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Photoadditions of *o*-Quinones to 1,4-Diphenyl-1,3-butadiene

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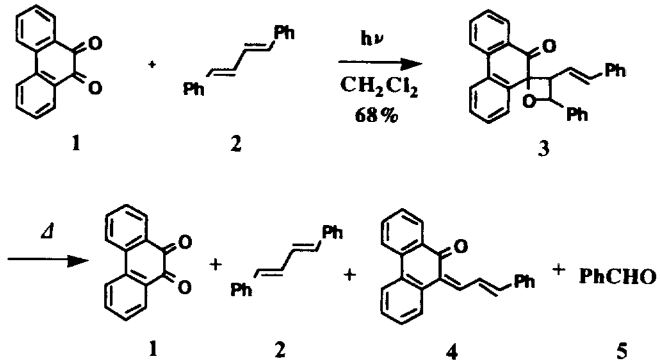
Quinones are an important class of compounds in industry, in organic synthesis, and in Nature.[1] Due to their various spectral properties, the photochemistry of quinones has been a subject of interest in many areas.[2-4] Phenanthrenequinone (PQ) **1** is known to react with substituted acetylenes to give 1,4-dioxenes or 1,3-dioxoles.[5] The photochemical reactions of PQ and olefins give rise to dioxenes or keto oxetanes.[6-8]

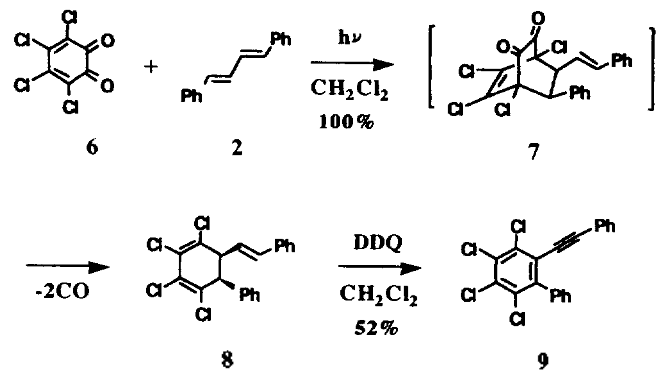
In connection with our investigation of the scope of these reactions, we examined the photochemistry of *o*-quinones and conjugated systems such as 1,4-diphenyl-1,3-butadiyne (DPBy) and *trans,trans*-1,4-diphenyl-1,3-butadiene (DPBe) **2**. Although no adduct was found in the photoreactions of PQ with diphenylacetylene and DPBy, a 1 : 1 adduct **3** was obtained in 68% yield when irradiated PQ **1** and DPBe **2** in dichloromethane.[9]

A solution of 150 mg (7.2×10^{-4} mol) of PQ **1** and 222 mg (1.08×10^{-3} mol) of DPBe **2** in 100 mL of dichloromethane was deoxygenated using nitrogen gas and irradiated with 350 nm UV light for 12 h. After evaporation of the solvent, the residue was chromatographed on silica gel (230-400 mesh) using *n*-hexane and ethyl acetate as eluents. Elution with *n*-hexane afforded unreacted DPBe **2**. Elution with 2% ethyl acetate in *n*-hexane afforded 205 mg (68% based on PQ) of adduct **3**.

The structure of 1 : 1 adduct **3** was characterized by UV, IR, 400 MHz ^{1}H-NMR, ^{13}C-NMR, and mass spectra. ^{1}H-^{13}C correlation spectrum of **3** shows that the peaks at 134.3 ppm



Scheme 1.



Scheme 2.

and 123.3 ppm in the ^{13}C dimension correspond to the vinyl protons (PhC<u>H</u>= and PhCH=C<u>H</u>-) in the ^{1}H dimension; the two methine ^{1}H resonances at 3.78 ppm and near 6.06 ppm[10] correspond to the two ^{13}C signals at 62.8 ppm and 81.2 ppm, respectively. **3** undergoes slow thermal dissociation at room temperature. Standing **3** at room temperature for 15 h gave rise to not only starting materials, PQ **1** and DPBe **2**, but also benzaldehyde **5** and its corresponding decomposition compound **4**. The three vinyl protons of **4** were observed at 6.85 ppm (d, J=16.12 Hz), 6.19 ppm (d, J=16.16 Hz), and 5.99 ppm (dd, J=16.16 and 16.12 Hz).

Refluxing a dichloromethane solution of tetrachloro-1,2-benzoquinone (*o*-TCBQ) **6** and DPBe **2** for 18 h gave rise to tetrachloro-1,3-cyclohexadiene derivative **8** in 99% yield.

Photochemical reaction of *o*-TCBQ **6** and DPBe **2** in dichloromethane with 350 nm UV light only for 2 h also afforded **8** quantitatively.[11] The stereochemistry of the *cis*-adduct **8** was rationalized by using the result of MMX data.[12] The magnitude of the coupling constant (J) between two adjacent CH bonds is depend directly on the dihedral angle between these two bonds, in which the magnitude is largest when the angle is 0° or 180°, and is smallest when the angle is 90°. ^3J of the *cis*-adduct **8** was 7.65 Hz.[11,12] The formation of **8** probably proceeds *via* [4+2] adduct **7**[13,14], which would be expected to undergo rapid photobisdecarbonylation.[13,14] ^{1}H-^{13}C correlation spectrum was also obtained to assign the exact positions of the carbon atoms of **8**.[15]

Refluxing a dichloromethane solution of **8** in the presence of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) for 12 h gave rise to the oxidized product **9** in 52% yield.[16]

^{1}H-NMR spectrum of **9** shows that all the four proton signals of **8** at 6.21 ppm, near 6.02 ppm and 3.78 ppm were disappeared. The formation of an aromatic system could be the driving force in this reaction.

The extension of the photoaddition reactions of *o*-quinones to conjugated systems, and the chemistry of these photoproducts, will be investigated.

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9. Spectral data of **3**: IR (KBr), 3064, 3029, 2917, 1693, 1595, 1447, 1278, 969, 786, 758, 695 cm^{-1}; UV (*n*-hexane), λ_{max} 330, 277, 263, 251, 222 nm; ^{1}H-NMR ($CDCl_3$), δ 8.12-7.02 (18H, aromatic), 6.21 (1H, d, J=16.0 Hz, PhC$\underline{H}$=CH-), 6.09-6.03 (2H, m, PhCH=C$\underline{H}$- and PhC$\underline{H}$(O)-), 3.78 ppm (1H, dd, PhCH(O)C$\underline{H}$-); ^{13}C-NMR ($CDCl_3$), δ 199.3 ppm ($\underline{C}$=O), 134.7, 129.4, 128.8, 128.5 (2 C's), 128.2, 128.1, 127.8, 126.3, 126.2, 125.3, 123.9, 123.0 ppm (14 different aromatic $\underline{C}$H's), 134.3 (Ph$\underline{C}$H=CH-), 123.3 (PhCH=$\underline{C}$H-), 81.2 (Ph$\underline{C}$H(O)-), 62.8 ppm (PhCH(O)$\underline{C}$H-), 140.5, 138.8, 136.9, 135.9, 130.0, 129.6, 89.7 ppm (7 quaternary C's); Mass (EI), m/e 414 (M), 206 (100%, DPBe), 77.
10. The two overlapped ^{1}H signals of a vinyl proton (PhCH=C$\underline{H}$-) and a methine proton (PhC$\underline{H}$(O)-) was well resolved into two distinct signals at 123.3 ppm and 81.2 ppm in the ^{13}C dimension.
11. Spectral data of **8**: UV (*n*-hexane) λ_{max} 356, 338, 310, 302, 294, 270 nm; IR (KBr) 3029, 2917, 1560, 1426, 969, 786, 758, 695 cm^{-1}; ^{1}H-NMR ($CDCl_3$), δ 7.39-7.23 (10H, m), 6.67 (1H, d, J=16.0 Hz, PhC$\underline{H}$=CH-), 5.96 (1H, dd, J=16.0 Hz and 5.92 Hz, PhCH-C$\underline{H}$-) 4.87 (1H, d, J=7.65 Hz, PhC$\underline{H}$-CH-), 4.70 ppm (1H, m, PhCH-C$\underline{H}$-); Mass (EI), m/e 394 (M).
12. MMX calculation using PC Model (v. 3.2) showed different coupling constants for two isomers. The calculated values, ^3J(*cis*) and ^3J(*trans*), for the two adjacent CH bonds of Ph-CH-CH- moiety were 4.77 Hz and 0.59 Hz, respectively, in which the calculated dihedral angles were 48° for *cis*-adduct **8** and 81° for *trans*-adduct.
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15. Carbon peaks at 135.2, 121.3, 80.13, and 78.77 ppm were correlated with proton peaks at 6.67 (PhC$\underline{H}$=CH-), 5.96 (PhCH=C$\underline{H}$-), 4.87 (PhC$\underline{H}$-CH-), and 4.70 ppm (Ph-CH-C$\underline{H}$-), respectively. All aromatic carbons were observed between 129.4 ppm and 126.2 ppm.
16. Spectral data of **9**: UV (*n*-hexane), λ_{max} 292, 285, 233, 223 nm; IR (KBr), 3064, 2959, 1595, 1461, 744, 702 cm^{-1}; ^{1}H-NMR ($CDCl_3$), δ 7.72-7.68 (5H, m, aromatic) and 7.54-7.50 ppm (5H, m, aromatic); Mass (EI), m/e 390 (M).

Epoxidation of β,γ-Unsaturated Carboxylic Acids by Dimethyldioxirane

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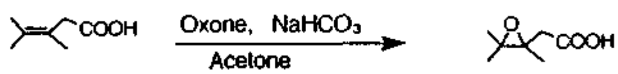
Peroxy acids, one of the most commonly used electrophilic epoxidizing agents, are not effective in the epoxidation of olefins containing carboxyl groups because of electron withdrawing property of the carboxyl group[1]. Moreover the acid generated from the peroxyacid is difficult to separate from the desired product, epoxy acid. Nucleophilic epoxidizing agents, hydrogen peroxide together with various catalysts (base, tungsten, etc.), are effective only to α,β-unsaturated acids[2]. Recently dimethyldioxirane[3] has been employed for epoxidation of α,β-unsaturated ketones[4], acids[5] and esters. Not only electron rich alkenes such as enol ethers[6] and lactones[7] but also electron poor alkenes such as vinyltetrazoles[8], flavons[9] are also epoxidized by dimethyldioxirane in high yield. But not many unsaturated carboxylic acids have been epoxidized by dimethyldioxirane. Here we report this powerful agent, which can be generated *in situ* from potassium peroxomonosulfate (oxone) and acetone[10], is effective in the epoxidation of β,γ-unsaturated acids.



Most β,γ-unsaturated acids tested in this study were rapidly reacted with dimethyldioxirane to give the corresponding epoxy acids in good yield (Table 1). The product yield decreased when there were two carboxyl groups or an amide group in the molecule. We confirmed that the epoxidation of α,β-unsaturated carboxylic acids are smoothly carried out by dimethyldioxirane, as reported previously[4]. But under the same reaction condition, a γ,δ-unsaturated carboxylic acid was transformed to the lactone instead of the epoxide. This is probably due to the spontaneous opening of epoxide.

The procedure[8] for epoxidation of β,γ-unsaturated acids was very simple and convenient: Ansaturated acid (0.001