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Photochemical Rearrangement of Chloranil

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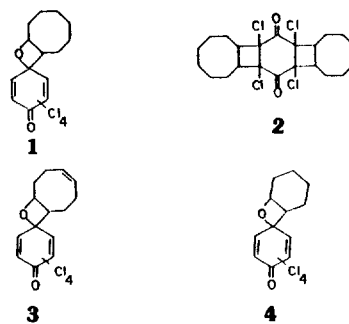
Sang Chul Shim

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Irradiation of a solution of chloranil and cycloheptatriene, or 1,3-cyclohexadiene, in dichloromethane yielded unexpected photorearrangement products as the major product, while chloranil with cyclohexene gave the photorearrangement product as well as 1:1 adduct.

Introduction

The photochemical addition of p-quinones to olefinic compounds has been the subject of some interest.¹⁻⁴ Photodimerization of p-quinone gives either cyclobutanes or spirooxetanes depending on the nature of the quinone. Cyclooctene forms spiro-oxetane(**1**) by photoaddition to chloranil.³ An excess of cyclooctene and chloranil in benzene gives 2:1 adduct (**2**) as the major product.³ The photoreaction of chloranil with 1,5-cyclooctadiene afforded the expected oxetane(**3**).⁵ Irradiation of chloranil and



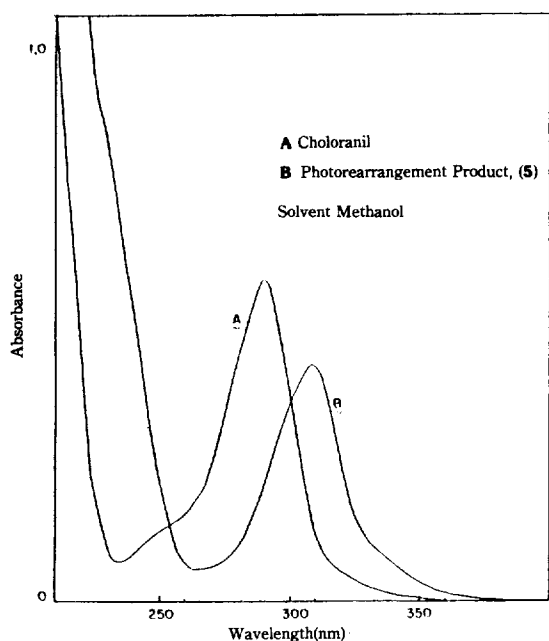


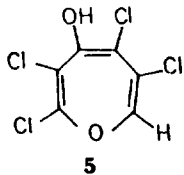
Figure 1. UV Spectra of Chloranil and Photorearrangement Product, 5.

cyclohexene in dichloromethane gave the expected 1:1 adduct(4)⁵ and also the photochemical rearrangement product(5). On the other hand, irradiation of chloranil and 1,3-cyclohexadiene in dichloromethane gave the photochemical rearrangement product(5) as the major product.

We now report that the unexpected photorearrangement product of chloranil was formed during the photoreaction of chloranil with cyclic olefins such as cyclohexene, cycloheptatriene, and 1,3-cyclohexadiene.

Results and Discussion

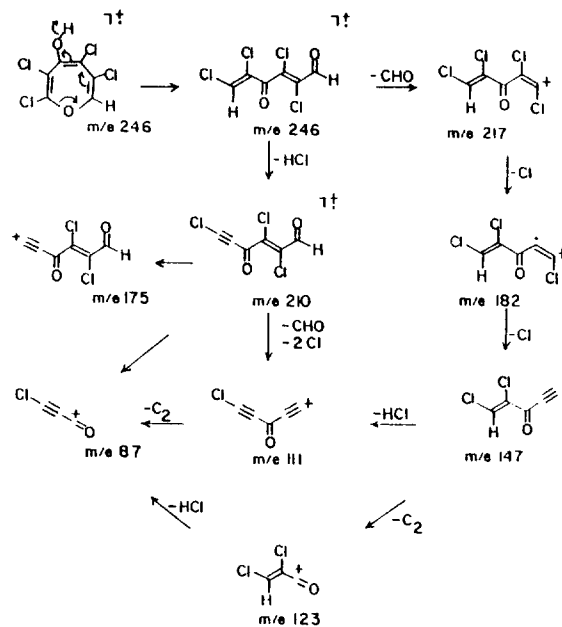
Irradiation of chloranil and cycloheptatriene in dichloromethane gave the unexpected photorearrangement product (5) in ca. 70% yield. The same type of rearrangement product was also obtained in higher yield (>95%) from the photoreaction of chloranil and 1,3-cyclohexadiene. The structure of 5 was identified by the following spectroscopic data.



The absorption maximum was observed at 308 nm in methanol (Fig. 1). The calculated value from empirical rules for conjugated dienes was 309 nm.^{6,7}

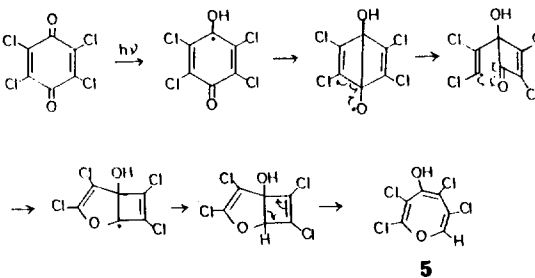
IR spectrum showed OH stretching band at 3400 cm^{-1} , C-O stretching band at 1207 cm^{-1} , C-Cl stretching band at 715 cm^{-1} and 708 cm^{-1} , and C-H out-of-plane bending vibration for the trisubstituted alkene at 887 cm^{-1} . The $^1\text{H-NMR}$ spectrum obtained in acetone- d_6 showed that the chemical shift (δ 8.90 ppm, singlet) of OH proton and that (δ 3.75 ppm, singlet) of vinyl proton are shifted to upfield region because of the paramagnetic ring current of the product(5). This phenomenon was also found in a number of planar or nearly planar

compounds possessing cyclic arrays of p-orbitals containing $4n\pi$ electrons, such as cycloheptatrienyl anions.⁸ The molecular ion peak was observed at m/e 246 in the mass spectrum (EI method). The base peak in the tetrachloro compound (5) showed prominent peaks at masses 246(M^+), 246($M^+ + 2$), 250($M^+ + 4$), and 252($M^+ + 6$) of relative abundance 79.6: 100.0: 42.3: 10.1. The peak at m/e 217, 182, 147, 123, 111, and 87 may result from the following fragmentation patterns (Scheme 1).



Scheme 1

The photorearrangement of chloranil probably undergoes *via* the diradical like (n, π^*) excited state⁹ as shown in scheme 2.



Scheme 2

Irradiation of chloranil and cyclohexene in dichloromethane gave the unexpected photorearrangement product(5) in ca. 30% as well as the 1:1 adduct(4). Without cyclic olefins, such as cyclohexene, cycloheptatriene, and 1,3-cyclohexadiene, the photorearrangement product of chloranil was not formed in dichloromethane. This may be due to the active hydrogen atoms at the allylic position of cyclic olefins. The studies on the mechanism and scope of the photoreaction are in progress.

Experimental

Materials. Dichloromethane and methanol were purified before use. Cyclohexene, 1,3-cyclohexadiene, cyclohepta-

triene, and chloranil were purchased from Aldrich Chemical Company and were used as received. The column chromatography was performed by using Kieselgel 60 (Merck, 70-230 mesh).

Instruments. Infrared spectra were recorded on a Perkin-Elmer 283B Grating Spectrophotometer in KBr pellets or NaCl cells. $^1\text{H-NMR}$ spectra were obtained on a Varian T-60A Spectrometer or Varian FT-80A Spectrometer at 79.542 MHz. Mass spectra were obtained on a Hewlett Packard 5985A GC/MS System using electron impact (EI) method. UV spectra were recorded on a Cary-17 Spectrophotometer.

Irradiation Apparatus. Irradiation was carried out in a Rayonet Photochemical Reactor (The Southern New England Ultraviolet Company) Model RPR-208 equipped with 350 nm UV lamps. The progress of the photoreactions was monitored by pre-coated TLC (silica gel; n-hexane: ethylacetate 4:1 v/v; UV visualization).

Photoreaction of Chloranil with Cyclic Olefins. 500 mg of Chloranil and 2.0 ml of cyclohexene dissolved in 120 ml of dichloromethane was deoxygenated for 30 min by bubbling nitrogen gas and irradiated with 350 nm UV light for 22 hours in a water-cooled reaction vessel. The photoadducts were separated by the column chromatography using n-hexane-ethylacetate (4:1 v/v) as an eluting solvent. 500 mg of chloranil and 2.0 ml of 1,3-cyclohexadiene in 120 ml of dichloromethane was degassed and irradiated for 6 hours in a water-cooled reaction vessel with 350 nm UV light. The excess of diene and dichloromethane were evaporated under reduced pressure. Filtration and recrystallization (chloroform-ethylacetate) yielded a solid(5). **5**; m.p., 240°C; UV (methanol), $\lambda_{\text{max}} = 308$ nm; IR (KBr), 3400 (ν_{OH}), 1207 ($\nu_{\text{C=O}}$), 887 ($\nu_{\text{C=C}}$ for trisubstituted alkene), and 715 cm^{-1} ($\nu_{\text{C=C}}$); $^1\text{H-NMR}$ (80 MHz, acetone- d_6), $\delta = 8.90$ (OH, s), and 3.75 ppm (vinyl proton, s); Mass (EI), m/e = 252 ($\text{M}^+ + 6$, rel. abund. 11.7), 250 ($\text{M}^+ + 4$, 46.7), 248 ($\text{M}^+ + 2$, 100.0). 246 (M^+

$\text{C}_6\text{H}_2\text{O}_2\text{Cl}_4$, 79.0), 217 ($\text{M}^+ - \text{CHO}$, C_5HOCl_4 , 2.0), 210 ($\text{M}^+ - \text{HCl}$, $\text{C}_5\text{HO}_2\text{Cl}_3$, 12.5), 182 (m/e 217-Cl, C_5HOCl_3 , 18.7), 175 (m/e 210-Cl, $\text{C}_5\text{HO}_2\text{Cl}_2$, 16.7), 147 (m/e 182-HCl, C_5HOCl_2 , 40.0), 111 (m/e 147-HCl, C_5OCl , 16.0), and 87 (m/e 111-C \equiv C, C_5OCl , 53.5). 500 mg of chloranil and 2.2 ml of cycloheptatriene in 120 ml of dichloromethane was degassed for 30 min. by bubbling nitrogen gas and irradiated with 350 nm UV light for 6 hours. The solvent was evaporated in vacuo. Filtration and recrystallization (methanol-n-hexane-dichloromethane) yielded a solid(5).

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Theoretical Studies on the Photocycloaddition Reaction of Psoralen with Thymidine

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The theoretical studies on the photocycloaddition reaction of 5,7-dimethoxycoumarin and 4',5'-dihydropsovalen with thymidine were carried out as a model for photosensitizing reaction of psoralen with DNA. The results are in reasonable agreement with experimental observations. The photoadducts between dimethoxycoumarin and thymidine were predicted to be C_4 -cycloadducts through the cycloaddition of 3,4-pyrone double bond of dimethoxycoumarin to 5,6 double bond of thymidine. The major photoadduct of 4',5'-dihydropsovalen with thymidine has the *anti* head-to-head stereochemistry.

Introduction

The photosensitization activity of psoralens is generally

correlated to their photoreactivity with pyrimidine bases in DNA. On irradiation with near UV light, the intercalated psoralen molecule can successively photoreact with two pyri-