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PHOTOCHEMICAL REACTION OF 2-ALKENOYL-3-ALKOXY-1,4-BENZOQUINONES. FORMATION OF 5H-PYRANO[4,3,2-de][1,3]BENZODIOXIN DERIVATIVES

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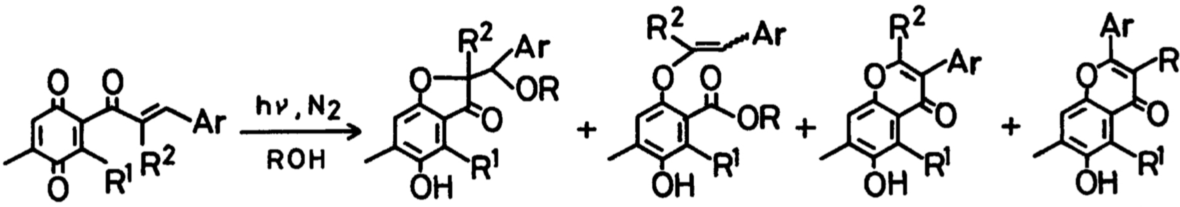
A number of 3-alkoxy-5-methyl-2-(α-methylcinnamoyl)-1,4-benzoquinones have been prepared by the reaction of 5-methyl-2-(α-methylcinnamoyl)-1,4-benzoquinone with alcohols. Irradiation of 3-methoxy-, 3-ethoxy-, and 3-isopropoxy-5-methyl-2-(α-methylcinnamoyl)-1,4-benzoquinones in solution gave 5H-pyrano[4,3,2-de][1,3]benzodioxins.

The photochemical reaction of 2-alkenoyl-1,4-benzoquinones (1 and 2) in alcohol under anaerobic conditions was reported to give the two isomeric adducts (3 and 4)[1)] and/or the two isomers of chromone derivatives (5 and 6).[2)] However, under the same conditions, 2-alkenoyl-3-alkoxy-1,4-benzoquinones (7) afforded another intramolecular cycloaddition compound, 5H-pyrano[4,3,2-de][1,3]benzodioxin (8), as main product. Photochemical reaction of alkoxyquinones with olefins has been intensively investigated.[3)] It has been reported that the irradiation of 2-alkenyl-3-alkoxy-1,4-quinones, which are formed as intermediates in the reaction, afforded intramolecularly cyclized products with the elimination of alkoxyl group. Thus, the photochemical reaction of 7 was noticeably different from that of other alkoxyquinones.



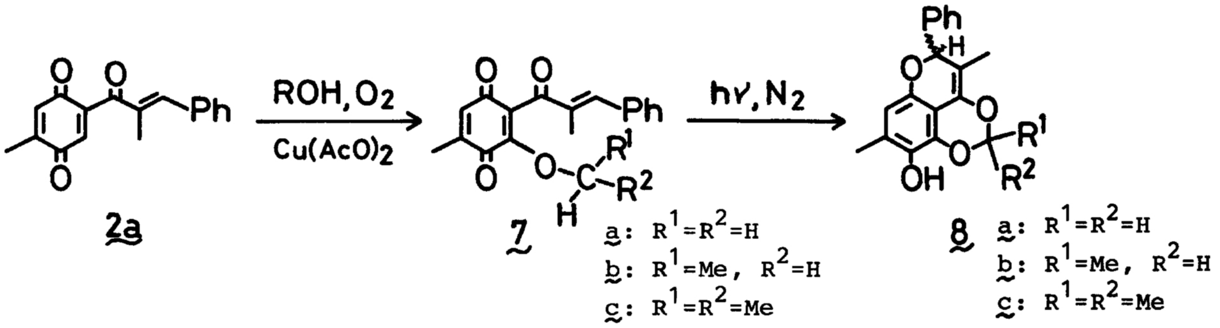
1: R^1=Me, R^2=H
2: R^1=H, R^2=Me

3 4 5 6

R=Me, Et, i-Pr, t-Bu

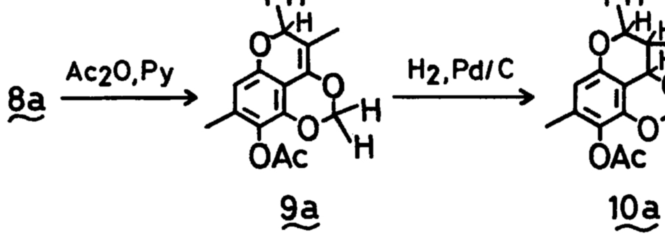
2-Alkenoyl-3-alkoxyquinones (7) were conveniently prepared from the reaction of 2-alkenoylquinone 2 with alcohol in the presence of equimolar $Cu(AcO)_2{:}H_2O$[4)] under oxygen atmosphere. For example, the reaction of 5-methyl-

2-(α-methylcinnamoyl)-1,4-benzoquinone (2a) with methanol gave 3-methoxy-5-methyl-2-(α-methylcinnamoyl)-1,4-benzoquinone (7a)5) as sole product in a 95% yield. The application of Farina and Valderrama's method6) for 2 to prepare 7 afforded a mixture of hydroquinone and 7 which could be hardly separated by usual ways.



When a solution of 7a in acetonitrile (0.01 mol cm^{-3}) was irradiated with a 300 W halogen lamp under the same conditions as described in the previous paper,1) an intramolecularly cyclized product, 9-hydroxy-4,8-dimethyl-5-phenyl-5H-pyrano[4,3,2-de][1,3]benzodioxin (8a),7) was obtained as the main product in a 50% yield. The ^{1}H NMR datum of 8a7) showed disappearance of characteristic signal at 3.88 ppm due to methoxyl group of 7a, appearance of an AB quartet signal at 5.19 and 5.28 ppm due to methylene protons resulting from the methoxyl group, and presence of singlet signal due to hydroxyl proton. The two signals of 7a at 6.38 and 2.02 ppm due to olefinic and methyl protons of the alkenoyl side chain shifted to higher field at 5.55 and 1.50 ppm, respectively. In addition, the IR spectrum of 8a indicated the presence of hydroxyl group and the absence of carbonyl group. The structure of 8a was further supported by the following chemical evidence. Positive bromine-addition reaction of methylated 8a in carbon tetrachloride suggested the presence of olefinic double bond. The product 8a gave the corresponding acetyl derivative 9a8) by acetic anhydride and pyridine and then catalytic hydrogenation of 9a afforded 9-acetoxy-3a,4-dihydro-4,8-dimethyl-5-phenyl-5H-pyrano[4,3,2-de][1,3]benzodioxin (10a)9) in a 77% yield.

Similarly 7b and 7c reacted under the same conditions to give 8b10) and 8c,11) respectively. As shown in Table 1, the yields of 8b and 8c were higher than that of 8a (Runs 2 and 3). By comparing the reactions of 7a, 7b, and 7c, the yields of 8a, 8b, and 8c were gradually increased in turn (Runs 4, 5, and 6). Compound 7a dissolved in methanol reacted to give 8a in a 43% yield (Run 7).12)



Thus, the reaction may proceed through γ-hydrogen abstractions by the excited quinone carbonyl13) at

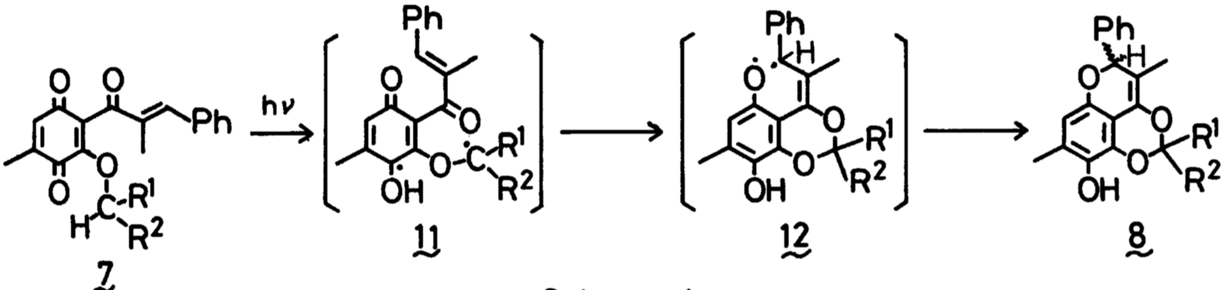
Table 1. Photochemical reaction of 3-alkoxy-5-methyl-2-(α-methylcinnamoyl)-1,4-benzoquinones (7a-c)

Run	Quinone	Solvent	Irradiation time/h	Recovered quinone/%[a)]	Yield of 8/%[b)]
1	7a	CH_3CN	3	31	50
2	7b	CH_3CN	3	6	75
3	7c	C_6H_6	3	1	77
4	7a	CH_3CN	1	74	25
5	7b	CH_3CN	1	46	50
6	7c	CH_3CN	1	20	73
7[c)]	7a	MeOH	2	0	43

a) Recovered quinone was a mixture of cis and trans isomers.

b) Isolated yield based on the quinone used.

c) Another compounds were obtained as minor products.[12)]



Scheme 1.

position 4 followed by intramolecular attack of the α-alkoxy radical 11 to the carbonyl group in the alkenoyl side chain.[14)] Cyclization of the resulting biradicals 12 gives 8 as shown in Scheme 1. This sort of bicyclo-cyclization reaction initiated by γ-hydrogen abstraction is quite novel and may be suggestive for the chemistry of polyhydroxyl compounds.

References

1) K. Maruyama, H. Iwamoto, O. Soga, and A. Takuwa, Chem. Lett., 1984, 1343.

2) K. Maruyama, H. Iwamoto, O. Soga, A. Takuwa, and A. Osuka, Chem. Lett., 1985, 595.

3) K. Maruyama, T. Otsuki, and K. Mitsui, J. Org. Chem., 45, 1424 (1980).

4) R. Baltzly and E. Lorz, J. Am. Chem. Soc., 70, 861 (1948).

5) 7a: yellow prisms, mp 103-104 °C. IR (CCl_4) 1670, 1655, and 1305 cm^{-1}; ^1H NMR (CCl_4) δ=2.02 (3H, s), 2.10 (3H, s), 3.88 (3H, s, OMe), 6.38 (1H, s), 7.12 (1H, s), and 7.28 (5H, s). 7b: yield 95%. yellow leaflet crystal, mp 78-80 °C. ^1H NMR (CCl_4) δ=1.26 (3H, t, J=7 Hz, $OCH_2\underline{Me}$), 4.14 (2H, q, J=7 Hz, $O\underline{CH_2}Me$). 7c: yield 60%. orange prisms, mp 103-105 °C. ^1H NMR

(CCl_4) δ=1.21 (6H, d, J=6 Hz, $OCH\underline{Me}_2$), 4.78 (1H, m, J=6 Hz, $OC\underline{H}Me_2$).

6) F. Farina and J. Valderrama, Synthesis, **1971**, 315.

7) **8a**: IR (CCl_4) 3575, 2910, 1700 (w), 1650, and 1190 cm^{-1}; ^1H NMR (CCl_4) δ=1.50 (3H, s, Me), 2.08 (3H, s, Me), 4.78 (1H, s, OH), 5.19 (1H, ABq, J=5 Hz, $C\underline{H}H$), 5.28 (1H, ABq, J=5 Hz, $CH\underline{H}$), 5.55 (1H, s, CH), 6.02 (1H, s, ArH), and 7.23 (5H, s, Ph).

8) 9-Acetoxy-4,8-dimethyl-5-phenyl-5H-pyrano[4,3,2-de][1,3]benzodioxin (**9a**): yield 81%. colorless prisms, mp 113-116 °C. IR ($CHCl_3$) 1760, 1705(w), and 1195 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.50 (3H, s), 2.02 (3H, s), 2.26 (3H, s, COMe), 5.26 (1H, ABq, J=5 Hz), 5.31 (1H, ABq, J=5 Hz), 5.74 (1H, s), 6.17 (1H, s), and 7.32 (5H, s). Found: C, 71.18; H, 5.64%. Calcd for $C_{20}H_{18}O_5$: C, 71.00; H, 5.36%.

9) **10a**: colorless needles (benzene-hexane), mp 214-215 °C, IR ($CHCl_3$) 1755, 1640, and 1195 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.67 (3H, d, J=7 Hz, $CH\underline{Me}$), 2.09 (3H, s, Me), 2.28 (3H, s, Me), 2.30-2.65 (1H, m, $C\underline{H}Me$), 5.22 (1H, d, J=3 Hz, CH), 5.25 (1H, s, CH), 5.40 (2H, s, CH_2), 6.34 (1H, s, ArH), 7.35 (5H, s, Ph). Found: C, 70.34; H, 5.89%; M^+, 340. Calcd for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92%; M, 340.

10) 9-Hydroxy-2,4,8-trimethyl-5-phenyl-5H-pyrano[4,3,2-de][1,3]benzodioxin (**8b**) (mixture of diastereoisomers; ca. 3:1): IR (CCl_4) 3575, 2905, 1700 (w), 1640, and 1190 cm^{-1}. ^1H NMR (CCl_4) δ=1.46 and 1.52 (3H, each s, Me), 1.63 (3H, d, J=5 Hz, $CH\underline{Me}$), 2.10 (3H, s, Me), 4.71 (1H, s, OH), 5.1-5.4 (1H, m, $C\underline{H}Me$), 5.53 and 5.63 (1H, each s, CH), 6.04 (1H, s, ArH), and 7.2-7.5 (5H, m, Ph).

11) 9-Hydroxy-2,2,4,8-tetramethyl-5-phenyl-5H-pyrano[4,3,2-de][1,3]benzodioxin (**8c**): IR ($CHCl_3$) 3550, 2990, 1695 (w), and 1640 cm^{-1}; ^1H NMR (CCl_4) δ=1.49, 1.54 and 1.60 (9H, each s, Me), 2.08 (3H, s, Me), 4.80 (1H, s, OH), 5.58 (1H, s, CH), 5.99 (1H, s, ArH), and 7.23 (5H, s, Ph).

12) Irradiation of **7a** in methanol gave **8a** (43%), 5-hydroxy-4-methoxy-2-(1-methoxybenzyl)-2,6-dimethylbenzofuran-3-one (type **3**, 18%), methyl 3-hydroxy-2-methoxy-4-methyl-6-(1-methylstyryloxy)benzoate (type **4**, 7%), 6-hydroxy-5-methoxy-2,7-dimethyl-3-phenylchromone (type **5**, 3%), 6-hydroxy-2,5-dimethoxy-2,7-dimethyl-3-phenylchromene (8%), and hydroquinone (10%).

13) The intramolecular γ-hydrogen-abstraction reactions by triplet ketones were well known. Hydrogen abstractions from ethers occur more rapidly than from alkanes because the resulting α-alkoxy radicals are stabilized by conjugation with a lone pair on oxygen: C. Walling and M. J. Mintz, J. Am. Chem. Soc., **89**, 1515 (1967). V. Malatesta and J. C. Scaiano, J. Org. Chem., **47**, 1455 (1982).

14) The preferred conformation of acetyl-1,4-benzoquinone has an acetyl group approximately perpendicular to the quinonoid ring: J. M. Bruce, F. Heatley, R. G. Ryles, and J. H. Scrivens, J. Chem. Soc., Perkin Trans. 2, **1980**, 860.

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