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Photodimerizations of 1,5- and 1,7-Azulenequinones: Solvent, Substituent, and Concentration Effects on the Product Distribution

Hiroko Kawakami, Yong Zhe Yan, Nobuo Kato, [†] **Akira Mori,**[*,†]
Hitoshi Takeshita,[††] **and the late Tetsuo Nozoe**[†††]

Graduate School of Engineering Sciences, 39, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816
†Institute of Advanced Material Study, 86, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816
††Tohwa Institute for Science, Tohwa University, Chikushi-ga-oka, Minami-ku, Fukuoka 815
†††Tokyo Research Laboratories, Kao Corporation, Bunka, Sumida-ku, Tokyo 131

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Azulenequinones gave dimers when they were irradiated with a high-pressure mercury lamp. In polar solvents, head-to-head dimers were predominant, whereas head-to-tail dimers increased in less polar solvents. From 3-methoxy-1,5-azulenequinone, four products were obtained, while bromoazulenequinones and 1,5-azulenequinone gave a single dimer. The product distribution was dependent on the polarity of solvents, substituents, and concentrations.

Azulenequinones, which are isomers of naphthoquinones, are examples of extended quinones and have a tropone structure in each molecule.[1)] We recently investigated thermal cycloaddition reactions of azulenequinones, in which azulenequinones reacted as a 4π component with such dienophiles[2)] as ethene, acrylonitrile, styrene, and *N*-phenylmaleiimide, and as 2π and 6π components with such dienes as isobenzofuran[3)] and 1, 3-diphenylisobenzofuran.[4)] Isobenzofurans added on both the tropone and cyclopentenone parts of azulenequinones to form 2 : 1 and 3 : 1 adducts, in which isobenzofurans reacted on the cyclopentenone part at first to follow the reaction on the tropone part. The cycloaddition proceeded not to form a cyclopentadienone chromophore in adducts. In the reaction of 3-bromo-1,5-azulenequinone and 1,3-diphenylisobenzofuran, there observed $[8+4]\pi$ adducts. But these are regarded to be derived from $[2+4]\pi$ adducts of the tropone carbonyl group. Thus, azulenequinones reacted thermally as 2π, 4π, and 6π-components as tropone does (Scheme 1).[5)]

The photochemistry of quinones has been widely investigated. Irradiation of quinones gave dimers,[6)] whereas adducts were formed in the presence of olefins as observed in the reaction of benzoquinone and cycloheptatriene (Scheme 2).[7,8)] Troponoids are also reactive photochemically. Tropone itself dimerizes by irradiation in various solvents and the reaction modes are dependent on the reaction conditions.[9)] In this paper, we report the photodimerization of azulenequinones, which have a quinone and a tropone structure in one molecule.

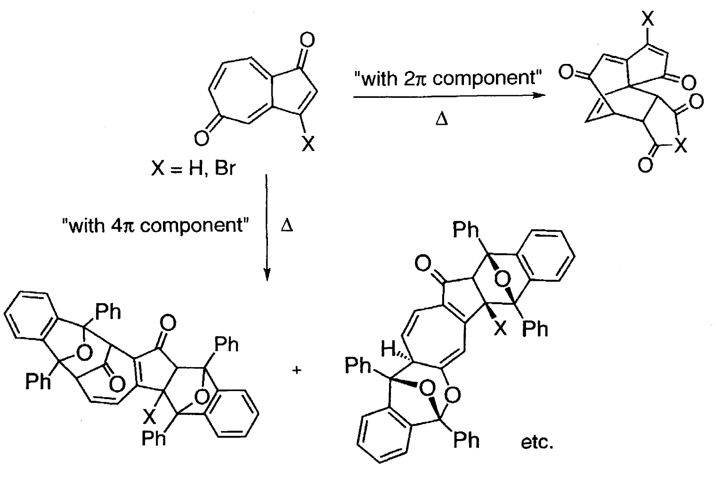
Results and Discussion

Irradiations of 3-Bromo-1,5-azulenequinone (B-5-AQ), 3-Bromo-1,7-azulenequinone (B-7-AQ), and 1,5-Azulenequinone (5-AQ). When an acetonitrile solution of 3-bromo-1,5-azulenequinone (**B-5-AQ**) was irradiated by means of an Hg lamp through an aqueous 0.7 mol dm^{-3} sodium nitrite layer to cut off the wavelength below 400 nm, a single product **1** was obtained in 32% yield (Scheme 3). The mass spectrum indicated that the product is a dimer of **B-5-AQ**. Its ^{1}H NMR spectrum showed five proton signals on the sp^2-carbons and five proton signals on the sp^3-carbons, indicating that **1** is an unsymmetrical heptacarbocyclic derivative. An analysis of the coupling sequence of the ^{1}H NMR spectrum led to the structure of a head-to-head (HH) dimer **1**. The X-ray crystallographic analysis of a single crystal obtained from a dichloromethane solution of **1** confirmed the structure, which is shown in Fig. 1.

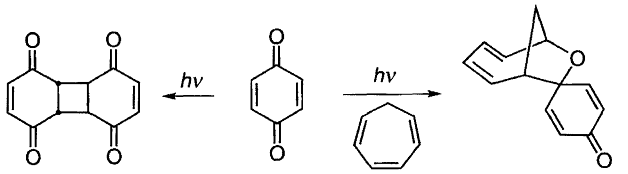
Similar irradiation of 3-bromo-1,7-azulenequinone (**B-7-AQ**) in acetonitrile afforded a single product **2**, a positional isomer of **1**, in 23% yield (Scheme 3).

While an acetonitrile solution of **B-5-AQ** was irradiated through a Pyrex glass filter, the color of the solution changed to brown. Dimer **1** was obtained in 27% yield together with insoluble brownish polymeric materials. Furthermore, when a dichloromethane solution of **B-5-AQ** was irradiated through an aqueous sodium nitrite layer, dimer **1** was obtained as a sole product in 4% yield.

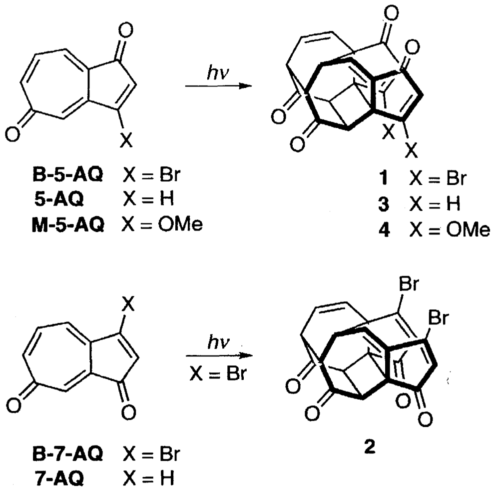
Irradiation of 1,5-azulenequinone (**5-AQ**) gave the parent dimer **3** in 30% yield through an aqueous sodium nitrite layer, while irradiation of 1,7-azulenequinone (**7-AQ**) gave



Scheme 1.



Scheme 2.



Scheme 3.

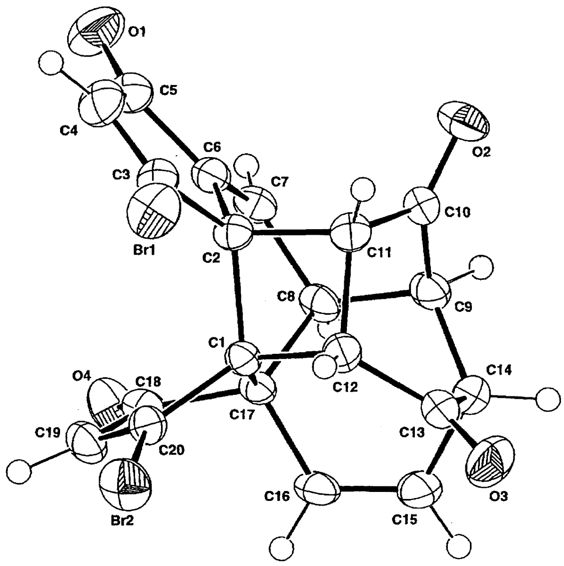


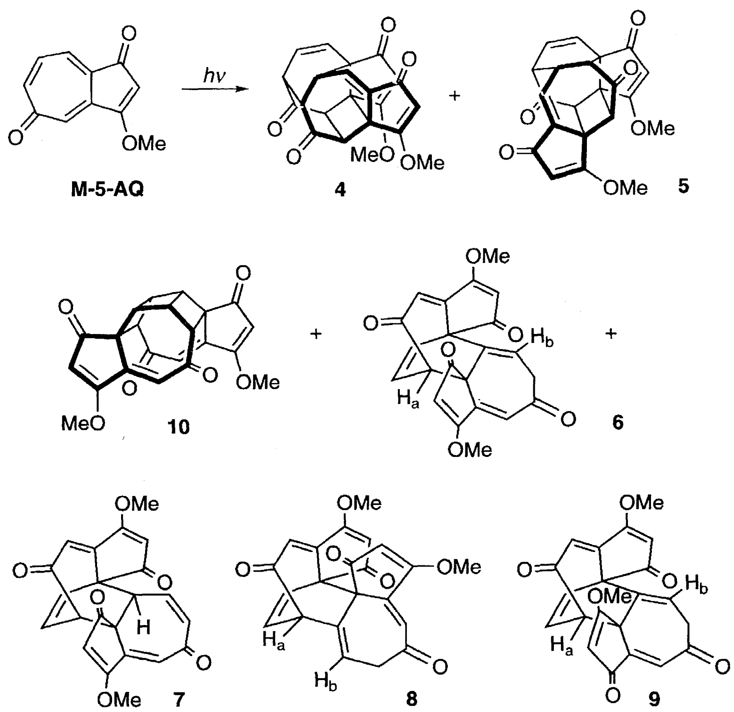
Fig. 1. Molecular structure of HH dimer **1**.

only polymeric materials.

Irradiations of 3-Methoxy-1,5-azulenequinone (M-5-AQ). When 3-methoxy-1,5-azulenequinone (**M-5-AQ**) was irradiated similarly in dichloromethane through an aqueous sodium nitrite layer, three products **4**—**6** were isolated in 6, 10, and 24% yields, respectively.[10] The structure of **4** was determined to be an HH dimer from the comparison of the spectral data with those of HH dimers **1**—**3**. Product **5** was also a dimer of **M-5-AQ**. The ^{1}H NMR spectrum of **5** showed five methine and five olefinic protons, which implies that **5** has an unsymmetrical structure. These are quite similar to the spectral features of dimers **1**—**4**. From these evidences, the structure of **5** was assigned to be a head-to-tail (HT) dimer as shown in Scheme 4.

The ^{1}H NMR spectrum of **6** showed a set of methylene protons, four singlet olefinic protons, two olefinic protons coupled to each other with a coupling constant of 8.4 Hz, and an olefinic proton coupled with the one of the methylene protons. The NMR data of the typical $[4+2]\pi$ cycloadducts of **B-5-AQ** or **B-7-AQ** and dienophiles suggest that[2] **6** must be the secondary product of a $[4+2]\pi$ cycloadduct of **M-5-AQ**. The cycloaddition would proceed photochemically in a *trans*-mode, as observed in the reaction of the photochemical dimerization of tropone,[9] and the photoinduced cycloaddition reaction of 9,10-dicyanoanthracene with tropone.[11] The relief of the ring strain in the primary *trans*-fused $[4+2]\pi$ cycloadduct **7** assisted migration of the double bond to give **6**.

The regiochemistry of **6** was speculated as shown in Scheme 4 from the NOE experiment result that the peak intensity of the proton (H_b) at $\delta = 6.81$ was not enhanced when the methine proton (H_a) at $\delta = 4.23$, which was assigned to the bridge-head proton, was irradiated. An alternative structure **8** could be eliminated. The stereochemistry of **6** was assigned from the chemical shift of H_b at $\delta = 6.81$, which appears at rather lower chemical shift as the proton at the γ position of a β,γ-unsaturated ketone system. The low chem-



Scheme 4.

ical shift can be explained on the basis that H_b in **6** is closer to the side of the carbonyl group of the cyclopentenone than the corresponding H_b in **9**, from inspections of molecular models.

Next, we investigated the photoreaction of **M-5-AQ** in less polar benzene, in which **4** did not form, as shown in Table 1. A new product **10** was obtained in 6% yield. In the ^{1}H NMR spectrum of **10**, three kinds of methine protons appeared at $\delta = 3.17$ (2H, tdd, $J = 5.3$, 3.3, 1.3 Hz), 3.33 (2H, m), and 3.73 (2H, t, $J = 5.3$ Hz) as well as two olefinic signals at $\delta = 5.62$ (2H) and 6.49 (2H) and a singlet methoxy signal at $\delta = 3.97$ (6H). The ^{13}C NMR spectrum showed eleven lines, which indicated that **10** had a symmetrical structure. The splitting patterns of three methine protons led the structure of **10** to an $[4+4]\pi$–$[2+2]\pi$ HT dimer.

Substituent Effects. **M-5-AQ** gave four products while bromoazulenequinones and **5-AQ** gave a single product, an HH dimer. There is a significant change in the product distribution of photodimerizations of azulenequinones when the substituent is changed from a methoxy group to a bromine atom.

The position of the carbonyl group also reflected on the reactivity. Irradiations of 1,7-azulenequinone (**7-AQ**) gave polymeric materials, although **5-AQ** gave **3**.

Solvent Effects. As summarized in Table 1, the HH dimer **4** was the main product in more polar acetonitrile. On the other hand, the yields of the HT dimer **5** and $[4+4]\pi$–$[2+2]\pi$ HT dimer **10** increased when the polarity of solvents is reduced. This result is parallel to those of photodimerizations of 2-cycloalkenones not only in solution[12,13] but also in micelle[14] and in zeolites.[15] Irradiations of 2-cyclohexenone (**CH**)[16,17] and 2-cyclopentenone (**CP**)[17,18] in several solvents at various concentrations gave HT and HH dimers via a triplet state where the *anti*-isomers were exclusively formed. In a less polar solvent, two molecules could orient as an HT arrangement to reduce repulsive dipole–dipole interaction. In a polar solvent, solvated molecules could come together to react in an HH arrangement. A similar explanation would be possible in the dimerization of **M-5-AQ**.

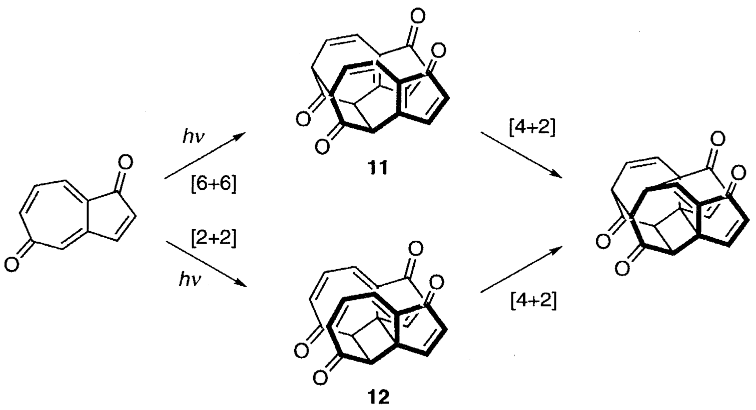
In **CH** and **CP**, the HH/HT dimer ratio increased when the concentration of cycloalkenone increased.[16,18] They explained the concentration dependence by a decrease of macroscopic and microscopic polarity as the concentration of **CH** is reduced. When the concentration of **M-5-AQ** was increased from 0.005 to 0.03 mol dm^{-3}, the ratio of the HH and HT dimers decreased from 1 to 0.75 (Table 2).[19] This is not so large, but different from the results of cycloalkenones. The reactive species involved in the reaction of **M-5-AQ** seemed to be independent of the concentration.

Table 1. Solvent Effects on Product Distribution of **M-5-AQ**

Solvent	Time (h)	4	5	6	10
Benzene	5.5	—	27	24	6
CH_2Cl_2	5.5	6	10	24	—
Acetone	5.5	21	6	9	—
CH_3CN	5.5	24	—	7	—

Table 2. Concentration Effects on Product Distribution of **M-5-AQ**

Concentration (mol dm^{-3})	4	5	6
0.005	17	17	11
0.01	12	16	19
0.03	9	12	23



Scheme 5.

Mechanistic Consideration of Photocycloadditions. Irradiations of **B-5-AQ** through a Pyrex glass filter gave only HH dimer **1** in 27% yield, which is similar to the yield through an aqueous sodium nitrite layer. Therefore, the lowest excited state is responsible for formation of the HH dimers.

Stereochemistry in the primary step of dimerization of azulenequinones was *syn* except for **6**. This is different from the result that 2-cycloalkenones give *anti*-fused dimers via a triplet state.[16—18] *Anti*-fused dimers, if formed in the reaction of azulenequinones, would cyclorevert to monomers under the conditions. *Syn*-fused dimers would form primarily via a triplet intermediate to follow intramolecular cyclization between neighboring chromophores to give the final products.

Two pathways are considered to be possible for the formation of the HH dimers, as shown in Scheme 5: a) *endo*-$[6+6]\pi$ cycloaddition to intermediate **11**, followed by an intramolecular $[4+2]\pi$ process, or b) *endo*-$[2+2]\pi$ cycloaddition to intermediate **12**, followed by an intramolecular $[4+2]\pi$ process.[20] Intermediate **11**, however, involves two unstable cyclopentadienone units in the molecule. Then, the *endo*-$[6+6]\pi$ cycloaddition process must be less favorable than the *endo*-$[2+2]\pi$ process. This conclusion is also supported by the result of the dimerization of **M-5-AQ**. The HT dimer **5** formed via an *endo*-$[2+2]\pi$ and the following intramolecular $[4+2]\pi$ cycloadditions. **M-5-AQ** dimerized not to form an unstable cyclopentadienone intermediate, which is consistent to the observation of thermal cycloaddition reactions.[2—4]

In conclusion, the photodimerizations of azulenequinones were quite sensitive to electronic factors and were certainly different from those of the monocyclic tropone derivatives. In other words, azulenequinones are not simply the perturbed tropone derivatives. Although stereochemistry of the initial step and concentration effect on the formation of the HH dimer were different from those of 2-cycloalkenones, it is certain that the HH and HT dimers were formed via a triplet state.

Experimental

The elemental analyses were performed at the elemental analysis laboratory in the Institute of Advanced Material Study, Kyushu University. The melting points were obtained on a Yanagimoto Micro Melting Point Apparatus and are uncorrected. The NMR spectra were measured on JEOL GSX 270H, LA 400, and LA 600 spectrometers in $CDCl_3$; the chemical shifts are expressed in δ units. The mass spectra were measured with JEOL 01SG-2 and JMS-70 spectrometers. The IR spectra were recorded on a JASCO IR-A102 spectrometer with KBr disks. The stationary phase for the column chromatography was Wakogel C-300 and the eluant was a mixture of ethyl acetate and hexane.

Photoreaction of 3-Bromo-1,5-azulenequinone. a) An acetonitrile solution (100 ml) of **B-5-AQ** (120 mg, 0.5 mmol), bubbled with N_2 gas for 30 min, was irradiated for 3.5 h by means of a 400 W high pressure lamp through an aqueous 0.7 mol dm^{-3} $NaNO_2$ filter (thickness: 0.6 cm). The solvent was removed under reduced pressure. The resultant residue was chromatographed on SiO_2 column (hexane/AcOEt = 4/1) to give **1** (38 mg, 0.16 mmol, 32%); **1**, mp 169—170 °C (decomp); ^{1}H NMR ($CDCl_3/C_6D_6$) $\delta =$ 2.89 (1H, td, $J=8.8$, 1.8 Hz), 2.91 (1H, dd, $J=8.8$, 7.1 Hz), 3.25 (1H, ddd, $J=8.8$, 7.1, 2.1 Hz), 3.38 (1H, dd, $J=9.0$, 2.1 Hz), 4.23 (1H, dd, $J=9.0$, 1.8 Hz), 5.76 (1H, dd, $J=8.4$, 7.1 Hz), 5.79 (1H, d, $J=8.4$ Hz), 5.96 (1H, s), 6.25 (1H, s), and 7.01 (1H, d, $J=7.1$ Hz); ^{13}C NMR $\delta=$ 39.3, 48.3, 48.8, 50.1, 54.6, 63.5, 66.4, 68.4, 127.2, 134. 8, 135.1, 138.0, 140.0, 142.6, 152.7, 158.9, 186.1, 191.4, 200.1, and 201.7; IR(KBr) ν 1728, 1702, 1569, and 1530 cm^{-1}; MS m/z (%) 474 (0.4), 418 (1.0), 238 (13), 237 (13), 236 (14), 210 (17), 209 (12), 208 (18), and 129 (100). Found: C, 50.41; H, 2.35%. Calcd for $C_{20}H_{10}O_4Br_2$: C, 50.65; H, 2.13%.

b) A dichloromethane solution (10 ml) of **B-5-AQ** (15 mg, 0.063 mmol) was irradiated similarly. The solvent was removed under reduced pressure. Tetracyanobenzene was added to the resultant residue as an internal standard to calculate the yield of **1** (0.4 mg, 4%) and the amount of the recovered **B-5-AQ** (4.9 mg).

c) An acetonitrile solution (25 ml) of **B-5-AQ** (20 mg, 0.084 mmol) was irradiated for 4 h by means of a 400 W high pressure lamp through a Pyrex glass filter. The solvent was removed under reduced pressure. The resultant residue was chromatographed on SiO_2 column (hexane/AcOEt = 4/1) to give **1** (5.4 mg, 0.011 mmol, 27%) and polymeric materials.

X-Ray Crystallographic Analysis of 1.[21] $C_{20}H_{10}Br_2O_4$, MW = 474.10, monoclinic, space group $P2_1/a$, $a=8.774(2)$, $b=24.541(5)$, $c=7.799(10)$ Å, $\beta=104.964(14)°$, $V=1622.4(5)$ Å^3, $Z=4$, $D_x=$ 1.941 g cm^{-3}, $wR(F^2)=0.1069$, $R[F^2>2\sigma(F^2)]=0.0393$. Program used to solve structure: SIR92.[22] Program used to refine structure: SHELXL93.[23]

Photoreaction of 3-Bromo-1,7-azulenequinone. a) An acetonitrile solution (100 ml) of **B-7-AQ** (80 mg, 0.34 mmol), bubbled with N_2 gas for 30 min, was irradiated for 3.5 h by means of a 400 W high pressure lamp through a 0.7 mol dm^{-3} $NaNO_2$ filter. The solvent was removed under reduced pressure. The resultant residue was chromatographed on SiO_2 column (hexane/AcOEt = 4/1) to give **2** (18.5 mg, 0.16 mmol, 23%), mp 228—229 °C (decomp); ^{1}H NMR $\delta = 3.33$ (1H, dd, $J = 8.2$, 2.4 Hz), 3.34 (1H, dd, $J = 8.2$, 7.3 Hz), 3.40 (1H, td, $J = 8.2$, 2.4 Hz), 3.63 (1H, ddd, $J = 8.2$, 7.5, 1.7 Hz), 4.28 (1H, dd, $J = 8.2$, 1.7 Hz), 6.19 (1H, d, $J = 8.6$ Hz), 6.28 (1H, dd, $J = 8.6$, 7.5 Hz), 6.36 (2H, s), and 6.79 (1H, d, $J = 7.3$ Hz); ^{13}C NMR $\delta = 42.7$, 44.9, 49.05, 49.08, 52.7, 54.6, 61.3, 65.1, 128.0, 129.1, 134.4, 134.7, 135.2, 143.5, 149.6, 158.8, 192.3, 192.6, 195.8, and 202.0; IR (KBr) ν 1719, 1700, 1657, 1553, and 1253 cm^{-1}; MS m/z (%) 474 (1.7), 447 (10), 446 (22), 445 (18), 339 (18), 338 (13), 337 (18), 311 (8), 309 (7), 202 (100), 201 (19), and 200 (86). Found: C, 50.56; H, 2.41%. Calcd for $C_{20}H_{10}O_4Br_2$: C, 50.65; H, 2.13%.

b) An acetonitrile solution (10 ml) of **B-7-AQ** (10 mg, 0.042 mmol), bubbled with N_2 gas for 30 min, was irradiated for 3.5 h by means of a 400 W high pressure lamp through a Pyrex glass filter. The solvent was removed under reduced pressure. The resultant residue was chromatographed on SiO_2 column (hexane/AcOEt = 4/1) to give **2** (0.4 mg, 4%) and polymeric materials.

Photoreaction of 1,5-Azulenequinone. a) An acetonitrile solution (15 ml) of **5-AQ** (15 mg, 0.095 mmol), bubbled with N_2 gas for 30 min, was irradiated for 2 h by means of a 400 W high pressure lamp through a 0.7 mol dm^{-3} $NaNO_2$ filter. The solvent was removed under reduced pressure. The resultant residue was chromatographed on SiO_2 column (hexane/AcOEt = 4/1) to give **3** (4.5 mg, 0.014 mmol, 30%), mp 162—163 °C (decomp); ^{1}H NMR ($CDCl_3/C_6D_6$) $\delta = 2.83$ (1H, td, $J = 8.2$, 2.2 Hz), 2.88 (1H, dd, $J = 8.2$, 7.2 Hz), 2.92 (1H, dd, $J = 8.2$, 2.2 Hz), 3.24 (1H, dd, $J = 8.2$, 7.7 Hz), 3.44 (1H, d, $J = 8.2$ Hz), 5.44 (1H, d, $J = 5.9$ Hz), 5.74 (1H, dd, $J = 8.4$, 7.7 Hz), 5.84 (1H, d, $J = 8.4$ Hz), 5.96 (1H, d, $J = 5.9$ Hz), 6.56 (1H, d, $J = 5.9$ Hz), 6.67 (1H, d, $J = 5.9$ Hz), and 6.97 (1H, d, $J = 7.2$ Hz); ^{13}C NMR ($CDCl_3$) $\delta = 39.9$, 48.3, 49.4, 51.3, 54.3, 57.5, 59.9, 63.8, 126.3, 131.9, 135.9, 137.4, 138.7, 139.2, 152.9, 161.3, 191.0, 192.9, 202.5, and 204.7; IR (KBr) ν 3052, 2958, 1736, 1703, 1652, and 1230 cm^{-1}; MS m/z (%) 316 (0.5), 288 (11), 260 (26), 231 (25), 203 (31), 202 (34), 158 (38), 130 (64), and 102 (100). Found: C, 75.98; H, 3.91%. Calcd for $C_{20}H_{12}O_4$: C, 75.94; H, 3.82%.

b) A dichloromethane solution (10 ml) of **5-AQ** (10 mg, 0.063 mmol), bubbled with N_2 gas for 30 min, was irradiated for 3 h by means of a 400 W high pressure lamp through a 0.7 mol dm^{-3} $NaNO_2$ filter to give **3** (0.6 mg, 12%) together with 5 mg of **5-AQ**.

Photoreaction of 1,7-Azulenequinone. a) An acetonitrile solution (10 ml) of **7-AQ** (7 mg, 0.044 mmol), bubbled with N_2 gas for 30 min, was irradiated for 1 h by means of a 400 W high pressure lamp through a 0.7 mol dm^{-3} $NaNO_2$ filter. The solvent was removed under reduced pressure to leave polymeric materials.

Photoreaction of 3-Methoxy-1,5-azulenequinone. a) A dichloromethane solution (10 ml) of **M-5-AQ** (15 mg, 0.08 mmol), bubbled with N_2 gas for 15 min, was irradiated for 5.5 h by means of a 400 W high pressure lamp through a 0.7 mol dm^{-3} $NaNO_2$ filter. The solvent was removed under reduced pressure. The resultant residue was chromatographed on SiO_2 column (hexane/AcOEt = 4/1) to give **4** (0.7 mg, 0.002 mmol, 6%), mp 232—234 °C (decomp); ^{1}H NMR $\delta = 3.32$ (2H, m), 3.46 (1H, dd, $J = 8.4$, 2.2 Hz), 3.62 (1H, m), 3.87 (3H, s), 3.92 (3H, s), 4.18 (1H, dd, $J = 8.4$, 1.8 Hz), 5.69 (1H, s), 5.90 (1H, s), 6.19 (1H, dd, $J = 8.4$, 7.3 Hz), 6.29 (1H, dd, $J = 8.4$, 1.1 Hz), and 7.14 (1H, m); ^{13}C NMR $\delta = 29.3$, 39.6, 47.6, 49.1, 53.6, 58.9, 59.0 (2C), 59.1, 63.9, 101.3, 108.7, 108.8, 126.2, 134.7, 136.7, 182.3, 184.3, 187.7, 193.4, 200.8, and 202.9; IR (KBr) ν 3084, 2942, 1711, 1660, 1593, 1352, and 1223 cm^{-1}; MS m/z (%) 376 (26), 188 (24), 160 (100), and 102 (72). Found: m/z 376.0947. Calcd for $C_{22}H_{16}O_6$: M, 376.0940.

5 (1.2 mg, 10%), mp 158—160 °C (decomp); ^{1}H NMR $\delta = 3.33$ (1H, br s), 3.34 (1H, dd, $J = 12.1$, 1.7 Hz), 3.46 (1H, ddd, $J = 12.1$, 7.7, 5.5 Hz), 3.60 (1H, m), 3.96 (3H, s), 3.99 (3H, s), 4.50 (1H, s), 5.23 (1H, s), 5.52 (1H, s), 6.16 (1H, d, $J = 8.8$ Hz), 6.29 (1H, dd, $J = 8.8$, 8.1 Hz), and 7.15 (1H, d, $J = 7.7$ Hz); ^{13}C NMR $\delta = 37.2$, 45.4, 49.0, 50.0, 53.1, 55.4, 57.2, 59.5, 59.7, 62.7, 100.6, 107.7, 128.3, 132.8, 134.2, 142.3, 183.6, 186.9, 188.0, 195.1, 201.0, and 207.4; IR (KBr) ν 3080, 2936, 1742, 1700, 1656, 1579, 1377, and 1224 cm^{-1}; MS m/z (%) 376 (17), 320 (100), 305 (38), 226 (37), 189 (35), and 102 (58). Found: m/z 376.0937. Calcd for $C_{22}H_{16}O_6$: M, 376.0940.

6 (2.9 mg, 24%), mp 92—93 °C; ^{1}H NMR $\delta = 3.11$ (1H, dd, $J = 10.6$, 3.3 Hz), 3.24 (1H, d, $J = 10.6$ Hz), 3.99 (3H, s), 4.07 (3H, s), 4.23 (1H, dm, $J = 7.3$ Hz), 5.69 (1H, s), 5.90 (1H, s), 6.14 (1H, d, $J = 2.2$ Hz), 6.33 (1H, dd, $J = 8.4$, 7.3 Hz), 6.38 (1H, dd, $J = 8.4$, 1.5 Hz), 6.47 (1H, s), and 6.81 (1H, d, $J = 3.3$ Hz); ^{13}C NMR $\delta = 43.1$, 49.7, 50.6, 54.7, 58.9, 60.4, 107.4, 110.9, 120.6, 121.0, 128.3, 134.6, 134.9, 135.4, 141.9, 151.7, 177.9, 179.6, 188.8, 195.0, 195.2, and 199.4; IR (KBr) ν 2940, 1702, 1669, 1573, 1327, and 1226 cm^{-1}; MS m/z (%) 376 (100), 348 (51), 333 (30), 305 (30), 263 (19), 198 (16), and 188 (18). Found: m/z 377.1029 $(M+1)^+$. Calcd for $C_{22}H_{17}O_6$: M + 1, 377.1025 and recovered **M-5-AQ** (3 mg).

b) A benzene solution (10 ml) of **M-5-AQ** (15 mg, 0.08 mmol) was similarly irradiated to give **5** (2.7 mg, 27%), **6** (2.4 mg, 24%), recovered **M-5-AQ** (5 mg), and **10** (0.6 mg, 6%), mp 132—134 °C (decomp); ^{1}H NMR $\delta = 3.17$ (2H, tdd, $J = 5.3$, 3.3, 1.3 Hz), 3.33 (2H, m), 3.73 (2H, t, $J = 5.3$ Hz), 3.97 (6H, s), 5.62 (2H, s), and 6.49 (2H, d, $J = 2.0$ Hz); ^{13}C NMR $\delta = 43.5$ (2C), 45.3 (2C), 53.8 (2C), 57.3 (2C), 59.0 (2C), 108.7 (2C), 123.3 (2C), 149.8 (2C), 177.8 (2C), 199.9 (2C), and 200.7 (2C); IR (KBr) ν 2940, 1703, 1658, 1590, 1327, and 1204 cm^{-1}; MS m/z (%) 376 (15), 348 (56), 305 (9), 189 (13), and 159 (100). Found m/z 377.1018 $[(M+1)^+]$. Calcd for $C_{22}H_{17}O_6$: M + 1, 377.1025.

c) An acetonitrile solution (10 ml) of **M-5-AQ** (15 mg, 0.08 mmol) was similarly irradiated to give **4** (2.6 mg, 24%), **6** (0.8 mg, 7%), and recovered **M-5-AQ** (4.2 mg).

d) An acetone solution (10 ml) of **M-5-AQ** (15 mg, 0.08 mmol) was similarly irradiated to give **4** (2.4 mg, 21%), **5** (0.7 mg, 6%), **6** (1.0 mg, 9%), and recovered **M-5-AQ** (3.5 mg).

e) A dichloromethane solution (10 ml) of **M-5-AQ** (9.4 mg, 0.05 mmol), bubbled with N_2 gas for 20 min, was similarly irradiated for 8 h to give **4** (1.4 mg, 17%), **5** (1.4 mg, 17%), **6** (0.9 mg, 11%), and recovered **M-5-AQ** (1.0 mg).

f) A dichloromethane solution (10 ml) of **M-5-AQ** (18.8 mg, 0.1 mmol) was similarly irradiated to give **4** (2 mg, 12%), **5** (2.6 mg, 16%), **6** (3.1 mg, 19%), and recovered **M-5-AQ** (2.3 mg).

g) A dichloromethane solution (10 ml) of **M-5-AQ** (56.4 mg, 0.3 mmol) was similarly irradiated to give **4** (4.2 mg, 9%), **5** (5.7 mg, 12%), **6** (10.8 mg, 23%), and recovered **M-5-AQ** (9.3 mg).

References

1) T. Nozoe and H. Takeshita, *Bull. Chem. Soc. Jpn.*, **69**, 1149 (1996).

2) T. Nozoe, H. Takeshita, Y. Z. Yan, and A. Mori, *Synlett*, **1995**, 375.

3) H. Takeshita, Y. Z. Yan, N. Kato, A. Mori, and T. Nozoe, *Tetrahedron Lett.*, **36**, 5195 (1995).

4) H. Takeshita, Y. Z. Yan, N. Kato, A. Mori, H. Wakabayashi, and T. Nozoe, *Tetrahedron Lett.*, **36**, 5199 (1995).

5) [2+4]: a) H. Takeshita, Y. Wada, A. Mori, and T. Hatsui, *Chem. Lett.*, **1973**, 335; [4+2]: b) Z.-H. Li, A. Mori, and H. Takeshita, *Bull. Chem. Soc. Jpn.*, **63**, 3713 (1990); c) G. Mehta and S. R. Karra, *J. Org. Chem.*, **54**, 2975 (1989); d) H. Meier, A. Pouli, and H. Kolsorn, *Chem. Ber.*, **122**, 101 (1989); e) G. R. Tian, S. Sugiyama, A. Mori, and H. Takeshita, *Bull. Chem. Soc. Jpn.*, **61**, 2398 (1988); f) T. Sasaki, T. Manabe, and E. Wakabayashi, *Tetrahedron*, **36**, 2119 (1980); g) K. N. Houk and R. B. Woodward, *J. Am. Chem. Soc.*, **92**, 4145 (1970); h) S. Itô, H. Takeshita, and Y. Shoji, *Tetrahedron Lett.*, **1969**, 1815; [6+4]: i) D. Forstmeyer, J. Bauer, E. Fontain, R. Herges, R. Herrmann, and I. Ugi, *Angew. Chem., Int. Ed. Engl.*, **27**, 1558 (1988); j) S. Itô, Y. Fujise, T. Okuda, and Y. Inoue, *Bull. Chem. Soc. Jpn.*, **39**, 1351 (1996); k) R. C. Cookson, B. V. Drake, J. Hudec, and A. Morrison, *J. Chem. Soc., Chem. Commun.*, **1966**, 15; [8+2]: l) H. Takeshita, H. Nakashima, S. Sugiyama, and A. Mori, *Bull. Chem. Soc. Jpn.*, **61**, 573 (1988); m) T. S. Cantrell, *Tetrahedron Lett.*, **1975**, 907.

6) D. Bryce-Smith and A. Gilbert, *J. Chem. Soc.*, **1964**, 2428; E. H. Gold and D. Ginsburg, *J. Chem. Soc. C*, **1967**, 15.

7) D. Bryce-Smith, A. Gilbert, and M. G. Johnson, *J. Chem. Soc. C*, **1976**, 383.

8) A. Mori and H. Takeshita, *Chem. Lett.*, **1975**, 599; A. Mori and H. Takeshita, *Bull. Chem. Soc. Jpn.*, **58**, 1581 (1985).

9) a) T. Mukai, T. Tezuka, and Y. Akasaki, *J. Am. Chem. Soc.*, **88**, 5025 (1966); b) A. S. Kende, *J. Am. Chem. Soc.*, **88**, 5026 (1966); c) T. Tezuka, Y. Akasaki, and T. Mukai, *Tetrahedron Lett.*, **1967**, 1397; d) T. Tezuka, Y. Akasaki, and T. Mukai, *Tetrahedron Lett.*, **1967**, 5003; e) I. D. Reingold, K. S. Kwong, and M. M. Menard, *J. Org. Chem.*, **54**, 708 (1989); f) A. S. Kende and J. E. Lancaster, *J. Am. Chem. Soc.*, **89**, 5283 (1967); g) T. S. Cantrell, *J. Am. Chem. Soc.*, **93**, 2540 (1971); h) P. J. Wagner and G. S. Hammond, *Adv. Photochem.*, **5**, 23 (1968).

10) A. Mori, H. Kawakami, H. Takeshita, and T. Nozoe, *Chem. Lett.*, **1996**, 985.

11) S. Wu, A. Mori, and H. Takeshita, *J. Chem. Soc., Chem. Commun.*, **1994**, 919.

12) P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2344 and 2454 (1962); P. E. Eaton and W. S. Hurt, *J. Am. Chem. Soc.*, **88**, 5038 (1966).

13) R. Reinfried, D. Bellus, and K. Schaffner, *Helv. Chim. Acta*, **54**, 1517 (1971).

14) K.-H. Lee and P. de Mayo, *J. Chem. Soc., Chem. Commun.*, **1979**, 493.

15) G. Lem, N. A. Karprinidis, D. I. Schuster, N. D. Ghatlia, and N. J. Turro, *J. Am. Chem. Soc.*, **115**, 7009 (1993).

16) E. Y. Y. Lam, D. Valentine, and G. S. Hammond, *J. Am. Chem. Soc.*, **89**, 3482 (1967).

17) P. J. Wagner and D. J. Bucheck, *J. Am. Chem. Soc.*, **91**, 5090 (1969).

18) J. L. Ruhlen and P. A. Learmakers, *J. Am. Chem. Soc.*, **89**, 4944 (1967).

19) When **6** was counted as a product from an HT dimer, the ratio of the HH and HT dimers decreased from 0.6 to 0.3.

20) Intermediates **11** and **12** might be mutually convertible via a [5,5] sigmatropy under the conditions.

21) Tables of fractional atomic coordinates and equivalent isotropic displacement parameters and geometric parameters including interatomic bond distances and angles for **1** are deposited as Document No. 71013 at the Office of Editor of Bull. Chem. Soc. Jpn.

22) M. C. Altomare, M. Burla, G. Camalli, C. Cascarano, A. Giacovazzo, G. Guagliardi, and J. Polidori, *J. Appl. Crystallogr.*, **27**, 435 (1994).

23) G. M. Sheldrick, "Program for the Refinement of Crystal Structure," University of Göttingen, Germany (1993).