

Figure 3. The α - β - α isomerism by protonation of $[\text{PtMo}_6\text{O}_{24}]^{8-}$ anion shown as polyhedra model. a) Present work. b) Reference 1. ●: Protonated O atom. ▲: Protonated O atom by acidic H atom. ■: Only a half protonated O atom in disorder.

drogen atom. It is very difficult to explain clearly that the isomerization occurs in the $[\text{PtMo}_6\text{O}_{24}]^{8-}$ polyanion. However, it seems that the gradual protonation of polyanion plays an important role in that isomerism. The α - β - α isomerism of hexa-

molybdoplatinate(IV) polyanion, $[\text{PtMo}_6\text{O}_{24}]^{8-}$ is the first example of isomerism caused by protonation in the heteropolyoxometalate.

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Photoreactions of Quinonoid Compounds with Alkynes and Cyclic Olefins

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Received February 19, 1988

The photochemical reactions of *p*-quinones to olefins have been reported as a widely-applicable reaction.¹⁻⁵ Photodimerization of *p*-benzoquinone (*p*-BQ) and some of its methyl derivatives give either cyclobutanes or spiro-oxetanes depending on the nature of the quinone. The photoaddition of diphenyl acetylene (DPA) to *p*-BQ forms a quinone methide (2,3), probably through an unstable intermediate, spiro-oxetane(1).¹⁻⁴

We recently reported that tetrachloro-*p*-benzoquinone (chloranil) readily forms a novel photorearrangement product by the reaction with some cyclic olefins, such as cyclohexene, 1,3-cyclohexadiene and cycloheptatriene.⁶ By contrast, irradiation of a solution of *p*-BQ and 1,3-cyclohexadiene in benzene yielded a Diels-Alder reaction product, which was found to be 1:1 adduct reacted at C=C double bond of *p*-BQ. In connection with our continuous studies toward the photoreactions of *p*-quinone derivatives with alkynes, we now report that irradiation of quinonoid compounds and DPA in dichloromethane gives the same type of photoadduct (4,5,8 and 9) as a major product. Irradiation was carried out in a cylindrical water-cooled Pyrex glass reaction vessels with 350 nm UV light (The Southern New England Ultraviolet Company). The photoproducts were isolated by column chromatography (silica gel) using *n*-hexane-diethyl ether-dichloromethane (4:1:1, v/v) as an eluting solvent. The structure for the photoproducts was identified by the mass spectra (electron impact method), ¹H-NMR, IR, UV, and fluorescence spectra. The 1:1 adduct from *p*-BQ and cyclohexadiene reacts with DPA giving 5. The mass spectrum (EI, 70 eV) shows a peak at *m/e* 286 ($\text{M}-\text{C}_5\text{H}_6$). The peaks at *m/e* 105 (100%) and 77 prove the existence of benzoyl group. The IR spectrum shows two C=O stretching bands at 1675 and 1668

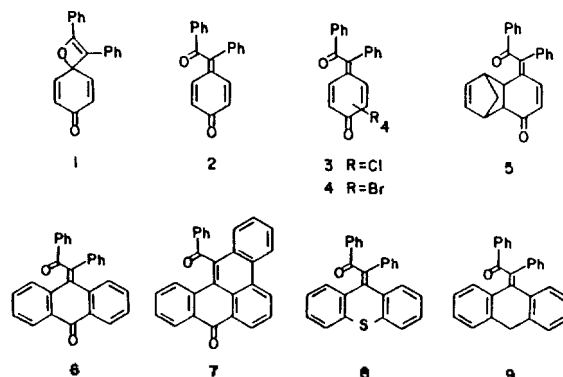


Figure 1. Photoproducts of the quinonoid compounds and 1,4-diphenylacetylene.

cm^{-1} . The two kinds of vinyl protons appear at 6.45 ppm (d. of d.) and 6.22 ppm (d. of d.) in ¹H-NMR spectrum (CDCl_3). On the other hand, the photochemical reaction of anthraquinone and DPA with 350 nm UV light afforded a photocyclization product(7), not 6. The structure of 7 was characterized by the following spectral data. The UV spectrum in methanol shows the different absorption bands in comparison with that of anthraquinone. The absorption bands of anthraquinone are observed at 324, 270, and 252 nm in methanol. The longest absorption band of 7 was shifted to 380 nm. This red shift results from the formation of phenanthrene moiety. The IR spectrum shows the presence of different carbonyl groups at 1660 and 1650 cm^{-1} . Mass spectrum (EI method) shows a parent ion peak at *m/e* 384, not at *m/e* 386. The base peak at *m/e* 105 is indicative of benzoyl group. Thioxanthone and

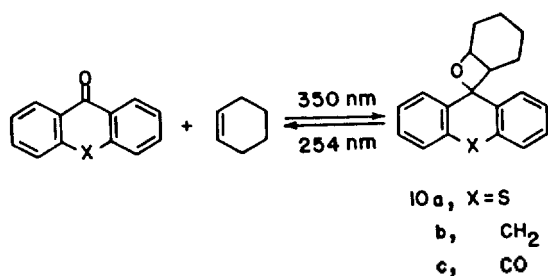


Figure 2. Photoreaction of thioxanthone with cyclohexene in dichloromethane.

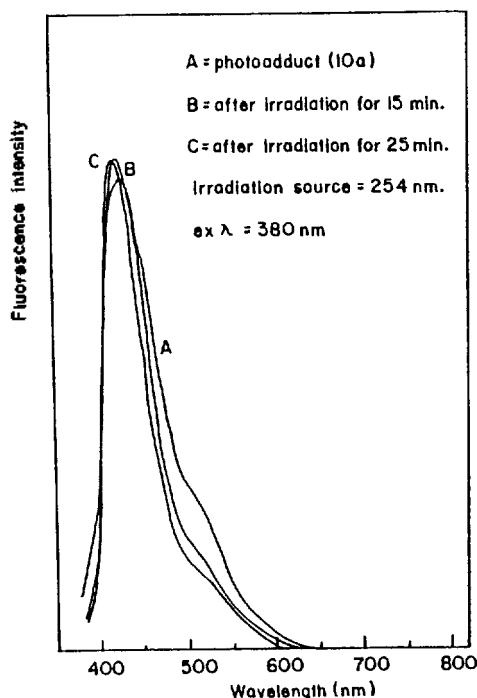


Figure 3. Photodecomposition of thioxanthone-cyclohexene photoadduct (10a) in dichloromethane.

anthrone also react with DPA to yield the same type of photoproducts, 8 and 9, respectively. These quinonoid compounds also react with cyclic olefins to give spiro-oxetanes.¹ Cyclic dienes, such as 1,5-cyclooctadiene, show closely parallel behaviour to that of cyclic olefins forming 1:1 adducts. When irradiated with 350 nm UV light, cyclohexene reacted with thioxanthone, anthrone, and anthraquinone to give 1:1 photoadducts, 10a, 10b, and 10c, respectively (Figure 2). The structure of the photoadducts (10a-10c) was identified by UV, IR, ¹H-NMR, and fluorescence spectra.

When irradiated with 254 nm UV light, the spiro-oxetanes decompose to the starting materials. It was analyzed by tlc, UV spectra, IR spectra, and fluorescence spectra (Figure 3). For example, 1:1 photoadduct (10a, A in Figure 3) of thioxanthone and cyclohexene was decomposed into the starting materials (C in Figure 3) by 254 nm UV light. Investigation of the mechanism and scope of the reaction is continuing.

Acknowledgement. This work was supported by a grant from the Basic Science Research Institute Program, Ministry of Education of Korea, 1987.

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Theoretical Studies on 1,2-Bispyrazinylethylene

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Received March 3, 1988

A quantum mechanical studies on pyrazine and other diazines show that two orbitals with lone-pair characters are in general delocalized throughout the system. These two orbitals interact, depending on geometry to raise the energy of the highest filled "n" orbital and this in turn causes the red shifts in $n-\pi^*$ transitions and leads to increase in the Van Vleck paramagnetic contributions.^{1,2}

The 1,2-bispyrazinylethylene(BPyE) is a tetraazastilbene which has both (n, π^*) and (π, π^*) excited states in contrast to

stilbenes. The replacement of phenyl rings with pyrazine would therefore enrich the photochemistry of the stilbene to the considerable extent. The (n, π^*) and (π, π^*) excited singlet states often lead to different reaction paths. Since the character of (n, π^*) and (π, π^*) states are quite different.³ In this system, $^1(n, \pi^*)$ state has about the same energy as $^1(\pi, \pi^*)$ state has about the same energy as $^1(\pi, \pi^*)$ state and consequently extensive mixing between these two states results in obscuring the (n, π^*) band.⁴ It is clear the EHT calculation⁵