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Photoaddition Reactions of 9,10-Phenanthrenequinone and Acenaphthenequinone to Conjugated Molecules

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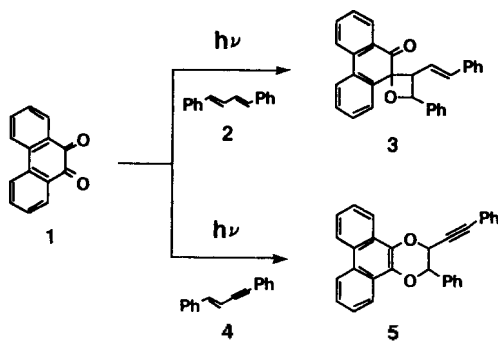Chonbuk National University,
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Quinones are an important class of compounds in organic synthesis, in industry, and in nature.[1~2] Due to their various spectroscopic properties, the photochemistry of quinones has been a subject of interest in many areas. 9,10-Phenanthrenequinone **1** is known to add to olefins to give two types of products, keto oxetanes and 1,4-dioxins.[3~5] Acetylenes also provide a useful route to synthesis of dioxole derivatives or α,β-unsaturated keto ester.[6~7]

In previous work, we have reported that 9,10-phenanthrenequinone **1** adds to *trans-trans*-1,4-diphenyl-1,3-butadiene **2** to give keto oxetane **3** as 1 : 1 adduct.[8] We now report that 9,10-phenanthrenequinone **1** adds to 1,4-diphenylbut-1-en-3-yne **4** to yield 1,4-dioxin **5**, as shown in Scheme 1. In contrast, acenaphthenequinone **6** added to **2** and **4** to yield keto oxetanes, **7** and **8**, as shown in Scheme 2. The difference between the reactivities of **1** and **6** was also discussed.

Preparative photochemical reactions 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 the mixture with nitrogen gas (purity; 99.9%) for 30 min.

Irradiation of 208 mg (1.0 mmol) of 9,10-phenanthrenequinone **1** and 204 mg (1.0 mmol) of 1,4-diphenylbut-1-en-3-yne **4** in 100 mL of dichloromethane with 300 nm UV light for 48 h yielded 1,4-dioxin **5** in 65% yield.[9] Photoadduct **5** was separated by flash column chromatography (silica gel, 230-400 mesh) using *n*-hexane and ethyl acetate (95 : 5, v/v) as the eluent. Mass spectrum (EI) of **5** showed a molecular ion peak at m/e 412. ^{1}H NMR analysis of **5** revealed a 2.3 : 1.0 ratio of *cis*-adduct and *trans*-adduct. Two methine protons of **5** (*cis*) were observed at δ 5.63 (d, $J=2.9$ Hz) and 5.54 (d, $J=2.9$ Hz) in ^{1}H NMR spectra ($CDCl_3$), whereas those of **5** (*trans*) were found at 5.30 (d, $J=7.3$ Hz) and 5.15 (d, $J=7.3$ Hz). The H-C-C-H dihedral angles φ of the two isomers were obtained by using Chem 3D Plus program, in which φ values of **5** (*cis*) and **5** (*trans*) were 62.7° and 173.1°, respectively. The magnitude of the splitting between the two H's, i.e., $^3J_{\text{H-C-C-H}}$ is the largest when φ=0° or 180°, and is the smallest when φ=90°.[10] Thus, it can be considered that $^3J_{trans}$ is larger than $^3J_{cis}$.

The photoadduct **3** may be formed via 1,4-diradical intermediate I, as shown in Figure 1, followed by coupling to give keto oxetane **3**.[8] Interestingly, irradiation of **1** and **4** gave 1,4-dioxin **5**, but not keto oxetane, like **3**. This fact implies that **5** is produced by the formation of 1,4-diradical intermediate III and then 1,6-diradical intermediate followed by coupling to give the final product **5**. These observations are consistent with the fact that phenylpropargyl radical is more stable than phenylallyl radical, that is, radical III is more stable than radical I.[11] The lifetime of the more stable 1,4-radical III is sufficiently long to give 1,6-diradical intermediate prior to cyclization to yield 6-membered ring compound **5**. Although the alternative radical intermediates II and IV have stable benzyl radical, the evidence for the involvement of these radicals was not observed. In other words, based on the experimental results, the preferred intermediate of **3** is not II but I, and that of **5** is not IV but III. Ethenylbenzene and ethynylbenzene moieties reduce the
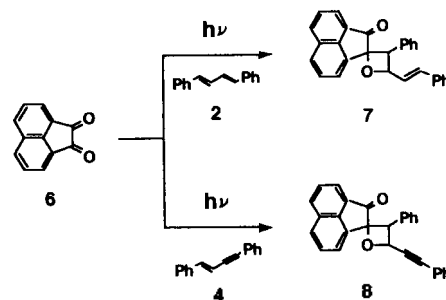
Scheme 2.
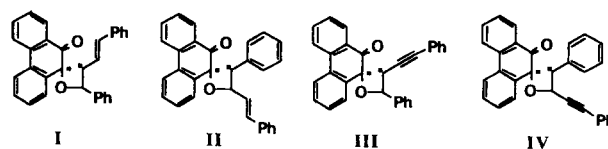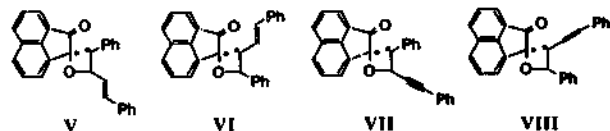
Figure 1.

Scheme 1.

Figure 2.

steric factor occurring in I and III, in comparison with phenyl groups in II and IV.

In contrast, photoaddition of acenaphthenequinone to some conjugated molecules, 2 and 4, gives only keto oxetanes, 7 and 8, as shown in Scheme 2. Irradiation (300 nm) of acenaphthenequinone 6 (182 mg, 1.0 mmol) and *trans, trans*-1,4-diphenyl-1,3-butadiene 2 (206 mg, 1.0 mmol) in dichloromethane (100 mL) yielded keto oxetane 7 in 32% yield.[12] H-C-C-H dihedral angles of 7 (*cis*) and 7 (*trans*) determined by Chem 3D Plus program were 16.75° and 105.9°, respectively. The coupling constants, $^3J_{cis}$ and $^3J_{trans}$, were 9.5 Hz and 8.1 Hz, respectively. With 1,4-diphenylbut-1-en-3-yne 4 (204 mg, 1.0 mmol), acenaphthenequinone 6 (182 mg, 1.0 mmol) also afforded the same type of keto oxetane 8 in 39% yield.[13] H-C-C-H dihedral angles of 8 (*cis*) and 8 (*trans*) were 5.62° and 106.8°, respectively. Actually, $^3J_{cis}$ and $^3J_{trans}$ were 8.1 Hz and 6.6 Hz, respectively.

In order to elucidate the difference between the typical reaction types of 1 and 6, bond angles of 9,10-dihydroxyphenanthrene and 1,2-dihydroxyacenaphthylene were calculated by using Chem 3D Plus program. The O-C-C bond angles of O-C-C-O moiety in 9,10-dihydroxyphenanthrene and 1,2-dihydroxyacenaphthylene were 120.2° and 125.6°, respectively. Thus, it can be thought that larger deviation of O-C-C bond angles from 120° prevent from the formation of 6-membered ring compounds. Consequently, larger O-C-C bond angles may reduce steric factor, as in the cases of V and VII. The electronic factors are considered to be more important in the formation of V and VII than in that of I and III. On the basis of the electronic factors, V and VII are more stable than VI and VIII, respectively, because benzyl radical moieties in V and VII are resonance-stabilized by four canonical forms.

This studies show that there are many factors, such as steric factor, electronic factor, bond angles, etc., governing the reaction pathways in the photoaddition reactions of *o*-quinones to some conjugated molecules. In the case of enyne system, it was found that carbon-carbon double bond is much more reactive toward *o*-quinones than carbon-carbon triple bond. In fact, the photoaddition reactions of *o*-quinones to 1,4-diphenylbytadiyne were also investigated. However, the chemical reactivity was found to be very low. Further studies are in progress to explore mechanistic factors responsible for the differences of the reaction pathways, as well as the photochemical synthesis of various kinds of quinone derivatives.

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12. Spectral data of 7: IR (KBr), 3057, 2924, 1728, 1602, 1496, 1454, 1271, 1194, 1060, 1004, 779, 702 cm^{-1}; ^{1}H NMR (CDCl$_3$) of 7 (*cis*), δ 8.40-7.20 (16H, aromatic), 6.70 (1H, PhCH=CH-, dd, J=16.1 Hz, J=8.1Hz), 6.07 (1H, Ph-CH=, d, J=16.1 Hz), 6.06 (1H, Ph-CH-, d, J=9.5 Hz), 4.42 (1H, Ph-CH-CH-, dd, J=9.5 Hz, J=8.1 Hz); ^{1}H NMR (CDCl$_3$) of 7 (*trans*), δ 8.40-7.20 (16H, aromatic), 6.67 (1H, Ph-CH=CH-, dd, J=16.1 Hz, J=9.5 Hz), 6.26 (1H, Ph-CH-, d, J=8.1 Hz), 6.19 (1H, Ph-CH=, d, J=16.1 Hz), 4.07 (1H, Ph-CH-CH-, dd, J=9.5 Hz, J=8.1 Hz); Mass (EI), m/e 388 (M), 206, 182.
13. Spectral data of 8: IR (KBr), 3057, 2924, 2228, 2200, 1728, 1602, 1496, 1454, 1271, 1194, 1060, 1004, 779, 702; ^{1}H NMR (CDCl$_3$) of 8 (*cis*), δ 8.29-7.51 (16H, aromatic), 4.73 (1H, d, J=8.1 Hz), 4.32 (1H, d, J=8.1 Hz); ^{1}H NMR (CDCl$_3$) of 8 (*trans*), δ 8.29-7.51 (16H, aromatic), 4.52 (1H, d, J=6.6 Hz), 4.29 (1H, d, J=6.6 Hz); Mass (EI), m/e 386 (M), 204, 182.