sterically bulky ether cleavage reagent, such as boron tribromide, to the *o*-methoxy group ought to be prevented in **4**.

In order to test this hypothesis 1,4-dimethoxybenzene was treated with hydrogen cyanide, aluminum chloride, and hydrogen chloride in methylene chloride to produce a soluble iminium complex **4**. Treatment of this complex with 2 equiv of boron tribromide gave exclusively 5-hydroxy-2-methoxybenzaldehyde (**3**), mp 114–116°. Hydrolysis of **4** gave **1**, which on treatment with 2 equiv of boron tribromide afforded 2,5-dihydroxybenzaldehyde (**5**) in excellent yield.

Since the 5-methoxy group in **1** is more nucleophilic than the 2-methoxy group, a certain degree of selectivity should also be achieved on treatment of **1** with concentrated sulfuric acid. Thus, heating of **1** with concentrated sulfuric acid at 50–54° for 46 hr indeed gave a 42% yield of **3**; the only other product isolated was **1** (20%).[2]

Experimental Section

5-Hydroxy-2-methoxybenzaldehyde (3). A. From the Iminium Complex 4 and Boron Tribromide. To 27.6 g (0.2 mol) of 2,5-dimethoxybenzene in 200 ml of methylene chloride with ice cooling and stirring, 28.4 g (0.22 mol) of aluminum chloride and 8.1 g (0.3 mol) of hydrogen cyanide were added. The cooling bath was removed and 21 g of hydrogen chloride was added slowly at room temperature over a period of 4 hr. After stirring for 40 hr one-quarter of the reaction mixture (85 ml) was stirred with 25 g (0.1 mol) of boron tribromide for an additional 20 hr. After hydrolysis with dilute hydrochloric acid (100 ml), 6.65 g of a mixture of hydroquinone and **3**, mp 145–155°, precipitated. Extraction of this solid with two 200-ml portions of methylene chloride and evaporation of the combined methylene chloride portions gave 4.55 g (60%) of **3**, mp 112–115°. Hydrolysis of the remaining reaction mixture (255 ml) with dilute hydrochloric acid, extraction of the methylene chloride layer with 5% sodium hydroxide, drying with magnesium sulfate, evaporation, and vacuum distillation of the residue gave a first fraction of 2,5-dimethoxybenzene and 20.2 g (91.5%) of **1**, bp 98° (0.1 mm), mp 49–52°.

B. From 2,5-Dimethoxybenzaldehyde (1) and Concentrated Sulfuric Acid. To 20.75 g (0.125 mol) of **1** with ice cooling, 112.5 ml of concentrated sulfuric acid was added and the mixture was heated at 50–54° for 46 hr. The reaction mixture was poured onto ice and the precipitated oil was extracted with diethyl ether. Extraction of the solvent with 200 ml of 5% sodium hydroxide, acidification, extraction with diethyl ether, drying over anhydrous $MgSO_4$, and evaporation of the solvent gave 8.15 g (42.3%) of **3**: mp 114–116° after recrystallization from aqueous alcohol; ir ($CHCl_3$) 1672 cm^{-1} (C=O); nmr (acetone-d_6) δ 3.88 (s, 3, OCH_3), 3.0–4.0 (s, 1, OH), 6.9–7.3 (m, 3, aromatic), 10.38 (s, 1, CHO).

Anal. Calcd for $C_8H_8O_3$: C, 63.15; H, 5.30. Found: C, 62.93; H, 5.31.

From the neutral diethyl ether layer 4.3 g (20.7%) of **1** was recovered.

2,5-Dihydroxybenzaldehyde (5). To 7 g (0.028 mol) of boron tribromide in 40 ml of methylene chloride, 3.32 g (0.02 mol) of 2,5-dimethoxybenzaldehyde was slowly added and the mixture was stirred at room temperature for 20 hr. Addition to ice water (70 ml), separation of the organic layer, and evaporation of the dried methylene chloride layer gave **5**, 0.8 g, mp 100–102° (lit.[3] mp 100–101°). Extraction of the aqueous layer with 100 ml of ethyl acetate produced another 1.8 g of **5**, total yield 2.6 g (92.2%).

Registry No.—**1**, 93-02-7; **3**, 35431-26-6; **4**, 51801-41-3; **5**, 1194-98-5.

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Light-Induced Reaction of 3,3′,5,5′-Tetramethyldiphenoquinone in Benzene

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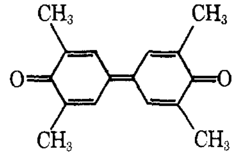
The irradiation of substituted *p*-benzoquinones, as solids or in solution, has been reported to yield photoaddition products as well as various types of dimers. These dimers include cyclobutanes,[2] spirooxetanes,[3] cage-like structures,[4] and unidentified products.[5]

In contrast to the photoinduced reactions of benzoquinone derivatives, no dimer was detected when **1** was irradiated in benzene in a nitrogen atmosphere. The products were 2,2′,6,6′-tetramethyl-*p*,*p*′-biphenol (**2**) and biphenyl (**3**).



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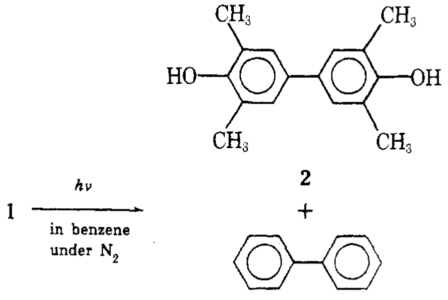


2

3

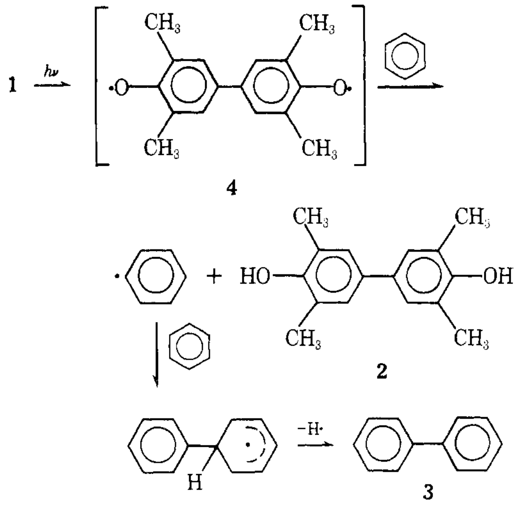
This result is surprising, since biphenyl formation is not common when benzoquinones are irradiated in benzene, which has been widely used as an inert solvent for photochemical reactions of benzoquinones.[6] For example, irradiation of 1,4-naphthoquinone in benzene gave only the dimer and no reduction products or biphenyl while 1,4-naphthoquinone in isopropyl alcohol gave the corresponding hydroquinone.[7]

The photolysis of iodoaromatic or bromoaromatic compounds in benzene solution results in a good yield of biphenyl or the result of the generation of an intermediate phenyl radical by the following photoinduced primary process.[8] The formation of biphenyl in the present work

$$\mathrm{PhX} \xrightarrow{h\nu} \mathrm{Ph}\cdot + \cdot\mathrm{X} \quad \mathrm{X} = \text{halogen atom}$$

indicates that here, too, a phenyl radical is generated as a reactive intermediate and that a benzene molecule may function as a hydrogen donor in the present photoinduced reaction of diphenoquinone.

Hay[9] has found that the thermolysis of molten 3,3′,5,5′-tetraphenyldiphenoquinone gave the corresponding biphenol as one of the products and demonstrated that diphenoquinones such as 3,3′,5,5′-tetraphenyldiphenoquinone were powerful oxidizing agents. Hence it appears reasonable to assume that species such as **4** are participating in the light-induced reaction. One possible route to the two products is the abstraction of a hydrogen atom from solvent benzene by the excited biradical (**4**)[10,11] followed by reaction of the resulting phenyl radical with a benzene molecule as follows, even though the possibility



of a dipolar transition state[6] consisting of diphenoquinone and benzene in place of 4 cannot be ruled out at present.

Experimental Section

Melting points are uncorrected. Infrared spectra were run on a Hitachi Model 215 grating spectrophotometer. Nmr spectra were recorded on a Varian HR-220 apparatus. Chemical shifts of the nmr spectra are reported in parts per million downfield from internal TMS. Mass spectra were obtained on a double-focusing mass spectrometer, Model JMS-01SG.

3,3′,5,5′-Tetramethyldiphenoquinone (1) was prepared by the oxidation of 2,6-xylenol with a copper(I) chloride–acetonitrile system. A solution of 0.5 g (0.005 mol) of copper(I) chloride in 50 ml of acetonitrile was stirred under an oxygen atmosphere, followed by addition of 1.22 g (0.01 mol) of 2,6-xylenol to the resulting homogeneous solution. The mixture was stirred for 2 hr at 30° while oxygen was being bubbled in and was chilled with an ice-water mixture. The resulting red crystals were filtered to yield 0.7 g of 1, mp 207–208° (lit.[12] mp 208–210°). The elementary analysis, ir, and nmr spectra were all in agreement with the reported structure. Reduction of 1 with zinc dust in acetic acid gave the corresponding biphenol (2): mp 220–223° (lit.[12] mp 223–225°); mass spectrum M^+ m/e 242 (calcd for $C_{16}H_{18}O_2$, 242); nmr ($CDCl_3$) 8.15, 8.26 (CH_3, s), 6.63 (OH, s), and 3.14 and 3.25 ppm (ring H, s); ir (KBr) 3380 (OH), 860 cm^{-1} (phenyl).

Irradiation of 3,3′,5,5′-Tetramethyldiphenoquinone. A solution of 0.4 g of diphenoquinone (1) in 1000 ml of benzene was purged with nitrogen for 2 hr and then irradiated by means of a 200-W high-pressure mercury arc surrounded by a quartz filter for 100 hr under a stream of nitrogen gas. After removal of the solvent *in vacuo*, the chloroform solution of the reaction mixture was chlomatographed over silica gel (300 g) using chloroform as eluent. The first fraction (50 ml of eluent) obtained contained 0.02 g of 3, whose ir (KBr) and nmr spectra were completely identical with those of authentic diphenyl. The second fraction (0.072 g, 75 ml of eluent) was identified as biphenol (2) by comparison with spectra of an authentic specimen. Starting material (0.250 g) was recovered as the third fraction by elution with 250 ml of chloroform.

Registry No.—1, 4906-22-3; 2, 2417-04-1; 3, 92-52-4; 2,6-xylenol, 576-26-1.

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Atomic Oxygen. III. Reaction of 1,3-Butadiene with Oxygen(^{3}P) Atoms[1]

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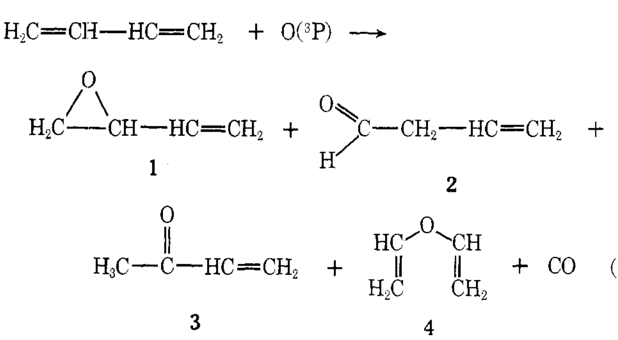
Atomic oxygen in its ground (triplet) state is produced by the gas-phase mercury-photosensitized decomposition of nitrous oxide.[2] The reaction of oxygen atoms with organic compounds is accomplished by photolysis of a mixture of mercury vapor, organic acceptor, and a large excess of nitrous oxide.[3] The generation of oxygen atoms by this technique produces one molecule of nitrogen per oxygen atom. Yields given below were calculated on the basis of nitrogen evolved during photolysis. Reactions were stopped with less than 25% of the reactant diene converted to products.

The reaction of 1,3-butadiene with O(^{3}P) has been studied by Cvetanovic and Doyle.[4] The oxygenated products that they isolated were carbon monoxide, 3,4-epoxy-1-butene, and crotonaldehyde. Crotonaldehyde may have been produced by rearrangement of 3-butenal during work-up.

We have examined the reaction of 1,3-butadiene with O(^{3}P) and have determined the product composition with very mild analytical techniques (*vide infra*). The oxygen-containing products of the reaction were carbon monoxide (14% yield); 3,4-epoxy-1-butene (1, 41%); 3-butenal (2, 23%); 3-buten-2-one (3, 1.5%); and vinyl ether (4, 0.5%) (eq 1). Total recovery of oxygenated material was 80%.



(1)

The hydrocarbons produced by formation of carbon monoxide were not quantitatively analyzed; however, propene was the major product of low molecular weight. Cvetanovic and Doyle[4] have shown that at a constant total pressure, product yields from the reaction of 1,3-butadiene with O(^{3}P) are independent of reactant ratio in the range nitrous oxide:1,3-butadiene = 9.6:137.

A search was made for the presence of 2,5-dihydrofuran in the product mixture. None of this product was detected upon injection of the product mixture on a vpc column known to separate an authentic sample of 2,5-dihydrofur-