

PHOTOCHEMICAL REACTION OF 2-ALKENOYL-3,5-DIMETHYL-1,4-BENZOQUINONES
WITH ALCOHOL

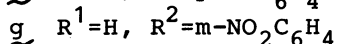
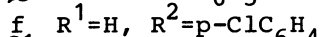
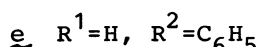
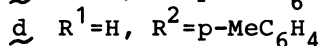
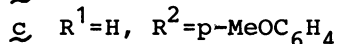
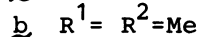
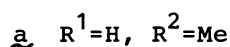
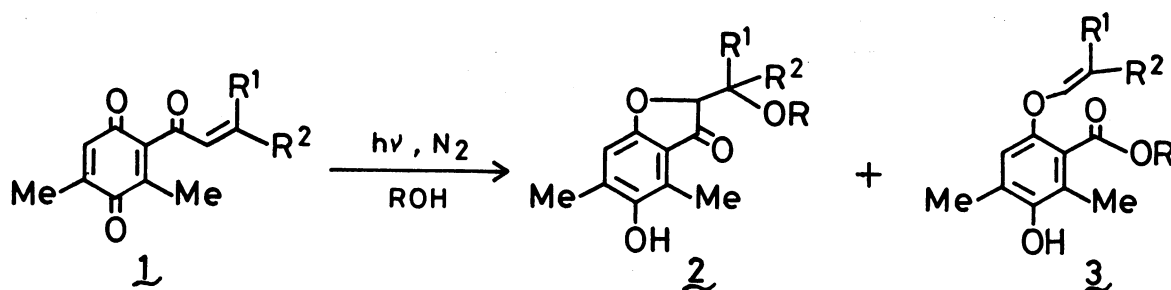
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Irradiation of 2-alkenyl-3,5-dimethyl-1,4-benzoquinones in alcohol under nitrogen atmosphere afforded the two isomeric adducts; benzofuranone derivatives and novel alkenyl ether derivatives. The mechanism of formation of these adducts is discussed.

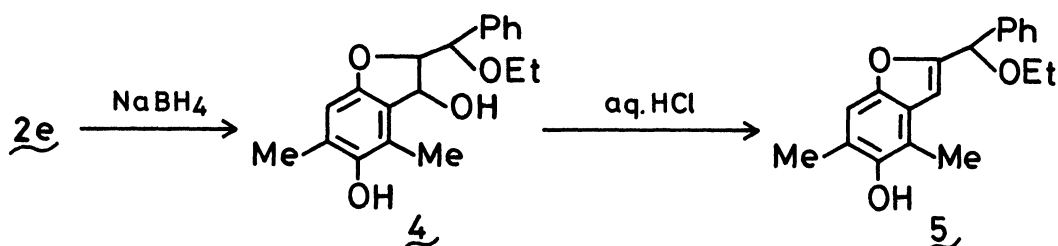
The quinones containing olefinic double bond in the side chain photochemically react to give the intramolecular cyclization products,¹⁾ while the acyl quinones give dimers.²⁾ However, the photochemical behavior of alkenyl-1,4-quinones which have both olefinic double bond and carbonyl group in the side chain is well not known. Recently, we reported that irradiation of alkenyl-1,4-quinones in benzene under aerobic conditions afforded the stable cyclic peroxides in fair to high yield.³⁾ In this letter, we wish to report the photochemical reaction of 2-alkenyl-3,5-dimethyl-1,4-benzoquinones (**1**) in alcohol under anaerobic conditions.

Upon irradiation of a solution of 2-cinnamoyl-3,5-dimethyl-1,4-benzoquinone (**1e**, ca. 0.01 M) in ethanol with a 300 W halogen lamp through a yellow glass

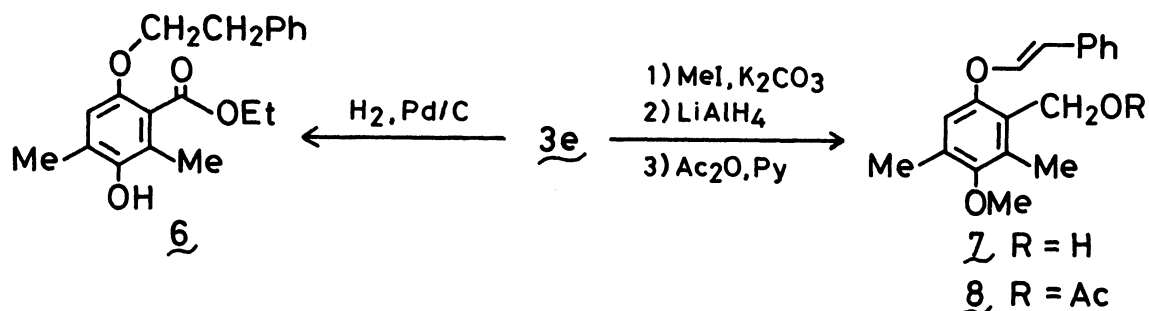


ROH = MeOH and EtOH

filter (Toshiba L-42; <410 nm cut off) at room temperature under nitrogen atmosphere for 3 h, a mixture of 2-(α -ethoxybenzyl)-5-hydroxy-4,6-dimethylbenzofuran-3(2H)-one (2e, 75%)⁴⁾ and ethyl 3-hydroxy-2,4-dimethyl-6-styryloxybenzoate (3e, 23%)⁵⁾ was obtained. After separation of the two products by column chromatography on silica gel, the structure of 2e was elucidated by the spectral data⁴⁾ and the following evidence. The product 2e was reduced with sodium borohydride followed by treatment with hydrochloric acid. The primary reduction product 4 was easily dehydrated to give 2-(α -ethoxybenzyl)-5-hydroxy-4,6-dimethylbenzofuran (5)⁶⁾ in a yield of 46%.



Another product was compatible with the structure 3e as described in the following. The spectral data of 3e⁵⁾ showed the presence of trans-vinyl protons [δ 6.00(1H, d, J=13 Hz) and 6.86(1H, d, J=13 Hz)]⁷⁾ and ester (ν 1735 cm⁻¹). Catalytic hydrogenation of 3e afforded ethyl 3-hydroxy-2,4-dimethyl-6-phenethylbenzoate (6)⁸⁾ in a yield of 80%. Positive bromine-addition reaction of 3e in carbon tetrachloride supported the presence of the ethylenic linkage. Reduction by lithium aluminum hydride of the methylated 3e gave 3-methoxy-2,4-dimethyl-6-styryloxybenzyl alcohol (7) which was acetylated to give the corresponding acetate 8⁹⁾ in a yield of 80%.



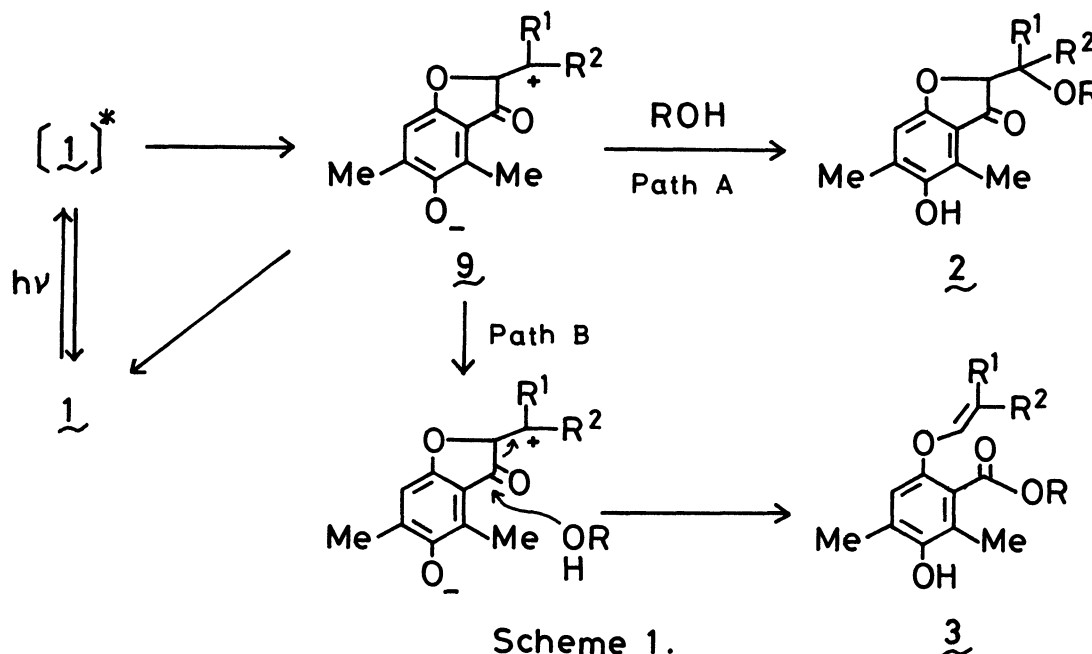
Similarly other 2-alkenoyl-3,5-dimethyl-1,4-benzoquinones (1a-1g) reacted with ethanol to give two isomeric adducts and their isomer distributions depending on the alkenoyl substituents (R¹ and R²) were summarized in Table 1.

In methanol 1a-1g gave the similar results under the same conditions (Table 1).

Table 1. Photochemical Reaction of 2-Alkenoyl-3,5-dimethyl-1,4-benzoquinones with Alcohol^{a)}

Compound	Substituent		In EtOH		In MeOH	
	R ¹	R ²	Yield/% ^{b)}		Yield/% ^{b)}	
			<u>2</u>	<u>3</u>	<u>2</u>	<u>3</u>
<u>1a</u>	H	Me	9	87	11	86
<u>1b</u>	Me	Me	73	21	87	9
<u>1c</u>	H	p-MeOC ₆ H ₄	93	0	97	0
<u>1d</u>	H	p-MeC ₆ H ₄	97	1	99	1
<u>1e</u>	H	C ₆ H ₅	75	23	82	17
<u>1f</u>	H	p-ClC ₆ H ₄	66	32	77	21
<u>1g</u> ^{c)}	H	m-NO ₂ C ₆ H ₄	9	84	18	74

a) Reaction conditions are cited in text. b) Isolated yields based on the quinone used. c) Concentration; 0.005 M, Reaction time; 4 h.



When an alcohol solution of 1 was allowed to stand for 12 h in the dark at room temperature, the starting quinone was quantitatively recovered. Thus, 1 reacted photochemically with alcohol to give 2 and 3 in good yields.

A possible mechanism of the reaction is considered to be as follows. Initially the photoexcited species of 1 cyclizes intramolecularly to form zwitterionic intermediate (2)^{1b,3)} and alcohol adds to 2 to give adduct 2 (path A) and adduct 3 (path B including a fission of C-C bond adjacent to carbonyl group) as shown in Scheme 1. The distribution of the products, 2 and 3, could be dependent on the stability of 2.

In the reaction of 1a and 1b as shown in Table 1 1a predominantly gave adduct

3a (87%), while 1b gave 2b (73%) as the major product. This is explainable by considering that 9b having tertiary carbonium ion is more stable than 9a having secondary carbonium ion.

Moreover, in the reaction of 1c-1f having a substituted phenyl group adducts 2 were predominantly formed, because of their intermediates 9 could be relatively stable. However, compound 1g which has a strong electron-withdrawing group (nitro) gave predominantly product 3g. Possibly this is due to the destabilizing effect of m-nitrophenyl group on 9g. Thus, the experimental results well support the reaction mechanism shown in Scheme 1.

References

- 1) a) J. M. Bruce, *Quart. Rev.*, 21, 405 (1967); b) D. Greed, H. Werbin, and F. T. Strom, *J. Am. Chem. Soc.*, 93, 502 (1971).
- 2) a) Y. Miyagi, K. Kitamura, K. Maruyama, and Y. L. Chow, *Chem. Lett.*, 1978, 33; b) K. Maruyama and N. Narita, *J. Org. Chem.*, 45, 1421 (1980).
- 3) K. Maruyama, M. Muraoka, and Y. Naruta, *J. Chem. Soc., Chem. Commun.*, 1980, 1282.
- 4) 2e: IR(CCl₄) 3610, 3400, 1708 cm⁻¹; ¹H NMR(CCl₄) δ=0.98(3H, t, J=7 Hz), 2.21(3H, s), 2.41(3H, s), 3.28(2H, m), 4.29(1H, d, J=2 Hz), 4.73(1H, d, J=2 Hz), 5.20(1H, bs), 6.60(1H, s), 7.1-7.4(5H, m). Found: m/z 312.1355. Calcd For C₁₉H₂₀O₄: M, 312.1360.
- 5) 3e: IR(CCl₄) 3620, 3450, 1735, 1655 cm⁻¹; ¹H NMR(CCl₄) δ=1.26(3H, t, J=7 Hz), 2.02(3H, s), 2.08(3H, s), 4.23(2H, q, J=7 Hz), 5.37(1H, bs), 6.00(1H, d, J=13 Hz), 6.52(1H, s), 6.86(1H, d, J=13 Hz), 7.08(5H, bs). MS m/z 312 (M⁺). Found: C, 72.91; H, 6.35%. Calcd for C₁₉H₂₀O₄: C, 73.06; H, 6.45%.
- 6) Spectral data on 5: IR(CCl₄) 3625, 3400 cm⁻¹; ¹H NMR(CCl₄) δ=1.23(3H, t, J=7 Hz), 2.14(3H, s), 2.19(3H, s), 3.52(2H, q, J=7 Hz), 4.36(1H, bs), 5.29(1H, s), 6.18(1H, s), 6.84(1H, s), 7.15-7.45(5H, m).
- 7) The other vinyl ether derivatives, 3a and 3c-3g, were all trans-isomers judging from their NMR spectra.
- 8) Spectral data on 6: IR(CCl₄) 3625, 3450, 1735 cm⁻¹; ¹H NMR(CCl₄) δ=1.25(3H, t, J=7 Hz), 1.94(3H, s), 2.02(3H, s), 2.69(2H, t, J=7 Hz), 3.94(2H, t, J=7 Hz), 4.16(2H, q, J=7 Hz), 4.95(1H, bs), 6.18(1H, s), 7.09(5H, s).
- 9) Spectral data on 8: IR(CCl₄) 1740, 1655 cm⁻¹; ¹H NMR(CCl₄) δ=1.91(3H, s), 2.22(6H, s), 3.61(3H, s), 5.05(2H, s), 6.10(1H, d, J=13 Hz), 6.65(1H, s), 6.97(1H, d, J=13 Hz), 7.14(5H, s).

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