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An Evidence for Remarkable Difference of the Electrophilicity between Two Carbonyl Groups in the Photoexcited 1,2-Naphthoquinone. Photocycloaddition Reaction of 1,2-Naphthoquinone with Olefins

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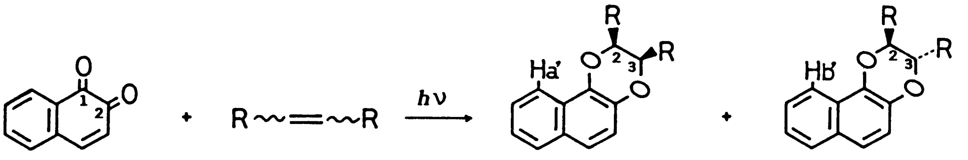
The [4+2]photocycloaddition reactions between 1,2-naphthoquinone and olefins have been investigated. From the results of the stereochemistry and the regiochemistry of the adducts, it is concluded that the carbonyl oxygen atom at the position 2 in the photoexcited triplet state of 1,2-naphthoquinone attacks selectively one of the olefinic carbons.

From synthetic and theoretical viewpoints, elucidation of the photochemical behavior of quinones would be fruitful since quinones play an important role in nature. In these investigations, 1,4-benzoquinone, 1,4-naphthoquinone, 9,10-anthraquinone, tetrachloro-1,2-benzoquinone, 9,10-phenanthrenequinone, and their analogues have been frequently used as a representative p- or o-quinone.$^{1)}$ However, a photochemical reactivity of the two carbonyl groups in these quinones is indistinguishable owing to their symmetrical structures. In contrast, a different reactivity between the two carbonyl groups in 1,2-naphthoquinone (**1**) can be expected owing to its unsymmetrical structure. In this paper the author describes the regioselective photocycloaddition of olefins to **1** in order to firmly establish the difference in electrophilicity between the two carbonyl oxygen atoms of **1**.

Since the mechanism of the [4+2]photocycloaddition of **1** with olefins has remained obscure,$^{1,2)}$ the author examined at first the reaction with symmetric olefins. Irradiation of a benzene solution of **1** and a large excess amount of cis- (**2a**) or trans-2-butene (**2b**) in a Pyrex tube at 15 °C using a 300 W high-pressure mercury lamp gave a stereoisomeric mixture of [4+2]cycloadducts, **4a** and **5b** in 49%

and 62% yields, respectively (Eq.1).$^{3)}$ The stereoisomeric ratios of cis- and trans-adducts (see Table 1) were determined by both ^{1}H NMR integrations and GLC analyses of the crude cycloadducts (see Table 1).$^{4)}$

Similarly, cis-stilbene (**2c**) and trans-stilbene (**2d**) also afforded both cis-cycloadduct (**4c**) and trans-cycloadduct (**5d**)$^{5)}$ when a benzene solution of **1** and each geometrical isomer of stilbene was irradiated.$^{6)}$ The stereoisomeric ratios of the cycloadducts are summarized in Table 1.$^{7)}$ These nonstereospecific additions show that the cycloaddition reactions of **1** with olefins proceed undoubtedly by way of a triplet 1,4-diradical intermediate.$^{2)}$



1 **2** **4** **5**

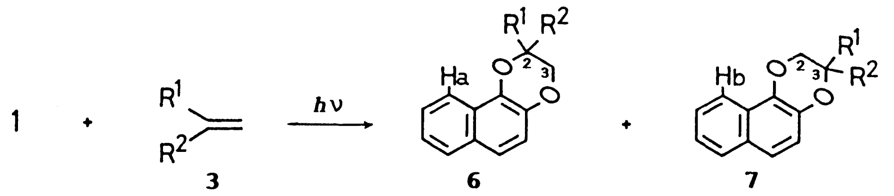
(1)

a: R=cis-CH_3; b: R=trans-CH_3; c: R=cis-C_6H_5; d: R=trans-C_6H_5

Table 1. Photochemical Reaction of **1** with Olefins (Eq. 1 and Eq. 2) at 15 °C

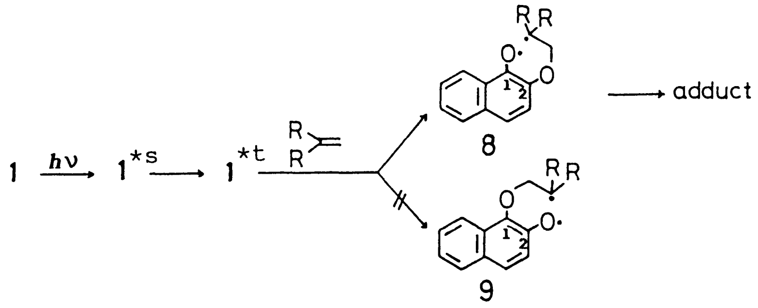
Olefin	Product	Yield/%	Stereoisomer ratio (**4**/**5**)	Regioisomer ratio(**6**/**7**)	Chemical shift(δ)	
					Ha(Ha')	Hb(Hb')
2a	**4a** + **5b**	49	65/35		8.07	8.07
2b	**4a** + **5b**	62	63/37			
2c	**4c** + **5d**	59	56/44		8.17	8.15
2d	**4c** + **5d**	45	23/77			
3a	**6a** + **7a**	40		83/17	8.15	8.07
3b	**6b** + **7b**	43		88/12	8.14	8.07
3c	**6c**	58		100/0	8.36	
3d	**6d**	46		100/0	8.31	
3e	**6e**	50		100/0	8.33	

We next investigated the photocycloaddition between **1** and unsymmetrical olefins. Upon irradiation of a benzene solution of **1** and styrene (**3a**), regioisomeric mixtures of cycloadducts (**6a**/**7a**=87/13) were obtained. The configuration of each isomer was determined by the ^{1}H NMR chemical shifts of Ha and Hb on naphthalene-ring (see Eq. 2). The Ha in **6a** resonates at δ 8.15, whereas the signal of Hb in **7a** appears at δ 8.07. Although the chemical shift of Hb is same with those of Ha' and Hb' in **4a** and **5b**, the chemical shift of Ha is similar with those of Ha' and Hb' in **4c** and **5d** (Eq.1 and Table 1). From these results, it is concluded that Ha of **6a** is resonates at lower field than Hb of **7a** probably due to a deshielding effect of the phenyl group at the position 2. Similar situations are also observed in the regioisomers of **6b** and **7b**.



a: R^1=H, R^2=C_6H_5; b: R^1=H, R^2=p-$CH_3C_6H_4$; c: R^1=R^2=C_6H_5;
d: R^1=R^2=p-$CH_3OC_6H_4$; e: R^1=R^2=p-$CH_3C_6H_4$

On the other hand, 1,1-diarylethylenes, **3c**-**3e**, gave exclusively a single regioisomer of the photocycloadduct upon irradiation with **1** in benzene. No another regioisomer could be detected even by ^{1}H NMR, GLC, or HPLC analyses. In order to elucidate the regiochemistry of the adduct, ^{1}H NMR chemical shift of the peri-hydrogen on naphthalene-ring of the photocycloadducts was examined and the results are summarized in Table 1. The extremely low field shift of the proton indicates that the cycloadducts should be **6c**-**6e**,[8)] because if they were another isomer (**7c**-**7e**) the chemical shift of the peri-hydrogen (Hb) should be similar with that of **4a**, **5b**, **7a**, or **7b**.



It is well known that the distributions of the regioisomers formed via a diradical intermediate depend on the stability of the intermediate. The regioisomer distributions in the present reactions can be clearly explained by the stability of the diradical intermediate **8**. If both **8** and **9** were formed simultaneously, the regioisomeric adducts should be obtained from the reaction with **3c**-**3e**. If **9** was the intermediate, another regioisomer (**7**) should be predominant or exclusive adduct. It is therefore concluded that the carbonyl oxygen atom at the position 2(C_2=O) of the photoexcited triplet state of **1**[9)] selectively add to an ethylenic carbon. That is to say, it should have a larger electrophilic character than that of C_1=O.

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References

1) J.M.Bruce, Quart. Revs., 21, 405 (1967); J.M.Bruce, "Photochemistry of Quinones," in "The Chemistry of the Quinonoid Compounds," ed by S.Patai, John Wiley (1974), Part 1, p. 465.

2) In contrast to the present results, Horspool reported that the [4+2]photocycloaddition of 1,4-dioxene to **1** gave a stereospecific cycloadduct, cis-dihydrodioxin. No other reports on the stereochemical aspects of the photocycloaddition of olefin to **1** have been so far. W.M.Horspool and G.D.Khandelwal, J. Chem. Soc., Chem. Commun., 1967, 1203.

3) A hydrogen abstraction product and an oxetane were not detected by the inspection of ^{1}H NMR analysis of the irradiated mixture.

4) The stereochemistry of cis-adduct(**4a**) and trans-adduct(**5b**) could be determined by the chemical shifts of the methine protons of the adducts. Y.L.Chow and T.C.Joseph have reported that the methine protons of trans-adduct resonates at higher field than those of cis-adduct which are produced in the [4+2]photocycloaddition reactions of 9,10-phenanthrenequinone with 2-butene. Y.L.Chow and T.C.Joseph, J. Chem. Soc., Chem. Commun., 1968, 604. See also K.Maruyama, T.Iwai, Y.Naruta, T.Otsuki, and Y.Miyagi, Bull. Chem. Soc. Jpn., 51, 2052(1978), and G.Pfundt and S.Farid, Tetrahedron, 22, 2237(1966). **4a**: ^{1}H NMR($CDCl_3$) δ=1.32(d, CH_3, J=6.4 Hz), 1.35(d, CH_3, J=6.4 Hz), 4.40(m, CH-CH), and 7.07-8.07(m, aromatic protons). **5a**: ^{1}H NMR($CDCl_3$) δ=1.41(d, CH_3, J=5.1 Hz), 1.47(d, CH_3, J=5.1 Hz), 3.98(m, CH-CH), and 7.09-8.07(m, aromatic protons).

5) The mixture of cycloadducts (**4c** and **5d**) could be separated into each stereoisomer by fractional recrystallization from ethanol. **4c**: needles, mp 125-126 °C; ^{1}H NMR($CDCl_3$) δ=5.56(d, CH, J=2.9 Hz), 5.65(d, CH, J=2.9 Hz), 6.99-7.81(m, aromatic protons), and 8.17(dd, Ha', J=0.8 and 8.4 Hz). **5d**: prisms, mp 150-151 °C; ^{1}H NMR($CDCl_3$) δ=4.96(d, CH, J=7.9 Hz), 5.05(d, 1H, J=7.9 Hz), 7.09-7.81(m, aromatic protons), and 8.15(bd, Hb', J=8.8 Hz).

6) In order to prevent the participation of pre-isomerized stilbene, the reactions of stilbene with **1** were carried out at wavelength longer than 400 nm and in the presence of a large excess amount of cis-stilbene or trans-stilbene. J.J.Bohning and K.Weiss, J. Am. Chem. Soc., 88, 2893 (1966).

7) Although a quite same distribution of the stereoisomeric adducts was obtained in the reactions with 2-butenes, different stereoisomer ratios of the adducts were observed in the reaction with cis- and trans-stilbenes as shown in Table 1. The origin of these facts will be discussed in elsewhere.

8) For example, compound **6c**: prisms from benzene-hexane, mp 164-166 °C; ^{1}H NMR($CDCl_3$) δ=4.68(s, 2H, CH_2), 7.01-7.74(m, 15H, aromatic protons), and 8.36(d, 1H, Ha, J=8.30 Hz); IR(KBr) 3070(w), 1630(m), 1600(s), 1470(s), 1443(s), 1385(s), 1257(vs), and 1063(m) cm^{-1}; MS m/z 338(M^+).

9) It has been clarified that **1** reacts photochemically from the triplet state. A.Takuwa, O.Soga, and K.Maruyama, J. Chem. Soc., Perkin Trans. 2, 1985, 409, and other references cited therein.

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