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PHOTOCHEMICAL REACTION OF CYCLOHEPTATRIENE WITH SOME AROMATIC QUINONES

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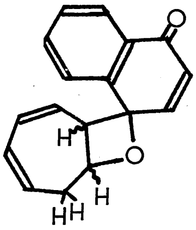
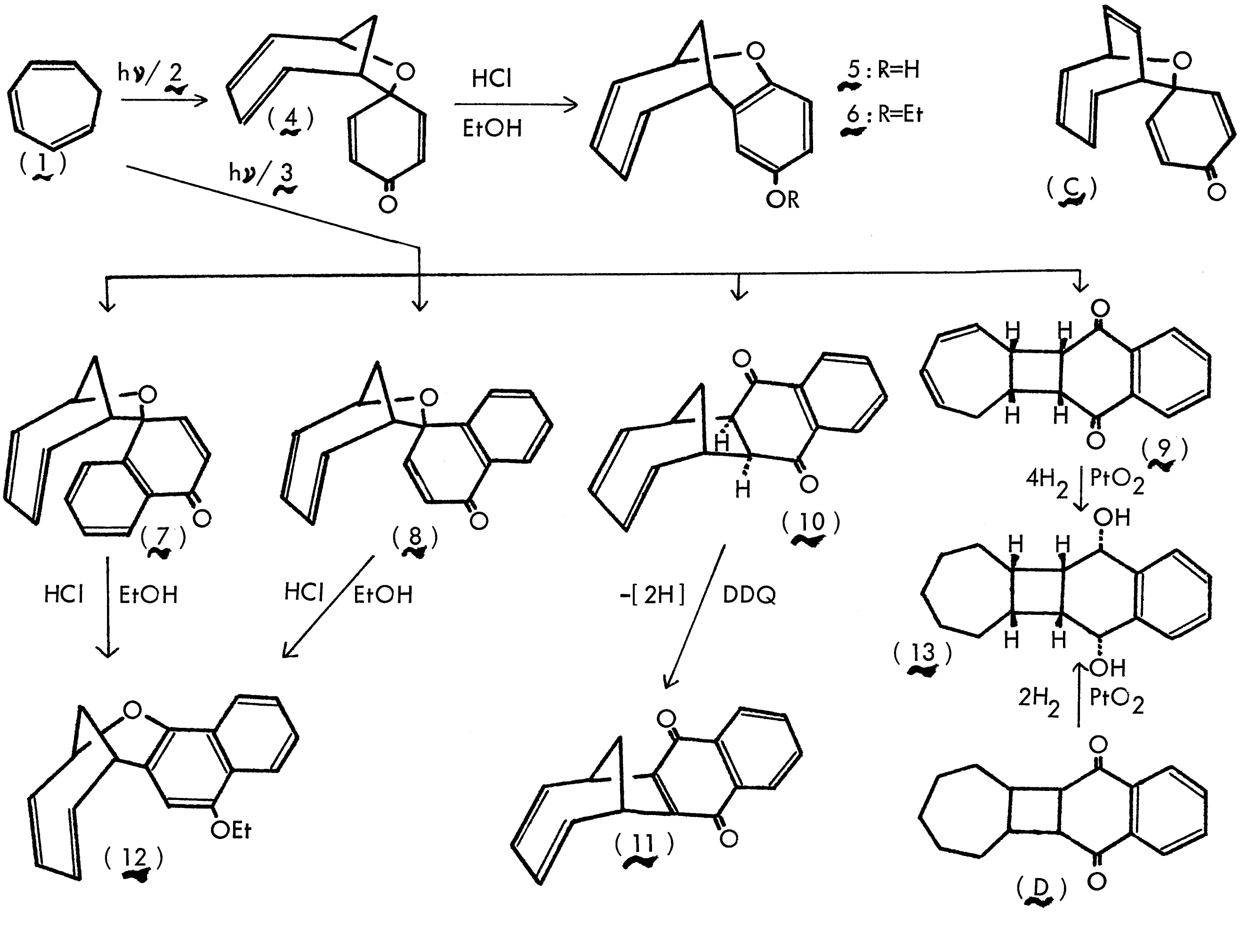
The photochemical addition reaction of cycloheptatriene with *p*-benzoquinone and 1,4-naphthoquinone yielded the spiro-ethers having 7-oxa-bicyclo[4,2,1]nonadiene moiety by the characteristic (6+2)π addition process. The latter quinone further produced the carbocyclic (2+2)π- and (6+2)π cycloadducts. Either (4+2)π adducts or dioxetanes were undetectable in both cases. The photoadducts were stable under their formation conditions, showing no tendency to cause the isomerization.

As a part of our series of studies of the photocycloaddition reactions of conjugated olefins with various carbonyl functions,1) we have extended the investigation to that of cycloheptatriene (**1**) with two quinones, *p*-benzoquinone (**2**) and 1,4-naphthoquinone (**3**), in order to know the pericyclic mode of the reaction in general, and to check the photochemical hydrogen abstraction to give ene-products or bis-cycloheptatrienyl (**A**) in connections with the ground state properties of quinones. On the photocycloaddition reaction of **1** with **3**, in fact Gandhi *et al.*2) have already reported the results which described a formation of a 1 : 1-adduct, as bright-red crystals, whose structure has been claimed to be a (2+2) π adduct (**B**) derived from the carbonyl chromophore, on the basis of 100 MHz NMDR spectral evidences. The purpose of this communication is to show our own results on the photocycloaddition of **1** and **3** in addition to that of **1** and **2**.3)



(**B**)

When a benzene solution of **1** and **2**4) was irradiated by means of a 450 W high-pressure mercury lamp through a Pyrex glass filter, an oily 1 : 1-cycloadduct (m/e : 200) (**4**) was obtained in 56 % yield. No other product was detectable despite an intensive survey for the every chromatographic fraction. The structure of **4** was determined as follows: The NMR [δ: 2.75(3H, m), 4.70(1H, t, J=6.5 Hz), 5.90(6H, overlapped m), 6.71(1H, dd, J=9.5, 3.0 Hz), and 7.01(1H, dd, J=9.5, 3.0 Hz)] spectrum revealed a presence of the dienone moiety as like as that of the reported cyclooctatetraene-2 adduct (C),5) however, an incidental overlapping of the aliphatic proton signals made impossible to discern the structure to determine the pericyclic mode of the addition, $(6+2)\pi$-, $(4+2)\pi$- or $(2+2)\pi$ process. The NMDR [δ :3.21(1H, d, J=12.8 Hz), 3.64(1H, dt, J=12.8, 6.5 Hz), 4.00(1H, t, J=6.5 Hz), 5.48(1H, t, J=6.5 Hz), 6.40(4H, m), 8.22(1H, dd, J=9.5, 3.0 Hz), 8.58(1H, dd, J=9.5, 3.0 Hz), 10.64(1H, d, J=9.5 Hz), and 10.76(1H, d, J=9.5 Hz)] spectrum in the presence of a shift reagent [4(31.4 mg)/Eu(DPM)$_3$(60.7 mg)] revealed that among the four aliphatic protons, two allylic methine protons did not spin-couple in each other, and the observed magnitude of the gem-coupling constant for the non-allylic methine protons(12.8 Hz) should be appropriate for that of a tetrahydrofuran. Therefore, 4 must be a $(6+2)\pi$ cycloadduct. The observed UV spectrum (λ_{max}^{MeOH} :228 nm(ε:15500), 264.5(4400))6) was also in accord with this view. When an ethanolic solution of 4 was treated with small amounts of hydrochloric acid at room temperature, a phenolic compound (5, mp 85-87°C) and its ethyl ether (6, a colorless oil) were obtained in 23 % and 56 % yields respectively. Again, the NMR spectra of 5 [δ:1.98(1H, ddd, J=14.0, 2.0, 1.0 Hz), 2.56(1H, ddd, J=14.0, 6.5, 4.0 Hz), 3.68(1H, dd, J=8.5, 6.5 Hz), 4.9(1H, OH), 4.94(1H, m),



5.90(3H, m), and 6.3-6.8(4H, m)] and **6** [δ:1.33(3H, t), 1.96(1H, ddd, J=14.0, 2.5, 1.2 Hz), 2.58(1H, ddd, J=14.0, 6.5, 4.5 Hz), 3.65(1H, br. t, J=6.5 Hz), 3.93(2H, q), 4.93(1H, m), 5.7-6.1(3H, m), and 6.2-6.9(4H, m)] clearly excluded the (2+2)π structure.(6)

On the other hand, the reaction of **1** and **3** under the similar conditions with the above showed rather complicated features; a formation of a stereoisomeric mixture of (6+2)π ethers (**7**, a colorless oil (35 %) and **8**, a colorless oil (2.5 %)), a (2+2)π cycloadduct (**9**, pale yellow needles, mp 103-104°C (10 %)) and a (6+2) π cycloadduct (**10**, pale yellow needles, mp 87-88°C (13 %)) together with a dehydro-derivative of **10** (**11**, yellow needles, mp 158-160°C (4 %)) was recognized. These products were identified by the spectroscopic and chemical methods of analyses.

The NMR spectra of **7** [δ:2.68(1H, d, J=12.5 Hz), 2.73(1H, t, J=7.0 Hz), 3.00(1H, dt, J=12.5, 7.0 Hz), 4.76(1H, t, J=7.0 Hz), 5.10(1H, dd, J=11.0, 7.0 Hz), 5.6-6.2(3H, m), 6.05(1H, d, J=10.5 Hz), 7.18(1H, d, J=10.5 Hz), and 7.24-8.00(4H, m)] and of **8** [δ:2.40(1H, d, J=12.5 Hz), 2.5-3.1(2H, m), 4.87(1H, br. t, J= 7.0 Hz), 5.7-6.4(4H, m), 6.18(1H, d, J=10.5 Hz), 7.30(1H, d, J=10.5 Hz), and 7.2-8.1(4H, m)] were closely resembled in each other, and comparisons of chemical shift of the corresponding pairs of hydrogens, i. e. one of the methylene protons of **8** (2.40) appeared in higher field than that of **7** (2.68), and one of the four vinyl protons of **7** (5.10) caused a marked up-field shift, while the four protons of **8** (5.7-6.4) behaved as usual, the stereostructures of **7** and **8** were deduced as indicated in the chart. It is interesting that the sterically more clowded isomer, **7**, was predominant over the other. **7** also gave an aromatized ethyl ether (**12**) by treatment with hydrochloric acid in ethanol at room temperature, while **8** needed to reflux for 2 hr to give the same product. The NMR [δ: 1.47(3H, t), 2.04(1H, ddd, J=13.8, 2.5, 1.0 Hz), 2.68(1H, ddd, J=13.8, 5.5, 4.0 Hz), 3.68(1H, dddd, J=8.5, 5.5, 2.0, 1.0 Hz), 4.08(2H, q), 5.14(1H, m), 5.7-6.1(3H, m), 6.2-6.5(1H, m), 6.40(1H, s), 7.3-7.6(2H, m), and 8.0-8.3(2H, m)] spectrum of **12** (colorless plates, mp 129-130°C) again confirmed the pericyclic mode of the addition process; especially, an observed change of the magnitude of the gem-coupling constant for the methylene protons is in a range of the expectation.

9 [δ:2.49(1H, ddd, J=13.0, 6.5, 4.0 Hz), 2.74(1H, ddd, J=13.0, 9.0, 4.0 Hz), 3.0-3.6(3H, m), 3.80(1H, dd, J=9.0, 7.5 Hz), 5.95(4H, m), and 7.6-8.2(4H, m)] showed rather poorly resolved NMR spectrum, but the methylene protons were proven to be at an allylic carbon by spin-decoupling experiments, thus, **9** can not be a (6+2)π cycloadduct. A catàlytic reduction of **9** with platinum oxide gave an octahydro-derivative (**13**, colorless needles, mp 248-250°C) which was identical with the tetrahydro-derivative of the one (**D**) of the photoadducts of **3** with cycloheptene.(7) Therefore, **9** is a (2+2)π cycloadduct.

On the other hand, 10 [δ: 1.87(1H, br. dt, J=13.0, 2.0 Hz), 2.04(1H, dtm, J=13.0, 6.0 Hz), 3.25(2H, br. dd, J=7.5, 6.0 Hz), 3.74(2H, br. s), 5.84(2H, dm, J=12.0 Hz), 6.0-6.2(2H, dm, J=12.0 Hz), 7.6-7.9(2H, m), and 8.0-8.2(2H, m)] was deduced to be a symmetrical *exo*-(6+2)π cycloadduct on the basis of the coupling patterns of protons at the ring juncture. 11, prepared also by dehydrogenation of 10 with 2,3-dichloro-5,6-dicyanobenzoquinone, exhibited also a symmetrical NMR spectrum [δ: 1.69(1H, d, J=12.0 Hz), 2.36(1H, dtt, J=12.0, 7.0, 1.5 Hz), 3.98(2H, t, J=7.0 Hz), 5.9(2H, m), 6.2(2H, m), 7.6(2H, m), and 8.2(2H, m)].

It is remarkable that the formation of cyclic ethers is not stereospecific but perispecific, while, the formation of carbocyclic products is stereospecific but not perispecific. The oxetane, and the ene-products or those related product, A, were undetectable. No (4+2)π cycloaddition process has occurred. With some contrasting features, the reaction of 1 with methyl acetopyruvate[8] has afforded the stereospecific (4+2)π - and (6+2)π cycloadducts and the ene-product.

When this cycloaddition was performed by means of a 500 W tungsten lamp, the composition of the photoproducts showed no difference with that by a mercury lamp, and the product ratio was constant during the irradiation.[9]

Although our reaction conditions seem to cover those of Gandhi,[2] we have failed to identify the crystalline C.

References and Notes

1) H. Takeshita, A. Mori, and Y. Toyonaga, *Bull. Chem. Soc. Japan*, 48, 307 (1975).

2) R. P. Gandhi, S. N. Dhawan, and S. M. Mukherji, *Ind. J. Chem.*, 9, 283 (1971).

3) An attempted reaction of 1 with chloranil under the similar conditions gave no adduct.

4) All the experiments in this paper were undertaken as one mole solution of quinones with two- to five-fold excess of 1 at 10-15°C under nitrogen atmosphere. The compounds described here gave satisfactory elemental analyses. The NMR spectra were measured in $CDCl_3$ solutions.

5) D. Bryce-Smith, A. Gilbert, and M. G. Johnson, *J. Chem. Soc., C*, 383 (1967).

6) The structure of C has recently been revised to the (6+2)π structure. *Cf.* R. M. Wilson, E. J. Gardner, R. C. Elder, R. H. Squire, and L.R. Florian, *J. Amer. Chem. Soc.*, 96, 2955 (1974). They reported λ_{max}^{MeOH} of C: 199 nm(ε: 11400), 223(16200), 260(5400).

7) Photocycloaddition of 3 with cycloheptene gave the carbocyclic (2+2)π adduct, D, and an isomeric mixture of dioxetanes.

8) H. Takeshita, A. Mori, and S. Itô, *Bull. Chem. Soc. Japan*, 47, 1767 (1974).

9) Generally, the irradiations by tungsten lamp gave better results due to diminishment of polymerization; at one instance, 1 and 2 gave 4 in 68 % yield.

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