Photodimerizations of 3-Methoxy-1,5-azulenequinone *via* Consecutive Pericyclic Reactions

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(Received August 5, 1996)

3-Methoxy-1,5-azulenequinone gave dimers when irradiated with a high-pressure mercury lamp. The product distribution was dependent on the polarity of the solvent. In a polar solvent, a head-to-head dimer was predominant whereas a head-to-tail dimer was mainly formed in a nonpolar solvent.

Previously, we have observed that irradiation of 3-bromo-1,5-azulenequinone (**1**) and 3-bromo-1,7-azulenequinone (**2**) gave the corresponding head-to-head dimers **3** and **4** in acetonitrile, respectively.[1] It was speculated that they were formed through [2+2]π or [6+6]π and the following [4+2]π cycloadditions. In this paper, we report photodimerization of 3-methoxy-1,5-azulenequinone (**5**), whose product distributions were dependent on the solvent polarity.

When **5** was irradiated in dichloromethane with a 400 W mercury lamp, three products (**6**-**8**) were isolated in 6, 10, and 24% yields, respectively. The structure of **6** was determined to be a head-to-head dimer from the comparison of the spectral data[2] with those of the dimer **3**. Product **7** was also a dimer of **5**. The ^{1}H NMR spectrum of **7** showed five methine and five olefinic protons, which implied that **7** has an unsymmetrical structure. The ^{1}H NMR spectral features of **7** are quite similar to those of **3** and **6**. From these evidences, the structure of **7** was assigned to be a crisscross type dimer as shown in Scheme.

The ^{1}H NMR spectrum of **8** showed a set of methylene protons, four singlet olefinic protons, two olefinic protons coupled each other with a coupling constant of 8.4 Hz, and an olefinic proton coupled with the one of the methylene protons. Compared with the NMR data of the typical [4+2]π cycloadducts of **1** or **2** and dienophiles,[3] **8** must be the secondary product of a [4+2]π cycloadduct of **5**. The cycloaddition would proceed photochemically in a *trans*-mode as observed in the reaction of the photochemical dimerization of tropone[4] and the photoinduced cycloaddition reaction between 9,10-dicyanoanthracene and tropone.[5] The relief of the ring strain in the primary *trans*-fused [4+2]π cycloadduct (**9**) assisted migration of the double bond.

The regiochemistry of **8** was speculated as shown in Scheme from the NOE experiment that the peak intensity of the proton (H_b) at δ 6.81 was not enhanced when the methine proton (H_a) at δ 4.23, which was assigned to the bridge head proton, was irradiated. An alternative structure **10** could be eliminated.

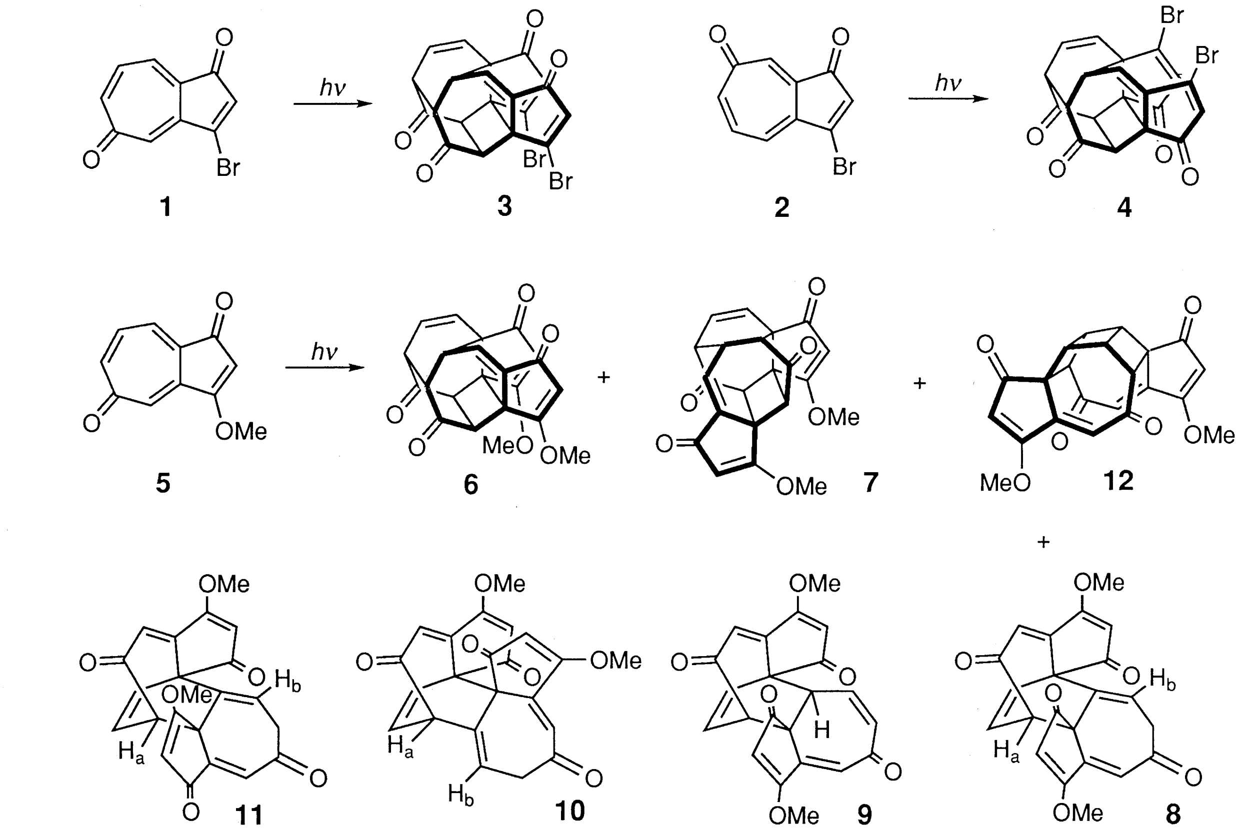

Table 1. Product distribution (%)^a of photodimerization of **5**

Solvent (ε)^b	Time (h)	**6**	**7**	**8**	**12**
Benzene (2.27)	5.5	-	27	24	6
CH_2Cl_2 (8.9)	5.5	6	10	21-24	-
Acetone (20.5)	5.5	21	6	9	-
CH_3CN (37.5)	5.5	24	-	7	-

^{a}Yields were determined by the ^1H NMR spectrum of the reaction mixture after removal of **5**. ^{b}Numbers in parentheses are dielectric constants of solvents.

The stereochemistry of **8** was assigned from the chemical shift of H_b at δ 6.81, which appears at rather lower magnetic field as the proton at the γ-position of a β,γ-unsaturated ketone system. The low chemical shift can be explained on the basis that H_b in **8** is closer to the side of the carbonyl group of the cyclopentenone than the corresponding H_b in **11** from inspections of molecular models.

Next, we investigated photoreaction of **5** in a less polar benzene, in which the head-to-head dimer **6** did not form as shown in Table 1. A new product **12** was obtained in 6% yield. In the ^1H NMR spectrum of **12**, three kinds of methine protons appeared at δ 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 δ 5.62 (2H) and 6.49 (2H) and a singlet methoxyl signal at δ 3.97 (6H). The ^{13}C NMR spectrum showed eleven lines, which indicated that **12** had a symmetrical structure. The splitting patterns of three methine protons led the structure of **12** to a [4+4]π-[2+2]π head-to-tail dimer.

As summarized in Table 1, the head-to-head dimer **6** was the main product in a more polar acetonitrile. When the polarity of solvents is reduced, the yields of the head-to-tail dimer **12** and the crisscross type product **7** were increased. In a less polar solvent, a head-to-tail and a crisscross alignments should be favored over a head-to-head approach to reduce dipole-dipole interactions. In a polar solvent, solvated molecules could come together to react in a head-to-head arrangement. These are quite similar to the solvent effects[6] of the photochemical dimerization of 2-cycloalkenones, in which the *anti* isomers were formed in a less polar solvent.

Thus, the product distributions were sensitive to the solvent polarity.

References and Note

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2 NMR spectra were measured in $CDCl_3$. **6**: ^1H NMR δ=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 δ=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. **7**: ^1H NMR δ=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, m), 5.52 (1H, m), 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 δ=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. **8**: ^1H NMR δ=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 δ=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. **12**: ^1H NMR δ=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 δ=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).

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