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Photoaddition Reactions of Alkynes to Quinonoid Compounds

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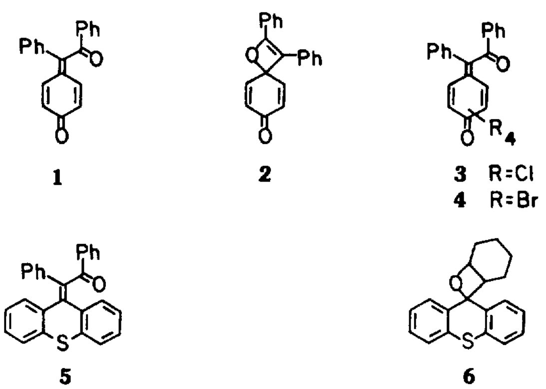
UV irradiation of anthraquinone and diphenylacetylene in benzene gave 1:1 photoadduct (**7**) and cyclization product (**8**). The photoreaction of anthrone and diphenylacetylene in dichloromethane afforded the photooxidation products (**7, 8,** and **9**) in air. The photoproduct (**7**) underwent the cyclization reaction during the purification by the column chromatography (silica gel). When irradiated with 350 nm UV light, the product (**11**) of benzil reacted with diphenylacetylene to give a photoadduct (**12**).

Introduction

The photochemical addition reactions of *p*-quinones to compounds containing olefinic or acetylenic linkages have been the subject of a number of publications.[1-11] Photodimerization of *p*-benzoquinone gives either cyclobutanes or spirooxetanes depending on the nature of the quinone.[1-4] The photoaddition of diphenylacetylene to *p*-benzoquinone forms a quinone methide(**1**), probably through an unstable intermediate, spiro-oxetene(**2**). In contrast to *p*-benzoquinone, methoxy-*p*-benzoquinone gives the cyclobutene.[4]



Scheme 1

We recently reported that chloranil readily forms a novel photorearrangement product by the photoreaction with some cyclic olefins.[12] Irradiation of the quinonoid compounds and diphenylacetylene in dichloromethane gives the photoproducts, such as (**3**), (**4**), or (**5**).[1-8,13] When irradiated with 350 nm UV light, cyclohexene reacts with thioxanthone, anthrone, and anthraquinone, to give 1:1 photoadducts, such as (**6**).[13] These spiropoxetanes decompose to the starting materials by 254 nm UV light.[13]

In connection with our continuous studies toward the photoaddition reactions of *p*-quinone derivatives with alkynes, we now report that irradiation of the quinonoid compounds and diphenylacetylene gives not only 1:1 photoaddut (**7**), but also the photocyclization product(**8**) of (**7**).

The purpose of this paper is to describe the photochemical formation of the polynuclear aromatic compounds from the quinonoid compounds. It is also worth to notice that the photooxidation products are formed by the photoreaction of anthrone and diphenylacetylene in air.

Experimental

Materials. Dichloromethane, *n*-hexane, ethylacetate, chloroform, and benzene were purified before use. Diphenylacetylene, anthrone, anthraquinone, and benzil were purchased from Aldrich Chemical Company and used as received. The column chromatography was performed by using Kiesel gel (Merck Co., 70-230 mesh). Kiesel gel 60 F_{254} (Merck Co., silica gel) was used for the thin layer chromatography.

Instruments. Infrared spectra were recorded on a Perkin-Elmer 283B Grating Spectrophotometer in KBr pellets. ^{1}H-NMR spectra were obtained on a Bruker AC-100 Spectrometer. Mass spectra were obtained on a Jeol GC/MS System (JMS-DX 300) using electron impact(EI) method. UV spectra were recorded on a Hitachi 556 Spectrophotometer. Fluorescence spectra were obtained on a JASCO Spectrofluorometer (FP 770).

Irradiation Apparatus. Irradiation was carried out in a Rayonet Photochemical Reactor (The Southern New England Ultraviolet Company, Model RPR 208) equipped with 350 nm, 300 nm, or 254 nm UV lamps. The progress of the photoreactions was monitored by the precoated TLC (silica gel, Kiesel gel 60 F_{254}, Merck Co.; UV visualization).

Photoreactions of the Quinonoid Compounds and Diphenylacetylene. 42 mg (0.2 mmol) of anthraquinone and 53 mg (0.3 mmol) of diphenylacetylene dissolved in 300 m*l* of benzene was degassed for 30 min by bubbling nitrogen gas and irradiated with 350 nm UV light for 48 hours. The photoproducts (**7** and **8**, 40% and 45%, respectively) were separated by the column chromatography using *n*-hexane-ethylacetate (10:1, v/v) as an eluting solvent.

7: UV(MeOH), λ_{max} = 306, 296, 270, 250, and 220 nm; IR (KBr), 3060-3020(ν_{CH}, aromatic), 1660($\nu_{C=O}$), and 1600 cm^{-1} ($\nu_{C=C}$, aromatic); ^{1}H-NMR(100 MHz, $CDCl_3$), δ = 8.50-7.50 ppm (18H, m); Mass(EI, 70ev), *m/e* = 77($C_6H_5^+$), 105 ($C_6H_5CO^+$, 100%), 281(M-105), and 386(M); Fluorescence(MeOH), λ_{max} = 500 and 470 nm(λ_{ex} = 400 nm).

8: UV(MeOH), λ_{max} = 380, 300, 290, 248, and 240 nm; IR (KBr), 3060-3020(ν_{CH}, aromatic), 1660($\nu_{C=O}$), and 1600 cm^{-1} ($\nu_{C=C}$, aromatic); ^{1}H-NMR(100 MHz, $CDCl_3$), δ = 9.40-7.46 ppm (16H, m); Mass(EI, 70ev), *m/e* = 77($C_6H_5^+$), 105 ($C_6H_5CO^+$), 279(M-105), and 384(M, 100%); Fluorescence (MeOH), λ_{max} = 501 and 471 nm(λ_{ex} = 420 nm). 58 mg(0.3 mmol) of anthrone and 53 mg(0.3 mmol) of diphenylacetylene dissolved in 40 m*l* of dichloromethane was irradiated with 300 nm UV light for 40 hours. The photoproducts (**7, 8,** and **9**, 35%, 40% and 15%, respectively) were isolated by the column chromatography using n-hexane-ethylacetate (10:1, v/v) as an eluting solvent.

9: UV(MeOH), λ_{max} = 304, 278, and 272 nm; IR(KBr), 3060-3020(ν_{CH}, aromatic), 2970-2860(ν_{CH}, aliphatic), and 1660 cm^{-1}($\nu_{C=O}$); ^{1}H-NMR(100 MHz, $CDCl_3$), δ = 8.30-7.03(12H, m), and 4.90 ppm(2H, s); Mass(EI, 70eV), *m/e* = 165(M/2-CO), 193(M/2, 100%), and 386(M); Fluorescence(MeOH), λ_{max} = 457, 450, and 430 nm(λ_{ex} = 370 nm). 500 mg of benzil in 100 m*l* of methanol was irradiated with 350 nm UV light under nitrogen gas for 28 hours to obtain a solid product(**11**, 23%).

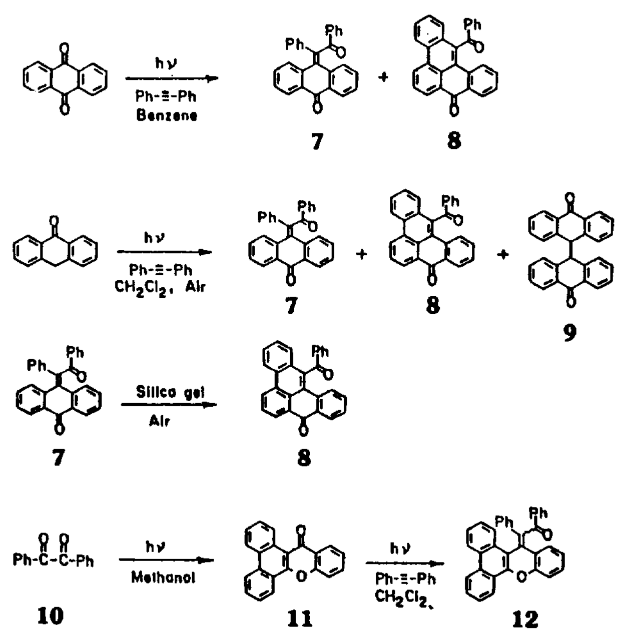
11: UV(MeOH), λ_{max} = 362, 342, 326, 310, 292, 271, 264, and 247 nm; IR(KBr), 3070-3020(ν_{CH}, aromatic), 1648($\nu_{C=O}$), and 1243 cm^{-1}(ν_{C-O}); ^{1}H-NMR(100 MHz, $CDCl_3$), δ = 8.68-7.30 ppm(12H, m); Mass(EI, 70eV), *m/e* = 120(M-phenanthrene moiety), 176(phenanthrene), 268(M-CO), and 296(M); Fluorescene(MeOH), λ_{max} = 373, 358, 343, and 330 nm(λ_{ex} = 300 nm). 88 mg(0.3 mmol) of (**11**) and 53 mg(0.3 mmol) of diphenylacetylene dissolved in 40 m*l* of dichloromethane was degassed for 30 min by bubbling nitrogen gas and irradiated with 350 nm UV light for 120 hours. The photoproduct(**12**, 90%) was isolated by the column chromatography using chloroform as an eluting solvent.

12: UV(MeOH), λ_{max} = 334, 280, 256, and 220 nm; ^{1}H-NMR (100 MHz, $CDCl_3$), δ = 8.50-7.30 ppm(22H, m); Mass(EI, 70eV), *m/e* = 105($C_6H_5CO^+$), 178($C_{14}H_{10}^+$), 296(M-178, 100%), and 474(M); Fluorescence(MeOH), λ_{max} = 500, 430, and 400 nm(λ_{ex} = 350 nm).

Results and Discussion

The photoaddition of *p*-quinones to olefins or alkynes has been reported as a widely-applicable reaction.[1-10] The products in general are spiro-oxetanes or spiro-oxetenes, respectively, in which the latter form quinone methides, such as (**1**), (**3**), or (**4**). The previous paper reported that anthraquinone undergoes photoaddition of diphenylacetylene to form (**8**), not (**7**).[13]

In our detailed studies, the photoaddition of diphenylacetylene to anthraquinone forms (**7**) besides (**8**) (ca. 1:1, molar ratio). The photoproducts were isolated by the column chromatography using n-hexane-ethylacetate(10:1, v/v) as an eluting solvent. Irradiation of a solution of anthraquinone, diphenylacetylene, and iodine in dichloromethane gave (**8**) as a major product, and (**7**) as a minor product. The product (**7**) readily undergoes cycloaddition to (**8**) during the purification by the column chromatography (silica gel). The structures of (**7**) and (**8**) were identified by UV, fluorescence, IR, ^{1}H-NMR, and mass spectra. The absorption band at the longer wavelength (380 nm) in the UV spectrum of the compound (**8**) exhibited absorption ascribable to the presence of phenanthrene moiety. The mass spectra of the products, (**7**) and (**8**), showed the molecular ion peaks at *m/e* 386 ($C_{28}H_{18}O_2$) and *m/e* 384($C_{28}H_{16}O_2$), respectively. The peaks at *m/e* 105 and *m/e* 77 prove the existence of benzoyl group. The photoreaction of anthrone and diphenylacetylene in dichloromethane afforded the photooxidation products (**7, 8** and the dimer (**9**)) in air (Scheme 2).



Scheme 2

Similarly, irradiation of a solution of anthrone, diphenylacetylene, and iodine in dichloromethane gave (**8**) as a major product. The isolated photoproduct (**7**) of anthrone and diphenylacetylene also underwent the cyclization reaction during the purification by the column chromatography (silica

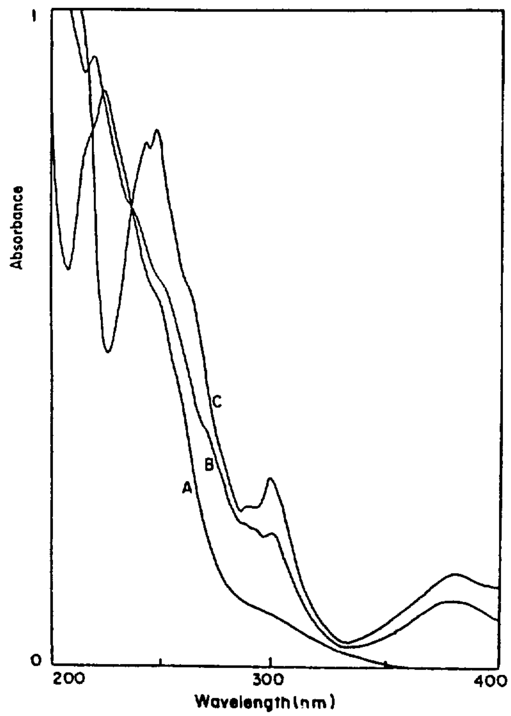


Figure 1. UV spectral change of the photoproduct (**7**) of anthrone and diphenylacetylene by silica gel in air. A: **7**, B: after the elution of **7** on silica gel using n-hexane-diethyl ether(4:1, v/v), C: **8**. Solvent: Methanol.

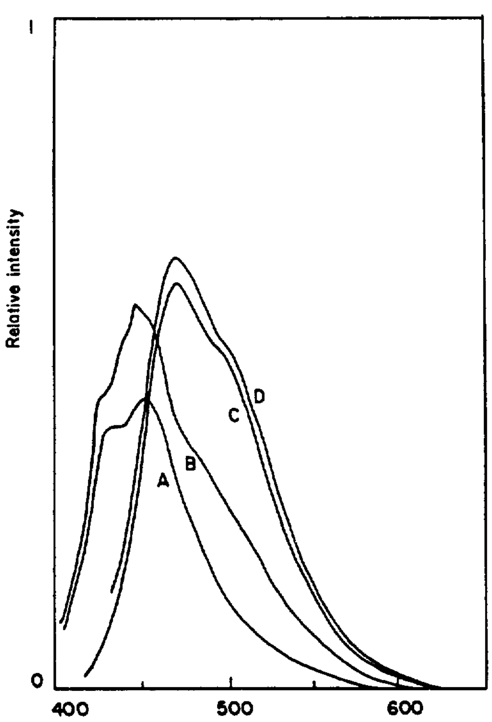


Figure 2. Fluorescence spectra of anthrone(A), dimer (B = **9**) of anthrone, and the photoproducts of anthrone and diphenylacetylene (C = **7**, D = **8**) in methanol.

gel) as shown in Figure 1.

Fluorescence spectra of (**7**), (**8**), anthrone, and the dimer of anthrone (**9**) were observed in methanol (Figure 2).

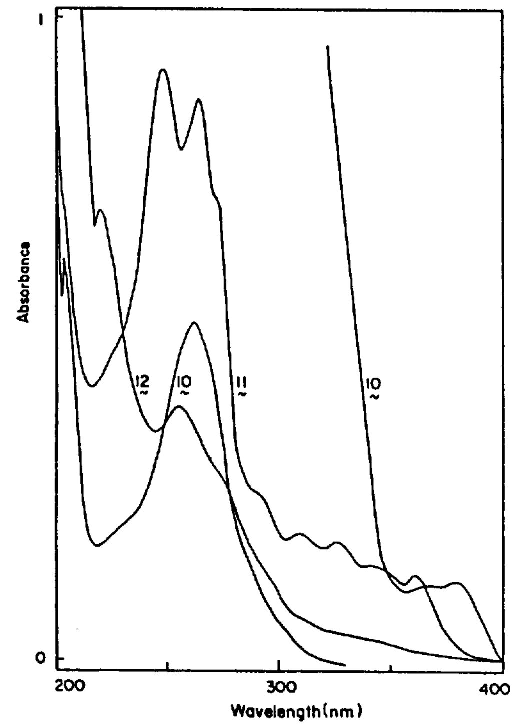


Figure 3. UV spectra of benzil (**10**), the photoproduct (**11**) of benzil, and the photoproduct (**12**) of (**11**) and diphenylacetylene in methanol.

The compound (**11**) is formed by the photoreaction of benzil (**10**) in methanol.[14] Irradiation of (**11**) and diphenylacetylene in dichloromethane gave (**12**) (isolation yield: 90%). The structure for the photoproduct (**12**) is supported by the mass spectrum. The mass spectrum of (**12**) exhibited, in addition to the parent systems at *m/e* 474, peaks at *m/e* 296(M-178, 100%), 178(phenanthrene moiety), and 105 ($C_6H_5CO^+$). The UV spectra of (**10**), (**11**), and (**12**) were observed in methanol as shown in Figure 3.

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Lone Pairs in the 1,3-Sigmatropic Group Rearrangements[1]

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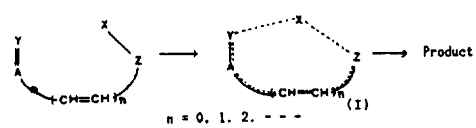
Semiempirical computations using the AM1 and MNDO methods were carried out in order to elucidate allowed mechanisms for 1,3-group(X) rearrangement processes with X = BH_2, CH_3, CN, F, NH_2, OH, Cl and SH. The reactivity of the group migration was largely controlled by the steric effect in the 4-membered ring transition state, an antarafacial process having a greater energy barrier due to a greater steric repulsion. For the groups with lone pair electrons, the participation of the lone pair orbital is found to ease the steric effect by enabling the FMO interation with highly polarizable, high lying, lone pair electrons at relatively distant range; the involvement of lone pairs in the transition state causes an alteration of the symmetry selection rule to that of a 6-electron system with an allowed 1,3-suprafacial migration in contrast to an allowed 1,3-antarafacial migration for a 4-electron system. Various stereoelectronic aspects were analysed in some detail.

Introduction

In a sigmatropic rearrangement, an atom or a group migrates from one end of a conjugated π system to the other through a cyclic transition state (TS), I, (Scheme 1).[2] In our previous papers, various types of sigmatropic hydrogen rear-



Scheme 1

rangements have been reported; Y and Z in scheme 1 have been varied to give 1,3- and 1,5-(Y, Z)-H shifts[3] and the system with A = nitrogen has also been dealt with[4].

In this work, we report the results of our semiempirical MO studies on the group(X) migration in propene, X-CH_2 - CH = CH_2 with X = CH_3, BH_2, NH_2, OH, CN, F, Cl, and SH; by examining frontier MO(FMO) patterns[5], symmetry rules[6], and electronic charge shifts, we attempted to explain the reactivity trend in this work. We made special reference to the change of symmetry rules for the goups with lone pairs for which the TS (I) becomes a 6-electron system and the 1,3-sigmatropic retentive migration involves a suprafacial process in contrast to an allowed 1,3-antarafacial process in the 4-electron system.

Calculation

Computations were performed using the AM1[7,8] and MNDO[7,9] methods. Geometries of the ground state (GS) and the TS were fully optimized by the method of gradient norm minimization[10]; whenever applicable, symmetry elements were introduced in the optimization of the TS structure. In the force constant matrix calculations[11] for the TS characterization, three cases were found to arise: (i) zero negative eigenvalue; for the 6-electron migration, with X = F and NH_2, a shallow minimum is obtained so that no negative eigenvalue appeared. For this type of behavior, McIver *et al.*, reported that the TS has a symmetric structure[12], the energy difference between the minimum and the TS being 0.5 — 1.0 kcal/mol with a rapid energy drop near the products (or reactants). The PMO analysis of Dewar *et al.*[13] have shown that pericyclic reactions are continuous, and synchronous processes, but the shallow minimum found in the Cope rearrangement had energy difference which is well within the computational error[14]. On the other hand, such shallow minimum obtained with a low level ab initio calculations turned out to be a maximum (TS) when a full CI calculations were carried out[15]. (ii) One negative eigenvalue; this is the normal case for the TS in the symmetry allowed processes. (iii) Two negative eigenvalues; when a migration group (X) with lone pairs was forced to be located within the molecular plane in an antarafacial migration, which was considered only for the comparison with the allowed suprafacial process, two negative eigenvalues appeared, one for the stretching and the other for the out-of plane bending modes of the C-X bond. However for X = NH_2, one negative eigenvalue was obtained for the antarafacial process, since zero negative eigenvalue was found for the suprafacial TS.

For the GS, the most stable, s-cis, conformers only were considered, since these are the crowded forms of heavy atom