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Hydroxyl Radical as a Strong Electrophilic Species

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Abstract—In order to clarify an index which could be used as proof of the presence of hydroxyl radical, a new standard isomer distribution ratio of phenols formed from aromatic hydroxylation with [(4-bromophenyl)diazenyl](phenyl)methyl hydroperoxide **4**, which is a stable source of hydroxyl radical, under a new appropriate photolysis condition in the presence or absence of benzoquinones is reported. We also demonstrated the strong electrophilic properties of hydroxyl radical in reference to earlier results of electron density calculations.

Introduction

Oxidative stress[1,2] and the damage[3] that results from it have been implicated in a wide number of disease processes including atherosclerosis,[4] autoimmune disorders,[5,6] rheumatoid arthritis,[7] neuronal degeneration,[8] cardiovascular diseases[9] and cancer.[10] Reactive oxygen species (ROS) are ubiquitous and occur naturally in all aerobic species, coming from both exogenous and endogenous sources.[11] In particular, hydroxyl radical among a number of ROS is quite reactive[12] and readily damages biological molecules[13] including DNA.[14,15] A number of compound[16–18] have been demonstrated in in vitro and in vivo experiments to protect against oxidative damage by inhibiting or quenching hydroxyl radical. As such, there is a need to establish proof[19] regarding the presence or absence of the hydroxyl radical as a reactive intermediate species in chemical and biological processes. In vivo measurement of highly reactive hydroxyl radicals in humans is very difficult and specific markers are currently under investigation (amino acid hydroxylation, protein, DNA adducts, and aromatic probes).[20] These are all based on the ability of hydroxyl radical to attack the benzene rings of aromatic compounds smoothly and produce hydroxylated compounds, particularly isomer ratios of phenols that can be measured directly.[21–23]

However, even in chemical processes where the isomer ratios in aromatic hydroxylation have been used as proof for the presence of hydroxyl radical as Walling and Johnson studied,[24] there still remain many ambiguities[25] concerning whether or not, or which isomer ratio of phenols reveals the participation of hydroxyl radical correctly. Various *ortho:meta:para* isomer ratios of phenols have been reported in aromatic hydroxylation with hydroxyl radicals generated from Fenton's reagent[26–28] or by radiolysis of water.[29–31] Variation in the ratios is thought to arise from positional isomerization of the initially formed hydroxycyclohexadienyl radicals **6** under aqueous acidic conditions, for example, via radical cations[24] **7** prior to oxidation to phenols as shown in Scheme 3 or by NIH shift rearrangements[32] via arene oxide intermediates[33] and so on. In addition, molecular oxygen present in the reactant was found to be incorporated into phenols and changed the isomer ratios.[34] Although many trials to clarify the mechanism have also been put forward, several reactive species are produced together with hydroxyl radical in the reactions,[31,35] which make the analysis of the reaction mechanism more complicated. Furthermore, even with Fenton's reagent, there are some papers describing production of another reactive intermediate[36,37] instead of hydroxyl radical.

In order to prevent positional isomerization and hence to get intrinsic isomer ratios which accurately reflect the position of hydroxyl radical attack, it is desirable to carry out reaction in an anhydrous medium in the presence of a good oxidant under deaerated conditions, with argon or nitrogen gas. In 1975 Tezuka et al.[38] found that α-azohydroperoxide such as [(4-bromophenyl)diazenyl](phenyl)methyl hydroperoxide **4**[39]

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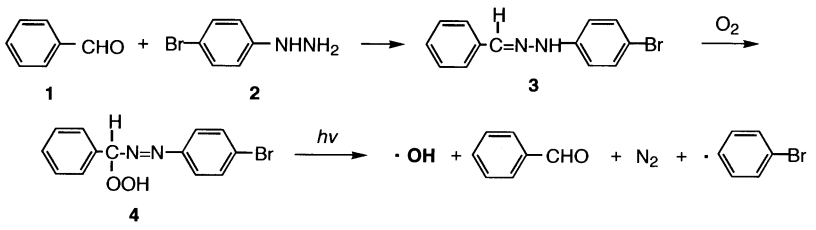
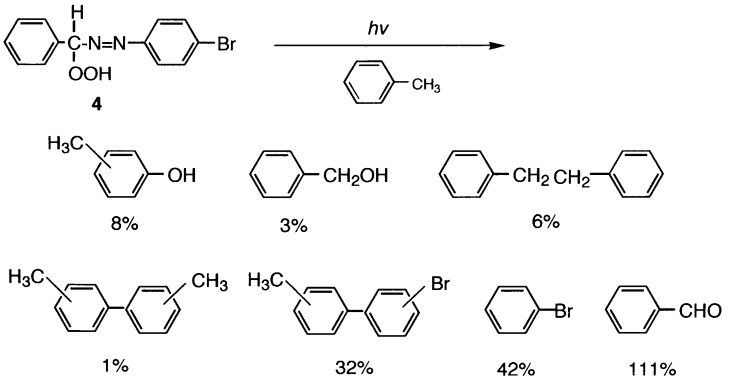
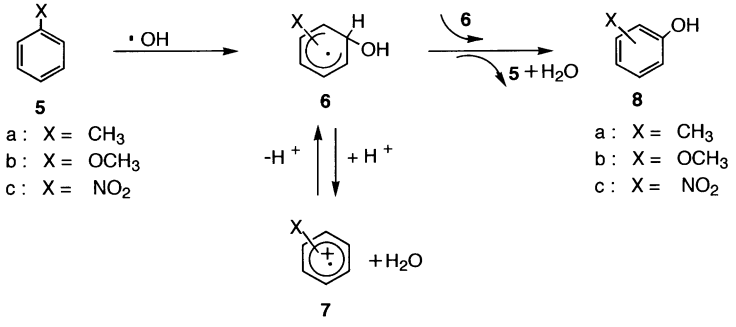


Scheme 1.



Scheme 2.



Scheme 3.

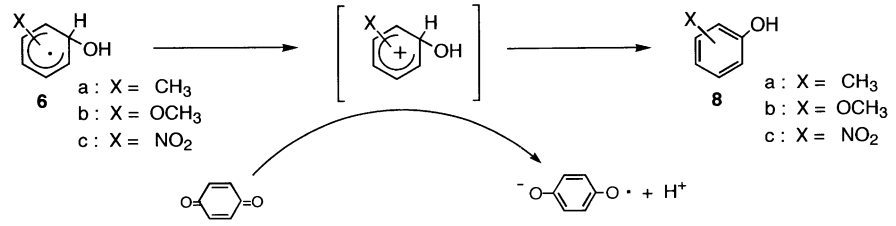
generates the hydroxyl radical by photolysis instead of thermolysis[40] under anhydrous conditions and we subsequently investigated aromatic hydroxylation[41] using **4** as an efficient hydroxyl radical generator. In this report, we describe a new standard isomer ratio of phenols formed from aromatic hydroxylation with 4 under a new appropriate photolysis condition in the presence or absence of benzoquinones as a good oxidant and demonstrate the strong electrophilic properties of hydroxyl radical in reference to previous results[42,43] of electron density calculations.

Chemistry

Hydrazone **3** derived from *p*-bromophenylhydrazine **2** and benzaldehyde **1** was oxidized by molecular oxygen in benzene to give α-azohydroperoxide **4** as yellow crystals as shown in Scheme 1. α-Azohydroperoxide **4** in toluene **5a**, anisole **5b** or nitrobenzene **5c** were photodecomposed in the presence or absence of benzoquinones under argon gas, and yielded cresol **8a**, methoxyphenol **8b** or nitrophenol **8c**, respectively together with benzaldehyde, bromobenzene and so on. All products in the reaction of **4** in toluene are shown in Scheme 2. During hydroxylation in the absence of benzoquinones, the initially formed isomeric hydroxycyclohexadienyl radicals **6** disproportionate to give phenols **8a**–**8c**, as shown in Scheme 3. In the presence of oxidant such as benzoquinones on the other hand, the isomeric radicals **6a**–**6c** are converted to phenols **8a**–**8c** efficiently by an electron transfer oxidation as shown in Scheme 4.

Results and Discussion

We initially selected $K_3Fe(CN)_6$ as an oxidant for cyclohexadienyl radical intermediate **6** because it is often used in aqueous media to prevent hydration and/or



Scheme 4.

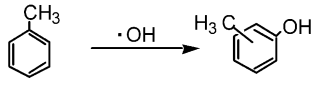
rearrangement reactions,[44] and tried to compare an isomer distribution ratio of phenols in this system with that with Fenton's reagent. We chose toluene as the substrate and carried out the reaction with hydroxyl radicals generated from **4** by photolysis with a high pressure mercury lamp through a Pyrex filter in toluene and water (1:1) in the absence or presence of $K_3Fe(CN)_6$ as the oxidant with vigorously stirring and thorough bubbling of argon gas constantly, and analyzed the isomer ratios and yields of the produced cresols, as indicated in Table 1. The isomer ratios in both cases were found to be almost the same while the yield of cresols increased in the presence of $K_3Fe(CN)_6$. This result was the desired outcome, even though the increase is small. We thus moved on to experiments in anhydrous media to increase the efficacy of the oxidant.

We tried to find a new standard isomer distribution ratio of phenols that would be obtained by the reaction with hydroxyl radicals generated from **4** by photolysis in anhydrous media in the absence or presence of an oxidant. We chose *p*-benzoquinone as the oxidant because there was a report[30] that the rate of electron transfer oxidation of cyclohexadienyl radical **6b** by *p*-benzoquinone under radiolytic conditions in aqueous media is fast and nearly equal to the diffusion controlled rate ($k \fallingdotseq 10^9$ M^{-1} s^{-1}). In order to investigate the substituent group effect for hydroxyl radical attack at a benzene ring, we selected toluene **5a**, anisole **5b** and nitrobenzene **5c** as substrates. The photolysis of **4** in these aromatics with a high pressure mercury lamp through a Pyrex filter under argon gas gave cresol, methoxyphenol and nitrophenol, respectively, in the isomer ratios and yields listed in Table 2.

It can be clearly seen from Table 2 that the yield of both cresol and methoxyphenol increased in the presence of *p*-benzoquinone while that of nitrophenol did not increase. The *ortho:meta:para* ratio of each phenol, on the other hand, showed a constant value within experimental error in the absence or presence of *p*-benzoquinone. It is important to note that the yield of phenols was more than doubled, except for nitrophenol, in the case of coexistence with the oxidant, while the isomer ratios remained constant in each case. This implies that the oxidation of the cyclohexadienyl radicals **6a** and **6b** by *p*-benzoquinone is so efficient that the isomer ratio of cresol and hydroxyanisole reflects the isomer ratio of the position at which hydroxyl radical first attacked. In other words, the isomer ratio in the case of the oxidation is almost the same as that of disproportionation,[26] and so we confirmed that this system with **4** in anhydrous media works very well for eliciting the correct isomer ratio regardless of oxidant. In terms of why the yield of both cresol and methoxyphenol increased more than doubled, we think that the intermediate cyclohexadienyl radicals **6**, which actually should have converted into biphenyls[41] as byproducts, might also form phenols instead in the presence of *p*-benzoquinone. In addition, it seemed that *p*-benzoquinone did not abstract a hydrogen atom from **4** and not interfere with the photodecomposition of **4**.

Furthermore, in order to minimize absorption of light by *p*-benzoquinone, reaction was next carried out using

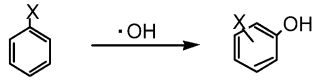
Table 1. The isomer ratios and yields of cresols in the presence or absence of $K_3Fe(CN)_3$[a–d]



$K_3Fe(CN)_3$[e] (M)	Cresol *ortho:meta:para*	Yield (%)
0	70:10:20	5
0.05	71:10:19	7

[a] A Pyrex filter was used.
[b] Yields are based on the original amount of **4** (0.01 M).
[c] Data obtained by repeating the experiment several times.
[d] Heterogeneous reaction system (water/toluene = 1:1).
[e] Concentration of $K_3Fe(CN)_3$ in toluene and water (1:1).

Table 2. The isomer ratios and yields of cresols, methoxyphenols and nitrophenols in the presence or absence of *p*-benzoquinone[a,b]



X	CH_3		OCH_3		NO_2	
p-Benzoquinone[c]	0 M	0.05 M	0 M	0.05	0 M	0.05 M
ortho	71	73	84	80	26	29
meta	9	11	0[d]	2	48	46
para	21	16	16	18	26	25
Yield[e] (%)	8	25	14	51	16	14
SOMO **6** (ev)[f]	−8.6∼9.0[g]		−8.5∼8.9[h]		−9.8∼−10.0[i]	

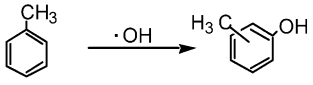
[a] A Pyrex filter was used.
[b] Data obtained by repeating the experiment several times.
[c] Concentration of *p*-benzoquinone in aromatics.
[d] Only a trace of *m*-methoxyphenol was detected by GLC.
[e] Yields are based on the original amount of **4** (0.01 M).
[f] Electron density of the HOMO of these aromatics was calculated by CNDO/2.
[g] *ortho* (−8.6990eV):*meta* (−9.0337eV):*para* (−8.6201eV).[45]
[h] *ortho* (−8.5603eV):*meta* (−8.8541eV):*para* (−8.4977eV).
[i] *ortho* (−10.0119eV):*meta* (−9.8419eV):*para* (−10.0106eV).[45]

a Corning glass filter 5–60 which passes only light between 360 and 490 nm. We selected toluene as a typical example for the solvent and performed the appropriate photolysis of **4** in toluene with *p*-benzoquinone with a high pressure mercury lamp through this filter whereby more than 90% of light was absorbed by **4** (*p*-benzoquinone: $\varepsilon_{420} = 12$; **4**: $\varepsilon_{420} = 180$ in toluene). We chose a 0.005 M concentration of *p*-benzoquinone so as to minimize absorption by the oxidant. In addition, we also used 2-methylbenzoquinone and 2,5-di-*tert*-butylbenzoquinone as an oxidant instead of *p*-benzoquinone and performed the same irradiation experiments with the Corning filter as the new appropriate photolysis condition.

As shown in Table 3, the isomer ratio of cresol in this case was found to be almost the same as that observed with the Pyrex filter within experimental error. In addition, the yields of cresol had the same tendency to increase when oxidant was added. All the observations in Tables 2 and 3 demonstrate that benzoquinone acts as the oxidant for **6** in its ground state and also do not resist photodecomposition of **4**. In other words, we confirmed that at least the intermediate radicals **6a** and **6b** were converted to the phenols **8a** and **8b** efficiently by electron transfer oxidation by benzoquinones, as shown in Scheme 4.

Finally, we consider further the data in Table 2 to demonstrate the electrophilic property of hydroxyl radical in reference to the previous results of electron density calculations. Comparison of the yields in Table 2 indicates that oxidation by *p*-benzoquinone is very effective in the toluene and anisole cases, but not in the case of nitrobenzene, supporting the proposition that an electron transfer oxidation by *p*-benzoquinone occurs when an electron-donating group is substituted in **5**. This probably is related to the fact that **6a** and **6b** possess a higher SOMO energy (−8.6–−9.0 eV[45] and −8.5–−8.9 eV, respectively) compared with **6c** (−9.8–−10.0 eV)[45] calculated by CNDO/2, and **6a** and **6b** might interact more easily with the LUMO (−2.1 eV) of *p*-benzoquinone. In other words, it seems that **6c** is more stabilized to delocalize the radical charge between the nitro substituent group and the ring, and that such an electron transfer oxidation did not take place.

Table 3. The isomer ratios and yields of cresols in the presence of *p*-benzoquinone derivatives[a,b]



Oxidant	Concentration[c] (M)	*ortho:meta:para*	Yield[d] (%)
None	—	71:9:20	8
p-Benzoquinone	0.005	67:13:20	18
2-Methyl-*p*-benzoquinone	0.005	66:11:23	21
2,5-di-*tert*-Butyl-*p*-benzoquinone	0.005	67:14:19	19

[a]A Corning 5-60 filter was used.
[b]Data obtained by repeating the experiment several times.
[c]Concentration of *p*-benzoquinone in toluene.
[d]Yields are based on the original amount of **4** (0.01 M).

The isomer ratios observed in this study are consistent with those under argon in the absence of oxidant within experimental errors, as reported by us.[41] On the basis of our present and previous studies, we propose a new standard isomer distribution ratio of cresol, methoxyphenol and nitrophenol as *ortho:meta:para* = 72:10:18, 82:1:17 and 27:47:26, respectively, in which the error is less than 10%, as shown in Table 4. The isomer ratios reported in this study, therefore, provide a correct value for the position of aromatics attacked by hydroxyl radical in anhydrous organic media. As for the derived ratios, additional factors need to be considered. As we reported, the HOMO electron density of aromatics strongly controls the site of hydroxyl radical attack at the aromatic ring.[42] We therefore also calculated the *ortho:meta:para* values of the HOMO coefficients for anisole by CNDO/2 according to the method of Eberhardt and Yoshida[45] and made a comparison between the calculated results, including their data,[45] and the experimental isomer ratios for hydroxylation of toluene, anisole and nitrobenzene observed in this study. As shown in Table 4, the experimental ratios are fairly consistent with the HOMO coefficients, but the *ortho* isomer values of **8a** and **8b** in this study are a little higher than the values of HOMO coefficients, as well as in the case of **5a** and **5b**. This fact, together with a high HOMO electron density and coefficient at the *ipso*-position[45] of these aromatics and formation of a small amount of phenol in the reaction of **5a** and **5b** with **4** in Table 5, suggests that the *ipso* isomer[46,47] must be taken into account. Therefore, we think that the rearrangement of the *ipso* to *ortho* isomers increases and this derives a high isomer ratio of the *ortho*-oriented isomer of **6a** and **6b** in this study.

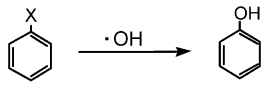
Comparing these new standard isomer distribution ratios with those obtained from radiolysis of water or reaction with Fenton's reagent, it is interesting to note

Table 4. The standard isomer ratio of phenols observed and the calculated HOMO coefficients of the aromatics

Benzenes	Isomer ratio observed[a] *ortho:meta:para*[b] (%)	HOMO coefficients[c] *ortho:meta:para*
Toluene	72:10:18	0.6392 (39%):0.4646 (28%):0.5282 (32%)[45]
Anisole	82:1:17	0.6754 (41%):0.4408 (27%):0.5295 (32%)
Nitrobenzene	27:47:26	0.0287 (36%):0.0374 (47%):0.0136 (17%)[45]

[a]Data obtained by the observed isomer ratio of phenols.
[b]Data obtained by repeating the experiment several times.
[c]HOMO coefficients were calculated by CNDO/2.

Table 5. The yields of phenol in the presence or absence of *p*-benzoquinone[a,b]



X	CH_3		OCH_3	
p-Benzoquinone[c] (M)	0	0.005	0	0.005
Yield[d] (%)	2	5	9	15

[a]A Corning 5-60 filter was used.
[b]Data obtained by repeating the experiment several times.
[c]Concentration of *p*-benzoquinone in toluene or anisole.
[d]Yields are based on the original amount of **4** (0.01 M).

Table 6. The isomer ratios of phenols in the reaction of toluene, anisole and nitrobenzene with α-azohydroperoxide **4**, radiolysis of water and Fenton's reagent

Phenols	α-Azohydroperoxide **4** *ortho:meta:para*[a]	Radiolysis of water *ortho:meta:para*	Fenton's reagent *ortho:meta:para*
Cresol	**72:10:18**	49:20:31[29]	71:5:24[26]
Methoxyphenol	**82:1:17**	46:0[b]:54[30]	85:4:11[27]
Nitrophenol	**27:47:26**	30:9:61[31]	24:30:46[28]

[a]Data obtained by repeating the experiment several times.
[b]Only a trace of *m*-methoxyphenol was detected.

that the ratios in this study differs from those by radiolysis, while there is a similar tendency with those from the Fenton's reagent, except for the ratios of nitrophenols, as shown in Table 6. It seems to us that the discrepancy of these values between radiolysis of water and this study is strongly associated with facile formation of the radical cation **7** in aqueous media ($k \fallingdotseq 10^8$ M^{-1} s^{-1}).[30] As described, we could not achieve electron transfer oxidation in this system with nitrobenzene and *p*-benzoquinone, and are unable to deduce which ratio is more precise. However, it is clearly demonstrated in this study that attack of hydroxyl radical takes place mainly at *ortho–para* positions when an electron-donating group is substituted in **5** and it occurs mainly at the *meta* position when an electron-withdrawing group is substituted in **5**. It is interesting to note that the ionization potential of hydroxyl radical (−13.0 eV)[48] is the lowest among other radicals such as phenyl radical (−9.24 eV)[48] and methyl radical (−9.84 eV),[48] and it suggests that hydroxyl radical has a strong electron accepting property. In addition to this, we also recognized that a 2×para/meta (p/m) value of **5b** calculated from the new isomer ratio was found to be 34.0 and this value is much higher than that of phenyl radical (2p/m = 1.44),[49] methyl radical (2p/m = 1.47) [49] and so on. Therefore, we could finally confirm the strong electrophilic properties of hydroxyl radical from both the observed and calculated data.

Conclusion

We discovered that **4** is a very good source for generation of hydroxyl radical in anhydrous media by photolysis, and determined the new standard isomer distribution ratio of phenols in aromatic hydroxylation by using this system under the appropriate photolysis condition. In the presence of oxidant, the yield of phenols with an electron-donating group in the aromatic increased while the isomer ratio of the phenols is almost the same as in the absence of the oxidant. In addition to this, the yield and isomer ratio of phenol with an electron-withdrawing group is almost constant in the presence or absence of oxidant. Therefore it is demonstrated that the new standard isomer distribution ratio should be correct and that hydroxyl radical possesses stronger electrophilic properties, compared to others such as phenyl and methyl radicals.

Experimental

Toluene and benzene were treated with concentrated sulfuric acid, washed with H_2O, 5% NaOH aqueous solution and H_2O, dried over calcium chloride, and then distilled. Anisole of guaranteed grade was treated with 5% NaOH aqueous solution, washed with H_2O, dried over calcium chloride, and distilled. Nitrobenzene of guaranteed grade was dried over calcium chloride, and distilled. These solvents were prepared by bubbling argon gas for at least 10 min prior to use. *p*-Benzoquinone and 2,5-di-*tert*-butylbenzoquinone were recrystallized from a mixture of ethanol and *n*-hexane (1:1) and 2-methylbenzoquinone was sublimed before use. Potassium ferricyanide, 1,1,1,3,3,3-hexamethyldisilazane and pyridine were of guaranteed grade. A glass column (3.0 mm×3.0 m) or a glass capillary column (20 m) was used in a Shimadzu 6-AM gas chromatograph, with a flame ionization detector (FID). Nitrogen was used as the carrier gas. The packing materials and operating conditions for separation of phenols are described below. The average isomer ratios and yields of phenols were obtained by repeating the same reaction run two or three times. The proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 60 MHz on a Varian EM360A Spectrometer using tetramethylsilane (TMS) as an internal reference. The infrared (IR) spectra were recorded on a Hitachi 215 infrared spectrophotometer. The ultraviolet (UV) spectra were recorded on a JASCO UVIDEC-1 spectrophotometer. The ESI mass spectra (ESI-MS) were recorded on a Plateform LC-MS Spectrometer (Micromass). The mass spectra (MS) were recorded on a Hitachi RMU-6M mass spectrometer by GC-mass system.

Preparation of [(4-bromophenyl)diazenyl](phenyl)methyl hydroperoxide 4. To a solution of 4-bromophenylhydrazine hydrochloride (3.58 g, 16.0 mmol) and sodium acetate (1.97 g, 24.0 mmol) in water (50 mL) and ethanol (50 mL) was added dropwise benzaldehyde (1.63 mL, 16.0 mmol) at room temperature and the resulting precipitate was filtered and purified by recrystallization from carbon tetrachloride to give 3.90 g (89.0%) of benzaldehyde 4-bromophenylhydrazone as milk-white crystals. A suspension of benzaldehyde 4-bromophenylhydrazone (2.12 g, 7.70 mmol) in dry benzene (20 mL) was stirred at room temperature in the

shade while oxygen gas was bubbled through the solution until 4-bromophenylhydrazone was completely converted to **4**. The suspension gradually turned yellow. After stirring for 6 h, the resulting precipitate was filtered and purified by recrystallization from benzene to give 1.43 g (60.5%) of **4** as yellow crystals: mp 114–115 °C (dec., lit.[50,51] mp 107–108 °C). ^{1}H NMR (60 MHz, CD_3CN)] δ 6.05 (1H, s), 7.4–7.6 (5H, m), 7.7–7.8 (4H, m), 10.35 (1H, s). IR (KBr, cm^{-1}) 845 (*o–o*). UV–vis [(CH_3CN) λ_{max}, nm (log ε)]: 287 (4.22), 413 (2.36). ESI-MS *m/z*: 308 $(M-H)^-$. Anal. Calcd for $C_{13}H_{11}O_2N_2Br$: C 50.81, H 3.58, N 9.12, Br 26.06. Found: C 51.01, H 3.98, N 9.34, Br 25.98.[50,51] The molecular structure of **4**, $BrO_2N_2C_{13}H_{11}$[52] was identified by X-ray crystal graphic analysis. Compound **4** is stable at room teperature and can be stored at 4 °C in the dark for a couple of months. Biological activity tests such as chemical carcinogen and inhibition of photosynthesis were done.[53,54]

Photodecomposition of [(4-bromophenyl)diazenyl](phenyl)methyl hydroperoxide 4 in toluene and water or aqueous potassium ferricyanide solution. To a toluene solution (10 mL) of **4** (61.5 mg, 0.20 mmol) in a Pyrex tube was added distilled water (10 mL) or 1.0 mM potassium ferricyanide solution (329 mg in 10 mL distilled water, pH = 6.2). The mixtures were stirred vigorously while they were irradiated with a 400 W high-pressure mercury lamp (UVL-400P, Rikougakusangyo) under argon gas at 12–15 °C for 3 h. After removal of the aqueous solution by filtration, each organic layer was separated and dried over calcium chloride. To each solution was added naphthalene as an internal standard, and the mixture was directly analyzed by GLC (3 mm×3 m glass column, KG02 on Uniport HP60–80; FID with temperature programing for 3 °C/min from 80 to 180 °C) and the yield of *o*-cresol was determined. From each solution utilized above, the solvent was removed under reduced pressure and the resulting residue was treated with 1,1,1,3,3,3-hexamethyldisilazane. The mixtures including the trimethylsilyl ethers of cresols were analyzed by GLC (3 mm×3 m glass column, KG02 on Uniport HP60–80; FID at 80 °C constant) and the *ortho*/*meta*/*para* isomer ratio of cresols was determined.

Photodecomposition of 4 in toluene in the absence or presence of *p*-benzoquinone. 4 (92 mg, 0.30 mmol) and various concentrations of *p*-benzoquinone [(0 mg, 0 mmol), (64.9 mg, 0.60 mmol), (162 mg, 1.5 mmol) or (324 mg, 3.00 mmol)] were dissolved in toluene (30 mL), respectively, and the mixtures in a Pyrex tube were irradiated for 3 h in the same manner as above. Each reaction mixture was analyzed by GLC (KG-02 glass column) in the same manner described above. The reaction mixture in the absence of *p*-benzoquinone was devided into the two parts of equal volume and one was used to analyze cresol as described above. The other was used for analyzing bromobenzene, benzaldehyde, benzyl alcohol, bromomethyldiphenyl, dibenzyl, ditolyl as follows.

a. To the reaction mixture was added naphthalene as an internal standard, and the mixture was directly analyzed by GLC (3 mm×3 m glass column, KG02 on Uniport HP60–80; FID at 80 °C constant) and the yields of bromobenzene and benzaldehyde were determined.

b. From the solution utilized above, the solvent was removed under the reduced pressure at room temperature, and the resulting residue was analyzed by GLC (3 mm×3 m, glass column, KG02 on Uniport HP60–80; FID with temperature programing for 1 °C/min from 130 to 180 °C) and the yields of cresol, benzyl alcohol and bromomethyldiphenyl (X) were determined.

c. To the above residue was added fluorenone as an internal standard, and the products were analyzed by GLC (3 mm×3 m glass column, SF-96 on Uniport B 10% 60–80; FID at 160 °C constant) and the yields of dibenzyl and ditolyl were determined.

The structure assignment of these compounds was made by GC-mass and GLC in comparison with the authentic samples. Bromomethyldiphenyl (X) was separated from the reaction mixture as a mixture of two components A and B (a mixture of isomers) which have the following spectroscopic properties. A: ^{1}H NMR (60 MHz, CD_3CN) δ 2.13 (3H, s; CH_3), 7.10–7.47 (8H, m; aromatic). MS *m/z*: 248, 246 (1:1) $(M)^+$, 167, 152. B: ^{1}H NMR (60 MHz, CD_3CN) δ 2.35 (3H, s; CH_3), 7.20–7.35 (8H, m; aromatic). MS *m/z*: 248, 246 (1:1) $(M)^+$, 167, 152.

Photodecomposition of 4 in anisole in the absence or presence of *p*-benzoquinone. 4 (92 mg, 0.30 mmol) and various concentrations of *p*-benzoquinone [(0 mg, 0 mmol), (64.9 mg, 0.60 mmol), (162 mg, 1.5 mmol) or (324 mg, 3.00 mmol)] were dissolved in anisole (30 mL), respectively, and the mixtures in a Pyrex tube were irradiated for 3 h in the same manner as in the case of toluene. After removal of excess solvent under reduced pressure at room temperature, each resulting residue was treated with 1,1,1,3,3,3-hexamethyldisilazane and pyridine to analyze methoxyphenols. After addition of naphthalene as an internal standard, each trimethylsilyl ether of *o*-, *m*-, *p*-methoxyphenol was analyzed by GLC (OV-101 glass capillary column, 20 m; FID at 110 °C constant) and the yield and isomer ratio of the methoxyphenols were determined.

Photodecomposition of 4 in nitrobenzene in the absence or presence of *p*-benzoquinone. 4 (92 mg, 0.30 mmol) and various concentrations of *p*-benzoquinone [(0 mg, 0 mmol), (64.9 mg, 0.60 mmol), (162 mg, 1.5 mmol) or (324 mg, 3.00 mmol)] were dissolved in nitrobenzene (30 mL), respectively and the mixtures in a Pyrex tube were photolyzed in the same manner as described above. To each reaction mixture was added 1,1,1,3,3,3-hexamethyldisilazane and pyridine to analyze nitorophenols. After addition of benzophenone as an internal standard, each trimethylsilyl ether of *o*-, *m*-, *p*-nitorophenol was analyzed by GLC (3 mm×3 m glass column, SF-96 on Uniport B 10% 60–80; FID at 160 °C constant) and the yield and isomer ratio of the nitrophenols were determined.

Photodecomposition of 4 in toluene in the absence or presence of *p*-benzoquinone by using a 400 W high pressure mercury lamp with a Corning glass filter 5–60. 4 (92 mg, 0.30 mmol) and each concentration of *p*-benzoquinone

[(0 mg, 0 mmol) or (16.2 mg, 0.15 mmol) were dissolved in toluene (30 mL), respectively, and the mixtures in a Pyrex tube were irradiated through a Corning glass filter with a 400 W high pressure mercury lamp under argon gas at 22 °C for 3 h. To each reaction mixture was added naphthalene as an internal standard, then the mixture was analyzed by GLC (3 mm×3 m glass column, KG02 on Uniport HP60–80; FID with temperature programing for 3 °C/min from 70 to 180 °C) and the yield and isomer ratio of cresols, and the yield of phenol were determined.

Photodecomposition of 4 in toluene in the presence of 2-methylbenzoquinone by using a 400 W high pressure mercury lamp with a Corning glass filter 5–60. 4 (92 mg, 0.30 mmol) and 2-methylbenzoquinone (18.3 mg, 0.15 mmol) were dissolved in toluene (30 mL) and the mixture was photolyzed by the same procedure as described above. The yield and isomer ratio of cresols were analyzed as above.

Photodecomposition of 4 in toluene in the presence of 2,5-di-*tert*-butylbenzoquinone by using a 400 W high pressure mercury lamp with a Corning glass filter 5–60. 4 (92 mg, 0.30 mmol) and 2,5-di-*tert*-butylbenzoquinone (33.0 mg, 0.15 mmol) were dissolved in toluene (30 mL) and the mixture was photolyzed by the same procedure as above. The yield and isomer ratio of cresols were analyzed in a similar manner.

Photodecomposition of 4 in anisole in the absence or presence of *p*-benzoquinone by using a 400 W high pressure mercury lamp with a Corning glass filter 5–60. 4 (92 mg, 0.30 mmol) and each concentration of *p*-benzoquinone [(0 mg, 0 mmol) or (16.2 mg, 0.15 mmol) were dissolved in toluene (30 mL), respectively, and the mixtures in a Pyrex tube were irradiated through a Corning glass filter with a 400 W high pressure mercury lamp under argon gas at 22 °C for 3 h. To each reaction mixture was added naphthalene as an internal standard, then the mixture was analyzed by GLC (3 mm×3 m glass column, KG02 on Uniport HP60–80; FID with temperature programing for 3 °C/min from 70 to 180 °C) and the yield of phenol was determined.

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