The Thermal Addition Reactions of Cycloheptatriene with Aromatic *p*-Quinones[1)]

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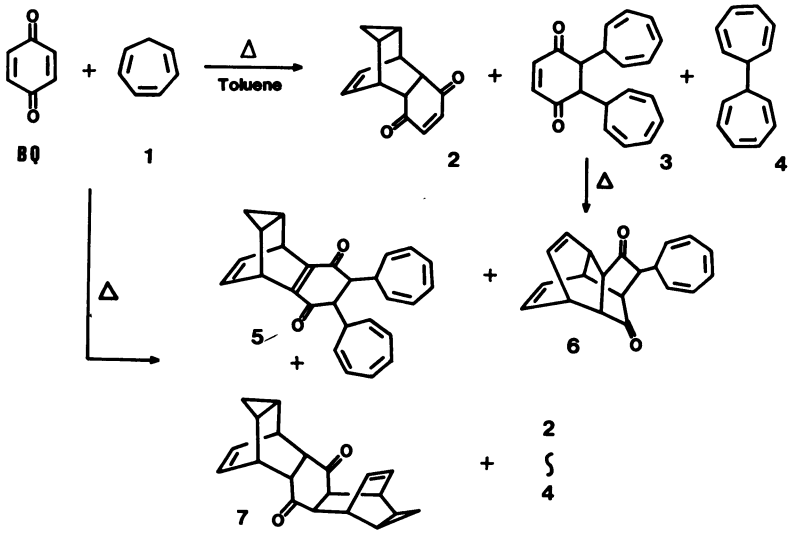
Thermal addition reactions of cycloheptatriene with several aromatic *p*-quinones gave the Diels-Alder adducts as minor products; the most characteristic feature was the formation of the *vic*-ditropylation products. The mechanism of their formation was clarified to be a sequential ene-reaction and dehydrogenation by means of chemical conversion from the isolated intermediates. Several new other additions, *e.g.*, successive Diels-Alder reactions, were also noted.

Previously, we have reported the characteristic behavior of cycloheptatriene (tropylidene, **1**) in reactions with several carbonyl compounds[2)] and aromatic quinones[3)] upon UV-light irradiations. Under these circumstances, the methylene hydrogens of **1** are extremely reactive toward the hydrogen-abstraction process because of the stability of the resultant symmetrical cycloheptatrienyl (tropyl) radical. In this connections, the thermal behavior of **1** toward aromatic quinones, which are frequently-used dienophiles[4)] and typical oxidizing agents, must also be interesting; once the stable tropyl radical is formed, it may behave differently to give products other than the Diels-Alder adducts. Herein, we wish to report our findings.

Results and Discussion

The Reaction of 1 with p-*Benzoquinone.* When a toluene solution of **1** and *p*-benzoquinone (BQ) was refluxed for 1 h, two products, 1:1-adduct (**2**) and 1:2-adduct (**3**), were isolated, along with some amounts of 1,1′-bi(cyclohepta-2,4,6-trienyl) (bitropyl, **4**)[5)] and BQ and hydroquinone (H_2BQ), which were precipitated as quinhydrone. The **2** was shown to be the ordinary Diels-Alder adduct by the appearance of four cyclopropane ring protons in the ^1H NMR spectrum. The **3** (21% yield)[6)] was shown to be a *vic*-ditropylation product; its ^1H NMR spectrum revealed a symmetrical element in its structure, showed signals ascribable to tropyl groups, and overlapped two olefinic protons. The presence of an enedione chromophore was evidenced by the IR carbonyl stretching vibration absorption peak at ν: 1685 cm^{-1}.

On the other hand, the thermal reaction of **1** and BQ without a solvent gave more complicated results. In addition to **2** (4%), **3** (6%), and **4** (15%), new products (**5**, **6**, and **7**) were isolated after repeated silica-gel column chromatography; another *vic*-ditropylation product, **5** (5%), showed its molecular



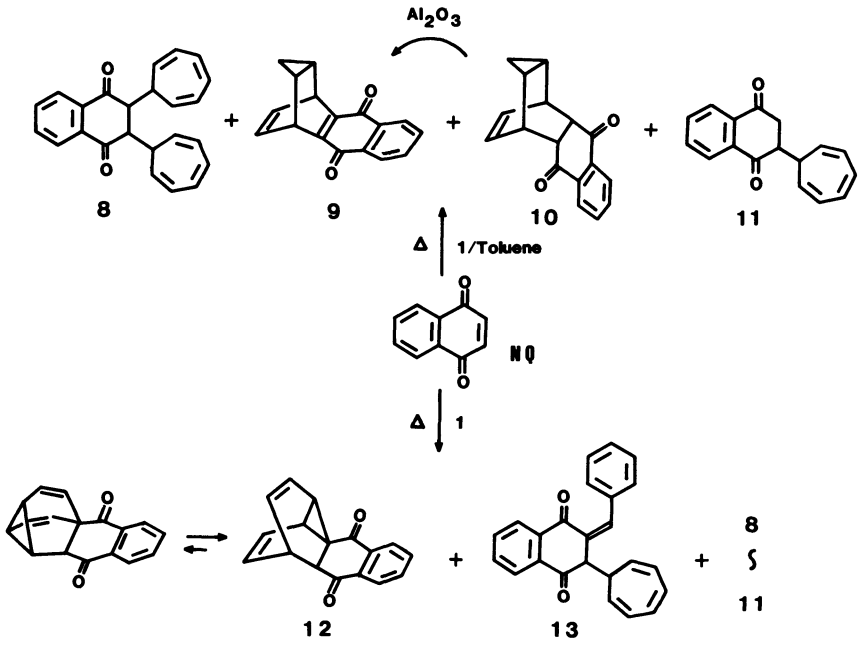
Scheme 1.

weight to be 380, and disclosed four cyclopropane ring protons and an enedione chromophore [ν: 1665, 1582 cm^{-1}]. Therefore, **5** must correspond to the ditropylation product derived from the dehydrogenation products of **2**. A cage compound, **6** (1%), revealed four olefinic protons other than those of the tropyl group in the ^1H NMR spectrum, while a carbonyl absorption at ν: 1730 cm^{-1} in the IR spectrum indicated it to be a strained cycloalkanone derivative. These feature requires the formation of two more C–C bonds. In fact, **6** could be prepared by a thermal isomerization reaction, an intramolecular Diels-Alder process, of **3** by refluxing in **1**.

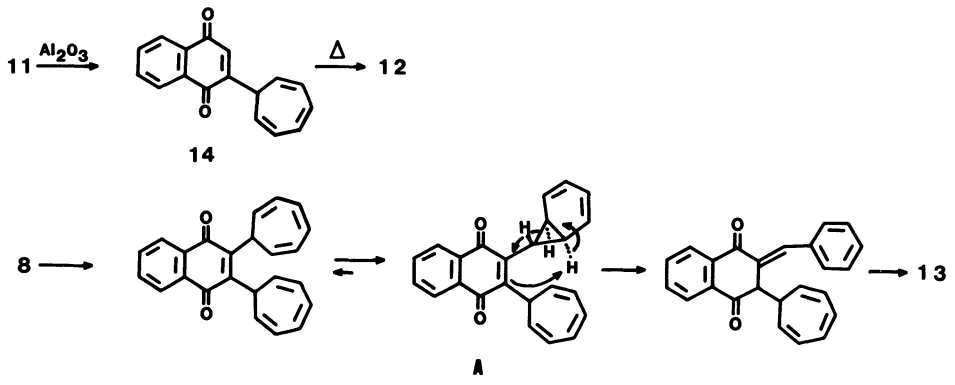
The structure of the remaining product, **7** (2%), a 1:2-adduct, showed the presence of a symmetrical element in the ^1H- and ^{13}C NMR spectra; it was deduced to be the two-fold Diels-Alder adduct of BQ with the norcaradiene form of **1**. Scheme 1 shows the deduced structures.

The Reaction of 1 with 1,4-Naphthoquinone. When a toluene solution of **1** and 1,4-naphthoquinone (NQ) was refluxed for 12 h, a complicated mixture was obtained. After repeated chromatographic work-ups, the products characterized, besides **4**, were a colorless oil (**8**, 0.6%), yellow needles (**9**, 16%), colorless plates (**10**, 22%), and a yellow oil (**11**, 5%). Their structures were unambiguously determined by NMR spectral analysis; **8** was the ditropylation product, **10** was the Diels-Alder product of NQ and the norcaradiene form of **1**, **9** was the dehydrogenation product of **10**,[7] and **11** was the monotropylated intermediate.

The reaction without any diluent yielded, together with **8** (2%), **9** (10%), **10** (7%), and **11** (1%), two more



Scheme 2.



Scheme 3.

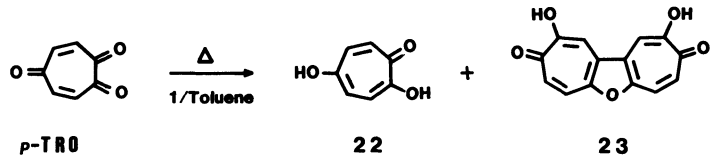
by-products, faintly brownish crystals (**12**, 3%) and a colorless oil (**13**, 6%). The **12**[8] was determined to be the intramolecular Diels-Alder product of the dehydrogenated derivative (**14**) of **11**. In fact, the heating of **14**, obtained by placing **11** in contact with a basic alumina, gave **12**. The **13** was deduced to be a benzylidene derivative derived from **8**. Its formation can be explained in terms of a sterically-favored valence tautomerization to the norcaradiene form for one of the tropyl group in dehydrogenated 2,3-ditropyl-1,4-naphthoquinone, **A**, and its isomerization *via* a $2\pi+2\sigma+2\sigma$-process.

The Reaction of 1 with p-*Toluquinone, Phenyl*-p-*benzoquinone, Chloro*-p-*benzoquinone, and 2,6-Dimethyl*-p-*benzoquinone.* When **1** was allowed to react with *p*-toluquinone (TQ) in toluene, two products, a Diels-Alder adduct (**15**, 18%) and a *vic*-ditropylation product (**16**, 14%) were obtained, while without the diluent, again, the formation of an additional compound (**17**, 6%) was observed, together with **4** (1.6%), **15** (15%), and **16** (18%). Similar products (**18**—**21**) were obtained from phenyl-*p*-benzoquinone (PQ), chloro-*p*-benzoquinone (CQ), and 2,6-dimethyl-*p*-benzoquinone (XQ). The structures of these adducts are illustrated in Chart 1.

It is also known to form cycloheptatrienium ion by the action of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) to **1** in an acidic solution,[9] and the formation of two-electron oxidized products from **1** must be important in the organic syntheses. *p*-Tropoquinone (*p*-TRQ), whose oxidation potential is higher than those of the corresponding *p*-benzoquinones,[10] should be interesting from a comparative point of view; in fact, the reaction resulted in the reductive formation of 5-hydroxytropolone (**22**) and 2,10-dihydroxydicyclohepta[*b*,*d*]furan-3,9-dione (**23**),[11] showing an occurrence of the oxidation of **1** rather than of the addition reaction. On the contrary, *p*-TRQ is known to give the Diels-Alder adducts with cyclopentadiene.[12]

It is well known that **1** gives the Diels-Alder adducts, mostly having a tautomeric norcaradiene form, by reactions with many dienophiles. However, the reaction with aromatic quinones, *e.g.*, *p*-benzoquinones, under the Diels-Alder conditions predominantly yielded the hydrogen-abstraction products, as one can see from the production of quinhydrone. Moreover, the formation of the ditropylation products might also be such a case, for it requires one mole of the dehydrogenation process.

Previously, we have proven the electrocyclic formation of **8** from NQ and **4** under photochemical conditions;[13] the irradiation of NQ and **4** in benzene by means of a high-pressure mercury lamp by cutting off the light shorter in wavelength than 300 nm with a Pyrex glass filter. However, the ditropylation with **4** does not occur under thermal conditions; it merely results in the production of a complicated intractable mixture, and **8** is undetectable. Whatever the mechanisms are, the ditropylation products must be formed *via* a sequential, step-by-step mechanism. In this point, an independent addition reaction of **1** to a monotropylation product like **14** seemed worth trying. Unfortunately, such an experiment went far beyond our expectations; when **14** was heated with **1**, the only product, obtained in a 28% yield from the



Scheme 4.

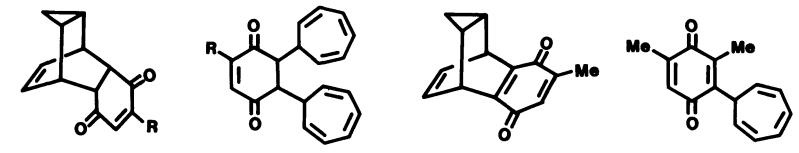
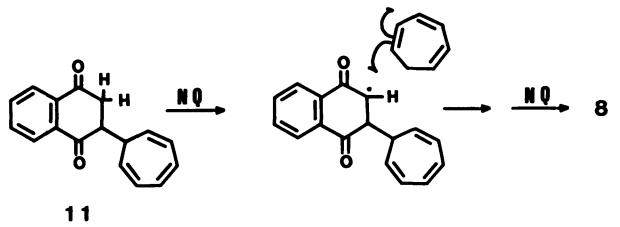


Chart 1.



Scheme 5.

mixture, was the barbaralane derivative, **12**. Moreover, when a mixture of **1**, **11**, and NQ was heated to reflux, the products isolated were **8**, **9**, and **10**, while a similar treatment of **11** and NQ in toluene instead formed **9** and **12**; the formation of **12** from **11** and the formation of **9** and **10**, at the same time, proved it easy for NQ-dehydrogenation to occur, though the resultant dehydro intermediates were reluctant to give 1:2-products because of a competitive intramolecular reaction.

In conclusion, it is clear that the quite active methylene group of **1** determines the predominant course of the reaction depending on the nature of the other cycloaddends, *i.e.*, with quinones, the formation of the symmetrical tropyl radical *via* the abstraction of hydrogen is the primarily favored step.

Experimental

All the mps, which were measured by means of a Yanagimoto Micro-mp Apparatus, were uncorrected. The elemental analyses were performed either at the Research Institute or at the Analyses Center, Faculty of Science, Kyushu University. The NMR spectra were measured by means of a JEOL FX 100 Spectrometer in $CDCl_3$ unless otherwise specified, and the chemical shifts are expressed in δ units from the internal Me_4Si. The mass spectra were measured by means of a JEOL OISG-2 Spectrometer. The IR spectra were measured by means of a Jasco IR-A 102 Model Spectrometer. The UV spectra were measured by means of a Hitachi 124 Model Spectrophotometer in methanol. The silica-gel used in this study was Wako Gel C 300.

Thermal Reaction of 1 with BQ. *a)* A toluene solution (8 cm^3) of **1** (2 cm^3) and BQ (1.08 g) was refluxed for 1 h. The mixture was then filtered to remove the insoluble material, from which quinhydrone (375 mg) was isolated. The subsequent evaporation of the filtrate *in vacuo* left a residual mass, which was chromatographed on a silica-gel column, with benzene–ether (8:2) as the eluent, to yield colorless, crystalline **4** (mp 62.5—63.5 °C (lit, [5] 61 °C), 10.4 mg; 0.9%), pale yellow crystalline **2** (mp 113—114 °C, 150.6 mg; 11% [Found: C, 77.83; H, 6.04%. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04%. ^{1}H NMR δ=0.04 (1H, dt, J=5.5, 4 Hz), 0.14 (1H, td, J=7, 5.5 Hz), 1.12 (2H, m), 3.02 (2H, t, J=1.5 Hz), 3.48 (2H, ddm, J=4.5, 1.5 Hz), 5.76 (2H, dd, J=4.5, 3.5 Hz), and 6.62 (2H, s). ν: 1665, 1615 cm^{-1}. λ_{max}^{MeOH}: 233 nm (ε=11700)]), and pale yellow crystalline **3** (mp 112—113.5 °C; 205 mg; 21% [Found: C, 82.53; H, 6.21%. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25%. ^{1}H NMR δ=1.90 (2H, dt, J=11, 6 Hz), 3.30 (2H, d, J=11 Hz), 5.20 (2H, dd, J=9.5, 6 Hz), 5.27 (2H, dd, J=9.5, 6 Hz), 6.23 (2H, dt, J=9.5, 3 Hz), 6.32 (2H, dt, J=9.5, 3 Hz), 6.59 (2H, s), 6.70 (2H, d, J=3 Hz), and 6.73 (2H, d, J=3 Hz). ν: 1685, 1600 cm^{-1}. λ_{max}^{MeOH}: 234 nm (ε=11100), 266 (4300)]). Additional amounts of BQ (166 mg; 15%) and H_2BQ (72 mg; 7%) were then obtained from the later elutions.

b) A mixture of **1** (20 cm^3) and BQ (3.25 g) was refluxed for 5 h. The mixture was then filtered to remove polymeric materials (3.25 g), and the filtrate was chromatographed on a silica-gel column with benzene–ether (9:1), after the evaporation of the volatile material, to give **5** (pale yellow crystals; mp 161—162 °C; 199 mg; 5% [Found: M$^+$, 380.1790. Calcd for $C_{27}H_{24}O_2$: 380.1775. ^{1}H NMR δ=0.57 (1H, q, J=7 Hz), 0.80 (1H, dm, J=7 Hz), 1.16 (2H, m), 1.72 (2H, dt, J=10.5, 7 Hz), 3.28 (2H, ddd, J=10.5, 3, 1.5 Hz), 4.22 (2H, m), 5.22 (4H, m), 5.97 (2H, m), 6.2 (4H, m), and 6.65 (4H, m). ν: 1665, 1582 cm^{-1}. λ_{max}^{MeOH}: 257 nm (ε=10500)]), **6** (colorless crystals; mp 198—201 °C; 44 mg; 1% [Found: C, 82.51; H, 6.22%. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25%. ^{1}H NMR δ=2.21 (1H, dt, J=10, 7 Hz), 2.38 (1H, d, J=5.5 Hz), 2.79 (1H, ddd, J=9, 5.5, 3 Hz), 3.10 (5H, m), 5.22 (1H, dd, J=9, 7 Hz), 5.66 (2H, t, J=9 Hz), 6.04 (1H, t, J=9 Hz), 6.24 (2H, m), 6.44 (2H, dd, J=9, 7 Hz), and 6.64 (2H, t, J=3 Hz). ν: 1730 cm^{-1}. λ_{max}^{MeOH}: 220 nm (ε=18800), 250 (sh. 6000)]), and **7** (colorless crystals; mp 177—180 °C; 208 mg; 2% [Found: M$^+$, 292.1475. Calcd for $C_{20}H_{20}O_2$: 292.1462. ^{1}H NMR δ=0.0 (4H, m), 0.9 (4H, m), 2.8 (4H, br. s), 3.25 (4H, m), and 5.87 (4H, dd, J=5, 3 Hz), ν: 1690 cm^{-1}]). The later fractions, eluted with benzene–ether (8:2), contained **2** (4%), **3** (6%), and **4** (15%).

Further Conversion of 3 to 6. A mixture of **3** (107 mg) and **1** (0.7 cm^3) was heated to reflux for 2 h with an occasional check of the reaction by means of thin-layer chromatography. Subsequent silica-gel column chromatography of the mixture, with benzene as the eluent, afforded crystalline **6** (16.5 mg; 18%), whose identity with an authentic sample was established by direct comparisons, and the recovered **3** (15.3 mg; 14%).

Thermal Reaction of 1 with NQ. *a)* A toluene solution (8 cm^3) of **1** (2.1 cm^3) and NQ (1.59 g) was refluxed for 12 h. After the removal of the solvent *in vacuo*, the residue was chromatographed on a silica-gel column, with benzene–ether (9:1) as the eluent, to give **8** (colorless crystals; mp 130—132 °C; 7 mg; 0.6% [Found: C 84.27; H, 5.92%; M$^+$, 340.1487. Calcd for $C_{24}H_{20}O_2$: C, 84.67; H, 5.93%; M$^+$, 340.1462. ^{1}H NMR δ=1.88 (2H, dt, J=11, 6 Hz), 3.50 (2H, d, J=11 Hz), 5.29 (4H, m), 6.22 (4H, m), 6.62 (4H, t, J=2.5 Hz), 7.72 (2H, m), and 8.09 (2H, m). ν: 1668, 1595 cm^{-1}]), **9** (yellow needles; mp 188—189 °C; 146 mg; 16% [Found: C, 82.49; H, 4.89%. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87%. ^{1}H NMR δ=0.70 (1H, dd, J=7, 6 Hz), 0.93 (1H, dd, J=6, 3.5 Hz), 1.36 (2H, m), 4.58 (2H, m), 6.12 (2H, dd, J=5, 3.5 Hz), 7.7 (2H, m), and 8.12 (2H, m). ^{13}C NMR δ=16.2, 17.8, 35.9, 126.2, 130.0, 132.3, 133.3, 156.2, and 181.7. ν: 1658, 1593 cm^{-1}]), **10** (colorless plates; mp 165—166.5 °C; 408 mg; 22% [Found: C, 81.63; H, 5.69%. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64%. ^{1}H NMR δ=0.12 (2H, m), 1.20 (2H, m), 3.23 (2H, dm, J=1.5 Hz), 3.58 (2H, ddd, J=5, 3.5, 1.5 Hz), 5.67 (2H, dd, J=5, 3.5 Hz), 7.66 (2H, m), and

8.00 (2H, m). *v*: 1670, 1596 cm^{-1}]), **11** (a yellow oil; 100 mg; 5% [Found: M^+, 250.0993. Calcd for $C_{17}H_{14}O_2$: 250.0993. ^1H NMR δ=2.24 (1H, dt, *J*=9, 6 Hz), 3.1—3.7 (3H, m), 5.28 (1H, dd, *J*=10, 6 Hz), 5.40 (1H, dd, *J*=10, 6 Hz), 6.23 (2H, m), 6.62 (2H, t, *J*=3 Hz), 7.70 (2H, m), and 8.02 (2H, m). *v*: 1694, 1598 cm^{-1}]), and the recovered NQ (423 mg; 26.6%).

b) A mixture of **1** (30 cm^3) and NQ (6.37 g) was heated to reflux for 11 h. After the removal of the solvent by distillation *in vacuo*, the residue was chromatographed on a silica-gel column, with benzene–ether (9:1) as the eluent; together with the already described **8** (128 mg; 2%), **9** (508 mg; 10%), **10** (727 mg; 7%), and **11** (90 mg; 1%), two products, **12** (faintly brown crystals; mp 131—132.5 °C; 151 mg; 3% [Found: C, 82.18; H, 4.89%. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87%. ^1H NMR δ=2.48 (1H, dd, *J*=8.5, 6 Hz), 2.84 (1H, d, *J*=3 Hz), 3.54 (2H, m), 5.67 (1H, dd, *J*=9.5, 6 Hz), 5.80 (1H, dd, *J*=9.5, 6 Hz), 6.06 (2H. dd, *J*=9.5, 6 Hz), 7.7 (2H, m), and 8.1 (2H, m). ^{13}C NMR δ=30.2, 30.8, 33.6, 38.2, 42.0, 120.2, 121.1, 126.4, 126.6, 126.9, 128.2, 133.9, 134.1, 134.6, 135.2, 195.6, and 195.7. *v*: 1700, 1670, 1595 cm^{-1}]), and **13** (a yellow oil; 250 mg; 6% [Found: M^+, 338.1302. Calcd for $C_{24}H_{18}O_2$: 338.1304. ^1H NMR δ=2.26 (2H, dt, *J*=12, 6 Hz), 4.73 (2H, dd, *J*=12, 1 Hz), 5.14 (4H, q, *J*=5 Hz), 6.16 (4H, m), 6.71 (4H, t, *J*=2.5 Hz), 6.77 (1H, d, *J*=1 Hz), 7.25 (5H, br. s), 7.7 (4H, m), and 8.0 (4H, m). ^{13}C NMR δ=42.0, 45.6, 123.7, 123.9, 124.9, 125.5, 125.9, 126.8, 127.2, 128.3, 128.8 (4C), 130.9, 131.2, 131.8, 132.2, 133.7, 134.6, 140.0, 151.9, 184.5, and 185.2. *v*: 1659, 1596 cm^{-1}]), were isolated.

Thermal Reaction of 1 with TQ. *a)* A toluene solution (8 cm^3) of **1** (2 cm^3) and TQ (1.25 g) was refluxed for 2.5 h. The insoluble solid was then filtered off, the filtrate was evaporated *in vacuo*, and the residue was chromatographed on a silica-gel column, with benzene–ether (8:2) as the eluent, to give **15** (pale yellow needles; mp 81—82 °C; 327 mg; 18% [Found: C, 78.38; H, 6.63%. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59%. ^1H NMR δ=0.80 (2H, m), 1.08 (2H, m), 1.98 (3H, d, *J*=2 Hz), 2.98 (2H, t, *J*=2 Hz), 3.40 (2H, br. s), 5.68 (2H, dd, *J*=5, 4 Hz), and 6.46 (1H, q, *J*=2 Hz). *v*: 1660 cm^{-1}. λ_{max}^{MeOH}: 239 nm (ε=8200)]) and **16** (pale yellow crystals, mp 107—108 °C; 172 mg; 14% [Found: C, 82.45; H, 6.80%. Calcd for $C_{21}H_{20}O_2$: C, 82.85; H, 6.63%. ^1H NMR δ=1.80 (2H, m), 1.92 (3H, d, *J*=1.5 Hz), 3.26 (1H, dt, *J*=11, 2 Hz), 3.32 (1H, dd, *J*=11, 2 Hz), 5.20 (4H, m), 6.17 (2H, dt, *J*=9.5, 3 Hz), 6.28 (2H, dt, *J*=9.5, 3 Hz), 6.42 (1H, quint, *J*=1.5 Hz), and 6.67 (4H, t, *J*=3 Hz). *v*: 1680, 1618 cm^{-1}. λ_{max}^{MeOH}: 247 nm (ε=12300)]). From the more polar fractions, eluted with a benzene–ether mixture (7:3), H_2TQ (284 mg) and TQ (241 mg; 19%) were obtained.

b) A mixture of **1** (14 cm^3) and TQ (2.44 g) was heated at 120 °C for 1.5 h. The subsequent removal of the volatile material by distillation *in vacuo* and the silica-gel chromatography of the residue with benzene–ether (9:1) gave **4** (29.5 mg; 1.6%), and **17** (a faintly brown oil; 121 mg; 6% [Found: M^+, 212.0811. Calcd for $C_{14}H_{12}O_2$: 212.0837. ^1H NMR δ=0.66 (1H, q, *J*=7 Hz), 0.87 (1H, dt, *J*=7, 3 Hz), 1.24 (2H, m), 2.06 (3H, d, *J*=1.5 HZ), 4.36 (2H, m), 6.05 (2H, dd, *J*=5, 4 Hz), and 6.45 (1H, q, *J*=1.5 Hz). *v*: 1650 cm^{-1}. λ_{max}^{MeOH}: 263 nm (ε=12100)]), together with **15** (644 mg; 15%) and **16** (541 mg; 18%). From the later eluent of the benzene–ether mixture (7:3), H_2TQ (1.04 g; 42%) was obtained.

Thermal Reaction of 1 with PQ. A mixture of **1** (3 cm^3) and PQ (416 mg) was heated at 95 °C for 1.5 h. The mixture was then filtered to remove the insoluble solid, the filtrate was evaporated *in vacuo*, and the residue was chromatographed on a silica-gel column, with benzene–ether (9:1) as the eluent, to give **18** (yellow crystals; mp 139—140.5 °C, 59.5 mg; 12.5% [Found: C, 82.20; H, 5.88%. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84%. ^1H NMR δ=0.12 (1H, tm, *J*=4 Hz), 0.24 (1H, tm, *J*=6 Hz), 1.19 (2H, ddm, *J*=6, 4 Hz), 3.17 (2H, t, *J*=3 Hz), 3.52 (2H, m), 5.82 (2H, dd, *J*=5, 4 Hz), 6.73 (1H, s), and 7.40 (5H, s). *v*: 1664 cm^{-1}. λ_{max}^{MeOH}: 228 nm (ε=15600), 307 (7300)]) and **19** (a pale yellow oil; 56.5 mg; 18% [Found: M^+, 366.1607. Calcd for $C_{26}H_{22}O_2$: 366.1619. ^1H NMR δ=2.05 (2H, dt, *J*=11, 6 Hz), 3.39 (1H, t, *J*=11 Hz), 3.41 (1H, t, *J*=11 Hz), 5.70 (4H, dm, *J*=6 Hz), 6.27 (4H, m), 6.67 (5H, m), and 7.39 (5H, s). *v*: 1690, 1595 cm^{-1}. λ_{max}^{MeOH}: 230 nm (ε=13300), 313 (5600)]). The later fractions afforded recovered PQ (99 mg; 24%).

Thermal Reaction of 1 with CQ. A mixture of **1** (5 cm^3) and CQ (1.38 g) was heated at 60 °C for 50 min. After the removal of the volatile material *in vacuo*, the residue thus obtained was chromatographed on a silica-gel column, with benzene–ether (9:1) as the eluent, to give **20** (pale yellow crystals; mp 98—98.5 °C; 368 mg; 16% [Found: C, 66.43; H, 4.76%. Calcd for $C_{13}H_{11}O_2Cl$: C, 66.53; H, 4.72%. ^1H NMR δ=0.12 (1H, tm, *J*=4 Hz), 0.21 (1H, tm, *J*=6 Hz), 1.16 (2H, ddm, *J*=6, 4 Hz), 3.04 (2H, t, *J*=2 Hz), 3.49 (2H, m), 5.80 (2H, dd, *J*=4, 3.5 Hz), and 6.81 (1H, s). *v*: 1665 cm^{-1}. λ_{max}^{MeOH}: 254 nm (ε=8500)]) and H_2CQ (377 mg; 27%).

Thermal Reaction of 1 with XQ. A toluene solution (2 cm^3) of **1** (2 cm^3) and XQ (1.36 g) was refluxed for 1.5 h. After the subsequent evaporation of the solvent *in vacuo*, the residue was chromatographed on a silica-gel column, with benzene–ether (8:2) as the eluent, to give **4** (30 mg; 6%) and **21** (yellow crystals; mp 90—93 °C; 91 mg; 14% [Found: M^+, 226.0975. Calcd for $C_{15}H_{14}O_2$: 226.0993. ^1H NMR δ=2.05 (3H, s), 2.09 (3H, d, *J*=2 Hz), 3.16 (1H, t, *J*=6 Hz), 5.16 (2H, dd, *J*=9, 6 Hz), 6.17 (2H, dm, *J*=9 Hz), and 6.62 (3H, m). *v*: 1645 cm^{-1}. λ_{max}^{MeOH}: 262 nm (ε=10600)]). Subsequently, H_2XQ (40 mg) and the recovered XQ (663 mg; 49%) were obtained from the polar fractions by elution with benzene-ether (5:5).

Dehydrogenation of 10 to 9. A benzene solution of **10** (35.6 mg) was held on an alumina column for 1 h. Subsequent elution with ether yielded **9** (22.6 mg; 67%).

Dehydrogenation of 11 to 14. The **11** (81 mg) was chromatographed on a basic alumina column with hexane–benzene (1:1) to give **14** (a colorless oil; 58.6 mg; 73% [Found: M^+, 248.0851. Calcd for $C_{17}H_{12}O_2$: 248.0837. ^1H NMR δ=3.64 (1H, td, *J*=7, 1.5 Hz), 5.41 (2H, dd, *J*=9.5, 7 Hz), 6.34 (2H, dt, *J*=9.5, 4 Hz), 6.64 (2H, t, *J*=4 Hz), 6.84 (1H, d, *J*=1.5 Hz), 7.75 (2H, m), and 8.1 (2H, m). *v*: 1664, 1596 cm^{-1}]).

Further Conversion of 14 to 12. A mixture of **1** (0.5 cm^3) and **14** (30 mg) was heated at 100 °C for 7 h. Subsequent silica-gel column chromatography of the mixture with benzene yielded **12** (8.4 mg; 28%).

Reaction of 14 and 11. A mixture of **1** (0.5 cm^3), **11** (20.5 mg), and **14** (22.8 mg) was heated at 100 °C for 5.5 h. Subsequent silica-gel column chromatography of the mixture with benzene afforded **8** (5.5 mg; 20%) and **12**

(2.5 mg; 16%).

Further Reaction of 11 and NQ. *a)* A mixture of **1** (0.5 cm^3), **11** (16 mg), and NQ (7 mg) was heated at 110 °C for 11 h. Subsequent silica-gel column chromatography of the mixture, with benzene–ether (5:5) as the eluent, yielded **8** (0.7 mg; 6%), together with **9** (1.5 mg) and **10** (2.5 mg).

b) A toluene solution (1 cm^3) of **11** (70.4 mg) and NQ (32.2 mg) was refluxed for 13 h. Subsequent silica-gel column chromatography of the mixture, with hexane–benzene (5:5) as the eluent, yielded **9** (7.4 mg; 11%) and **12** (4.9 mg; 7%).

Thermal Reaction of 1 with p-*TRQ.* A toluene solution of **1** (0.8 cm^3) and *p*-TRQ (545 mg) was heated to reflux for 10 min. The precipitates (287 mg, 56%), removed by filtration and washed with benzene and MeOH, were identical with **23**.[11] From the MeOH washings, **22** (124 mg; 22%) was obtained. From the benzene washings, a trace of **4** was isolated.

References

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6) The yields of the product were based on the stoichiometry of the quinones required for their formation.

7) For deduction of the stereochemistry, the argument based on the *J* values would necessarily be ambiguous in the bicyclo[2.2.2]octene system. However, the chemical shift differences of the olefinic protons, $\Delta\delta$, between the bicyclooctenes and bicyclooctadienes must provide information. Thus, $\Delta\delta$ for norbornadiene and norbornane is 6.65−5.93=0.72, which could be calculated from the figures given in the literature,[14] but our $\Delta\delta$ value for **9** and **10** is 6.12−5.67=0.45, while for **17** and **15** it is 6.05−5.68=0.37. The differences can probably be explained in terms of the induced ring current effect from the naphthoquinone moiety; therefore, the stereostructures for the products are as depicted. We admit that, in this case, there is no reason why the adducts, which are formed stereospecifically, must have an unfavorable *exo*-configuration against the secondary orbital overlappings.

8) This product is a barbaralane derivative; however, in the ^1H and ^{13}C NMR spectra, there is no indication of the occurrence of valence isomerization, which is well known in the case of the parent skeleton.

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