of 2.650 Å is reasonable, the small angle of 113° suggests that a hydrogen bond does not exist. However, the N···O distance of 2.65 Å is shorter than that found in molecule A, lending credence to the idea of an attractive force between NB and OB-3.

All the intermolecular distances less than 3.9 Å were computed and surveyed but no unusually short contacts (other than hydrogen bonds) were found.

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Photochemistry of Electron-Transport Quinones. II.[1] Model Studies with Plastoquinone-1 [2,3-Dimethyl-5-(3-methylbut-2-enyl)-1,4-benzoquinone]

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Abstract: A number of photoproducts have been characterized from near-uv irradiation of plastoquinone-1 (**1**, $n = 1$) under several conditions. In benzene or isopropyl alcohol under oxygen the naphthoquinone **2**, the novel tricyclic peroxide **3**, and the benzofuranone **7** were formed. In the same solvents but under nitrogen, irradiation afforded **2**, the chromenol (**9a**, $n = 0$), and the benzoxepin **10**. Two additional photoproducts isolated from irradiation in isopropyl alcohol under nitrogen were the isomeric spiroenones **13** (A and B). These oxidized dimers were not only interconvertible upon treatment with triethylamine but also gave rise to the pyranoxanthene **18**. Irradiation in methanol or aqueous acetonitrile under nitrogen resulted in formation of the dihydrobenzofurans **4a** and **c** in addition to **10** and, in methanol, **2**. The characterization of these photoproducts will facilitate future studies on the photochemistry of the photosynthetic electron-transport quinones.

Electron-transport quinones located in membranous cellular substructures such as mitochondria and chloroplasts which perform, respectively, respiratory and photosynthetic functions, are redox components of electron-transport chains. The loss or diminution of some biological functions, such as growth, oxidative phosphorylation, and photosynthesis following ultraviolet irradiation of cells, has been attributed[3] to photochemical disruption of electron transport, the photolabile electron-transport quinones being the most likely targets for the radiation.

Considerable evidence[4] has accumulated that plastoquinone-9 (PQ-9, **1**, $n = 9$) is an essential transport quinone in photosynthetic processes. Far-uv irradiation of autotrophic cells leads to destruction of PQ-9 and the concomitant loss of several partial photosynthetic reactions.[5] The more energetic radiations in the 300-nm region of sunlight reaching the earth can also modify plastoquinone-9. Therefore, autotrophic cells must have evolved mechanisms for protecting plastoquinones from the harmful radiations, or alternatively, if the quinones are destroyed, evolved processes for their restoration.

These considerations prompted our initiation of studies to unravel the *in vitro* and *in vivo* photochemistry of PQ-9. There appears to be only one report on photodamage to PQ-9 *in vitro*, that of Eck and Trebst,[6] who prepared a PQ-9 dimer by irradiating the quinone as a thin film. They isolated the same dimer—one in which the quinone ring of one molecule has added to one of the nine double bonds of a second molecule—from horse chestnut leaves but were uncertain whether it occurred naturally or was an artifact of the isolation procedure.

Because of the limited availability of PQ-9 and other naturally occurring plastoquinones, we chose to study a model quinone PQ-1[7] (**1**, $n = 1$), which has the main structural features of the plastoquinones except for the presence of only one isoprene unit in the side chain. We expected that characterization of PQ-1 photoproducts, the subject of this report, would greatly facilitate our projected studies of the naturally occurring plastoquinones.

Results

Near-Uv Irradiation of Plastoquinone-1 under Oxygen. Following irradiation of PQ-1 (**1**, $n = 1$) in dry benzene

(1) Part I: H. Werbin and E. T. Strom, *J. Amer. Chem. Soc.*, **90**, 7296 (1968).

(2) (a) University of Texas at Dallas; (b) Mobil Research and Development Corporation.

(3) (a) A. F. Brodie in "Biochemistry of Quinones," R. A. Morton, Ed., Academic Press, London, 1965, p 384; (b) J. Jagger in "Research Progress in Organic-Biological and Medicinal Chemistry," U. Gallo and L. Santamaria, Ed., North-Holland Publishing Co., Amsterdam, in press.

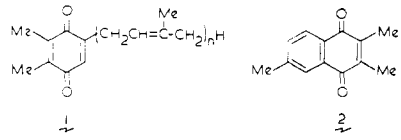
(4) Summarized by F. L. Crane in "Biological Oxidations," T. P. Singer, Ed., Interscience, New York, N. Y., 1968, p 563.

(5) (a) K. E. Mantai and N. I. Bishop, *Biochim. Biophys. Acta*, **131**, 350 (1967); (b) N. Shavit and M. Avron, *ibid.*, **66**, 187 (1963); (c) A. Trebst and E. Pistorious, *Z. Naturforsch. B*, **20**, 885 (1965); (d) K. E. Mantai, J. Wong, and N. I. Bishop, *Biochim. Biophys. Acta*, **197**, 257 (1970).

(6) V. H. Eck and A. Trebst, *Z. Naturforsch. B*, **18**, 446 (1963).

(7) P. M. Scott, *J. Biol. Chem.*, **240**, 1374 (1965).

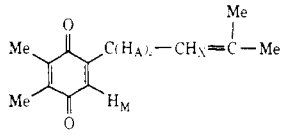
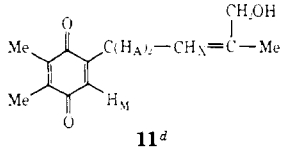
or dry isopropyl alcohol, five photoproducts were detected by thin-layer chromatography (tlc). Three of these have been separated by preparative tlc and identified as 2,3,6-trimethyl-1,4-naphthoquinone (**2**), R_f 0.66, 4,5-dihydro-3,3,8,9-tetramethyl-4,9a-epoxy-9a*H*-1,2-benzodioxepin-7(3*H*)-one (**3**), R_f 0.29, and 5-hydroxy-6,7-dimethylbenzofuran-3(2*H*)-one (**7**), R_f 0.06.



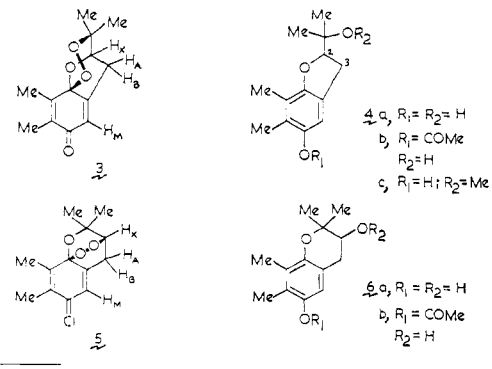
The photoproduct with R_f 0.66 was a yellow crystalline compound and had an ultraviolet spectrum (λ_{max} 334, 273, 264, 255 nm; sh, 250 nm) typical[8] of 2,3-dialkyl-1,4-naphthoquinones. Its infrared spectrum (ν_{max} 1664, 1620, 1596 cm^{-1}) was almost identical in the 1550–1700-cm^{-1} region with that of 2,3-dimethyl-1,4-naphthoquinone. These data and the molecular ion at *m/e* 200 (also the base peak) observed in the mass spectrum were indicative of a trimethyl-1,4-naphthoquinone. A strong peak at *m/e* 118 (36% of the base peak) was attributed to loss of (CH_3)—C=C—(CH_3)—C=O (*m/e* 82) from M^+. This mode of fragmentation is typical[9] of 2,3-dialkyl-1,4-naphthoquinones and allowed assignment of two of the methyl groups to the 2 and 3 positions of the naphthoquinone ring. Thus the photoproduct was either 2,3,5- or 2,3,6-trimethyl-1,4-naphthoquinone. That it was the latter was shown by its melting point,[10] 100°, and nmr spectrum. A singlet (6 H) at δ 2.16 was attributed to the 2- and 3-methyl groups, a singlet (3 H) at δ 2.47 to the 6-methyl group,[11] and complex absorption (3 H) between δ 7.42 and 8.00 to the aromatic protons.

The second photoproduct, R_f 0.29, the novel tricyclic peroxide **3**, has been the subject of a preliminary communication.[12] Its structure was assigned on the basis of its spectroscopic properties and its reduction to the dihydrobenzofuran **4a** which was characterized as the acetate **4b**. Elemental analysis and M^+ at *m/e* 236 in the mass spectrum corresponded to the molecular formula $C_{13}H_{16}O_4$ and indicated photoaddition of one oxygen molecule to PQ-1. A peak at *m/e* 204 ($M^+ - 32$, 62% of the base peak) supported this notion. These data, its positive reaction to a starch–iodide test, and the absence of an OH group in its ir and nmr spectra proved that the photoproduct was a peroxide. A more rigid conformation of the side chain of the photoproduct than that of PQ-1 (see Table I for the nmr spectrum of PQ-1) and probable saturation of the olefinic double bond were inferred by analysis of its nmr spectrum. It consisted of singlets (each 3 H) at δ 1.12 and 1.70 (*gem*-dimethyls), quartets (each 3 H) at δ 1.87 and 2.07 (vinylic methyls, $J_{homoallylic}$ = 1.3 Hz), an octet (1 H) and an ill-defined octet (1 H) centered at δ 2.77 and 3.10, respectively (H_A, H_B portion of an ABMX spectrum with J_{AB} = 18 Hz, J_{AX} = 6 Hz, J_{BX} = 1.2 Hz, J_{BM} = 2 Hz), a quartet (1 H) at δ 4.30 (H_X, J_{XA} = 6 Hz, J_{XB} = 1.2 Hz), and a triplet (1 H) at δ 6.12 (H_M, $J_{MA} = J_{MB}$ = 2 Hz). These data supported either **3** or **5** as the struc-

Table I. Nuclear Magnetic Resonance Assignments[a] for Plastoquinone-1 (**1**, $n = 1$) and 2,3-Dimethyl-5-(3-hydroxymethylbut-3-enyl)-1,4-benzoquinone (**11**)

Compd	Solvent	Me	$-CH_2O$	H_A	H_X	H_M
 **1**, $n = 1$	$CDCl_3$	1.63, s, 3 1.79, s, 3 2.02, s, 6		3.10,[b] d, J = 7.5, 2	5.18,[b] t, J = 7.5, 1	6.47,[c] t, J = 1.5, 1
 **11**[d]	$CDCl_3$	1.83,[e] d, J = 1.3, 3 2.01, s, 6	4.17, s, 2	3.19,[b] d, J = 7.7, 2	5.24,[b] t, J = 7.7, 1	6.51,[c] t, J = 1.5, 1
	$(CD_3)_2SO$	1.74, d, J = 1.1, 3 1.95, s, 6	3.94,[f] d, J = 5.3, 2 (3.95, s, 2)	3.12,[b] d, J = 7.7, 2	5.20,[b] t, J = 7.7, 1	6.49,[c] t, J = 1.5, 1

[a] δ (relative to internal TMS, δ = 0), followed by signal multiplicities, coupling constants (J, hertz), and relative intensities. [b] Broadened by unresolved allylic and homoallylic coupling. [c] Allylic coupling to H_A. [d] The stereochemistry about the side-chain double bond is not known. [e] Allylic coupling to H_X. [f] Hydroxyl proton gives rise to a triplet, J = 5.3 Hz at δ 4.60, disappearing on addition of D_2O.



(8) 2,3-Dimethyl-1,4-naphthoquinone has λ_{max} 330, 269, 260, 249, and 243 nm; menaquinone-9 has λ_{max} 325, 270, 260, 249, and 243 nm. Taken from ref 3a, p 49.

(9) (a) J. H. Bowie, D. W. Cameron, and D. H. Williams, *J. Amer. Chem. Soc.*, **87**, 5094 (1965); (b) S. J.Di Mari, J. H. Supple, and H. Rapoport, *ibid.*, **88**, 1226 (1966).

(10) 2,3,6-Trimethyl-1,4-naphthoquinone, mp 100°, E. Bergmann and F. Bergmann, *J. Org. Chem.*, **3**, 125 (1938); 2,3,5-trimethyl-1,4-naphthoquinone, mp 128°, O. Kruber, *Ber. Deut. Chem. Ges. B*, **73**, 1174 (1940).

(11) Methyl substituents in the 5 and 8 positions of 1,4-naphthoquinones and in the 1, 4, 5, and 8 positions of 9,10-anthraquinones are deshielded by the quinonoid carbonyl group. Thus in the nmr spectrum of 1,3-dimethyl-9,10-anthraquinone, singlets at δ 2.78 and 2.45 are attributed to the 1- and 3-methyl substituents, respectively. Spectrum No. 650 in "High Resolution N.M.R. Spectra Catalogue," Vol. 2, Varian Associates, Palo Alto, Calif., 1963. See also J. E. Bowie, D. W. Cameron, P. E. Schütz, D. H. Williams, and N. S. Bhacca, *Tetrahedron*, **22**, 1771 (1966), and references therein.

(12) D. Creed, H. Werbin, and E. T. Strom, *Chem. Commun.*, 47 (1970).

ture of the peroxide; the uv (234 nm, ϵ 10,250) and ir (1685, 1640 cm^{-1}) data were also consistent with either one but did not distinguish between them.

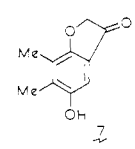
Examination of molecular models of **3** and **5** revealed that on the basis of the relative magnitudes of the dihedral angles between H_A, H_B, and H_X, that for **3**, J_{AX} should be larger than J_{BX}, whereas for **5**, J_{AX} and J_{BX} should be about equal.[13] The finding that J_{AX} = 6 Hz and J_{BX} = 1.2 Hz favored structure **3**.

Identification of the sodium borohydride reduction product of the peroxide as the dihydrobenzofuran **4a** rather than the chromanol **6a** proved that the peroxide was **3**. The reduction, carried out at pH 7–8 owing to the lability of the peroxide to alkali, yielded a phenolic product that had a uv maximum at 300 nm which shifted to 315 nm on addition of alkali and reverted to 300 nm on subsequent acidification. Since this product was somewhat unstable and difficult to purify, it was acetylated under mild conditions (dry pyridine and acetic anhydride for 18 hr at room temperature or for 30 min at 100°). The acetylated material, a colorless oil (λ_{max} 283 nm, ϵ 3000; 289 nm, ϵ 3100), showed hydroxyl and ester carbonyl stretching frequencies (3450 and 1760 cm^{-1}, respectively) in the infrared, indicating that monorather than diacetylation had occurred. Had the chromanol **6a** been the reduction product of the photoproduct it would have been diacetylated under these conditions, which normally acetylate secondary alcohols having a similar *gem*-dimethyl substitution pattern.[14]

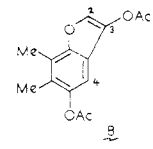
Confirmation of **4b** as the structure for the acetylated reduction product was provided by analysis of its nmr and mass spectra. The nmr spectrum consisted of singlets (each 3 H) at δ 1.20 and 1.33 (*gem*-diMe), δ 2.01 and 2.14 (ArMe), and δ 2.29 (COMe), a doublet (2 H) at δ 3.12 (3 protons,[15] J = 9 Hz), a triplet (1 H) at δ 4.57 (2 proton, J = 9 Hz), and a singlet (1 H) at δ 6.66 (ArH). The 2 and 3 protons gave rise to a splitting pattern and coupling constants comparable to those observed for the similarly substituted dihydrobenzofuran columbianetin[16] and the dihydrobenzofuran obtained by mild aerobic oxidation of colupulone.[17] Furthermore, in the nmr spectrum run in $(CD_3)_2SO$, the hydroxyl proton gave rise to the singlet at δ 4.52 that would be expected[18] for the tertiary alcohol **4b** but not for the secondary alcohol **6b**.

The mass spectrum of the acetylated reduction product had a strong peak at *m/e* 59, that was attributed to the ion $(CH_3)_2C{=}OH^+$, resulting from the simple fragmentation of the molecular ion (*m/e* 264) that would be expected for the tertiary alcohol **4b** but not for the secondary alcohol **6b**.

The third photoproduct, R_f 0.06, a crystalline fluorescent compound, is probably not a primary photoproduct since it was not detectable after aerobic irradiations of PQ-1 for short intervals. Its molecular formula, $C_{10}H_{10}O_3$, was established by mass spectrometry. Its uv spectrum with λ_{max} (ϵ) 267 (12,800), and 366 nm (6150) was similar to that of 5-hydroxybenzofuran-3(2*H*)-one.[19] The nmr spectrum, run in $(CD_3)_2SO$, consisted of four sharp singlets at δ 2.17, 4.67, 6.76, and 9.48 with relative intensities of 6:2:1:1, respectively. The singlet at δ 9.48 disappeared on addition of D_2O and was attributed to a phenolic hydroxyl proton. These data left little doubt that the photoproduct was the benzofuran-3(2*H*)-one (**7**), and this was confirmed by its conversion to the enol acetate **8**, 3,5-diacetoxy-6,7-dimethylbenzofuran.[20]



7



8

The acetylation of **7** was performed at 100° in acetic anhydride with anhydrous sodium acetate as catalyst. The white crystalline product thus obtained had M^+ at *m/e* 262 in the mass spectrum that corresponded to the addition of two acetate functions to **7**; these were also detected in the ir spectrum (1768 and 1758 cm^{-1}). The aryl-substituted carbonyl streching frequency observed at 1672 cm^{-1} in the ir spectrum of **7** was no longer present. The nmr spectrum of the diacetate consisted of singlets (each 3 H) at δ 2.17, 2.34, 2.36, and 2.43 (ArMe, –COMe), a singlet (1 H) at δ 7.07 (aromatic 4 proton), and a singlet (1 H) at δ 7.80 (2 proton). The 2 proton was deshielded by the adjacent acetoxy group, since it was found downfield with respect to the 2-proton signal at δ 7.52 in the nmr spectrum of benzofuran.[21] These data allowed unequivocal assignment of **8** to the diacetate. It reverted to the photoproduct **7** upon acid hydrolysis.

Near-Uv Irradiation of Plastoquinone-1 under Nitrogen. Six photoproducts were detected by tlc in solutions of PQ-1 in benzene irradiated for 15 hr. Three of these were isolated by preparative tlc and identified as **2**, plastochromenol-0 (**9a**, n = 0), R_f 0.34, and 3,8,9-trimethylbenzoxepin-7-(2,5*H*)-ol (**10**), R_f 0.31.

The uv spectra of the unstable photoproduct with R_f 0.34 (λ_{max} 332, 266, 232, sh 274 nm) and its acetate (λ_{max} 314, 266, 228, sh 276, 234 nm) were almost identical with those[22] of plastochromenol-8 (**9a**, n = 8) and its acetate (**9b**, n = 8) and indicated that the photoproduct was plastochromenol-0 (**9a**, n = 0). The mass and nmr spectra of the acetylated photoproduct confirmed the structure (**9b**, n = 0). In its mass spectrum M^+ appeared at *m/e* 246. The nmr spectrum consisted of a singlet (6 H) at δ 2.28 (–COMe), doublets (1 H) centered at δ 5.57 and 6.22 (3 and 4 protons, respectively, $J_{3,4}$ = 10 Hz), and a singlet (1 H) at δ 6.51 (ArH). The acetylated photoproduct was also identical (R_f, ir and uv spectra)

(13) S. Sternhell, *Quart. Rev., Chem. Soc.*, **23**, 236 (1969), and references cited therein.

(14) R. B. Woodward, A. A. Patchett, D. H. R. Barton, D. A. J. Ives, and R. B. Kelly, *J. Chem. Soc.*, 1131 (1957).

(15) The equivalence of these two protons is unexpected in view of the bulky 2 substituent but also is observed in the nmr spectra of columbianetin[16] and the oxidation product of colupulone,[17] benzofurans having the same 2 substituent. The expected ABX splitting pattern for the 2 and 3 protons is, however, observed in the nmr spectrum of 2-methyl-2,3-dihydrobenzofuran, where J_{AX} = J_{2-3} = 8.6 Hz, comparable to J_{2-3} = 9 Hz observed for **4b**; J. Gripenberg and T. Hase, *Acta Chem. Scand.*, **20**, 1561 (1966).

(16) Spectrum No. 310 in "High Resolution N.M.R. Spectra Catalogue," Vol. 1, Varian Associates, Palo Alto, Calif., 1962.

(17) D. N. Cahill and P. V. R. Shannon, *J. Chem. Soc. C*, 936 (1969).

(18) O. L. Chapman and R. W. King, *J. Amer. Chem. Soc.*, **86**, 1256 (1964).

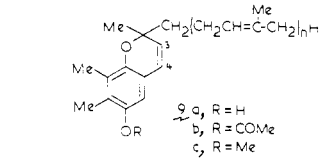
(19) λ_{max}^{MeOH} 252 and 366 nm: G. Schenck, M. Huke, and K. Gorlitzer, *Tetrahedron Lett.*, 2375 (1968).

(20) For the enol acetate of 5-hydroxybenzofuran-3(2*H*)-one see M. C. Kloetzel, R. R. Dayton, and B. Y. Abadir, *J. Org. Chem.*, **20**, 38 (1955).

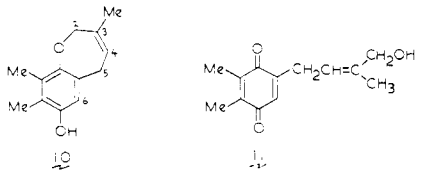
(21) P. J. Black and M. L. Heffernan, *Aust. J. Chem.*, **18**, 353 (1965).

(22) F. W. Hemming, R. A. Morton, and J. F. Pennock, *Biochem. J.*, **80**, 445 (1961).

with a sample of plastochromenol-0 (**9b**, $n = 0$) synthesized by a method similar to that used by McHale and Green[23] for the preparation of chromenols of several isoprenoid-1,4-quinones.



9 a, R = H
b, R = COMe
c, R = Me



10 **11**

The uv spectrum of the photoproduct with R_f 0.31 had a maximum at 284 nm (ϵ 2400) that shifted to 300 nm (ϵ 3200) on addition of base; acidification restored the original spectrum. These data suggested the photoproduct was a monoalkyl ether of a hydroquinone.[24] The ir spectrum showed weak absorption at 1620 cm^{-1} (nonconjugated C=C). In the mass spectrum M^+ appeared at *m/e* 204. These data suggested structure **10** for the photoproduct and this was proved by its nmr spectrum and oxidative ring opening to the quinone **11**. The nmr spectrum of the photoproduct, run in $(CD_3)_2SO$, consisted of a doublet (3 H) at δ 1.46 ($J_{allylic}$ = 1 Hz, 3-Me), singlets (each 3 H) at δ 2.02 and 2.09 (ArMe), a broad singlet (2 H) at δ 3.24 (5 proton, $ArCH_2$), a broad singlet (2 H) at δ 4.22 (2 proton, $-OCH_2-$), a broad singlet (1 H) at 5.53 (4 proton), a singlet (1 H) at 6.37 (ArH), and a singlet (1 H), disappearing on addition of D_2O, at δ 8.77 (-OH); the data are in complete accord with structure **10**.

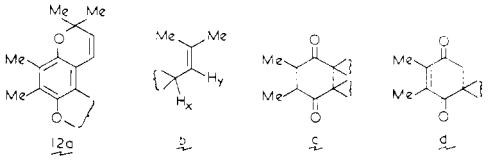
The oxidative ring opening of **10** to **11** was carried out in a manner analogous to the oxidations[25] of chromanols of a number of isoprenoid-1,4-quinones. A methanolic solution of **10** oxidized with ferric chloride yielded a yellow crystalline material having a uv spectrum (λ_{max} 254 nm, ϵ 18,700, λ_{sh} 260 nm, ϵ 18,000, and 310 nm, ϵ 800) similar to that of plastoquinone-1[26] and M^+ at *m/e* 220 in its mass spectrum. The nmr data for the oxidation product and plastoquinone-1 are given in Table I and leave no doubt that the assignment of **11** to the former is correct.

Seven photoproducts were detected by tlc in solutions of PQ-1 in isopropyl alcohol that had been irradiated under nitrogen for 15 hr. Five of these were isolated by preparative tlc and identified as **2** (**9a**, $n = 0$), **10**, and two diastereoisomers of 1′,7′-dihydro-3,4,4′,-5′,7′,7′-hexamethyl-1′-(2-methylpropenyl)spiro[3-cyclohexene-1,2′-[2*H*]furo[3,2-*f*][1]benzopyran]-2,5-dione (**13**), R_fs 0.49 and 0.44. The latter were designated A and B, respectively. That they were isomers was shown by their spectroscopic properties described in Table II and the Experimental Section. The molecular formula $C_{26}H_{30}O_4$, obtained from their mass spectra (M^+ at *m/e* 406) and elemental analyses, suggested both were oxidized dimers of PQ-1. Similarities in the uv spectra of A and B with that of plastochromenol-0 indicated both had a benzochromene configuration as one structural feature and nmr spectral data supported this notion.

A and B showed λ_{max} at 242, 278, and 338 nm, near to the maxima in the uv spectrum of plastochromenol-0 (**9a**, $n = 0$) at 232, 266, and 332 nm (and sh 274 nm). The red shifts of the maxima indicated additional substitution of the benzochromene chromophore, while the width of the 242-nm maximum suggested the presence of another chromophore.

The nmr data are presented in Table II. The AB doublets[27] centered at δ 6.14 and 5.53 (J = 9.8 Hz) in the spectrum of A, and at δ 5.97 and 5.54 (J = 10 Hz) in that of B, were assigned to the olefinic protons of a 2,2-dimethylbenzochromene ring, and are comparable with the doublets due to the 3 and 4 protons at δ 5.57 and 6.22 (J = 9.8 Hz) in the spectrum of plastochromenol-0 acetate (**9b**, $n = 0$). The additional finding of four singlets (each 3 H) in the spectra of A and B at positions close to those observed for the *gem*-2,2-dimethyls and aromatic methyls of **9b** ($n = 0$), supported **12a** as a partial structure for A and B and allowed the assignment of 14 of the 30 protons.

In the spectrum of A there were doublets (each 3 H) centered at δ 1.59 (J = 0.9 Hz) and 1.53 (J = 1.3 Hz), and in the spectrum of B, a doublet (3 H) was centered at δ 1.53 (J = 1.2 Hz) and a broad singlet (3 H) at δ 1.45. These signals were attributed to the *gem*-dimethyl groups of an isoprenoid side chain. The allylic coupling to a single olefinic proton was shown by spin decoupling: irradiation at δ 5.14, the position of a one-proton doublet (J = 10.2 Hz) in the spectrum of A, caused the doublets at δ 1.59 and 1.53 to collapse to singlets. In the same experiment another one-proton doublet (J = 10.2 Hz) at δ 4.51 also collapsed to a singlet. These data confirmed the presence in A, and therefore in B since A and B are isomers, of the partial structure **12b**. The doublet at δ 5.14 was assigned to H_Y, and that at δ 4.51 to H_X; both signals were broadened by unresolved long-range coupling, allylic and homoallylic, respectively, to the protons of the terminal methyl groups.



12a **b** **c** **d**

The partial structures **12a** and **b** left eight protons unassigned in both A and B, in a fragment $C_8H_8O_2$. Six of these protons gave rise to methyl quartets (J = 1.0 Hz) centered at δ 1.90 and 1.98 in the spectrum of A run in a 1:4 mixture of C_6D_6 and $CDCl_3$, each split by homoallylic coupling[13,27] to the other. In $CDCl_3$ these signals appeared as a quartet at δ 1.99 and part of broad absorption (9 H) centered at δ 2.07. In the spec-

(23) D. McHale and J. Green, *Chem. Ind. (London)*, 1867 (1963).

(24) The uv spectrum of plastohydroquinone-1 has λ_{max} 290 (ϵ 3300), but undergoes irreversible changes at alkaline pH.

(25) (a) P. Karrer, E. Escher, H. Fritzsche, H. Keller, B. H. Ringier, and H. Salomon, *Helv. Chim. Acta*, 21, 939 (1938); (b) M. Tishler, L. F. Fieser, and N. L. Wendler, *J. Amer. Chem. Soc.*, 62, 1982 (1940); (c) E. C. Slater, H. Rudney, J. Bouman, and J. Links, *Biochem. Biophys. Acta*, 47, 497 (1961).

(26) Plastoquinone-1 has λ_{max}^{EtOH} (ϵ) 254 (16,700) and 318 nm (661), according to Scott.[7] We find λ_{max}^{EtOH} (ϵ) 254 (17,700), 315 nm (625), and λ_{sh} 262 nm (17,000), and λ_{max}^{hexane} (ϵ) 252 (19,200), 259 (17,900), 308 (385), and 441 nm (30).

(27) In spin decoupling experiments the resolution and multiplicities of these signals in the spectrum of A were not affected by irradiation at the positions of other signals in the spectrum.

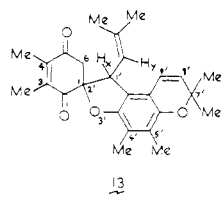
Table II. Nuclear Magnetic Resonance Assignments[a] for Isomeric Photoproducts **13** (A and B) and Plastochromenol-0 Acetate (**9b**, $n = 0$)

Compd	Solvent	7′,7′-diMe	=C(Me)$_2$	3,4-diMe	4′,5′-diMe
A	$CDCl_3$	1.34, s, 3	1.59,[b] d, J = 0.9, 3	1.99,[c] q, J = 1.0, 3	2.07,[d] bs, 6
		1.39, s, 3	1.71,[b] d, J = 1.3, 3		2.10, s, 3
	20% C_6D_6 in $CDCl_3$	1.32, s, 3	1.53,[b] d, J = 1.3, 3	1.90,[c] q, J = 1.0, 3	2.04, s, 3
		1.36, s, 3	1.66,[b] d, J = 0.9, 3	1.98,[c] q, J = 1.0, 3	2.07, s, 3
B	$CDCl_3$	1.35, s, 3	1.53,[b] d, J = 1.2, 3	1.96,[e] m, 6	2.08, s, 3
		1.39, s, 3	1.61,[b] d, J = 1.2, 3		2.16, s, 3
	20% C_6D_6 in $CDCl_3$	1.33, s, 3	1.45,[b] bs, 3	1.88,[e] bs, 6	2.08, s, 3
		1.34, s, 3	1.54,[b] bs, 3		2.16, s, 3
9b, $n = 0$	$CDCl_3$	1.40, s, 6			2.03, s, 3
					2.12, s, 3

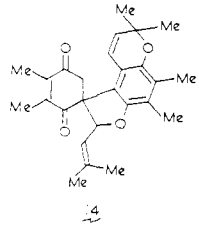
[a] δ (relative to internal TMS, δ = 0), followed by signal multiplicities, coupling constants (J, hertz), and relative intensities. [b] Allylic coupling to H_Y. [c] Homoallylic coupling between *vic*-methyls of the cyclohexenedione ring. [d] Overlap with 3- or 4-Me. [e] Unresolved

trum of B these six protons gave rise in $CDCl_3$ to an unresolved multiplet centered at δ 1.96 and in a 1:4 mixture of C_6D_6 and $CDCl_3$ to a broad singlet at δ 1.88. These signals were assigned to the 2- and 3-methyl groups of a cyclohex-2-enone on the basis of their positions, the shifts induced[28] by C_6D_6, and in the case of A, their multiplicities. In addition since two carbonyl stretching frequencies were observed for both A (1700 and 1670 cm^{-1}) and B (1700 and 1675 cm^{-1}), and both could be reduced to the same hydroquinone, the 2,3-dimethylcyclohex-2-ene-1,4-dione configuration **12c** seemed likely as the third partial structure for A and B. The uv data supported this conclusion. Thus cyclohex-2-ene-1,4-dione[29] and its 2,6,6-trimethyl derivative[30] have λ_{max} (due to an allowed π–π^* transition) at 233 and 238 nm, respectively; on the basis of these data one would expect the 2,3-dimethylcyclohex-2-ene-1,4-dione chromophore **12c** to have λ_{max} at about 243 nm; both A and B showed λ_{max} at 242 nm.

The remaining two unassigned protons in A and B gave rise, in their nmr spectra, to AB quartets centered at δ 3.06 (J = 16.5 Hz) and 3.16 (J = 16.0 Hz), respectively. The large coupling constants showed that these signals were due to nonidentical methylene protons. Their positions and the absence of any coupling to other protons, indicated by their resolution and from spin-decoupling data, showed that this methylene group was α to one of the enedione carbonyls and permitted expansion of the partial structure **12c** to the spiroenone **12d**.



13



14

Thus three fragments **12a**, **12b**, and **12d** were identified as parts of the structures of A and B, and when these are linked together only two gross structures **13** and **14** are possible. Characterization of the single derivative formed by the reduction of either A or B with zinc and hydrochloric acid permitted tentative assignment of the structure **13** to A and B.

The uv spectrum of the reduced material had λ_{max} (ϵ) 332 (4000), 280 (9800), 272 nm (9400), and λ_{sh} (ϵ) 296 nm (6000), similar to that of an equimolar mixture of plastohydroquinone-1 and plastochromenol-0 methyl ether[31] (**9c**, $n = 0$), and its ir spectrum showed no carbonyl absorption. In the nmr spectrum, run in $(CD_3)_2SO$, there were three sharp singlets (each 1 H) at δ 7.18, 7.63, and 8.29 that disappeared on addition of D_2O. These signals were assigned to the hydroquinone and chromenol hydroxyl protons. A singlet (1 H) at δ 6.55 was attributed to the single aromatic proton. The characteristic AB quartet that appeared in the nmr spectra of both A and B, at δ 3.06 and 3.16, respectively, was no longer present, and the doublets in the spectra of A and B assigned to H_X and H_Y were replaced by a complex multiplet between δ 5.4 and 5.7 consistent with the additional deshielding of these protons. Indeed, this multiplet overlapped a doublet (J = 9.8 Hz) centered at δ 5.57 that was assigned to one proton of the benzochromene ring (8′-H in A or B). The other proton (9′-H in A or B) gave rise to a doublet (J = 9.8 Hz) centered at δ 6.63. The spectrum is detailed fully in the Experimental Section. The data leave no doubt that **15a** represents the reduction product of A and B.

The acetate of the reduced A or B had M$^+$ at m/e 534 in its mass spectrum, consistent with the triacetate **15b**. Its uv spectrum with λ_{max} (ϵ) 317 (2900), 278 (6600), 270 (7900), 225 nm (23,400), and λ_{sh} (ϵ) 240 nm (17,000), was very similar to that of plastochromenol-0 acetate which had λ_{max} (ϵ) 314 (2900), 266 (5900), 228 nm (24,000), and λ_{sh} (ϵ) 276 (5000), 234 nm (21,000). In its nmr spectrum (Experimental Section), H_X and H_Y gave rise to broad doublets (J = 8.2 Hz) centered at δ 5.07 and 5.36, respectively. The signal due to H_X was shifted upfield with respect to the signal due to H_X in **15a** as a result of acetylation of the adjacent hydroquinone and hydroxybenzochromene functions.

The characterization of **15a** as the reduction product of both A and B supported **13** rather than **14** as the structure for A and B since, to yield **15a** upon reduction, **14** would have to undergo considerable rearrangement (cleavage of one C–C and one C–O bond and formation of a new C–C bond), whereas **13** would not (Chart I). These data and the finding that **15a** can be oxidized under several conditions to a mixture of A and B excluded **14** as a possible structure for A and B since the oxidation of **15a** to **14** would require a further rearrangement (breakage of two C–C bonds and formation of a C–C and C–O bond). However, the oxidation of

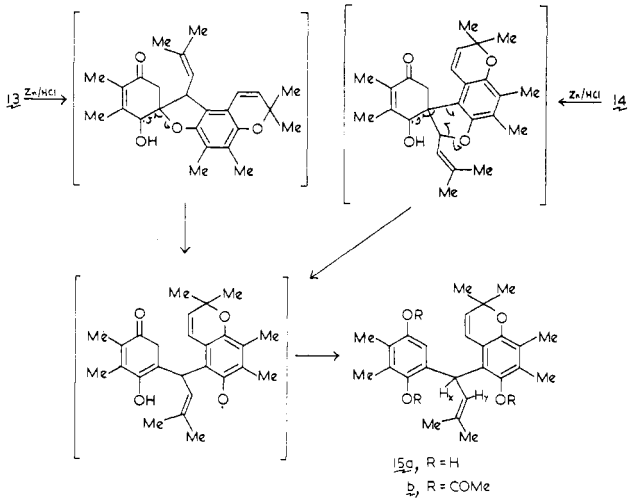
(28) See J. E. Bowie, *et al.*, ref 11.
(29) E. W. Garbisch, Jr., *J. Amer. Chem. Soc.*, **87**, 4971 (1965).
(30) T. Wada, *Chem. Pharm. Bull.*, **13**, 43 (1965).

(31) Owing to the difficulty in obtaining a pure sample of plastochromenol-0 (λ_{max} 331, 274, 266, 232 nm), its methyl ether (λ_{max} 328, 276, 268, 231 nm) was used in these uv studies.

6-CH_2	H_X (1′-H)	H_Y	8′-H	9′-H
3.06, q, J = 16.5, 2	4.51,[f] d, J = 10.2, 1	5.14,[g] d, J = 10.2, 1	5.53, d, J = 9.8, 1	6.14, d, J = 9.8, 1
3.00, q, J = 16.5, 2	4.53,[f] d, J = 10.2, 1	5.05,[g] d, J = 10.2, 1	5.48, d, J = 9.8, 1	6.16, d, J = 9.8, 1
3.16, q, J = 16.0, 2	4.05,[f] d, J = 11.0, 1	4.93,[g] d, J = 11.0, 1	5.54, d, J = 10.0, 1	5.97, d, J = 10.0, 1
3.13, q, J = 16.0, 2	4.06,[f] d, J = 11.0, 1	4.94,[g] d, J = 11.0, 1	5.52, d, J = 10.0, 1	6.01, d, J = 10.0, 1
			5.57, d, J = 9.8, 1	6.22, d, J = 9.8, 1

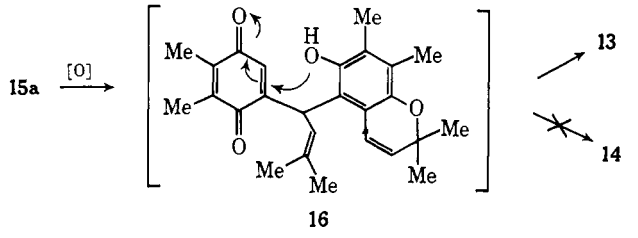
homoallylic coupling. [f] Broadened by homoallylic coupling to $=C(Me)_2$. [g] Broadened by allylic coupling to $=C(Me)_2$.

Chart I. Reduction of Spiroenone Photoproducts A and B (**13**)



15a to **13** can be envisaged as having occurred *via* the intermediate quinone **16** through intramolecular nucleophilic β addition of its benzochromene hydroxyl group to the 1,4-benzoquinone nucleus (Chart II). This novel cyclization may be a consequence of steric crowding in **16**.

Chart II. Oxidation of **15a** to **13**

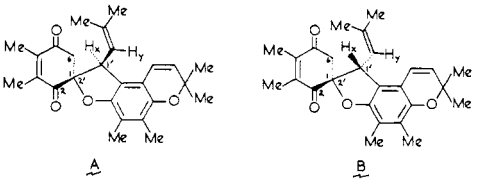


Examination of molecular models of the stereoisomers of **13** allowed us to assign the relative stereochemistry of A and B on the basis of the chemical shifts of the 1′ proton (H_X). In one pair of enantiomers, H_X lay above the plane of the 2-carbonyl group and would be expected[32] to resonate at a higher field (diamagnetic shift) than in the other pair of enantiomers where H_X points away from the 2-carbonyl group. In isomer A the 1′ proton gave rise to a doublet centered at δ 4.51 and in B at δ 4.05; accordingly the relative stereochemistry of A and B was assigned as shown in Chart III.

The isomeric photoproducts **13** have a potentially enolizable carbonyl group, but several attempts to pre-

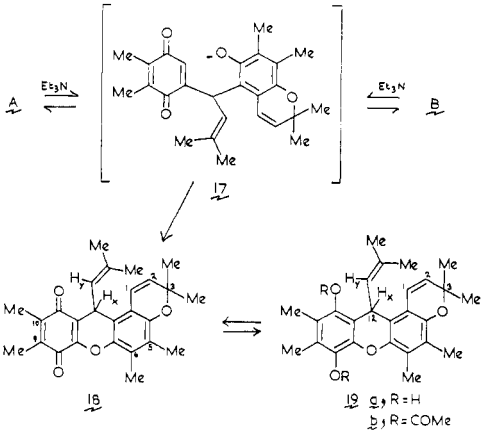
(32) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969, pp 88–92.

Chart III. Relative Stereochemistry of Photoproducts **13**



pare their enols or enol acetates failed. Instead by addition of a trace of triethylamine, either A or B in benzene could be converted to a mixture of A, B, and a red derivative. The latter was the major product from acid treatment of both A and B. We envisaged this isomerization as having occurred *via* removal of a proton from the 6 position of A or B by triethylamine followed by ring opening to the anion **17** (rather than formation of an enol anion). The latter then reverted to A or B by intramolecular nucleophilic addition (Chart IV). On the basis of this mechanism the red deriva-

Chart IV



tive should be the 1,4-benzoquinone **18** formed by intramolecular nucleophilic addition to the other nuclear position (6 position in **13**) of **17**. This conclusion was supported by the spectroscopic properties of the red derivative and its hydroquinone diacetate.

The red derivative had M^+ at m/e 404 in its mass spectrum. It had strong absorption (ν_{max} 1670, 1658, 1640 cm^{-1}) in the ir ascribable[33] to quinonoid carbonyl stretching, and in the uv λ_{max} (ϵ) 475 (1400), 324 (4000), 270 (18,500), and 242 nm (19,600). The 475-nm band was attributed to charge-transfer interaction between the quinone and benzochromene chromophores, the 324- and 242-nm bands to the benzochromene chromo-

(33) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, Methuen, London, 1966, p 150.

phore, and the 270-nm band to the allowed $\pi-\pi^*$ transition of the 1,4-benzoquinone chromophore.[34] That the derivative was the 1,4-quinone **18** was further supported by its nmr spectrum, detailed fully in the Experimental Section. A singlet (6 H) at δ 2.04 shifted to δ 1.65 when the spectrum was run in C_6D_6 rather than $CDCl_3$. This large shift ($\Delta = \delta_{CDCl_3} - \delta_{C_6D_6} = +0.39$) was comparable to those observed[28] for the benzene-induced shifts in the nmr spectra of a number of methyl-1,4-quinones and the singlet was therefore assigned to the 9- and 10 methyls of **18**. Broad singlets at δ 1.59 and 2.32 were assigned to the terminal *gem*-dimethyls (=C(Me)$_2$). The anomalous position at δ 2.32 of one of these signals was attributed to deshielding by the 2-carbonyl group,[35] since examination of a molecular model of **18** revealed that when it was in its least-hindered conformation (with the isopropene side chain axial to the pyran ring) one of the side-chain methyls was close to the plane of the 2-carbonyl group. The side-chain protons H_X and H_Y have almost identical chemical shifts and gave rise, in $CDCl_3$, to a broad singlet (2 H) centered at δ 4.84, and in C_6D_6 to a complex multiplet between δ 4.9 and 5.1.

The reduction of **18** by a standard procedure for 1,4-quinones gave the hydroquinone **19a** as a white solid. Because it was prone to revert upon aerobic oxidation to **18**, the hydroquinone was acetylated. The acetate had M^+ at *m/e* 490 in the mass spectrum consistent with the triacetate **19b** and showed only ester absorption (ν_{max} 1760 cm^{-1}) in the carbonyl region of the infrared. The nmr spectrum (Experimental Section) was consistent with the structure **19b**. The side-chain protons H_Y and H_X (12 proton) were sufficiently nonequivalent to give rise to two doublets (J = 11.1 Hz) centered at δ 4.88 and 5.06 and broadened by allylic and homoallylic coupling to the side-chain methyls.

Solutions of PQ-1 irradiated in methanol gave rise to three photoproducts that were detected by tlc and, after isolation by preparative tlc, identified as **2**, **10**, and 2-(5-hydroxy-6,7-dimethyl[2,3*H*]benzofuran-2-yl)-2-methoxypropane (**4c**), R_f 0.12. The photoproduct with R_f 0.12 was shown by its mass spectrum (M^+ at *m/e* 236) and elemental analysis to have a molecular formula of $C_{14}H_{20}O_3$, corresponding to a photoadduct of methanol and PQ-1. Its uv spectrum had λ_{max} (ϵ) 300 nm (4500) which shifted to 318 nm (5000) on addition of base and reverted to 300 nm on subsequent reacidification, comparable to the behavior of the dihydrobenzofuran **4a**. The above data strongly suggested that the photoproduct was **4c** and this was confirmed by its nmr spectrum which was very similar to that of **4b**. It consisted of singlets (each 3H) at δ 1.20 and 1.27 (*gem*-diMe), a singlet (6 H) at δ 2.11 (ArMe), a singlet (3 H) at δ 3.29 (–OMe), a doublet (1 H) at δ 3.10 (3 proton, J = 8.7 Hz), a triplet (1 H) at δ 4.59 (2 proton, J = 8.7 Hz), and a singlet (1 H) at δ 6.48 (ArH).

Two photoproducts were detected by tlc in solutions of PQ-1 in aqueous acetonitrile irradiated under nitrogen. They were identified as **10** and 2-(5-hydroxy-6,7-dimethyl[2,3*H*]benzofuran-2-yl)-propan-2-ol (**4a**), R_f 0.05. The latter was characterized as the acetate **4b**.

Discussion

The Photochemistry of Plastoquinone-1. I. Mechanistic Aspects. The photochemistry of plastoquinone-1, a trisubstituted isoprenoid-1,4-benzoquinone, is quite different from that reported for other tetrasubstituted isoprenoid-1,4-quinones such as the ubiquinones and menaquinones. Thus the irradiation of PQ-1 under oxygen gave rise to the peroxide **3** as the major photoproduct rather than to a hydroperoxide or chromenol as was observed for phylloquinone[36] and the ubiquinones,[37,38] respectively. There are no comparable photochemical reactions in the menaquinone or ubiquinone series to the formation of the dihydrobenzofurans **4a** and **c**, the spiroenones **13**, the naphthoquinone **2**, or the benzoxepin **10**, observed in our studies.

The one photochemical reaction that PQ-1 and the other isoprenoid-1,4-quinones thus far studied have in common is chromenol formation; this occurs under nitrogen for PQ-1 and phylloquinone[39] and under both oxygen[37] and nitrogen[38] with the ubiquinones. Quinone methide intermediates have been invoked[38,40] to explain the photochemical formation of ubichromenols and isoubiquinones,[40] and the conversion of PQ-1 to plastochromenol-0 (**9a**, n = 0) may proceed analogously *via* the anion **20**. Furthermore nucleophilic attack by **20** on PQ-1 leading to **21** (Chart V) and **16** would explain the formation of the spiroenones **13** since **16** is the most likely intermediate in the oxidation of **15a** to **13** (Chart II).

The dihydrobenzofurans **4a** and **c** and the tricyclic peroxide **3** can be envisaged as having arisen from addition of ROH (R = H or Me) or oxygen to a common zwitterionic intermediate **22** engendered by an intramolecular photocyclization of the excited PQ-1. We consider the oxygen molecule involved in formation of **3** to have been in its ground state since PQ-1 was not converted to **3** with singlet oxygen ($^1\Delta$ or $^1\Sigma$) generated by methylene blue or eosin photosensitization.

The photocyclizations of PQ-1 to the naphthoquinone **2** and the benzoxepin **10** are typical examples of photochemical reactions of a 1,4-quinone carrying a side chain from which hydrogen atoms may be abstracted,[41,42] and are analogous to the visible-light-induced photocyclizations[43] of but-3′-enyl-1,4-benzoquinone and benzyloxymethyl-1,4-benzoquinone to 1,4-dihydro-5,8-dihydroxynaphthalene and 6-hydroxy-2-phenylbenzo-1,3-dioxan, respectively. Thus **2** and **10** probably arise from *intra*molecular scavenging of the free-radical **23** formed by hydrogen abstraction from the side-chain methyl group of one molecule of PQ-1 by another molecule of photoexcited PQ-1. *Inter*molecu-

(34) 2-Methoxy-3,5,6-trimethyl-1,4-benzoquinone has $\lambda_{max}^{CCl_4}$ (ϵ) 271 nm (17,400) due to the "allowed" $\pi-\pi^*$ transition: W. Flaig and J.-Ch. Salfeld, *Justus Liebigs Ann. Chem.*, **618**, 117 (1958).

(35) In the hydroquinone diacetate **19b** of **18** the gem dimethyls (=C(Me)$_2$) gave rise to broad singlets at δ 1.56 and 1.89; the position of the latter suggested some deshielding in **18** by π systems other than of the 2-carbonyl group.

(36) (a) C. D. Snyder and H. Rapoport, *J. Amer. Chem. Soc.*, **91**, 731 (1969); (b) M. Ohmae and G. Katsui, *Bitamin*, **35**, 116 (1967).

(37) I. Imada and H. Morimoto, *Chem. Pharm. Bull.*, **12**, 1047 (1964).

(38) H. W. Moore and K. Folkers, *Justus Liebigs Ann. Chem.*, **684**, 212 (1965).

(39) S. Fujisawa, S. Kawabata, and R. Yamamoto, *Yakugaku Zasshi*, **87**, 1451 (1967).

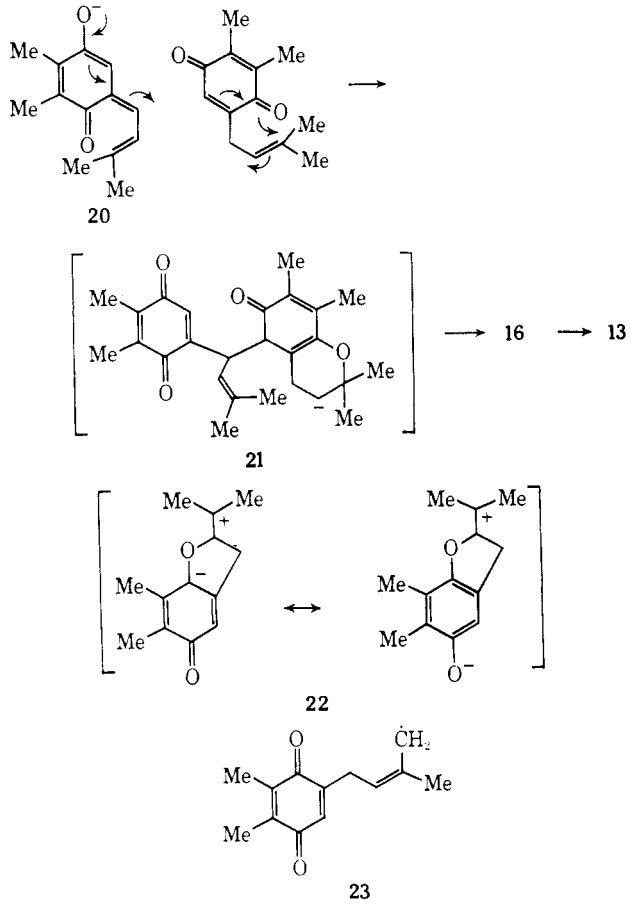
(40) H. Morimoto, I. Imada, and G. Goto, *Justus Liebigs Ann. Chem.*, **729**, 184 (1969).

(41) J. M. Bruce, *Quart. Rev., Chem. Soc.*, **21**, 405 (1967).

(42) J. M. Bruce and D. Creed, *J. Chem. Soc. C*, 649 (1970).

(43) J. M. Bruce and P. Knowles, *ibid.*, *C*, 1627 (1966).

Chart V



lar scavenging of **23** and other radicals derived by hydrogen abstraction reactions of excited PQ-1 could be responsible for the low overall conversions of PQ-1 to identifiable photoproducts observed upon irradiation of PQ-1 in benzene and isopropyl alcohol under nitrogen.

II. Biological Significance. Photosynthesis occurs in subcellular membranous organelles of plant cells known as chloroplasts where the energy of sunlight removes an electron from water in photosystem II and the electron is shuttled through a series of carriers until it reduces Pigment 700 in photosystem I.[44] Plastoquinone-9 (PQ-9) is one of these carriers and is thought to lie between two others, one unknown, designated Q, and cytochrome b.

The spectrum of sunlight between 300 and 900 nm inducing photosynthesis[45] includes wavelengths (300–400 nm) deleterious to plastoquinone-9. Hence mechanisms are present in photosynthetic cells that either prevent the damage by light or if it occurs, remove the photoproducts and restore PQ-9. Thus the damage may be prevented simply because of preferential absorption by other pigments of the harmful rays impinging on the cells. Alternatively, by analogy with the role of carotenoids and phycobilins in some photosynthetic organisms, photoexcited PQ-9 may transfer its excitation energy to chlorophyll *a* for use in photosynthesis or dissipation by luminescence. The formation of PQ-9 photoproducts under natural conditions—the work of Eck and Trebst[6] indicates that this may occur—could be a consequence of saturation of such protective mechanisms.

The isolation and identification of PQ-9 photoproducts, arising either naturally or induced by uv light, should help define the molecular environment ("nearest neighbors") of PQ-9. For example, if PQ-9 is a mobile electron carrier, it may photochemically react intramolecularly, or, intermolecularly with the lipoprotein matrix in which it is embedded. Alternatively, if it is "locked" in the transport chain within a molecular radius of two other carriers Q and cytochrome *b*, the quinone may become covalently bound to one of these.

Our work on the photochemistry of PQ-1 delineates a spectrum of the photochemical reactions that this isoprenoidquinone undergoes and provides a basis upon which to carry on the more difficult work of identifying photoproducts of the photosynthetic transport quinones.

Experimental Section[46]

Aerobic Irradiations. A solution of PQ-1 (0.158 g) in benzene (80 ml) was irradiated for 3 hr, the solvent was distilled *in vacuo*, and the brown oily residue was chromatographed on eight plates. Observation of the plates with near-uv showed bands at R_f's 0.06, 0.29, and 0.61–0.75. After elution of the band, R_f 0.06, with ether, the solvent was removed and the residue was crystallized from methanol, yielding orange crystals of **5-hydroxy-6,7-dimethylbenzofuran-3(2*H*)-one (7)**: mp 248–252° dec; ν_{max} 3280 s, 1672 vs, 1610 s cm^{-1}; *m/e* (%) at 178 (M^+, 100) 163 (12), 149 (55), 121 (20), 107 (18); molecular weight from M^+ in mass spectrum, 178.0632; calcd for $C_{10}H_{10}O_3$, 178.0630.

Acetylation of **7** with pyridine and acetic anhydride yielded **3,5-diacetoxy-6,7-dimethylbenzofuran (8),** obtained from a hexane–benzene mixture as white crystals: mp 91–93°; λ_{max} nm (ϵ) 287 (3300), 282 (2800), 277 (3300), 250 (14,200); *m/e* (%) at 262 (M^+, 11), 220 (18), 178 (100), 163 (7), 149 (5).

Material with R_f 0.29 was eluted with ether and, after evaporation of the solvent, the residue was recrystallized from a hexane–benzene mixture yielding white crystals (0.022 g, 42%) of **4,5-dihydro-3,3,8,9-tetramethyl-4,9a-epoxy-9a*H*-1,2-benzodioxepin-7(3*H*)-one (3)**: mp 153–155°; ν_{max} 3000 w, 1685 s, 1640 vs cm^{-1}; *m/e* at 236 (M^+, 21), 221 (5), 204 (62), 189 (100), 163 (33), 162 (36), 150 (34), 122 (41).

Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.10; H, 6.78. Found: C, 65.72; H, 6.89.

(44) M. Avron in "Current Topics in Bioenergetics," Vol. 2, D. R. Sanadi, Ed., Academic Press, New York, N. Y., 1967, p 1. An alternative view of the photosynthetic process is described by A. Arnon in "Biological Oxidations," T. P. Singer, Ed., Interscience, New York, N. Y., 1968. p 123.

(45) R. K. Clayton, "Molecular Physics in Photosynthesis," Blaisdell, New York, N. Y., 1965, p 3.

(46) Melting points are corrected. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Ir spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer, uv spectra on a Hitachi Perkin-Elmer Coleman 124 spectrophotometer equipped with a Sargent SRG recorder or a Cary 14 spectrophotometer, for Nujol mulls or solutions in ethanol, respectively, unless stated otherwise. Nuclear magnetic resonance spectra were taken, unless specified otherwise, in solutions in chloroform with tetramethylsilane as internal standard, on a Varian HA-100 spectrometer. Frequencies were measured, to an accuracy of ±0.1 Hz, with a Hewlett-Packard 522-B electronic counter. Resonances assigned to OH groups disappeared on addition of D_2O. Mass spectra were recorded on a Varian CH5 mass spectrometer. Spectral data given in the Results are not repeated in this section. Preparative thin-layer chromatography (ptlc) was carried out on 20 × 20 cm glass plates coated with a 1-mm thick layer of silica gel PF_{254}, Brinkmann Instruments Inc., Westbury, N. Y. The plates were dried at room temperature overnight and activated for 1 hr at 125°. These silica gel coated plates are designated as *plates* throughout the experimental section. The solvent for all ptlc runs was 5% ether in benzene unless otherwise indicated. Plastoquinone-1 (PQ-1) was prepared by the method of Scott.[7] Benzene was double distilled, the second time over P_2O_5. Acetonitrile was purified by the method of Coetzee, *et al.*[47] Anhydrous Na_2SO_4 was used to dry solutions. Solutions of PQ-1 were flushed with nitrogen (Matheson, prepurified) or oxygen for a period of 20 min prior to and then during irradiation, in Pyrex glassware, at room temperature, at a distance of 3 cm from five General Electric 15-W F15T-8-BLB "black light" lamps mounted in parallel.

(47) J. F. Coetzee, G. P. Cunningham, D. K. McGuire, and G. R. Padmanabhan, *Anal. Chem.*, **34**, 1139 (1962).

Sodium borohydride converted **3** to **4b**. Carbon dioxide was bubbled into a mixture of water (30 ml) and ethanol (15 ml) for 10 min. To this solution were then added sufficient sodium borohydride to raise the pH to 8 and **3** (0.026 g) in ethanol (10 ml). The mixture was stirred 5 min, acidified to pH 4 with 1 *N* HCl, stirred an additional 15 min, and then was extracted with ether. The ether extracts were washed with water and saturated aqueous $NaHCO_3$ and dried. After filtration and evaporation of the solvent, the residue was chromatographed on two plates (8% ether in benzene). The slowest moving fraction (R_f 0.0–0.10) contained a brown oil **4a** which was acetylated (pyridine–acetic anhydride overnight at room temperature or for 30 min at 100°) and rechromatographed on two plates. The band at R_f 0.10 was eluted and after removal of the solvent, **4b** was obtained as a colorless oil (0.015 g, 52% yield), **2-(5-acetoxy-6,7-dimethyl[2,3*H*]benzofuran-2-yl)propan-2-ol**: ν_{max}^{film} 3450 s, 2975 s, 2930 s, 1760 vs, 1630 w, 1590 w cm^{-1}; *m/e* (%) at 264 (M^+, 16), 222 (88), 204 (35), 202 (37), 189 (81), 164 (100), 151 (59), 59 (56); δ [$(CD_3)_2SO$] 1.13 (broad s, *gem*-diMe), 1.92, 2.07 (s, ArMe), 2.24 (s, $-COCH_3$), 3.09 (d, J = 8.5 Hz, $-CH_2-$), 4.50 (t, J = 8.5 Hz, –CH–), 4.53 (s, –OH), 6.68 (s, ArH).

One-third (0.034 g) of the fastest moving fraction (0.108 g), R_f 0.65–0.75, was rechromatographed on four plates. PQ-1 separated from **2,3,6-trimethyl-1,4-naphthoquinone (2)** which was accumulated from several experiments and then recrystallized from hexane, yielding yellow crystals: mp 100° (lit.[10] 100°); *m/e* (%) at 200 (M^+, 100), 185 (6), 172 (43), 157 (22), 129 (33), 128 (23), 118 (36), 90 (27), 89 (28).

The irradiation of solutions of PQ-1 in either benzene or isopropyl alcohol under oxygen for periods longer than 3 hr resulted in slightly increased yields of **2** and **4** at the expense of the peroxide **3**.

Dye-Sensitized Photooxidation of PQ-1. Oxygen was bubbled for 10 min in the dark through a solution of PQ-1 (0.08 g) and methylene blue (4 mg) in isopropyl alcohol (20 ml). The solution was then transferred to a Pyrex Petri dish in which it was illuminated (four General Electric 15-W cool white fluorescent lamps) for 15 hr at room temperature through a red filter of Sudan IV in mineral oil. PQ-1 (0.074 g, 92%) and six minor products, none of which was the peroxide **3** or the benzofuranone **4**, were isolated by ptlc of the reaction mixture on four plates. Under the same conditions, phylloquinone gave rise to phylloquinone hydroperoxide (52%). In a similar experiment neither **3** nor **4** was isolated from an eosin Y sensitized photooxidation of PQ-1 using a Corning 3-69 yellow filter.

Irradiation in Benzene under Nitrogen. A solution of PQ-1 (0.245 g) in benzene (50 ml) was irradiated for 16 hr. After removal of solvent, the residue was chromatographed on five plates. Two fluorescence quenching bands were observed by near-uv at R_f 0.30–0.35 and 0.65–0.75. Elution of the slower moving band with ether and removal of the ether afforded a mixture (0.019 g) of a yellow oil and a white solid. The latter, when washed with hexane (three 1-ml portions) and recrystallized from the same solvent, afforded white crystals (6 mg) of **3,8,9-trimethylbenzoxepin-7(2,5*H*)-ol (10)**: mp 156–157°; ν_{max} 3280 s, 1620 w, 1585 w cm^{-1}; *m/e* (%) at 204 (M^-, 50), 189 (100), 174 (14), 141 (18), 131 (23).

Anal. Calcd for $C_{13}H_{16}O_4$: C, 76.47; H, 7.84. Found: C, 76.32; H, 7.53.

The oxidative ring cleavage of **10** was performed by adding ferric chloride (0.1 g) in water (1 ml) to a solution of **10** (0.014 g) in methanol (8 ml). The mixture was stirred in the dark for 2 hr at room temperature, water (20 ml) was added, and the mixture was extracted with ether (three 10-ml portions). The combined extracts were washed with water and saturated sodium chloride and dried. The residue obtained after removal of the ether was chromatographed on one plate (10% ether in benzene). In addition to **10** (3.0 mg), a substance having an R_f of 0.14 was recovered. After recrystallization from a hexane–benzene mixture **2,3-dimethyl-5-(3-hydroxymethylbut-3-enyl)-1,4-benzoquinone (11)** was obtained as yellow crystals: mp 78–80°; ν_{max} 3390 s, 3330 s, 1645 vs, 1630 vs, 1615 s cm^{-1}; *m/e* (%) at 220 (M^+, 10), 218 (6), 202 (7), 200 (21), 189 (100), 172 (11).

Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.91; H, 7.27. Found: C, 70.86; H, 7.35.

When the hexane washings of **10** were chromatographed on two plates two bands were observed, one with an R_f of 0.31, **10**, and one with an R_f of 0.34. The material in the latter was converted by acetylation (pyridine–acetic anhydride overnight at room temperature) to plastochromenol-0 acetate (**9b**), n = 0 [0.01 g, 5% **9a**, n = 0] identical (R_f, uv and ir spectra) with a sample that was synthesized as follows: PQ-1 (0.109 g) in dry pyridine (10 ml) was held at room temperature for 12 hr. The brown oily residue obtained after removal of the pyridine was chromatographed on three plates. The two major fractions, R_f 0.70 and 0.35, afforded PQ-1 (0.034 g) and a yellow oil (0.042 g), respectively. The latter was acetylated overnight, the solvents were vacuum distilled, and the residual oil was rechromatographed on three plates. Two major fractions were obtained with R_f 0.35 and 0.64. The former yielded a yellow, crystalline material (0.014 g) that was not characterized, the latter a colorless oil, **plastochromenol-0 acetate** (0.033 g, represents 0.027 g, 36% yield of plastochromenol-0 from PQ-1) (**9b**, n = 0); ν_{max}^{film} 2972 m, 2965 s, 2922 m, 1748 vs, 1640 w, 1614 w, 1576 w cm^{-1}; *m/e* (%) at 246 (M^+, 15), 231 (19), 204 (12), 189 (100).

Irradiation in Isopropyl Alcohol under Nitrogen. In a typical experiment PQ-1 (0.215 g) in isopropyl alcohol (50 ml) was irradiated for 15 hr. The solvent was removed and the oil remaining was chromatographed on five plates. Seven photoproducts were observed. From the band with an R_f of 0.65–0.75, PQ-1 (0.06 g) and **2** (3 mg, 2%) were isolated, while **10** (0.017 g, 10%) and **9a**, n = 0 (0.011 g, 7%), were identified in the band with R_f 0.30–0.35. Materials in two other bands with R_f 0.47–0.51 (0.017 g) and 0.44–0.46 (0.011 g) were purified by rechromatography and crystallization from hexane and afforded in each case yellow crystals of **1′,7′-dihydro-3,4,4′,5′,7′,7′-hexamethyl-1′-(2-methylpropenyl)spiro[3-cyclohexene-1,2′[2*H*]-furo[3,2-*f*][1]benzopyran]-2,5-dione (13).** The compound (0.012 g, 8%) with the higher R_f (0.49) was designated A: mp 149–150°; ν_{max} 3040 w, 1700 s, 1670 vs, 1615 w, 1580 w cm^{-1}; λ_{max} nm (ε) 338 (4040), 278 (8700), 242 (29,300); *m/e* (%) at 407 (12), 406 (M^-, 39), 392 (29), 391 (100), 279 (8), 267 (9), 204 (10), 202 (18), 201 (8), 200 (13), 199 (10), 189 (41), 188 (12).

Anal. Calcd for $C_{26}H_{30}O_4$: C, 76.84; H, 7.39. Found: C, 76.62; H, 7.71.

The compound (6 mg, 4%) with the lower R_f (0.44) was designated B: mp 180–181°; ν_{max} 3040 s, 1700 s, 1675 vs, 1612 w, 1580 w cm^{-1}; λ_{max} nm (ε) 338 (4300), 278 (9000), 242 (32,000); *m/e* (%) at 407 (11), 406 (M^+, 40), 392 (27), 391 (100), 267 (7), 239 (4), 202 (4), 189 (13), 188 (5).

Anal. Calcd for $C_{26}H_{30}O_4$: C, 76.84, H, 7.39. Found: C, 76.54; H, 7.63.

Reduction of A and B to 15a. To a solution of A or B (5 mg) in ethanol (5 ml) were added 1 *N* hydrochloric acid (1 ml) and zinc dust (0.040 g). The mixture was stirred 5 min at room temperature and, after addition of water (10 ml), extracted with ethyl acetate. The combined extracts were washed with water and saturated aqueous $NaHCO_3$ and dried. The residue obtained after removal of the ethyl acetate at room temperature was recrystallized from aqueous ethanol and afforded white crystals (4.5 mg, 82%) of **5-[1-(6-hydroxy-2,2,7,8-tetramethyl-2*H*-1-benzopyran-5-yl)-3-methyl-2-butenyl]-2,3-dimethylhydroquinone (15a)**: mp 194–197°; ν_{max} 3260 s, 1601 w cm^{-1}; δ [$(CD_3)_2SO$] 1.26, 1.30 (each s, 3, pyran *gem*-diMe), 1.51 (broad s, 3, Me attached to olefinic side chain), 1.69 (d, $J_{allylic}$ = 0.5 Hz, 3, Me attached to olefinic side chain), 1.97, 2.01, 2.07 (each s, 3, 6, and 3, respectively, ArMe), 5.4–5.7 (m, 2, –CH—CH=), 5.57 and 6.63 (each d, J = 10.0 Hz, 1, pyran ring H's), 6.55 (s, 1, ArH), 7.18, 7.63, 8.29 (–OH). The triacetate **15b** was obtained, as a colorless oil, by treatment of **15a** with pyridine and acetic anhydride overnight at room temperature followed by ptlc (R_f 0.32): ν_{max} 1760 s, 1595 w cm^{-1}; *m/e* (from 534–400 only) at 534 (M^+), 519, 492, 476, 435, 433; δ 1.36 (s, 6, pyran *gem*-diMe), 1.54 and 1.72 (broad s, 3, $=C(Me)_2$), 1.9–2.2 (m, 21, ArMe, –COMe), 5.07 and 5.36 (each d, J = 8.2 Hz, broadened by allylic and homoallylic coupling to $=CMe_2$, 1, –CH—CH=), 5.52 and 6.39 (each d, J = 10.1 Hz, 1, pyran ring H's), 7.25 (s, 1, ArH).

Anal. Calcd for $C_{32}H_{38}O_7$: C, 71.91; H, 7.12. Found: C, 71.95; H, 7.09.

Interconversion of A and B. Triethylamine (0.1 ml) was added to a solution of either A or B (0.018 g) in methanol (5 ml). The mixture was allowed to stand 12 hr at room temperature or was refluxed for 30 min. The solvent was removed and the residue was chromatographed on three plates. A (7.5 mg), B (6.4 mg), and the quinone **18** (2 mg) were isolated in the usual manner. The latter was identical (R_f, ir and uv spectra) with **18** that was prepared by the method described in the next section.

Preparation of 18. To a solution of A or B (0.0265 g) in methanol (40 ml) was added a 1:1 mixture of concentrated HCl and water (2 ml). The mixture was refluxed for 2 hr and then the bulk of the methanol was distilled off. Water (20 ml) was added to the remainder and the mixture was extracted with ether. The extracts

were washed with water and saturated aqueous NaCl and dried. The total product was chromatographed on two plates. The red fraction, R_f 0.80, when recrystallized from a hexane–benzene mixture, afforded red crystals (8.7 mg, 33%) of **3,12-dihydro-3,3,5,6,9,10-hexamethyl-12-(2-methylpropenyl)pyrano[3,2-*a*]xanthene-8,11-dione (18)**: mp 186.5–188°; ν_{max} 1670 s, 1658 vs, 1640 s, 1620 s, 1600 w cm^{-1}; *m/e* (%) at 405 (6), 404 (M^+, 18), 390 (28), 389 (100), 187.5 (7), 187 (27); δ 1.35, 1.45 (each s, 3, 3,3-diMe), 1.59, 2.32 (each broad s, 3, =C(Me)$_2$), 2.04 (s, 6, 5,6-diMe), 2.00, 2.12 (each s, 3, 9,10-diMe), 4.84 (broad s, 2, –CH—CH=), 5.65 and 6.39 (each d, 1, J = 10.1 Hz, 1- and 2-H of pyran); δ (C_6D_6) 1.27, 1.29 (each s, 3, 3,3-diMe), 1.49 (broad s, 3, one Me of propenyl side chain), 2.39 (d, $J_{allylic}$ = 1.0 Hz), 1.65 (s, 6, 5,6-diMe), 2.13 (s, 6, 9,10-diMe), 4.9–5.1 (m, 2, –CH—CH=), 5.38 and 6.54 (each d, 1, J = 10.2 Hz, 1- and 2-H of pyran).

Reduction of 18 to the Hydroquinone Diacetate 19b. A solution of **18** (0.011 g) in ether (10 ml) was shaken for 1 min with a solution of sodium dithionite (0.050 g) in water (10 ml). The colorless ether layer was washed with water and saturated aqueous NaCl and dried for 1 hr (the solution becomes red if left too long in the air indicating oxidation back to **18**). After removal of ether the residue was acetylated with pyridine–acetic anhydride and the product was chromatographed on one plate. There were isolated in the usual manner **18** (2 mg) and a colorless oil, R_f 0.43. The latter on recrystallization from hexane afforded white crystals (9.5 mg, 86%) of **3,12-dihydro-3,3,5,6,9,10-hexamethyl-12-(2-methylpropenyl)pyrano[3,2-*a*]xanthene-8,11-diol acetate (19b)**: mp 176–178°; ν_{max}^{KBr} 3000–2850 m, 1760 vs, 1625 w, 1580 w cm^{-1}; *m/e* (%) at 491 (19), 490 (M^+, 59), 476 (31), 475 (100), 433 (22), 391 (37), 389 (17), 349 (17), 189 (36); δ 1.38, 1.42 (s, 3, 3,3-diMe), 1.56 (d, $J_{allylic}$ = 0.5 Hz, 3, side-chain Me), 1.89 (d, $J_{allylic}$ = 1.0 Hz, 3, side-chain Me), 2.00, 2.22 (s, 3, two Ar-Me), 2.11 (s, 6, two ArMe), 2.39, 2.42 (s, 3, COMe), 4.88, 5.06 (each d, 1, AB quartet with J_{AB} = 11.1 Hz, –CH—CH=, broadened by long-range coupling to =C(Me)$_2$), 5.64 and 6.42, (each d, 1, J = 10.0 Hz, 1- and 2-H of pyran); δ (20% C_6D_6 in $CDCl_3$) 1.32, 1.39 (s, 3, 3,3-diMe), 1.54 (d, $J_{allylic}$ = 0.5 Hz, 3, side-chain Me), 1.87 (broad s, 3, side-chain Me), 1.95, 2.07, 2.11, 2.21 (each s, 3, 5,6,9,10-tetra-Me) 2.28, 2.32 (s, 3, COMe), 4.85, 5.04 (each d, 1, AB quartet with J_{AB} = 10 Hz, –CH—CH=, broadened by long-range coupling to =C(Me)$_2$), 5.59 and 6.44 (each d, 1, J = 9.9 Hz, 1- and 2-H of pyran).

Anal. Calcd for $C_{30}H_{34}O_6$: C, 73.47; H, 6.94. Found: C, 73.11; H, 7.07.

Irradiation in Methanol under Nitrogen. PQ-1 (0.050 g) in methanol (30 ml) was irradiated for 3.5 hr. The light brown oily residue obtained after evaporation of the methanol was chromatographed on three plates. The fraction with R_f 0.65–0.75 contained PQ-1 (4 mg) and **2** (0.5 mg, 1%) identical (R_f and uv) with the same material isolated previously. The fraction with R_f 0.25–0.35 gave **10** (4 mg, 9%) identical (mixture melting point, R_f, uv) with **10** previously characterized. The fraction with R_f 0.05–0.20 (detected by spraying the plates with $CeSO_4$ in 2 N H_2SO_4) was eluted and obtained as a colorless oil (0.032 g, 64%) which crystallized from a hexane–chloroform mixture as white crystals of **2-(5-hydroxy-6,7-dimethyl[2,3*H*]benzofuran-2-yl)-2-methoxypropane (4c)**: mp 88.5–89.5°; ν_{max} 3320 s, 1626 w, 1601 w cm^{-1}; *m/e* (%) at 236 (M^+, 14), 189 (9), 164 (9), 163 (6), 73 (100); δ [$(CD_3)_2SO$] 1.08, 1.14 (s, 3, *gem*-diMe), 1.99 (s, 6, ArMe), 3.00 (d, J = 8.8 Hz, 2, $-CH_2-$), 3.16 (s, 3, –OMe), 4.51 (t, J = 8.8 Hz, 1, –CH–), 6.46 (s, 1, ArH), 8.42 (–OH).

Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.19; H, 8.47. Found: C, 70.92; H, 8.24.

Irradiation in Aqueous Acetonitrile under Nitrogen. To a solution of PQ-1 (0.009 g) in acetonitrile (5 ml) was added water (20 ml). The mixture was irradiated for 1 hr and then extracted with ethyl acetate. The combined extracts were washed with water and saturated aqueous NaCl and dried. The material isolated by chromatography on one plate proved to be **10** (10.4 mg, 4%). From a fraction hardly moving from the starting line, a colorless oil (8.2 mg) was obtained. It was acetylated overnight at room temperature and identified as **4b** (9.4 mg). The photoproduct is thus **2-(5-hydroxy-6,7-dimethyl[2,3*H*]benzofuran-2-yl)propan-2-ol (4a)** (7.8 mg, 86%, based on yield of acetate).

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Communications to the Editor

Brønsted Coefficients and ρ Values as Guides to Transition-State Structures in Deprotonation Reactions

Sir:

In order to apply transition-state theory to the correlation of changes in rates of reactions with changes in structures it is necessary to visualize transition-state structural models. One of the most useful guides in this respect is Leffler's approximation, which states that the transition state bears the "greater resemblance to the less stable of the species (reactants or products) of a chemical equilibrium."[1] Other guiding postulates have been proposed which lead to the same general conclusion,[2,3] and it is current practice in organic chemistry to consider that in "uphill" reactions the transition state is product-like and that in "downhill" reactions it is reactant-like.[4] In deprotonations of carbon acids, such as nitroalkanes, ketones, etc., by bases the "crossover" point will come when the attacking base is approximately equal in strength to the anion being formed, *i.e.*, when $\Delta pK = pK_{HA} - pK_{BH^+} = 0$.[4] For "downhill" reactions ΔpK will be negative and for "uphill" reactions ΔpK will be positive. Thus, in the reaction of 1-phenylnitroethane with hydroxide ion, since $\Delta pK = -8.6$, one would expect a reactant-like transition state, and this viewpoint can be supported on several grounds.[5] As we change to progressively weaker bases the transition state should become progressively more product-like. According to the usual interpretation, the Brønsted coefficient might then be expected to increase as ΔpK approaches zero.[6] With $ArCHMeNO_2$ systems the Brønsted α is related to the Hammett ρ by the equation, $\alpha = \rho_{k_1}/\rho_{K_a}$, where ρ_{k_1} refers to the rate of deprotonation

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(2) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

(3) C. G. Swain and E. R. Thornton, *ibid.*, **84**, 817 (1962).

(4) See, for example, R. P. Bell, and D. M. Goodall, *Proc. Roy. Soc., Ser. A*, **294**, 273 (1966).

(5) F. G. Bordwell, W. J. Boyle, Jr., and K. C. Yee, *J. Amer. Chem. Soc.*, **92**, 5926 (1970).

(6) (a) Reference 1b, pp 156–168, 238–242; (b) T. C. Bruice and S. J. Benkovic, "Biorganic Mechanisms," Vol. 1, W. A. Benjamin, New York, N. Y., 1966, pp 37–38; (c) J. O. Edwards, "Inorganic Reaction Mechanisms," W. A. Benjamin, New York, N. Y., 1964, Chapter 3; (d) R. P. Bell and B. G. Cox, *J. Chem. Soc. B*, 194 (1970).