The Photochemistry of Polyhaloarenes XIII.
The Photohydrodehalogenation of 3,4-Dibromobiphenyl

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Abstract: Irradiation of 3,4-dibromobiphenyl (**BpBr$_2$**) in acetonitrile resulted in the formation of 4-bromobiphenyl (**BpBr**) and 3-bromobiphenyl (**3-BpBr**) in a ratio of 7.6 ± 0.1 up to 22% conversion of starting material. The dependence of the reciprocal of the quantum yield (1/Φ) upon 1/**BpBr$_2$** is linear. Reduction of **BpBr$_2$** with lithium di-*tert*-butylbiphenylide generates a 3.6:1.0 ratio of **BpBr** to **3-BpBr**, while photohyrodebromination of **BpBr$_2$** in the presence of triethylamine produces a similar ratio of 1.8:1.0. Product determining radical stability was assessed by radical debromination of **BpBr$_2$** using Ph$_3$SnH in THF, which resulted in a **BpBr:3-BpBr** ratio of 1.5:1.0. AM1 calculations on the product determining radicals provide the basis for rationalization of products via excimer and radical anion intermediates. Copyright © 1996 Elsevier Science Ltd

Our interest in the photochemistry of polybromoarenes is stimulated by the importance of these substrates as environmental contaminants,[1] their absorption of light in the sunlight range[2] and by the opportunity to test mechanistic features for these polybromobiphenyls against those we have proposed earlier for polychlorobenzenes.[3] Our earlier studies on the photodechlorination of aryl chlorides have revealed that the chemical outcome is very sensitive to mechanism. For example, in the photohydrodehalogenation of penta, tetra and tri-chlorobenzenes in the presence of an electron transfer agent, the regiochemistry of dehalogenation of the haloarene radical anion generated is significantly different from the regiochemistry observed during the direct irradiation of these halides without electron transfer agent. The radical anion loses a chloride ion to generate a phenyl radical species which abstracts hydrogen from solvent to form product.[4] This is illustrated for chlorobenzene (Scheme I).
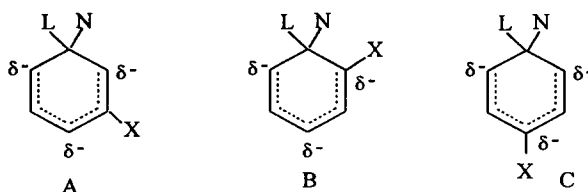
Scheme I
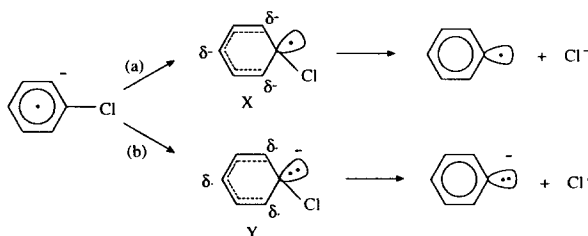
Negative chemical ionization mass spectral studies on polychlorobenzenes have shown that up to pentachlorobenzene, path (a) is preferred over path (b). The latter is dominant only for hexachlorobenzene. The difference in the regiochemistries has been explained on the basis of the relative stabilities of the transition states involved during this loss of chloride ion along path (a) (Scheme I). The transition state for this reaction route (**X**) may possess the character of a delocalized anion with a bent localized radical center. The reactivity pattern has been rationalized by the suggestion that the stability of the transition state is related to that of the analogous

Wheland intermediate for S_NAr reactions (Scheme II), which is decreased by placement of a halogen on a carbon with a partial negative charge, and the most stable intermediate (or transition state) is the one which possesses the minimum value for the sum of the charge densities for carbon substituted with halogen in the HOMO (stability order A>B>C).[4] This explanation, known as the I_π effect, has been useful in rationalizing orientation in aromatic nucleophilic substitution[5] and correctly predicts the regiochemistries in the case of photohydrodechlorination of polychlorobenzenes.

Scheme II

Based on this approach, it should be possible to predict the relative ease of formation of the two possible isomers from the photohydrodebromination of 3, 4-dibromobiphenyl (**BpBr₂**) via a radical anion intermediacy as shown in Scheme III. A consideration of the two possible transition states **E** and **D** reveals that **E** should have a smaller negative charge placed on the carbon with bromine substituted due to the extended charge delocalization through the adjacent phenyl ring and is therefore expected to be more stable than the related transition state **D**. This leads to the prediction that 3-bromobiphenyl (**3-BpBr**) will be formed in greater amounts. In addition, it seemed reasonable that the extent of formation of **3-BpBr** would indicate the degree of polarization of the excimer species involved in the direct irradiations, if indeed, such a species is supported by the dependence of quantum yield upon substrate concentration.

Scheme III
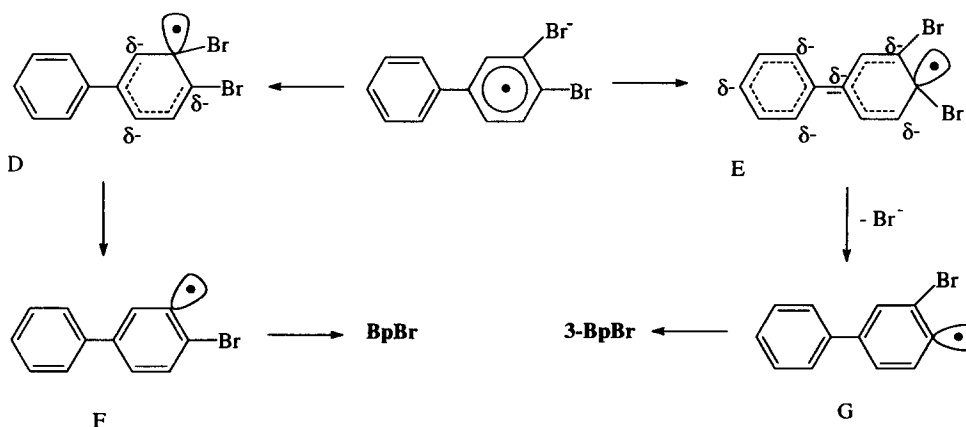
Results and Discussion

Irradiation of **BpBr₂** in acetonitrile resulted in the formation of 4-bromobiphenyl (**BpBr**) as the major product at up to 40 min irradiation and 22% conversion of the starting material, generating a ratio of **BpBr / 3-BpBr** of 7.6 ± 0.1 (Table 1). Kinetic studies were used to elucidate the mechanism of photodebromination. Dependence of the quantum yield of debromination on the concentration of **BpBr₂** in acetonitrile was studied at 300 nm. The degassed samples were irradiated for 20 min in order to avoid secondary product formation. The steady state assumption for the mechanism of Scheme IV, viewed as a likely hypothesis, leads to the quantum yield dependence of eq 1 and 2. Thus, the reciprocal of the quantum yield of product formation for Scheme IV ($1/\Phi_{prod}$) is linear with respect to $1/(\mathbf{BpBr_2})$ (eq 2). In harmony with this, a plot of $1/\Phi_{prod}$ versus the inverse of concentration of **BpBr₂** is linear with a correlation coefficient of 0.993 and a positive slope (Figure 1). Thus, a mechanism similar to that of photohydrodebromination of **BpBr**[6] is operative during the analogous debromination of **BpBr₂**. This fits with the assumption that there is only one reactive spin state which is the triplet state, since **BpBr** has Φ_{isc} close to one (0.98 ± 0.05)[6] and an extra bromine will increase the efficiency of intersystem crossing due to the heavy atom effect.[7] Even though the concentration dependence study suggests the involvement of excimer species during the debromination of **BpBr₂**, the formation of **BpBr** as the major product does not agree with the prediction based on the I_π effect on the fragmentation of the radical anion intermediate, which would represent one component of the excimer, if charge transfer is extensive. Therefore, it seemed reasonable to reinforce our view of probable fragmentation pathway for cleavage of the radical anion of **BpBr₂** by generating it in a nonphotochemical reduction process.

Table 1. Product Formation Resulting from the Irradiation of **BpBr₂** in Acetonitrile (300 nm).

time (min)	percent Reaction[a]	BpBr/3BpBr[a]
1	1.5 ± 0.1	7.7 ± 0.5
2.5	2.0 ± 0.3	7.9 ± 0.4
5	6.7 ± 0.9	7.5 ± 0.2
10	14.0 ± 4.0	7.5 ± 0.0
20	16.2 ± 0.1	7.3 ± 0.1
40	22.2 ± 0.5	7.4 ± 0.1

[a] Standard deviation of the mean of three runs

Lithium di-*tert*-butylbiphenyl (**LiDBB**)[8] was used for the reduction of **BpBr₂**. **LiDBB** was chosen due the fact that coupling reactions of the radical, generated subsequent to the electron transfer with **LiDBB**, with reagent are held to a minimum. A possible side reaction in the case of lithium naphthalene as a reducing agent is the coupling of the resulting aryl radical with the naphthalene radical anion.

Scheme IV
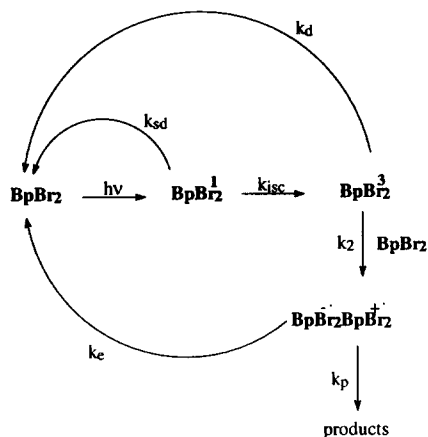
$$\Phi_{prod} = \frac{k_2 FG[BpBr_2]}{k_d + k_2[BpBr_2]} \quad (1)$$

$$\frac{1}{\Phi_{prod}} = \frac{1}{F \cdot G} + \frac{k_d}{k_2 FG[BpBr_2]} \quad (2)$$

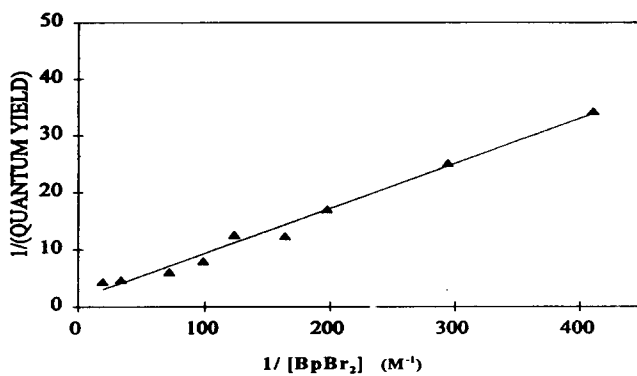$$F = \frac{k_p}{k_p + k_e} \qquad G = \frac{k_{isc}}{k_{isc} + k_{sd}}$$

Figure 1.
Plot of the inverse of quantum yield of photodebromination of **BpBr$_2$**
in acetronitrile versus the inverse of the concentration of **BpBr$_2$**.

The steric bulkiness of two *tert*-butyl groups prohibits this side reaction from occurring. The reduction of **BpBr$_2$** with one equivalent of **LiDBB** gave **BpBr** as a major product: a 1 to 3.6 ratio of **3-BpBr** against **BpBr** for less than 1 % of starting material disappearance (Scheme V). The reaction was quenched quickly so that there was no secondary reaction to generate biphenyl from the resulting monobromobiphenyls.

Scheme V

4-Bromobiphenyl   :   3-Bromobiphenyl

3.6   :   1
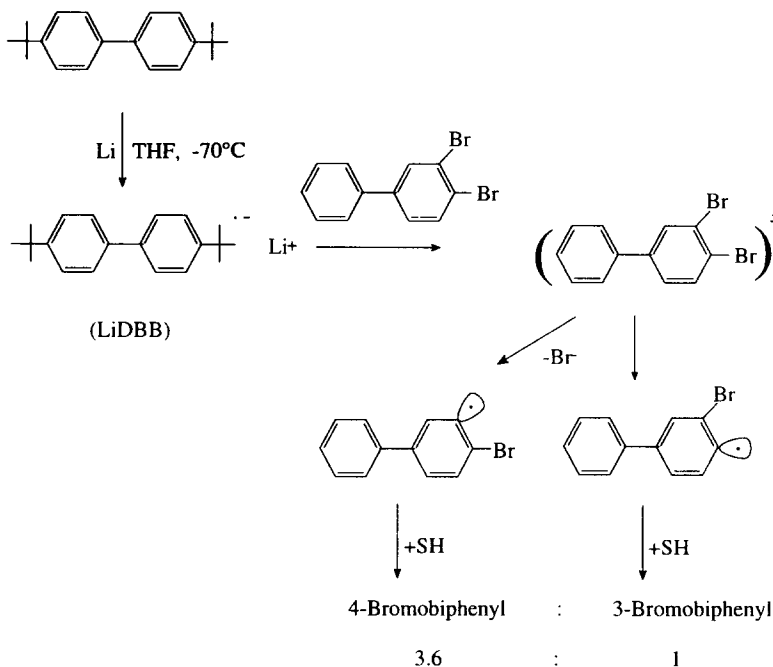
The prediction based on Scheme III suggests that the pathway leading to product via the more stable transition state **E** should be dominant over that for the less stable **D** and consequently **3-BpBr** should be the major product. Contrary to this prediction, **BpBr** is the major product and the results are similar instead to those obtained from the photochemical reaction. It is possible that the difference in the predicted and observed results of chemical reduction of **BpBr₂** may be reflecting the difference in the stabilities of the resulting radical species (**F** and **G**) instead of the model radical anion fragmentation transition states (**D** and **E**). The difference in the stabilities of the radical species, **F** and **G**, was tested by induced radical debromination using Ph₃SnH in THF[9] and the result is shown in Scheme VI. This result indicates that the radical **F** is probably more stable than **G**, which would lead to the formation of **BpBr** as the major product. As before, the reaction was quenched quickly to prevent any secondary reaction from the resulting monobromobiphenyls. In using this competition to estimate the relative stabilities of radicals **F** and **G**, it must be appreciated that there is a degree of heterolytic character in the transition state for bromine abstraction by the tin radical.[9]

Our earlier study of the photohydrodebromination of **BpBr**, in the presence of triethylamine, provided evidence supporting the derivation of product via an exciplex formed by electron transfer to give a solvent separated radical anion species of **BpBr**. Irradiation of **BpBr₂** in the presence of triethylamine was expected to behave similarly. Photodebromination in the presence of triethylamine revealed a linear relationship for 1/φ versus 1/ (triethylamine) (r = 0.993). Thus photohydrodebromination is enhanced in the presence of triethylamine and the formation of exciplex is supported. The ratio of **BpBr** to **3-BpBr** is weakly dependent upon extent of conversion. Extrapolation to 0% conversion provides a **BpBr / 3-BpBr** ratio of 1.81 (Table 2). Formation of a larger fraction of **3-BpBr** even at very short irradiation time (3 min) is in contrast to the results observed during

the direct photolysis of **BpBr$_2$**. Furthermore, the regiochemistry of debromination was similar to that obtained in the **LiDBB** and triphenyltin hydride mediated reactions. The results of these reactions are summarized in Scheme VII.

Table 2. Product Formation from **BpBr$_2$** at Different Irradiation Times in the Presence of Triethylamine in Acetonitrile (300 nm).

time (min)	% of reaction	BpBr/3BpBr [a]
2.5	2	1.84 ± 0.01
5	17	1.72 ± 0.05
10	30	1.69 ± 0.07
20	57	1.54 ± 0.16
40	88	1.49 ± 0.19

[a] Mean and standard deviation of the mean of three runs

The similar ratio of products from photodebromination in the presence of triethylamine, in the reduction with **LiDBB**, and in the reduction with Ph$_3$SnH is noteworthy. The NBMO coefficients for the transition states (**D** and **E** in Scheme III) leading to **BpBr** and **3-BpBr**, respectively, were calculated according to the Longuet-Higgin's mnemonic.[10] For **D** and **E** the values of the relevant coefficients are 0.33 (carbon-4 of **D**) and 0.27 (carbon-3 of **E**). AM1 calculations[11] support this where the coefficients, 0.36 for carbon-4 of **D** and 0.30 for carbon-3 of **E**,
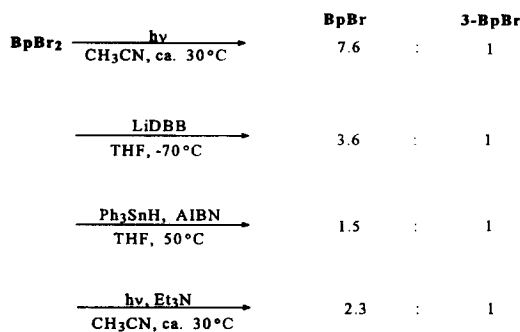
Scheme VI

Ph$_3$SnH, AIBN
THF, 50 °C

+SH   +SH

4-Bromobiphenyl   :   3-Bromobiphenyl

1.5   :   1
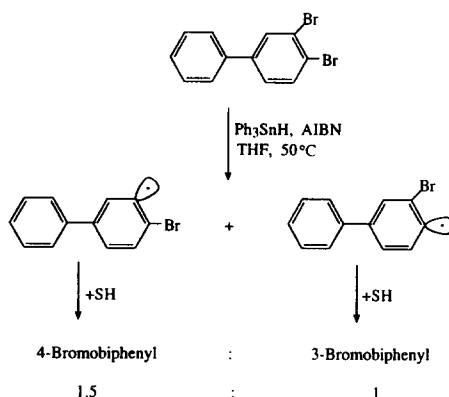
are similar in magnitude and order. For the AM1 calculations, a hydrogen atom was used in place of the radical center in order to have a four-centered carbon. This small difference in the coefficients probably explains, in part, the lack of strong preference for any one isomer in the fragmentation of the radical anion generated during the irradiation with triethylamine. However, the regiochemistries observed for the processes proceeding through a radical anion and also through an excimer are reversed from that anticipated. Why is this? Our original view that transition state **E** would be favored over **D** (Scheme III) depends upon coplanarity for **E**. AM1 calculations show that coplanar **G** is 49 kcal/mol less stable than twisted **G** (scheme VIII). The additional conjugation anticipated
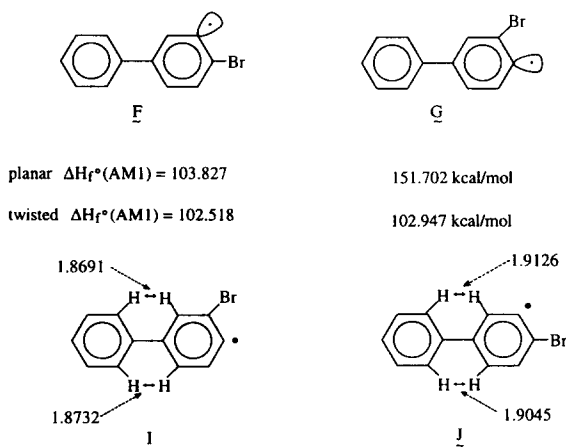
for **E** will be reduced and perhaps subtle nonbonded interactions will control the outcome. Twisted radical **F** is more stable than twisted **G** (Scheme VIII) and the energy difference, twisted **F** versus twisted **G** may control. To compare with the results of Scheme VII using the calculated energy difference ΔH_f° (twisted **G**) - ΔH_f° (twisted **F**) and assuming an Arrhenius relationship for the LiDBB, the Ph_3SnH, and the Et_3N runs, the calculated ratios are 2.90:1; 1.95:1 and 2.04:1, which provides a nice fit to the observed ratios.

Scheme VII

|		BpBr		3-BpBr
BpBr₂ $\xrightarrow[\text{CH}_3\text{CN, ca. 30°C}]{h\nu}$		7.6	:	1
$\xrightarrow[\text{THF, -70°C}]{\text{LiDBB}}$		3.6	:	1
$\xrightarrow[\text{THF, 50°C}]{\text{Ph}_3\text{SnH, AIBN}}$		1.5	:	1
$\xrightarrow[\text{CH}_3\text{CN, ca. 30°C}]{h\nu, \text{Et}_3\text{N}}$		2.3	:	1

The question remains, however, as to why the photochemical outcome without electron transfer reagent produces such a large fraction of 4-bromobiphenyl. The triplet state of **BpBr₂** may reasonably be assumed to be planar in agreement with views of the structure of triplet biphenyl, o-, m-, p-methylbiphenyl and

Scheme VIII

F

planar $\Delta H_f^{\circ}(AM1) = 103.827$

twisted $\Delta H_f^{\circ}(AM1) = 102.518$

1.8691

1.8732

H

G

151.702 kcal/mol

102.947 kcal/mol

1.9126

1.9045

J

o-, m-, and p-chlorobiphenyl.[12] This suggests that the triplet excimer is a complex of a planar 3,4-dibromobiphenyl unit with a twisted 3,4-dibromobiphenyl unit (**H** for example). An AM1 calculation provides a structural minimum, with no imaginary frequencies, which is reasonably well described by a complex of a coplanar dibromobiphenyl with a twisted dibromobiphenyl in which the dibromobenzene rings are face to face as in **H**. If the C-Br fission can take place from either the planar moiety or the twisted one, then some **3-BpBr** should be formed as is observed. Note that a comparison of planar **G** and planar **F** reveals that 48 kcal/mol more strain energy would be

H
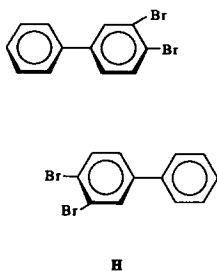
relieved in forming **F** leading to the prediction that fission from a planar **BpBr$_2$** unit should form **BpBr** as the sole product. If one assumes that fission from **H** proceeds with no relaxation, single point AM1 calculations on the radicals formed by fission in the planar moiety reveal that loss of the meta bromine provides 9.3 kcal/mol more strain relief than fission of the para bromine. This, if fully realized in the transition state would provide a 10^6:1 ratio of **BpBr:3-BpBr**, while a complete relaxation leading to twisted **F** and twisted **G** would result in a 2:1 **BpBr:3-BpBr** ratio. Since the experimentally determined ratio is 7.6 ± 0.1, complete relaxation in the coplanar 3,4-dibromobiphenyl unit clearly is not achieved during fission. If one assumes that fission either takes place (a) from the planar unit or (b) by energy transfer to the twisted unit with fission to produce products via twisted aryl radicals, then 65% of the fragmentation occurs in the top planar unit and 35% from the twisted bottom unit. Finally, an intriguing question arises as to why planar **F** is 48 kcal/mol more stable than planar **G**. The AM1 calculations show that there is a buttressing effect of the bromine when it is in the meta position pushing the ortho hydrogens closer together as revealed in representations **I** and **J**. (Scheme VIII).

Experimental Section

General Procedure for Photolysis. Irradiation of the samples in duplicate was carried out in a Rayonet merry-go-round reactor (The Southern New England Co.) equipped with eight lamps (300 nm) while being cooled by an overhead fan to maintain a constant temperature of ca. 30°C. The photolysis samples (1mL) were placed in Pyrex tubes (Ace Glass, 170 mm @ 15 mm), each screwed to a nylon adapter bushing containing a Pyrex glass sliding stopper valve and degassed through three or four freeze-pump-thaw cycles. The tubes were sealed under vacuum and irradiated at 300 nm for the desired time period. Quantum yields of products were determined by using 3 azoxybenzene actinometer solutions (1 mL each).[13]

Quantum Yield Dependence of BpBr on Concentration of BpBr$_2$. Appropriate amounts of **BpBr$_2$** were weighed into 5 mL volumetric flasks and the solutions were made up to the mark with acetonitrile to obtain concentrations from 0.00244 to 0.0513 M. Two samples of each of the solutions were degassed and irradiated at 300 nm in the presence of azoxybenzene actinometer. At the concentrations employed for both **BpBr$_2$** and the actinometer solutions, the optical densities were greater than 2 thus ensuring complete absorption of incident light.

Three actinometer tubes each containing 1 mL of azoxybenzene solution (ca. 0.006 M) were used for each irradiation run. After irradiation was completed (20 min), a stock solution of octadecane internal standard was added such that the ratio of the product concentration of **BpBr** to the concentration of the internal standard was within the range of the calibration curve. Quantum yields of products were determined by using 3 sets of azoxybenzene actinometers (1 mL each). Reported quantum yields are averages of two samples for each **BpBr** concentration.

Product Analyses: Photolysis mixtures were analyzed by GLC on a Varian 3300 and/or 3400 capillary gas

chromatograph equipped with an FID, a 30 m @ 0.25 mm capillary column (J&W Scientific Inc.) and a Spectra physics 4290 integrator. The capillary column used was either a DB-5 (5% phenyl-methylsilicone) or a DB-624 (cyanopropylphenyl-dimethypolysiloxane) column (Alltech Associates Inc.) and helium was used as carrier gas at 30 mL/min. The photoproduct was identified by comparing its GC retention time with that of an authentic sample and by mass spectral analyses carried out with a Finnigan 4023 mass spectrometer equipped with a Finnigan 9610 or Varian 3400 capillary gas chromatograph.

Synthesis of 3,4-Dibromobiphenyl.[14] A mixture of 2.15 g of 3,4-dibromoaniline (8.6 mmol) and 2.5 g of pentyl nitrite (2.6 eq., 22.4 mmol) in benzene was stirred at room temperature until a vigorous reaction with evolution of gas set in. This was allowed to proceed without heating until it had subsided in 30 min. The mixture was boiled under reflux for 30 min (70% yield of dibromobiphenyl). A longer period of reflux (2 h) resulted in formation of several byproducts which were not identified The resulting mixture was purified by flash column chromatography. Hexane was used as eluent initially and was followed progressively by a combination of 4 : 1 and 1 : 1 of hexane and $CHCl_3$ (60% yield): 1H NMR (400 MHz, CDCl3) d 7.38 (dd, 1H(H6), J = 2.3, 7.7 Hz), 7.40 - 7.55 (m, 5ArH), 7.67 (d, 1H(H5), J = 8.2 Hz) and 7.84 (d, 1H(H2), J = 2.0 Hz); 13C NMR (400 MHz, CDCl3) d 123.58, 125.17, 126.93, 127.19, 128.15, 129.00, 132.17, 133.85, 133.81, 138.67, 140.30 and 141.99; MS (m/e) 314, 312, 310 (M+), 152 (100), 126, 102 and 76.

Radical Anion Reduction of 3,4-Dibromobiphenyl using Lithium Di-tert-Butylbiphenylide in THF.[8] A 100-mL, three-necked Morton flask containing a 2.5-cm glass-covered magnetic stir bar was flame dried under a stream of argon gas. After the flask had cooled under argon, 270 mg (0.387 mol) of p,p'-di-tert-butylbiphenyl was added followed by syringing in 20 mL of dry THF. To this stirred solution, 6.3 mg of lithium ribbon cut into 3 small pieces was quickly added under a fast stream of argon. The solution turned green within 5 min due to the formation of the radical anion of the biphenyl and acquired a dark green color within 30 min. The stirring was continued for 4 h until all the lithium had reacted. The green solution was cooled down to -70 °C and 15.1 mg of 3,4-dibromobiphenyl in THF was added and immediately quenched by adding water. The reaction mixture was extracted with hexane (3 @ 20 mL). The organic layer was washed with water and dried with anhydrous sodium sulfate. After concentration, the ratio of products was determined by GC analysis using a capillary DB-WAX (Carbowax) column. The column was held at 60 °C for 5 min and then raised to 220 °C at 5 °C/min. The products were identified by comparing their GC retention times and mass spectra with those of authentic samples.

Induced Radical Debromination of 3,4-Dibromobiphenyl using Ph₃SnH in THF.[9] A mixture of 3,4-dibromobiphenyl (6.5 mg, 0.021 mmol), 0.33 eq. of Ph₃SnH (2.3 mg, 0.0064 mmol) and AIBN (10% of Ph₃SnH, 0.1 mg) was heated to reflux (approximately 50 °C) for 2 h. The resulting mixture was directly injected into the GC and analyzed using a capillary DB-WAX (carbowax) column and the products were identified by comparing their GC retention times and mass spectra with those of authentic samples. The total yield of monobromobiphenyls was approximately 9% with a 1.5 : 1 ratio in favor of 4-bromobiphenyl.

Photolysis of 3,4-Dibromobiphenyl in the presence of Triethylamine. In a 20 mL volumetric flask, a solution of 31.2 mg (0.00555 M) of **BpBr₂**, 346.8 mg (0.171 M) of triethylamine, 7.6 mg (0.0203 M) of hexadecane and 8.6 mg (0.00263 M) of octadecane was prepared. Two samples of degassed solution (1 mL each) were irradiated for 2.5, 5, 10, 20 and 40 min (Table II); the **BpBr/3-BpBr** ratio extrapolated to zero percent reaction is 1.81 (Table 2). The products were identified by comparing GC retention times and mass spectra with those of authentic samples.

Computational Methods. Calculations were performed on an IBM RISC 6000 Workstation using the

SPARTAN computation and graphics software (Wavefunction, Inc., Irvine, CA). Calculation of excimer structures were performed in three steps, as follows: First, ground state and triplet state structures were geometrically optimized at the desired level. Second, the intitial orientation 'guess' of the excimer structure was specified. Third, the 'excimer' structure was defined as a triplet state and geometrically optimized. When convergence criteria were met, the optimized structure was examined. A wide diversity of initial guess structures was attempted; the converged structure is discussed in this report.

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