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PHOTO-CYCLOADDITION OF 1,4-NAPHTHOQUINONE WITH 2-NORBORNENE
—— A NOVEL TYPE OF PHOTO-CYCLOADDITION

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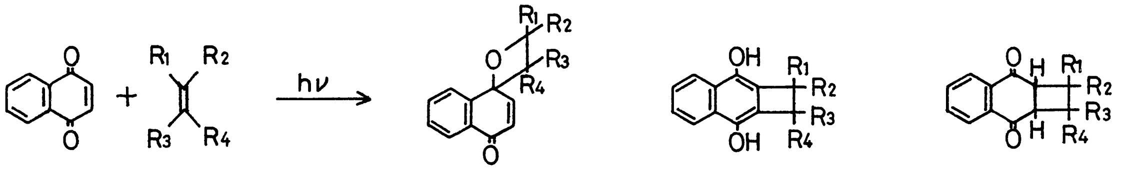
Photo-cycloaddition compound composed of two molecules of 1,4-naphthoquinone and one molecule of 2-norbornene was obtained in the photochemical reaction of 1,4-naphthoquinone with 2-norbornene. Structure of the photo-cycloaddition compound was determined as (4). This type of photo-cycloaddition compound involving the formation of six membered carbon ring has never been reported.

In the photochemical reaction of 1,4-naphthoquinone with olefins cycloaddition forming the four membered ring compounds has been reported so far.1,2,3) The photo-cycloaddition compounds which have been reported can be classified into three structural types: (1), (2) and (3). All these photo-cycloaddition compounds are characteristic as they are composed of each one molecule of 1,4-naphthoquinone and olefins.



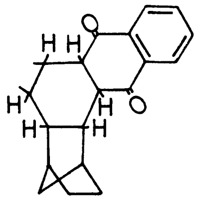
(1) (2) (3)

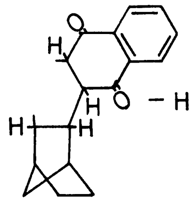
We shall report here on photo-cycloaddition reaction of two molecules of 1,4-naphthoquinone with one molecule of 2-norbornene involving the formation of six membered carbon ring as the main reaction product, although a half amount of accompanying spiro-oxetan was also produced.

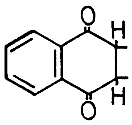
1,4-Naphthoquinone (10 mmol) and 2-norbornene (20 mmol) were dissolved in benzene (20 ml) and irradiated in a glass tube by high pressure Hg arc lamp (300 W) through 5 cm thick of water layer. After the usual work-up photo-cycloaddition compounds (Compound (I) and (II)) were isolated from the reaction mixture.

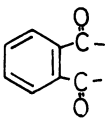
The photo-cycloaddition compound (I) is white needles, mp.277.5-278.5°C, after recrystallization from chloroform. The compound (I) was subjected to the following examinations:

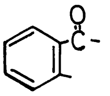
Elemental analysis: Calcd. for $C_{27}H_{22}O_4$; C: 79.00, H: 5.40 %
Found; C: 78.84, H: 5.39 %.

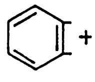
Mass spectrum: m/e = 410 (M^+, 100 %), 278 ([

]$^+$, 16 %), 251 ([

− H]$^+$, 16 %), 160 ([

+ 2H]$^+$, 29 %), 133 ([

+ H]$^+$, 26 %), 104 ([

]$^+$, 34 %), 77 ([ +H]$^+$, 28 %).

NMR spectrum (Fig.1) showed five characteristic groups of lines: 0.60-1.70ppm(8H, aliphatic-H, multiplet), 2.03 ppm (2H, aliphatic-H, broad doublet), 3.13 ppm (1H, Hc, double doublet), 3.37 ppm (1H, Hb, double doublet), 4.56 ppm (2H, Ha, doublet), 7.70-8.24 ppm (8H, aromatic-H, multiplet). Chemical shifts were measured by using TMS as an internal standard in the solution of chloroform-d. Spin-spin interaction of Ha with Hb (J= 5.0 Hz) and with Hc (J= 5.0 Hz) could be confirmed by the spin decoupling technique of irradiation on Ha (see Fig.1 (A)). The other doublet coupling of Hb (J= 14.0 Hz) and Hc (J= 12.0 Hz) was based to the spin-spin interaction with aliphatic protons (see Fig.1 (B) and (C)).

IR spectrum of the photo-cycloaddition compound (I) indicated the existence of the carbonyl group ($\nu_{C=O} = 1670\ cm^{-1}$) and aliphatic C-H group ($\nu_{C-H} = 2870,\ 2950\ cm^{-1}$) but none of the hydroxyl group.

Electronic spectrum of the photo-cycloaddition compound (I) in the solution of chloroform had two absorptions in the ultra-violet region: λ_{max}= 256 nm(log ε=4.38), λ_{max}= 307 nm(log ε=3.70).

Oxidation of the photo-cycloaddition compound (I) by potassium dichromate in the solution of chloroform resulted phthalic acid. Moreover, when the photo-cycloaddition compound (I) was submitted to the Baeyer-Villiger oxidation by pertrifluoroacetic acid in the solution of methylene dichloride, cyclohexane tetracarboxylic acid derivative (see structure (5)) was isolated. The subsequent esterification with diazomethane resulted to the methyl ester of the tetracarboxylic acid derivative. Structure (5) was confirmed through the measurement of its Mass, NMR and IR

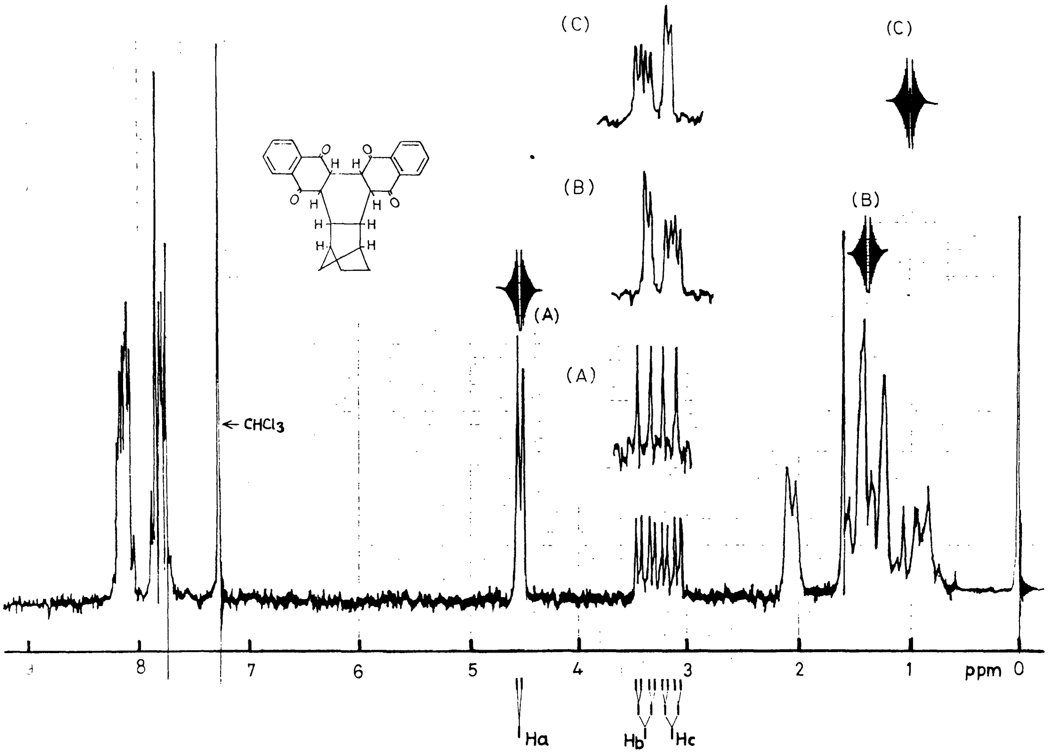
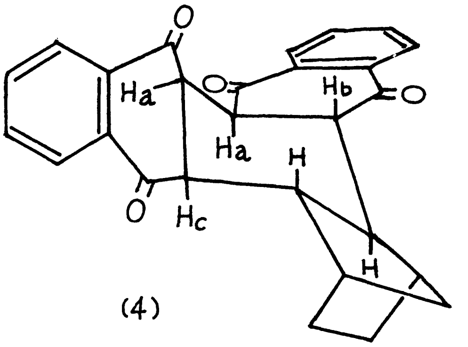


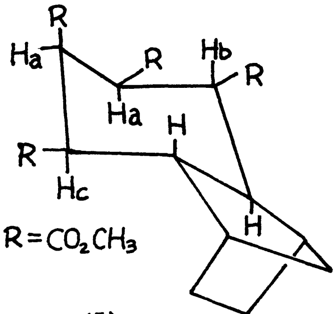
Fig.1. NMR spectrum of the photo-cycloaddition compound (I) in the solution of chloroform-d

spectrum ($\nu_{C-H} = 2940\ cm^{-1}$, $\nu_{C=O} = 1730\ cm^{-1}$). NMR spectrum of the ester (5) resembled closely to that of the parent photo-cycloaddition compound (I) in the region of aliphatic protons: 1.06-1.85 ppm (8H, aliphatic-H, multiplet), 2.20 ppm (1H, aliphatic-H, broad singlet), 2.44 ppm (1H, aliphatic-H, broad singlet), 2.81 ppm (1H, Hc, double doublet), 2.99 ppm (1H, Hb, double doublet), 3.36 ppm (2H, Ha, doublet), 3.58 ppm (12H, methyl-H, singlet).

Taking into account of these results the photo-cycloaddition compound (I) must be composed of two molecules of 1,4-naphthoquinone and one molecule of 2-norbornene and the structure should be consistent with (4).



(4)



(5)

The photo-cycloaddition compound (II) is colorless cubes, mp.101.0-102.0°C, after recrystallization from petroleum ether. The compound (II) was subjected to the following examinations:

Elemental analysis: Calcd. for $C_{17}H_{16}O_2$; C: 80.92, H: 6.39 %

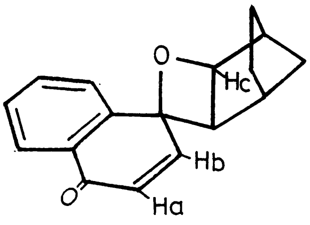
Found; C: 80.76, H: 6.25 %.

Mass spectrum showed molecular peak at mass number (m/e) = 252.

NMR spectrum:0.80-2.90 ppm (9H, aliphatic-H, multiplet), 5.05 ppm (1H, Hc, double doublet), 6.16 ppm (1H, Hb, doublet), 7.70 ppm (1H, Ha, doublet), 7.20-8.10 ppm (4H, aromatic-H, multiplet). The assignment to the structure (6) was confirmed by the spin decoupling technique.

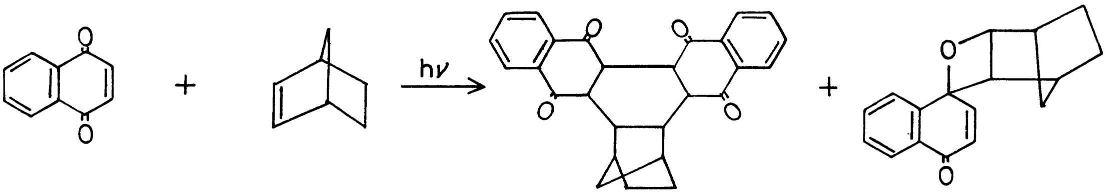
IR spectrum of the photo-cycloaddition compound (II) indicated the existence of the carbonyl group ($\nu_{C=O}$ = 1668 cm^{-1}), spiro-oxetan ring (ν_{C-O} = 977 cm^{-1}) and aliphatic C-H group (ν_{C-H} = 2950 cm^{-1}).

From these results the photo-cycloaddition compound (II) must be spiro-oxetan, which structure is consistent with (6).



(6)

The yield of the photo-cycloaddition compound (I) was at least 10 % for thirty hours' irradiation and was about twice as much as that of the compound (II). Summarizing the results explained above the photo-cycloaddition reaction can be formulated as the followings:



Relative amount (about); 2 : 1

We have confirmed that several other olefins can give the same type of (2 + 2 + 2)π photo-cycloaddition compound.

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