One-Pot Formation of a Cyclobutane from the Double Photocycloaddition Reactions of 1,4-Diethynylbenzene to Some *o*-Quinones

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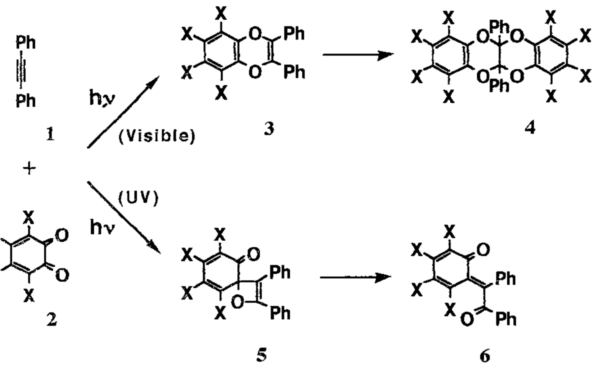
A cyclobutane was produced in one pot, when irradiated 1,4-diethynylbenzene and some *o*-quinones, such as tetrahalo-1,2-benzoquinones, phenanthrenequinone and acenaphthenequinone, in dichloromethane with 300 nm UV light.

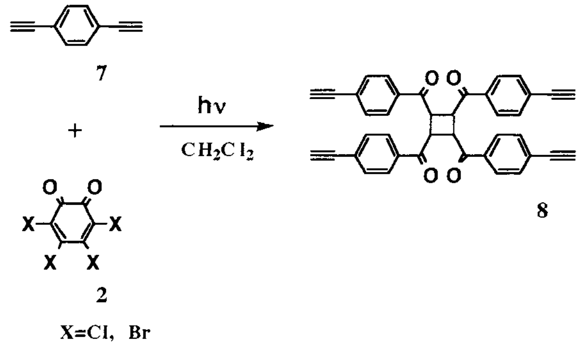
Quinones are an important class of compounds as quinone dye-stuffs in industry or dehydrating agents in organic synthesis in addition to a vital role in biological systems.[1,2] Due to their various spectroscopic properties, the photochemistry of quinones has been a subject of interest in many areas.[3-5] Alkynes are known to react photochemically with *o*-quinones to give 1,4-dioxins, 1,3-dioxoles, or *o*-quinomethanes.[6-8] Bryce-Smith *et. al* have reported that the photoaddition reaction of diphenylacetylene **1** and tetrachloro-1,2-benzoquinone **2a** (X=Cl) in acetone or acetonitrile at > 400 nm gave 1:1 adduct **3** as a dioxin which undergoes further photochemical reaction with the quinone to give 1:2 adduct **4**.[9]



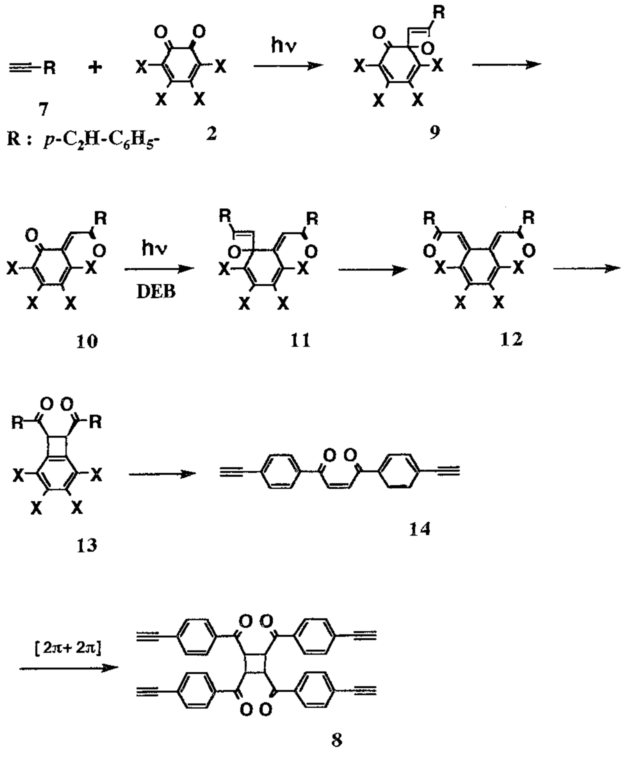
Scheme 1.

Recently, we found that, when irradiated diphenylacetylene **1** and tetrahalo-1,2-benzoquinones **2** in dichloromethane with 300 nm UV light, *o*-quinomethanes **6**, *p*-quinomethanes and *p*-quinodimethanes are produced through another reaction pathway, that is, *via* spiro-oxetene intermediates **5**.[10] As a matter of fact, the *p*-quinodimethanes have served in many synthetic applications.[11] In addition, quinomethanes have been extensively studied over the last few decades.[2,12] The *o*-quinomethane **6** was found to undergo *cis-trans* one-way isomerization to give its geometric isomer. These three types of photoproducts were also isolated, when irradiated a dichloromethane solution of diphenylacetylene **1** and phenanthrenequinone **15** (or acenaphthenequinone **16**) under the similar condition.[10]

We now report very interesting results that a cyclobutane **8**[13] was produced in one pot, when irradiated 1,4-diethynylbenzene (DEB) **7**,[14] and some *o*-quinones in dichloromethane with 300 nm UV light. Preparative photoreactions were conducted in a photoreactor composed of a water-cooled system and a Pyrex reaction vessel with 300 nm UV lamps (Rayonet Photochemical Reactor, Model RPR-208), after purging with dry nitrogen gas (purity: 99.9%) for 30 min.



Scheme 2.



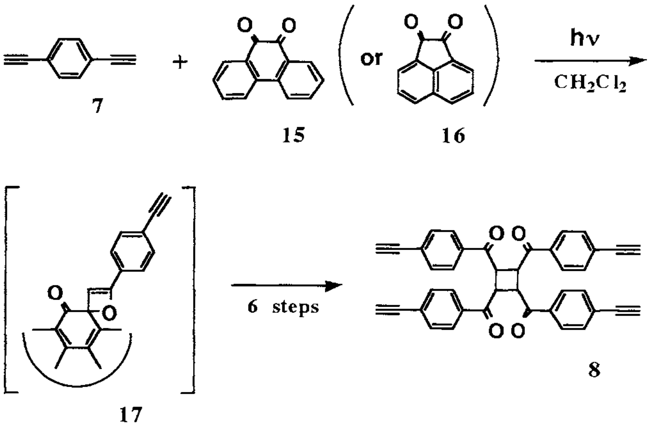
Scheme 3.

Irradiation of a dichloromethane solution (50 mL) of DEB **7** (59 mg, 0.4 mmol) and tetrachloro-1,2-benzoquinone **2a** (X=Cl, 116 mg, 0.4 mmol) with 300 nm UV light for 24 h afforded a cyclobutane **8** in 37% yield as the major product, as shown in Scheme 2.[13] The alkyne **7** and tetrabromo-1,2-benzoquinone **2b** (X=Br) was also irradiated in the similar condition to give the cyclobutane **8** in 45% yield. The photoproduct was isolated by flash column chromatography (silica gel, 230 - 400 mesh) using hexane and ethyl acetate as the eluent (from 97:3 to 9:1, v/v).

The one-pot photochemical formation of the cyclobutane **8** from DEB **7** and *o*-quinones **2** could be accounted *via* consecutive reaction pathways, including double photocycloaddition reactions, as shown in Scheme 3. The first event is thought to be [2+2] photocycloaddition reaction of a carbon-carbon triple bond of DEB **7** and a carbon-oxygen double bond of *o*-quinones **2**, in which unstable spiro-oxetenes **9** are formed, and then undergo rearrangement to give *o*-quinomethanes **10**. On the basis of the experimental results, the remaining carbonyl group in the *o*-quinomethanes **10** is so reactive as to add to another DEB molecule **7** to give the 1:2 adduct **12**, *via* the corresponding spiro-oxetene intermediates **11**. Now the electrocyclic reaction of the 1,3-diene **12** gives rise to a cyclobutane intermediate **13**, which is then cleaved to give an ethylene **14**. A [2π+2π] photocycloaddition reaction of the olefin **14** finally yields a cyclobutane **8**. ^{1}H and ^{13}C NMR spcrtra shows that four methine protons in the cyclobutane ring appeared at δ 6.61 (s) and δ 67.5, respectively. Mass spectrum (EI) also confirms the exact structure of the cyclobutane **8**, in which the molecular ion peak was observed at m/e 498.

The cyclobutane **8** was also produced from the photoreactions of DEB **7** with phenanthrenequinone **15** (or acenaphthenequinone **16**) in dichloromethane. Irradiation of a dichloromethane solution (50 mL) of DEB **7** (63 mg, 0.5 mmol) and phenanthrenequinone **15** (104 mg, 0.5 mmol) with 300 nm UV light for 24 h gave the cyclobutane **8** in 28% yield, as shown in Scheme 4.[13] DEB **7** (63 mg, 0.5 mmol) and acenaphthenequinone **16** (91 mg, 0.5 mmol) were also rradiated in dichloromethane (50 mL) in the similar condition to give the cyclobutane **8** in 25% yield.

In summary, we found that any alkynes having two terminal acetylenes may undergo double photocycloaddition reactions to *o*-quinones which also have two carbonyl groups in the structure as the functional groups. This means that new polymers may be produced from the photoreactions of the two bifunctional molecules. In fact, an insoluble polymeric compound was obtained from the reaction mixtures of DEB **7** and *o*-quinones, such as **2a** and **2b**, **15**, and **16**.



Scheme 4.

Extension of the characterization of the polymeric materials and the photochemical reactivities of a variety of diynes having terminal acetylenes towards *o*-quinones will be investigated. The exact stereochemistry of the cyclobutane and the photoaddition reactions of other acetylene derivatives to *o*-quinones will also be investigated.

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13 **8**: UV(MeOH) λ_{max} 280, 270, 255, 243 nm; IR(KBr) 3313, 2978, 2110, 1716, 1608, 1459, 1077, 859 cm^{-1}; 400 MHz ^{1}H-NMR(CDCl$_3$), δ 8.06 (4x2H, aromatic, d, J = 8.1 Hz), 7.61 (4x2H, aromatic, d, J = 8.1 Hz), 6.61 (4x1H, 4CH's, s), 3.31 (4x1H, 4CCH's, s); ^{13}C-NMR(CDCl$_3$), δ 185.1 (CO), 133.0 (aromatic CH), 131.5 (aromatic C), 129.8 (aromatic CH), 125.4 (aromatic C), 82.3 ($\underline{C}$CH), 81.3 (C$\underline{C}$H), 67.5 (CH); Mass (EI), m/e 498 (M).

14 DEB **7** was found to add to *p*-quinones to give cyclobutenes or *p*-quinomethanes. For the photoaddition reactions of DEB to *p*-quinones, see a) S. S. Kim, A. R. Kim, K. J. O, D. J. Yoo, and S. C. Shim, *Chem. Lett.*, **1995**, 787. b) S. S. Kim, K. J. O, and S. C. Shim, *Bull. Korean Chem. Soc.*, **15(4)**, 270 (1994).