Type II Photoreaction of 1a,2a-Dihydro-2*H*-cyclopropa[*b*]naphthalene-1,3-dione

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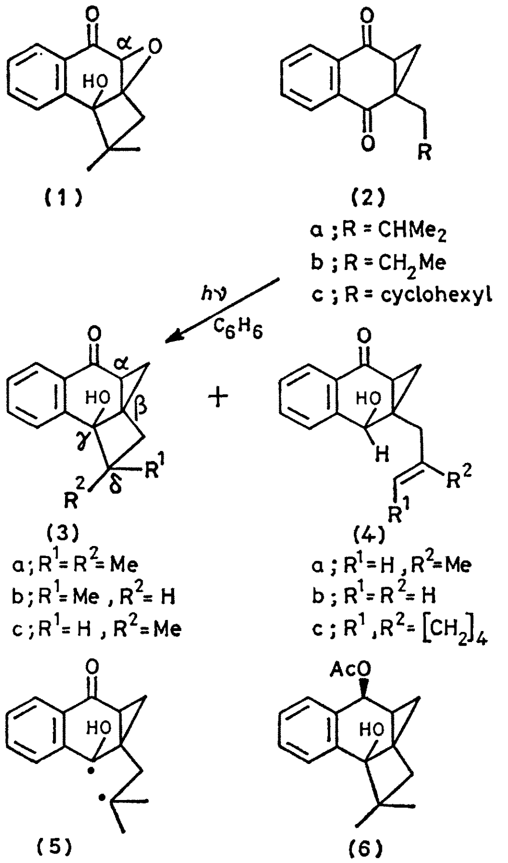
Summary Type II photoreaction of the title compound gave a cyclobutanol (**3**) and an unsaturated alcohol (**4**); the latter was presumably formed by an unusual disproportionation of a type II biradical.

RECENTLY we have reported the photorearrangements with C(α)–O bond cleavage of the cyclobutanol (**1**) which is obtained from the type II photocyclization of 2-alkyl-2-3-epoxy-2,3-dihydro-1,4-naphthoquinone.[1] We now describe the type II photoreaction of the naphthoquinone derivative (**2**) leading to the formation of the cyclobutanol (**3**) and the unsaturated alcohol (**4**). It is noteworthy in that a type II biradical (**5**) is photochemically generated from (**3**) and finally collapses to (**4**) by reverse disproportionation.



(1)

(2)
a ; R = $CHMe_2$
b ; R = CH_2Me
c ; R = cyclohexyl

(3)
a; R^1 = R^2 = Me
b; R^1 = Me , R^2 = H
c; R^1 = H , R^2 = Me

(4)
a ; R^1 = H , R^2 = Me
b ; R^1 = R^2 = H
c ; R^1 , R^2 = $[CH_2]_4$

(5)

(6)

Irradiation of compound (**2a**) in C_6H_6 or C_6H_6–Bu^{t}OH (1 : 1) with a 300 W high-pressure Hg lamp in a Pyrex vessel furnished a mixture of (**3a**) and (**4a**), which were separated by silica gel column chromatography. The structure of (**4a**) was firmly established by oxidation (CrO_3–pyridine) to a diketone which, on hydrogenation (Pd/C; EtOH), was converted back into (**2a**).†

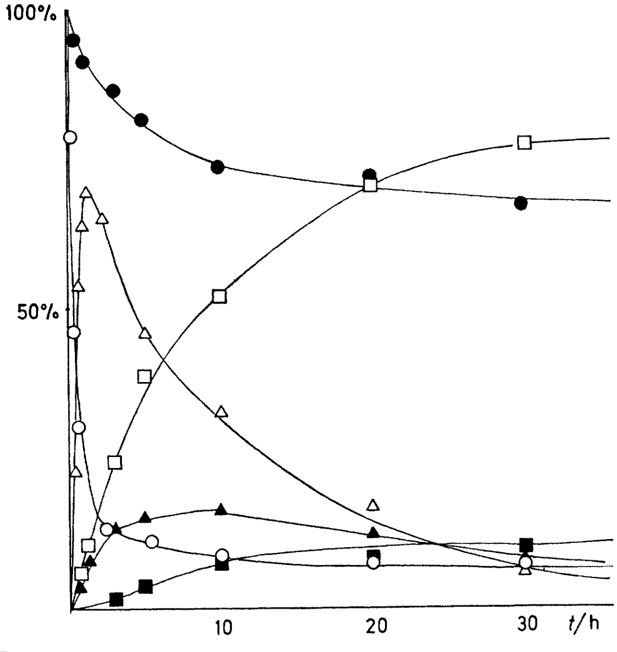


FIGURE. Dependence of the product distribution on the solvent and irradiation time. Filled symbols ●, ▲, and ■ show the amount of (**2a**), (**3a**), and (**4a**) in the photolysis of (**2a**) in benzene, respectively, while open symbols ○, △, and □, represent the amount of (**2a**), (**3a**), and (**4a**) in the photolysis in C_6H_6–Bu^{t}OH (1 : 1), respectively.

The product distribution was found to depend on both the solvent and irradiation time (Figure). The amount of (**3a**) reached a maximum after 1 h in C_6H_6–Bu^{t}OH (after 10 h in C_6H_6) and then decreased, while the amount of (**4a**) increased steadily. These results suggest the photochemical production of (**5**) from (**3a**) as well as by the normal type II pathway from (**2a**). In fact, irradiation of (**3a**) in benzene produced (**2a**) very efficiently by the disproportionation of (**5**), with the concurrent formation of (**4a**). Similar irradiation of (**2b**) in C_6H_6 up to 65% conversion gave the cyclobutanols (**3b**) (22%) and (**3c**) (15%), and the unsaturated alcohol (**4b**) (11%). Both (**3b**) and (**3c**), on irradiation in benzene, efficiently gave (**2b**) with concurrent interconversion and formation of (**4b**). In the reaction of (**2c**), only the unsaturated alcohol (**4c**) was obtained, in 85% yield. The acetate (**6**) was quite stable under the irradiation conditions. Therefore, the C(γ)–C(δ) bond rupture in (**3a**) may be brought about as a result of excitation energy

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† All new compounds gave satisfactory elemental analyses and spectral data.

transfer to the cyclobutane ring through the cyclopropane ring or through the π-electron systems of the benzene ring. The photochemical behaviour of (**3**) is in marked contrast to that of (**1**).[1]

The unsaturated alcohol (**4**) presumably arises from hydrogen transfer from the δ-carbon to the benzylic radical centre. However, this process in type II biradicals is quite rare and we are unaware of any other examples. The reactivity for hydrogen abstration of the ketyl radical site in type II biradicals is negligibly small, compared with that of alkyl radical sites.[2] One possible explanation for the formation of (**4**) may be that under the irradiation conditions there is formed a photoequilibrium between (**2**) and (**3**) *via* (**5**) as a common intermediate with (**4**) being formed slowly from the latter.

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[1] K. Maruyama, A. Osuka, and H. Suzuki, *J. Chem. Soc., Chem. Commun.*, 1980, **323**.

[2] P. J. Wagner, *Acc. Chem. Res.*, 1971, **4**, 168.