

Photoaddition of Allenes to *p*-Quinones

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p-Benzoquinone, 2-methyl-*p*-benzoquinone, tetrachloro-*p*-benzoquinone, and 1,4-naphthoquinone undergo photochemical addition to tetramethyl- or 1,1-dimethyl-allene to form 5-hydroxyindan-2-one derivatives. The kinetics of the photoaddition of *p*-benzoquinone to tetramethylallene was investigated by quantum yield measurements in the absence and presence of anthracene, and the rate of addition of triplet *p*-benzoquinone to tetramethylallene was estimated. A mechanism is proposed involving addition and rearrangement.

RECENTLY attention has been given to the photoaddition of ketones or thioketones to allenes. Aldehydes and ketones undergo photochemical cycloaddition to allenes to give oxetans.^{1,2} Thioketones also react with allenes to yield thietans.^{3,4}

The photochemical cycloaddition of the carbonyl group

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¹ D. R. Arnold and A. H. Glick, *Chem. Comm.*, 1966, 813.

² H. Gotthardt, R. Steinmetz, and G. S. Hammond, *Chem. Comm.*, 1967, 480; *J. Org. Chem.*, 1968, **33**, 2774.

³ H. Gotthardt, *Chem. Ber.*, 1972, **105**, 2008.

of *o*- or *p*-quinones to olefins is well known⁵ and gives dioxin, oxetanone, or dioxol derivatives. On the other hand, there are relatively few reports on the photochemical cycloaddition of quinones to allenes. Boleij and Bos⁶ reported that allenes add photochemically to

⁴ H. J. Bos, H. Schinkel, and Th. C. M. Wijsman, *Tetrahedron Letters*, 1971, 3905.

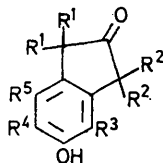
⁵ For reviews of quinone photochemistry, see J. M. Bruce, *Quart. Rev.*, 1968, **21**, 405; M. B. Rubin, *Fortschr. Chem. Forsch.*, 1969, **13**, 251.

⁶ J. S. M. Boleij and H. J. T. Bos, *Tetrahedron Letters*, 1971, 3201.

9,10-phenanthraquinone to yield 2-alkylidene-2,3-dihydrophenanthro[9,10-*b*]-*p*-dioxin, and we have found that photoreaction of tetramethylallene (TA) with *p*-benzoquinone (BQ) or 1,4-naphthoquinone (NQ) forms 5-hydroxyindan-2-one derivatives (1a) or (2a).⁷ In connection with our investigation of these photoadditions we were led to examine the scope and mechanism of photo-reactions of *p*-quinones (BQ, 2-methyl-*p*-benzoquinone, tetrachloro-*p*-benzoquinone, and NQ) to TA or 1,1-dimethylallene (DA).

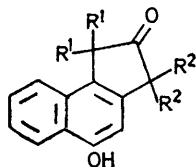
RESULTS

A mixture of DA, and BQ or NQ in benzene was irradiated with 360⁸ or 436 nm light (see Experimental section). In each case only one product was isolated in significant quantity and was shown to be the 1:1 adduct from the *p*-quinone and DA on the basis of elemental and mass spectral analyses. The photoadducts were identified as 5-hydroxy-1,1-dimethylindan-2-one (Ib) and 1,3-dihydro-5-hydroxy-3,3-dimethylbenz[*e*]inden-2-one (IIb), respectively, from their spectral (i.r. and n.m.r.) data which were similar to those of the photoadducts from *p*-quinones (BQ or NQ) and TA,⁷ whose structures were confirmed by an



(I)

- a; R¹ = R² = Me, R³ = R⁴ = R⁵ = H
 b; R¹ = Me, R² = R³ = R⁴ = R⁵ = H
 c; R¹ = R³ = R⁴ = R⁵ = H, R² = Me
 d; R¹ = R² = R³ = Me, R⁴ = R⁵ = H
 e; R¹ = R² = R⁴ = Me, R³ = R⁵ = H
 f; R¹ = R² = R⁵ = Me, R³ = R⁴ = H
 g; R¹ = R⁴ = Me, R² = R³ = R⁵ = H
 h; R¹ = R³ = Me, R² = R⁴ = R⁵ = H
 i; R¹ = R² = Me, R³ = R⁴ = R⁵ = Cl
 j; R¹ = R² = Me, R³ = R⁴ = R⁵ = D



(II)

- a; R¹ = R² = Me
 b; R¹ = H, R² = Me
 c; R¹ = Me, R² = H

independent synthesis of 1,1,3,3-tetramethylindan-2-one.⁹ The possible alternative isomers (Ic) and (Iic) were eliminated as follows. Comparison of the n.m.r. spectrum of the photoadduct from DA and NQ with that of (IIa) ruled out

* These esters might act as a bifunctional substrate, in which the ester oxygen and the carbonyl oxygen of indan-2-one can be co-ordinated by Eu(fod)₃. However, preferential complexation at the ester oxygen appears to occur, since no splitting of the methyl protons for 1,1,3,3-tetramethylindan-2-one⁹ was observed at least at the concentrations of Eu(fod)₃ used for its ester.

† The assignment of structure as (Ib) rather than (Ic) by n.m.r. comparison with (Ia) would not be conclusive because of the lack of shift data for its isomer (Ic). The difference in the slopes for C-1 and -3 in Table 1, however, is large enough to deduce the structure, while Δδ is small.

(Iic) as the structure. In (IIa) the 1-methyl protons resonate at δ 1.65, downfield from the 3-methyl protons (δ 1.37).⁷ The signal at δ 1.30 in the photoadduct from NQ and DA is, therefore, attributed to the 3-methyl protons. Structure (Ib) is preferred to (Ic) for the photoadduct from BQ and DA on the basis of studies on the lanthanide shift reagent, tris-(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato)europium, Eu(fod)₃.¹⁰ The C-methyl signal of the acetate of (Ia) [δ 1.24 (12H, sharp s)]⁸ was shifted downfield on addition of Eu(fod)₃ and was observed as two singlets (6H each). On the other hand, in the acetate of the photoadduct from BQ and DA a downfield shift induced by Eu(fod)₃ was observed without splitting. In the presence of Eu(fod)₃, protons are shifted according to the relationship Δδ = $\hbar(3 \cos^2 \theta - 1)/R^3$.¹¹ A Dreiding model of the acetate of (Ia) indicates that the methyl protons at C-3 are substantially closer to the shift reagent than those at C-1, assuming that the lanthanide complex is located near the ester oxygen.* Comparison of the slopes in plots of δ against [Eu(fod)₃]/[Substrate] (Table 1) suggests that the methyl groups are on C-1 in the photoadduct from BQ and DA.†

TABLE 1

Effect of adding Eu(fod)₃ to solutions of 5-acetoxyindan-2-ones in CCl₄

| 5-Acetoxyindan-2-one | Signal for Me at | [Eu(fod) ₃]/M | | | | Slopes of plots against [Eu(fod) ₃]/[Substrate] |
|----------------------|------------------|---------------------------|------|------|------|---|
| | | 0.01 | 0.02 | 0.03 | 0.06 | |
| 1,1,3,3-Tetramethyl- | C-1 | 0.17 | 0.32 | 0.63 | 0.96 | 2.64 |
| 1,1-Dimethyl- | C-3 | 0.18 | 0.36 | 0.71 | 1.08 | 2.97 |
| | C-1 | 0.16 | 0.32 | 0.62 | 0.93 | 2.64 |

* Δδ = δ (shifted spectrum) - δ (unshifted spectrum).

Photolysis of 2-methyl-*p*-benzoquinone (MBQ) and TA or DA in benzene gave one product in significant quantity in each case. The adduct from TA was identified as 5-hydroxy-1,1,3,3,4-pentamethylindan-2-one (Id), and that from DA as 5-hydroxy-1,1,6-trimethylindan-2-one (Ig). Comparison of the n.m.r. spectrum of the former with that of (Ia) is informative. The n.m.r. spectrum (Id) showed three methyl singlets at δ 1.29 (6H), 1.45 (6H), and 2.28 (3H), a hydroxy-proton at 5.20 (1H), and an AB quartet at 6.67 and 6.97 (2H) (*J* 7.5 Hz) which corresponds to the *ortho*-phenyl protons. The magnitude of the coupling constant of the phenyl protons ruled out (Ie) or (If) as a possible structure, since *meta*- and *para*-coupling constants in benzene derivatives should be much smaller.¹² The methyl protons at C-1 and -3 in (Id) were observed as two singlets, whereas the methyl protons of (Ia) were detected as a sharp singlet. The steric effect between the 3- and 4-methyl protons might cause the 3-methyl protons to lie in a region deshielded by the carbonyl group.¹³ The resonances at δ 1.29 and 1.45, then, can be attributed to the methyl protons on C-1 and -3,

⁷ N. Ishibe and I. Taniguchi, *Tetrahedron*, 1971, **27**, 4883.

⁸ N. Ishibe, M. Sunami, and M. Odani, *Tetrahedron*, 1973, **29**, 2005.

⁹ H. A. Bruson, F. W. Grant, and E. Bonko, *J. Amer. Chem. Soc.*, 1953, **80**, 3633.

¹⁰ R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, 1971, **93**, 1522.

¹¹ B. L. Shapiro, I. R. Hlubucek, and G. R. Sullivan, *J. Amer. Chem. Soc.*, 1971, **93**, 3281.

¹² L. M. Jackman and S. Sternhell, 'Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry', Pergamon Press, London, 1969, p. 305.

¹³ J. A. Pople, *J. Chem. Phys.*, 1962, **37**, 60; R. H. Martin, N. Defay, and F. Greets-Evrard, *Tetrahedron*, 1964, **20**, 1505.

respectively. This assignment is in agreement with the observation that C-1 methyl protons in (Ib) resonate at δ 1.22.

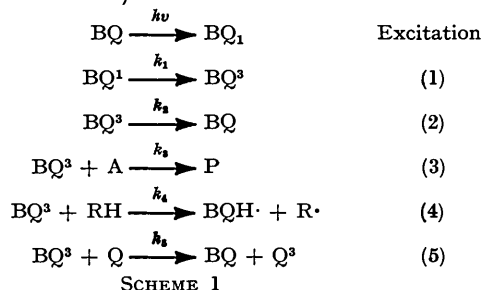
The n.m.r. spectrum of (Ig) showed two singlets at δ 1.24 (6H) and 2.20 (3H), the former value being consistent with that of (Ib) or (Id) which was attributed to the methyl protons at C-1. The absence of *ortho*- and *meta*-coupling indicates the presence of *para*-aromatic protons.

U.v. irradiation of TA and tetrachloro-*p*-benzoquinone in benzene afforded 4,5,7-trichloro-6-hydroxy-1,1,3,3-tetramethylindan-2-one (Ii). The mass spectrum of the photoadduct showed molecular ion peaks at m/e 313/311/309/307 (relative abundance 1 : 9 : 27 : 27), indicating that the photo-product contains three chlorine atoms. The i.r. spectrum of the photoadduct was similar to that of (Ia) except for the bands due to the chlorine atom.

DISCUSSION

In our investigations, irradiation of *p*-quinones with allenes were conducted with 360 or 436 nm light. Under these conditions only the $^1(n,\pi^*)$ state of *p*-quinones¹⁴ is excited. Intersystem crossing gives the $^3(n,\pi^*)$ state ($E_T = 50$ and 57 kcal mol⁻¹ for BQ and NQ,¹⁵ respectively). Energy transfer from this state to allenes used cannot occur efficiently, since the triplet excitation energy is 100–104 kcal mol⁻¹ for the antiplanar allene triplet¹⁶ and 83 kcal mol⁻¹ for the planar allene.¹⁷ Either of these states (*p*-quinone excited singlet or triplet) could, in principle, be responsible for the photochemical cycloaddition. The addition of BQ to TA was quenched by anthracene. Examination of the u.v. spectra of mixtures of BQ and anthracene whose concentrations were kept similar to those used in the quantum yield determinations (see Experimental section) did not give evidence for the formation of a charge-transfer complex. These results indicate that the reactive excited state is the n,π^* triplet state of BQ.

Many cases of oxetan formation are known in which attack on a triplet excited carbonyl compound occurs on a ground state olefin molecule.¹⁸ It seems reasonable that this kind of mechanism might hold for the *p*-quinone-allene reaction, as set out in Scheme 1, where BQ, BQ¹, and BQ³ are the ground state, first excited singlet state, and lowest triplet state, respectively, of *p*-benzoquinone; A is the ground state of the allene; P is product; and Q is quencher (anthracene).



¹⁴ S. Nagakura and A. Kuboyama, *J. Amer. Chem. Soc.*, 1954, **76**, 1003.

¹⁵ M. Kasha, *Radiation Res. Suppl.*, 1960, **2**, 243.

¹⁶ J. M. Borden, *J. Chem. Phys.*, 1966, **45**, 2512

¹⁷ O. Rodriguez and H. Morrison, *Chem. Comm.*, 1971, 679.

¹⁸ D. R. Arnold, *Adv. Photochem.*, 1968, **6**, 301.

Excitation of BQ is followed by intersystem crossing to the triplet [equation (1)] and by unimolecular deactivation of the triplet state of BQ to the ground state [equation (2)]. The triplet BQ reacts with the ground state allene to afford to product [equation (3)], or with solvent to give the semiquinone radical¹⁹ which proceeds to hydroquinone or polymeric material [equation (4)]. The triplet BQ is quenched by anthracene *via* a diffusion-controlled process [equation (5)]. The steady-state approximation on BQ¹ and BQ³ leads to equation (6),

$$1/\phi = 1 + \frac{k_2 + k_5[Q]}{k_3[A] + k_4[RH]} \quad (6)$$

where ϕ is the quantum yield of disappearance of BQ. In order to evaluate the magnitude of k_3 , the rate of hydrogen abstraction from the solvent k_4 , has to be determined. In the absence of the allene, equation (6) becomes (7) and a plot of $1/\phi$ against $[Q]$ at a fixed volume of solvent would be expected to be linear.

$$1/\phi = 1 + \frac{k_2}{k_4[RH]} + \frac{k_5[Q]}{k_4[RH]} \quad (7)$$

Preparative irradiation of BQ in benzene with 360 or 436 nm light afforded a small amount of hydroquinone and polymeric material. No formation of a benzoquinone dimer was observed at low concentrations of BQ in this study, while *p*-quinones form dimers²⁰ upon irradiation in the solid state or in concentrated solution. It was shown that the disappearance of BQ in benzene using 436 nm light was completely quenched by 10⁻²M-anthracene ($E_T = 42$ kcal mol⁻¹) and partially quenched at low anthracene concentrations. A plot of the reciprocal of quantum yield for disappearance of BQ *vs.* [anthracene] gives a good straight line with a least-squares slope of 1.22×10^4 l mol⁻¹ and an intercept of 284 (Figure 1). Assuming diffusion-controlled quenching by anthracene ($k_5 = 3.2 \times 10^9$ l mol⁻¹ s⁻¹),²¹ the use of equation (7) together with a slope obtained from Figure 1 leads to $k_4 = 2.3 \times 10^4$ l mol⁻¹ s⁻¹. The use of this value together with an intercept of 284 leads to the rate of radiationless decay of the BQ triplet (k_2) 7.3×10^7 s⁻¹. This value is consistent with the reported values for the rate of radiationless decay of the cyclic enone triplet (10^7 – 10^8 s⁻¹).²²

Scheme 1 predicts that the reciprocal of the quantum yield should be dependent on the reciprocal of the allene concentration. This is in agreement with the observed result (Figure 2). The use of the value of $k_2 = 7.3 \times 10^7$ s⁻¹ together with a slope of 0.4 mol l⁻¹ in equation (6) leads to $k_3 = 1.8 \times 10^8$ l mol⁻¹ s⁻¹, assuming $k_3[A] \gg k_4[RH]$.

In order to investigate the quantum yield of BQ disappearance as a function of the concentration of quencher,

¹⁹ H. Yoshida, K. Hayashi, and T. Warashina, *Bull. Chem. Soc. Japan*, 1972, **45**, 3515.

²⁰ R. C. Cookson and J. Hudec, *Proc. Chem. Soc.*, 1959, 11; R. C. Cookson, D. A. Cox, and J. Hudec, *J. Chem. Soc.*, 1962, 1717; D. Bryce-Smith and A. Gilbert, *J. Chem. Soc.*, 1964, 2428.

²¹ W. D. Clark, A. D. Litt, and C. Steel, *J. Amer. Chem. Soc.*, 1969, **91**, 5413; G. Porter and M. R. Topp, *Proc. Roy. Soc.*, 1970, **A**, **315**, 163.

²² P. de Mayo, *Accounts Chem. Res.*, 1971, **4**, 41.

Pyrex tubes containing known concentrations of BQ, TA, and anthracene in benzene were irradiated with 436 nm light in a merry-go-round reactor. Plots were obtained for the reciprocal of the quantum yield of BQ disappearance against the concentration of quencher (Figure 3). Least-squares analysis gave a slope of 185 l mol^{-1} and an intercept of 4.5. The use of equation (6) together with the values mentioned earlier of k_4 and k_5 gives an approximate value for k_3 , the rate of cycloaddition reaction, of $1.7 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$. This magnitude agrees well with that estimated previously from Figure 2. From this magnitude and an intercept of 4.5 the rate of radiationless decay of the BQ triplet is $6.0 \times 10^7 \text{ s}^{-1}$ and is in good agreement with that obtained from Figure 1.

The rate of disappearance of BQ in benzene is of the

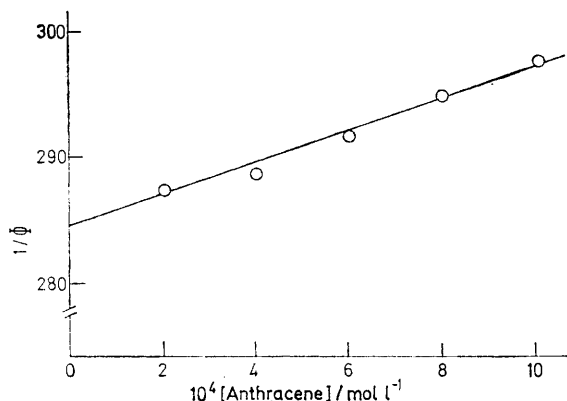


FIGURE 1 Plot of reciprocal of quantum yield for disappearance of BQ vs. concentration of added anthracene in the photo-reaction of BQ with benzene

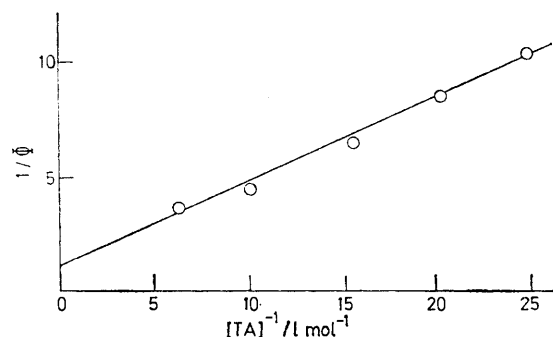


FIGURE 2 Dependence of reciprocal of the quantum yield for disappearance of BQ on reciprocal of TA concentration

same order as that²³ with which triplet phenanthrene-quinone abstracts hydrogen from benzene, indicating that

* The quantum yield of disappearance of BQ in methanol was 19.8. This value suggests a chain mechanism for this reaction. A plot of the reciprocal of quantum yield for disappearance of BQ vs. [anthracene] gave a straight line. Equation (7) cannot, however, be used to determine k_4 , since quenching of this photo-reaction by anthracene might be due to the reaction of a radical intermediate with anthracene, as has been observed in the reaction of ketyl radical with dienes. (N. J. Turro and D. M. McDaniel, *Mol. Photochem.*, 1970, 2, 98.)

† One possible explanation for the absence of (Ia) in methanol is the ease with which hydrogen is abstracted from methanol.¹⁹

‡ We thank Dr. E. D. Becker, National Institute of Health, for informing us of the experimental conditions for the preparation of [²H₄]-*p*-benzoquinone.

benzene is a very poor hydrogen donor. BQ abstracts hydrogen very effectively from methanol and the semi-quinone radical formed is stable in methanol.^{19,*} Irradiation of a mixture containing BQ and TA in methanol, indeed, did not give (Ia), but gave hydroquinone as

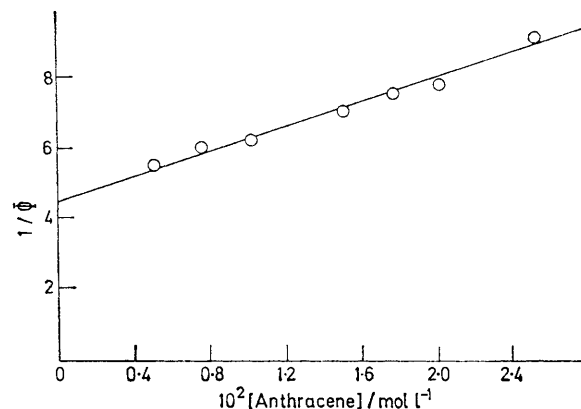
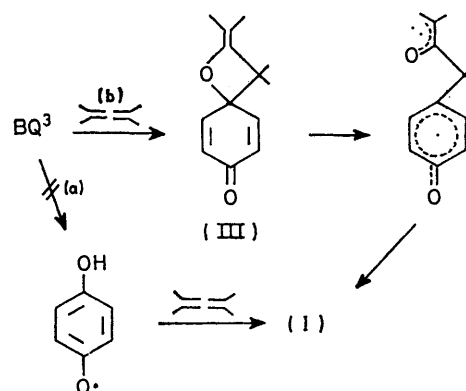


FIGURE 3 Plot of reciprocal of quantum yield for disappearance of BQ vs. concentration of added anthracene in the photo-reaction of BQ with TA

an isolable product.† The rate of cycloaddition reaction, k_3 , in benzene is much faster than that of disappearance of BQ in benzene, k_4 , suggesting that hydrogen abstraction by the BQ triplet from the solvent is not an important step for the reaction of BQ and allenes as a primary process [path (a) in Scheme 2]. Consequently, a triplet quinone molecule attacks a ground state allene to give an intermediate (III) which would rearrange to (I) in a photochemical or thermal process. Acid-catalysed rearrangement of (III) to (I) on silica gel chromatography could not occur, because (Ia)⁷ and (Ij) were isolated from the reaction mixture without using silica gel chromatography. Intramolecular hydrogen migration to a carbonyl oxygen could be excluded, because photo-reaction of [²H₄]-*p*-benzoquinone^{24,‡} with TA in benzene



SCHEME 2

gave the 5-hydroxy-2-indanone derivative (Ij), in which a deuterium was not incorporated in the hydroxy-group.

²³ M. B. Rubin and Z. Neuwirth-Weiss, *J. Amer. Chem. Soc.*, 1972, 94, 6048.

²⁴ E. Charney and E. D. Becker, *J. Chem. Phys.*, 1965, 42, 910.

EXPERIMENTAL

I.r. spectra were recorded with a JASCO DS 402G spectrophotometer, u.v. spectra with a Hitachi 124 spectrophotometer, mass spectra with a Hitachi RMU-6L spectrometer, and n.m.r. spectra with a JEOL PS-100 spectrometer at 100 MHz or a Varian T-60A spectrometer at 60 MHz using tetramethylsilane as internal standard. All elemental analyses were determined by the Microanalytical Laboratory of Kyoto University, Kyoto, Japan.

Commercially available *p*-benzoquinone, 1,4-naphthoquinone, and tetrachloro-*p*-benzoquinone were purified by recrystallization. 1,1-Dimethylallene and tetramethylallene (Chemical Samples Co.) were used without further purification. 2-Methyl-*p*-benzoquinone was prepared by oxidation of 2-methylhydroquinone²⁵ and [²H₄]-*p*-benzoquinone was synthesized by the method described by Charney and Becker.²⁴

Irradiation of p-Quinones with Allenes.—A typical procedure is described, with the results for the remaining cases listed in Table 2. A solution of *p*-benzoquinone (0.7 g) and

203 and 190. 5-Hydroxy-1,1,6-trimethylindan-2-one (Ig); δ (CCl₄) 1.24 (6H, s), 2.20 (3H, s), 3.40 (2H, s), 6.53 (1H, s), 6.93 (1H, s), and 7.24 (1H, s); ν_{\max} (liquid film) 3390 (OH) and 1740 cm⁻¹ (CO); *m/e* 190 (*M*⁺) and 162. 4,5,7-Trichloro-6-hydroxy-1,1,3,3-tetramethylindan-2-one (Ii); δ [(CD₃)₂CO] 1.47 (12H, s) and 6.08 (1H, s); ν_{\max} (KBr) 3300 (OH) and 1740 cm⁻¹ (CO); *m/e* 311/309/307 (*M*⁺) and 292.

Irradiation of [²H₄]-p-Benzoquinone with Tetramethylallene.—A mixture of [²H₄]-*p*-benzoquinone (0.7 g) and tetramethylallene (2.0 g) in benzene (180 ml) was irradiated under nitrogen with 360 nm light for 50 h. The mixture was concentrated to 20 ml under vacuum and cooled, and the precipitate formed was filtered off. Recrystallization from ethyl acetate afforded [4,5,7-²H₃]-6-hydroxy-1,1,3,3-tetramethylindan-2-one, m.p. 267—270° (45%); δ [(CD₃)₂SO] 1.26 (12H, s) and 8.25 (1H, s); ν_{\max} (KBr) 3270 (OH) and 1730 (CO); *m/e* 207 (*M*⁺).

Irradiation of p-Benzoquinone with Tetramethylallene in Methanol.—A mixture of *p*-benzoquinone (0.7 g) and tetramethylallene (2.0 g) in methanol (180 ml) was irradiated

TABLE 2
Photoreaction of *p*-quinones and allenenes in benzene (180 ml)

| Quinone (g) | Allene (g) | Irradiation time (h) | Product (%) | M.p. (°C) | Analysis * | | | |
|---|------------|----------------------|-------------|-----------|----------------|--------------|----------------|----------------|
| | | | | | C (%) | H (%) | O (%) | Cl (%) |
| NQ 1.3 | DA 1.44 | 48 | (IIb) 35 | 88—90 | 79.8 (79.6) | 6.5 (6.2) | 14.0 (14.2) | |
| MBQ 0.72 | TA 2.0 | 46 | (Id) 8 | 128—129 | 76.9 (77.1) | 8.3 (8.3) | | |
| MBQ 0.72 | DA 1.4 | 24 | (Ig) 18 | Liquid | 75.6 (75.8) | 7.7 (7.4) | | |
| Tetrachloro- <i>p</i> -benzoquinone 1.1 | TA 1.8 | 50 | (Ii) 27 | 175—178 | 50.6 (50.8) | 4.2 (4.2) | | 34.7 (34.6) |

* Required values in parentheses.

1,1-dimethylallene (1.44 g) in benzene (180 ml) was irradiated under nitrogen with 360 nm light⁸ for 50 h, using a filter solution of CuSO₄·5H₂O—CoSO₄·7H₂O. The solvent was removed by rotary evaporation to leave a solid, which was chromatographed on silica gel. 20% Ethyl acetate-cyclohexane eluted a solid which was recrystallized from the eluant to give 5-hydroxy-1,1-dimethylindan-2-one (Ib), m.p. 165—166° (35% yield, based on *p*-benzoquinone), δ [(CD₃)₂CO] 1.22 (6H, s), 3.44 (2H, s), 6.7—6.85 (2H, m), 7.1—7.25 (1H, m), and 8.25 (1H, s); ν_{\max} (KBr) 3300 (OH) and 1730 cm⁻¹ (CO); λ_{\max} (MeOH) 287 nm (log ϵ 3.47); *m/e* 176 (*M*⁺) and 148 (Found: C, 74.6; H, 7.0; O, 18.4. C₁₁H₁₂O₂ requires C, 75.0; H, 6.8; O, 18.4%).

A solution of *p*-benzoquinone (0.5 g) and 1,1-dimethylallene (1.5 g) in benzene (180 ml) was irradiated under nitrogen for 70 h with 436 nm light, which was isolated with a combination of filter solutions of CuSO₄·5H₂O in NH₄OH and NaNO₂.²⁶ Similar work-up as above afforded (Ib) in (39%).

The spectral data of the photoadducts are as follows. 1,3-Dihydro-5-hydroxy-3,3-dimethylbenz[e]inden-2-one (IIb); δ [(CD₃)₂CO] 1.30 (6H, s), 3.73 (2H, s), 6.92 (1H, s), and 7.4—8.4 (5H, m); ν_{\max} (KBr) 3300 (OH) and 1725 cm⁻¹ (CO); λ_{\max} (MeOH) 232 (log ϵ 3.48), 302 (2.77), 318 (2.65), 340 nm (2.65); *m/e* 226 (*M*⁺), 211 and 198. 5-Hydroxy-1,1,3,3,4-pentamethylindan-2-one (Id); δ (CCl₄) 1.29 (6H, s), 1.45 (6H, s), 2.28 (6H, s), 5.20 (1H, s), and 6.67 and 6.97 (each 1H, d, *J* 7.5 Hz); ν_{\max} (KBr) 3340 (OH) and 1735 cm⁻¹ (CO); λ_{\max} (MeOH) 271 (log ϵ 3.04) and 280 nm (3.01); *m/e* 218 (*M*⁺).

²⁵ A. I. Vogel, 'Practical Organic Chemistry,' Longmans Green, New York, 1957, p. 745.

under nitrogen with 436 nm light for 55 h. After concentration of the reaction mixture, (Ia) was not detected by t.l.c. (silica gel). The mixture was chromatographed on silica gel with 20% ethyl acetate-benzene to yield hydroquinone in 45% yield. Its m.p. and i.r. spectrum were identical with those of an authentic sample.

Irradiation of p-Benzoquinone in Benzene.—A solution of *p*-benzoquinone (0.7 g) in benzene (180 ml) was irradiated under nitrogen with 360 nm light for 120 h or 436 nm light for 140 h. After concentration of the reaction mixture, t.l.c. (silica gel) showed three spots corresponding to *p*-benzoquinone, hydroquinone, and polymeric compounds.

Quantum Yield Determinations.—Solutions containing various weights of anthracene and *p*-benzoquinone (6.25 × 10⁻⁴ mol) were made up to 25 ml with spectrograde benzene or methanol, and poured into the Pyrex tubes. Solutions containing various weights of tetramethylallene and *p*-benzoquinone (2.5 × 10⁻⁴ mol) were made up to 25 ml with spectrograde benzene and poured into the Pyrex tubes. The tubes were deoxygenated by nitrogen bubbling for 15 min, sealed off, and irradiated in a merry-go-round assembly using a 100 W medium-pressure mercury arc lamp as the central light source. The light source was filtered by a combination of two filter solutions; CuSO₄·5H₂O (0.4 g) in 2.7M-NH₄OH (100 ml) (1 cm path length) and NaNO₂ (60 g) in H₂O (100 ml) (1 cm path length).²⁶ These solutions permitted light of the following wavelength distribution to pass through: 0% 4045—4078 Å, 81% 4358 Å, and 5% 5461 Å.

²⁶ A similar filter solution is recommended for generation of 4358 Å light; J. J. Calbert and J. N. Pitts, jun., 'Photochemistry,' John Wiley, New York, 1966, p. 733.

The temperature of the tubes during irradiation was *ca.* 25 °C. Potassium ferrioxalate actinometry²⁷ was used to determine the lamp intensity. A reliable, reproducible output rate of $1.95\text{--}2.15 \times 10^{15}$ quanta s^{-1} was recorded. The disappearance of *p*-benzoquinone was allowed to run to 15% or less. At the end of the irradiation, naphthalene or benzophenone was added as an internal standard. G.l.c. (20% Silicone DC-550 at 100 °C or Apiezon grease L at 220 °C) allowed the area of the *p*-benzoquinone or 5-hydroxy-1,1,3,3-tetramethylindan-2-one peak to be measured relative to that of internal standard.

5-Acetoxy-1,1-dimethylindan-2-one.—A mixture of (Ib) (0.06 g) and acetyl chloride (10 ml) was refluxed for 1 h. The excess of acetyl chloride was distilled off under reduced pressure, and the crude residue was dissolved in ether (50 ml), washed with saturated aqueous NaHCO_3 and water, and dried (MgSO_4). Evaporation of the solvent under reduced

pressure gave *5-acetoxy-1,1-dimethylindan-2-one* as a viscous liquid (75% yield); δ (CCl_4) 1.24 (6H, s), 2.18 (3H, s), 3.40 (2H, s), and 6.8—7.3 (3H, m); ν_{max} (CCl_4) 1765 (CO) and 1695 cm^{-1} (CO) (Found: C, 71.4; H, 6.5. $\text{C}_{13}\text{H}_{14}\text{O}_3$ requires C, 71.5; H, 6.5%).

Lanthanide-induced Shift Experiments.—Carbon tetrachloride solutions [0.16M in 5-acetoxy-1,1,3,3-tetramethylindan-2-one or 5-acetoxy-1,1-dimethylindan-2-one and 0.01—0.06M in $\text{Eu}(\text{fod})_3$] were prepared. Plots of the chemical shifts (δ) from tetramethylsilane for each of the observed resonances of the methyl protons in the indan-2-ones against $[\text{Eu}(\text{fod})_3]/[\text{Substrate}]$ gave straight lines and their slopes are summarized in Table 1.

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²⁷ C. H. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, 1956, *A*, **235**, 518.