hydrogenation of 5-nitro-2-methylisoquinolinium *p*-toluenesulfonate, *i.e.*, *trans*-9,10-*trans*-5-H-5-amino-2-methyldecahydroisoquinoline (**2b**). A dipicrate of the amine melted at 261.8–263.8°.

*Anal.* Calcd for $C_{22}H_{26}N_8O_{14}$: C, 42.17; H, 4.18; N, 17.89. Found: C, 42.23; H, 4.34; N, 17.90.

**Deamination with Nitrous Acid[10] of *cis*-5,9,10-H-5-Amino-2-methyldecahydroisoquinoline to *cis*-5,9,10-H-5-Hydroxy-2-methyl decahydroisoquinoline.**—To a solution of sodium nitrite (5.0 g) in water (4.0 ml) was added *cis*-5,9,10-H-5-amino-2-methyldecahydroisoquinoline (**1b**, 6.1 g) and acetic acid (8.0 g). The mixture was heated with stirring to 60° and acetic acid (0.87 g) in water (4 ml) was added over a period of 30 min. The mixture was heated with stirring for 13 hr at 55–65°. Then NaOH pellets (5.0 g) were added; the mixture was heated near reflux for 4 hr. More NaOH pellets were added, and the mixture was cooled and extracted with ether in a continuous extractor for 48 hr. The ether solution was dried over $K_2CO_3$ and concentrated to yield 5.5 g of viscous oil. Vapor phase chromatography (column, 20 ft, 30% SE-30 on Chromosorb W) of the crude oily product prior to distillation showed 2% olefins, 92% *cis*-5,9,10-H-5-hydroxy-2-methyldecahydroisoquinoline (**1a**), and 6% unidentified product. This oil crystallized on standing and was distilled to yield *cis*-5,9,10-H-5-hydroxy-2-methyldecahydroisoquinoline (**1a**, 4.4 g), mp 94–95°. Examination of the ir and nmr spectra of this alcohol showed them to be consistent with the proposed structure. An nmr ($CDCl_3$) peak appeared at 3.75 ppm (half-band width of 15 cps), >CH–OH.

**Deamination with Nitrous Acid[10] of *trans*-9,10-*trans*-5-H-5-Amino-2-methyldecahydroisoquinoline to *trans*-9,10-*trans*-5-H-5-Hydroxy-2-methyldecahydroisoquinoline.**—*trans*-9,10-*trans*-5-H-5-Amino-2-methyldecahydroisoquinoline (**2b**, 6 g) was deaminated in a procedure identical with that described above for the *cis* isomer. A viscous oil (5.8 g) was recovered from the continuous ether extraction and was shown by vapor phase chromatography to contain 87% *trans*-9,10-*trans*-5-H-5-hydroxy-2-methyldecahydroisoquinoline (**2a**), 7% olefins, and 6% unidentified product. Distillation of this material yielded 4.7 g of **2a**, bp 120–124° (0.3 mm). The ir and nmr spectra of this alcohol were consistent with the proposed structure. An nmr ($CDCl_3$) peak appeared at 3.75 ppm (half-band width of 16 cps), >CH–OH.

It was found that seeding of the above oil with a crystal of *trans*-9,10-*cis*-5-H-5-hydroxy-2-methyldecahydroisoquinoline[11] caused crystallization of 90 mg (2%) of this isomer, mp 131–132°. An nmr ($CDCl_3$) peak appeared at 3.8 ppm (half-band width of 6 cps), >CH–OH.

**Registry No.**—**1b**, 16336-19-9; dipicrate of **1b**, 16336-20-2; **1c**, 16336-21-3; **2b**, 16336-22-4; dipicrate of **2b**, 16336-23-5; **2c**, 16336-24-6.

**Acknowledgment.**—The authors are indebted to Marion Laboratories, Inc., Kansas City, Mo., for their financial assistance in the support of this project and also to Drs. F. C. Chang and J. G. Beasley for useful discussions during the course of this work and to Mrs. M. Petrie for recording the nmr spectra.

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[10] W. Hückel and M. Hanack, *Angew. Chem. Intern. Ed. Engl.*, **6**, 534 (1967).

[11] Prepared from 5-hydroxy-2-methylisoquinolinium *p*-toluenesulfonate and isolated by the chromatographic procedure of Kimoto and Okamoto.[2]

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# Photoreactions. V. Mechanism of the Photorearrangement of Alkyl-*p*-benzoquinones[1]

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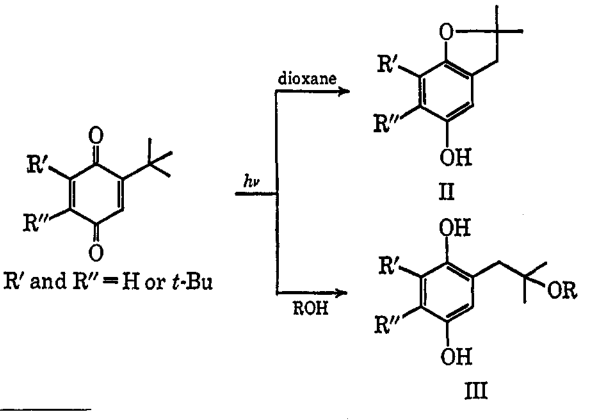
*Kay-Fries Chemicals, Inc., West Haverstraw, New York 10993, and the*
*Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey 07030*

*Received November 2, 1967*

Photolysis of *p*-benzoquinones with various side chains have been studied in alcoholic solution. The identical ether was obtained by the photorearrangement of *t*-butyl- and isobutyl-*p*-benzoquinone. The rearranged side chain was the same from *n*-propyl- and isopropyl-substituted *p*-benzoquinones. Since light of wavelength longer than 400 mμ is capable of initiating the photolysis, it is assumed that the n → π* transition of the quinone system is involved. A spirocyclopropyl intermediate has been postulated to account for the observations on the photorearrangement of the side chain.

Previous investigations[1] in our laboratories have uncovered the photorearrangement of the side chain of mono- and di-*t*-butyl-*p*-benzoquinones (I) in various solvents. In nonalcoholic media, the *t*-butyl group undergoes rearrangement to generate the 2,2-dimethyl-5-hydroxycoumaran system (II), while in alcoholic solvents an analogous rearrangement leads to the formation of the 2-alkoxy-2-methyl-1-propyl side chain (III). We have now examined the effect of the side chain on the course of the photorearrangement and attempted to formulate a mechanism to account for the observations.



## Results

The photolysis of dilute solutions of various alkyl-substituted *p*-benzoquinones (IV) was carried out under a sun lamp. For completeness of sequence, the following side chains were studied: methyl, ethyl, isopropyl, *n*-propyl, and isobutyl. The reaction mixtures were treated with alkaline dimethyl sulfate to convert the phenolic components into methyl ethers which were easily separated by gas chromatography. In general, spectral data (nmr, mass, ir, uv) were ade-

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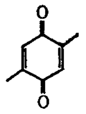
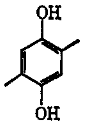
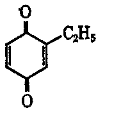
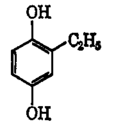
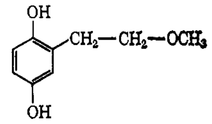
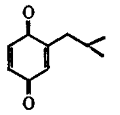
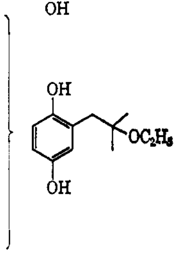
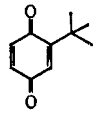
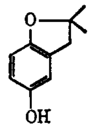
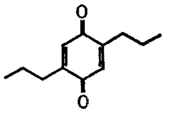
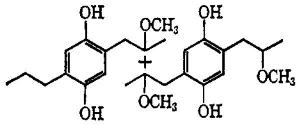
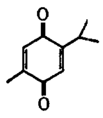
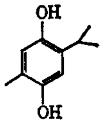
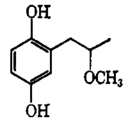
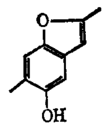
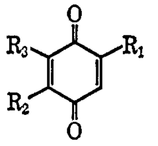
[1] For part IV, see C. M. Orlando, H. Mark, A. K. Bose, and M. S. Manhas, *J. Amer. Chem. Soc.*, **89**, 6527 (1967).

[2] (a) Kay-Fries Chemicals, Inc.; (b) General Electric Research and Development Center, Schenectady, N. Y. 12301; (c) Stevens Institute of Technology.

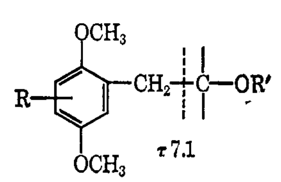
TABLE I

| Quinone | Alcohol | Hydroquinone | Ether | Benzofuran derivative |
|---|---|---|---|---|
|  | $C_2H_5OH$ |  | | |
|  | $CH_3OH$ |  |  | |
|  | $C_2H_5OH$ | |  | |
|  | $C_2H_5OH$ | | |  |
|  | $CH_3OH$ | |  | |
|  | $CH_3OH$ |  |  |  |

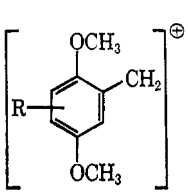


IVa, $R_1 = R_2 = CH_3$; $R_3 = H$
b, $R_1 = C_2H_5$; $R_2 = R_3 = H$
c, $R_1 = i\text{-}C_4H_9$; $R_2 = R_3 = H$
d, $R_1 = t\text{-}C_4H_9$; $R_2 = R_3 = H$
e, $R_1 = R_2 = n\text{-}C_3H_7$; $R_3 = H$
f, $R_1 = i\text{-}C_3H_7$; $R_2 = CH_3$; $R_3 = H$

quate for deducing the structure of the products. Advantage was taken of the earlier observation[1,3] that the benzylic methylene protons in a hydroquinone derivative of type V resonate at about $\tau$ 7.1 and the major mode of fragmentation of V under electron impact leads to the ion VI. The phenolic products



V



VI

from the photolysis of substituted quinones are listed in Table I. No information was collected at this stage on the nonphenolic products.

All the photolyses in this and the previous[1] study were carried out in Pyrex vessels using either a 275-W G.E. sun lamp or sunlight. Therefore, in these experiments light of wavelength greater than 295 mμ was responsible for the phototransformations. In one experiment a filter[4] was employed to eliminate wavelengths lower than 400 mμ while irradiating an ethanol solution of 2,6-di-*t*-butyl-*p*-benzoquinone (I, R′ = *t*-Bu; R″ = H). Even under these conditions the usual photorearrangement product III (R′ = *t*-Bu; R″ = H; R = $C_2H_5$) was obtained.

## Discussion

The ultraviolet spectra of benzoquinone and alkyl-*p*-benzoquinones[5] possess four distinct absorption regions: $\lambda_{max}$, mμ ($\epsilon$), 540 (0.2), 400–500 (20–30), 300 (320), 250 (20,000). The higher intensity absorptions at 300 and 250 mμ have been ascribed to $\pi \rightarrow \pi^*$ transitions.[5b] Further analyses of the weak absorptions at 400–500 and 540 mμ have established them as $n \rightarrow \pi^*$ transitions.[5a,6] The former transition has been attributed to a $n \rightarrow \pi^*$ singlet[5b,7] and the latter to an $n \rightarrow \pi^*$ triplet.[5-7] The ultraviolet spectra of all the alkyl-*p*-benzoquinones employed in our study displayed the characteristic *p*-benzoquinone absorptions as discussed above (see Experimental Section).

Since photorearrangement was observed using wavelengths longer than 400 mμ, the $n \rightarrow \pi^*$ excitation of the quinone system appears to be involved. We have not established whether the singlet state is formed initially; however, it has been reported[8] that, for quinones, the singlet–triplet intersystem crossing is relatively frequent. If $n \rightarrow \pi^*$ carbonyl excitation is the

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[3] C. M. Orlando, Jr., H. Mark, A. K. Bose, and M. S. Manhas, *Chem. Commun.*, 714 (1966).

[4] The filter solution employed was an aqueous sodium hydrogen phthalate–sodium nitrite solution which did not transmit light below 400 mμ. Information describing the preparation of this filter solution was kindly supplied by Professor A. Gilbert of the University of Reading, U. K.

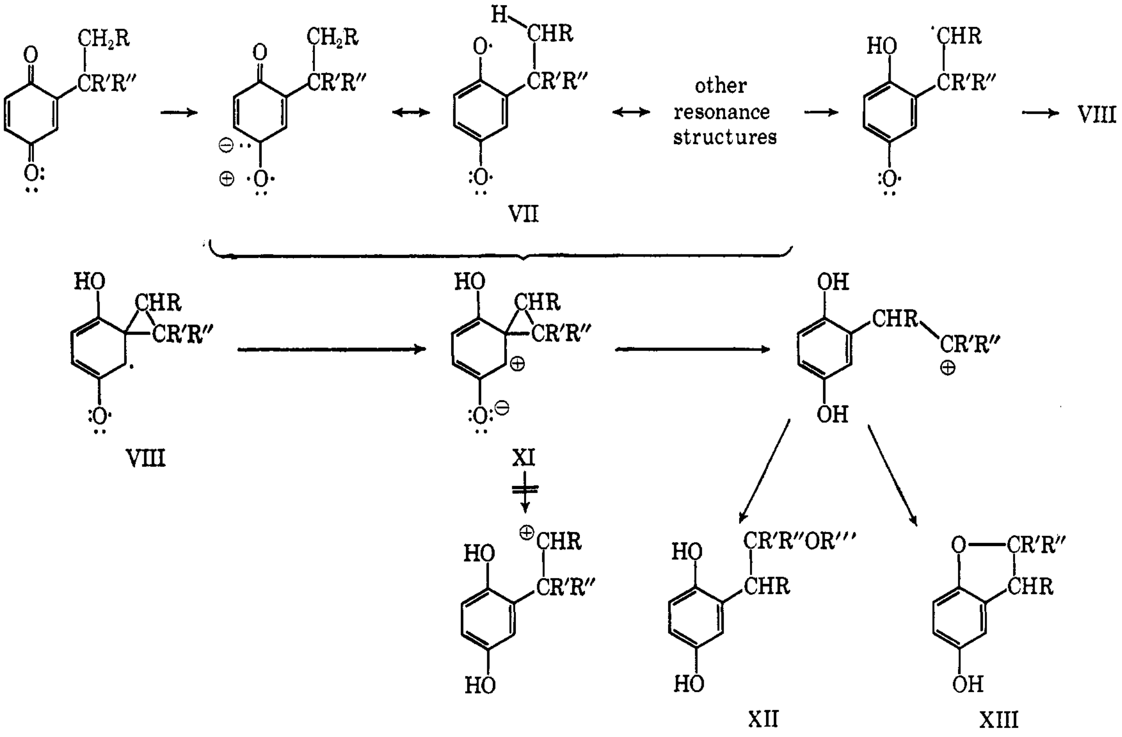
[5] (a) A. Kuboyama, *Bull. Chem. Soc. Jap.*, **35**, 295 (1962); (b) J. W. Sidman, *J. Amer. Chem. Soc.*, **78**, 2363 (1956).

[6] H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

[7] J. A. Barltrop and B. Hesp, *J. Chem. Soc.*, 5182 (1965).

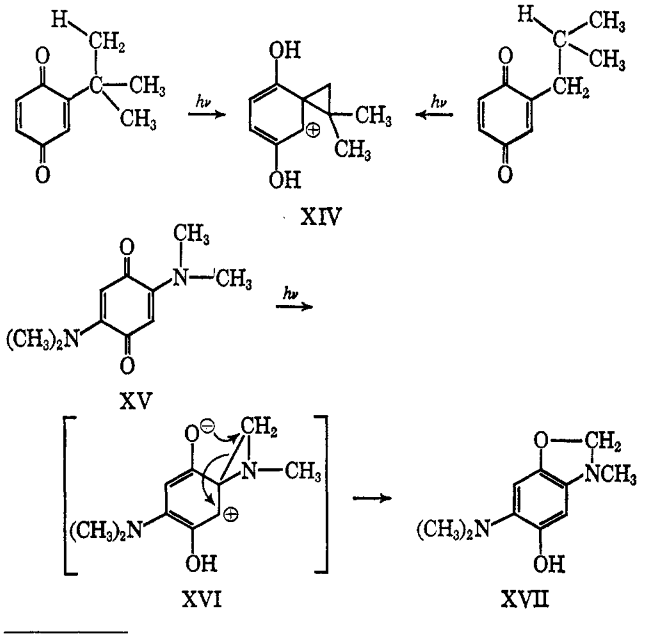
[8] J. W. Sidman, *Chem. Rev.*, **58**, 689 (1958).

CHART I



first step in the photolysis of quinones, some of the subsequent steps should be analogous to those postulated by Zimmerman and Schuster[9] for dienone photochemistry. The presence of a suitable 2-alkyl group could easily lead to intramolecular hydrogen abstraction. An examination of Table I reveals that a six-membered transition state appears to be essential for such hydrogen abstraction. For example, in thymoquinone the methyl group is unaffected while the isopropyl group participates in hydrogen abstraction.

The intramolecular hydrogen abstraction leads to the diradical VII and its resonance forms (see Chart I). All the data in Table I can be rationalized by postulating that a spirocyclopropyl intermediate[10] VIII is formed at this stage. Electron demotion would then afford an ionic intermediate XI which would have a strong tendency for aromatization. Interaction of the spirocyclopropyl group with an alcohol would cleave the three-membered ring and bond isomerization will eventually yield a rearranged hydroquinone (XII). Alternatively, one of the cyclopropyl bonds could also be ruptured by intramolecular interaction with the adjacent oxygen and lead to a coumaran (XIII). Of the two alternative modes of cleavage of the spirocyclopropyl group, the one leading to the more substituted ether will be favored because this involves the formation of more stable tertiary carbonium ion as the intermediate. This postulate fully accounts for the same photoproduct from isobutyl-$p$-benzoquinone (IVc) and $t$-butyl-$p$-benzoquinone (I, $R' = R'' = H$) as the same cyclopropyl intermediate (XIV) would be involved in both cases. This postulate also explains why there is no rearrangement of the side chain when $n$-propyl-$p$-benzoquinone is photolyzed. The lack of rearrangement[13] of the side chain during the photolysis of XV can be explained by invoking the formation of a spiroaziridine intermediate, XVI, which undergoes selective cleavage (${}^{\oplus}CH_2\text{–}N\text{–}$ favored over $CH_3N^{\oplus}\text{–}CH_2\text{–}$) leading to the formation of XVII.



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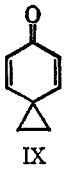
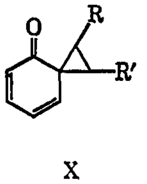
[9] H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **83**, 4486 (1961), and other papers in this series.

[10] The analogous compound, spiro[2.5]octa-2,5-dien-1-one (IX), has been synthesized.[11] Evidence has been presented[12] for the intermediacy of the isomeric spiro compound X in the abnormal Claisen rearrangement.



IX



X

[11] R. Baird and S. Winstein, *J. Amer. Chem. Soc.*, **85**, 567 (1963); **79**, 4238 (1957).

[12] E. N. Marvell and B. Schatz, *Tetrahedron Lett.*, 67 (1967).

[13] D. W. Cameron and R. G. F. Giles, *Chem. Commun.*, 573 (1965).

It is desirable to have more direct evidence for the spirocyclopropyl intermediate postulated above. Work is in progress for gathering further information on this type of photorearrangement.

## Experimental Section

Infrared, nmr, and mass spectra were recorded on a Perkin-Elmer Model 21 spectrometer, a Varian A-60A spectrometer and a C.E.C. 21-103 mass spectrometer, respectively. Ultraviolet absorption spectra were determined in methanol using a Cary Model 14 spectrophotometer. Gas chromatographic analyses were carried out on an F & M Model 500 vapor fractometer with a 2-ft silicone rubber column (10% on Chromosorb W). Melting points were determined on a Thomas–Hoover capillary melting point apparatus and were corrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Photolyses were carried out in water-cooled Pyrex reactors equipped with magnetic stirring. Sunlight or a G.E. 275-W sun lamp were used as light sources. For nmr signals the following data are reported in sequence: chemical shift of the center of the signal, the multiplicity (s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet) of the signal, the area under the peaks, and coupling constant (*J*). The ultraviolet absorption data were recorded in methyl alcohol unless otherwise stated and are reported in the form $\lambda_{max}$, m$\mu$ ($\epsilon$).

**Materials.**—Thymoquinone [mp 43–45°; $\lambda_{max}$ 253 (18,687), 260 sh (17,187), 312 (287), 428 (27)] and 2,5-dimethyl *p*-benzoquinone [mp 124–125°; $\lambda_{max}$ 253 (15,789), 260 sh (14,474), 313 (244), 425 (24.2)] were obtained from City Chemical Corp., New York, N. Y. Ethyl-*p*-benzoquinone [mp 34–37°, lit.[14] mp 38.5–39.5°; $\lambda_{max}$ 246 (13,953), 308 (531), 425 (50.6), 447 (50.9)] and isobutyl-*p*-benzoquinone [mp 35–36°;[15] $\lambda_{max}$ 248 (16,235), 313 (692), 425 (65.9), 447 (82.3)] were prepared by silver oxide oxidation of the corresponding ethyl-[16a] and isobutylhydroquinone.[16b]

**Preparation of 2,5-Di-*n*-propyl-*p*-benzoquinone (IVe).**—2,5-Diallyl-*p*-benzoquinone[17] was catalytically hydrogenated (5% Pd–C) to 2,5-di-*n*-propylhydroquinone (mp 150–152°). A solution of 2,5-di-*n*-propylhydroquinone (3.0 g, 0.015 mol) in 100 ml of ether was stirred for 4 hr at 25° with silver oxide (10 g, 0.043 mol). The solid was filtered and the filtrate evaporated to an orange liquid, 2.2 g (76%), which was the title compound: $\lambda_{max}$ 255 (18,367), 315 (363), 431 (39).

*Anal.* Calcd. for $C_{12}H_{16}O_2$: C, 75.00; H, 8.33. Found: C, 75.80; H, 8.3.

**Preparation of the Filter Solution.**[4]—A saturated solution (250 ml) of sodium nitrite in distilled water was added to a solution of 5 g of sodium hydrogen phthalate in 1 l. of distilled water with uniform stirring. This solution was brought to pH 12 by dilute sodium hydroxide and then used as a filter for all light below 400 m$\mu$.

**Photolysis of 2,5-Dimethyl-*p*-benzoquinone (IVa) in Ethanol.**—A solution of 2.0 g (0.015 mol) of 2,5-dimethyl-*p*-benzoquinone in 200 ml of absolute ethanol was irradiated for 49 hr with a 275-W G.E. sun lamp. Evaporation of the solvent gave a solid which upon crystallization from ethyl acetate–benzene gave 0.56 g (29%) of 2,5-dimethylhydroquinone, mp 212–217°.

**Photolysis of Ethyl-*p*-benzoquinone (IVb) in Methanol.**—A solution of 1.6 g of IVb in 160 ml of methanol was irradiated 19 hr at 25° with a 275-W G.E. sun lamp. After solvent evaporation 2.08 g of an oil was isolated. This reaction product was methylated with 3.15 g of dimethyl sulfate in 10 ml of water containing 1 g of sodium hydroxide for 1 hr at 25°. Extraction of this reaction mixture with ether provided 2.32 g of product. Vacuum distillation of this liquid at 140° (0.1 mm) gave 0.683 g of a yellow distillate. Gas chromatographic separation of the distillate on a silicone rubber column at 150° gave two products: (1) **ethylhydroquinone dimethyl ether** [0.549 g (30%); mass spectrum, molecular ion *m/e* 166 (M, calcd for $C_{10}H_{14}O_2$); uv $\lambda_{max}^{THF}$ 290 m$\mu$ ($\epsilon$ 3520); nmr ($CDCl_3$) $\tau$ 8.8 (t, 3 H), 7.4 (q, 2 H), 6.27 (s, 3 H), 3.27 (m, 3 H)] and (2) **$\beta$-methoxyethylhydroquinone dimethyl ether** [6.134 g (6.2%); mass spectrum, molecular ion *m/e* 196 (M, calcd for $C_{11}H_{16}O_3$); $\lambda_{max}^{THF}$ 291 m$\mu$ ($\epsilon$ 3100); nmr ($CDCl_3$) $\tau$ 7.12 (t, 2 H), 6.67 (s, 3 H), 6.41 (t, 2 H), 6.25 (s, 3 H), 3.25 (s, 3 H)].

**Photolysis of Isobutyl-*p*-benzoquinone (IVc) in Ethanol.**—A solution of 1.0 g of isobutyl-*p*-benzoquinone in 100 ml of absolute ethanol was irradiated with a 275-W G.E. sun lamp for 25 hr. The solvent was evaporated to 1.14 g of dark brown oil. Trituration of this oil with hexane gave 0.293 g (23%) of 2-ethoxy-2-methyl-*n*-propylhydroquinone, mp 142–145°, identical with the product isolated from the irradiation of *t*-butyl-*p*-benzoquinone in ethanol.

**Photolysis of 2,5-Di-*n*-propyl-*p*-benzoquinone (IVe) in Methanol.**—A solution of 1 g of 2,5-di-*n*-propyl-*p*-benzoquinone in 100 ml of methanol was irradiated with a G.E. sunlamp for 75 hr. Evaporation of the solvent gave 1 g of an oil. Methylation of this oil with 1.26 g of dimethyl sulfate and 0.5 g of sodium hydroxide in 10 ml of water gave 0.226 g of distilled product. Gas chromatographic separation of this reaction product on a 2-ft silicone rubber column (10% on Chromosorb W) at 160° gave three products: (1) **dimethyl-2-(2-methoxy-1-propyl)-5-*n*-propylhydroquinone** [0.105 g (8.0%); nmr ($CDCl_3$) $\tau$ 8.75 (m), 8.20 (m), 7.20 (m), 6.55 (s), 6.05 (s), 3.15 (broad s)], (2) **dimethyl-bis-2,5-(2-methoxy-1-propyl)hydroquinone** [0.045 g (3.0%); nmr ($CDCl_3$) $\tau$ 8.88 (d, 6 H), 7.30 (m, 4 H), 6.50 (s, 6 H), 5.50 (m, 2 H), 6.22 (s, 6 H), 3.35 (s, 2 H)], and (3) **methyl-2-(2-methoxy-1-propyl)-5-*n*-propylhydroquinone** [0.045 g (3.6%); nmr ($CDCl_3$) $\tau$ 9.00 (m), 7.4 (m), 6.65 (s), 6.25 (s), 3.55 (s), 3.32 (s), 2.15 (s)].

**Photolysis of Thymoquinone (IVf) in Methanol. A. Gas Chromatographic Product Isolation.**—A solution of 11.5 g of thymoquinone in 1150 ml of anhydrous methanol was irradiated in sunlight for 12 days.[18] Evaporation of the solvent provided 14.7 g of a crude oil. A suspension of 14.7 g of this oil in 100 ml of water containing 23.2 g of dimethyl sulfate and 7.4 g of sodium hydroxide was stirred at room temperature for 24 hr. The reaction mixture was extracted with 150 ml of ethyl acetate, and the extract was dried over anhydrous magnesium sulfate after washing with water to neutrality. Removal of the solvent and vacuum distillation of the product afforded 7.4 g of distillate. Gas chromatographic separation of this distillate on a 2-ft silicone rubber column at 150° gave four components: (1) **dimethyl-2-(2-methoxy-1-propyl)-5-methylhydroquinone** [3.83 g (20%); mass spectrum, molecular ion *m/e* 224 (M, calcd for $C_{13}H_{20}O_3$), base peak, *m/e* 165 $[M - CH(OCH_3)CH_3]^{\oplus}$; nmr ($CDCl_3$) $\tau$ 8.91 (d, 3 H), 7.88 (s, 3 H), 7.38 (m, 2 H), 6.78 (s, 3 H), 6.52 (m, 1 H), 6.35 (s, 6 H), 3.55 (s, 2 H)], (2) **methyl-2-(2-methoxy-1-propyl)-5-methylhydroquinone** [0.154 g (10%); mass spectrum, molecular ion *m/e* 209 (M, calcd for $C_{12}H_{18}O_3$); nmr pattern similar to that for other derivatives in this series], (3) **2,6-dimethyl-5-methoxybenzofuran** [1.58 g (13%); mass spectrum, molecular ion *m/e* 176 (M, calcd for $C_{11}H_{12}O_2$); nmr[19] ($CDCl_3$) $\tau$ 7.70 (s, 3 H), 7.55 (s, 3 H), 6.18 (s, 3 H), 3.75 (s, 1 H), 2.85, s.14 (d, 2 H)], and (4) **dimethylthymohydroquinone** [2.01 g (15%), identical with an authentic sample].

**B. Column Chromatographic Product Isolation.**—A solution of 4.0 g of thymoquinone in 400 ml of methanol was irradiated for 53 hr with a 275-W G.E. sun lamp. Evaporation of the solvent gave an oil (5.5 g) which upon chromatography on 150 g of silica gel (100–200 mesh) gave three products (eluted with 1:1 carbon tetrachloride–chloroform): (1) **2-(2-methoxy-1-propyl)-5-methylhydroquinone** [0.36 g (7.8%); mp 97.9–98.3° (hexane–benzene); $\lambda_{max}$ 294 m$\mu$ ($\epsilon$ 4500); nmr ($CD_3COCD_3$) $\tau$ 8.90 (d, 3 H), 7.85 (s, 3 H), 7.35 (m, 2 H), 6.67 (s, 3 H), 6.35 (m, 1 H), 3.67 (s, 2 H) (*Anal.* Calcd for $C_{11}H_{16}O_3$: C, 67.34; H, 8.16. Found: C, 67.38; H, 8.02)], (2) **2,6-dimethyl-5-hydroxybenzofuran** [0.091 g (2.1%); mp 98–99.6° (hexane); $\lambda_{max}^{THF}$ 250 m$\mu$ ($\epsilon$ 10,634), 257 sh (8730), 297 (5238), 305 (4603); nmr ($CD_3COCD_3$) $\tau$ 7.75 (s, 3 H), 7.65 (s, 3 H), 3.75 (s, 1 H), 3.15 (s, 1 H), 2.90 (s, 1 H), 2.2 (s, 1 H) (*Anal.* Calcd for $C_{10}H_{10}O_2$: C, 74.02; H, 6.17. Found: C, 74.20; H, 5.80)], and (3) **thymohydroquinone** [0.096 g (2.4%); mp 141–144° (hexane–benzene); lit.[20] mp 142–142.5°; $\lambda_{max}$ 293 m$\mu$ ($\epsilon$ 4357)].

**Photolysis of 2,6-Di-*t*-butyl-*p*-benzoquinone in Ethanol Using**

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(14) R. K. Ladisch, *Chem. Abstr.*, **52**, 20061*d* (1958); U. S. Patent 2,840,-571.

(15) M. F. Hawthorne and M. Reintjes, *J. Amer. Chem. Soc.*, **86**, 951 (1964).

(16) (a) Prepared according to the method described by T. B. Johnson and W. W. Hodge, *ibid.*, **35**, 1014 (1913); (b) Prepared by the catalytic reduction of $\beta$-methallylhydroquinone.

(17) L. F. Fieser, W. P. Campbell, and E. M. Fry, *ibid.*, **61**, 2206 (1939).

(18) Comparable results were obtained when a 1% solution of thymoquinone in methanol was irradiated with a 275-W G.E. sun lamp for 53 hr.

(19) For the chemical shifts of protons in the furan ring system, see A. R. Katritzky, "Physical Method of Heterocyclic Chemistry," Vol. II, Academic Press Inc., New York, N. Y., 1963, p 124.

(20) E. Zavarin and A. B. Anderson, *J. Org. Chem.*, **20**, 82 (1955).

**Sodium Nitrite–Sodium Hydrogen Phthalate Filter Solution.**—A solution of 1 g of 2,6-di-*t*-butyl-*p*-benzoquinone in 100 ml of ethanol was irradiated through a sodium nitrite–sodium hydrogen phthalate filter solution (λ >400 mμ) for 48 hr with a 275-W G.E. sun lamp. Evaporation of the solvent gave an orange oil which when triturated with hexane afforded a solid. This solid upon recrystallization from benzene–hexane gave 2-(2-ethoxy-2-methyl-1-propyl)-6-*t*-butylhydroquinone,[1] 0.277 g (23%), mp 125–127°.

**Registry No.**—IVa, 137-18-8; IVb, 4754-26-1; ethylhydroquinone dimethyl ether, 1199-08-2; β-methoxyhydroquinone dimethyl ether, 16162-59-7; IVc, 4197-79-9; IVe, 16162-61-1; dimethyl-2-(2-methoxy-1-propyl)-5-*n*-propylhydroquinone, 16162-62-2; dimethylbis-2,5-(2-methoxy-1-propylhydroquinone, 16203-63-7; IVf, 490-91-5; dimethyl-2-(2-methoxy-1-propyl)-5-methylhydroquinone, 14753-10-7; 2,6-dimethyl-5-methoxybenzofuran, 14753-09-4; 2-(2-methoxy-1-propyl)5-methylhydroquinone, 16162-65-5; 2,6-dimethyl-5-hydroxybenzofuran, 16162-66-6; 2,6-di-*t*-butyl-*p*-benzoquinone, 719-22-2.

# *Notes*

## The Cuprous Chloride–Amine Catalyzed Oxidation of 2,6-Di-*t*-butyl-*p*-cresol with Oxygen

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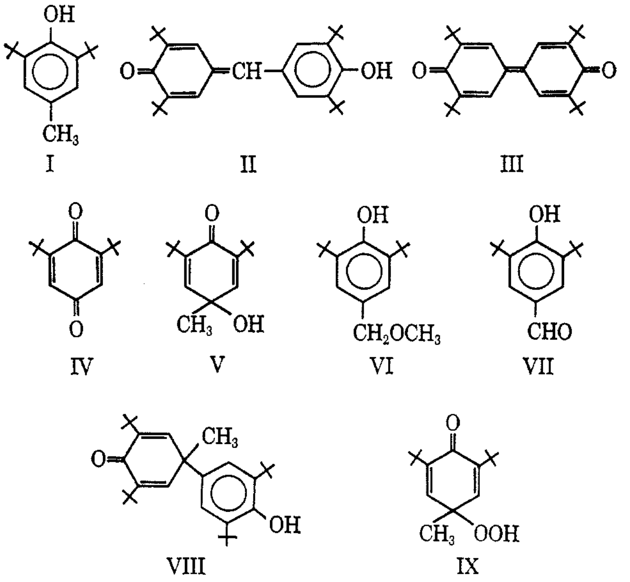
Recently, the air oxidation of 2,6-di-*t*-butyl-*p*-cresol (I) in alkaline ethanol was reported to give the demethylated dimers 2,6-di-*t*-butyl-4-(4-hydroxy-3,5-di-*t*-butylbenzylidene)-2,5-cyclohexadien-1-one (II) and 3,5,3′,5′-tetra-*t*-butyldiphenoquinone (III) (Chart I).[1] We now describe the formation of III and a different demethylated dimer, 2,6-di-*t*-butyl-4-methyl-4-(3,5-di-*t*-butyl-4-hydroxyphenyl)-2,5-cyclohexadien-1-one (VIII), among six identifiable products in the cuprous chloride–amine catalyzed reaction of I with oxygen.[2a] Based upon the earlier work of Kharasch and Joshi[2b] and the data obtained in the present investigation, a reasonable mechanism has been proposed to account for the over-all oxidation reaction.

The oxygenation of I in methanol solution using a cuprous chloride–amine catalyst gave six identifiable products which constituted 73% (weight) of the total reaction mixture. These products were (1) 3,5,3′,5′-tetra-*t*-butyldiphenoquinone (III, 5%); (2) 2,6-di-*t*-butyl-*p*-benzoquinone (IV, 27%); (3) 2,6-di-*t*-butyl-4-methyl-4-hydroxy-2,5-cyclohexadien-1-one (V, 14%); (4) 3,5-di-*t*-butyl-4-hydroxybenzylmethyl ether (VI, 14%); (5) 3,5-di-*t*-butyl-4-hydroxybenzaldehyde (VII, 12%); (6) 2,6-di-*t*-butyl-4-methyl-4-(3,5-di-*t*-butyl-4-hydroxyphenyl)-2,5-cyclohexadien-1-one (VIII, 2%) (see Chart I). All of these compounds have been previously described as low-yield oxidation products of I under varied conditions.[1,3] The hydroperoxide IX which was isolated in the reaction of I with oxygen in ethanolic potassium hydroxide was observed to decompose to V (45%) and an unknown compound, mp 159–160° (20%).[2] This latter compound was identical with the product VIII (mp 154–156°) isolated from the oxygenation described herein, based upon the identity of the infrared, ultraviolet, and nmr spectra.

CHART I



I II III IV V VI VII VIII IX

Conclusive evidence for the structural assignment VIII to the compound, mp 154–156°, was provided by several spectroscopic methods. The dimeric structure of VIII was evident on the basis of molecular weight determination [Calcd for $C_{29}H_{44}O_2$: mol wt, 424. Found: mol wt, 424 (mass spectrometry)]. The infrared spectrum possessed both a nonbonded hydroxyl absorption at 3640 cm$^{-1}$ and a cross-conjugated dienone absorption at 1660 and 1640 cm$^{-1}$. The ultraviolet spectrum had absorption maxima at 237 mμ (ε 21,188) and 274 (2510) and is consistent

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[1] C. H. Brieskorn and K. Ullmann, *Chem. Ber.*, **100**, 618 (1967).

[2] (a) For a recent review of the cuprous chloride–amine–oxygen system in phenol oxidation see, A. S. Hay, *Adv. Polymer Sci.*, **4**, 496 (1967); (b) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1439 (1957).

[3] (a) L. V. Gorbunova, N. S. Vasileiskaya, M. L. Khidekel, and B. A. Razuvaev, *J. Org. Chem. USSR*, **2**, No. 7, 1227 (1967); (b) J. I. Wasson and W. M. Smith, *Ind. Eng. Chem.*, **45**, 197 (1953); (c) S. J. Metro, *J. Amer. Chem. Soc.*, **77**, 2901 (1955); (d) E. Muller, A. Rieker, K. Ley, R. Mayer, and K. Scheffler, *Ber.*, **92**, 2278 (1959); (e) J. Sugita, *Nippon Kagaku Zasshi*, **87**, 1082 (1966) [*Chem. Abstr.*, **66**, 9477*w* (1967)].