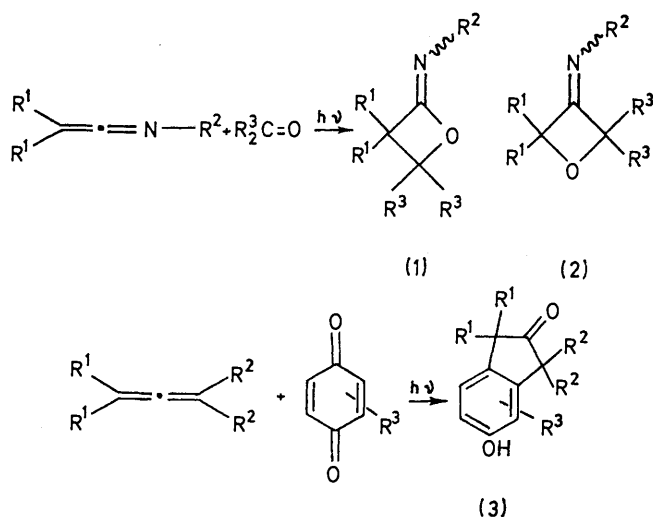


Photoaddition of *p*-Quinones to *N*-(Cyclohexyl)dimethylketenimine

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N-(Cyclohexyl)dimethylketenimine on photoreaction with *p*-benzoquinone and *p*-naphthoquinone forms the 1:1 adducts 1-cyclohexyl-5-hydroxy-3,3-dimethylindolin-2-one and 1-cyclohexyl-1,3-dihydro-5-hydroxy-3,3-dimethylbenz[*g*]indol-2-one, respectively. A mechanism involving addition and rearrangement is proposed.

IN recent years, considerable attention has been directed towards the photoinduced cycloaddition of aldehydes and ketones to olefins and acetylenes to give oxetans and their rearranged products.¹ Allenes also undergo photochemical cycloaddition to aldehydes, ketones,^{2,3}



and thioketones⁴ to form oxetans and thietans. Singer⁵ extended this reaction to ketenimines and obtained imino-oxetans (1) and (2) which result from both possible

directions of addition of aldehydes and ketones to ketenimines. There has been, however, no report on the photochemical addition of *p*-quinones to ketenimines. It was anticipated that ketenimines would undergo cycloaddition to the carbonyl group or the carbon-carbon double bond of *p*-quinones. We recently found⁶ that the photoreaction of *p*-quinones with allenenes afforded 5-hydroxyindan-2-ones (3) which possibly result from rearrangement of a methyleneoxetan intermediate. We report here the photoaddition of *p*-benzoquinone and *p*-naphthoquinone to *N*-(cyclohexyl)dimethylketenimine.

RESULTS AND DISCUSSION

A mixture of *N*-(cyclohexyl)dimethylketenimine and *p*-benzoquinone (BQ) or *p*-naphthoquinone (NQ) was irradiated with a medium-pressure mercury lamp using a filter solution containing CuSO₃·5H₂O and CoSO₄·7H₂O to isolate 330–360 nm light.⁷ In each case chromatography of the reaction mixture yielded one product in significant quantity which was shown to be a 1:1 adduct of the *p*-quinone and the ketenimine on the basis of elemental and mass spectral analysis. The i.r. spectra of the photoproducts exhibited a hydroxy-band at 3200 cm⁻¹ and strong carbonyl bands of a disubstituted amide at 1660 cm⁻¹ for the adduct from BQ and at 1635 cm⁻¹ for that from NQ. The u.v. spectrum of the adduct from BQ showed maxima at 262 (log ε 4.01) and 302 nm (3.35) suggesting the presence of a *p*-

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¹ D. R. Arnold, *Adv. Photochem.*, 1968, **6**, 301, and references cited therein.

² D. R. Arnold and A. H. Glick, *Chem. Comm.*, 1966, 813.

³ H. Gotthardt, R. Steinmetz, and G. S. Hammond, *J. Org. Chem.*, 1968, **33**, 2774.

⁴ H. Gotthardt, *Tetrahedron Letters*, 1971, 2343, 2345; *Chem. Ber.*, 1972, **105**, 2008; H. J. T. Bos, H. Schinckel, and Th. C. M. Wijsman, *Tetrahedron Letters*, 1971, 3905.

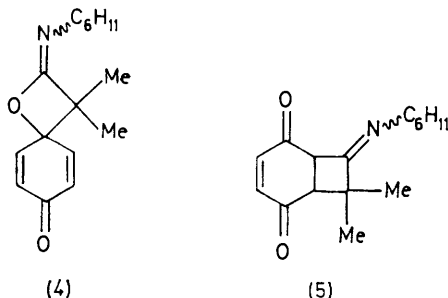
⁵ (a) L. A. Singer and P. D. Bartlett, *Tetrahedron Letters*, 1964, 1887; (b) L. A. Singer and G. A. Davis, *J. Amer. Chem. Soc.*, 1967, **89**, 598; (c) *ibid.*, p. 941; (d) L. A. Singer, G. A. Davis, and V. P. Muralidhar, *ibid.*, 1969, **91**, 897; (e) L. A. Singer, G. A. Davis, and R. L. Knutsen, *ibid.*, 1972, **94**, 1188.

⁶ N. Ishibe and I. Taniguchi, *Tetrahedron*, 1971, **27**, 4883; N. Ishibe, Y. Yamaguchi, and K. Hashimoto, unpublished data.

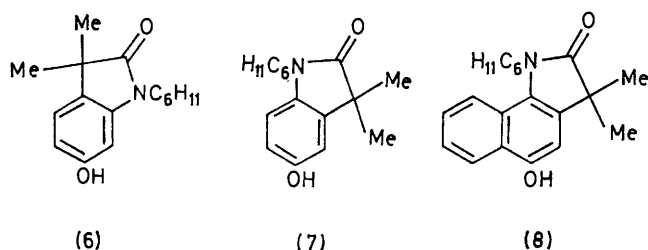
⁷ N. Ishibe, M. Sunami, and M. Odani, *Tetrahedron*, 1973, **29**, 2005.

aminophenol group.⁸ The u.v. spectrum of the adduct from NQ displayed maxima at 238 ($\log \epsilon$ 4.41), 300 (3.80), 311 (3.71), and 324 nm (3.56), indicating an aminonaphthol group.⁹ The presence of the hydroxy-group in the adduct from BQ was confirmed by the formation of an acetate with acetic anhydride. The n.m.r. spectrum of the adduct from BQ exhibited a methyl singlet at δ 1.21 (6H), a cyclohexyl multiplet at 1.4–2.1 (11H), phenyl multiplets at 6.6–6.9 (2H) and 7.0–7.15 (1H), and a broad hydroxy-singlet at 8.15 (1H). The n.m.r. spectrum of the adduct from NQ showed a cyclohexyl multiplet at δ 1.3–1.9 (11H), a methyl singlet at 1.42 (6H), a hydroxy-singlet at 6.95 which disappeared upon addition of deuterium oxide, and a multiplet at 7.2–7.8 (5H).

These spectral properties rule out the possibility of both an imino-oxetan derivative such as (4) and an iminocyclobutane derivative such as (5) for the structure of the photoadduct. The presence of an aminophenol function and the disubstituted amide group in



their spectra suggests that the adducts are indolin-2-ones. The possible structures of the adduct from BQ are (6) and (7). The adduct was identified as (7) by an independent synthesis of (7) and from comparison of its

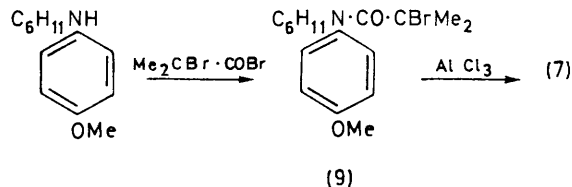


m.p. and mixed m.p., and i.r. and n.m.r. spectra with those of the photoadduct from BQ. An authentic sample of (7) was prepared by treating the anilide (9) with anhydrous aluminum chloride¹⁰ as shown in

* A possibility that thermal rearrangement of an imino-oxetan derivative such as (4) to (7) at room temperature cannot be excluded, since thermal rearrangement of cyclohexa-2,5-dienones is well known.

† The photoaddition of fluorenone to *N*-(cyclohexyl)dimethylketenimine proceeds by way of a singlet fluorenone-ketenimine complex as well as by triplet fluorenone addition.^{5d} Both singlet and triplet states of excited *p*-quinones are, in principle, responsible for the photoaddition of *p*-quinones to *N*-(cyclohexyl)dimethylketenimine.

Scheme 1. The structure of the adducts from BQ and NQ are then assigned as 1-cyclohexyl-5-hydroxy-3,3-dimethylindolin-2-one (7), and 1-cyclohexyl-1,3-dihydro-5-hydroxy-3,3-dimethylbenz[*g*]indol-2-one (8).



SCHEME 1

There was a possibility that the initial photoproduct from BQ is an imino-oxetan derivative such as (4) which isomerizes to (7) during silica gel chromatography. Isomerization of an α -imino-oxetan to a β -lactam occurs during Florosil chromatography of the photoproduct from fluorenone and *N*-(phenyl)ethylphenylketenimine.^{5c} Attempts at direct crystallization of the reaction mixture of BQ and *N*-(cyclohexyl)dimethylketenimine were unsuccessful. The i.r. spectrum of the mixture, after removal of the solvent and starting materials at 70° under reduced pressure (0.1 Torr), did not show a strong absorption band higher than 1700 cm^{-1} which corresponds to the C=N stretching vibration of an imino-oxetan⁵ or the carbonyl band of a β -lactam. The n.m.r. spectrum of this mixture did not exhibit signals due to olefinic protons of a cyclohexa-2,5-dienone function but showed aromatic protons due to (7). These results suggest that 2-indolinone derivatives are formed during irradiation of *p*-quinones and *N*-(cyclohexyl)dimethylketenimine.*

U.v. spectral analysis of BQ and *N*-(cyclohexyl)dimethylketenimine solutions under the preparative conditions revealed that the primary light absorption process is excitation of BQ. This is also supported by the fact that irradiation of a mixture of BQ and *N*-(cyclohexyl)dimethylketenimine at wavelengths longer than 400 nm gave (7). Under these conditions, only the n,π^* state of *p*-quinones is excited,¹¹ since the u.v. spectrum of *N*-(cyclohexyl)dimethylketenimine shows a maximum at 300 nm.^{5b} The lowest triplet energies of BQ and NQ in the n,π^* configuration are 50¹² and 57 kcal mol^{-1} ,¹³ whereas the lower limit on the triplet level of ketenimine was placed at *ca.* 50 kcal mol^{-1} .^{5c} High photoreactivity of BQ towards *N*-(cyclohexyl)dimethylketenimine suggests that energy transfer of excited *p*-quinones to ground-state ketenimine is not important. This was the case in the photocycloaddition of benzophenone and fluorenone to various ketenimines.^{5b,c} Consequently, excited *p*-quinone † adds to ground-state ketenimine to

⁸ R. A. Friedel and M. Orchin, 'Ultraviolet Spectra of Aromatic Compounds,' Wiley, New York, 1951.

⁹ K. Hirayama, 'Constants of Organic Compounds,' ed. M. Kotake, Asakura, Tokyo, 1963, p. 111.

¹⁰ M. N. Kolosov and N. A. Preobrazhenskii, *Zhur. obshchei Khim.*, 1953, **23**, 1179 (*Chem. Abs.*, 1955, **49**, 295g).

¹¹ S. Nagakura and A. Kuboyama, *J. Amer. Chem. Soc.*, 1954, **76**, 1003.

¹² M. Kasha, *Radiation Res.*, 1960, **2**, 243.

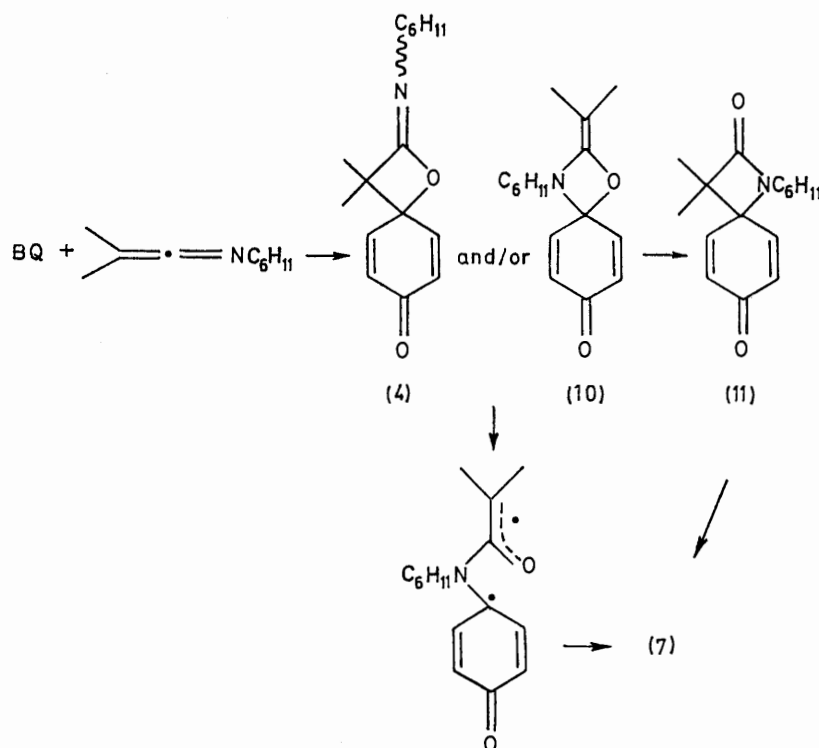
¹³ J. M. Hallas and L. Goodman, *J. Chem. Phys.*, 1965, **42**, 760.

form intermediate (10) and/or (4), although these intermediates were not isolated from the reaction mixture. Photochemical or thermal rearrangement of this adduct to (7) might occur directly and/or *via* the β -lactam (11), as has been observed in the rearrangement of cyclohexa-2,5-dienones to phenol derivatives.¹⁴ In the photoaddition of *p*-quinones to the ketenimine, the formation of an intermediate (10) which results from the cycloaddition of *p*-quinones across the carbon-nitrogen double bond of ketenimine appears to be possible, although the photochemical cycloaddition of aldehydes and ketones across the carbon-nitrogen double bond of ketenimine has not been observed.⁵ In the latter case only cycloaddition of carbonyl compounds across the carbon-carbon double bond of ketenimine occurs. Intermediates (4) and (10) might isomerize

hydroquinol-2(1*H*)-ones is known,¹⁵ the photochemical reaction of *p*-quinones and ketenimines is another example of the photochemical cyclization to indolin-2-ones. It seems to be general that the photoreaction of *p*-quinones with cumulenes, at least such as allenes⁶ and ketenimines, gives the cyclized products through addition-rearrangement reaction.

EXPERIMENTAL

Commercially available *p*-benzoquinone and *p*-naphthoquinone were purified by recrystallization. *N*-(Cyclohexyl)dimethylketenimine was prepared by dehydration of *N*-(cyclohexyl)isobutyramide with phosphorus pentoxide in triethylamine.^{5b} I.r. spectra were obtained using a JASCO DS-402G spectrophotometer. N.m.r. spectra were obtained using a JEOL PS-100 spectrometer with chemical



SCHEME 2

mainly to (6) and (7), respectively. Only (7) was isolated in significant quantity.* While lack of additional evidence prevents identification of the structure of an intermediate, we believe that the photoaddition of *p*-quinones across the carbon-nitrogen double bond of ketenimine is a primary reaction for the formation of 2-indolinone.†

While the photocyclization of acrylanilides to 3,4-di-

* A failure to isolate (6) does not exclude the possibility of the formation of (6), since t.l.c. of the reaction mixture showed several weak spots besides (7). The yield of any (6) formed, however, would be <2%.

† If the β -lactam (11) is an intermediate for the formation of indolin-2-ones, both (4) and (10) are equally important.

shifts reported in p.p.m. downfield of internal tetramethylsilane. U.v. spectra were obtained using a Hitachi 124 spectrophotometer. All mass spectral data were obtained from a Hitachi RMU-6L spectrometer. Microanalytical data were obtained from the Microanalytical Laboratory of Kyoto University.

Irradiation of p-Benzoquinone with N-(Cyclohexyl)dimethylketenimine.—A solution of *p*-benzoquinone (2.3 g) and *N*-(cyclohexyl)dimethylketenimine (2.9 g) in benzene (180 ml) was purged with nitrogen for 1 h before irradiation,

¹⁴ For a review, see A. J. Waring, *Adv. Alicyclic Chem.*, 1966, 1, 241; P. J. Kropp, *Org. Photochem.*, 1967, 1, 1.

¹⁵ Y. Ogata, K. Takagi, and I. Ishino, *J. Org. Chem.*, 1971, 36, 3975, and references cited therein.

and continuously during irradiation. The solution was irradiated for 24 h with a 100 W medium-pressure mercury lamp using a filter solution of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O} - \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ to isolate 330–360 nm light.⁷ After irradiation, the solvent was removed by distillation *in vacuo*, and the residual liquid was chromatographed on a silica gel column, packed as a slurry in benzene. Elution with benzene gave unchanged *p*-benzoquinone and *N*-(cyclohexyl)dimethylketenimine and with ethyl acetate–cyclohexane (2 : 8) a solid (1.30 g, 26% based on the ketenimine). Recrystallization from benzene gave 5-hydroxy-3,3-dimethyl-1-cyclohexylindolin-2-one (7), m.p. 238–239°, mixed m.p. 235–237°, ν_{max} (KBr), 3200, 2910, 2850, 1660, 1600, 1485, 1370, 1355, 1300, 1200, 1140, 895, and 820 cm^{-1} , δ [$(\text{CD}_3)_2\text{SO}$] 1.21 (6H, s), 1.4–2.1 (11H, m), 6.6–6.9 (2H, m), 7.0–7.15 (1H, m), and 8.15 (1H, s), λ_{max} (MeOH) 262 (log ϵ 4.01), 3.2sh nm (3.35), *m/e* 259 (M^+ , 53%), 176 (100), 151 (41), 97 (50), 96 (34), 83 (63), 82 (38), 81 (34), 71 (47), 69 (44), 67 (38), 57 (72), 55 (97), 43 (91), and 41 (75) (Found: C, 74.2; H, 8.35; N, 5.3. $\text{C}_{18}\text{H}_{21}\text{NO}_2$ requires C, 74.15; H, 8.1; N, 5.4%).

Irradiation of a mixture of *p*-benzoquinone (2.1 g) and *N*-(cyclohexyl)dimethylketenimine (2.9 g) in benzene (180 ml) was carried out using a filter solution containing *trans*-, *trans*-1,4-diphenylbutadiene in cyclohexane to cut off light at ca. 400 nm.^{16,*} After irradiation for 24 h similar work-up as above gave (7) in 21% yield.

Irradiation of p-Naphthoquinone with N-(Cyclohexyl)dimethylketenimine.—A solution of *p*-naphthoquinone (3.1 g) and *N*-(cyclohexyl)dimethylketenimine (2.6 g) in benzene (180 ml) was irradiated under nitrogen with 330–360 nm light⁷ for 24 h. After removal of the solvent *in vacuo*, the residual viscous liquid was chromatographed on a silica gel column packed as a slurry in benzene. Elution with benzene gave unchanged *p*-naphthoquinone and *N*-(cyclohexyl)dimethylketenimine and with ethyl acetate–benzene (2 : 8) a solid (1.27 g, 24% based on the ketenimine). Recrystallization from cyclohexane gave 1-cyclohexyl-1,3-dihydro-5-hydroxy-3,3-dimethylbenz[g]indol-2-one (8), m.p. 92–93°, ν_{max} (KBr) 3200, 2920, 2860, 1635, 1590, 1505, 1450, 1350, 1220, 1150, 1055, 825, and 715 cm^{-1} , δ (CCl_4) 1.42 (6H, s), 1.3–1.9 (11H, m), 6.95 (1H, s), and 7.2–7.8 (5H, m), λ_{max} (MeOH) 238 (log ϵ 4.41), 300 (3.80), 311 (3.71), 324 nm (3.56), *m/e* 309 (M^+ , 5%), 307 (7), 226 (19), 211 (16), 183 (69), 88 (28), 86 (47), 84 (57), 68 (53), 56 (100), 55 (66), 43 (33), 42 (32), and 41 (90) (Found: C, 77.6; H, 7.6; O, 10.25. $\text{C}_{20}\text{H}_{23}\text{NO}_2$ requires C, 77.65; H, 7.5; O, 10.35%).

Acetylation of (7).—A mixture of (7) (0.1 g) and acetic

* This filter solution cannot be used to isolate light at 256 nm,¹⁷ but can be used as a cut-off filter.

anhydride (2.5 g) in pyridine (10 g) was refluxed for 3 h. After removal of acetic anhydride and pyridine *in vacuo*, preparative t.l.c. of the residue on silica gel and elution with ethyl acetate–benzene (2 : 8) gave a solid. Recrystallization from petroleum afforded 0.05 g (46%) of 1-cyclohexyl-3,3-dimethyl-2-oxoindolin-5-yl acetate, m.p. 133–137°, ν_{max} (KBr), 2940, 2880, 1765, 1670, 1600, 1485, 1445, 1370, 1340, 1200, 1175, 1015, and 940 cm^{-1} , δ (CCl_4) 1.33 (6H, s), 1.4–2.2 (11H, m), 2.25 (3H, s), 6.7–6.9 (2H, m), and 7.1–7.2 (1H, m) (Found: C, 71.55; H, 7.55; O, 15.9. $\text{C}_{18}\text{H}_{23}\text{NO}_3$ requires C, 71.75; H, 7.65; O, 15.95%).

N-Cyclohexyl-N-(p-methoxyphenyl)- α -bromoisobutyramide (9).— α -Bromoisobutyryl bromide (4.5 g) was added to a solution of *N*-cyclohexyl-*p*-anisidine (2.5 g) in benzene (50 ml) at 0°. The mixture was refluxed for 3 h and the precipitate formed was filtered off. The filtrate was washed with water, 10% hydrochloric acid, and water, and dried (Na_2SO_4). After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel and eluted with ethyl acetate–cyclohexane (2 : 8) to give a solid. Recrystallization from petroleum afforded *N*-cyclohexyl-*N*-(*p*-methoxyphenyl)- α -bromoisobutyramide (0.85 g, 20%), m.p. 84–85°, ν_{max} (KBr) 2920, 2870, 1630, 1505, 1455, 1395, 1360, 1295, 1240, 1165, 1100, 1030, 845, and 750 cm^{-1} , δ (CCl_4) 0.7–2.4 (11H, m), 1.60 (6H, s), 3.78 (3H, s), and 6.73 and 7.07 (each 1H, d, *J* 9.0 Hz) (Found: C, 57.6; H, 6.7; O, 9.2; Br, 22.6. $\text{C}_{17}\text{H}_{24}\text{BrNO}_2$ requires C, 57.65; H, 6.85; O, 9.05; Br, 22.55%).

1-Cyclohexyl-5-hydroxy-3,3-dimethylindolin-2-one.—Anhydrous aluminium chloride (0.63 g) was added slowly to the amide (9) (0.84 g) at 0°. After copious evolution of hydrogen chloride ceased, more anhydrous aluminium chloride (0.63 g) was added at 80°, stirring being begun as soon as the mass liquefied sufficiently. The mixture was then heated for 10 min at 180°, and poured into water. After extraction with ether, the extract was dried (Na_2SO_4). Removal of the solvent *in vacuo* gave 1-cyclohexyl-5-hydroxy-3,3-dimethylindolin-2-one (7) (70%), m.p. 235–236° (from benzene). Spectral properties (i.r., n.m.r., and mass) were identical with those of the photoproduct (7).

We thank Professor F. Mashio of this department for his encouragement during this work.

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¹⁶ M. Koizumi, S. Shida, S. Kato, N. Mataga, and A. Imamura, 'Zikken Kagaku Koza,' ed. M. Kotake, Maruzen, Tokyo, 1956, vol. 6, p. 268.

¹⁷ J. G. Calvert and J. N. Pitts, jun., 'Photochemistry,' Wiley, New York, 1966, p. 730.