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Mechanisms of the Photochemical Rearrangement of Diphenyl Ethers

Naoki Haga* and Hiroaki Takayanagi

School of Pharmaceutical Sciences, Kitasato University, 5-9-1 Shirokane, Minato-ku, Tokyo 108, Japan

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The mechanism of the photochemical rearrangement of diphenyl ether (**1a**) was studied. Irradiation of **1a** in ethanol gave 2-phenylphenol (**2**, 42%) and 4-phenylphenol (**3**, 11%) as rearrangement products, in addition to phenol (**4**, 30%) and benzene (**5**, 25%) as diffusion products. Cross-coupling experiments employing [$^2H_{10}$]**1a** demonstrated that the formation of 2- and 4-phenylphenol was an intramolecular process. Irradiation of **1a** in benzene or in toluene gave biphenyls in good yields. The combined yields of rearrangement products (**2** and **3**) increased with increase of solvent viscosity, with a concomitant decrease in the formation of **4**. All the results can be rationalized in terms of excitation of **1a** to the singlet state and dissociation to a radical pair intermediate involving phenoxy and phenyl radicals. Intramolecular recombination of these radicals gives rearrangement products, and escape followed by hydrogen abstraction from the solvent gives diffusion products. When position 4 of **1a** was occupied by an electron-donating substituent (**1b**−**e**), aryloxy−phenyl bond cleavage to give the corresponding rearrangement products prevailed over phenoxy−aryl bond cleavage. The opposite was the case for substrates with an electron-withdrawing substituent at position 4 (**1h,i**).

Introduction

Several rearrangements of aromatic compounds, for instance the Claisen rearrangement,[1,2] the Fries rearrangement,[3,4] and the benzidine rearrangement,[5,6] are widely known to proceed *via* a photochemical process as well as by acid-catalyzed (thermal) reaction. The mechanisms of these photochemical rearrangements can be clearly distinguished from the ground state process. Most of them proceed *via* homolytic cleavage of a carbon−heteroatom or heteroatom−heteroatom bond in the excited state to generate radical species, as demonstrated by direct detection of radical intermediates by flash photolysis,[7] by chemically induced dynamic nuclear polarization studies,[8] and by measuring the solvent viscosity effect on product distribution.[9] These radical pairs may undergo rapid recombination to give rearrangement products, or the radicals may escape to afford free radicals. Quantum yields of these processes are relatively high because the bond dissociation energies of the severed bonds are relatively low, and the resulting radicals are stabilized by delocalization of their odd electron through the conjugated system.

Although diphenyl ether (**1a**) is stable to acids[10] or high temperatures,[11] it is converted on UV irradiation in 2-propanol into **3** and **4** in a low quantum yield.[12] Though this reaction is formally classified as a photo-Claisen rearrangement, this [1,3] rearrangement is different from the [3,3] photo-Claisen rearrangement. During the two decades after the above discovery, photolability of **1a** and its derivatives has been investigated by only a few workers,[2b,13−17] owing to its low reactivity upon UV irradiation and limited synthetic utility. Kelly *et al.*[2b] and Hageman *et al.*[13] used a high-pressure mercury lamp to irradiate **1** in ethanol and found that **2** was formed, in addition to **3** and **4**. In 1970, Ogata *et al.*[14] found that the formation of **2** was essentially an intramolecular process *via* a singlet excited state, and the product distribution of this rearrangement depended somewhat on the hydrogen-bonding ability of the solvent used. Photolyses of asymmetrically substituted diphenyl ethers

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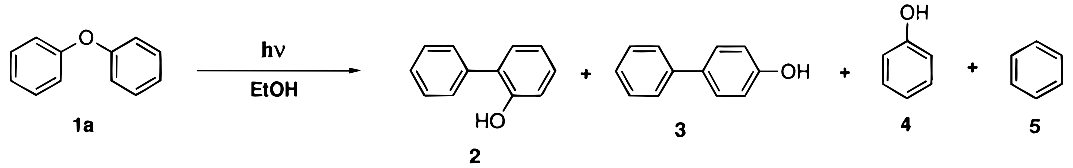
Scheme 1



were carried out by several workers,[15–17] but there is no apparent consistency in their results. Through these studies, it was inferred that the photolysis of **1a** proceeds *via* a radical pair (phenyl radical and phenoxy radical) intermediate, and the radicals either recombine or escape to afford free radicals. Though the radical pair mechanism has been widely accepted, little evidence is available to support (or contradict) this hypothesis. Our aims were therefore (1) to reinvestigate the intramolecularity of this rearrangement and (2) to identify the intermediate(s).

The cross-coupling experiment by Ogata *et al.* [14] is unsatisfactory in two respects. Firstly, they employed **1a** and *p,p′*-ditolyl ether, but did not examine all of the possible intermolecular products which might be formed. Secondly, the quantum yields differed between the two substrates. To avoid these problems, we carried out a cross-coupling experiment employing **1a** and $[^2H_{10}]$**1a** as substrates, and the resulting products (**2** and **3**) were analyzed by whole molecular ion mass spectrometry (WMIMS).

In the case of the photochemical rearrangement of benzyl phenyl ether (a kind of photo-Claisen rearrangement),[18] the benzyl radical generated undergoes dimerization to give 1,2-diphenylethane or abstracts hydrogen to give toluene, as well as coupling with the phenoxy radical to give 2- and 4-benzylphenol.[2b] If a similar mechanism operates in the photochemical rearrangement of **1a**, the corresponding intermediate is a phenyl radical which may dimerize to give biphenyl or abstract hydrogen to give benzene, as well as being converted into **2** and **3**. However, the phenyl radical is much less stable than the benzyl radical, which can be stabilized by delocalization of its odd electron into the aromatic ring. In order to test the intermediacy of the short-lived phenyl radical, we irradiated **1a** in benzene or toluene as a phenyl radical scavenger and examined the solvent viscosity dependence of the product distribution. Further, to evaluate the involvement of a radical pair in this reaction, solvent viscosity effects on the distribution between rearrangement products and **4** were investigated.

Results

Quantitative Analyses of the Reaction Products in Ethanol. Ogata *et al.* reported that upon unfiltered light irradiation from a high-pressure mercury lamp in ethanol for 25 h, **1a** rearranged to give **2** (20.4%), **3** (12.7%), and a trace amount of **4**.[14] We repeated irradiation of **1a** in degassed ethanol and confirmed their results, except that we obtained higher yields of the products. Thus, internal irradiation for 4 h converted **1a** into **2**, **3**, and **4** in yields of 40%, 12%, and 19%, respectively, after isolation by column chromatography. The structures of products were identified by comparison of the spectral properties with those of authentic samples. No other product was detected by TLC, though small amounts of unidentified polymeric products with low R_f values were formed.[4d] Examination of the possibility of secondary photochemical reaction of the primary photochemical products revealed that **2** and **3** were somewhat unstable to irradiation. Upon independent irradiation of **2**, **3**, and **4**, 7% of **2** and 15% of **3** were lost, and more than 35% of **4** decomposed to unidentified polymeric products after 8 h of internal irradiation. This photolability of **4** should be taken into consideration in assessing yields after prolonged irradiation.

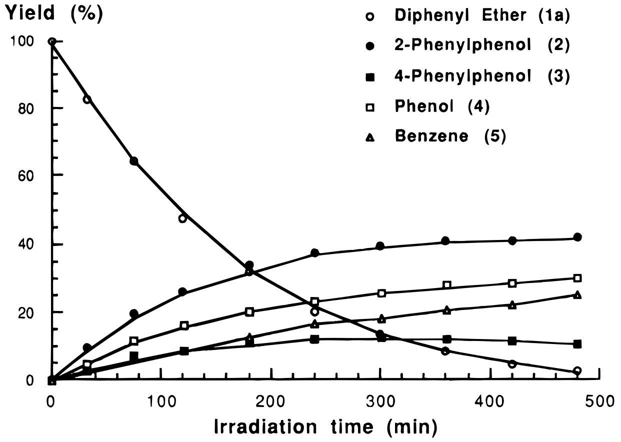


Figure 1. Time course of irradiation of **1a** in ethanol.

For identification and quantification of volatile products, the reaction mixture was analyzed by GC. The time courses of consumption of **1a** and formation of the products are illustrated in Figure 1. Surprisingly, besides **2**, **3**, and **4**, benzene (**5**) was formed in a yield comparable with that of **4** (Scheme 1). The yields of the four products and recovered **1a** after 4.0 and 8.0 h of irradiation were 37.2% and 41.8% for **2**, 12.1% and 11.5% for **3**, 23.4% and 30.1% for **4**, 16.9% and 25.0% for **5**, and 22.2% and 2.3% for **1a**, respectively. Prolongation of the irradiation from 4.0 to 8.0 h increased the yields of **2, 4,** and **5**, with a slight decrease of **3**, and the total yield decreased from 94.9% to 85.7%.

Irradiation of **1a** in the presence of *cis*-1,3-pentadiene, a typical triplet quencher, was carried out, and the resulting mixture was analyzed by GC. The yields after 4.0 h of irradiation were 32.0%, 12.1%, 20.5%, 15.3% and 33.0% for **2, 3, 4, 5**, and recovered **1a**, respectively. The presence of *cis*-1,3-pentadiene had no influence on the photochemical reaction of **1a**.

Irradiation in Benzene. If a free phenyl radical intervened as an intermediate, it would be trapped as biphenyl (**6**) in benzene.[19] When **1a** was irradiated in benzene, the reaction proceeded sluggishly because of intense absorption of incident light by benzene in the region of 230–260 nm,[20] and more than 90% of **1a** was

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Table 1. Solvent Effects on the Product Distribution in the Rearrangement of 1a

			yield (%)				
solvent	viscosity[a]	conversion (%)	**2**	**3**	**4**	**2/3**	**(2 + 3 + 4)/(2 + 3)**
1,2-propanediol	46.5	55.9	40.2	4.2	1.2	9.57	1.03
1,2-ethanediol	17.73	71.2	54.7	6.8	2.2	8.04	1.04
2-propanol	2.151[b]	57.2	28.6	13.8	14.9	2.07	1.35
acetic acid	1.139	44.7	19.5	6.6	19.1	2.95	1.73
ethanol	1.078	64.7	29.2	14.7	19.5	1.99	1.45
methanol	0.5445	66.9	28.0	13.8	24.4	2.03	1.58
1,4-dioxane	1.204	51.7	19.5	6.1	16.7	3.20	1.65
THF	0.460	62.5	14.5	5.0	35.0	2.90	2.79
diethyl ether	0.2234[b]	49.0	6.5	2.2	33.8	2.95	2.95
cyclohexane	0.898	22.3	6.2	2.0	4.7	3.10	1.57
n-heptane	0.3967	17.2	2.5	1.3	6.3	1.92	2.66
n-hexane	0.2985	18.2	1.9	1.0	6.1	1.90	3.10
acetonitrile	0.342	90.2	18.1	7.9	40.5	2.29	2.56

[a] cP at 25 °C. [b] Calculated value according to Bingham's equation.[48]

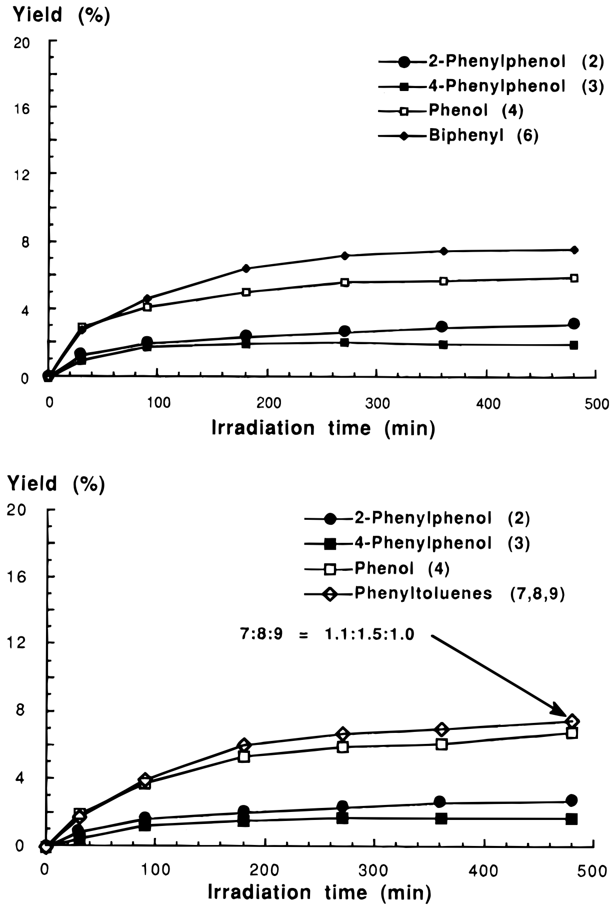
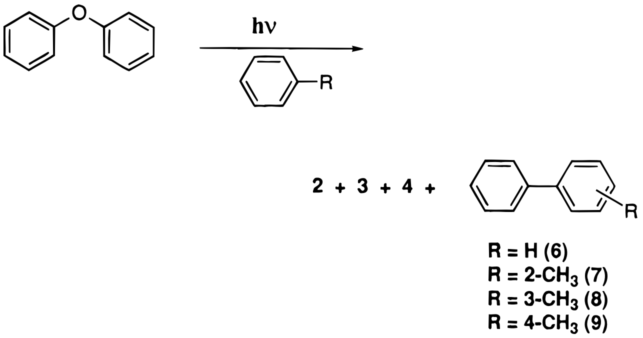


Figure 2. Time course of irradiation of **1a** in benzene (top) and in toluene (bottom).

Scheme 2



recovered unchanged even after 8.0 h of internal irradiation. However, in this reaction it turned out that **6** was formed in a high yield compared to the rearrangement products (**2** and **3**) (Scheme 2). The time courses of formation of the products are shown in Figure 2. Components of the reaction mixture after 8.0 h of irradiation were **1a** (71.8%), **2** (3.1%), **3** (2.0%), **4** (5.9%), and **6** (7.9%) by GC analyses. Polyphenyls such as quaterphenyl were not detected by GC.[19a] Unidentified polymeric products with low R_f values were formed in a higher yield than in the reaction in ethanol. A similar result was obtained on irradiation of **1a** in toluene (Figure 2). In addition to recovered **1a** (70.1%), **2** (2.8%), **3** (1.8%), and **4** (6.8%), 2-, 3-, and 4-phenyltoluene (**7**, **8**, and **9**) were formed in yields of 2.3% (**7**), 3.1% (**8**), and 2.1% (**9**) after 8.0 h.

Influence of Solvent Viscosity on Product Distribution. If a radical pair intervened as an intermediate in this reaction, the yields and product distribution would depend significantly on the solvent, as has been observed for many radical reactions.[2a,9,21] Thus, formation of the rearrangement products (**2** and **3**) would increase in going to a more viscous solvent, accompanied with a decrease of diffusion products (**4** and **5**). Ogata *et al.* found that formation of **2** and **3** from **1a** was facilitated in ethanol rather than in diethyl ether and that the rearrangement/diffusion ratio (the ratio of the combined yields of **2** and **3** to that of phenol) was essentially independent of solvent viscosity.[14] They concluded that the pathway *via* solvation by alcohol at the oxygen atom of **1a** is favored because the C−O bond cleavage is facilitated, and solvent viscosity plays a limited role. However, this result should be reexamined because they employed solvents of a limited viscosity range (from 0.33 to 2.95 cP). We used 13 solvents with a viscosity range from 0.223 (diethyl ether) to 46.5 cP (1,2-propanediol). External irradiation of **1a** in these solvents was conducted simultaneously, and the resulting mixture was analyzed by GC (for details, see the Experimental Section). Yields of products (**2**, **3**, and **4**) together with amounts of recovered **1a** are listed in Table 1. Two features were noted. First, varying the solvent caused a dramatic variation of product distribution. Thus, the more viscous the solvent, such as 1,2-propanediol and 1,2-ethanediol, the higher the yields of **2** and **3**. To the contrary, in solvents with low viscosity, such as aceto-

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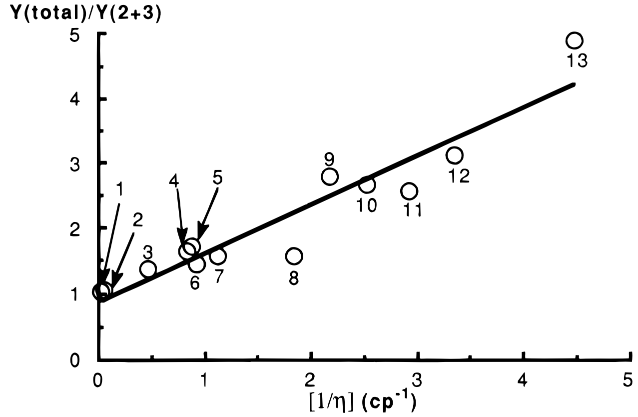
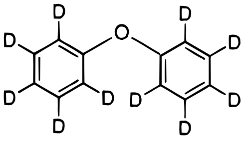


Figure 3. Plot of the reciprocal ratio of the combined yield of **2** and **3** to that of **2, 3**, and **4** against the reciprocal solvent viscosity: Y(total), combined yield of **2**, **3**, and **4**; Y(2 + 3), combined yield of **2** and **3**; solvents, (1) 1,2-propanediol, (2) 1,2-ethanediol, (3) 2-propanol, (4) 1,4-dioxane, (5) acetic acid, (6) ethanol, (7) cyclohexane, (8) methanol, (9) THF, (10) *n*-heptane, (11) acetonitrile, (12) *n*-hexane, and (13) diethyl ether.

Chart 1



[$^2H_{10}$]1a

nitrile, *n*-hexane, and diethyl ether, yields of rearrangement products (**2** and **3**) were lower and formation of diffusion products (**4**) increased to a significant degree. For example, reaction in 1,2-ethanediol gave yields of 38% for **2**, 4% for **3**, and 1% for **4**, whereas yields of 7%, 2%, and 35%, respectively, were obtained in diethyl ether. Figure 3 plots the reciprocal ratio of the combined yield of **2** and **3** to that of **2, 3**, and **4** against the reciprocal viscosity of solvents at 25 °C, giving a linear relation with an intercept of 0.87 and a slope of 0.75 cP. Secondly, the conversion efficiency of **1a** decreased from 71.0% in 1,2-ethanediol to 17.2% in *n*-heptane. In general, conversion decreased in the order of reaction in hydroxylic solvents (alcohols and acetic acid), in ethers, and in hydrocarbons.

Cross-Coupling Experiments. To examine precisely the intramolecularity of the rearrangements to the ortho and to the para position, positions 2, 4, and 6 of **1** must be free of a substituent. Thus, we chose the combination of **1a** and [$^2H_{10}$]**1a** as substrates for a cross-coupling experiment (Chart 1). The labeled substrate was prepared from [$^2H_5$]bromobenzene and [$^2H_6$]phenol according to the modified method of Milyakh *et al.*[22] In a preliminary experiment, **1a** and [$^2H_{10}$]**1a** were found to undergo rearrangement in nearly equal quantum yield. For the purpose of testing the possibility of proton exchange of [$^2H_{10}$]**1a** during irradiation, [$^2H_{10}$]**1a** was irradiated independently in ethanol, and the deuterium abundance of the resulting **2** and **3** as well as that of recovered **1a** was analyzed by multiscan WMIMS, which was devised for evaluating heavy atom isotope ratios.[23] Calculations of hydrogen isotope abundance of [$^2H_{10}$]**1a** (both for the initial and for the recovered sample) were carried out on the basis of relative peak intensities in the range of *m*/*e* 177 (M − 3) to 181 (M + 1), as described for determining the deuterium abundance of *O*-phenylhydroxylamines.[24] Details of the calculation are described in the Experimental Section. Similarly, the deuterium abundances of [$^2H_9$]**2** and [$^2H_9$]**3** were calculated in the range of *m*/*e* 175 (M − 4) to 180 (M + 1). The results are summarized in Table 2. For the recovered **1a** and **3**, deuterium abundance did not vary from that of the initial **1a**, which shows that no exchange of deuterium on the aromatic ring with protons of the solvent or the unlabeled substrate occurred during irradiation. Though a decrease of deuterium abundance of approximately 5% was observed for **2**, it was assumed that this did not significantly affect the mass analyses of cross-coupling experiments.

Table 2. Deuterium Abundance of 1a, 2, and 3 after Irradiation of [$^2H_{10}$]1a[a]

compound	^{2}H abundance (%)
1a (initial)	95.73 ± 0.04
1a (recovered)	94.54 ± 0.22
2	90.04 ± 0.21
3	95.70 ± 0.29

[a] Mean value of three or four runs. Each run involved 180−450 scans.

Cross-coupling experiments were carried out by internal irradiation of an equimolar mixture of **1a** and [$^2H_{10}$]-**1a** (0.01 M total substrate) in ethanol for 45 min. Conversion of **1a** was 25%. The isolated **1a**, **2**, and **3** were analyzed by multiscan WMIMS. For **2** and **3**, relative peak intensities of *m*/*e* 168−180 were measured to evaluate the contents of [$^2H_9$]**2(3)**, [$^2H_5$]**2(3)**, [$^2H_4$]**2(3)**, and unlabeled **2(3)**. The results are presented in Table 3. Deuterium abundance was 87.5% and 95.5% for **2** and **3**, respectively. In the case of **3**, relative peak intensities in the range of 176−180 did not vary from those in the range of 177−181 in **1a**. Peaks with *m*/*e* 175 and 174 resulting from the formation of hybridized products, 4-$OHC_6H_4C_6D_5$ ([$^2H_5$]**3**) and 4-$OHC_6D_4C_6H_5$ ([$^2H_4$]**3**), were not found. On the other hand, the peak composition of **2** is complicated in that a significant decrease of peak intensity at *m*/*e* 179 was observed, accompanied with an increase of those with *m*/*e* 175−178. Two factors contribute to this result: the intense peak of M − 1 and the deuterium exchange of **2** with the solvent. Notwithstanding, the peaks with *m*/*e* 175 and 174, due to formation of hybridized products 2-$OHC_6H_4C_6D_5$ ([$^2H_5$]-**2**) and 2-$OHC_6D_4C_6H_5$ ([$^2H_4$]**2**), are negligible. For recovered **1a**, relative peak intensities in the range of *m*/*e* 169−181 were measured in order to evaluate the contents of [$^2H_{10}$]**1a**, [$^2H_5$]**1a**, and unlabeled **1a**. The results are summarized in Table 4. Because [$^2H_{10}$]**1a** used for this experiment contains 5.0% protons, the relative peak intensities of *m*/*e* 179 ([$^2H_9$]**1a**) and 178 ([$^2H_8$]**1a**) are moderately large (22.4% of *m*/*e* 180 for *m*/*e* 179 and 10.9% for *m*/*e* 178). As expected, relative peak intensities of **1a** did not vary before and after the irradiation. No peak with *m*/*e* 175 ([$^2H_5$]**1a**) was detected in the recovered substrate. Thus, no hybridization between labeled and

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Table 3. Variation of Relative Peak Intensities (±Standard Deviation) of 2 and 3 in Cross-Coupling Experiments

compound	relative peak intensity[b] at the following *m*/*e*												
	180	179	178	177	176	175	174	173	172	171	170	169	168
2	8.25 ± 1.85	42.24 ± 1.51	37.21 ± 0.86	21.53 ± 1.04	12.25 ± 1.39	3.43 ± 0.65	0	0	0	20.53 ±1.21	100	50.54 ± 1.75	3.22 ± 1.60
3	11.95 ± 0.98	86.85 ± 2.73	22.45 ± 1.34	8.76 ± 0.75	2.92 ± 0.58	0	0	0	0	14.16 ± 0.35	100	11.79 ± 1.92	0

[a] Mean value of three or four runs. Each run involved 280−440 scans. [b] Relative value on the basis of *m*/*e* 170 as 100.

Table 4. Variation of Relative Peak Intensities (±Standard Deviation) of [$^2H_{10}$]1a and Unlabeled 1a of Cross-Coupling Experiments

compounds	relative peak intensity[b] at the following *m*/*e*											
	181	180	179	178	177	176	175	174	173	172	171	170	169
1a(initial)	11.09 ± 0.13	84.82 ± 2.41	22.54 ± 0.38	10.88 ± 0.65	2.53 ± 0.86	0	0	0	0	0	13.34 ± 0.13	100	15.87 ± 1.23
1a(recovered)	10.99 ± 0.25	83.90 ± 2.56	22.95 ± 0.45	11.67 ± 0.70	3.86 ± 0.55	0	0	0	0	0	13.45 ± 0.86	100	16.05 ± 0.62

[a] Mean value of three or four runs. Each run involved 180−220 scans. [b] Relative value on the basis of *m*/*e* 170 as 100.

Scheme 3

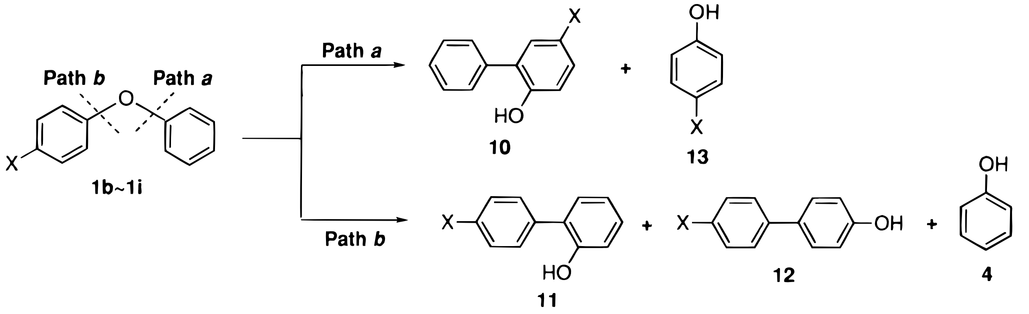


Table 5. Product Distribution in the Photochemical Rearrangement of 4-Substituted Diphenyl Ethers (1b−1j) in Ethanol

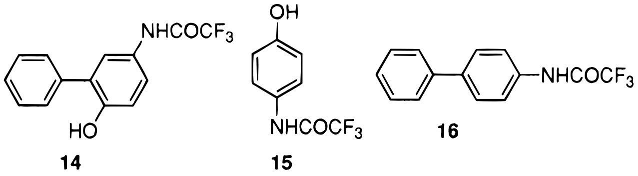
X	irrad time (h)	yield (%)[a]					
		10	11	12	13	4	others
Me(**1b**)	3.0	47	0	7	15	0	
OCH_3(**1c**)	2.0	33	0	0	9	0	15[b]
OH(**1d**)	1.0	37	0	0	32	0	10[b]
NH_2(**1e**)	0.3	37[c]	0	0	27[d]	0	10,[b] 6[e]
C_6H_5(**1f**)	8.0	9	0	0	6	5	50[f]
F(**1g**)	2.5	20	3	5	0	0	6,[b] 4[g]
CO_2CH_3(**1h**)	2.5	0	42	29	0	14	
CN(**1i**)	2.0	0	43	30	0	13	

[a] Isolated yields. [b] 4-Phenylphenol (**3**). [c] Isolated as **14**. [d] Isolated as **15**. [e] 2-Phenylaniline, which was isolated as **16**. [f] Recovery of **1f**. [g] 2-Phenylphenol (**2**).

unlabeled phenyl groups to generate $C_6D_5OC_6H_5$ ([$^2H_5$]-**1a**) occurred during the irradiation.

Substituent Effect on the Regioselectivity. In order to evaluate the substituent effect on the regioselectivity of C−O bond fission, asymmetric ethers (**1b**−**i**) whose para position is occupied by a substituent were irradiated in ethanol. As shown in Scheme 3, the two possible pathways will give independent products. Thus, if path a (phenyl−aryloxy cleavage) operates in preference to path b (aryl−phenoxy cleavage), **10** would be produced as the rearrangement product, provided that the substituent remained in the benzene ring during the rearrangement. Product distributions in these reactions are listed in Table 5. A distinct substituent effect on the regioselectivity of the C−O bond cleavage was observed. Reaction of substrates that have an electron-donating substituent, **1b** (X = Me), **1c** (X = OMe), **1d** (X = OH), and **1e** (X = NH_2), proceeded predominantly *via* path a, except for the formation of **12b** from **1b** in a low yield (minor involvement of path b). That is, the 4-substituted-2-phenylphenols (**10**), which were formed by phenyl migration to the ortho position of the aryloxy group, were isolated as a major product. In the reaction of **1e**, the amino group of the products was converted into trifluoroacetamide (**14**, **15**, and **16**) by treatment with trifluoroacetic anhydride (TFAA) to facilitate isolation and purification (Chart 2). In all cases, phenols (**4** and/or **13**) were formed. Unexpectedly, elimination of the substituent occurred during the reaction on irradiation of **1c**, **1d**, **1e**, and **1g**, which gave rise to the formation of 4-phenylphenol (**3**). Formation of 4-phenylaniline (isolated as **16**) from **1e** and formation of **2** from **1g**, though they are minor in relation to the overall reaction, are abnormal. The structures were established unambiguously on the basis of elemental analyses and spectral properties or by direct comparison with an authentic sample.

Chart 2



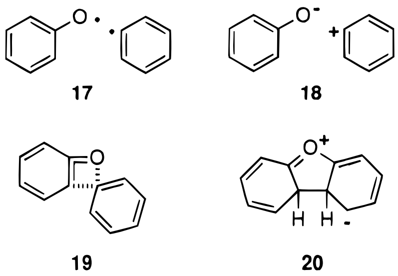
In contrast, irradiation of substrates that have an electron-withdrawing substituent, **1h** (X = CO_2CH_3) and **1i** (X = CN), gave products exclusively *via* path b. The aryl group rearranged to the ortho position and the para position with respect to the phenoxy group to give **11** and **12**, respectively. Formation of the former prevailed over formation of the latter.

Reaction of **1f** (X = Ph) and **1g** (X = F) was borderline. That is, 9% yield of **10f** as a product *via* path a and 6% yield of **13f** as a product *via* path b were formed. Similarly, 20% yield of **10g** as a product *via* path a and 3% yield of **11g** and 5% yield of **12g** as products *via* path b were formed, together with small amounts of **2** and **3**.

Discussion

Intramolecularity of the Rearrangement. Both the ortho and the para rearrangements were proved to

Chart 3



be essentially intramolecular by the cross-coupling experiments. The absence of peaks at *m/e* 175 and 174, which are the molecular ions of the hybridized products, 4-$OHCH_4CD_5$ ([$^2H_5$]**3**) and 4-$OHCD_4CH_5$ ([$^2H_4$]**3**), in **3** provides convincing evidence that the para rearrangement proceeds completely intramolecularly (Table 3). In the formation of **2**, the significant decrease of peak intensity at *m/e* 179 accompanied with increases of those at *m/e* 175−178 can be attributed to partial deuterium exchange of [$^2H_5$]**2** and the contribution of the intense M − 1 peak of this compound, rather than to mixing of an intermolecular process. The deuterium abundance was reduced from 95.3% for the initial **1a** to 87.2% for **2** resulting from formation of [$^2H_8$]**2**−[$^2H_5$]**1a**, and the peak at *m/e* 169 has 50.5% of the intensity of that at *m/e* 170 (Table 3). Therefore, the ortho rearrangement also turned out to be intramolecular.

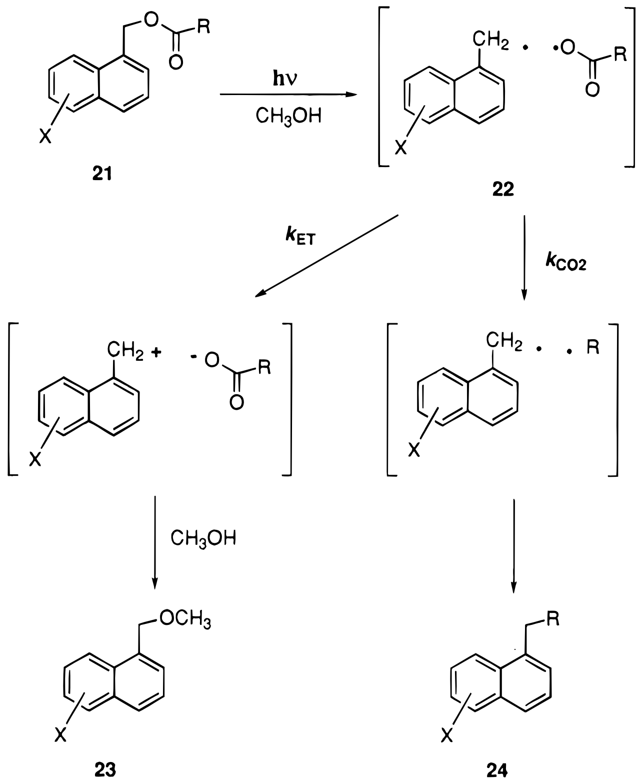
For the recovered substrate, relative peak intensities in the range of *m/e* 169−181 did not vary from those of the initial substrate (Table 4). This indicates that [$^2H_{10}$]-**1a** did not undergo phenyl group exchange with unlabeled **1a** to generate hybrid substrate ($C_6D_5OC_6H_5$) during the reaction.

Multiplicity of the Excited State. Identical results for yields of the products in the presence and in the absence of *cis*-1,3-pentadiene indicate that the singlet excited states of **1a** are undoubtedly major species in the reaction. Energy transfer from the triplet state of **1a** to *cis*-1,3-pentadiene is 92 kJ mol^{-1} exothermic as estimated from the triplet excitation energies of **1a** and *cis*-1,3-pentadiene of 339 kJ mol^{-1}[25] and 247 kJ mol^{-1},[26] respectively. If the triplet state of **1a** were the intermediate, the reaction would be quenched by *cis*-1,3-pentadiene.

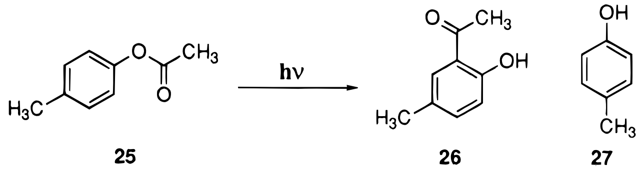
Mode of Bond Cleavage and Bond Formation. As regards the mode of C−O bond cleavage and C−C bond formation in this rearrangement, four possible intramolecular processes (Chart 3) can be considered for formation of **2** and **3**: (i) a dissociative process *via* a radical pair intermediate (**17**), (ii) a dissociative process *via* an ion pair intermediate (**18**), (iii) a concerted process *via* a transition state (**19**), and (iv) a ring closure and cleavage process *via* a dibenzofuran-type intermediate (**20**). Among them, **19** and **20** are disadvantageous for the para rearrangement (formation of **3**). Our present data support the radical pair process, as discussed in detail below.

The finding that irradiation of **1a** in ethanol gave radical-derived products **2**, **3**, **4**, and **5** stoichimetrically and that no ionic-derived product was produced provides convincing evidence that the C−O bond dissociates entirely homolytically, because if **1a** underwent heterolytic C−O bond cleavage to generate an ion pair (**18**) involving the phenyl cation and phenoxy anion, the former would be trapped by ethanol as ethoxybenzene.

Scheme 4



Scheme 5



Our results also eliminate the pathway involving generation of an ion pair by electron transfer from a radical pair (**17**). This is in contrast to the photolysis of α-naphthylmethyl esters (**21**) in methanol (Scheme 4),[25] where competitive reactions, i.e., electron transfer from a radical pair (**22**) followed by dissociation to free ions and decarboxylation followed by radical coupling, give both ionic- (**23**) and radical-derived products (**24**). The proportion of **23** to **24** may depend on both the oxidation potential of the α-naphthylmethyl radical and the rate constant for the decarboxylation.

The observed solvent viscosity effect on the ratio of formation of **2** and **4** seems to disfavor the concerted process. In the case of photo-Fries rearrangement of 4-methylphenyl acetate (**25**),[9] the independence of the quantum yield for formation of 2-hydroxy-5-methylacetophenone (**26**, in-cage product) on solvent viscosity and the decrease of quantum yield for formation of 4-methylphenol (**27**, out-of-cage product) with increase of solvent viscosity were attributed to the distinct mechanisms of these processes (Scheme 5), i.e., formation of **26** by concerted rearrangement *via* a transition state with a four-membered ring, in contrast with formation of **27** by dissociation into a radical pair followed by diffusion to

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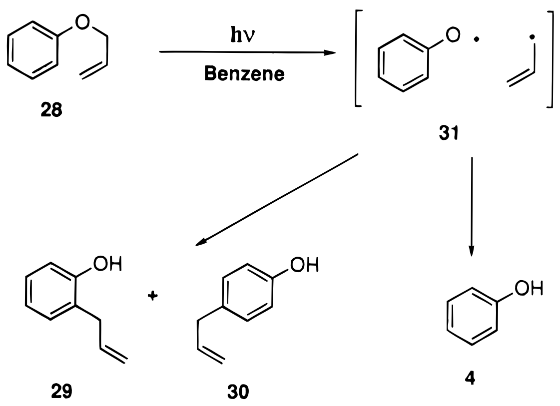
[25] Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd Ed.; Marcel Decker, Inc.: New York, 1993; p 71.

[26] Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Decker, Inc.: New York, 1993; p 71.

[27] DeCosta, D. P.; Pincock, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 8948−8950.

Scheme 6



afford free radicals. On the other hand, the effect of solvent viscosity on the formation of **2** from **1a** was opposite to that in the formation of **26**: the yield of **2** increased from 1.9% in *n*-hexane to 55% in 1,2-ethanediol on irradiation (Table 1). This variation in the yield of **2** shows that the efficiency of conversion of **1a** into **2** depends appreciably on the nature of the solvent. This favors a dissociative process rather than the concerted process.

It is noteworthy that ratio of ortho to para rearrangement is significantly larger in 1,2-ethanediol (**2**/**3** = 9.6) and in 1,2-propanediol (**2**/**3** = 8.0) than in other solvents, where an approximately constant value of the ratio of 1.8−3.0 is noted (Table 1). This may suggest that the concerted process, which leads to the ortho rearrangement alone, competes with the radical pair process in viscous solvents such as 1,2-ethanediol and 1,2-propanediol.[4a] In fact, the ortho migration of the phenyl group to the phenoxy radical is a [1,3] rearrangement, which is an allowed process in an excited state, in terms of the orbital symmetry restriction, whereas the para migration is a [1,5] process, which is forbidden. A clear interpretation of the preference for ortho rearrangement over para rearrangement, however, cannot be derived from the solvent viscosity effect.

A fourth possibility for C−O bond cleavage and C−C bond formation, i.e., dibenzofuran derivative (**20**) formation followed by the C−C bond cleavage, must be considered. It was reported that irradiation in the presence of iodine as an oxidizing agent converted **1a** into dibenzofuran in 70% yield without formation of other products.[28] However, for the same reason as in the case of the concerted process, this process can be ruled out in the absence of an oxidizing agent. If this mechanism were operating in the ortho rearrangement of **1a**, formation of **2** should proceed regardless of the solvent.

The solvent viscosity effect on product distribution distinguishes between the radical pair mechanism and the other mechanisms. In the case of photo-Claisen rearrangement of allyl phenyl ether (**28**) in benzene,[2a] the more viscous the solvent used, the higher the quantum yields for allylphenols (**29** and **30**), while the quantum yield for formation of phenol (**4**) remained unchanged (Scheme 6). A plot of reciprocal ratio of quantum yields for formation of rearrangement product against reciprocal viscosity of the solvent gave a straight line.[29] A radical pair (**31**) involving a phenoxy radical and an allyl radical, which recombine in the pair to give **29**, has been proposed for the reaction mechanism. Our experiments employing 13 different solvents revealed a dramatic solvent viscosity effect on the product distribution in the photolysis of **1a**. As shown in Figure 3, the observed variation of product distribution on varying the solvent (the more viscous the solvent, the higher the yields of **2** and **3** and the lower the yield of **4**) demonstrates the intervention of a radical pair in this reaction, as in the photo-Claisen rearrangement of **28**. That is, because the rate constant for diffusion of the resulting radical pair is small in viscous solvents, in-cage recombination to give **2** and **3** is favored over diffusion to afford free radicals.

The radical pair mechanism described above is in accord with the formation of biphenyl (**6**) in a high yield in the reaction of **1a** in benzene. This result shows that the radical pair dissociates to a free phenyl radical, which is then trapped by benzene. Though this reaction was extremely slow because of competitive absorption of incident light between **1a** and benzene, formation of **4** and **6** in relatively higher yields than those of **2** and **3** shows that in this reaction, diffusion of the initial radical pair to afford free radicals prevails over recombination. Reaction of **1a** in toluene gave a similar result: three isomeric phenyltoluenes and **4** were produced in preference to **2** and **3.** The formation of **7**, **8**, and **9** with a ratio of 1.1:1.5:1.0 is considerably different from the outcome in thermal aromatic substitution by a phenyl radical generated by dissociation of benzoyl peroxide.[19] For example, phenylation of toluene by phenyl radical generated by thermolysis of *N*-nitrosoacetylarylamine gave three phenyltoluene isomers with a ratio of **7**:**8**:**9** = 1.9:0.8:1.7.[19a] The reason for this difference is unclear, but we tentatively attribute this lower yield of **7** partially to secondary reactions of the phenylcyclohexadienyl radical, as yet unknown, to give products other than phenyltoluenes.

Mechanism of the Rearrangement. As shown in Scheme 7, the primary chemical process is excitation from the ground state **1** to a singlet state followed by homolytic C−O bond cleavage to give a singlet radical pair (**17**) involving a phenoxy radical and a phenyl radical. In this pair, recombination of the phenyl radical at the ortho and the para positions of the phenoxy radical gives quinoid intermediates (**32** and **33**), followed by aromatization to **2** and **3**, respectively. In viscous solvents the concerted process for the ortho rearrangement may compete with the radical pair process. When the radical pair dissociates to free radicals (**34** and **35**), they cannot recombine either intramolecularly or intermolecularly. Instead, they abstract a hydrogen atom from the solvent to afford phenol (**4**) and benzene (**5**). When benzene is employed as the solvent, the free phenyl radical (**35**) undergoes substitution with benzene to give biphenyl (**6**). The radical mode for this reaction is not affected by substitution at the para position of **1a**, since products derived from an ionic intermediate were not isolated in the photolysis of **1b**−**1j** (Table 5).

Formation of **3** from **1c**, **1d**, **1e**, and **1g** is noteworthy. We attribute this to para rearrangement *via* path a (intramolecular rearrangement of the phenyl group to the *ipso* position of the substituent) followed by removal of the substituent, rather than to photolytic removal of the substituent in the substrates and/or products. Independent irradiation of **10c**, **10d**, **10e**, and **10g** in ethanol

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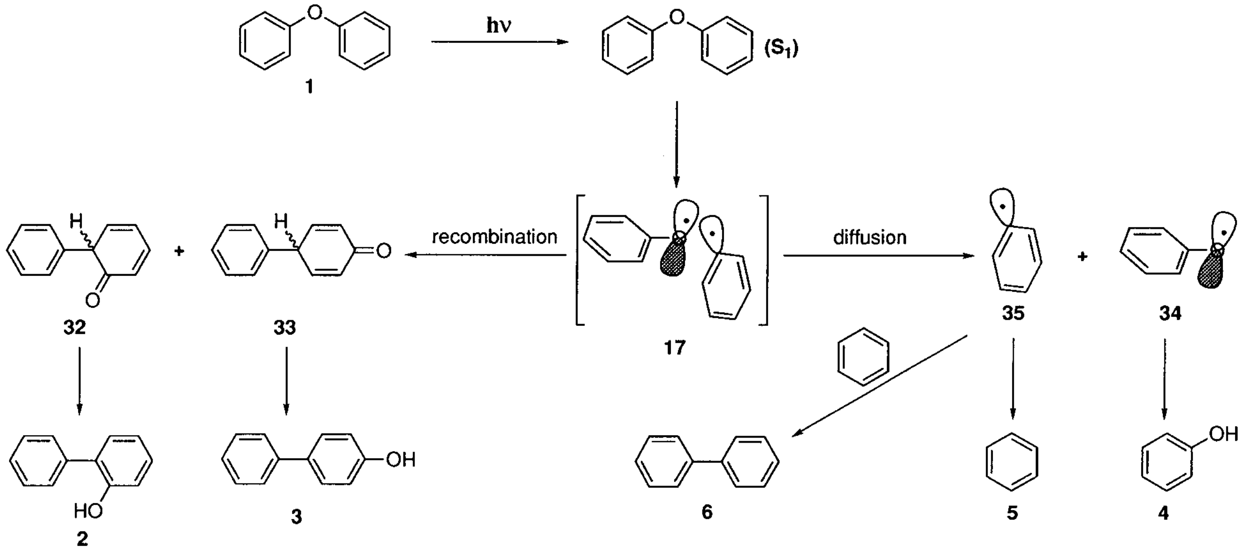
(28) (a) Zeller, K. P.; Petersen, H. *Synthesis* **1975**, 532−533. (b) Zeller, K. P.; Gauglitz, G. Z. *Naturforsch.* **1977**, *32B*, 285−288.

(29) Booth, D.; Noyes, R. M. *J. Am. Chem. Soc.* **1960**, *82*, 1868−1872.

Scheme 7



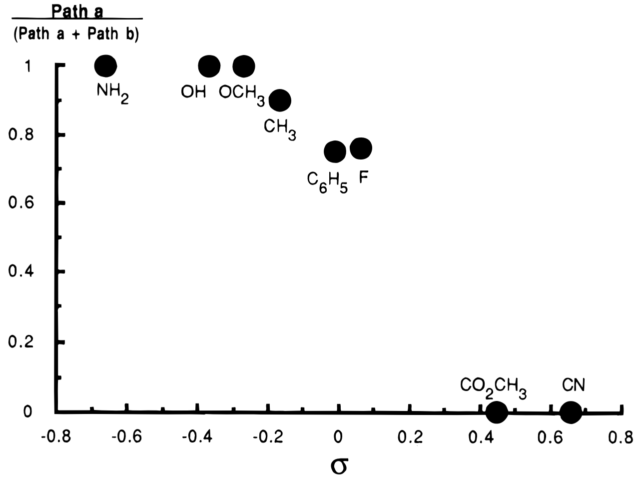


Figure 4. Hammett plot of σ vs the ratio of the combined yield of products *via* path a to that of total products: path a, combined yield of the products formed *via* path a; path b, combined yield of the products formed *via* path b.

revealed that each of them is photostable. Formation of 4-phenylaniline (isolated as **16**) from **1e** and formation of **2** from **1g** cannot be explained at present. These processes seem to be independent of coupling or diffusion of the radical pair (**17**).

Regarding the solvent effect for facilitation of dissociation of the C–O bond of **1a**, our observations agree with those of Ogata *et al.* Among the solvents we used, alcohols and acetic acid afforded product yields of more than 65% on irradiation for 16 h (Table 1). On the other hand, in ethers and in hydrocarbons, the conversion was 40–50% and 18–30%, respectively. This inefficiency (especially in hydrocarbons) may be explained in terms of hydrogen bonding of hydroxylic solvents to the oxygen atom of singlet **1** to facilitate the C–O bond cleavage or to the quinoid intermediates (**32** and **33**) to stabilize them.

Finally, a comment is needed on the distinct substituent effect on the regioselectivity observed in the photolyses of the asymmetrically substituted ethers (**1b**–**1j**). Preference of aryloxy–phenyl cleavage for substrates with an electron-donating substituent and preference of aryl–phenoxy cleavage for those with an electron-withdrawing substituent (Scheme 3, Table 5) seem to be correlated with the Hammett σ values in spite of the radical nature of this reaction. The Hammett plot of σ vs the ratio of the combined yield of products *via* path a to that of total products is presented in Figure 4. Though the influence of a substituent at position 4 on the regioselectivity is clear, we have no explanation as yet for these fascinating phenomena.

Conclusion

We have conducted preparative photolyses to elucidate the mechanism of the photochemical rearrangement of diphenyl ether (**1a**) and found that 2-phenylphenol (**2**) and 4-phenylphenol (**3**) are formed as rearrangement products in higher yields than those obtained in earlier studies, together with phenol (**4**) and benzene (**5**) as diffusion products. The stoichiometrical formation of radical-derived products **2**, **3**, **4**, and **5** provides convincing evidence for homolytic C–O bond cleavage, but not for heterolytic cleavage.

An intramolecular mechanism for both the ortho and the para rearrangement was unambiguously demonstrated by cross-coupling experiments employing [$^2H_{10}$]-**1a** and unlabeled **1a**.

Plots of the reciprocal ratio of the combined yield of **2** and **3** to that of **2, 3**, and **4** against the reciprocal viscosity of solvents gave a linear relation. This, together with formation of biphenyls in photolyses of **1a** in benzene and toluenes, suggests that the reaction involves a dissociation process, but not a concerted process.

All the results described above indicate intermediacy of a radical pair involving a phenoxy radical and a phenyl radical. Intramolecular recombination in the cage gives rearrangement products, and escape from the cage followed by hydrogen abstraction from the solvent gives diffusion products.

Finally, we evaluated the substituent effect on the regioselectivity of C–O bond fission in asymmetric ethers (**1b**–**1i**) and found that electron-donating substituents favor aryloxy–phenyl cleavage, in contrast to electron-withdrawing substituents. This distinct substituent effect seems to be correlated with the Hammett σ values in spite of the radical nature of this reaction.

Experimental Section

General. Melting points were obtained on a Yazawa melting point apparatus (type BY-10) without correction. ^{1}H-NMR spectra were determined with a Varian UNITY 400 spectrometer in various solvents, with tetramethylsilane as an internal reference. UV spectra were obtained on a Hitachi UV-VIS 340 spectrophotometer. Low-resolution electron ionization mass spectra (EI-MS) were taken on a JMS-DX 300. Multiscan WMIMS were taken on a JMS AX 505 HA. Flash column chromatography was performed on silica gel (Merck Art 9385 Kieselgel 60). Thin layer chromatography was performed on silica gel (Merck Art 11696 TLC-Kieselgel 60 HF). GC was taken on a Shimadzu GC 14-A equipped with a Chromatopac C-R5A. Microanalyses were carried out in the microanalytical laboratory of our school.

Solvents. Spectral-grade ethanol, methanol, and acetonitrile and infinity-grade 2-propanol, acetic acid, diethyl ether, tetrahydrofuran, 1,4-dioxane, *n*-hexane, *n*-heptane, and cyclohexane were used for photolysis without further purification. Special-grade 1,2-ethanediol and 1,2-propanediol were dried over calcium hydride and distilled under reduced pressure (1,2-ethanediol, 62 °C, 2.0 Torr; 1,2-propanediol, 65 °C, 1.3 Torr).

Apparatus for Photolysis. For preparative-scale irradiation, a 400 W high-pressure mercury lamp (RIKO UVL-400-HA, internal irradiation type) with a quartz jacket was placed in a cylindrical irradiation flask (Pyrex, 170 or 500 mL). We have found that all of **1** used in this study except 4-phenoxyaniline (**1e**) are inert on irradiation at wavelengths longer than 300 nm from this lamp through a Pyrex filter. So the unfiltered light from this lamp was used directly except in the irradiation of **1e**. Irradiation of **1e** through a Pyrex filter (passing wavelengths longer than 300 nm) for 6 h gave similar results to those obtained by use of unfiltered light. Cooling water was passed through the quartz jacket. The irradiation flask was fitted with a nitrogen inlet, a magnetic stirrer bar, and a gas outlet with a calcium chloride tube.

For analytical-scale irradiation, sample solutions in quartz test tubes (10 mL) were irradiated simultaneously for the same length of time in a merry-go-round apparatus (RIKO RH400-10W) equipped with a 400 W high-pressure mercury lamp (RIKO UVL-400-HA, external irradiation type) through a quartz sleeve. Temperature of the solutions was maintained at 25 °C in a thermostat.

Preparation of Diphenyl Ethers (1). Commercially available **1a** was used after distillation under reduced pressure (bp 75 °C/2.5 Torr, lit.[30] bp 73−74 °C/1 Torr). Commercially available 4-phenoxyphenol (**1d**) and 4-phenoxyaniline (**1e**) were purified by repeated recrystallization from dichloromethane−hexane to give analytical purity (mp **1d**, 85.0−85.5 °C, lit.[31] 75−80 °C; mp **1e**, 84.5−85.0 °C, lit.[32] 83−85 °C). Other substrates (**1b**, **1c**, **1f**, **1g**, **1h**, and **1i**) were prepared by Ullmann synthesis[33] from the corresponding phenols and bromobenzenes with freshly prepared copper powder as the catalyst. Potassium *tert*-butoxide was employed instead of potassium hydroxide.

(4-Methylphenoxy)benzene (1b): prepared from bromobenzene and *p*-cresol; colorless oil, yield 74%, bp 92 °C/1.5 Torr (lit.[34] bp 110−111 °C/2 Torr). Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.56; N, 0.00; O, 8.68. Found: C, 84.83; H, 6.55; N, 0.00. EI-MS *m/e* 184 (M^+). ^1H-NMR ($CDCl_3$): δ 7.32 (dd, 2H, J = 8.9, 7.1 Hz), 7.15 (d, 2H, J = 8.1 Hz), 7.08 (tt, 1H, J = 7.1, 1.8 Hz), 6.99 (dd, 2H, J = 8.1, 1.8 Hz), 6.93 (d, 2H, J = 8.1 Hz), 2.35 (s, 3H). **(4-Methoxy-1-phenoxy)benzene (1c):** prepared from bromobenzene and 4-methoxyphenol; colorless oil, yield 29%, bp 111 °C/1.5 Torr (lit.[35] bp 105−115 °C/0.5 Torr) Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04; N, 0.00; O, 15.98. Found: C, 78.12; H, 6.00; N, 0.00. EI-MS *m/e* 200 (M^+). ^1H-NMR ($CDCl_3$): δ 7.30 (dd, 2H, J = 8.9, 7.7 Hz), 7.04 (tt, 1H, J = 7.7, 1.6 Hz), 6.99 (d, 2H, J = 9.0 Hz), 6.95 (dd, 2H, J = 8.9, 1.6 Hz), 6.89 (d, 2H, J = 9.0 Hz), 3.81 (s, 3H). **4-Phenoxybiphenyl (1f):** prepared from bromobenzene and **3a**; recrystallized from hexane, colorless plates, yield 24%, mp 68.0−69.5 °C (lit.[36] mp 67−68 °C). Anal. Calcd for $C_{18}H_{14}O$: C, 87.78; H, 5.73; N, 0.00; O, 6.50. Found: C, 88.00; H, 5.87; N, 0.00. EI-MS: *m/e* 246 (M^+). ^1H-NMR ($CDCl_3$): δ 7.57 (dd, 2H, J = 8.8, 2.0 Hz), 7.56 (d, 2H, J = 9.0 Hz), 7.43 (t, 2H, J = 8.8 Hz), 7.36 (dd, 2H, J = 8.9, 7.1 Hz), 7.33 (tt, J = 8.8, 2.0 Hz), 7.13 (tt, 1H, J = 7.1, 1.2 Hz), 7.08 (d, 2H, J = 9.0 Hz), 7.06 (dd, 2H, J = 8.9, 1.2 Hz). **(4-Fluoro-1-phenoxy)benzene (1g):** prepared from bromobenzene and 4-fluorophenol; colorless oil, yield 58%, bp 78 °C/2.5 Torr (lit.[37] bp 96−98 °C/2 Torr). Anal. Calcd for $C_{12}H_9FO$: C, 76.58; H, 4.82; F, 10.09; N, 0.00; O, 8.50. Found: C, 76.85; H, 4.79; F, 10.15; N, 0.00. EI-MS: *m/e* 200 (M^+). ^1H-NMR ($CDCl_3$): δ 7.32 (dd, 2H, J = 8.6, 7.5 Hz), 7.09 (dt, 1H, J = 7.5, 1.3 Hz), 7.03 (dd, 2H, J = 9.2, 7.7 Hz), 6.99 (dd, 2H, J = 7.7, 4.9 Hz), 6.97 (dt, 2H, J = 9.2, 1.3 Hz). **Methyl 4-Phenoxybenzoate (1h)**: prepared from methyl 4-bromobenzoate and phenol; colorless prisms, yield 62%, mp 62.5−63.0 °C (lit.[38] mp 58−60 °C). Anal. Calcd for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30; N, 0.00; O, 21.03. Found: C, 73.91; H, 5.56; N, 0.00. EI-MS: *m/e* 228 (M^+). ^1H-NMR ($CDCl_3$): δ 8.03 (d, 2H, J = 9.0 Hz), 7.39 (dd, 2H, J = 8.6, 7.3 Hz), 7.06 (dd, 2H, J = 8.6, 1.2 Hz), 6.98 (d, 2H, J = 9.0 Hz), 3.90 (s, 3H). **4-Phenoxybenzenecarbonitrile (1i):** prepared from bromobenzenecarbonitrile and phenol; pale yellow prisms, yield 80%, mp 32.0−33.0 °C (lit.[31] mp 47 °C). This compound was not recrystallized because of its low mp. Anal. Calcd for $C_{13}H_9NO$: C, 79.98; H, 4.65; N, 7.17; O, 8.20. Found: C, 80.07; H, 4.67; N, 7.13. EI-MS: *m/e* 195 (M^+). ^1H-NMR ($CDCl_3$): δ 7.60 (d, 2H, J = 8.6 Hz), 7.42 (dd, J = 8.5, 7.3 Hz), 7.23 (tt, 1H, J = 7.3, 1.2 Hz), 7.07 (dd, 2H, J = 8.5, 1.2 Hz), 7.00 (d, 2H, J = 8.6 Hz).

Photochemical Rearrangement of 1 (Preparative Irradiation). As a typical example, irradiation of **1b** in ethanol will be described. After 30 min of nitrogen bubbling prior to the irradiation, a solution of 314 mg (1.70 mmol) of **1b** in 170 mL of absolute ethanol was irradiated at ambient temperature for 3.0 h. Nitrogen bubbling was continued during the irradiation. When the substrate was no longer detectable by TLC, the solvent was removed by evaporation under reduced pressure. The residual oil (348 mg) was flash-chromatographed (silica gel, eluent: *n*-hexane then *n*-hexane-ethyl acetate, 15:1, finally 8:1) to give 176 mg (47%) of **10b**, 28 mg (15%) of **13b**, and 23 mg (7%) of **12b**. A pale yellow colored unidentified solid (35 mg) was discarded. Irradiation time and product yields of other substrates are given in Table 5.

In the case of irradiation of 4-phenoxyaniline (**1e**), the amino group of the products (**10e**, **13e**, and 4-phenylaniline) was converted to the corresponding trifluoroacetamide (**14**, **15**, and **16**, respectively) as follows. After irradiation of 315 mg (1.70 mmol) of **1e** in 170 mL of ethanol and removal of the solvent, the residual tarry mixture (343 mg) was suspended in 20 mL of dichloromethane. To the solution was added 3.57 g (17.0 mg, 10 equiv) of TFAA at 0 °C. Stirring was continued for 2 h. After removal of the solvent under reduced pressure, the residue was extracted with 150 mL of 2 N sodium hydrogen carbonate and dichloromethane (100 mL twice). The combined organic phase was dried over magnesium sulfate and filtered. Evaporation of the solvent gave a brown solid (498 mg), which was flash-chromatographed (silica gel, eluent: *n*-hexane−ethyl acetate, 8:1, then 4:1) to afford 28 mg (6.2%) of **16**, 30 mg (10.4%) of **3**, 176 mg (36.8%), of **14** and 96 mg (27.5%) of **15.**

The structures of **11i** and **12i** were determined by comparison with authentic samples which were prepared by an alternative method,[39] and those of other products were established by comparison of the melting points and/or the spectral properties with reported values.

In the case of the reaction of **1a** in toluene, methylbiphenyls formed (**7**, **8**, and **9**) could not be separated by silica-gel flash

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chromatography. So they were obtained as a mixture and identified by comparison of the spectral properties with those of authentic samples. In this reaction, some unidentified products, though in lower yields than the phenyltoluenes, were detected by GC. They could not be isolated by column chromatography, so we did not pursue them further.

4-Methyl-2-phenylphenol (10b): colorless oil (lit. mp 68−68 °C,[40] 65−67 °C [39]). This compound did not solidify in our experiments, but combustion analysis and spectral properties support this structure. Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.56; O, 8.68. Found: C, 77.97; H, 6.04. EI-MS: *m/e* 184 (M^+). ^{1}H-NMR ($CDCl_3$): δ 7.37−7.54 (m, 5H), 7.10 (dd, 1H, J = 8.8, 2.3 Hz), 7.09 (d, 1H, J = 2.3 Hz), 6.92 (d, 1H, J = 8.8 Hz), 5.15 (br s, 1H), 2.37 (s, 3H). **4-(4′-Methylphenyl)phenol (12b):** pale brown powder, mp 153.0−154.5 °C (lit.[41] mp 155 °C). EI-MS: *m/e* 184 (M^+). ^{1}H-NMR ($CDCl_3$): δ 7.46 (d, 1H, J = 9.0 Hz), 7.44 (dd, 1H, J = 8.2 Hz), 7.23 (d, 1H, J = 8.2 Hz), 6.89 (d, 1H, J = 9.0 Hz), 4.7 (br s, 1H), 2.39 (s, 1H). **4-Methoxy-2 phenylphenol (10c)**: colorless oil (lit. bp 116 °C/0.1 Torr,[42] mp 132−132.8 °C [39]). This compound did not solidify, but combustion analysis and spectral properties support this structure. Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04; O, 15.98. Found: C, 77.97; H, 6.04. EI-MS: *m/e* 200 (M^+). ^{1}H-NMR ($CDCl_3$): δ 7.28−7.53 (m, 5H), 6.92 (dd, 1H, J = 8.0, 1.1 Hz), 6.84 (dd, 1H, J = 8.0, 2.9 Hz), 6.82 (dd, 1H, J = 2.9, 1.1 Hz), 4.7 (br s, 1H), 3.80 (s, 3H). **2-Phenylhydroquinone (10d)**: recrystallized from dichloromethane and hexane, colorless needles, mp 103.0−104.0 °C (lit.[43] mp 101 °C). Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41; N, 0.00; O, 17.18. Found: C, 77.13; H, 5.44; N, 0.00. EI-MS: *m/e* 186 (M^+). ^{1}H-NMR ($CDCl_3$): δ 7.38−7.51 (m, 5H), 6.86 (dd, 1H, J = 9.5, 1.0 Hz), 6.75 (m, 2H), 4.84 (s, 1H), 4.43 (s, 1H). ***N*-(4-Phenylphenyl)trifluoroacetamide (16)**: recrystallized from dichloromethane and hexane; pale brown needles, mp 207−210 °C (lit.[44] mp 200−201 °C). Anal. Calcd for $C_{14}H_{10}F_3NO$: C, 63.40; H, 3.80; F, 21.49; N, 5.28; O, 6.03. Found: C, 63.33; H, 3.97; F, 21.74; N, 5.23. EI-MS: *m/e* 265 (M^+). ^{1}H-NMR ($CDCl_3$): δ 7.85−7.94 (br s, 1H), 7.66 (d, 2H, J = 7.9 Hz), 7.64 (d, 2H, J = 7.9 Hz), 7.58 (dd, 2H, J = 7.2, 1.3 Hz), 7.45 (t, 2H, J = 7.2 Hz), 7.36 (tt, 1H, J = 7.3, 1.3 Hz). ***N*-((4-Hydroxy-3-phenyl)phenyl)trifluoroacetamide (14)**: recrystallized from dichloromethane and hexane; colorless needles, mp. 184 °C. Anal. Calcd for $C_{14}H_{10}F_3NO_2$: C, 59.79; H, 3.58; F, 20.27; N, 4.98; O, 11.38. Found: C, 59.74; H, 3.53; F, 20.05; N, 4.96. EI-MS: *m/e* 281 (M^+). ^{1}H-NMR ($CDCl_3$): δ 7.72−7.82 (br s, 1H), 7.43−7.54 (m, 7H), 7.01 (d, 1H, J = 8.5 Hz), 5.25 (s, 1H). **2,4-Diphenylphenol (10f)**: recrystallized from hexane; colorless prisms, mp 89.0−89.5 °C (lit.[45] mp 89 °C). Anal. Calcd for $C_{18}H_{14}O$: C, 87.78; H, 5.73; N, 0.00; O, 6.50. Found: C, 87.86; H, 5.73. EI-MS: *m/e* 246 (M^+). ^{1}H-NMR ($CDCl_3$): δ 7.57 (dd, 2H, J = 8.9, 1.4 Hz), 7.47−7.52 (m, 6H), 7.38−7.45 (m, 3H), 7.31 (tt, 1H, J = 8.9, 1.4 Hz), 7.05 (dd, 1H, J = 8.0, 0.7 Hz), 5.25 (s, 1H). **4-Fluoro-2-phenylphenol (10g)**: colorless oil.[46] Anal. Calcd for $C_{12}H_9FO$: C, 76.58; H, 4.82; F, 10.09. Found: C, 76.57; H, 4.83; F, 9.99. EI-MS: *m/e* 188 (M^+). ^{1}H-NMR ($CDCl_3$): δ 7.52 (dd, 2H, J = 8.2, 7.4 Hz), 7.45 (dd, 2H, J = 7.4, 2.0 Hz), 7.42 (tt, 1H, J = 8.2, 2.0 Hz), 6.90−6.98 (m, 2H), 6.92 (dd, 1H, J = 8.9, 5.0 Hz), 5.03 (s, 1H). **2-(4′-Fluorophenyl)phenol (11g)**: colorless oil (lit.[47] mp 45 °C). This compound did not solidify, but combustion analysis and spectral properties support this structure. Anal. Calcd for $C_{12}H_9FO$: C, 76.58; H, 4.82; F, 10.09. Found: C, 76.38; H, 4.83; F, 10.23. EI-MS: *m/e* 188 (M^+). ^{1}H-NMR ($CDCl_3$): δ 7.46 (dd, 2H, J = 8.9, 5.5), 7.27 (dt, 1H, J = 7.4, 2.0 Hz), 7.23 (dd, 1H, J = 7.4, 2.0 Hz), 7.17 (t, 2H, J = 8.9 Hz), 7.00 (dt, 1H, J = 7.4, 1.2 Hz), 6.97 (dd, 1H, J = 7.4, 1.2 Hz), 5.09 (s, 1H). **4-(4′-Fluorophenyl)phenol (12g)**: recrystallized from ethyl acetate and hexane, colorless prisms, mp 165−168 °C (lit.[47] mp 166 °C). Anal. Calcd for $C_{12}H_9FO$: C, 76.58; H, 4.82. Found: C, 76.37; H, 4.82. EI-MS: *m/e* 188 (M^+). ^{1}H-NMR ($CDCl_3$): δ 7.48 (dd, 2H, J = 9.0, 5.8 Hz), 7.42 (d, 2H, J = 8.7 Hz), 7.09 (t, 2H, J = 9.0 Hz), 6.90 (d, 2H, J = 8.7 Hz), 4.84 (s, 1H). **Methyl 4-(2′-Hydroxyphenyl)benzoate (11h)**: recrystallized from dichloromethane and hexane; colorless needles, mp 133.0−133.5 °C (lit.[38] mp 129−131 °C). Anal. Calcd for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30; N, 0.00; O, 21.03. Found: C, 73.91; H, 5.56; N, 0.00. EI-MS: *m/e* 228 (M^+). ^{1}H-NMR ($CDCl_3$): δ 8.14 (d, 2H, J = 8.6 Hz), 7.59 (d, 2H, J = 8.6 Hz), 7.26−7.31 (m, 2H), 7.02 (ddd, 1H, J = 7.0, 7.1, 1.2 Hz), 6.97 (dt, 1H, J = 7.9, 1.2 Hz), 5.12 (s, 1H), 3.95 (s, 3H). **Methyl 4-(4′-Hydroxyphenyl)benzoate (12h)**: recrystallized from methanol; pale yellow prisms, mp 230.0−231.0 °C (lit.[38] mp 224−225 °C). Anal. Calcd for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30; N, 0.00; O, 21.03. Found: C, 73.62; H, 5.59; N, 0.00. EI-MS: *m/e* 228 (M^+). ^{1}H-NMR (DMSO-d_6): δ 9.66−9.75 (br s, 1H), 7.96 (d, 2H, J = 8.7 Hz), 7.72 (d, 2H, J = 8.7 Hz), 7.57 (d, 2H, J = 9.0 Hz), 6.86 (d, 2H, J = 9.0 Hz), 3.84 (s, 3H). **4-(3′-Hydroxyphenyl)benzenecarbonitrile (11i)**: recrystallized from dichloromethane and hexane, pale yellow prisms, mp 111.0−112.0 °C (lit.[39] mp 113.5 °C). Anal. Calcd for $C_{13}H_9NO$: C, 79.98; H, 4.65; N, 7.17; O, 8.20. Found: C, 79.70; H, 4.69; N, 7.07. EI-MS: *m/e* 195 (M^+). ^{1}H-NMR ($CDCl_3$): δ 7.75 (d, 2H, J = 8.6 Hz), 7.65 (d, 2H, J = 8.6 Hz), 7.30 (ddd, 1H, J = 8.5, 7.9, 2.0 Hz), 7.27 (dd, 1H, J = 7.9, 2.0 Hz), 7.04 (dt, 1H, J = 7.9, 1.9 Hz), 6.94 (dd, 1H, J = 8.5, 1.9 Hz), 5.06 (s, 1H). **4-(4′-Hydroxyphenyl)benzenecarbonitrile (12i)**: recrystallized from dichloromethane and hexane, pale yellow prisms, mp 202.5−203.0 °C (lit.[39] mp 198.5−199.0 °C). Anal. Calcd for $C_{13}H_9NO$: C, 79.98; H, 4.65; N, 7.17. Found: C, 79.72; H, 4.65; N, 7.16. EI-MS: *m/e* 195 (M^+). ^{1}H-NMR ($CDCl_3$): δ 7.70 (d, 2H, J = 8.2 Hz), 7.63 (d, 2H, J = 8.2 Hz), 7.50 (d, 2H, J = 8.3 Hz), 6.94 (d, 2H, J = 8.3 Hz), 4.98 (s, 1H).

Independent Syntheses of 11i and 12i. These two compounds were prepared according to Petrillo's method.[39]

Irradiation of 1a (GC Analyses). Irradiation of **1a** (0.01 M solution in ethanol, benzene, or toluene) was done in a similar manner to that described above. At each irradiation period in Figures 1 and 2, an aliquot was taken out and subjected to GC analyses without an internal reference. Conditions of measurement were as follows: column, H30B-PM50 (Shinwa Chemical Industries); column diameter, 0.25 mm; injection port, 180 °C; detector, 200 °C; column temperature, initially 150 °C, elevated at 7 °C/min to 200 °C. Retention times (min) were 4.48 (**1a**), 6.90 (**2**), 12.24 (**3**), 4.19 (**6**), 4.29 (**7**), 5.21 (**8**), 5.47 (**9**), 2.31 (**4**), and 1.71 (**5**). Yields of recovered **1a** and products were determined according to calibration curves, prepared by using appropriate concentrations of the samples.

In the triplet quenching experiment, **1a** (0.01 M) in ethanol in the presence of *cis*-1,3-pentadiene (Aldrich, 5.0 × 10^{-3} M) was irradiated internally, and the resulting mixture was analyzed by GC.

Solvent Viscosity Effect (GC Analyses). Solutions of **1a** (0.01 M in each solvents) in 10 mL quartz test tubes were degassed to about 10^{-3} Torr in three freeze−pump−thaw cycles, sealed, and irradiated simultaneously in a merry-go-round apparatus for 16 h. The resulting mixture was injected into the GC column directly without an internal reference. When 1,2-ethanediol and 1,2-propanediol were used as solvents, pretreatment for GC column injection was done as follows to remove the solvents. After irradiation, the mixture was extracted with 60 mL of diethyl ether and with cold water (30 mL × 3), dried over magnesium sulfate, and evaporated to give an oil, which was diluted with ethyl acetate to 10 mL in a volumetric flask and used for GC analyses.

Preparation of [$^2H_{10}$]1a. A solution of [$^2H_6$]phenol (630 mg, 6.3 mmol) in 2.0 mL of methanol was prepared, and 706

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mg (6.3 mmol) of potassium *tert*-butoxide was carefully dissolved in it. Methanol was evaporated, and the residue was dried in vacuo under heating. Removal of residual *tert*-butyl alochol is essential. A pale brown solid was obtained, and to this, 171 mg (1.7 mmol) of [$^2H_6$]phenol, cupric sulfate monohydrate (18 mg), and [$^2H_5$]bromobenzene (989 mg, 6.1 mmol) were added. The mixture was heated in an oil bath, which had been preheated to 200−210 °C. Heating was continued for 1 h with vigorous stirring. The blackish brown residue was extracted with hexane (50 mL) and 1 N sodium hydroxide (30 mL), washed with brine (30 mL × 2), and dried over magnesium sulfate. Evaporation of the solvent gave 988 mg of a pale yellow oil. Purification by flash chromatography (silica gel, *n*-hexane as an eluent) afforded 935 mg of [$^2H_{10}$]**1a** (5.19 mmol, yield 85% based on [$^2H_5$]bromobenzene), which was used for cross-coupling experiments without further purification.

Cross-Coupling Experiments. A solution containing [$^2H_{10}$]**1a** (189.3 mg, 1.05 mmol) and unlabeled **1a** (188.3 mg, 1.11 mmol) in 170 mL of absolute ethanol was irradiated for 45 min in the same manner as described for the irradiation of **1a**−**i**. After evaporation of the solvent, the residual yellow oil (378 mg) obtained was flash-chromatographed (silica gel, eluent: *n*-hexane−ethyl acetate, 30:1, then 20:1, and finally 8:1) to afford 285.0 mg (75%) of **1a**, 41.2 mg (11%) of **2**, 5.8 mg (2%) of **4**, and 23.0 mg (6%) of **3** in that order. For **1a**, **2**, and **3**, multiscan WMIMS was conducted with a JEOL JMS AX 505 HA mass spectrometer. Samples of about 30 μg in a quartz reservoir (volume, 2 mL) were introduced into the mass spectrometer in the solid state. Data collection was achieved by monitoring the relative abundance with respect to the molecular ion at 70 eV. For each compound, three or four samples were analyzed. The range of *m*/*z* 165−185 was monitored at 10 s/scan. Conditions of analyses were as follows. The ionization source was heated as follows: initially 26 °C for **1a** and **2**, 50 °C for **3**, and elevated at 3 °C/min for **1a** and **2**, 10 °C/min for **3**, to obtain an appropriate ion current. In this way, 180−220 scans (**1a**), 280−360 scans (**2**), and 380−440 scans (**3**) were collected. The data were analyzed in sets of 20 scans to yield relative peak intensities and standard deviations. For **1a**, peak intensities at *m*/*z* 180 ([$^2H_{10}$]**1a**), *m*/*z* 175 ([$^2H_5$]**1a**), and *m*/*z* 170 (unlabeled **1a**) were used to diagnose the scrambling of the phenyl group in **1a**. Similarly, for **2a** and **3**, *m*/*e* 179([$^2H_9$]**2** or [$^2H_9$]**3**), *m*/*z* 175 ([$^2H_5$]**2** or [$^2H_5$]-**3**), *m*/*z* 174 ([$^2H_4$]**2** or [$^2H_4$]**3**), and *m*/*z* 170 (unlabeled **2** or **3**) were used to diagnose the intramolecularity of the rearrangement. The results are summarized in Tables 3 and 4.

Deuterium abundance of [$^2H_{10}$]1a, [$^2H_9$]2, and [$^2H_9$]3. Irradiation of a solution of [$^2H_{10}$]**1a** (190.5 mg, 1.06 mmol) in 170 mL of absolute ethanol (0.005 M) for 45 min gave 138.5 mg (72.7%) of **1a**, 20.0 mg (10.5%) of **2**, 5.8 mg (5.5%) of **4**, and 8.8 mg (4.6%) of **3**. For **1a**, **2**, and **3**, relative peak intensities were determined by multiscan WMIMS as described for the cross-coupling experiment. Calculations of deuterium abundance have been described in detail in an earlier publication.[24] The results are summarized in Table 2.

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