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Cyclization of Type II Diradicals from 3-Alkoxy-1,2-naphthoquinones. Photochemical Transformation of an Alkoxyl Group into a Methylenedioxy Group[†]

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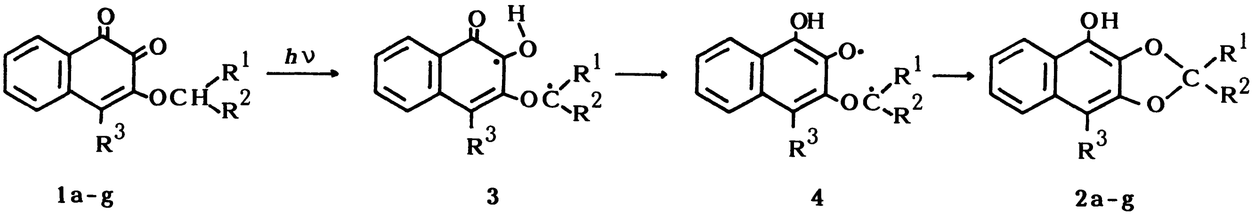
Photo-induced intramolecular hydrogen abstraction of 3-alkoxy-1,2-naphthoquinones afforded methylenedioxy compounds. The efficiency of the reactions was strongly affected by introducing a substituent at the position 4 of the quinones.

Methylenedioxy compounds are widespread in nature. An intramolecular hydrogen abstraction of guiacol residue has been suggested for the formation of the methylenedioxy compounds in biological system,$^{1)}$in which the phenoxy radical derived from guiacol function might abstract hydrogen intramolecularly from the methoxyl group. However chemically produced phenoxy radicals, unlike alkoxy radicals, tend not to abstract hydrogen from saturated carbon.$^{2)}$ We now report that the transformation of alkoxyl group into methylenedioxy function has been achieved by the photochemical process(in vitro), i.e., intramolecular hydrogen abstraction reaction of 3-alkoxy-1,2-naphthoquinones.

Irradiation of 3-methoxy-1,2-naphthoquinone(**1a**) in N_2-purged benzene with a



Scheme 1.

[†]This paper is dedicated to the late Professor Ryozo Goto, Kyoto University.

high pressure mercury lamp through a Pyrex filter afforded 1-hydroxy-2,3-methylenedioxynaphthalene(**2a**, 17%).[3] The structure of **2a** was deduced from the spectral data.[4] Under similar conditions, other 3-alkoxy-1,2-naphthoquinones(**1b**-**c**) yielded methylenedioxy derivatives, **2b**-**c**, in 34-36% yields(Scheme 1 and Table 1).

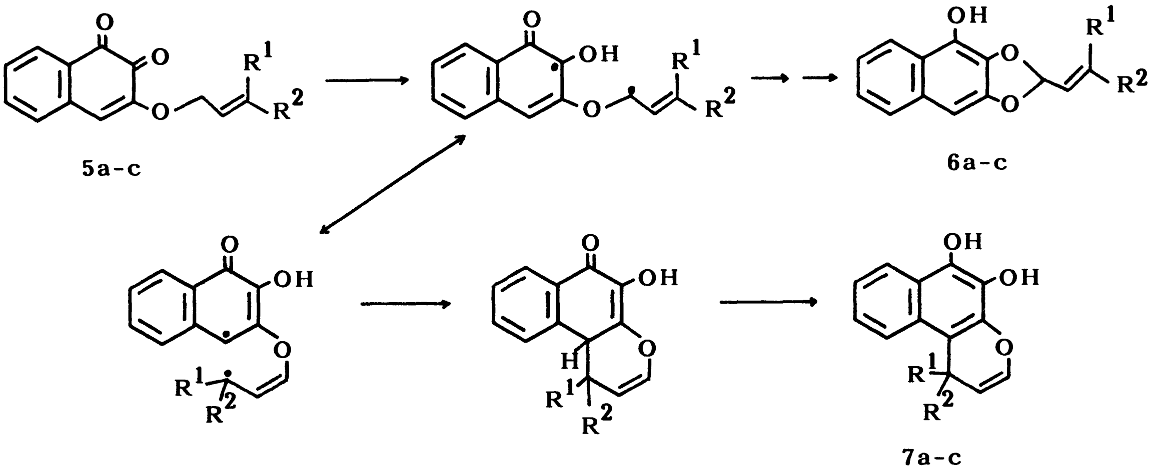
Table 1. Photochemical Reaction of 3-Alkoxy-1,2-naphthoquinones

Run	Quinone	Substituent R^1	R^2	R^3	Product (yield/%)[a]	Relative reactivity[b]	Chemical shift[c]
1	**1a**	H	H	H	**2a** (17)	1.0	3.01
2	**1b**	H	CH_3	H	**2b** (34)	5.3	3.29
3	**1c**	CH_3	CH_3	H	**2c** (36)	25.0	3.99
4	**1d**	H	H		**2d** (90)	14.0	3.59
5	**1e**	H	CH_3		**2e** (83)	43.0	3.96
6	**1f**	CH_3	CH_3		**2f** (80)	92.0	4.73
7	**1g**	H	H		**2g** (92)	d)	3.63

a)Isolated yields after acetylation. b)Determined by UV spectral changes. c)Chemical shift of alkoxyl protons(OCH); δ-values in C_6D_6. d)Not determined.

The simplest mechanism consistent with these findings is that of Scheme 1. As a 3-alkoxy-1,2-naphthoquinone, **1** upon excitation should undergo intersystem crossing and abstraction of alkoxylic hydrogen[5] to furnish a 1,4-diradical(**3**), and subsequent rearrangement of the hydroxylic hydrogen can produce a 1,5-diradical(**4**), and the resulting **4** can cyclize to yield **2**. The efficient Type II process is expected when achievement of a cyclic six-membered transition state is constrained by structural requirements.[6] These requirements is not satisfactory for **1a** because of the free rotation around Ar-OCH_3 bond being allowed. In order to compress the carbonyl oxygen at the position 2 and the hydrogen of methoxyl group in the requisite conformation, we introduced an allyl group into the 4-position of **1a**. The more favorable conformation for Type II process of 4-allyl-3-methoxy-1,2-naphthoquinone(**1d**) than that of **1a** was supported by the chemical shift of methoxyl protons of these quinones(Runs 1 and 4 in Table 1). The low chemical shift of the methoxyl protons of **1d** relative to that of **1a** (Δδ=0.58 ppm) suggests that the methoxyl protons of **1d** are located in the anisotropic deshielding region of the carbonyl group,[7] and therefore the free rotation of around Ar-OCH_3 bond should be relatively restricted. Similar situations are also observed between **1b**-**c** and **1e**-**f**, respectively(Table 1). In the event, Type II process of **1d**-**g** occurred more efficiently than that of **1a**-**c**, respectively (see Table 1).

For further supporting the proposed reaction mechanism, we examined the reaction of 3-allyloxy-1,2-naphthoquinones(**5a**-**c**). Irradiation of **5a** in benzene yielded methylenedioxy derivative(**6a**,41%) and 4H-pyrane derivative(**7a**, 27%). The structure of **7a** was deduced from spectroscopic data[8] and the following chemical transformations. The oxidation, acetylation, or hydrogenation of **7a** afforded quinone(**8**), diacetate(**9**), or chroman derivative(**10**),respectively.[9] The formation of **7a** can be rationalized by cyclization of 1,6-diradical, followed by enolization as shown in Scheme 2. These results also support the reaction proceeds via Type II process. Other quinones, **5b** and **5c**, gave similarly two isomeric products(**6** and **7**) and the distribution of the isomeric products was controlled by both diradical stabilities and steric influences(Table 2 and Scheme 2).



Scheme 2.

Table 2. Photochemical Reaction of 3-Allyloxy-1,2-naphthoquinones

Quinone	Products (yield/%)[a]	Distribution 6 : 7
5a ($R^1=R^2=H$)	**6a**(41); **7a**(27)	60 : 40
5b ($R^1=H$; $R^2=CH_3$)	**6b**(34); **7b**(38)	47 : 53
5c ($R^1=R^2=CH_3$)	**6c**(45); **7c**(13)	77 : 23

a)Isolated yields.

These nobel photocyclizations of 3-alkoxy-1,2-naphthoquinones will open an easy synthetic access to dioxymethylene function.

References

1) G.H.N. Toweres,"Metabolism of Phenolics in Higher Plants and Micro-organisms," in "Biochemistry of Phenolic Compounds," ed by J.B. Harborne, Academic Press, London (1964), Chap. 7, p. 249; A.R. Battersby "Oxidative Coupling of Phenols," ed by W.I. Taylor and A.R. Battersby, Marcel Dekker, New York(1967), p. 119.

2) P. Gray and A. Williams, Chem. Rev., 59, 239(1959); J.K. Kochi,"Oxygen Radicals," in "Free Radicals," ed by J.K. Kochi, Jhon Willey, New York (1973), Vol. 2, p. 665-710.

3) Cyclization product of 1,4-diradical(**3**), 1,3-epoxy derivative, was not detected in the reaction mixture(from NMR). The UV spectral changes of the reaction also showed a isosbestic point at 320 nm.

4) Compound **2a** was isolated as acetate after acetylation: needles from hexane, mp 109-110 °C; ^{1}H NMR(CCl$_4$) δ 2.36(s, 3H), 6.00(s, 2H), 6.92(s, 1H), and 7.12-7.63(m, 4H); IR(KBr) 1760, 1462, 1445, and 1205 cm^{-1}.

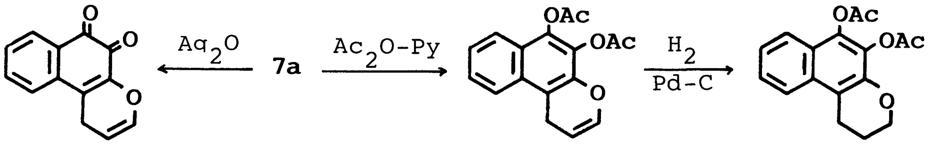
5) Recently, we reported the photoexcited 1,2-naphthoquinone molecule in the triplet state could abstract hydrogen from hydrogen donors such as xanthene or aldehydes. A. Takuwa, Bull. Chem. Soc. Jpn., 49, 2790(1976), 50, 2973(1977); K. Maruyama, A. Takuwa, and O. Soga, J. Chem. Soc., Perkin Trans. 2, 1979, 255; K. Maruyama, A. Takuwa, S. Matsukiyo, and O. Soga, Perkin Trans. 1, 1980, 1414.

6) N.J. Turro,"Modern Molecular Photochemistry," Benjamin, California(1978), p. 362.

7) The low field shift of the methoxyl protons in **1d** is not owing to the deshielding effect of the double bond of allyl group at the position 4, because the methoxyl protons in 3-methoxy-4-propyl-1,2-naphthoquinone(**1g**) also resonate at lower field than those in **1a** (Run 7 in Table 1).

8) Compound **7a**: ^{1}H NMR(CDCl$_3$) δ 3.50(m, 2H), 5.00(m, 1H), 5.10(br, 2H), 6.52(m, 1H), 7.20-7.72(m, 4H).

9) Compounds, **8**, **9**, and **10** were obtained after treatment of **7a** with silver(I) oxide or acetic anhydride-pyridine mixture, or by hydrogenation of the diacetate in the presence of Pd-C catalyst.
Compound **8**: red needles, mp 200 °C(decomp.); ^{1}H NMR(CDCl$_3$) δ 3.18(m, 2H), 4.98(m, 1H), 6.50(m, 1H), and 7.25-8.03(m, 4H); IR(KBr) 1670 cm^{-1}. Compound **9**: prisms, mp 182-183 °C; ^{1}H NMR(CDCl$_3$) δ 2.27(s, 3H), 2.35(s, 3H), 3.55(m, 2H), 5.04(m, 1H), 6.47(m, 1H), and 7.30-7.72(m, 4H); IR(KBr) 1770, 1205, and 1120 cm^{-1}. Compound **10**: prisms, mp 167-168 °C; ^{1}H NMR(CDCl$_3$) δ 2.10(quintet, 2H, J=6 Hz), 2.30(s, 3H), 2.40(s, 3H), 3.01(t, 2H, J=6 Hz), 4.22(t, 2H, J=6 Hz), and 7.35-7.85(m, 4H); IR(KBr) 1770, 1370, 1205, 1187, and 1123 cm^{-1}.



8 **9** **10**

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