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Synthetic Photochemistry. XXX.[1] The Addition Reactions of Cycloheptatriene with Some Aromatic *p*-Quinones[2]

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The photochemical reactions of cycloheptatriene with *p*-benzoquinone and 1,4-naphthoquinone yielded the spirocyclic ethers, which had 7-oxabicyclo[4.2.1]nona-2,4-diene structures, by the characteristic (6+2)π cycloaddition process. The latter quinone further produced the carbocyclic (2+2)π and (6+2)π cycloadducts.

Previously, we have investigated the photoaddition reactions of cycloheptatriene (**1**) with methyl 2,4-dioxopentanoate, an enolized β-diketone,[3] and benzil and methyl pyruvate, α-dicarbonyl compounds,[4] to give the ene-reaction products in the major process; in the cases of the β-diketone, the (4+2)π and (6+2)π cycloadducts were also produced. From cyclic α-dicarbonyl compounds such as acenaphthenequinone and 1,2-naphthoquinone,[5] various kinds of cycloadducts were formed; the former gave the (2+2)π and (6+2)π cycloadducts along with the ene-reaction products, and the latter, the (6+2)π, (4+2)π, and (4+4)π cycloadducts. Thus, since **1** is remarkable in giving various *peri*-cycloadducts in the photoinduced reactions, we have been interested in *p*-quinones, the conjugated dicarbonyl compounds. Although the photochemical reactions of aromatic quinones with olefins have been widely studied,[6] studies of the reactions of **1** with *p*-quinones have been limited to those of 1,4-naphthoquinone (NQ) in benzene to give the so-called "1:1-spirooxetane adduct" (**2**),[7] which does, however, seem to lack a sound rationale for its structure deduction. Other than this, the recent photo-induced cycloaddition of duroquinone has been reported to form cage compounds (**3** and **4**).[8]

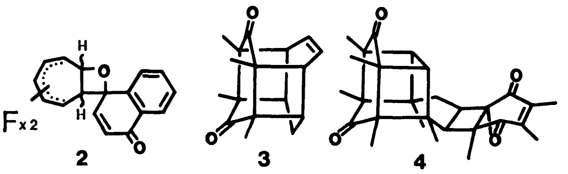
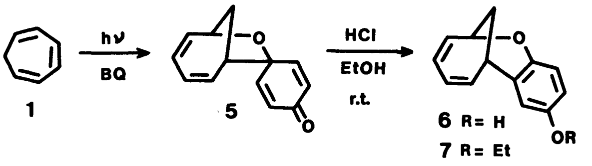


Chart 1.

Results and Discussion

Upon the irradiation of a benzene solution of *p*-benzoquinone (BQ) and **1**, an oily 1:1-adduct (**5**) was obtained in 50—70% yields. Its structure was determined by the following spectroscopic data: the appearance of eight olefinic protons and four aliphatic protons in the ^{1}H NMR and only one carbonyl carbon at the ^{13}C NMR spectra indicated it to be a 1:1-adduct between the carbonyl part of BQ and the olefinic part of **1**. In order to determine the pericyclic mode of the addition, the decoupling experiments by double irradiation (NMDR) were performed in the presence of a lanthanoide-shift reagent. The irradiation of the doublet (*J*=13 Hz) at δ=3.21 (H-a) caused the doublet of triplets (*J*=13, 6.5 Hz) at 3.64 (H-b) to collapse to a triplet (*J*=6.5). The irradiation of H-b caused both the doublet of H-a and the triplet (*J*=6.5 Hz) at 5.48 (H-d), which was assigned to the proton at the ethereal carbon, to collapse to a singlet and a doublet (*J*=6.5 Hz) respectively. The irradiation of the triplet (*J*=6.5 Hz) at 4.00 (H-c) caused H-b to collapse to a doublet of doublets (*J*=13, 6.5 Hz). Therefore, the two allylic protons (H-d and H-c) did not spin-couple in each other. The observed magnitude (*J*=13 Hz) of the gem-coupling constant for the non-allylic methylene protons should be appropriate for that of a tetrahydrofuran. Consequently, **5** must be the (6+2)π cycloadduct.

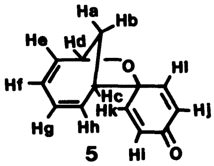
The treatment of the adduct **5** with hydrogen chloride in ethanol resulted in its conversion to a phenol derivative (**6**) and its ethyl ether (**7**) *via* the dienone-phenol rearrangement.



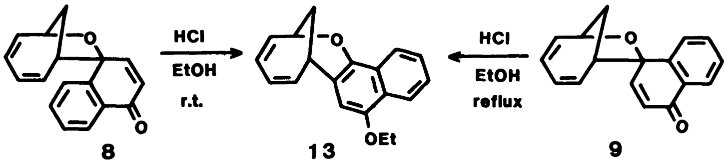
Scheme 1.

Subsequently, the photoreaction of **1** with 1,4-naphthoquinone (NQ) was investigated. In the literature,[7] the formation of an oxetane derivative (**2**), as orange crystals, has been described, but this mode of the reaction was quite different from that in our present study. This might be also worth reinvestigating. Thus, when a benzene solution of NQ and **1** was exposed to a 400-W high-pressure mercury lamp, four 1:1-adducts (**8**, **9**, **10**, and **11**) were formed in a ratio of 58:4:17:21, in addition to a dehydro derivative (**12**) of **11**. The structures of these compounds were confirmed by the chemical and spectroscopic evidence. The ^{1}H NMR spectra of **8** and **9** closely resemble each other; when we compare

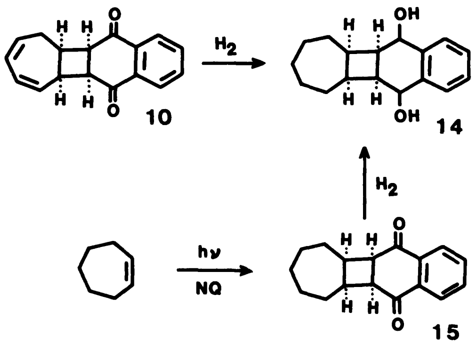
Table 1. The NMR data of 5 and the NMDR data of 5(31.4 mg) and Eu(dpm)$_3$(60.7 mg) in CDCl$_3$

	5	5+Eu(dpm)$_3$					
Ha		3.21, d(13)	irr	s	x	x	x
Hb	2.75, m	3.64, dt(13, 6.5)	t(6.5)	irr	dd(13, 6.5)	dd(13, 6.5)	x
Hc		4.00, t(6.5)	x	—	irr	x	d(6.5)
Hd	4.70, t(6.5)	5.48, t(6.5)	x	d(6.5)	x	irr	d(6.5)
He							
≀		6.40, m	x	x	o	o	irr
Hh	5.90, m				 5		
Hi		10.64, d(9.5)					
Hj		10.76, d(9.5)					
Hk	6.71, dd(9.5, 3)	8.22, dd(9.5, 3)					
Hl	7.01, dd(9.5, 3)	8.58, dd(9.5, 3)					

The symbols used here are defined as follows: o, changed; x, unchanged; —, unobserved. The values shown in parentheses are the coupling constants (J)/Hz.



Scheme 2.



Scheme 3.

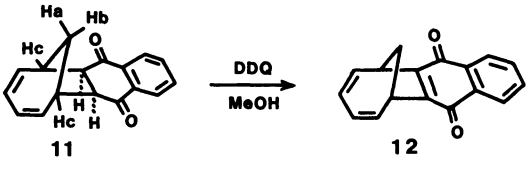
the chemical shifts of the corresponding pairs of hydrogens, one of the methylene protons of **9**, at 2.40, appeared in a higher field than that of **8**, at 2.68, and one of the four vinyl protons of **8**, at 5.10, caused a marked up-field shift, while all four vinyl protons of **9**, from 5.7 to 6.7, behaved normally. Therefore, the stereochemistries of **8** and **9** were deduced to be as depicted in Scheme 2. It is interesting that the sterically more crowded isomer, **8**, was predominant over the less crowded isomer, **9**.

The addition of hydrogen chloride in ethanol at room temperature also caused the dienone-phenol rearrangement of **8** to an aromatized ethyl ether (**13**), while it was necessary to reflux **9** to get the same product (**13**).

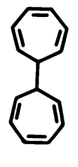
The third photoproduct (**10**) showed a rather poorly resolved ^{1}H NMR spectrum. However, since the methylene protons at 2.49 and 2.74 were proven to be allylic carbon by NMDR experiments, **10** can not be a (6+2)π cycloadduct. The catalytic reduction of **10** with platinum(IV) oxide gave an octahydro derivative (**14**), which was identical with the reduction product, a tetrahydro derivative, of one of the photoproducts (**15**) of NQ with cycloheptene. Therefore, **10** is a (2+2)π cycloadduct.

Next, the fourth product, **11**, was deduced from the NMDR experiments to be a symmetrical *exo*-(6+2)π cycloadduct. The irradiation of olefinic protons caused the broad doublet of doublets (J=7.5, 6 Hz) at 3.25 (H-c) to collapse to a broad doublet (J=6 Hz), but it did not affect the broad doublet signal (J=13 Hz) at 1.87 (H-a) or the doublet of triplets (J=13, 6 Hz) at 2.04 (H-b). The coupling constant between H-c and H-d, being nearly zero, led us to conclude that the geometry of the ring juncture was that of the *exo*-adduct.

The remaining product, **12**, also exhibited a symmetrical ^{1}H NMR spectrum; the results of the elemental analysis suggested that it was a dehydrogenation product of **11**. Indeed, the DDQ (2,3-dichloro-5,6-dicyano-*p*-benzoquinone)-treatment of **11** afforded **12**.



Scheme 4.



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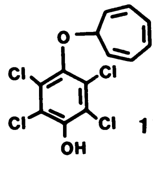

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Chart 2.

The attempted photoreaction of **1** with 2,3,5,6-tetrachloro-*p*-benzoquinone (CB) gave no cycloadduct; the only products identified were the hydroquinone of CB and 1,1′-bicycloheptatrienyl (1,1′-bitropyl, **16**),[5,9] not the formerly reported monotropyl ether of tetrachlorohydroquinone (**17**).[10] Thus, CB behaved as an oxidizing agent rather than as a photocycloaddend toward **1**.

In conclusion, the photoreaction of **1** with BQ gave the single (6+2)π photoproduct, which coupled at the carbonyl group and the triene function of **1**, while the photoproducts of **1** with NQ, (6+2)π and (2+2)π cycloadducts, were derived from both the C=O group and the C=C group. This can be explained in terms of the nature of the excited species; that is, the lowest triplet of BQ is an n,π* excited state, while that of NQ is thought to be considerably mixed with the n,π* and π,π* excited states.[11] The absence of any (4+2)π adduct in the photoproducts is consistent with the prediction based on the Woodward-Hoffmann rule,[12] but is in contrast to the reaction with a unique photocycloaddend, methyl 2,4-dioxopentanoate.[3]

Experimental

All the mps, which were measured by means of a Yanagimoto Micro-mp Apparatus, are uncorrected. The irradiations were performed by means of a 400-W high-pressure mercury lamp through a Pyrex glass filter, with running water-cooling under a nitrogen atmosphere. Elemental analyses were performed either at the Research Institute of Industrial Science or at the Analyses Center, Faculty of Science, Kyushu University. The NMR spectra were measured by the use of a JEOL FX 100 Spectrometer in a $CDCl_3$ solution, unless otherwise specified; the chemical shifts were expressed in δ unit from the internal Me_4Si. The mass spectra were measured by means of a JEOL 01SG-2 Spectrometer. The IR spectra were taken in either as KBr disks or as inserted liquid film between NaCl plates using a Jasco IR-A 102 spectrometer. All the UV spectra were taken by means of a Hitachi 124 Spectrophotometer in methanol.

Photoaddition of 1 with BQ. An anhydrous benzene solution (5 cm^3) of **1** (916 mg) and BQ (541 mg) was irradiated for 8.5 h. The mixture was filtered to remove the polymeric solid, and then, the filtrate was evaporated *in vacuo* to a give viscous syrup (1.2 g), which was chromatographed on a silica-gel column with benzene to yield a pale yellow oil; bp 115—118 °C (bath temp)/2 mm Hg, 681 mg (68%), **5** [Found: C, 77.72; H, 6.12%. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04%. ^{13}C NMR δ=31.1, 47.3, 75.0, 89.1, 125.0, 126.8, 127.4, 127.8, 133.1, 133.6, 148.1, 149.9, and 184.6. λ_{max}: 228 nm (ε=15500), 264.5 (4400). *m/z*: 200 (M^+)].

Acid-catalyzed Rearrangement of 5. The photoadduct **5** (36.8 mg) was dissolved in EtOH (3 cm^3) containing concd HCl (0.03 cm^3), after which the mixture was kept at room temperature for 80 min with stirring. The mixture was then poured into water and extracted with ether. The extract was dried on $MgSO_4$ and chromatographed on a silica-gel column with benzene to yield a colorless oil; 23.2 mg (55%), **7** [Found: C, 79.07; H, 7.11%. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06%. ^1H NMR δ=1.33 (3H, t, *J*=7 Hz), 1.96 (1H, ddd, *J*=14, 2.5, 1 Hz), 2.58 (1H, ddd, *J*=14, 6, 4.5 Hz), 3.68 (1H, br. t, *J*=6 Hz), 3.93 (2H, q, *J*=7 Hz), 4.93 (1H, m), and 5.75—6.9 (7H, m). ^{13}C NMR δ=14.9, 28.9, 29.7, 33.5, 63.7, 114.0, 115.4, 117.9, 124.1, 125.0, 128.5, 131.9, 137.8, 146.2, and 152.6. λ_{max}: 222 nm (ε=12500), 249 (5000), 292 (2900). *m/z*: 228 (M^+)], and colorless crystals; mp 85—87 °C; 8.3 mg (23%); **6** [Found: 78.08; H, 6.02%. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04%. ^1H NMR δ=1.98 (1H, ddd, *J*=14, 2, 1 Hz), 2.56 (1H, ddd, *J*=14, 6.5, 4 Hz), 3.68 (1H, dd, *J*=8.5, 6.5 Hz), 4.94 (1H, m), and 5.7—6.1 (3H, m). ^{13}C NMR δ=28.9, 33.3, 70.7, 114.8, 116.2, 118.1, 124.4, 125.1, 128.7, 131.8, 137.7, 146.1, and 149.0. ν: 3460, 3360 cm^{-1}. *m/z*: 200 (M^+)].

Photoaddition of 1 to NQ. An anhydrous benzene solution (10 cm^3) of **1** (920 mg) and NQ (790 mg) was irradiated for 1.5 h. The resultant mixture was chromatographed on a silica-gel column with hexane-benzene to afford a colorless oil; 292 mg (35%); **8** [Found: C, 81.37; H, 5.85%. Calcd for $C_{17}H_{14}O_2$: C, 81.58, H, 5.64%. ^1H NMR δ=2.68 (1H, d, *J*=12.5 Hz), 2.73 (1H, t, *J*=7 Hz), 3.00 (1H, td, *J*=12.5, 7 Hz), 4.76 (1H, t, *J*=7 Hz), 5.10 (1H, dd, *J*=11, 7 Hz), 5.6—6.2 (3H, m), 6.05 (1H, d, *J*=10.5 Hz), 7.18 (1H, d, *J*=10.5 Hz), and 7.2—8.0 (4H, m). ^{13}C NMR δ=32.4, 52.3, 74.6, 95.3, 125.8, 125.9, 127.2, 127.6, 128.2, 128.9, 130.9, 131.3, 133.0, 134.9, 141.0, 152.2, and 184.4. λ_{max}: 224 nm (ε=12500), 242.5 (9500), 253 (10200), 270 (sh., 7600). *m/z*: 250 (M^+)], a colorless oil; 20.5 mg (2.4%); **9** [Found: C, 81.49; H, 5.72%. ^1H NMR δ=2.40 (1H, d, *J*=12 Hz), 2.5—3.2 (2H, m), 4.85 (1H, br. t, *J*=6 Hz), 5.7—6.7 (4H, m), 6.17 (1H, d, *J*=10.5 Hz), 7.28 (1H, d, *J*=10.5 Hz), and 7.2—8.2 (4H, m). ν: 1680, 1607 cm^{-1}], colorless crystals; mp 103—104 °C; 108 mg (13%); **10** [Found: C, 81.37; H, 5.72%. ^1H NMR δ=2.49 (1H, ddd, *J*=13, 6.5, 4.5 Hz), 2.74 (1H, ddd, *J*=13, 9, 4 Hz), 3.0—3.6 (3H, m), 3.80 (1H, dd, *J*=9, 7.5 Hz), 5.95 (4H, m), and 7.6—8.2 (4H, m). ν: 1680, 1600 cm^{-1}], colorless crystals; mp 87—88 °C; 81.2 mg (10%); **11** [Found: C, 81.48; H, 5.67%. ^1H NMR δ=1.87 (1H, br. d, *J*=13 Hz), 2.04 (1H, dtm, *J*=13, 6 Hz), 3.25 (2H, dd, *J*=7.5, 6 Hz), 3.74 (2H, br. s), 5.84 (2H, dt, *J*=12, 3.5 Hz), 6.0—6.2 (2H, m), 7.6—7.9 (2H, m), and 8.0—8.2 (2H, m). ^{13}C NMR δ=31.3, 44.0, 62.1, 125.1, 126.7, 133.9, 134.9, 136.8, and 195.8. ν: 1673, 1588 cm^{-1}], and yellow crystals; mp 160—162 °C; 35 mg (8%); **12** [Found: C, 82.14; H, 4.83%. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87%. ^1H NMR δ=1.69 (1H, d, *J*=12 Hz), 2.36 (1H, dtt, *J*=12, 7, 1.5 Hz), 3.98 (1H, t, *J*=7 Hz), 5.8—6.3 (4H, m), 7.6 (2H, m), and 8.2 (2H, m). ν: 1645, 1590, 1583 cm^{-1}], and recovered NQ, 260 mg.

Acid-catalyzed Rearrangement of 8. The photoadduct **8** (65.7 mg) was dissolved in EtOH (5 cm^3) containing concd

HCl (0.03 cm^3), after which the mixture was kept at room temperature for 22 h. Then, the mixture was poured into water and extracted with ether. After drying on $MgSO_4$, the extract was chromatographed on a silica-gel column with benzene to yield colorless plates; mp 129—130 °C; 15.4 mg (21%); **13** [Found: C, 81.79; H, 6.52%. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52%. ^{1}H NMR δ=1.47 (3H, t, J=7 Hz), 2.04 (1H, ddd, J=14, 2.5, 1 Hz), 2.68 (1H, ddd, J=14, 5.5, 4 Hz), 3.68 (1H, dddd, J=8.5, 5.5, 2, 1 Hz), 4.08 (2H, q, J=7 Hz), 5.14 (1H, m), 5.7—6.5 (4H, m), 6.40 (1H, s), and 7.2—8.2 (4H, m). ν: 1628, 1595 cm^{-1}].

Acid-catalyzed Rearrangement of 9. Similarly, an EtOH solution (5 cm^3) of **9** (36.1 mg) and concd HCl (0.03 mg) was refluxed to yield colorless crystals (mp 129—130 °C; 17 mg (42%)), which were identical in every respect with the sample of **13** obtained from **8**.

Photoreaction of Cycloheptene with NQ. An anhydrous benzene solution (10 cm^3) of cycloheptene (1.95 g) and NQ (1.58 g) was irradiated for 22.5 h. Silica-gel column chromatography of the reaction mixture afforded colorless crystals; mp 71.5—72 °C; 140 mg (11%); **15** [Found: C, 80.08; H, 7.08%. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13%. ^{1}H NMR δ=1.0—2.2 (10H, m), 2.4—2.9 (2H, m), 3.0—3.2 (2H, m), and 7.6—8.1 (4H, m). ν: 1680, 1595, 1295, 1280 cm^{-1}], and recovered NQ, 786 mg (50%).

Catalytic Reduction of 10. An MeOH solution (4 cm^3) of **10** (46.1 mg) was hydrogenated with PtO_2. The subsequent removal of the solvent left the octahydro derivative (**14**) of **10**; 46.8 mg (100%); colorless crystals; mp 248—250 °C [Found: C, 78.69; H, 8.67%. Calcd for $C_{17}H_{22}O_2$: C, 79.03, H, 8.58%. ν: 3420, 2940, 1460, 1325, 1040, 750 cm^{-1}].

Catalytic Reduction of 15. An MeOH solution (2 cm^3) of **15** (23 mg) was similarly hydrogenated with PtO_2. The product isolated consisted of colorless crystals (mp 248—250 °C, 22.1 mg (95%)), which were identical in every respect with the authentic **14**.

Dehydrogenation of 11 with DDQ. An MeOH solution (2 cm^3) of **11** (51.7 mg) was refluxed with DDQ (50.2 mg) for 2 h. After the solvent had been removed *in vacuo,* the residue was chromatographed on a silica-gel column to give colorless crystals (mp 158—160 °C; 40.1 mg (78%)), which were identical in every respect with **12**.

Photoreaction of 1 with CB. An anhydrous benzene solution of **1** (2 g) and CB (1.22 g) was irradiated for 3 h. The reaction mixture was then filtered to remove an insoluble solid, which consisted of recovered CB and its hydroquinone (1.04 g (85%)); the filtrate was then chromatographed on a silica-gel column to give **16** (33 mg; colorless plates; mp 62.5—63.5 °C), whose identity with an authentic sample (lit,[5] mp 64—67 °) was confirmed by direct comparisons.

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