Photoreactions. IV.[1] Photolysis of *t*-Butyl-Substituted *p*-Benzoquinones

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Abstract: Photolysis of 2-*t*-butyl-, 2,5-di-*t*-butyl-, and 2,6-di-*t*-butyl-*p*-benzoquinone has been studied in a variety of solvents. Besides reduction to the corresponding hydroquinone, rearrangement of the side chain was found to occur leading to an ether and a coumaran.

The photochemical reactions of a variety of carbonyl compounds have been studied extensively,[3] but the *p*-benzoquinone system has received only limited attention. Early investigations on the photolysis of *p*-benzoquinone established their reduction to hydroquinone in alcoholic solvents[4] and reductive acylation to acylhydroquinones and hydroquinone monoesters in aldehyde solvents.[5] More recently several investigators have reexamined the quinone–aldehyde systems.[6]

In the past several years, various substituted *p*-benzoquinones have been shown to undergo photodimerization to cyclobutanes[7] and to "cage dimers."[7a] Photocycloadditions of olefins and dienes to the carbonyl group of the quinone have been found to lead to spirooxetanes[8] and spiropyrans,[9] respectively. The photoaddition of diphenylacetylene to *p*-benzoquinone has been reported.[10] Photocyclizations have been observed very recently with dialkylamino-*p*-benzoquinones[11] and alkenyl-*p*-benzoquinones.[12]

In the course of our investigation of the photolysis of substituted *p*-benzoquinones in different solvents, we have discovered instances of photorearrangement of the side chain. Brief reports of some of our findings were published earlier.[13] We present here some further observations and details of our studies on *t*-butyl-substituted *p*-benzoquinones.

Photolysis of 2-*t*-Butyl-*p*-benzoquinone (I)

Irradiation of a dilute solution of this quinone in absolute ethanol produced in 52% yield a colorless product (II) which corresponds to a 1:1 addition of the quinone and ethanol. The infrared spectrum of II showed hydroxy absorption, and the nmr spectrum indicated the presence of three aromatic protons, an ethoxy group [quartet (2 H) at τ 6.48 and triplet (3 H) at τ 8.82], two methyl groups (τ 8.76), and a methylene group (τ 7.08). Obviously, the ethoxy group was on the side chain and the *t*-butyl group had been modified. The chemical shift of the methylene group (τ 7.08) is inconsistent with the structure IIb in which the two methylene groups linked to the ether oxygen should have essentially the same chemical shift (*ca.* τ 6.5). Therefore, it was postulated that the side chain had undergone photorearrangement, and the product had the structure IIa. Photolysis of I in acetic acid followed by column chromatography afforded in about 1% yield a phenolic product III isomeric with the starting *t*-butylquinone. The same substance was obtained in good yield on warming for a few minutes an ethanolic solution of II with hydriodic acid.

The nmr spectrum of III is fully in accord with the coumaran structure IIIa but not with IIIb. Unequivocal evidence for the correctness of structure IIIa was obtained by the synthesis of the same compound by the reaction of 2-(β-methallyl)hydroquinone (IV) with hydriodic acid. The interrelationship of I, II, III, and IV is shown in Chart I.

Photolysis of 2,6-Di-*t*-butyl-*p*-benzoquinone (VI)

The irradiation with a sun lamp of a 5% solution of VI in ethanol produced a mixture of at least five components, three of which were identified as the 1:1 addition product VII (42.5%), the coumaran VIII isomeric with VI (9.5%), and 2,6-di-*t*-butylhydroquinone (IX) (20.5%). When sunlight was used for irradiation, at least seven products were formed including VII (80.5%), VIII (4.5%), and IX (9.0%).

The hydroquinone VII was converted into VIII in nearly quantitative yield on treatment with hot hydriodic acid. Spectroscopic evidence in favor of the structure VII for the 1:1 addition product of the quinone VI and ethanol has been discussed previously.[13a] The coumaran structure VIII is also supported by nmr data.[13b] The similarity between the nmr spectra of II and VII and of III and VIII is further evidence for the photorearrangement of the *t*-butyl side chain when VI is irradiated.

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[2] (a) Kay-Fries Chemicals, Inc. (b) Stevens Institute of Technology.

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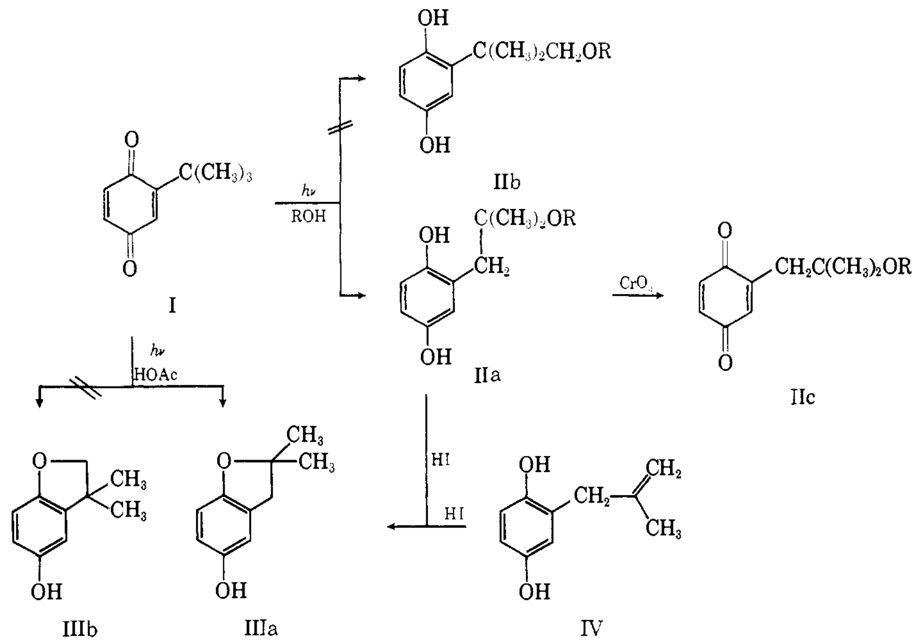
Chart I



In the hydroquinone VII, the hydroxy group flanked by two large *ortho* substituents can be expected to be sterically hindered. As a consequence, the nmr spectrum of VII clearly distinguishes between the two hydroxy groups: one produces a very broad signal characteristic of rapid proton exchange, and the other displays a very sharp peak; when shaken with D_2O, the rate of disappearance of the broad peak is much faster than that of the sharp peak. Acetylation of VII with acetic anhydride and pyridine produced only one monoacetate X; no diacetate appeared to be formed. The nmr spectrum of X also showed a sharp peak for the hydroxy group which disappeared very slowly on shaking with D_2O. The oxidation of VII to quinone XI could be carried out without difficulty. Long-range coupling ($J = <1$ cps) between one of the ring protons and the methylene group in the side chain in X was established by a double-resonance experiment.[13a]

The photolysis of VI was studied in a variety of solvents; the results are summarized in Tables I and II. It is seen that the yield of the 1:1 adduct VII gets progressively smaller as the size of the primary alcohol increases (Table I). The yield of VII is small when the alcohol component is a secondary alcohol; it is almost negligible when a tertiary alcohol is used. The nmr spectrum of the adduct VII from each of these alcohols shows the benzylic methylene signal (τ 7.1–7.2) characteristic of the rearranged side chain.

Table I. Photolysis[a] of 2,6-Di-*t*-butyl-*p*-benzoquinone (VI) in Alcoholic Solvents (ROH)

ROH	Product: VII, R =	% yield
CH_3OH	CH_3	50
C_2H_5OH	C_2H_5	38
$CH_3CH_2CH_2OH$	$CH_3CH_2CH_2$	14
$(CH_3)_2CHOH$	$(CH_3)_2CH$	11
$(CH_3)_3COH$	$(CH_3)_3C$	0.01
$CH_3(CH_2)_4OH$	$CH_3(CH_2)_4$	*b*
Cyclohexanol	C_6H_{11}	6

[a] In a Pyrex vessel at 25–30°: under a GE 275-w sun lamp for methanol and cyclohexanol, under sunlight for the others. [b] Structure determined from nmr spectra without isolation of the pure photoproduct.

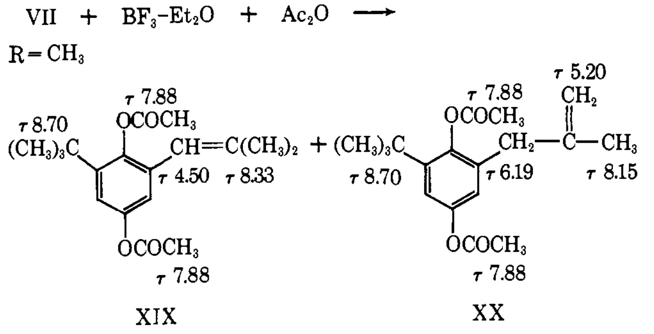
The irradiation of VI in nonalcoholic media (see Table II) led to photoisomerization to the coumaran VIII. An exception was thiophenol which produced only the reduction of the quinone to the hydroquinone in 43% yield.

Table II. Photolysis[a] of 2,6-Di-*t*-butyl-*p*-benzoquinone (II) in Other Protic Solvents (R)

R	Product	% yield
CH_3COOH	VIII	16
$CH_2(COOEt)_2$	VIII	*b*
H_2O (dioxane)	VIII	1.3
HCN (hexane)	VIII	2
C_6H_5SH	2,6-Di-*t*-butyl-hydroquinone	
CF_3COOH	VIII	*b*

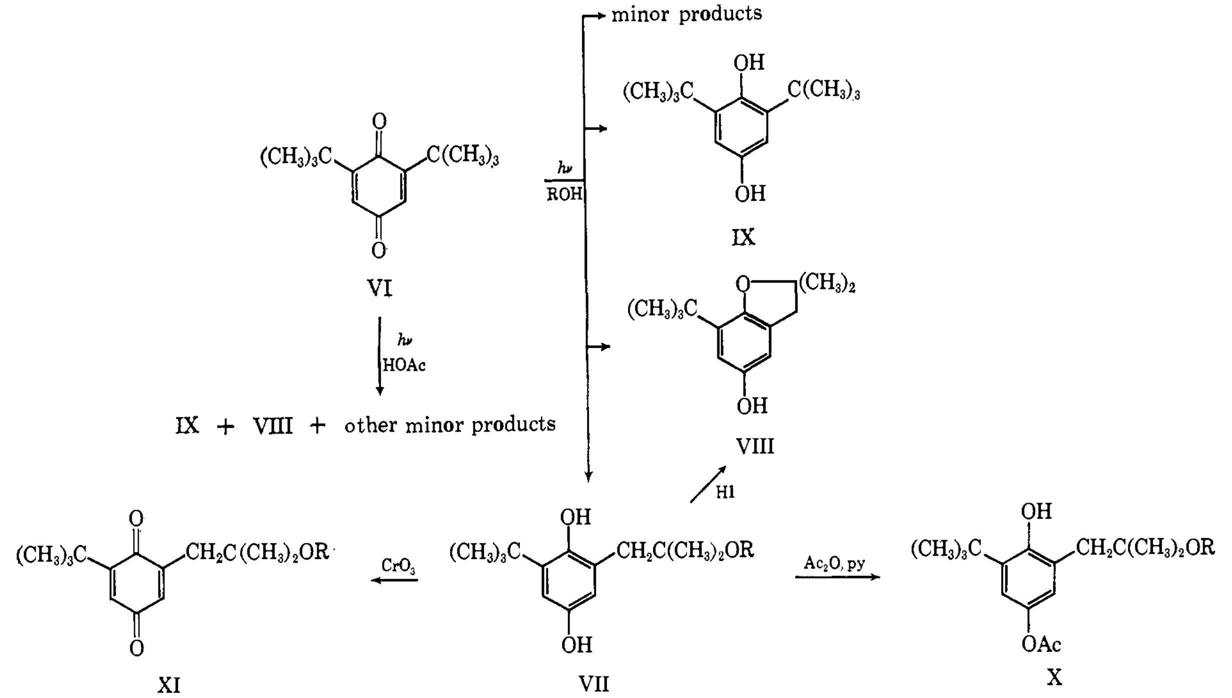
[a] In a Pyrex vessel at 25–30°: under a GE 275-w sun lamp for acetic acid, thiophenol, and trifluoroacetic acid; under sunlight for the others. [b] Structure determined from nmr spectra without isolation of the pure photoproduct.

The acidity of the medium did not appear to influence the course of the photoreaction of VI. The photolysis of this quinone in trifluoroacetic acid was studied in some detail. Since this acid is devoid of proton nmr signals in the τ 0–10 region, nmr spectroscopy was found to be a convenient method for monitoring the progess of the photoreaction. A solution of VI in trifluoroacetic acid was sealed in an nmr tube under nitrogen and photolyzed. Periodic examination of the nmr spectrum showed that changes in the reaction mixture ceased after 24 hr. The irradiated solution was subjected to vpc on an Apiezon column; three fractions, A, B, and C, and traces of other products were obtained. Fraction B was found to be the starting material. The product C was identified as VIII on the basis of its infrared and mass spectra. Compound A which displayed an ester carbonyl absorption in the infrared spectrum and a molecular weight of 220 (mass spectral) was deduced to be the trifluoroacetyl derivative of VIII. When the irradiated solution was allowed to stand in contact with air, the peak in the vpc corresponding to A decreased



with time while that due to C increased, signifying easy hydrolysis of the trifluoroacetate of VIII. If the irradiation of a solution of VI was carried out in the presence of air instead of under nitrogen, the same products were obtained but more of the starting material was recovered.

Chart II



Recently it was reported[14] that steroid methyl ethers can be cleaved to steroid alcohols by reaction with boron trifluoride etherate and acetic anhydride at 0°. Before definitive evidence had been obtained for skeletal rearrangement in the conversion of VI to VII, it was decided to use this cleavage reaction to obtain the alcohol corresponding to the ether VII (R = CH_3). In the absence of rearrangement during photolysis of VI, this alcohol would be primary in nature while photorearrangement would be indicated by the formation of a tertiary alcohol.

The main product from the reaction of VII (R = CH_3) with boron trifluoride etherate and acetic anhydride was separated by vpc. Its infrared spectrum indicated it to be an acetate and the mass spectrum showed the molecular ion at m/e 304. The nmr spectrum corresponded to a mixture of XIX and XX in approximately equal proportions. The mass spectral fragmentation was consistent with this structural assignment. These observations provide further support for the rearrangement of the *t*-butyl side chain during photolysis of VI. The course of the photolysis of VI in various solvents and related reactions is illustrated in Chart II.

Photolysis of 2,5-Di-*t*-butyl-*p*-benzoquinone (XII)

While our studies on the irradiation of XII in alcoholic media were in progress, reports from two other laboratories appeared on the same subject.[15,16] In the absence of nmr data, one group of investigators assumed that the 1:1 addition of an alcohol leads to nuclear alkoxylation. The second group[16] located the alkoxy substituent on the side chain but did not consider the possibility of a side-chain rearrangement either for the 1:1 adduct or the coumaran formed by photoisomerization.

The major products from the photolysis of XII in ethanol are a 1:1 addition product, XIII (*ca.* 52%), and a 2:1 ethanol–quinone adduct, XV (*ca.* 17%). Of the several other products formed in minor amounts, one has been reported to be XIV which is isomeric with XII.

Both alcohol adducts, XIII and XV, displayed the characteristic benzylic methylene signal in the τ 7.2 region. In the light of the nmr data and our findings on the photolysis of 2-*t*-butyl- and 2,6-di-*t*-butyl-*p*-benzoquinone (*vide supra*), the structure for the adducts from XII must be as shown in XIII and XV in Chart III. The immediate precursor to XV should be the quinone XVI which would arise in the reaction mixture through the dehydrogenation of XIII by a quinone or air. When XIII was oxidized with chromic acid, the quinone XVI was obtained in 60% yield. Photolysis of XVI in ethanol afforded the 2:1 adduct XV in 88% yield. The low yield of XV from the photolysis of XII reflects the slow rate of oxidation of XIII under the reaction conditions.

The irradiation of XII in glacial acetic acid resulted in the isolation of two products, XIV (4%) and XVII (4%).

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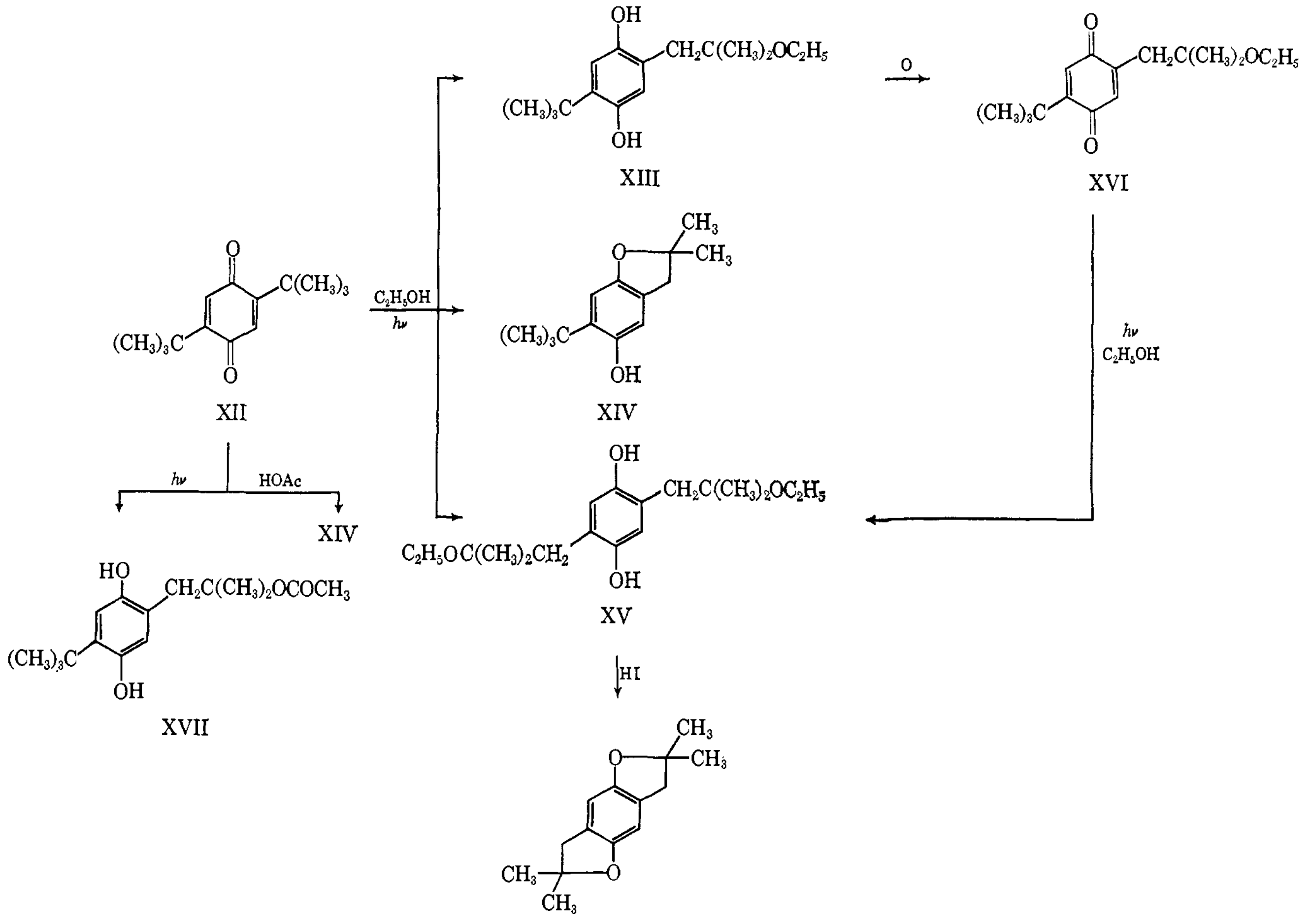
Chart III



The compound XIV was identical with a minor product obtained[16] from the photolysis of XII in ethanol; it could also be prepared by the reaction of XIII with hot hydriodic acid.[16] From its nmr spectrum and by analogy with the chemistry discussed earlier, the structure XIV (Chart III) involving a rearrangement of the side chain can be assigned to it. The compound XVII was shown to be a hydroxy acetate by its infrared spectrum. The nmr spectrum revealed that a rearrangement of one side chain had occurred. Since the coumaran ring is stable to hot hydriodic acid, it is unlikely that XVII is not a genuine photoproduct but arises from the reaction of acetic acid with XIV.

The present investigation has established that the products from the photolysis of *t*-butyl-substituted *p*-benzoquinones (other than the corresponding hydroquinones) arise through a skeletal rearrangement of the *t*-butyl side chain. A spirocyclopropyl intermediate appears to be involved in this process.[13b] Further observations on the photolysis of substituted *p*-benzoquinones and comments on mechanism will be the subject of future communications.

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 95% ethanol using a Perkin-Elmer Model 202 or a Beckman-DK-2A spectrometer. Gas chromatographic analyses were carried out on a F & M Model 500 vapor fractometer with a 2-ft silicone rubber (SE 30) column. 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 GE 275-w sun lamp were used for irradiation.

For describing nmr spectra the following data are reported: chemical shift of the center of a 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*).

Materials. 2-*t*-Butyl-*p*-benzoquinone (mp 55–57°, $\lambda_{max}^{C_2H_5OH}$, mμ: 247 (ε 16,326), 311 (183), 438 (24.6)) and 2,5-di-*t*-butyl-*p*-benzoquinone (mp 150–151°, $\lambda_{max}^{C_2H_5OH}$, mμ: 254 (ε 18,383), 262 sh (16,712), 310 (302), 451 (28.6)) were prepared in good yield by the chromium trioxide–acetic acid oxidations of the corresponding hydroquinones. 2,6-Di-*t*-butyl-*p*-benzoquinone (mp 65–67°, $\lambda_{max}^{C_2H_5OH}$, mμ: 254 (ε 16,540), 317 (464), 450 (29.5)) and 2,6-di-*t*-butylhydroquinone were obtained from Ethyl Corporation, Baton Rouge, La., and 2,5-di-*t*-butyl- and 2-*t*-butylhydroquinones from Eastman Chemical Products, Inc., Kingsport. Tenn.

Photolysis of 2-*t*-Butyl-*p*-benzoquinone (I). A. 2-(2-Ethoxy-2-methyl-1-propyl)hydroquinone (IIa, R = C_2H_5). A solution of I (2 g) in absolute ethanol (200 ml) was irradiated with a 275-w GE sun lamp for 24 hr. Evaporation of the solvent left a dark solid which was crystallized from benzene–hexane to give colorless crystals of IIa (R = C_2H_5), 1.3 g (51%), mp 144–147°; λ_{max}^{Nujol}, μ: 2.95 (OH), 6.25 (ArC=C), 9.42 (COC); λ_{max}^{THF}, mμ: 298 (ε 4000); nmr (CD_3COCD_3), τ: 8.82 (t, 3 H, OCH_2CH_3), 8.76 (s, 6 H, $C(CH_3)_2$), 7.08 (s, 2 H, $ArCH_2$), 6.48 (q, 2 H, OCH_2), 3.31 (m, 2 H, aromatic protons), 1.90 (s, 1 H, OH); one hydroxy proton signal was absent because of rapid exchange with the solvent.

Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.57; H, 8.57. Found: C, 68.86; H, 9.07.

B. 2,2-Dimethyl-5-hydroxycoumaran (IIIa). A solution of I (2 g) in (200 ml) glacial acetic acid was irradiated for 66 hr with a 275-w GE sun lamp. The solvent was removed under reduced pressure, and the dark, oily residue was chromatographed on 60 g of 100–200 mesh silica gel. Elution with carbon tetrachloride–chloroform (1:4) provided colorless crystals of IIIa, 0.0185 g

(0.9%), mp 85–95°. The infrared and nmr spectra of this material were essentially identical with those of pure IIIa prepared in the following experiment.

Reaction of IIa (R = C_2H_5) and IV with Hydriodic Acid. A suspension of 1.2 g of IIa (R = C_2H_5) in a mixture of 1 ml of 95% ethyl alcohol and 4 ml of 47% aqueous hydriodic acid was heated to 70° for 5 min. At that temperature the solid went into solution. After cooling the reaction mixture was diluted with 30 ml of water and extracted with ether. The ether layer was dried over anhydrous magnesium sulfate and the solvent removed from it by evaporation. The residual oil was distilled under vacuum. The distillate crystallized to give 0.6 g (64%) of IIIa, mp 99–101°;[17] λ_{max}^{neat}, μ: 3.0 (OH), 6.2 (ArC=C), 8.7 and 9.1 (ArOC); λ_{max}^{THF}, mμ: 307 (ϵ 4200); nmr ($CDCl_3$), τ: 8.55 (s, 6 H, $C(CH_3)_2$), 7.08 (s, 2 H, $ArCH_2$), 4.18 (s, 1 H, OH), 3.33–3.45 (m, 3 H, aromatic H).

In a similar experiment 3 g of IV was heated with 15 ml of aqueous hydriodic acid (47%) at 50° for 0.5 hr, and the product was extracted with ethyl acetate and purified by crystallization from hexane–benzene to give 0.9 g (30%) of IIIa, mp 96–99°.

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.17; H, 7.31. Found: C, 73.00; H, 7.20.

2-(β-Methallyl)hydroquinone (IV). This compound was prepared according to the method in the literature,[18] mp 82–84°; nmr (CD_3COCD_3), τ: 8.30 (s, 3 H, CH_3), 6.67 (s, 2 H, $ArCH_2$), 5.23 (broad s, 2 H, $C{=}CH_2$), 3.20 (s, 1 H), 2.92 (s, 1 H), and 2.70 (s, 1 H), aromatic protons; hydroxy protons were exchanged with the solvent.

2-(2-Ethoxy-2-methyl-1-propyl)-*p*-benzoquinone (IIc, R = C_2H_5). A suspension of IIa (R = C_2H_5) (4.0 g, 0.019 mole) in 25 ml of glacial acetic acid was stirred at 25° while solid chromium trioxide (2.0 g, 0.02 mole) was added gradually over a 30-min period. The temperature of the reaction mixture rose gradually to 65°. After cooling to 25°, this solution was diluted with 50 ml of water and extracted with 100 ml of benzene. The organic layer was dried over anhydrous magnesium sulfate and distilled to give 2.8 g (71%) of IIc, bp 105° (0.01 mm).

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.23; H, 7.69. Found: C, 69.90, H, 8.00.

Photolysis of 2,6-Di-*t*-butyl-*p*-benzoquinone (VI). A. 2-(2-Methyl-2-ethoxy-1-propyl)-6-*t*-butylhydroquinone (VII, R = C_2H_5). A solution of 4.5 g of VI in 100 ml of absolute ethanol was irradiated for 24 hr using a sun lamp. Repeated crystallizations of the crude product from hexane–benzene gave 2 g (38%) of colorless needles, mp 128–130°; λ_{max}^{KBr}, μ: 2.97 and 3.17 (OH), 6.24 (ArC=C), 9.02 and 9.46 (COC); λ_{max}^{THF}, mμ: 295 (ϵ 4600);[19] nmr ($CDCl_3$), τ: 8.77 (t, 3 H, OCH_2CH_3), 8.77 (s, 6 H, $C(CH_3)_2$), 8.60 (s, 9 H, $C(CH_3)_3$), 7.20 (s, 2 H, $ArCH_2$), 6.47 (q, 2 H, OCH_2), 5.00 (broad peak, 1 H, OH), 3.48 and 3.15 (AB patterns, *J* = 3 cps, 2 H, aromatic H), 1.25 (s, 1 H, OH); mass spectrum, *m/e*: 266 $(M)^+$, 179 $(M - C(CH_3)_2OC_2H_5)^+$, and others.

Anal. Calcd for $C_{16}H_{26}O_3$: C, 72.10; H, 9.77. Found: C, 71.50; H, 9.92.

Acetylation of 0.5 g of VII (R = C_2H_5) was carried out by heating with 0.65 g of acetic anhydride and 5 ml of pyridine for 1 hr at 100°. Addition of 10 ml of ice water to the cooled reaction mixture led to the separation of 0.55 g (99%) of the *monoacetate* X (R = C_2H_5) which was recrystallized from hexane, mp 63.5–65.5°; λ_{max}^{KBr}, μ: 3.15 (OH), 5.70 (OCO), 6.15 (ArC=C), 8.96 and 9.45 (COC). The nmr spectrum was very similar to that of VII (R = C_2H_5) except for the replacement of the broad peak at τ 5.0 with a three-proton singlet corresponding to the acetyl group. The signal of the hindered hydroxy group (singlet at τ 1.58) disappeared very slowly (more than 1 hr for 50% disappearance) on shaking a $CDCl_3$ solution with D_2O.

Anal. Calcd for $C_{18}H_{28}O_4$: C, 70.10; H, 9.09. Found: C, 70.19; H, 9.11.

B. 2,2-Dimethyl-5-hydroxy-7-*t*-butylcoumaran (VIII). Gas chromatography (using an S.E. 30 column) of the mother liquor (62% of the reaction product by weight) from the previous experiment indicated the presence of five components, two of which, comprising 22% of the mixture, were not identified. The other three components were found to be the following: 2,6-di-*t*-butylhydroquinone (IX, 48%), 2-(2-ethoxy-2-methyl-1-propyl)-6-*t*-butylhydroquinone (VII, R = C_2H_5, 8%), and 2,2-dimethyl-5-hydroxy-7-*t*-butylcoumaran (VIII, 22%). The last compound (VIII) was also obtained by heating for 1.5 hr 57 g of VII (R = C_2H_5) with 300 ml of aqueous hydriodic acid (47%). The hot reaction mixture was homogeneous but on cooling 46 g (100%) of VIII crystallized out, mp 150–152°; λ_{max}^{KBr}, μ: 3.1 (OH), 6.25 (ArC=C), 8.75, 8.95, and 9.10 (ArOC); λ_{max}^{THF}, mμ: 305 (ϵ 5000); nmr ($CDCl_3$), τ: 8.70 (s, 9 H, $C(CH_3)_3$), 8.56 (s, 6 H, $C(CH_3)_2$), 7.15 (s, 2 H, $ArCH_2$), 5.58 (s, 1 H, OH), 3.58 (m, 2 H, aromatic H).

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.36; H, 9.09. Found: C, 75.80; H, 9.28.

Irradiation of a solution of 2 g of VI in 200 ml of glacial acetic acid under a sun lamp for 18 hr gave 2.9 g of a colored product. Chromatography of this over silica gel using a benzene–carbon tetrachloride mixture as eluent afforded 0.32 g (16%) of VIII.

C. 2,6-Di-*t*-butylhydroquinone (IX). A solution of 1 g of VI in 7 ml of redistilled benzenethiol was irradiated for 72 hr under a sun lamp. The orange color of the reaction mixture changed to yellow during this time. Removal of benzenethiol under reduced pressure and distillation [bp 130° (0.2 mm)] of the residue gave a colorless material which was crystallized from hexane to give 0.43 g (43%) of IX, mp 100–103°.

Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.68; H, 10.00. Found: C, 75.60; H, 10.00.

When a solution of VI in benzenethiol was stored in the dark for 8 days and worked up as above, 0.24 g (24%) of IX and 0.4 (40%) of diphenyl disulfide, mp 53–56°, were obtained.

D. 2,2-Dimethyl-5-trifluoroacetoxy-7-*t*-butylcoumaran. A solution of 0.15 g of VI in 2 ml of trifluoroacetic acid was sealed in an nmr tube and exposed to a sun lamp with air cooling. The nmr spectrum was recorded periodically. After 24 hr no further changes were noticed, and the irradiation was discontinued. Gas chromatography of the reaction mixture over a 10% Apiezon L column gave three major fractions. The first fraction (44%) was deduced to be the title compound on the basis of its infrared (5.55 μ) and mass spectra (M^+ at *m/e* 316 and expected fragmentation patterns). The other two fractions corresponded to the starting material (42%) and VIII (14%).

E. 2-(2-Methyl-2-methoxy-1-propyl)-6-*t*-butylhydroquinone (VII, R = CH_3). Irradiation under a sun lamp for 20 hr of a solution of 4.5 g of VI in 100 ml of methanol afforded 2.5 g (50%) of VII (R = CH_3), mp 119.6–121.6° (recrystallized from hexane–benzene); λ_{max}^{KBr}, μ: 3.00, 6.25, 9.02; λ_{max}^{THF}, mμ: 298 (ϵ 4660); nmr (CCl_4), τ: 8.85 (s, 6 H), 8.68 (s, 9 H), 7.33 (s, 2 H), 6.75 (s, 3 H), 5.17 (broad peak, 1 H), 3.78 and 3.42 (m, 2 H), 1.9 (s, 1 H).

Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.42; H, 9.52. Found: C, 70.79; H, 9.78.

F. 2-(2-Cyclohexyloxy-2-methyl-1-propyl)-6-*t*-butylhydroquinone (VII, R = C_6H_{11}). The product from the irradiation of a solution of 2 g of VI in 200 ml of cyclohexanol was chromatographed over silica gel. The fraction eluted with a benzene–carbon tetrachloride mixture provided 0.17 g (6%) of VII (R = cyclohexyl), mp 138–142°; λ_{max}^{KBr}, μ; 2.84, 3.15, 6.25, 8.95, 9.44; λ_{max}^{THF}, mμ: 289 (ϵ 4250); nmr ($CDCl_3$), τ: 8.68 (s, 6 H), 8.59 (s, 9 H), 8.4 (m, 10 H), 7.28 (s, 2 H), 6.80–6.63 (m, 1 H, H on C-1 of $c\text{-}C_6H_{11}O\text{–}$), 3.65–3.31 (AB pattern, *J* = 3 cps, 2 H, aromatic H), 1.34 (s, 1 H).

Anal. Calcd for $C_{20}H_{32}O_3$: C, 75.00; H, 10.00. Found: C, 75.13; H, 10.10.

G. 2-(2-Methyl-2-*n*-propyloxy-1-propyl)-6-*t*-butylhydroquinone (VII, R = $CH_3CH_2CH_2$). The product from the irradiation of a 1% solution of VI in 1-propanol in sunlight for 87 hr crystallized partially on long standing. Trituration with hexane gave the title compound in 15% yield, mp 85–87.4°; λ_{max}^{KBr}, μ: 2.95, 3.15, 6.45, 8.98, 9.35; λ_{max}^{THF}, mμ: 295 (ϵ 4350); nmr (CCl_4), τ: 9.10 (t, 3 H, CH_2CH_3), 8.77 (s, 6 H), 8.64 (s, 9 H), 8.2–8.9 (m, 2 H, CH_2CH_3), 7.28 (s, 2 H), 6.60 (t, 2 H, OCH_2CH_2), 6.08 (broad peak, OH), 3.75–3.45 (AB patterns, *J* = 2 cps, 2 H, aromatic H).

Anal. Calcd for $C_{17}H_{28}O_3$: C, 72.85; H, 10.00. Found: C, 72.84; H, 10.26.

H. 2-(2-Isopropyloxy-2-methyl-1-propyl)-6-*t*-butylhydroquinone (VII, R = $(CH_3)_2CH$). Using the same experimental conditions as in G and irradiation for 48 hr, the title compound was obtained in 31% yield, mp 108–110°; λ_{max}^{THF}, mμ: 296 (ϵ 4220); nmr (CCl_4), τ: 8.94–8.60 (m, 21 H, all seven methyl groups), 7.35 (s, 2 H, $ArCH_2$), 6.5–5.5 (very broad peak, 2 H, OH and $OCH(CH_3)_2$), 3.80 and 3.47 (AB pattern, *J* = 3 cps, 2 H, aromatic protons), 2.70 (s, 1 H, OH).

Anal. Calcd for $C_{17}H_{28}O_3$: C, 72.85; H, 10.00. Found: C, 72.60; H, 10.18.

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(17) Private communication from W. K. T. Gleim, Universal Oil Products, Des Plaines, Ill.: 2,2-dimethyl-5-hydroxycoumaran mp 99°; 2,2-dimethyl-5-hydroxy-6-*t*-butylcoumaran mp 154–155°.

(18) A. Gaydasch and W. K. T. Gleim, U. S. Patent, 2,681,371; *Chem Abstr.*, **49**, 7595c (1955).

(19) The ultraviolet absorption data reported earlier[13] was in error because of instrumental difficulty.

I. 2-(2-*t*-Butyloxy-2-methyl-1-propyl)-6-*t*-butylhydroquinone (VII R = $(CH_3)_3C$). Irradiation under sunlight for 48 hr decolorized a 1% solution of VI in *t*-butyl alcohol. On chromatography of the product on a silica gel column using a mixture of chloroform and carbon tetrachloride for elution, the title compound was obtained in 0.01% yield as colorless needles, mp 135–138°; $\lambda_{\max}^{\mathrm{KBr}}$, μ: 2.93, 3.00, 6.45, 9.00; mass spectrum, *m/e:* 294 (M^+), 238 ($M^+ - C_4H_8$), 220 ($M^+ - C_4H_9OH$). Because of a lack of adequate quantity of this material elemental analysis and further characterization were not attempted.

J. 2-(2-Methyl-2-*n*-pentyloxy-1-propyl)-6-*t*-butylhydroquinone (VII, R = $CH_3(CH_2)_4$). Using the same technique as in the previous experiment and irradiation time of 24 hr, a noncrystalline product was obtained which had a satisfactory nmr spectrum for the rearranged hydroquinone structure VII (R = *n*-pentyl); nmr ($CDCl_3$), τ: 8.82 (s, $C(CH_3)_2$), 8.62 (s, $(CH_3)_3$, 7.30 (s, ACH_2), 3.60 and 3.30 (AB pattern, J = 2.5 cps, aromatic protons), and other signals with multiple splitting.

Photolysis of VI under Sunlight. A solution of 150 g of VI in 10 l. of absolute ethanol was irradiated with direct sunlight for 5 days. Evaporation of the solvent and trituration of the residue with hexane gave 134 g (74%) of VII (R = C_2H_5), mp 127.6–129.6°. Gas chromatography of the mother liquor showed the presence of the following components: IX (32%), VIII (17%), VII (R = C_2H_5, 14%), and four other fractions (37%) which were not identified.

Photolysis of VI in dimethyl malonate solution under sunlight for 40 days gave a noncrystalline product, the nmr spectrum of which showed that the main component was VIII. Irradiation for 18 hr in aqueous dioxane solution led to the isolation of VIII in 1.3% yield after chromatography. The same product was obtained in 2% yield after chromatographic purification when a solution of 1 g of VI in a mixture of 10 ml of hydrocyanic acid and 90 ml of hexane was exposed to direct sunlight for 22 days.

2-(2-Methyl-2-alkoxy-1-propyl)-6-*t*-butyl-1,4-benzoquinone (XI). A. A solution of 1.7 g of VII (R = C_2H_5) in 10 ml of glacial acetic acid was stirred at 25° while a solution of 0.44 g of chromium trioxide in 2 ml of glacial acetic acid was added dropwise during 10 min. The resulting dark solution was stirred for an additional 2 hr at 25°. Dilution of the reaction mixture with 30 ml of water resulted in the separation of an orange oil which was extracted with ether and purified by vacuum distillation to give 1.2 g (71%) of XI (R = C_2H_5), bp 145° (0.09 mm); $\lambda_{\max}^{\mathrm{neat}}$, μ: 6.07 (C=CC=O), 9.05 and 9.35 (COC); $\lambda_{\max}^{\mathrm{THF}}$, m$\mu$: 257 ($\epsilon$ 17,000), 289 sh (ϵ 1700), 450 (ϵ 37); the nmr spectrum has been reported previously.[13a]

Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.72; H, 9.09. Found: C, 72.96; H, 9.22.

B. Using the same method as above, 1.6 g of VII (R = CH_3) was oxidized to 1.1 g (69%) of XI (R = CH_3), bp 130–135° (0.3 mm); $\lambda_{\max}^{\mathrm{neat}}$, μ: 6.05 (C=CC=O), 9.05 and 9.30 (COC); $\lambda_{\max}^{\mathrm{THF}}$, m$\mu$: 257 ($\epsilon$ 26,650), 450 (ϵ 30); nmr ($CDCl_3$), τ: 8.88 (s, 6 H, $C(CH_3)_2$), 8.72 (s, 9 H, $C(CH_3)_3$), 7.35 (s, 2 H, $ArCH_2$), 6.80 (s, 3 H, OCH_3), 3.35 (m, 2 H, aromatic H). A double resonance experiment showed that one of the aromatic protons was coupled (J = <1 cps) with the methylene protons.[13a]

Anal. Calcd for $C_{15}H_{22}O_3$: C, 72.00; H, 8.88. Found: C, 72.11; H, 8.95.

Reaction of VII (R = CH_3) with Boron Trifluoride Etherate and Acetic Anhydride. To an ice-cold solution of 0.05 g of VII (R = CH_3) in 5 ml of acetic anhydride was added 1 ml of boron trifluoride etherate under anhydrous conditions. After standing overnight in an ice box, the reaction mixture was poured on crushed ice and extracted with ether. The ether layer was dried and evaporated, and the residue was subjected to gas chromatography over a 10% Apiezon L column. Only one major peak was obtained, the infrared spectrum of which showed the presence of an acetate group (5.7 μ). The nmr spectrum (see structures XIX and XX for assignments) indicated the presence of XIX and XX in nearly equal amounts. The mass spectrum showed the molecular ion at *m/e* 304 (mol wt calcd for $C_{18}H_{24}O_4$: 304).

Photolysis of 2,5-Di-*t*-butyl-*p*-benzoquinone (XII). A. 2,5-Bis-(2-ethoxy-2-methyl-1-propyl)hydroquinone (XV). A solution of 4.8 g of XII in 330 ml of absolute ethanol was irradiated for 18 hr using a sun lamp. During this period a white solid separated. Filtration of the reaction mixture gave 0.9 g (14%) of the title compound,[16] mp 208.6–210.2°; $\lambda_{\max}^{\mathrm{KBr}}$, μ: 3.15, 6.18, 9.00, 9.47; $\lambda_{\max}^{\mathrm{THF}}$, m$\mu$: 300 ($\epsilon$ 4650).

Anal. Calcd for $C_{18}H_{30}O_4$: C, 69.67; H, 9.67. Found: C, 69.66; H, 9.57.

This compound was obtained in much higher yield by irradiating for 16 hr under a sun lamp a solution of 1 g of XVI in 68 ml of absolute ethanol. Filtration of the reaction mixture afforded 1 g (88%) of XV, mp 207–212°.

B. 2-(2-Ethoxy-2-methyl-1-propyl)-5-*t*-butylhydroquinone (XIII, R = C_2H_5). The mother liquor after the separation of XV from the previous experiment was evaporated and the crystalline residue (5.2 g) was recrystallized from a mixture of hexane and benzene to give 3.4 g (61%) of XIII (R = C_2H_5) as fine, colorless needles, mp 167.2–168.6°;[16] $\lambda_{\max}^{\mathrm{KBr}}$, μ: 3.00, 3.25, 6.15, 8.97, 9.45; $\lambda_{\max}^{\mathrm{THF}}$, m$\mu$: 297 ($\epsilon$ 4650).

Anal. Calcd for $C_{16}H_{26}O_3$: C, 72.18; H, 9.77. Found: C, 71.90; H, 9.80.

C. 2,2-Dimethyl-5-hydroxy-6-*t*-butylcoumaran (XIV). Photolysis of a solution of 2 g of XII in 200 ml of glacial acetic acid was carried out under a sun lamp for 6 hr. The solvent was then removed under reduced pressure at 50° and the residual oil extracted with ether. The ether layer was washed several times with 10% sodium carbonate solution and finally with water until the washings were neutral. After drying over anhydrous magnesium sulfate the ether solution was stripped of solvent, and the oil (2.5 g) so obtained was chromatographed over silica gel. Elution with 1:4 chloroform–carbon tetrachloride solution gave two crystalline fractions, the earlier of which was 0.08 g (4%) of XIV as colorless needles, mp 155–157° (lit.[16] mp 157°); $\lambda_{\max}^{\mathrm{KBr}}$, μ: 2.95, 6.15, 8.62, 8.85.

The same compound was also obtained by heating under reflux 2 g of XIII with 10 ml of 95% ethyl alcohol and 10 ml of 47% aqueous hydriodic acid. After 0.5 hr of heating the homogeneous reaction mixture was allowed to cool when 1 g (65%) of XIV, mp 147–151°, crystallized out and was collected by filtration.

D. 2-(2-Acetoxy-2-methyl-1-propyl)-5-*t*-butylhydroquinone (XVII). The later fraction from the chromatography mentioned in the above experiment was found to be 0.1 g (4%) of colorless needles of XVII, mp 105–108°; $\lambda_{\max}^{\mathrm{KBr}}$, μ: 2.95, 5.77, 8.35, 9.05; nmr ($CDCl_3$), τ: 8.63 (s, 6 H, $C(CH_3)_2$), 8.47 (s, 9 H, $(CH_3)_3$), 7.96 (s, 3 H, $COCH_3$), 7.15 (s, 2 H, $ArCH_2$), 5.50 (s, 1 H, OH), 3.62 (s, 1 H, aromatic H), 3.18 (s, 1 H, aromatic H).

Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.55; H, 8.57. Found: C, 68.47; H, 8.55.

Photolysis of XII under Sunlight. A solution of 9.6 g of XII in 650 ml of absolute ethanol was exposed to a sun lamp for 3 hr. The solid that separated during the reaction was collected by filtration to give 1.4 g (11%) of XV, mp 208–210°. The mother liquor afforded 8.9 g (78%) of XIII, mp 145–150°.

2,2,6,6-Tetramethylbenzo[1,2-*b*:4,5-*b′*]difuran (XVIII). A suspension of XV (0.7 g) in 5 ml of 47% aqueous hydriodic acid and 1 ml of ethanol was heated to 100°. In 5 min at 100°, the solid dissolved, and the solution was heated at this temperature for an additional 10 min. The reaction mixture was cooled and filtered and 0.3 g (64%) of XVIII[16] was obtained, mp 123–125°; $\lambda_{\max}^{\mathrm{KBr}}$, μ: 6.24, 7.25, 7.35, 8.85, 9.15; $\lambda_{\max}^{\mathrm{THF}}$, m$\mu$: 316 ($\epsilon$ 5400).

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.06; H, 8.25. Found: C, 77.00; H, 9.00

2-(2-Ethoxy-2-methyl-1-propyl)-5-*t*-butyl-*p*-benzoquinone (XVI). A suspension of 3.4 g of XIII in 30 ml of glacial acetic was stirred at 25° while a solution of chromium trioxide (1.27 g, 0.012 mole) in 2 ml of water was added dropwise over a 10-min period. The resulting dark solution was stirred for an additional 2 hr at 25°. The reaction mixture was diluted with 30 ml of water and extracted with ether. The ether layer was washed until neutral, dried, and evaporated to give 2 g (60%) of an orange liquid; nmr ($CDCl_3$), τ: 8.55–9.00 (m, 18 H, all six methyl groups), 7.35 (s, 2 H, $ArCH_2$), 6.60 (q, 2 H, OCH_2CH_3), 3.48 (m, 2 H, ArH).

Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.72; H, 9.09. Found: C, 72.70; H, 9.10.