2 Hz, 1 H); 7.40 (d, J = 8.5 Hz, d, J = 8 Hz, d, J = 2 Hz, 1 H); 7.67 and 7.74 (A_2B_2, J_{app} = 9 Hz, 4 H). ^{13}C NMR: δ 55.3 (OCH_3); 110.2 (C); 111.3 (CH); 119.0 (C); 120.9 (CH); 128.4 (C); 129.8 (CH); 130.0 (2 CH); 130.4 (CH); 131.5 (2 CH); 143.2 (C); 156.2 (C).

4'-Methoxy-1,1'-biphenyl-4-carbonitrile (minor isomer): mp 103 °C (lit.[37] mp 104 °C). MS, m/z 209 (mass peak), 194, 166, 140. ^1H NMR (250 MHz): δ 3.87 (s, 3 H); 7.02 (d, J = 9 Hz, 2 H); 7.56 (d, J = 9 Hz, 2 H); 7.67 and 7.74 (A_2B_2, J_{app} = 9 Hz, 4 H). ^{13}C NMR: δ 55.3 (OCH_3); 110.1 (C); 114.5 (2CH); 118.9 (C); 127.0 (2CH); 128.2 (2CH); 131.4 (C); 132.4 (2CH); 145.1 (C); 160.2 (C). The reaction mixture did not contain any detectable amount of the oxygen-coupling ether: p-$CNC_6H_4OC_6H_5$ as shown by comparison with an authentic sample.[38]

Reaction of 4-Chlorobenzonitrile with 2,6-Di-*tert*-butylphenoxide in Liquid NH_3. Direct Electrochemical Induction. The electrolysis was performed in a compartmented cell containing 80 mL of NH_3 and 1.67 g of potassium bromide. A magnesium rod was used as the anode; the cathode was a platinum grid. 2,6-Di-*tert*-butylphenol (18.05 mmol, 3.72 g), water (3.24 mmol, 58.3 mg), and then potassium *tert*-butoxide (21.3 mmol, 2.39 g) were added. 4-Chlorobenzonitrile (3.01 mmol, 413.8 mg) was added just before electrolysis. The current density was kept constant throughout the electrolysis (13.3 mA/cm^2 at the cathode), until 436 C (1.5 F per mole of chlorobenzonitrile) was consumed. After addition of excess ammonium chloride and evaporation of the solvent, the crude residue was extracted with acetonitrile. The reaction mixture was purified by chromatography (silica gel, dichloromethane/pentane as the eluent). The starting unreacted phenol is eluted first. Then the following eluted.

4'-Hydroxy-2',6'-di-*tert*-butyl-1,1'-biphenyl-4-carbonitrile: yield, 203 mg, 22%; mp 155 °C. MS m/z 307 (mass peak), *292*, 57, 84, 264. ^1H NMR (250 MHz): δ 1.50 (s, 18 H); 5.47 (s, 1 phenolic H); 7.47 (s, 2 H); 7.70 and 7.77 (A_2B_2, J_{app} = 9 Hz, 4 H). ^{13}C NMR: δ 30.3 (6 CH_3); 34.4 (2 C); 109.8 (C); 119 (C); 124.0 (2 CH); 127.3 (2 CH); 130.4 (C); 132.4 (2 CH); 136.8 (2 C); 146.6 (C); 154.6 (C). IR (KBr pellet): 3650, 2245, 1620, 1445, 847 cm^{-1}. Anal. Calcd C, 82.08; H, 8.15; N, 4.56. Found: C, 81.87; H, 8.23; N, 4.84.

4-Chlorobenzamide: yield, 56 mg, 12%; compared (mp, NMR) with a commercial sample.

Redox-Mediated (4,4'-Bipyridine) Electrochemical Induction. The experimental procedure was the same as described above except that 4,4'-bipyridine (2.07 mmol, 323 mg) was added before electrolysis. The electrolysis was stopped after consumption of 0.3 F per mole of substrate (87.2 C), leading to the following.

4'-Hydroxy-2,6'-di-*tert*-butyl-1,1'-biphenyl-4-carbonitrile: 720.7 mg, 78%.

4-Chlorobenzamide: 6%.

Reaction of 2-Chloroquinoline with Phenoxide Ions in DMSO. 2-Chloroquinoline (6.1 mmol) was mixed with 14 mmol of tetramethylammonium phenoxide in 50 mL of DMSO containing 0.1 M NBu_4BF_4. Electrolysis was carried out at −1.75 V vs SCE (reduction of 2-chloroquinoline). The resulting solution was analyzed by reverse-phase HPLC (Lichrosorb R18, 70–30 MeOH–H_2O). In addition to 68% quinoline, 27% of the 2-(2-quinolinyl)phenol coupling product was found as shown by comparison with authentic samples of this compound and of the 4-isomer.[39]

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Ceric Ammonium Nitrate Oxidative-Cleavage Reaction of Some Lignin Model Compounds: Role of the Benzylic Hydroxyl Group

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A series of β-1 lignin model compounds was synthesized and then oxidized with ceric ammonium nitrate (CAN) in aqueous acetonitrile. The compounds studied were 1,2-diarylethanols with either a p-hydroxy (**1a–e**) or a p-methoxy (**2a–e**) on the 1-ring and the following para substituents on the 2-ring: (a) H, (b) Cl, (c) Me, (d) OMe, and (e) NO_2. Reactions of p-hydroxyl compounds **1a–e** with CAN resulted in the formation of a red cerium complex that did not oxidize under the conditions of the reaction. In contrast, all of the methoxy compounds **2a–e** were rapidly oxidized by CAN at room temperature to give p-anisaldehyde in near quantitative yield. The relative rates of these oxidative-cleavage reactions were found to be 0.11, 0.16, 1.00, 1.58, and 2.37 for the 1,2-diarylethanols **2e**, **2b**, **2a**, **2c**, and **2d**, respectively. A Hammett treatment of this data revealed an excellent correlation with σ (ρ = −1.24). Methylation of the benzylic hydroxy group of **2a** gave 1-methoxy-1-(4-methoxyphenyl)-2-phenylethane, which was found to be inert to CAN oxidation.

The alkaline oxidative-cleavage reaction of softwood lignin to vanillin using such oxidants as nitrobenzene and copper(II) is one of the more important reactions of wood chemistry. Until recently the mechanism of this reaction was assumed to be a two-electron process involving quinone methide intermediates.[1] Evidence from our laboratories[2-5] is more consistent with a one-electron process that does not involve quinone methide intermediates. The precise roles that the p-hydroxy and benzylic hydroxy groups of lignin play in this reaction are also not clearly established.

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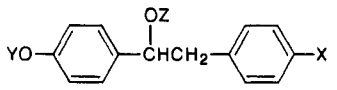
One approach to help further elucidate the mechanism of this reaction is to choose an oxidant whose reaction mechanism has already been clearly established to be one electron and then to study the reaction of that oxidant on some lignin model compounds. On the basis of an extensive series of studies, Trahanovsky[6] proposed that the ceric ammonium nitrate (CAN) cleavage of 1,2-diarylethanols to benzaldehydes is an excellent prototype for one-electron oxidative cleavages of alcohols. Consequently, we chose CAN as the one-electron oxidant for this study.

The β-1 lignin model compounds chosen for this oxidation study include 1-(4-hydroxyphenyl)-2-(4-substituted-phenyl)ethanols **1a–e**, 1-(4-methoxyphenyl)-2-(4-substituted-phenyl)ethanols **2a–e**, and 1-methoxy-1-(4-methoxyphenyl)-2-phenylethane (**3a**).



1, Y = Z = H
2, Y = Me, Z = H
3, Y = Z = Me

a, X = H; **b**, X = Cl; **c**, X = Me; **d**, X = OMe; **e**, X = NO_2

Results and Discussion

Nave and Trahanovsky[7,8] carried out a substituent effect study on the CAN oxidative-cleavage reaction of some 2-aryl-1-phenylethanols and reported a ρ^+ value of −2.0 for the *p*-methyl, *p*-chloro, and *p*-nitro substituents. These competitive relative rates were determined in a 75% aqueous acetonitrile solution that was heated on a steam bath for 20 min. Oxidative cleavage, a one-electron process, was the only reaction found in this series of compounds. Trahanovsky has also observed[6] that "there are no clearly documented two-electron oxidative cleavages of alcohols." However, when the 2-aryl ring of the 2-aryl-1-phenylethanols contained a *p*-methoxy, a *m*-methoxy, or a *p*-acetamido substituent, a fast side reaction was observed,[6,7] which was suspected of being an electron-transfer oxidation of the activated 2-aryl ring into a cation radical.

The attempted CAN oxidation of 2-aryl-1-(4-hydroxyphenyl)ethanols **1a–e** under conditions analogous to those used by Trahanovsky failed to yield any oxidation products. A dark red color appeared and then persisted when ethanols **1** were mixed with CAN. Presumably, the Ce(IV) preferentially complexed with the phenolic group of **1** to form a complex that was not oxidized. The appearance of a red color has been cited[9] as a marker for complex formation between Ce(IV) and hydroxylic substrates.

The reaction of CAN with 2-aryl-1-(4-methoxyphenyl)ethanols **2a–e**, which are identical with **1** except that the phenolic group has been methylated, was dramatically different. Now the reaction was virtually instantaneous even at room temperature. A red color was again observed to form, but it immediately discharged, leaving a pale yellow solution. HPLC analysis confirmed that oxidative cleavage had occurred and that *p*-anisaldehyde was a common cleavage product of all ethanols **2a–e**.

One major adaptation to this reaction was made before the competitive kinetics were run. Both ethanols **1** and **2** are susceptible to acid-catalyzed dehydration, and the corresponding stilbene derivatives are the resulting dehydration products.[4] Dehydration was a concern because nitric acid is also generated during the course of this redox reaction. When sodium acetate was added to the reaction mixture prior to the addition of the CAN, the nitric acid byproduct was effectively buffered and dehydration was prevented.

Table I. Relative Rate Data for CAN Oxidations[a] of 1,2-Diarylethanols 2a–e

compd	X	k_X/k_H
2e	NO_2	0.11 ± 0.01
2b	Cl	0.61 ± 0.03
2a	H	1.00
2c	Me	1.58 ± 0.04
2d	OMe	2.37 ± 0.14

[a] In 75% aqueous acetonitrile at room temperature.

Substituent Effects. A near quantitative yield of anisaldehyde (>95%) was obtained from the oxidative cleavage of each 2-aryl-1-(4-methoxyphenyl)ethanols **2a–e**. In spite of the fact that all of the 1,2-diarylethanols **2** have a methoxy group on the 1-ring and **2d** has a methoxy group on both the 1- and 2-aryl rings, no ring oxidation products were found. These reactions were run in 75% aqueous acetonitrile at room temperature, in contrast to the steam bath conditions mentioned earlier.[7,8] Our HPLC studies also found no products resulting from the 2-aryl ring of **2**.

The average relative rates, k_X/k_H, found for the competitive CAN oxidations of **2** are given in Table I. The relative rate value found for the methoxy compound **2d** was 2.37, instead of the 100–1000 reported[6] for 2-(*p*-methoxyphenyl)-1-phenylethanol, indicating that the methoxy substituent is "well-behaved" in our study.

A Hammett plot of the relative rate data of Table I vs σ and σ^+ was carried out. The data was found to correlate best with σ giving a ρ value of −1.24 (r = −0.997). The relative rate data of Nave and Trahanovsky[6,7] for the CAN oxidation of 2-aryl-1-phenylethanols correlated best with σ^+ and gave a ρ value of −2.0. However, when the 2-aryl-1-phenylethanols were oxidized with Cr(IV), the best fit was found with σ, and a ρ value of −1.06 was obtained.[10] The oxidative-cleavage reactions of the 4-hydroxystilbene analogues of **2** with alkaline nitrobenzene and Cu(II) were found[5] to correlate best with σ^+, giving a ρ value of −0.48 for both oxidizing agents. All of these ρ values are in the 0 to −2 range normally found for free radical reactions involving benzyl-free radicals.[11] Reactions involving benzyl cations normally have much larger negative ρ values.[12]

The mechanism of the CAN oxidation of 1,2-diarylethanols, such as **2**, is believed[8] to involve a rapid equilibrium between the alcohol and Ce(IV) ion to form the Ce(IV) complex **4**. This Ce(IV) complex **4** then decomposes into an aryl aldehyde, a benzyl radical, and a Ce(III) ion by way of transition-state **5**, which involves a single electron transfer from the alkoxide ion of the complex to the Ce(IV) ion. The transition-state **5** is resonance stabilized by canonical forms **5b** and **5c**, which have a single electron and a positive charge on the benzylic 2-position of the ethanol, respectively. The facile nature of the CAN oxidation of **2**, over in seconds at room temperature, is clearly due to the presence of the *p*-methoxy group in the

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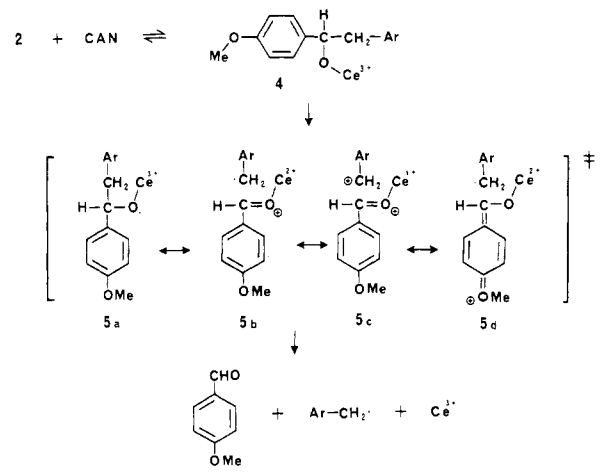

1-aryl ring. This electron-donating *p*-methoxy group can undergo direct resonance with the positive charge of **5b**, giving **5d**, in which the positive charge is now on the *p*-methoxy group. A similar direct resonance can also occur in the dicationic species **5c**, but such a delocalized species is not believed to be as important here as **5d** since σ not σ^+ dependence was found and dications are normally higher energy than cations.

An alternate mechanism can be postulated that involves an intermolecular loss of an electron from the 1-(*p*-methoxyphenyl) ring of **2** or complex **4** to form an aryl cation radical. This aryl cation radical would then decompose to products.

Next, an attempt to differentiate between these two mechanisms was made by treating **3a**, the methylated analogue of **2a**, with CAN. The results of this experiment are discussed in the next section.

Role of the Benzylic Hydroxy Group. In a series of studies on the oxidation of lignins that had alternately been methylated at the *p*-hydroxy group and at the benzylic hydroxy group, Leopold[13-15] concluded that methylation of the benzylic hydroxy group was the cause of the low yield of vanillin obtained in the oxidation reaction. Nevertheless, Snook and Hamilton[16] found that both Fenton's reagent and peroxydisulfate oxidatively cleave either methyl benzyl ether or 1-phenylalkanols to form benzaldehyde by a process thought to involve aryl cation radicals. Cation radicals have also been shown[17,18] to be intermediates in the C_α–C_β oxidative-cleavage reaction of lignin with the ligninase from the white-rot fungus *Phanerochaete chrysosporium*. In the latter reaction aryl rings with fewer than two alkoxy groups did not yield cation radicals with the ligninase.[17] Furthermore, the CAN oxidation of 1,2-diarylethanes[19] and 1-phenyl-2-(4-methoxyphenyl)ethanol[8] have been postulated to involve cation radical intermediates.

If the mechanism of our oxidative-cleavage reaction involves the resonance-stabilized transition-state **5**, then methylation of the ethanol hydroxy group of **2a** would prevent the reaction from occuring, since a cerium(IV) complex cannot form with **3a**. But if the mechanism involves the cation radical of **2**, then the reaction should proceed as usual. The reaction would also not proceed with **3a** if a cation radical was formed from complex **4**.

In order to further investigate this point, the CAN oxidation of 1-methoxy-1-(4-methoxyphenyl)-2-phenylethane (**3a**), the methyl ether of **2a**, was studied. A competitive method was again used. When a limiting quantity of CAN was added to a mixture of **2a** and **3a** in aqueous acetonitrile, 50% of **2a** was oxidized to anisaldehyde, and **3a** was quantitatively recovered. Benzyl ether **3a** was also treated with CAN for several minutes at room temperature, in the absence of **2a**, and the ether was again recovered unchanged. These experiments clearly show that the benzylic hydroxy group of diarylethanols **2** is necessary for the CAN oxidative-cleavage reaction to occur. This rules out a mechanism involving a cation radical of **2**. Also, since the *p*-methoxy compound **2d** was found to be "well-behaved" here, the Trahanovsky mechanism involving transition-state **5** best explains our data.

It is also important to note that quinone methide intermediates were not involved in the oxidative-cleavage reaction of diarylethanols **2** since such intermediates are prevented from forming by the presence of the *p*-methoxy groups on the 1-aryl ring. The speed of these CAN oxidations under such mild conditions is a dramatic illustration of the facile nature of this one-electron oxidative-cleavage reaction.

Experimental Section

Melting points were determined on a Mel-Temp apparatus and are uncorrected. ^{1}H NMR spectra were recorded with a Varian CFT-20 spectrometer. Infrared spectra were obtained using a Nicolet 20 DX-FTIR. All IR samples were analyzed as 1% dispersions in KBr disks. Reaction mixture analyses were determined on a HP-1090A liquid chromatograph equipped with a 5-μm IBSil C-18 reverse-phase packed column. A gradient mixture of acetonitrile and water was used to elute the column, and the UV detector was set at 230 nm. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. All UV spectra were run in absolute methanol.

Kinetics. Competitive kinetic runs were conducted by addition of approximately 175 μmol of both the substituted alcohol **2b–e** and the reference alcohol **2a**, dissolved in 2.0 mL of 75% aqueous acetonitrile solution, to a limiting amount of CAN. An excess (compared to the CAN present) of sodium acetate was placed in the reaction flask prior to the addition of the alcohols to buffer the nitric acid formed in the CAN oxidations. The oxidations were virtually instantaneous even at room temperature. The reaction flask was maintained at room temperature for 10 min with occasional swirling, at which time an accurately measured quantity of internal standard (biphenyl or benzophenone) was added volumetrically to the reaction mixture. The mixture was then diluted 15-fold with 75% aqueous acetonitrile. The dilute mixture was allowed to set for several hours, filtered through a 0.45-μm filter, and then analyzed by HPLC. The quantities of unreacted alcohols were determined by comparing their response-factor-corrected integrals to those of the internal standard. The amount of *p*-anisaldehyde present was determined in a similar fashion. Three to eight repetitions were run for each substituted alcohol. The competitive kinetic equation used is $k_X/k_H = \log (X_f/X_i)/\log (H_f/H_i)$, where X_f, X_i, H_f, and H_i represent the final and initial quantities of substituted alcohol and unsubstituted alcohol, respectively.

1-(4-Hydroxyphenyl)-2-(4-substituted-phenyl)ethanols 1a–e. The synthesis of these 1,2-diarylethanols was reported earlier.[4]

1-(4-Methoxyphenyl)-2-phenylethanol (2a). Ethanol **2a** was prepared from benzylmagnesium bromide and anisaldehyde in 49% yield, mp 55–56 °C (lit.[20] mp 58 °C).

2-(4-Chlorophenyl)-1-(4-methoxyphenyl)ethanol (2b). Alcohol **2b** was prepared from (*p*-chlorobenzyl)magnesium

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chloride and anisaldehyde by the method of Smith et al.[21] in 67% yield, mp 83-85 °C (lit.[21] mp 84-85.5 °C).

1-(4-Methoxyphenyl)-2-(4-methylphenyl)ethanol (2c). Ethanol **1c**, 6.0 g (22 mmol) in methanol, was methylated with 3.0 g (70 mmol) of freshly distilled diazomethane in ether. After the excess diazomethane was allowed to blow off in a hood, the ether solution was extracted with 2 N NaOH and dried over $MgSO_4$ and the ether removed at 50 °C. The alcohol **2c**, 5.6 g (87%), was obtained as a white amorphous solid from hexane, mp 42-44 °C. IR (KBr): 3328 (OH str), 3004 (Ar C-H str) 1250 (C-O str) cm^{-1}. NMR ($CDCl_3$): 2.29 (s, 3 H), 2.73 (d, J = 3.6 Hz, 1 H), 2.95 (d, J = 8.1 Hz, 2 H), 3.78 (s, 3 H), 4.79 (t of d, 1 H), 6.77-7.30 (m, 8 H) ppm. UV λ (log ϵ_{max}): 223 (4.25), 273 (3.33), 281 (3.23) nm.

Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.44. Found: C, 79.61; H, 7.52.

1,2-Bis(4-methoxyphenyl)ethanol (2d). Alcohol **2d** was prepared by the $NaBH_4$ reduction of desoxyanisoin in 87% yield, mp 112-113 °C (lit.[22] mp 110 °C).

1-(4-Methoxyphenyl)-2-(4-nitrophenyl)ethanol (2e). Ethanol **1e** was methylated with diazomethane using the procedure described above to give alcohol **2e** in 84% yield, mp 113-114 °C (lit.[23] mp 113-115 °C).

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1-Methoxy-1-(4-methoxyphenyl)-2-phenylethane (3a). The procedure of Johnstone[24] was used to methylate 1,2-diarylethanol **2a**. Ethanol **2a**, 0.91 g (4.0 mmol), was added to a suspension of 0.90 g (16 mmol) powdered KOH in 0.5 mL (8 mmol) of freshly distilled methyl iodide. After being stirred for 30 min, the mixture was poured into water, extracted with CH_2Cl_2, and then washed with water. Removal of CH_2Cl_2 and recrystallization from aqueous methanol yielded 0.82 g (84%) of pale yellow crystals, mp 46-47 °C. IR (KBr): 3034 (Ar C-H str), 2914 (R C-H str), 1240 (C-O str) cm^{-1}. NMR ($CDCl_3$): 2.9-3.6 (m, 5 H), 3.78 (s, 3 H), 4.27 (t, J = 8.1 Hz, 1 H), 6.8-7.2 (m, 9 H) ppm. UV λ (log ϵ_{max}): 225 (4.15), 274 (3.20), 281 (3.13) nm.

Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.44. Found: C, 79.46; H, 7.38.

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Registry No. **1a**, 73049-07-7; **1b**, 110995-89-6; **1c**, 110995-90-9; **1d**, 110995-91-0; **1e**, 110995-92-1; **2a**, 5422-47-9; **2b**, 6279-23-8; **2c**, 113160-00-2; **2d**, 20498-71-9; **2e**, 20498-72-0; **3a**, 113160-01-3; *p*-anisaldehyde, 123-11-5; benzylmagnesium bromide, 1589-82-8; (*p*-chlorobenzyl)magnesium chloride, 874-72-6; desoxyanisoin, 120-44-5.

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Photoinduced Reductive Addition Reactions of 2-Alkenoyl-1,4-benzoquinones with Alcohols

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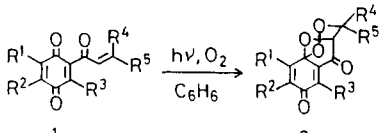
Irradiation of 2-alkenoyl-3,5-dimethyl-1,4-benzoquinones **1** in alcohol under a nitrogen atmosphere afforded two isomeric adducts: benzofuranone derivatives **4** and alkenyl ether derivatives **5**. The ratios of **4** to **5** depended both on the nature of the alkenoyl substituents and on the alcohols used as solvent. Irradiation of some quinones **1** dissolved in *tert*-butyl alcohol gave, however, 3-substituted chromone derivatives **13** as additional products.

Photochemical reactions of isoprenoid 1,4-quinones, e.g., plastoquinone,[1] ubiquinone (coenzyme Q)[2], and vitamin K analogues (menaquinone and phylloquinone)[3] have been extensively investigated under several conditions because these quinones are known to play an important role in biological processes such as electron transport and oxidative phosphorylation.[4] From the anaerobic photosynthetic bacterium, *Chlorobium thiosulphatophilum*, for example, chlorobiumquinone (1′-oxomenaquinone 7), which is an alkenoyl-1,4-quinone with an olefinic double bond and a carbonyl group in the side chain, was isolated.[5] Irradiations of isoprenoid 1,4-quinones under aerobic conditions give trioxane, hydroperoxide, and aldehyde, but under anaerobic conditions intramolecular cyclization products such as chromene are produced.[1-3] Investigation of the photochemical reactions of alkenoyl quinones **1** is therefore of interest from both the biological and the photochemical point of view.

Recently, it has been reported[6] that irradiation of alkenoyl quinones **1** in benzene under aerobic conditions affords the relatively stable cyclic peroxides **2** (eq 1). In



1 2 (1)

a preliminary paper we reported[7] that irradiation of 2-alkenoyl-3,5-dimethyl-1,4-benzoquinones in methanol or ethanol under anaerobic conditions gave two isomeric

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