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A NOVEL PHOTO-CYCLOADDITION REACTION OF 2-ALKOXY-1,4-NAPHTHOQUINONES WITH OLEFINS

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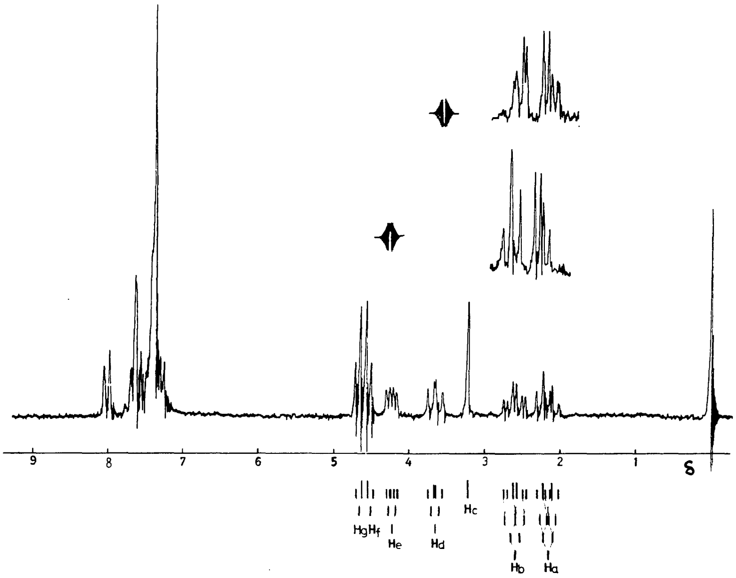
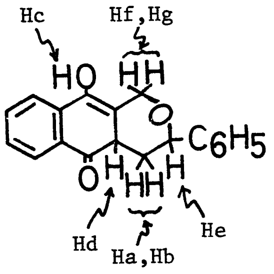
Photo-cycloaddition compounds, characterized by forming tetrahydropyran ring, were obtained in a good yield in the photochemical reaction of 2-alkoxy-1,4-naphthoquinones with several olefins. This type of photo-cycloaddition reaction between quinones and olefins has never been reported so far.

Although several 2-alkoxy-1,4-naphthoquinones and some olefins can give the novel type of photo-cycloaddition compound, we shall report here on the photo-cycloaddition reaction of 2-methoxy-1,4-naphthoquinone with styrene as a typical example$^{1)}$.

2-Methoxy-1,4-naphthoquinone(1 mmol) and styrene(2 mmol) were dissolved in benzene(20 ml) and irradiated in a glass tube by high pressure Hg arc lamp(300W) through 5 cm thick of water layer. After 2-methoxy-1,4-naphthoquinone was consumed(for 15 hrs. irradiation) photo-addition compound(I) was isolated from the reaction mixture by the usual work-up. The photo-addition compound(I) is white needles, mp.164.0-164.5°C, after recrystallization from benzene(yield: 69%). The compound(I) was subjected to the following examinations:

Elemental analysis: Found; C:78.03%, H:5.45%, Calcd. for $C_{19}H_{16}O_3$; C:78.08%, H:5.52%. Mass spectrum showed molecular peak (M^+) at m/e= 292. IR spectrum indicated the existence of hydroxyl group(ν_{OH}= 3250 cm^{-1}), aliphatic C-H group(ν_{CH}= 2940 cm^{-1}) and carbonyl group(ν_{CO}= 1675 cm^{-1}) (KBr disk). Electronic spectrum: λ_{max}= 290 nm($CHCl_3$)($\log\varepsilon$ = 3.48). NMR spectrum(Fig.1) showed seven characteristic groups of lines: δ :2.16(1H,Ha,multiplet), 2.58(1H,Hb,multiplet), 3.22(1H,Hc, broad singlet),3.62(1H,Hd,double doublet),4.18(1H,He,double doublet),4.56,4.64(2H,Hf,Hg,AB-quartet), 7.24-8.10(9H,aromatic-H,multiplet)(solvent:$CDCl_3$).The NMR signal corresponding to Hc was disappeared after treatment of the solution with D_2O. The spin-spin interactions were decoupled by using spin decoupling technique(see Fig.1). Spin-spin coupling constants were measured as follows: J_{AB}=12.0 Hz, J_{AD}=8.0 Hz, J_{AE}=10.0 Hz, J_{BD}=12.0 Hz, J_{BE}=6.0 Hz, J_{FG}=6.0 Hz. When deuterio-methoxy quinone was subjected to the same photochemical reaction, the NMR signals corresponding to Hf,Hg (Fig.1) of the



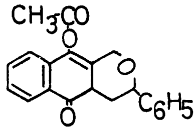


(1)

Fig.1. NMR spectrum of the photo-addition compound(I)

photo-addition compound(I) were disappeared. On the other hand, the NMR signal corresponding to Hd(Fig.1) was disappeared completely when 2-methoxy-1,4-naphthoquinone deuterated at position 3 was used in the reaction. These results indicated that the protons of the compound(I), indicated as Hd,Hf and Hg in Fig.1 were originated from 2-methoxy-1,4-naphthoquinone moiety.

When the compound(I) was treated with acetyl chloride, acetylated product (compound(II)) was obtained. The structure of the compound (II) was confirmed by its IR, NMR and Mass spectrum (see structure (2)). Clemmensen reduction of the compound(I) gave mixture of compound (III) (main) and (IV)2). Their structures were assigned to (3) and (4), respectively, by comparison of their IR,NMR and Mass spectrum. Taking into account of these results the structure of the photo-addition compound (I) should be consistent with (1). The reaction can be formularized as followings:



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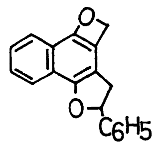

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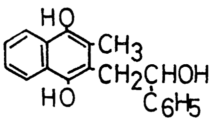

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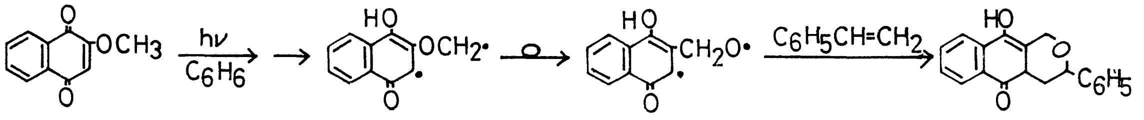

(1)

The scope and limitations of this type of photo-addition reaction will be reported in near future.

1) On another type of photo-addition reactions of 1,4-naphthoquinone with olefins; see K.Maruyama, T.Otsuki and Y.Naruta, Chem.Lett., (1973), 641.

2) H.Schmid, A.Ebnöther and Th.M.Meijer, Helv.Chim.Acta., 33, 1751 (1950).

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