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Photochemical Reaction of Allyl-1,4-benzoquinones. Trapping of Biradical Intermediates with Olefins

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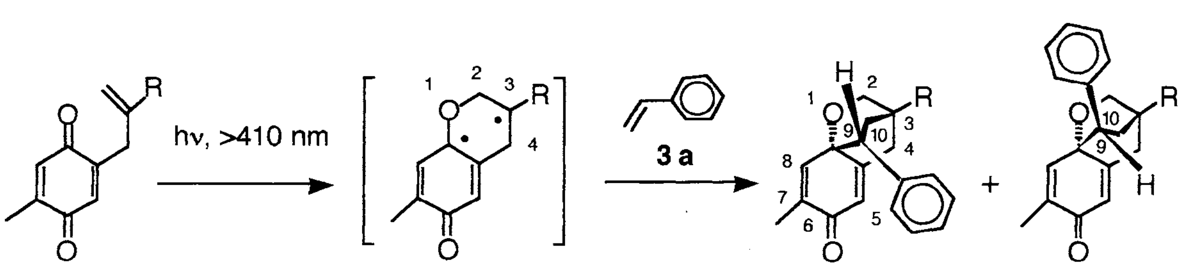
Irradiation of 2-allyl- and 2-(2-methylallyl)-5-methyl-1,4-benzoquinones in the presence of olefins gave tricyclic compounds in fair yields, which were the coupling products between the olefins and the biradical intermediate generated by the intramolecular photocyclization reaction of the quinone.

The trapping of biradical intermediates with molecular oxygen is well known to give cyclic oxygenation products.1-3) The trapping with olefins has been also investigated,4-6) but the examples are less than those of the trapping with oxygen. We now report that the biradical intermediate, generated from the photochemical reaction of 5-methyl-2-(2-methylallyl)- 1,4-benzoquinone (**1**, R=Me) and 2-allyl-5-methyl-1,4-benzoquinone (**1**, R=H), reacts regioselectively with olefins to give tricyclic compounds in considerable yields.

Typically, irradiation of a benzene solution (10 cm^3) of 5-methyl-2-(2-methylallyl)-1,4-benzoquinone (**1**, R=Me, 0.3 mmol) with styrene (**3a**, 1.5 mmol) through glass filter (Toshiba L-42, cut off <410 nm) under nitrogen atmosphere for 3 h afforded a mixture of two kinds of isomeric adducts, **4a** and **5a** (R=Me, 30%, 50:50) (Eq. 1). After isolation of each isomer by column chromatography on silica gel, the structures of the adducts were determined by their spectroscopic properties and elemental analyses.7) The ^{1}H NMR spectra of both adducts showed that the adducts were not the corresponding oxetane or cyclobutane derivatives but another type of the 1:1 adducts of **1** and **3a**.8) In the spectrum of **4a** a pair of characteristic signals due to oxymethylene

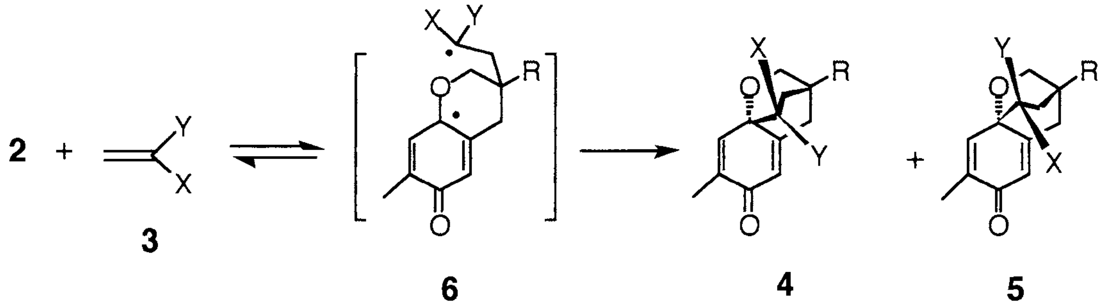


(1)

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

group was observed at δ 3.72 (1H, dd, J=8.5 and 3.2 Hz) and 3.93 (1H, d, J=8.5 Hz). The signal (δ 3.72) indicated the presence of longrange coupling with one of methylene protons at the 10-position [δ 1.73 (1H, ddd, J=13.4, 7.8 and 3.2 Hz)] by W-letter rule. Especially, for **5a** the similar longrange couplings were observed for each methylene protons at the 2-position with one of each methylene protons at the 4- and 10-positions (J=2.2 and 3.2 Hz, respectively). Another longrange coupling (J=2.4 Hz) between the methylene protons at the 10- and 4-positions was also detected.[7] These longrange couplings suggest the phenyl group should be located at the 9-position. The distinction between **4a** and **5a** was based on the following aspects. The signals of the phenyl group at the 9-position of **4a** appeared in the upfield [δ 6.99 (2H, dd) for ortho-protons] more than that of **5a** [δ 7.25-7.40 (5H, m)]. On the contrary, the signal of the methine proton at the 9-position of **5a** appeared in the upfield (δ 2.89) more than that of **4a** (δ 3.56) owing to magnetic anisotropy of the quinonoid moiety.

The results of photochemical reaction between **1** and some other olefins (**3b-k**) under similar conditions are summarized in Table 1.



(2)

As shown in Table 1, the photoinduced addition reaction of **1** with p-chloro (**3b**), p-methoxy (**3c**), and α-methylstyrenes (**3d**) proceeded regioselectively to give the corresponding tricyclic compounds, **4b-d** and **5b-d**, in similar yields. These results indicate that the localized radical at the 3-position of **2**, which was formed by the intramolecular addition of photoexcited quinone carbonyl to the γ-position of the allyl side chain, attacks the terminal olefinic carbon to give more stable radical intermediate **6** followed by ring closure to afford **4** and **5** (Eq. 2).

However, no addition products of **1** with 1,1-diphenylethylene (**3e**) were obtained. Probably, the diphenylalkyl radical of **6e** (X=Y=Ph) is too bulky for the coupling in spite of the stable radical. Isobutene (**3f**) and ethyl vinyl ether (**3g**) also gave no adducts. The results clearly indicate that the radical of **2** (3-position) has nucleophilic character, so that it hardly adds to the electron-rich olefins.[9] Actually, when the reactions of **1** were carried out with electlon-deficient olefins such as methyl acrylate (**3h**), methyl methacrylate (**3i**), acryronitrile

Table 1. Photoinduced Addition Reaction of Allyl-1,4-benzoquinones **1** with Olefins

Quinone **1**	Olefin	Substituents X	Substituents Y	Yield of **4** + **5** /%$^{a)}$	Ratio of (**4** : **5**)$^{b)}$	Conversion of **1** /%
R=Me	**3a**	H	Ph	35$^{c,d)}$	(50 : 50)	75$^{c)}$
	3b	H	p-ClC_6H_4	30$^{c)}$	(50 : 50)	80$^{c)}$
	3c	H	p-$MeOC_6H_4$	33$^{c)}$	(52 : 48)	70$^{c)}$
	3d	Me	Ph	29	(62 : 38)	90
	3e	Ph	Ph	0	-	90
	3f	Me	Me	1	-	97
	3g	H	OEt	0	-	92
	3h	H	COOMe	60	(56 : 44)	96
	3i	Me	COOMe	89	(54 : 46)	96
	3j	H	CN	77	(53 : 47)	91
	3k	Me	CN	84	(63 : 37)	96
R=H	**3i**$^{e)}$	Me	COOMe	50$^{f)}$	(58 : 42)	44

a) Isolated yields based on **1** consumed. b) Ratios were determined by ^1H NMR. c) Irradiation time was 1.2 h. d) Isolated yield was 30% after irradiation for 3 h. e) A large excess of **3i** was used. f) A small amount of other products was also produced.

(**3j**), and methacryronitrile (**3k**), the addition products, **4h**-**k** and **5h**-**k**, were obtained in high yields as shown in Table 1. In these cases, the nucleophilic additions of **2** to **3h**-**k** proceed easily[9] and the newly generated radicals, **6h**-**k**, must be stabilized by the resonance with adjacent methoxycarbonyl or cyano group.[10] Moreover, the cyclization of the biradicals **6h**-**k** occurs more smoothly compared with that of **6e**, because the methoxycarbonyl and cyano groups are sterically smaller than the phenyl group. In addition, the reaction of **1** with inner olefins such as crotononitrile (**3l**) and dimethyl maleate (**3m**) did not give the corresponding adducts. In these cases, the addition of **2** to **3l** and **3m** are prevented by the steric hindrance.[9]

In order to examine the generality of the present reaction, the photochemical reaction of 2-allyl-5-methyl-1,4-benzoquinone (**1**, R=H) was carried out in the presence of **3i**. The corresponding adducts, **4i** and **5i** (R=H, 50%, 58 : 42), could be also obtained.

Thus, the biradical intermediate **2** formed photochemically from **1** was able to be trapped by the terminal olefins having electron-deficient group and/or conjugated system such as methyl acryrate, acryronitrile, and styrene derivatives in considerable yields. The generality and limitation of this subject are being investigated.

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7) Spectral data of addition products; **4a**: Colorless prisms, mp 137-138 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.04 (3H, s, Me), 1.54 (3H, d, J=1.5 Hz, CH=C$\underline{\mathrm{Me}}$), 1.73 (1H, ddd, J=13.4, 7.8 and 3.2 Hz, CH_2), 2.15 (1H, bdd, J=13.4 and 10.7 Hz, CH_2), 2.66 (2H, s, CH_2), 3.56 (1H, dd, J=10.7 and 7.8 Hz, $CH_2C\underline{H}Ph$), 3.72 (1H, dd, J=8.5 and 3.2 Hz, OCH_2), 3.93 (1H, d, J=8.5 Hz, OCH_2), 6.08 (1H, t-like, J=2.0 Hz, $C\underline{H}=CCH_2$), 6.38 (1H, q, J=1.5 Hz, $C\underline{H}$=CMe), 6.99 (2H, dd, J=8.1 and 1.5 Hz, Ph), 7.1-7.2 (3H, m, Ph). IR (CCl_4) 1680 and 1645 cm^{-1}; Found: C, 81.57; H, 7.05. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. **5a**: Colorless prisms, mp 151-152 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.01 (3H, s, Me), 1.72 (3H, d, J=1.5 Hz, CH=C$\underline{\mathrm{Me}}$), 1.80 (1H, ddd, J=13.7, 5.9 and 2.4 Hz, CH_2), 2.12 (1H, ddd, J=13.7, 11.7 and 3.2 Hz, CH_2), 2.57 (1H, dt-like, J=18.8 and 2.4 Hz), 2.65 (1H, dt-like, J=18.8 and 2.2 Hz, CH_2), 2.89 (1H, dd, J=11.7 and 5.9 Hz, $CH_2C\underline{H}Ph$), 3.75 (1H, dd, J=8.6 and 3.2 Hz, OCH_2), 3.99 (1H, dd, J=8.6 and 2.2 Hz, OCH_2), 5.92 (1H, q, J=1.5 Hz, $C\underline{H}$=CMe), 6.09 (1H, t-like, J=2.2 Hz, $C\underline{H}=CCH_2$), 7.25-7.40 (5H, m, Ph). IR (CCl_4) 1675 and 1645 cm^{-1}; Found: C, 81.52; H, 7.22. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19.

8) Irradiation of 2,5-dimethyl-1,4-benzoquinone with styrene under the same conditions gave a mixture of diastereoisomers of the cyclobutane adducts in high yields. cf. K. Maruyama and N. Narita, Bull. Chem. Soc. Jpn., **53**, 757 (1980).

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