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Photoaddition Reactions of Duroquinone to Phenyl Substituted Ethylenes

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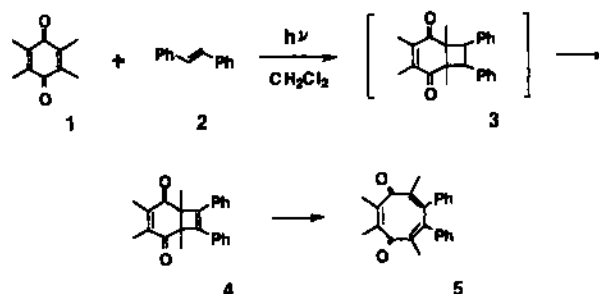
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Quinones are an important class of compounds in organic synthesis, in industry, and in nature. Due to their various spectroscopic properties and reactivities, the photochemistry of *p*-quinones has been a subject of interest in many areas.¹⁻⁴ Recently, an alkyne has been observed to add to duroquinone **1**, having electron donating methyl groups, to give 1:1 and 1:2 photoadducts.⁵ In connection with our investigation of the scope of these reactions, we examined the photoaddition reaction of duroquinone to phenyl substituted ethylenes, such as *trans*-stilbene **2** and styrene **6**.

We introduce here the formation of 8-membered ring compound **5** from the photoreaction of duroquinone **1** and stilbene **2**. We also introduce competitive pathways in the photoaddition of duroquinone **1** to styrene **6**. Preparative photochemical reactions were conducted in dry nitrogen atmosphere in a photochemical reactor composed of a water-cooled system and a Pyrex reaction vessel with 300 nm UV lamps (Rayonet Photochemical Reactor, Model RPR-208). The photoadducts were isolated by flash column chromatography on silica gel using *n*-hexane and ethyl acetate (10 : 1, v/v) as the eluent. Irradiation (300 nm) of duroquinone **1** (164 mg, 1.0 mmol) and *trans*-stilbene **2** (360 mg, 2.0 mmol) in dichloromethane (100 mL) for 76 h yielded 8-membered ring compound **5** (65%) in one pot, as shown in Scheme 1.⁶

In sharp contrast, competitive pathways were observed in the photoaddition reaction of duroquinone **1** to styrene **6**, as shown in Scheme 2. The photoproducts observed in this photoreaction was 1:1 adducts (**8** and **9**) and 1:2 adducts (**11** and other two isomers) as cyclobutanes, 1:2 adducts (**12** and **13**) as racemic cyclohexanes, and polystyrene-bound duroquinone (**14**). Irradiation (300 nm) of duroquinone **1** (328

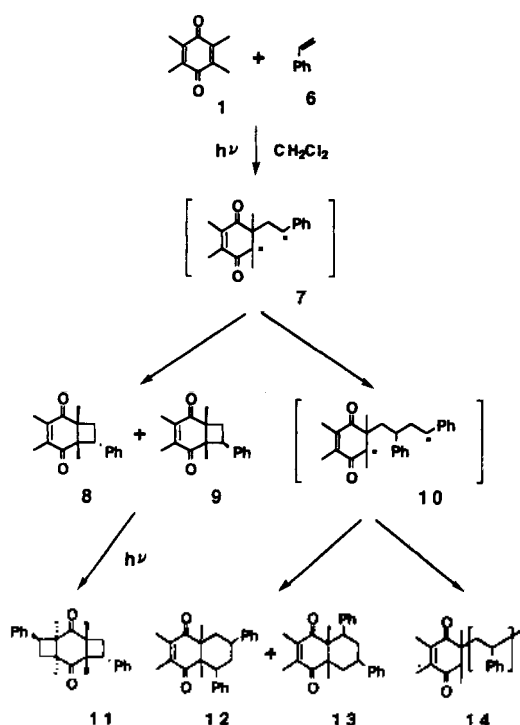


Scheme 1

mg, 2.0 mmol) and styrene **6** (0.05 mL, 0.44 mmol) in benzene (200 mL) for 24 h afforded only 1:1 photocycloadducts (**8** and **9**) in 83% yield. ¹H NMR analysis of the photoproducts revealed a 5.1:1.0 ratio of **8** to **9**. Proton signals at β and α position of methylene group of **8** were observed at δ 2.45 and 2.58, respectively. A proton signal at β position of methine group was observed at δ 3.59. The formation of 1:1 adducts and second intermediate **7** and that of cyclohexanes and polystyrene-bound duroquinone are the results of competition between ring closure and chain enlargement to give the corresponding products.

Increasing the relative amount of styrene decreases the formation of the 1:1 adducts. Instead, 1:2 adducts (**11** and other two stereoisomers) and another types of 1:2 adduct (**12** and **13**) were obtained in moderate yields.

Irradiation of **1** (164 mg, 1 mmol) and **6** (0.6 mL, 5.2 mmol) in benzene (200 mL) for 24 h yielded 1:1 adducts (**8** : **9** = 1.4 : 1.0) in 22% yield, 1:2 adducts (**11** and other two stereoisomers) in 38% yield, and two stereoisomeric mixture of **12** and **13** in 33% yield. ¹H NMR analysis revealed



Scheme 2

a 3.2:1.0:1.0 ratio of **11** to other two isomers and a 1.9:1.0 ratio of **12** to **13**. Small amount of polystyrene-bound duroquinone **14** was also observed and isolated.

When **1** (164 mg, 1 mmol) and **6** (10.0 mL, 87 mmol) were irradiated in benzene (200 mL) for 24 h, 1:2 adducts as cyclobutanes (**11** and other two isomers⁷) and cyclohexanes (**12** and **13**), and polystyrene-bound duroquinone **14** was produced in 35%, 39%, and 20% yield, respectively, where 1:1 adduct **8** was isolated only in 5% yield. All of duroquinone was consumed in this photoreaction. ¹H NMR analysis revealed a 3.6:1.0:1.0 ratio of **11** to other two isomers. The two stereoisomers, **12** and **13**, were obtained with a ratio of 1.9:1.0, as revealed by ¹H NMR.

In order to elucidate the exact structure of the major 1:2 adduct **11**, the nuclear Overhauser effect was exploited in the ¹H NMR experiment. Saturation of a CH₃ resonance (δ 1.50) brought about a 10.2% enhancement of CH(β) resonance of methine groups, a 5.3% enhancement of CH(β) resonance of methylene groups, and a 5.0% enhancement of CH(H_{ortho}) resonance of phenyl groups at the other position. The methyl groups at δ 1.50, therefore, must be positioned closest to the hydrogen atoms(β) of methine groups. Similarly, saturation of another CH₃ resonance (δ 1.06) produced a 4.69% enhancement of CH(β) resonance of methylene groups, a 2.93% enhancement of CH(β) resonance of methine groups, and a 3.77% enhancement of CH(H_{ortho}) resonance of phenyl group at the other side. So, the methyl groups at δ 1.06 must be positioned closest to the hydrogen atoms(β) of methylene groups. The enhancement of the two CH(H_{ortho}) resonance of phenyl group also implies that methyl groups(β) at one position and phenyl group at the other position are located in the same side. ¹H-¹³C correlation spectrum of **11** was also obtained in chloroform-d. Carbon peaks at δ 37.16 and 43.47 of the cyclobutane rings

were correlated with proton peaks at δ 2.49 and 2.71 (methylene protons), and δ 3.73 (methine protons), respectively.

Two diastereomers, **12** and **13**, could be differentiated by NMR spectra. The formation of these cyclohexanes, **12** and **13**, may result from two diradical intermediates, i.e., the first intermediate, 1,4-diradical **7**, and second intermediate, 1,6-diradical **10**.

It is also interesting to note that polystyrene-bound duroquinone **14** is produced in moderate yield, when duroquinone **1** and an excess of styrene **6** are irradiated. ¹H NMR spectrum of **14** showed smaller peaks of duroquinone moiety at δ 2.33 (q, 1H), 1.42 (s, 2 CH₃'s), 1.26 (d, CH₃) and 1.11 (s, CH₃), and, of course, larger peaks due to polystyrene skeleton at δ 7.07, 6.52, 2.20, 2.05, 1.83, and 1.42. The peaks were also compared to those of polystyrene standard. ¹³C NMR spectrum of **14** also showed carbon signals of the polymer chain at δ 145.3, 128.3, 125.6, 43.73, and 40.51. The average number of repeating units in the polymer chain of **14** was 18, which was determined by ¹H NMR spectral integral.

In conclusion, we have shown that 8-membered ring compound **5** were produced from duroquinone **1** and *trans*-stilbene **2** in one pot. We also have shown here that four types of photoadducts, including polystyrene-bound duroquinone **14**, are produced, when **1** and **6** are irradiated in benzene. The relative chemical yields of the adducts were found to depend upon the molar ratio of the starting materials. Two competitive reaction pathways are involved in the formation of the photoadducts. Production of 1:1 adducts, **8** and **9**, and second intermediate, **10**, may result from the competition between ring closure to give cyclobutanes and chain enlargement to give 1,6-diradical intermediate. Similarly, the formation of two stereoisomeric mixtures, **12** and **13**, and polystyrene-bound duroquinone **14** may also be the result of competition between ring closure and ring enlargement to yield the corresponding photoproducts. Once a styrene monomer adds to the second intermediate **10** to yield larger chain, the resultant chain radical is able to attack styrene monomers and finally to be terminated.

Further studies are in progress to get other types of photoadducts of duroquinone and various kinds of olefins.

Experimental

General Procedure for photoadditions of duroquinone to substituted ethylenes. Normal scale preparations of photoadducts were conducted in a photoreactor (Rayonet photochemical reactor, Model RPR-208) composed of a water-cooled reaction vessel and cooling fan. A solution of a 164 mg (1.0 mmol) of duroquinone and 360 mg (2.0 mmol) of *trans*-stilbene in 100 mL of dichloromethane was degassed with nitrogen for 30 min and then irradiated with 300 nm UV lamps in the apparatus described above. The photoreaction mixtures were concentrated in vacuo and chromatographed over silica gel (230-400 mesh, Merck Co.) using *n*-hexane and ethyl acetate as the eluents. A solution of duroquinone and styrene in benzene was also irradiated in the similar manner, and followed by column chromatography to give the photoadducts.

8: UV (MeOH) λ_{\max} 370, 254, 211, 208 nm; IR (KBr) 3029, 2980, 1658, 1454, 1377, 1264, 1032, 758, 702 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.32-7.17 (3H, Ph), 7.08 (d, 2H (ortho), Ph, $J=8.0$ Hz), 3.59 (dd, 1H (β) of CH , $J=12.0$ Hz, $J=8.0$ Hz), 2.58 (dd, 1H (α) of CH_2 , $J=12.0$ Hz, $J=8.0$ Hz), 2.45 (dd, 1H (β) of CH_2 , $J=12.0$ Hz, $J=12.0$ Hz), 2.10 (s, CH_3), 2.09 (s, CH_3), 1.23 (s, CH_3), 0.97 (s, CH_3); ^{13}C NMR (CDCl_3) δ 203.8, 200.1, 145.6, 145.5, 137.9, 128.2, 127.5, 126.7, 53.86, 48.42, 45.58, 33.43, 20.44, 13.52, 13.45, 13.44; Mass (EI) m/e 268 (M), 104 (100%).

9: UV (MeOH) λ_{\max} 370, 254, 211, 208 nm; IR (KBr) 3029, 2980, 1658, 1454, 1377, 1264, 1032, 758, 702 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.32-7.17 (3H, Ph), 6.99 (d, 2H (ortho), Ph, $J=8.0$ Hz), 3.63 (dd, 1H (α) of CH , $J=12.0$ Hz, $J=8.0$ Hz), 2.81 (dd, 1H (α) of CH_2 , $J=12.0$ Hz, $J=12.0$ Hz), 2.26 (dd, 1H (β) of CH_2 , $J=12.0$ Hz, $J=8.0$ Hz), 1.99 (s, CH_3), 1.69 (s, CH_3), 1.48 (s, CH_3), 1.46 (s, CH_3); ^{13}C NMR (CDCl_3) δ 201.3, 198.9, 145.8, 145.7, 144.9, 138.5, 128.1, 127.6, 126.9, 56.27, 47.98, 46.87, 34.80, 20.82, 18.00, 13.66, 12.95; Mass (EI) m/e 268 (M), 104 (100%).

11: UV (MeOH) λ_{\max} 320, 308, 249, 211, 208 nm; IR (KBr) 3029, 2987, 1679, 1447, 1377, 1222, 1086, 758, 702 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.32-7.21 ($2 \times 3\text{H}$, Ph), 6.96 (d, $2 \times 2\text{H}$ (ortho), Ph, $J=8.0$ Hz), 3.73 (dd, $2 \times 1\text{H}$ (β) of CH , $J=12.0$ Hz, $J=8.0$ Hz), 2.71 (dd, $2 \times 1\text{H}$ (α) of CH_2 , $J=12.0$ Hz, $J=8.0$ Hz), 2.49 (dd, $2 \times 1\text{H}$ (β) of CH_2 , $J=12.0$ Hz, $J=12.0$ Hz), 1.50 (s, $2 \times \text{CH}_3$), 1.06 (s, $2 \times \text{CH}_3$); ^{13}C NMR (CDCl_3) δ 215.2, 137.4, 128.3, 127.1, 126.9, 56.78, 51.79, 43.47, 37.16, 22.63, 12.74; Mass (EI) m/e 372 (M), 268, 104 (100%).

12: UV (MeOH) λ_{\max} 370, 241, 218, 211, 204 nm; IR (KBr) 3029, 2973, 1686, 1658, 1454, 1377, 1025, 899 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.43-7.06 (10H, Ph), 3.55 (1H of CH), 2.89 (1H of CH_2), 2.81 (1H of CH_2), 2.60 (1H of CH), 2.48 (1H of CH_2), 2.32 (1H of CH_2), 0.96 (s, CH_3), 0.74 (s, CH_3), 0.68 (s, CH_3), 0.64 (s, CH_3); ^{13}C NMR (CDCl_3) δ 213.2, 212.7, 139.1, 137.7, 128.5-126.6 (Ph, overlapped), 54.64, 49.26, 48.49, 42.69, 37.44, 33.42, 22.40, 19.97, 19.96, 15.10; Mass (EI) m/e 372 (M), 268, 104 (100%).

13: ^1H NMR (CDCl_3) δ 7.34-6.93 (10H, Ph), 3.65 (1H of CH), 3.52 (1H of CH), 2.96 (1H of CH_2), 2.65 (1H of CH_2), 2.37 (1H of CH_2), 2.27 (1H of CH_2), 1.69 (s, CH_3), 1.62 (s,

CH_3), 1.35 (s, CH_3), 0.71 (s, CH_3); ^{13}C NMR (CDCl_3) δ 211.2, 208.3, 146.6, 146.5, 138.6, 138.4, 146.6-126.8 (Ph, overlapped), 61.22, 49.81 (CH), 49.49, 42.90 (CH), 35.54, 34.31, 23.48 (CH_3), 22.11 (CH_3), 19.13 (CH_3), 12.81 (CH_3); Mass (EI) m/e 372 (M), 268, 104 (100%).

14: UV (MeOH) λ_{\max} 370, 357, 346, 245, 218, 212, 206 nm; IR (KBr) 3026, 2923, 1721, 1687, 1452, 1370, 908, 757, 700 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.07, 6.52, 2.20, 2.05, 1.83, 1.42 [polymer chain], and 2.33 (q, 1H), 1.42 (s, $2 \times \text{CH}_3$), 1.26 (d, CH_3), 1.11 (s, CH_3) [duroquinone].

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- In our previous results, **4** and **5** was prepared from the photoaddition reaction of **1** and diphenylacetylene. For spectral data of **4** and **5**, see Kim, S. S.; Kim, A. R.; Yoo, D. J.; Shim, S. C. *Bull. Korean Chem. Soc.* **1995**, *16*, 797.
- Two other stereoisomers were also found, and similar patterns of UV, IR, ^1H NMR, ^{13}C NMR spectra were observed. Mass (EI) spectra were also obtained to confirm the molecular weight (m/e 372).

Effect of Au and WO_3 on the Surface Structure and Photocatalytic Activity of TiO_2

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Heterogeneous photocatalysis with titanium oxide (TiO_2) is a promising method for the decomposition of organic pol-

lutants dissolved in water.¹⁻³ Previously, we have demonstrated that photocatalytic activity of TiO_2 can be greatly im-