Pressure-Accelerated Diels-Alder Reactions of Tropones with Aromatic *p*-Quinones

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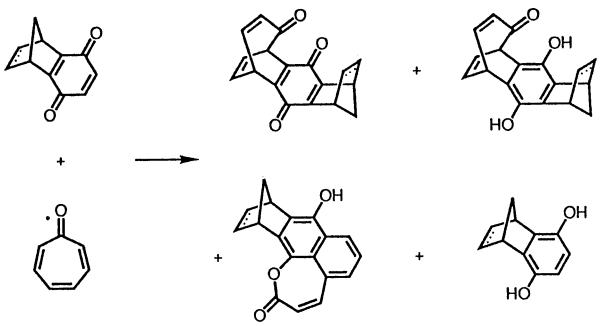
The Diels-Alder reactions of tropones with aromatic *p*-quinones under 3000 and 10000 bar gave enolized 1 : 1-adducts together with dehydrogenated products, homobarrelenone derivatives. The latter were isomerized to tetracyclo[6.5.0.0^{1,9}.0^{5,9}]trideca-2,6,11-triene-4,10,13-triones on exposure to diffused light. No cycloadduct was obtained when the reaction was carried out under 1 bar.

Recently, Mehta and Karra reported[1] that cycloaddition reactions between 5,8-methano-5,8-dihydro-1,4-naphthoquinone and 5,8-methano- 5,6,7,8-tetrahydro-1,4-naphthoquinone and 2,4,6-cycloheptatrien-1-one (tropone) gave an ε-lactone derivative through a [4+2] cycloaddition, dehydrogenation, and consecutive pericyclic reactions of [3s,3s] sigmatropy, [$\pi_s^2+\sigma_s^2+\pi_s^2$] cycloaddition, and a [1,7] hydrogen shift. As they mentioned, this was the first example of a cycloaddition reaction of tropone to an unactivated *p*-benzoquinone derivative, although the Diels-Alder reactions of troponoids with a wide variety of dienophiles have been reported.[2] It is not surprising that the Diels-Alder reactions between tropones and aromatic quinones, such as *p*-benzoquinones and 1,4-naphthoquinones, both electron-deficient C=C systems, have not been examined so far under ordinary conditions.[3] Since it is well-documented that a cycloaddition reaction can be pressure-accelerated,[4] we carried out the reactions of troponoids with aromatic quinones under 3000 and 10000 bar at 100 °C (1 bar=10^5 Pa). Herein, the findings will be described.

Results and Discussion

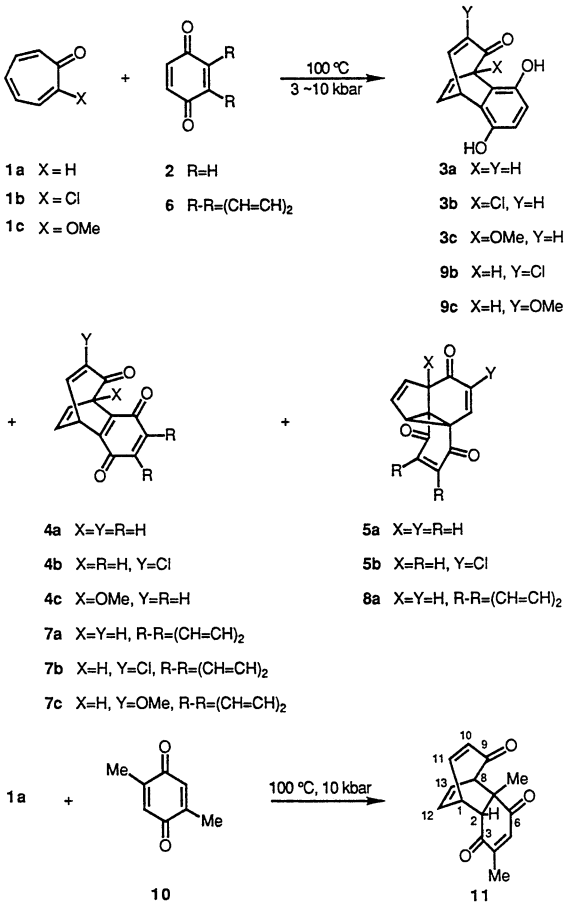
When a toluene solution of tropone (**1a**) and *p*-benzoquinone (**2**) was heated at 100 °C under 3000 bar, three products (**3a—5a**) were isolated by means of silica-gel column chromatography. However, no product was obtained from this combination at 30 °C under 3000 bar. Their structures were elucidated by means of NMR and other spectral measurements.



Scheme 1.

The main product, **3a**, was a 1 : 1-adduct which had six olefinic and two methine protons. The IR spectrum showed the presence of an α,β-unsaturated carbonyl group and a phenolic hydroxyl group. Therefore, **3a** was an enolized [4+2] adduct.[1,5] Product **4a** was a dehydrogenated form of **3a**, judging from its mass spectrum (*m/z*, 212: M$^+$). The DDQ (2,3-dichloro-5,6-dicyano-*p*-benzoquinone) oxidation of **3a** gave **4a** in 48% yield.

The ^{13}C NMR spectrum of product **5a** disclosed three cyclopropane carbons and nine sp^2-carbons, including three carbonyl carbons, while the ^{1}H NMR spectrum showed six vinyl protons and two methine



Scheme 2.

protons on the sp^3-carbons. The spin coupling sequences indicated that the structure of **5a** was tetracyclo[6.5.0.0^{1,9}.0^{5,9}]trideca-2,6,11-triene-4,10,13-trione. Similar photoisomerizations have been observed in the barbaralane derivatives.[6] The homobarrelenone quinone **4a** was photoisomerized to **5a** by means of external irradiation with a 100 W high-pressure mercury lamp or by exposure to diffused light.[7] However, **4a** was stable in the dark, i.e., at 100 °C under 3000 bar.

In the reaction of **1a** and 1,4-naphthoquinone (**6**), the two products characterized were a dehydrogenated product, a quinone **7a**, and a rearrangement product, **8a**. The irradiation of **7a** gave **8a**.

The high-pressure reactions of 2-chlorotropone (**1b**) and 2-methoxytropone (**1c**) with **2** gave isomeric pairs of adducts (**3b** and **9b** and **3c** and **9c**) and two dehydrogenated products, **4b** and **4c**. The structures of the isomeric pairs of adducts were elucidated from the ^{1}H NMR spectra. The DDQ dehydrogenation of **9b** and **3c** afforded **4b** and **4c** respectively. The reactions of **1b** and **1c** with **6** each gave only one isomer, **7b** and **7c** respectively.

Next, it seemed that the Diels-Alder reaction of **1a** and some alkyl derivatives of **2** was worth trying, since the adducts derived from some of them could not form dehydrogenation products. When a mixture of **1a** and 2,5-dimethyl-*p*-benzoquinone (**10**) was heated at 100 °C under 10000 bar, a [4+2] adduct (**11**) was formed in 29% yield. The regiochemistry of **11** was determined by the ^{1}H COSY spectrum, in which the methine signal on C_2 at δ=3.10 correlated with the olefinic proton at δ=6.55, assigned to the proton at C_{12}. No adduct was formed from the same treatment of **1c** and **10**, even under 10000 bar.

Thus, the high-pressure conditions were conveniently applied to the Diels-Alder reaction of tropones with quinones. However, the reaction courses were slightly different between **2** and **6**. The reactions between tropones and *p*-benzoquinones gave the enolized 1 : 1-adducts, in some cases, together with quinones, dehydrogenated secondary products, whereas the reactions with **6** gave only the quinones.[8] Since 1,4-naphthalenediol has a lower oxidation potential than the hydroquinone,[9] the dehydrogenation of the former is much easier than the latter; this is consistent with the experimental results.

In the case of the reaction of **1c** and **2**, the dehydrogenated product was not obtained. The ^{1}H NMR spectrum of **3c** showed the chelating hydroxyl proton signal at δ=8.49, while the unchelating proton signal appeared at δ=4.68. Therefore, the intramolecular hydrogen bonding between the methoxyl group at the bridgehead position and the adjacent hydroxyl hydrogen of hydroquinone part disfavored the dehydrogenation.

Explanations of the regiospecificities in the cycloadditions of 2-substituted tropones have already been attempted by means of molecular orbital calculation.[10] The present results were parallel to those of troponoids and acrylonitrile, an electron-deficient dienophile.[11]

Experimental

The elemental analyses were performed by Misses S. Hirashima and T. Mizoguchi of the Institute of Advanced Material Study, Kyushu University. The NMR spectra were measured by means of JEOL FX 100 Model and JEOL GSX 270 H Model spectrometers in a $CDCl_3$ solution (unless otherwise specified); chemical shifts are expressed in units of δ. The mass spectra were measured with a JEOL 01SG-2 spectrometer. The IR spectra were taken as KBr disks or as a liquid film inserted between NaCl plates using a Jasco IR-A 102 spectrometer. The UV spectra were measured by the

Table 1. Product Distributions of High-Pressure Diels-Alder Reactions of Tropones and *p*-Quinones[a]

Tropone	Quinone	Pressure /kbar[e]	Product (Yield/%)	Recovered Tropone
1a	**2**	3	**3a**(66), **4a**(7), **5a**(1)	(41)
1a[b]	**2**	3	**3a**(63), **4a**(5), **5a**(1)	(54)
1a	**2**	10	**3a**(60), **4a**(25)	(0)
1a[c]	**2**	10	No product	(99)
1b	**2**	3	**3b**(16), **9b**(23), **4b**(11)	(55)
1b	**2**	10	**3b**(16), **9b**(36), **4b**(26)	(0)
1c	**2**	3	**3c**(46), **9c**(7)	(47)
1c	**2**	10	**3c**(51), **9c**(13)	(0)
1a	**6**	3	**7a**(46), **8a**(8)	(79)
1a	**6**	10	**7a**(42)	(0)
1b	**6**	3	**7b**(16)	(59)
1b	**6**	10	**7b**(29)	(80)
1c	**6**	3	**7c**(27)	(80)
1c	**6**	10	**7c**(25)	(0)
1a[d]	**10**	10	**11**(29)	(0)

a) Reaction conditions: ratio of **1** and quinone, 1 : 3; solvent, toluene; reaction temperature, 100°C; reaction time, 10 h. b) The ratio of **1a** and **2** was 1 : 1. c) The reaction temperature was 25 °C in CH_2Cl_2. d) The ratio of **1a** and **10** was 1 : 1.6. e) kbar=10^8 Pa.

use of a Hitachi U-3200 spectrophotometer.

Reaction of 1a with 2. a) A toluene solution (7.5 cm³) of **1a** (128 mg) and **2** (392 mg) was heated at 100 °C under 3000 bar for 10 h. After the solvent had been evaporated under reduced conditions, the residue was chromatographed on a silica-gel column to give 101 mg (66%) of **3a**, 10.8 mg (7%) of **4a**, and 1.5 mg (1%) of **5a**.

3a: Yellow crystals, mp 214—216 °C; ^{1}H NMR (CD_3OD) δ=4.76 (1H, ddd, J=8.6, 7.2, 1.5 Hz), 5.00 (1H, dt, J=7.2, 1.5 Hz), 5.18 (1H, dd, J=10.7, 1.5 Hz), 6.46 (1H, d, J=8.6 Hz), 6.51 (1H, d, J=8.6 Hz), 6.55 (1H, ddd, J=7.3, 7.2, 1.5 Hz), 6.93 (1H, ddd, J=7.3, 7.2, 1.5 Hz), and 7.35 (1H, dd, J=10.7, 8.6 Hz); ^{13}C NMR (CD_3OD) δ=39.7, 56.9, 114.8, 115.7, 124.3, 126.1, 130.5, 131.9, 140.9, 146.5, 148.9, 155.6, and 193.8; IR (KBr) 3324 (br), 1656, 1627, 1493, and 1274 cm^{-1}; UV (MeOH) 202 (ε 27700), 231 (7200) and 293.2 nm (2700); MS m/z (%) 214 (M^+, 14), 171 (20), 131 (12), 99 (11), and 78 (100). Found: C, 72.70; H, 4.62%. Calcd for $C_{13}H_{10}O_3$: C, 72.89; H, 4.71%.

4a: Yellow crystals, mp 139—140 °C; ^{1}H NMR δ=4.61 (1H, ddd, J=8.4, 6.2, 1.5 Hz), 5.01 (1H, ddd, J=6.2, 1.8, 1.5 Hz), 5.28 (1H, dd, J=11.0, 1.5 Hz), 6.57 (1H, ddd, J=7.6, 6.2, 1.5 Hz), 6.78 (2H, s), 6.87 (1H, ddd, J=7.6, 6.2, 1.5 Hz), and 7.13 (1H, dd, J=11.0, 8.4 Hz); ^{13}C NMR δ=37.1, 55.4, 126.0, 128.6, 135.8, 136.1, 137.8, 142.1, 148.9, 150.6, 183.8, 183.9, and 185.4; IR (KBr) 1679, 1656, and 1590 cm^{-1}; UV (MeOH) 202 (ε 12500), 248.8 (10500), and 355.2 nm (460); MS m/z (%) 212 (M^+, 11), 184 (63), 183 (58), 156 (49), 155 (57), 128 (100), 102 (82), and 76 (94). Found: C, 73.32; H, 3.87%. Calcd for $C_{13}H_8O_3$: C, 73.58; H, 3.80%.

5a: Colorless crystals, mp 170—172 °C; ^{1}H NMR δ=3.87 (1H, dd, J=1.8, 0.7 Hz), 4.39 (1H, dd, J=2.2, 0.7 Hz), 5.87 (1H, ddd, J=5.5, 1.8, 0.7 Hz), 5.91 (1H, ddd, J=5.5, 2.2, 0.7 Hz), 6.27 (1H, d, J=10.3 Hz), 6.65 (1H, d, J=10.6 Hz), 6.70 (1H, d, J=10.6 Hz), and 7.17 (1H, d, J=10.3 Hz); ^{13}C NMR δ=44.5, 54.0, 55.1, 62.6, 128.5, 130.9, 135.5, 136.9, 137.1, 138.5, 188.8, 190.0, and 194.6; IR (KBr) 1670, 1603, 1304, and 832 cm^{-1}; UV (MeOH) 214.0 (ε 15200), 235 (10700, sh), 271 (4300, sh), and 386 nm (380); MS m/z (%) 212 (M^+, 42), 184 (63), 156 (34), 155 (24), 128 (100), and 102 (60). Found: m/z 212.0452 (M^+). Calcd for $C_{13}H_8O_3$: 212.0473 (M).

b) A toluene solution (4 cm³) of **1a** (119 mg) and **2** (121 mg) was heated at 100 °C under 3000 bar for 10 h. A similar work-up gave 68.7 mg (63%) of **3a**, 5.9 mg (5%) of **4a**, 0.7 mg (1%) of **5a**, and 65 mg of recovered **1a**.

c) A toluene solution (2 cm³) of **1a** (57 mg) and **2** (174 mg) was heated at 100 °C under 10000 bar for 10 h. A similar work-up gave 68.5 mg (60%) of **3a** and 28.2 mg (25%) of **4a**.

d) A dichloromethane solution (4 cm³) of **1a** (103 mg) and **2** (315 mg) was kept at 25 °C under 10000 bar for 10 h. 102 mg (99%) of **1a** were recovered.

Reaction of 1a with 6. a) A toluene solution (9 cm³) of **1a** (491 mg) and **6** (2.20 g) was heated at 100 °C under 3000 bar for 10 h. After the solvent had been evaporated, the residue was chromatographed on a silica-gel column to give 140 mg (46%) of **7a** and 23 mg (8%) of **8a**, together with 368 mg of the recovered **6**.

7a: Yellow crystals, mp 208—210 °C; ^{1}H NMR δ=4.84 (1H, ddd, J=8.4, 5.8, 1.5 Hz), 5.25 (1H, dt, J=6.2, 1.5 Hz), 5.31 (1H, dd, J=11.0, 1.5 Hz), 6.61 (1H, ddd, J=7.7, 6.2, 1.5 Hz), 6.91 (1H, ddd, J=7.7, 5.8, 1.5 Hz), 7.19 (1H, dd, J=11.0, 8.4 Hz), 7.7—7.8 (2H, m), and 8.1—8.15 (2H, m); ^{13}C NMR δ=37.5, 55.9, 126.1, 126.6, 126.8, 128.8, 131.9, 132.0, 133.9, 134.1, 137.9, 144.2, 150.9, 151.0, 181.6, 181.8, and 185.8; IR (KBr) 1663, 1651, 1297, and 714 cm^{-1}; UV (MeOH) 202.8 (ε 21800), 247.6 (16700), 253 (16600), 260 (10000, sh), 280 (4700, sh), and 341.2 nm (2600); MS m/z (%) 262 (M^+, 72), 234 (75), 233 (100), 206 (37), 205 (30), 178 (47), 152 (36), 151 (32), and 76 (49). Found: C, 77.61; H, 4.11%. Calcd for $C_{17}H_{10}O_3$: C, 77.86; H, 3.84%.

8a: Colorless crystals, mp 169—172 °C; ^{1}H NMR δ=3.81 (1H, dd, J=1.8, 1.2 Hz), 4.59 (1H, ddd, J=1.4, 1.2, 0.8 Hz), 5.89 (1H, dd, J=5.2, 1.8 Hz), 5.91 (1H, dd, J=5.2, 1.4 Hz), 6.33 (1H, dd, J=10.3, 0.8 Hz), 7.39 (1H, d, J=10.3 Hz), 7.75—7.8 (2H, m), and 8.15—8.2 (2H, m); ^{13}C NMR δ=45.1, 54.4, 55.9, 62.1, 127.2, 127.9, 128.4, 130.9, 131.8, 132.6, 134.6, 134.8, 136.4, 136.8, 187.8, 189.1, and 195.0; IR (KBr) 1678, 1299, and 712 cm^{-1}; UV (MeOH) 226.4 (ε 35800), 251 (13000), 308 (3200, sh), and 356 nm (1200); MS m/z (%) 262 (M^+, 100), 234 (55), 206 (29), 178 (37), 152 (35), and 76 (48). Found: m/z 262.0616 (M^+). Calcd for $C_{17}H_{10}O_3$: 262.0629 (M).

b) A toluene solution (2 cm³) of **1a** (24.5 mg) and **6** (110 mg) was heated at 100 °C under 10000 bar for 10 h. The same work-up gave 25.6 mg (42%) of **7a**.

Reaction of 1b with 2. a) A toluene solution (8 cm³) of **1b** (471 mg) and **2** (1.09 g) was heated at 100 °C under 3000 bar for 10 h. After the solvent had then been evaporated under the reduced conditions, the residue was chromatographed on a silica-gel column to give 59.5 mg (16%) of **3b**, 85.3 mg (23%) of **9b**, and 42.9 mg (11%) of **4b**. 258 mg of **1b** were also recovered.

3b: Colorless crystals, mp 204—206.5 °C; ^{1}H NMR (CD_3OD) δ=4.88 (1H, overlapped with the solvent signals), 5.41 (1H, dd, J=11.0, 0.7 Hz), 6.40 (1H, dd, J=8.2, 1.1 Hz), 6.52 (1H, d, J=8.4 Hz), 6.64 (1H, d, J=8.4 Hz), 6.92 (1H, dd, J=8.2, 7.0 Hz), and 7.36 (1H, dd, J=11.0, 8.4 Hz); ^{13}C NMR (CD_3OD) δ=38.7, 79.9, 117.6, 117.8, 121.9, 124.8, 129.2, 137.6, 138.7, 146.6, 150.4, 156.3, and 184.4; IR (KBr) 3438, 1680, 1486, 1203, and 823 cm^{-1}; MS m/z (%) 250 (M^+ for ^{37}Cl, 38), 248 (M^+ for ^{35}Cl, 100), 212 (56), 204 (94), 183 (70), 101 (31), and 28 (46). Found: C, 62.92; H, 3.84%. Calcd for $C_{13}H_9O_3Cl$: C, 62.79; H, 3.65%.

9b: Pale yellow crystals, mp 90—92 °C; ^{1}H NMR (CD_3OD) δ=4.85 (1H, overlapped with the solvent signals), 5.24 (1H, dd, J=6.9, 1.5 Hz), 6.50 (1H, d, J=8.4 Hz), 6.55 (1H, d, J=8.4 Hz), 6.59 (1H, ddd, J=7.8, 6.9, 1.5 Hz), 6.96 (1H, ddd, J=7.8, 6.8, 1.5 Hz), and 7.63 (1H, d, J=9.5 Hz); ^{13}C NMR (CD_3OD) δ=39.4, 56.0, 115.0, 116.1, 123.5, 128.8, 130.7, 131.0, 140.8, 146.6, 149.0, 151.7, and 186.8; IR (KBr) 3434, 3126, 3034, 1675, 1494, 1271, and 722 cm^{-1}; MS m/z (%) 250 (M^+ for ^{37}Cl, 38), 248 (M^+ for ^{35}Cl, 100), 213 (48), 185 (50), and 160 (66). Found: C, 63.12; H, 3.70%. Calcd for $C_{13}H_9O_3Cl$: C, 62.79; H, 3.65%.

4b: Yellow crystals, mp 123.5—124.5 °C; ^{1}H NMR δ=4.70 (1H, ddd, J=9.2, 6.2, 1.5 Hz), 5.24 (1H, dd, J=6.6, 1.5 Hz), 6.62 (1H, ddd, J=7.3, 6.6, 1.5 Hz), 6.81 (2H, s), 6.93 (1H, ddd, J=7.3, 6.2, 1.5 Hz), and 7.40 (1H, d, J=9.2 Hz); ^{13}C NMR δ=37.0, 54.5, 128.9, 135.8, 136.2, 136.6, 138.2, 141.8, 146.9, 148.8, 180.3, 183.3, and 183.4; IR (KBr) 1695, 1657, 1594, 1307, and 840 cm^{-1}: UV (MeOH) 201 (ε 12400), 249.2 (13000), and 354 nm (590); MS m/z (%) 248 (M^+ for ^{37}Cl, 23), 246 (M^+ for ^{35}Cl, 66), 218 (34), 211 (100), 183 (94), 155 (53), 127 (35), and 82 (41). Found: C, 63.52; H, 3.07%. Calcd for $C_{13}H_7O_3Cl$: C, 63.31; H, 2.86%.

b) A toluene solution (2 cm³) of **1b** (67 mg) and **2** (173 mg) was heated at 100 °C under 10000 bar for 10 h. The same

work-up gave 18.5 mg (16%) of **3b**, 42.8 mg (36%) of **9b**, and 30.1 mg (26%) of **4b**.

Reaction of 1b with 6. a) A toluene solution (9 cm³) of **1b** (222 mg) and **6** (750 mg) was heated at 100 °C under 3000 bar for 10 h. The solvent was then evaporated under reduced conditions and the residue was chromatographed on a silica-gel column to give 29.4 mg (16%) of **7b** and 131.4 mg of **1b**.

7b: Pale yellow crystals, mp 221—222.5 °C; ^{1}H NMR δ=4.93 (1H, ddd, J=9.2, 6.2, 1.5 Hz), 5.49 (1H, dd, J=6.6, 1.5 Hz), 6.65 (1H, ddd, J=7.3, 6.6, 1.5 Hz), 6.96 (1H, ddd, J=7.3, 6.2, 1.5 Hz), 7.46 (1H, d, J=9.2 Hz), 7.75—7.8 (2H, m), and 8.12—8.17 (2H, m); ^{13}C NMR δ=37.4, 55.0, 126.7, 127.0, 128.6, 129.1, 131.8, 131.9, 134.1, 134.3, 138.2, 143.9, 147.1, 150.9, 180.5, 181.2, and 181.4; IR (KBr) 1691, 1666, 1640, 1593, 1296, and 730 cm^{-1}; UV (MeOH) 246 (ε 23600, sh), 252.4 (26000), 274 (11600, sh), 333.6 nm (3700); MS m/z (%) 298 (M$^+$ for ^{37}Cl, 14), 296 (M$^+$ for ^{35}Cl, 36), 261 (53), 233 (100), 176 (28), and 151 (20). Found: C, 68.71; H, 2.91%. Calcd for $C_{17}H_9O_3Cl$: C, 68.82; H, 3.06%.

b) A toluene solution (2 cm³) of **1b** (34.7 mg) and **6** (117 mg) was heated at 100 °C under 10000 bar at 10 h. The same work-up gave 4.2 mg (29%) of **7b** and 27.9 mg of **1b**.

Reaction of 1c with 2. a) A toluene solution (9 cm³) of **1c** (347 mg) and **2** (827 mg) was heated at 100 °C under 3000 bar for 10 h. The residue of the reaction mixture was chromatographed on a silica-gel column to give 153 mg (46%) of **3c**, 22.2 mg (7%) of **9c**, and 164 mg of recovered **1c**.

3c: Pale yellow crystals, mp 204—207 °C (decomp); ^{1}H NMR δ=3.75 (3H, s), 4.68 (1H, br s), 4.83 (1H, dddd, J=8.4, 7.0, 1.5, 0.7 Hz), 5.41 (1H, dd, J=11.0, 0.7 Hz), 6.56 (1H, d, J=8.8 Hz), 6.61 (1H, d, J=8.8 Hz), 6.64 (1H, dd, J=8.8, 1.5 Hz), 6.94 (1H, dd, J=8.8, 7.0 Hz), 7.27 (1H, dd, J=11.0, 8.4 Hz), and 8.49 (1H, s): ^{13}C NMR δ=37.5, 54.2, 92.9, 115.8, 116.6, 120.3, 125.0, 127.3, 130.2, 136.4, 143.5, 150.0, 152.6, and 187.3; IR (KBr) 3320, 3210, 1675, 1465, 1225, 1020, and 827 cm^{-1}; MS m/z (%) 244 (M$^+$, 78), 201 (100), and 175 (23). Found: C, 68.62; H, 4.85%. Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95%.

9c: Yellow crystals, mp 115—117 °C; ^{1}H NMR (CD_3OD) δ=3.40 (3H, s), 4.57 (1H, br s), 4.81 (1H, ddd, J=9.2, 6.8, 1.5 Hz), 5.12 (1H, dd, J=6.8, 1.1 Hz), 6.44 (1H, d, J=8.8 Hz), 6.47 (1H, d, J=9.2 Hz), 6.50 (1H, d, J=8.8 Hz), 6.54 (1H, ddd, J=7.8, 6.8, 1.5 Hz), 6.99 (1H, ddd, J=7.8, 6.8, 1.1 Hz), and 7.89 (1H, s); ^{13}C NMR (CD_3OD) δ=36.5, 55.0, 56.0, 114.4, 115.9, 122.7, 124.2, 130.2, 133.1, 142.4, 146.1, 147.9, 148.9, and 190.3; IR (KBr) 3418, 3126, 3034, 1669, 1495, 1120, and 759 cm^{-1}; MS m/z (%) 244 (M$^+$, 70), 218 (37), 201 (43), 169 (100), 160 (58), 119 (51), and 69 (57). Found: m/z 244.0670 (M$^+$). Calcd for $C_{14}H_{12}O_4$: 244.0735 (M).

b) A toluene solution (2 cm³) of **1c** (71.1 mg) and **2** (169 mg) was heated at 100 °C under 10000 bar for 10 h. The subsequent chromatography of the reaction mixture gave 65.5 mg (51%) of **3c** and 17.1 mg (13%) of **9c**.

Reaction of 1c with 6. a) A toluene solution (7 cm³) of **1c** (410 mg) and **6** (1.43 g) was heated at 100 °C under 3000 bar for 10 h. The solvent was then removed under reduced pressure, and the residue was chromatographed on a silica-gel column to give 47.3 mg (27%) of **7c** and 328 mg of recovered **1c**.

7c: A yellow viscous oil; ^{1}H NMR δ=3.45 (3H, s), 4.87 (1H, ddd, J=9.5, 6.2, 1.5 Hz), 5.37 (1H, dd, J=6.6, 1.5 Hz), 6.18 (1H, d, J=9.5 Hz), 6.59 (1H, ddd, J=7.4, 6.6, 1.5 Hz), 6.97 (1H, ddd, J=7.4, 6.2, 1.5 Hz), 7.7—7.8 (2H, m), and 8.1—8.15 (2H, m); ^{13}C NMR δ=34.5, 54.6, 55.0, 117.3, 126.6, 126.8, 128.6, 131.9, 132.0, 133.9, 134.1, 139.6, 144.0, 146.6, 152.4, 181.4, 181.8, and 183.5; IR (KBr) 1693, 1664, 1640, 1296, and 1110 cm^{-1}; UV (MeOH) 222 (ε 14900, sh), 247.6 (15400), 253 (14700), 271 (8400), and 334.4 nm (2600); MS m/z (%) 292 (M$^+$, 73), 264 (50), 249 (100), 221 (83), 193 (28), and 104 (79). Found: m/z 292.0718 (M$^+$). Calcd for $C_{18}H_{12}O_4$: 292.0735 (M).

b) A toluene solution (2 cm³) of **1c** (45.4 mg) and **6** (159 mg) was heated at 100 °C under 10000 bar for 10 h. Subsequent silica-gel chromatography gave 24.3 mg (25%) of **7c**.

DDQ Oxidation of 3a. An acetone solution (10 cm³) of **3a** and DDQ (218 mg) was stirred at room temperature for 2 h. The solvent was then removed, and the residue was washed with benzene. The benzene-soluble part was chromatographed on a silica-gel column to give 65.1 mg (48%) of **4a**.

DDQ Oxidation of 9b. An acetone solution of **9b** (118 mg) and DDQ (162 mg) was stirred at room temperature for 1 h. The solvent was then evaporated, and the residue was washed with benzene. The benzene-soluble part was chromatographed on a silica-gel column to give 105 mg (90%) of **4b**.

DDQ Oxidation of 3c. An acetone solution (5 cm³) of **3c** (46 mg) and DDQ (64 mg) was stirred at room temperature for 5 h. The benzene-soluble part of the reaction mixture was chromatographed on a silica-gel column to give 25.1 mg (70%) of **4c** and 9.8 mg (21%) of **3c**.

4c: Pale brownish crystals, mp 82—84 °C; ^{1}H NMR δ=3.45 (3H, s), 4.73 (1H, dddd, J=8.1, 6.2, 1.5, 1.1 Hz), 5.43 (1H, dd, J=11.0, 1.1 Hz), 6.52 (1H, dd, J=8.1, 1.5 Hz), 6.74 (1H, d, J=9.9 Hz), 6.79 (1H, d, J=9.9 Hz), 6.90 (1H, dd, J=8.1, 6.2 Hz), and 7.09 (1H, dd, J=11.0, 8.1 Hz); ^{13}C NMR δ=36.9, 53.4, 91.2, 125.4, 133.4, 134.1, 134.7, 137.8, 141.5, 150.1 (2C), 182.8, 183.2, and 183.4; IR (KBr) 1689, 1658, and 1399 cm^{-1}; UV (MeOH) 201 (ε 13700), 228 (8300, sh), 246.4 (8700), and 382 nm (590); MS m/z (%) 242 (M$^+$, 28), 213 (100), 184 (31), 115 (22), and 43 (49). Found: m/z 242.0576 (M$^+$). Calcd for $C_{14}H_{10}O_4$: 242.0578 (M).

Thermal Reaction of 4a under 3000 bar. A toluene solution (3 cm³) of **4a** (9.5 mg) was heated at 100 °C for 10 h. The residue was then chromatographed on a silica-gel column to give 9 mg (94%) of **4a**.

Thermal Reaction of 7a under 10000 bar. A toluene solution (3 cm³) of **7a** (9 mg) was heated at 100 °C for 10 h. The subsequent chromatography of the residue gave 7.2 mg (80%) of **7a**.

Thermal Reaction of 7b under 3000 bar. A toluene solution (3 cm³) of **7b** (5.7 mg) was heated at 100 °C for 3 h. The subsequent chromatography of the residue gave 5.1 mg (89%) of **7b**.

Irradiation of 4a. A $CDCl_3$ solution (1 cm³) of **4a** (12.4 mg) in a NMR tube was irradiated for 10 min with a 100 W high-pressure mercury lamp. The chromatography of the residue gave 1.9 mg (15%) of **5a**.

Reaction of 1a and 10. A toluene solution (4 cm³) of **1a** (106 mg) and **10** (200 mg) was heated at 100 °C for 12 h under 10000 bar. The subsequent Florisil chromatography of the mixture gave 70 mg (29%) of **11**.

11: Colorless crystals, mp 160—162 °C; ^{1}H NMR δ=1.36 (3H, s), 2.03 (3H, d, J=1.6 Hz), 3.10 (3H, br s), 3.51 (1H, dm, J=7.4 Hz), 3.94 (1H, t, J=8.8 Hz), 5.94 (1H, ddd, J=8.4, 7.4, 0.9 Hz), 5.96 (1H, dd, J=11.0, 2.1 Hz), 6.55 (1H, ddd, J=8.8,

8.4, 0.9 Hz), 6.57 (1H, q, J=1.6 Hz), and 6.94 (1H, dd, J=11.1, 8.8 Hz); ^{13}C NMR δ=16.5, 26.9, 44.3, 52.8, 53.2, 56.4, 124.2, 131.1, 137.9, 141.3, 148.1, 150.4, 193.9, 198.6, and 200.2; IR (KBr) 2974, 1665, 1631, 1385, 1132, 901, 843, and 751 cm^{-1}; UV (MeOH) 234 (ε 14900) and 250 nm (10600, sh); MS m/z (%) 242 (M^+, 40), 214 (50), 171 (27), 131 (27), 96 (100), 91 (31), 78 (25), 68 (93), 40 (37), and 39 (39). Found: C, 74.54; H, 5.81%. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.83%.

Reaction of 1c and 10. A toluene solution (4 cm^3) of **1c** (276 mg) and **10** (400 mg) was heated at 100 °C for 11 h under 10000 bar. 200 mg (72%) of **1c** were thus recovered.

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7) The results of further investigation of related subjects will be reported separately.

8) There are two possible oxidizing agents in the dehydrogenated process; the oxygen molecule under the reaction conditions and under the separation processes, and an excess quinone under the reaction conditions. Since the oxidation-reduction potential difference between **2** and an enolized 1 : 1-adduct from **1** and **2** was the same as that between **6** and an enolized 1 : 1-adduct from **1** and **6**, however, we could exclude the possibility that a quinone was an oxidizing agent.

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