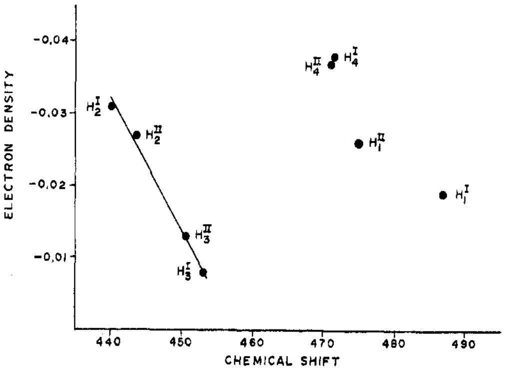

Figure 2.—Chemical shifts of protons in I and II *vs.* calculated electron densities. Electron densities are from ref 4 and the chemical shifts for I from ref 1.

different environments and there is observed a large chemical shift difference as well as a calculated electron density difference.

On the basis of the chemical shift data and transition state considerations,[5] one would predict a large preference for electrophilic aromatic substitution at H_2 with a much smaller reactivity at H_4 for each of these compounds. On the basis of the electron density calculations, one might expect the 2 and 4 positions to be about equally reactive or with a slight preference for the 4 position. Nitration, chlorination, bromination, and chlorosulfonation of I has been reported to give substitution at the 2 position.[5] Substitution at the 4 position is observed after positions 2 and 8 have been substituted. Although II has been nitrated and chlorosulfonated, the position of substitution has not been established.[6] These results suggest that the calculated electron densities at H_4 are too high relative to those at H_2.

Experimental Section

The nmr spectrum of II was taken in deuteriochloroform using a Varian A-56/60 spectrometer. The peak positions were determined relative to TMS by use of the side-band technique immediately preceding and immediately following the spectral scan. The initial peak assignments were based on similarities between the spectrum of II and the published spectrum of I.[1] The exact chemical shifts and couplings constants were calculated using the LAOCN-3 program.[3] In plotting the computed spectrum in Figure 1, lines closer together than 0.2 Hz were added together, since such lines would not normally be resolved.

5,12*H*-Dibenzo[*b*,*e*]-1,3a,6,6a-tetraazapentalene (II).—In 2 ml of decalin was placed 52.1 mg (0.221 mmol) of 1-(2-azidophenyl)benzotriazole.[2] The mixture was first warmed to dissolve the solid and then heated slowly up to the boiling point of the decalin. After 5 min of refluxing, the solution was cooled to room temperature. The needles which precipitated were filtered and washed thoroughly with petroleum ether, yield 26.5 mg (58%), mp 251–252° (lit.[2] 255°).

Registry No.—II, 2055-55-2.

Acknowledgment. –The author is indebted to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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(5) R. A. Carboni, J. C. Kauer, W. R. Hatchard, and R. J. Harder, *J. Amer. Chem. Soc.*, **89**, 2626 (1967).

(6) J. C. Kauer and R. A. Carboni, *ibid.*, **89**, 2633 (1967).

Thermolysis of 3,3′,5,5′-Tetraphenyldiphenoquinone

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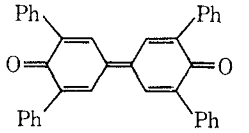
When 3,3′,5,5′-tetraphenyldiphenoquinone **1**[1] is heated above its melting point, the melt which initially is an intense red color gradually fades and becomes almost colorless. Thin layer chromatography on silica gel using xylene as eluent shows the presence of three compounds, **2**, **3**, and **4**, with R_f values of 1, 0.7, and 0.5, respectively. By comparison with an authentic sample, **4** was identified as 2,2′,6,6′-tetraphenyl-*p*,*p*′-biphenol.



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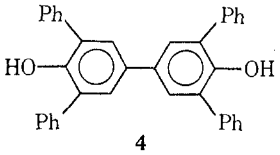

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Superposition of the infrared spectra (in CS_2) of **2** and **4** gives a spectrum that is essentially identical with that of **3**. This is shown in Table I which lists the principal absorption bands of the three compounds. Furthermore, the molar extinction coefficients of all the major bands of **3** are approximately one-half of the corresponding bands in **2** or **4**. The infrared spectrum of 2,6-diphenylphenol (**5**)[1] also shows a doublet at 685 and 695 cm^{-1} indicating the two phenyl groups are not equivalent.

TABLE I

PRINCIPAL INFRARED ABSORPTION BANDS (IN CM^{-1})

2			1188			772	745	691	
3	3538	1225	1188	1120	867	772	745	700, 691	565
4	3538	1225		1120	872	772		700, 691	571

The spectrum of **2** is exceptionally simple. The strong C–O stretching absorption at 1188 cm^{-1}, which is also present in **3**, is also found in 4-phenyldibenzofuran (**6**, ν 1184 cm^{-1}) and dibenzofuran (**7**, ν 1195 cm^{-1}). The former also has a strong absorption at 691 cm^{-1}.

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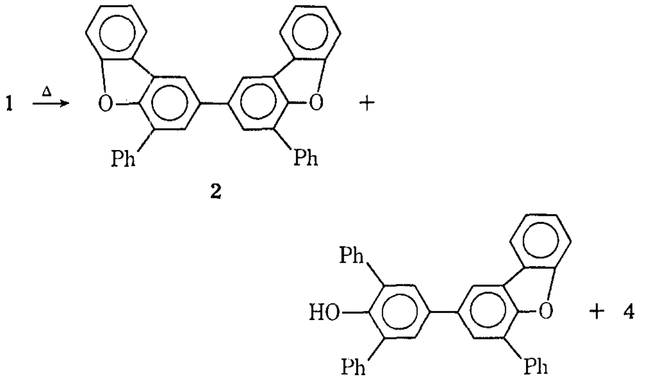
(1) J. Plesek, *Collect. Czech. Chem. Commun.*, **21**, 375 (1956).

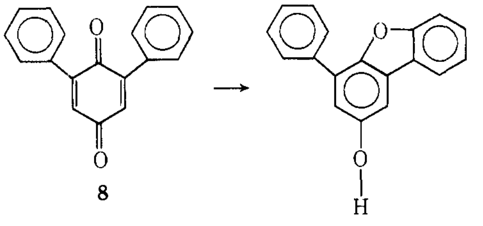
Thus it is apparent that the course of the reaction is



2

3

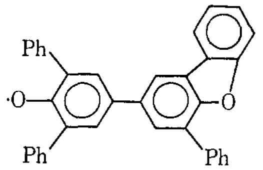
A related reaction has recently been observed. Hageman[2] irradiated 2,6-diphenyl-1,4-benzoquinone (**8**) in acetonitrile with ultraviolet light and isolated the dibenzofuran **9** in high yield.



8

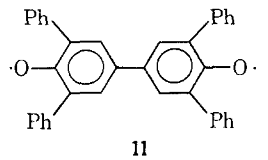
9

Separation of the bisdibenzofuran **2** from **3** and **4** is readily accomplished by column chromatography or alternatively by crystallization from benzene. Oxidation of the mixture of **3** and **4** with oxygen in alcohol solution in the presence of a copper–amine catalyst[3] converts **4** to insoluble **1**. By analogy, with the oxidation of 2,4,6-triphenylphenol to the stable phenoxy radical,[4] the oxidation of **3** should yield **10**, and thus reduction of the filtrate from the preceding step regenerates **3**.



10

Dimroth[5] has examined the esr spectrum of **1** and observed a weak signal at room temperature. It has also been demonstrated that diphenoquinones such as **1** are powerful oxidizing agents. The oxidation of diphenylmethane to *s*-tetraphenylethane proceeds readily in high yield at 150°.[6] Hence it appears reasonable to assume that species such as **11** on the quinhydrone are



11

present especially at elevated temperatures. In the absence of a species to dehydrogenate, attack would occur on the pendant phenyl and subsequent aromatization by dehydrogenation would yield **2** or **3**.

Experimental Section

Preparation of 1.—Oxygen was passed through a vigorously stirred solution of 50 g (0.20 mol) of 2,6-diphenylphenol and 4.0 g of copper(I) chloride in 500 ml of *n*-butyronitrile at 100° for 5 hr. The reaction mixture was cooled and filtered to yield 42 g (0.086 mol, 85% yield) of **1**, mp 290° dec. Reduction with hydrazine in hot acetic acid gave the corresponding biphenol **4**, mp 196°. *Anal.* Calcd for $C_{36}H_{26}O_2$: C, 88.13; H, 5.34. Found: C, 88.30; H, 5.28.

Thermolysis of 1.—To a test tube was added 9.80 g (0.02 mol) of **1** which was then heated to 300° for 0.5 hr at which point the melt was light amber in color. The reaction mixture was cooled and diluted with 2 vol of benzene. The solution was chromatographed over activated alumina (column 2 in. in diameter, 12 in. long) using benzene as eluent. The first fractions obtained contained 2.56 g (0.0053 mol, 26.5% yield) of **2**, mp 231–234°. *Anal.* Calcd for $C_{36}H_{22}O_2$: C, 88.86; H, 4.56; mol wt, 486. Found: C, 88.7; H, 4.7; mol wt, 495.

Elution with ethanol–benzene gave a mixture of the two products, **3** and **4**. After evaporation of the solvents, the residue was dissolved in 150 ml of ethanol. To this solution was added 0.5 g of CuCl and 2 ml of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine. Oxygen was passed through the vigorously stirred solution for 0.5 hr and then the green solid which separated was removed by filtration. The solid was dissolved in 250 ml of hot chloroform and filtered to separate copper salts, and the filtrate evaporated to yield 5.63 g (0.0115 mol, 57.5% yield) of **1**, identified by comparison with an authentic sample. The intense red-colored filtrate from the oxidation was treated with hypophosphorous acid until the red color of the reaction mixture disappeared and then flooded with water. The solid obtained was recrystallized from acetic acid to yield 1.24 g (0.0025 mol, 12.5% yield) of **3**, mp 196–198°. *Anal.* Calcd for $C_{36}H_{24}O_2$: C, 88.50; H, 4.95. Found: C, 88.6; H, 5.17.

Registry No. –**1**, 3550-01-4; **2**, 26675-14-9; **3**, 26675-15-0; **4**, 2416-96-8.

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[2] H. J. Hageman and W. G. B. Huysmans, *Chem. Commun.*, 837 (1969).

[3] A. S. Hay, *Advan. Polym. Sci.*, **4**, 496 (1967).

[4] K. Dimroth and A. Berndt, *Angew. Chem.*, **76**, 434 (1964).

[5] K. Dimroth, W. Unbach, and K. H. Blöcher, *ibid.*, **75**, 860 (1963).

[6] A. S. Hay, *Tetrahedron Lett.*, 4241 (1965).

Intramolecular Hydrogen Bonding in β-Amino α,β-Unsaturated Esters

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This note comprises studies on hydrogen bonding of 1-ethylpyrazolyl-5-aminomethylenemalonic acid diethyl ester (Ia) and of its 3-methyl derivative (Ib) utilizing nmr and ir spectroscopy. These compounds could exist as II, III, or IV, where R′ is the pyrazol ring. Although nmr studies have been reported on closely related Schiff bases[1] and vinylogous imides,[2] studies on our system have not been previously reported.

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[1] G. O. Dudek and E. P. Dudek, *J. Amer. Chem. Soc.*, **88**, 2407 (1966), and preceding papers of the series.

[2] D. L. Ostercamp, *J. Org. Chem.*, **30**, 1169 (1964), and references cited therein.