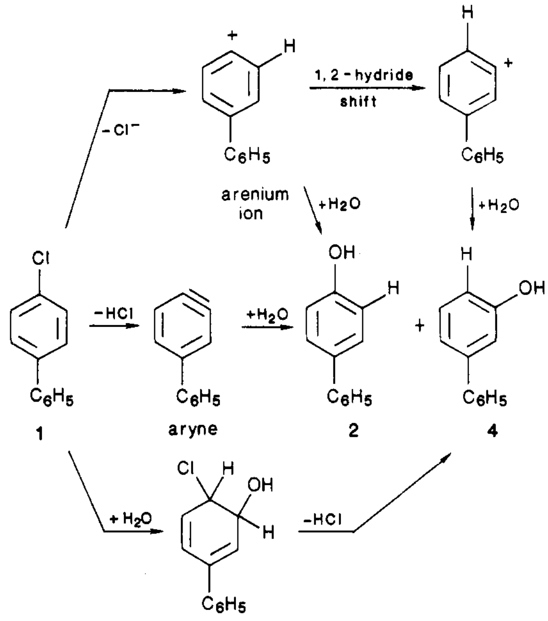


1 2 3 (4)

two ways. First, analysis of the product mixture, obtained from the photolysis of the unlabeled precursor, by capillary gas chromatography of the trichloroacetate derivative(s)[12] revealed the presence of equimolar amounts of both isomers. Second, analysis of the product mixture, obtained from the photolysis of ^{14}C-labeled 4-chlorobiphenyl, by isotopic dilution with unlabeled 3- and 4-hydroxybiphenyl also revealed the presence of both phenols in equal amounts. In addition, the gas chromatography experiment also revealed that 2-hydroxybiphenyl is not produced during the photolysis of 1 in water.

The 4-hydroxybiphenyl (2) clearly arose by one of any number of ionic mechanisms.[1,3a,d,g-k] How the 3-hydroxybiphenyl (4) arose was not immediately apparent. Even though photoinitiated nucleophilic aromatic substitution is a common reaction,[13] there are no examples to date in the literature where the nucleophile and nucleofuge appear to involve different carbon centers. As shown in Scheme I, reactions involving an aryne or arenium ion could yield 3-hydroxybiphenyl (4). If the reaction involved an aryne, photolysis of 1 in D_2O will incorporate one deuterium onto one of the benzene rings of both 2 and 4. When 1 was photolyzed in deoxygenated D_2O, mass spectral analysis of the phenols revealed that 94% were undeuterated and 6% monodeuterated. Clearly the aryne mechanism is not correct. The 6% of monodeuteration apparently arose by secondary photolysis of the undeuterated phenols. The results from the D_2O experiment also rule out an addition–elimination mechanism (Scheme I) because one deuterium will be incorporated onto one of the benzene rings of 4. Furthermore, control experiments demonstrated that the 3-hydroxybiphenyl does not arise by photoisomerization of 4-hydroxybiphenyl.[14]

Scheme I



The arenium ion mechanism involves the phenylphenylinium ion which either reacts with water to yield 4-hydroxybiphenyl or competitively undergoes a 1,2-hydride shift to give a new aryl cation which reacts with water to yield 3-hydroxybiphenyl (Scheme I). Even though the results for the photohydrolysis in D_2O are consistent with this pathway, it cannot be true. Although 1,2-hydride shifts of aryl cations occur in the gas phase, this reaction has never been documented in solution, even when the aryl cation is generated in very exothermic reactions involving β decay.[15]

Because none of the above mechanisms operates, the likely explanation for the results appeared to be that 4-chlorobiphenyl in part photoisomerizes[16] to 3-chlorobiphenyl (5) which then reacts with water in the normal way (eq 5).[17] Using the recently reported method of Mullin et al.,[18] it has been possible to separate 3- and 4-chloro-

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[11] For a leading reference on the application of isotopic dilution in photochemistry, see: Zimmerman, H. E.; Carpenter, C. W.; Weber, A. M. *J. Am. Chem. Soc.* **1985**, *107*, 1073. See also: Marshall, R. A. G. *J. Chem. Educ.* **1976**, *53*, 321. Pope, C. G. *Ibid.* **1975**, *52*, 343.

[12] Argauer, R. J. *Anal. Chem.* **1968**, *40*, 122.

[13] (a) Rossi, R. A. *Acc. Chem. Res.* **1982**, *15*, 164 and references cited therein. (b) Cornelisse, J.; Havinga, E. *Chem. Rev.* **1975**, *75*, 353. (c) Havinga, E.; Cornelisse, J. *Pure. Appl. Chem.* **1976**, *47*, 1. (d) Matsuura, T.; Omura, K. *Synthesis* **1974**, 173.

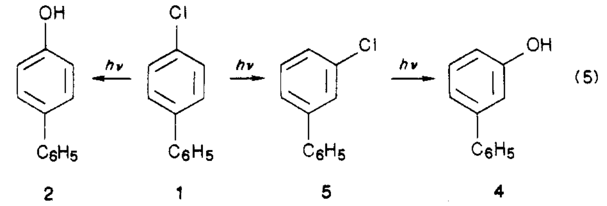
[14] It would have been mechanistically significant to know the ratio of 2 to 4 as a function of time. Unfortunately, the phenols are photolabile (yielding unknown, water soluble products) under the reaction conditions. Thus a meaningful ratio cannot be obtained.

[15] Angelini, G.; Fornarini, S.; Speranza, M. *J. Am. Chem. Soc.* **1982**, *104*, 4773.

[16] Methyl-substituted biphenyls are known to photoisomerize in toluene. Abromovitch, R. A.; Takaya, T. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1806.

[17] Photolysis of 3-chlorobiphenyl in water does generate 3-hydroxybiphenyl.

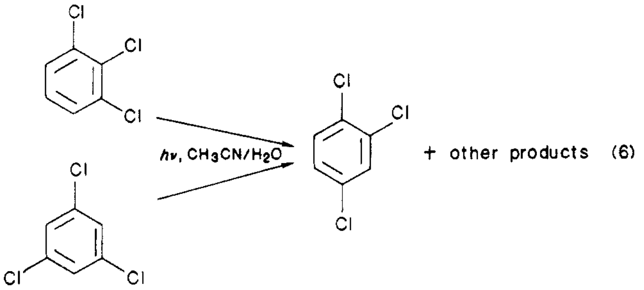
[18] Mullin, M. D.; Pochini, C. M.; McCrindle, S.; Romkes, M.; Safe, S. H.; Safe, L. M. *Environ. Sci. Technol.* **1984**, *18*, 468.



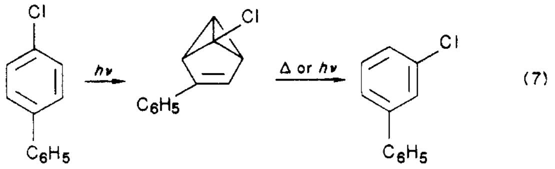
biphenyl by capillary gas chromatography and prove that the 3-chloro isomer is indeed formed during the photolysis of 4-chlorobiphenyl.[19]

Discussion

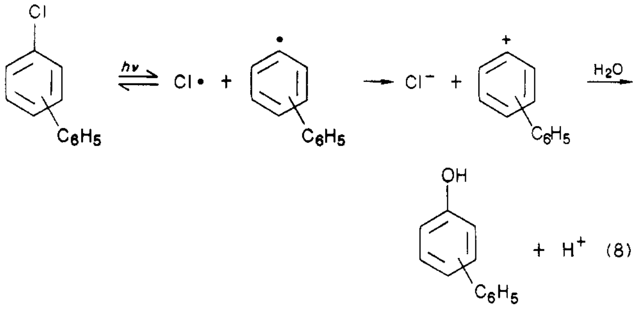
The photoisomerization of 4-chlorobiphenyl into 3-chlorobiphenyl is an unusual reaction. Only one other halogenated arene is known to behave similarly. Hutzinger and co-workers have shown[20] that photolysis of 1,2,3-trichlorobenzene and 1,3,5-trichlorobenzene yielded in small part 1,2,4-trichlorobenzene in 1:1 CH_3CN–H_2O (eq 6). In methanol, these two substrates yielded *p*-dichlorobenzene in low yield in addition to other products.



How does the isomerization of 4-chlorobiphenyl occur? This question cannot be answered with the data presently available, but a plausible mechanism is one in which 4-chlorobiphenyl is first converted into a benzvalene which then, either thermally or photochemically, isomerizes to the 3-chloro isomer (eq 7).[21-23] There is precedence for this sequence of steps in the photochemical behavior of benzene.[22] Additional work will be required to validate this sequence of steps in the photochemistry of 4-chlorobiphenyl in water.



The mechanism for the photohydrolysis of the chlorobiphenyls is on firmer ground. Because the photochemically induced homolytic cleavage of the carbon–chlorine bond in aryl halides occurs commonly, it is reasonable to believe that the same reaction occurs initially when 3- and 4-chlorobiphenyl are photolyzed in water. Because the aryl radical (and chlorine atom) cannot abstract a hydrogen atom efficiently from water, the two radicals either combine to regenerate the starting material or undergo electron transfer to give Cl^- and an aryl cation. The electron-transfer reaction will be facilitated by water's unusually large dielectric constant. Once the aryl cation is formed, it will react rapidly to form the phenol (eq 8). This reaction scheme has been well-documented in the work of Kropp on the photochemistry of alkyl and vinyl halides.[24]



Why has the photoisomerization of a chloroaromatic with one exception not been observed previously? Even in those few cases in which the reaction has been studied in water, the interest has commonly been on the disappearance of reactant and not in product identification.[25] In water, as mentioned previously, homolytic reactions are suppressed, permitting ionic and other types of reactions to become competitive or dominant. Because of the hydrophobic nature of most organic compounds, their photochemistry in water can only be studied at very low concentration. Low concentrations of substrates preclude or at least inhibit bimolecular electon-transfer reactions between the excited and ground state of the substrates; electron transfer has figured prominently in recent mechanistic schemes for photochemically induced nucleophilic aromatic substitution of aryl chlorides.[1,3d,k] If certain mechanisms are suppressed because of low substrate concentration, again other processes will begin to operate.

Whatever the ultimate explanation for the unusual chemistry observed here, it is clear that, because of water's high dielectric constant and HO bond strength, photoreactions in this medium may be significantly different than those in other solvents. If the photoisomerization of chloroaromatics in water is general, moreover, it could have important environmental consequences because the transposition of chlorine could transform a benign compound into a toxic one.

Experimental Section

Sample Preparation. Aqueous solutions of 4-chlorobiphenyl (Ultra Scientific) were prepared by adding a known amount of 4-chlorobiphenyl to doubly distilled water and stirring the solution magnetically for about 2 days. The mixture was then filtered through sintered glass before its introduction into the photolysis tube. Samples were also prepared by adding the reactant directly to the photolysis tube containing doubly distilled water. It is important not to use glassware cleaned with cleaning solution because residual chromium ions on the surface of the glass oxidize the substrate competitively with its dissolution.

In preparing solutions of ^{14}C-labeled 4-chlorobiphenyl, the compound itself was dissolved in a very small amount acetone. The desired amount was measured by syringe into the photolysis flask. Ring-uniformly labeled [^{14}C]-4-chlorobiphenyl was obtained from Pathfinder Laboratories. It was greater than 98% pure and

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[19] If one follows the reaction as a function of time, the ratio of 5:1 increase from 0 at the beginning of the reaction to approximately 1 after 60 min.

[20] Choudry, G. C.; Roof, A. A. M.; Hutzinger, O. *Tetrahedron Lett.* **1979**, 2059.

[21] The reaction could also proceed through a prismane, although a Dewar benzene would almost certainly be a precursor to the prismane.[22]

[22] Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; pp 499–503.

[23] It is also conceivable that there are no intermediates in the photoisomerization. These so called adiabatic photoreactions are not very common and almost always involve bond breaking. See ref 22, pp 608–609, for some examples.

[24] (a) Kropp, P.; Poindexter, G. S.; Pienta, N. J.; Hamilton, D. C. *J. Am. Chem. Soc.* **1976**, *98* 8135. (b) McNeely, S. A.; Kropp, P. J. *Ibid.* **1976**, *98*, 4319.

[25] See, for example: Boule, P.; Tissot, A.; Lemaire, P. *Chemosphere* **1985**, *14*, 1789.

had a specific activity of 9.86 mCi/mmol; it also did not contain 3-chlorobiphenyl. Typically, a concentration of approximately 1.25×10^{-3} mg/L or 5.65×10^{4} cpm per mL was prepared. There was no difference in photochemical behavior of samples prepared by using acetone and those added directly to the water.

Photochemistry. Sample irradiation was accomplished by exposure to a 450-W water-cooled, medium pressure Hanovia mercury lamp for a set time between 0 and 100 h. A Pyrex sleeve, which cuts off transmission below approximately 300 nm, was positioned around the lamp and both were fitted into a quartz well for cooling. The solutions were purged with prepurified N_2 (MG Scientific) that had been deoxygenated according to the procedure of Meites and Meites.[26]

After photolysis, the photoproducts were removed from the aqueous layer by extracting with four portions of ethyl acetate equal in volume to the aqueous layer. These were dried over magnesium sulfate and filtered, and the solvent was removed via rotary evaporation. An appropriate amount between 1 and 3 mL of methanol or ethyl acetate was reintroduced to the photoproducts in preparation for analysis.

Analytical Techniques. The samples were analyzed on a Perkin-Elmer Series 2 liquid chromatograph by using a C 18/10 0.46 × 25 cm LC column and a Perkin-Elmer LC-75 spectrophotometric detector. The following conditions were set as standards, unless specified otherwise: solvent ratio, 75% methanol–25% water; flow rate, 2 mL/min; detector wavelength, 247 nm. In addition, a Hewlett-Packard Model 3390A integrator–recorder was used.

For some experiments using ^{14}C-labled 4-chlorobiphenyl, fractions were collected by using a solvent gradient of 60–75% methanol which increased at a rate of 1% per minute. Fractions were collected at 1-min intervals by positioning a scintillation vial beneath the HPLC output. At the end of 1 min, another vial was put into the same position for the same time period. At the end of the run, 15 mL of scintillation cocktail (to each 1 L of dioxane was added 8 g of omnifluor which is a mixture of 98% PPO plus 2% bis-MSB) was pipetted into each vial containing the collected 2 mL. These vials were allowed to equilibrate overnight prior to counting.

These radiolabeled fractions were analyzed by using a Tracor Analytic Model 6892 liquid scintillation system which was programmed to count each vial for 2 min. The level of channel A was set to 90–620 while that for channel B was 350–620. Channel A levels were considered for data analysis. Reliable data are considered to be approximately four times background or about 300 counts per minute (cpm).

In order to separate the *m*- and *p*-phenylphenols for analysis by gas chromatography (GC), chloroacetate derivates were prepared by using the procedure of Argauer.[12] Following this procedure, 10 μL of the phenylphenol in benzene (approximate concentrations of 1 μg/μL) was introduced into a flask to which was added 15 mL of 0.25 N NaOH and 10 mL of reagent (1 g of chloroacetic anhydride per 200 mL of benzene). The flask was shaken for exactly 2 min on a mechanical shaker. The benzene and water layers readily separated and so 5-μL aliquots were removed directly from the benzene layer for injection into the gas chromatograph.

A Perkin-Elmer Model 3920 gas chromatograph was equipped with a capillary column containing dimethyl silicone polymer maintained at 140 °C. The injection heater was at 220 °C while the interface was at 180 °C. Nitrogen carrier gas was used. The electron capture detector was heated to 350 °C. Under these conditions retention time had to be sacrificed for better separation; therefore, the 3-hydroxybiphenyl derivative had an approximate retention time of 40.7 min while that of the 4-hydroxybiphenyl derivative was 44.5 min.

In order to separate 3- and 4-chlorobiphenyl, the procedure of Mullin et al.[18] was modified for use. The analysis was performed on a Varian 3700 gas chromatograph with ^{63}Ni electron capture detector using a 30-m fused silica gel capillary column (0.25-nm inner diameter). The oven was programmed to remain at 110 °C for 2 min after injection and then to increase at 2°/min until 160 °C was reached. The injector was at 270 °C and the detector at 330 °C. N_2 was used as the carrier gas at a flow rate of 2 mL/min with 30 psi flow through the detector at 30 mL/min. A 2–4-μL sample (in benzene) with splitless injection was used.

pH Measurements. Reactions in which pH was studied as a function of time were performed in a circulating photolysis apparatus in Figure 1. This apparatus allowed the pH to be measured with no interruption of the light. The combination electrode, Ross Model 81-02, and automatic temperature compensator, Fisher Model 13-636-17, were fitted into the upper right portion (through Ace Glass threaded connectors) and did not come into contact with the lamp. The lower left side was clamped next to the lamp and both were covered with aluminum foil during the irradiation. When desired, nitrogen was introduced as indicated. The magnetic stirrer kept the solution constantly circulating. A Fisher Accumet Model 810 pH meter was used for the measurements. Controls showed that water was deoxygenated in this device and remained so throughout a run.

Isotopic Dilution Experiments. 1. Biphenyl. A sample of ^{14}C-labeled 4-chlorobiphenyl (specific activity; 9.86 mCi/mmol; 5.50×10^{4} cpm/μL in acetone) in water was prepared, irradiated, and worked up as previously described. A portion of the product was added to 57.0 mg of unlabeled biphenyl. After recrystallizations from 3:1 CCl_4/toluene (to constant melting point), a 7.65-mg sample was dissolved in 1 mL of acetone and 1 mL of water in a scintillation vial to which was added the scintillation cocktail. The final count of 268 cpm was considered to be within background readings. As little as 5.33×10^{-9} g of labeled biphenyl would have been detected in this experiment.

2. Phenylphenols. A sample of 4-chlorobiphenyl (^{14}C ring labeled) in water was irradiated and worked up as previous described. During HPLC analysis, the eluent having the retention time of phenylphenols was collected. Meanwhile, 3- and 4-hydroxybiphenyl were separately purified by recrystallization in methanol. The procedure outlined for biphenyl was followed in this case. After several recrystallizations of 3-hydroxybiphenyl plus radioactive eluent and likewise 4-hydroxybiphenyl plus eluent, the final scintillation counting yielded an average of 44 676 cpm for 3-hydroxybiphenyl and an average of 46 858 cpm for 4-hydroxybiphenyl.

Photolyses in D_2O. 1. 4-Chlorobiphenyl. 4-Chlorobiphenyl was photolyzed in degassed D_2O as previously described. After workup and separation by HPLC, the resultant hydroxybiphenyl fraction was subjected to mass spectrometry at 25 eV (Hewlett-Packard Model GC quadrupole mass spectrometer with HP 3954 data system) and yielded the following [*m*/*e*, (abundance)]: 170 (100), 171 (19.3), 172 (1.5). Standard analysis[27] yields 94% d_0 and 6% d_1.

2. 3-Hydroxybiphenyl. Photolysis of 3-hydroxybiphenyl in D_2O was performed exactly as that of 4-chlorobiphenyl. After workup, the 3-hydroxybiphenyl was subjected to mass spectrometry and yielded the following [*m*/*e*, (abundance)]: 170 (100), 171 (21.6), 172 (2.2). This corresponds to 92% d_0 and 8% d_1.

3. 4-Hydroxybiphenyl. Results similar to 3-hydroxybiphenyl were observed.

Control Experiments. 1. 4-Hydroxybiphenyl. After photolysis in degassed H_2O and workup, the photolysis mixture was derivatized with trichloroacetic anhydride according Argauer.[12] Analysis by capillary GC revealed no 3-hydroxybiphenyl.

2. 3-Hydroxybiphenyl. The photolysis and analysis were performed exactly as reported for 4-hydroxybiphenyl. No 4-hydroxybiphenyl was detected.

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Registry No. 4-Chlorobiphenyl, 2051-62-9; 3-hydroxybiphenyl, 580-51-8; 4-hydroxybiphenyl, 92-69-3.

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