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Solvent Effect on the Product Distributions in the Photocycloaddition of Electron-rich Olefins to 1,2-Naphthoquinone

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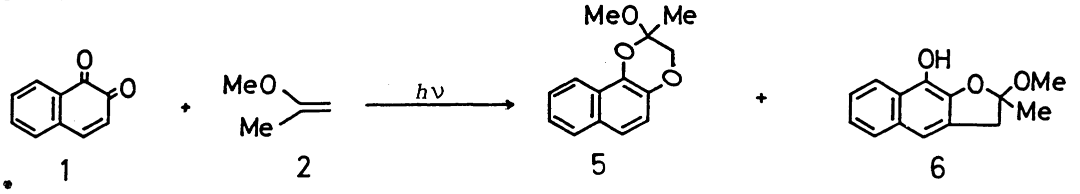
Irradiation of 1,2-naphthoquinone in the presence of electron rich olefins such as 2-methoxypropene, ethyl vinyl ether, or 2,3-dihydrofuran, afforded two isomers of cycloadducts, i.e., dihydrodioxins and dihydrofuran derivatives. The distributions of these two products strongly depended on the solvent polarities. In the reaction in benzene, dihydrodioxins were almost exclusively obtained, whereas in acetonitrile or methanol dihydrofuran derivatives were exclusively produced in high yields.

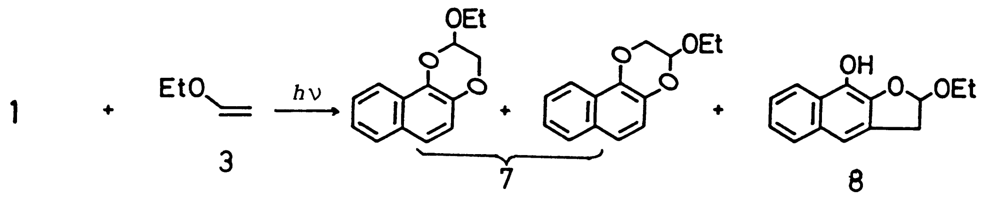
The photocycloaddition reactions of quinones to olefins have been much studied of interest in synthetic and mechanistic viewpoints,1) but the photochemical reaction of 1,2-naphthoquinone (**1**) with olefins has little been investigated so far. In our preceding paper, it was reported that irradiation of **1** with alkyl- or aryl-substituted ethylenes in benzene gave dihydrodioxins via a triplet diradical intermediate.2) During the course of the study, we found that the reaction-sites of **1** could be controlled by a reaction medium in the photocycloaddition reactions of **1** with electron-rich olefins. We wish to report herein that a novel solvent effect on the product distributions in the cycloaddition reactions of **1** with olefins.

Upon irradiation (>340 nm) of a benzene solution of **1** and 2-methoxypropene (**2**) with a high-pressure mercury lamp afforded two isomers of photocycloadducts, dihydrodioxin (**5**, 75%) and dihydrofuran derivative (**6**, 5%) after separation with preparative TLC [ether:hexane(V/V)=1:1]. The structures of the isolated products were elucidated by spectroscopic data.3) In contrast, when the reaction was carried out in acetonitrile the distribution of the two photocycloadducts was completely reversed; **5** and **6** were isolated in 3 and 87% yields, respectively (see Eq. 1).



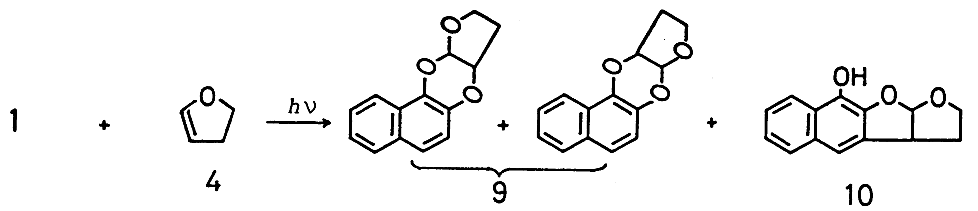
(1)

	5	6
C_6H_6	75%	5%
CH_3CN	3%	87%



(2)

	7	8
C_6H_6	87%	6%
CH_3CN	3%	85%



(3)

	9	10
C_6H_6	55%	6%
CH_3CN	4%	58%

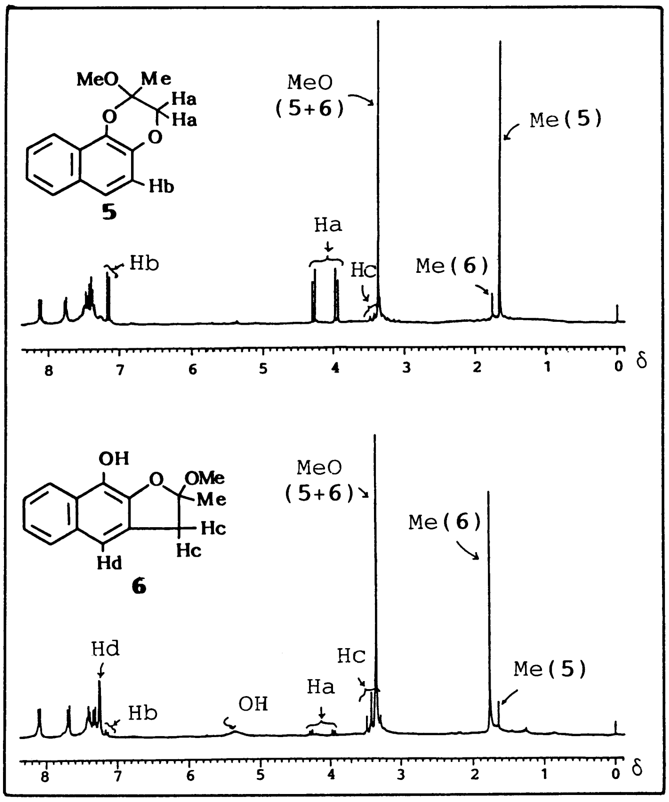


Fig. 1. ^1H NMR spectra (270 MHz) of the irradiated mixture of **1** and **2** in benzene (top) and in acetonitrile (bottom). Solvent : $CDCl_3$

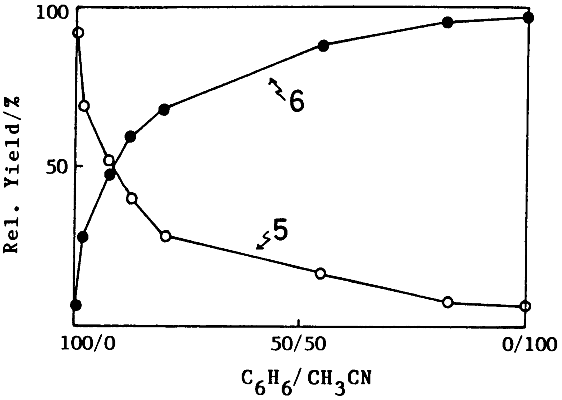


Fig. 2. Relative yields of **5** and **6** in the photochemical reaction of **1** with **2** in various proportions of benzene-acetonitrile.

The reactions proceeded very cleanly in both solvents and any other product could not be detected in irradiated mixture by inspection of ^{1}H NMR spectra as shown in Figure 1.

The other olefins, ethyl vinyl ether (**3**) and 2,3-dihydrofuran (**4**) also reacted smoothly with **1** in benzene to afford respectively dihydrodioxins, **7** and **9**, as major products.$^{4)}$ However, when acetonitrile was employed as solvent the predominant product changed respectively to dihydrofuran derivatives, **8** and **10**, as can be seen in Eqs. 2 and 3.

The relative ratios of **5** to **6** were measured in various proportions of benzene-acetonitrile solution, and they decreased with increasing the proportions of acetonitrile (see Fig. 2). Thus the distributions of the products might be drastically affected by the solvent polarity. In order to further establish the influence of the solvent polarity on the product distributions, the reaction of **1** with **2** was carried out in various solvents by the use of a merry-go-round irradiation apparatus.$^{5)}$ The relative yields for the formation of **5** to **6** were evaluated from ^{1}H NMR integrations and the results are tabulated in Table 1.

Table 1. Relative Ratios of **5** to **6** in the Photocycloaddition Reaction of **1** with **2** in Various Solvents

Solvent	$E_T$$^{a)}$	$\varepsilon$$^{b)}$	Rel. ratio$^{c)}$ **5** : **6**	Total yield/%$^{c)}$
CH_3OH	55.5	32.6	1 : 99	90
CH_3CH_2OH	51.9	24.3	3 : 97	86
CH_3CN	46.0	37.5	4 : 96	97
CH_3COCH_3	42.2	20.7	21 : 79	77
CH_2Cl_2	41.1	7.77	83 : 17	34
C_6H_6	34.5	2.28	94 : 6	85

a) Kosower's E_T parameter. b) Dielectric constant.
c) Determined by ^{1}H NMR spectroscopy.

In methanol, ethanol, and in acetonitrile **6** was almost exclusive product. Even though the relative yield of **6** would tend to be depressed in acetone, it was still preferential product. However, in the reaction in dichloromethane the relative yield of **6** was extremely depressed and **5** turned into the predominant product. These tendencies were more strikingly recognized in benzene which has the smallest polarity of solvent used in this work. Thus, the relative yields of **5** to **6** decrease with increasing of solvent polarity. Similar tendencies were also observed in the reactions of **1** with other olefins used in this work.

Next, we examined the reactions with 4-cyano-1,2-naphthoquinone (**11**) which has lower reduction potential (E_{red}=-0.02 V) than that of **1** (E_{red}=-0.27 V).$^{6)}$ The reaction of **11** with **2** or **3** in acetonitrile gave only dihydrofuran derivative (**13**) in almost quantitative yields, and even in the reaction in benzene **13** was also appreciably produced as shown in Table 2.

From these results and the evidence of no formation of a charge transfer complex of **1** or **11** with **2** both in benzene and acetonitrile being observed in the ground state, dihydrofuran derivatives may be produced from ionic process probably via a single electron-transfer reaction. On the other hand, the contribution of a diradical structure may be the most important intermediate in nonpolar solvent to afford dihydrodioxins as reported in our previous paper.[2)] However, the details of the reaction mechanism remain largely equivocal, and are under investigation.

Table 2. Relative Ratio of **12** to **13** in the Reaction of 4-Cyano-1,2-naphthoquinone (**11**) with Olefins in Benzene or Acetonitrile

Olefin	Solvent	Rel. ratio[a)]			Total yield/%[a)]
		Dihydrodioxin(**12**)	:	Dihydrofuran(**13**)	
2	C_6H_6	44	:	56	91
	CH_3CN	0	:	100	99
3	C_6H_6	41	:	59	90
	CH_3CN	0	:	100	95

a) Determined by ^{1}H NMR spectroscopy.

Thus it is particularly noteworthy that the reaction-sites of 1,2-naphthoquinones in the present reactions could be controlled by the solvent used.

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References

1) J. M. Bruce, Quart. Rev., 21, 405 (1967); J. M. Bruce, "Photochemistry of Quinones," in "The Chemistry of the Quinonoid Compounds," ed by S. Patai, Jhon Wiley (1974), Part 1, pp. 465-538. K. Maruyama, T. Otsuki, and H. Tai, J. Org. Chem., 50, 52 (1985) and other references cited therein.
2) A. Takuwa, Chem. Lett., 1989, 5.
3) All new compounds reported here gave satisfactory IR and NMR spectra, which will be reported elsewhere.
4) Unfortunately, in spite of several efforts the orientation of the regioisomers (**7** and **9**) could not be established, so the distributions of the regioisomers have not yet been determined.
5) A solution of **1** in a solvent (3 mmol dm^{-3}) was irradiated for 30 min.
6) Determined by a cyclic voltammetry using Ag/AgCl (in CH_3CN) as a reference.

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