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Novel Photocyclization between Quinone and 1,1-Diphenylcyclopropane

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Photochemical reaction of 2,3-dichloro-1,4-naphthoquinone with 1,1-diphenylcyclopropane gave a spirofuran adduct as the sole photoproduct.

Recently, photoreactions involving electron-transfer processes have received much attention from synthetic and mechanistic aspects of organic photochemistry.$^{1)}$ The electron-transfer photochemistry of cyclopropanes are particularly interesting because of unique structure and reactivity of the cation radicals.$^{1-3)}$ We have studied electron-transfer photoreactions of quinone with a variety of electron donors, such as 1,1-diphenylethenes,$^{4)}$ 2-alkoxy-1-alkenes$^{5)}$ and the related silyl cnol ethers,$^{6)}$ allylstannanes,$^{7)}$ and allenes.$^{8)}$ Now we wish to report the photochemistry of quinone with arylcyclopropanes.

Irradiation of an acetonitrile solution (25 ml) containing 2,3-dichloro-1,4-naphthoquinone (1a, 0.5 mmol) and 1,1-diphenylcyclopropane (2b, 1 mmol) with a high pressure mercury lamp through a Pyrex filter for 3 h afforded the spirofuran adduct 3b as the sole photoproduct in 53% yield. The novel spirocyclic structure of 3b was assigned from spectroscopic data, elemental analysis,$^{9)}$ and X-ray analysis (Fig. 1).$^{10)}$ We have reported that photoreaction of quinone 1a with 1,1-diphenylallene 4b gives the spiropyran adduct 5b via electron transfer (Fig. 2).$^{8)}$ The structure of 3b is similar to that of 5b, but the position of coupling is different; that is, in 5b the coupling occurs between the carbonyl carbon in quinone moiety and the ortho position of the one of two phenyl substituents on the allene skeleton, but in 3b it occurs between the carbonyl carbon and C_1 on the cyclopropane. Interestingly, none of the products were

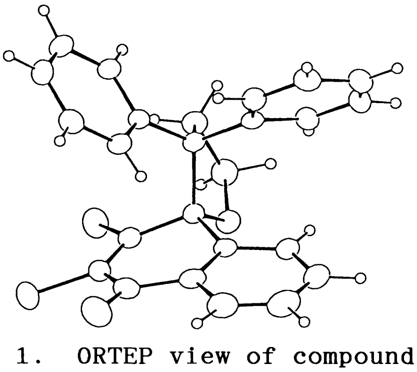


Fig. 1. ORTEP view of compound 3b.

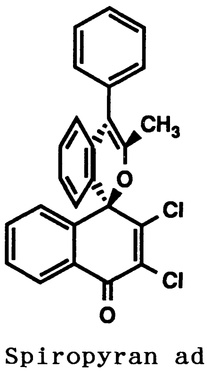
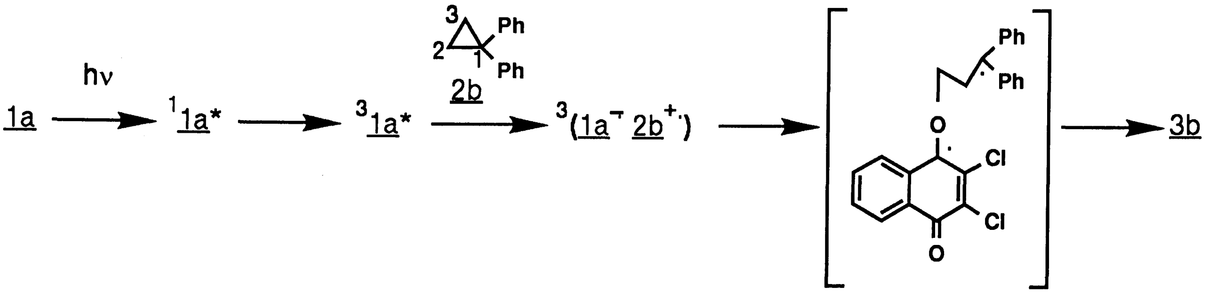


Fig. 2. Spiropyran adduct 5b.

obtained in the reaction in benzene. Furthermore, photoreactions of quinone 1a with 1,1-bis(4-fluorophenyl)cyclopropane 2a or 1,1-bis(4-methoxyphenyl)cyclopropane 2c gave no products in acetonitrile.

We propose the following electron-transfer mechanism.[11] This is analogous to the well-established mechanism for halo-1,4-naphthoquinone-electron donor photoreactions.[4-8] The reaction involves an ion radical pair resulting in the formation of spiro compound via 1,5-biradical intermediate.



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References

1) S.L.Mattes and S.Farid, "Organic Photochemistry," ed by A.Padwa, Marcel Dekker. Inc., New York (1983), Vol.6; P.S.Mariano and J.L.Stavinoha, "Synthetic Organic Photochemistry," ed by W.M.Horsepool, Plenum Press, New York (1984), p.145; G.J.Kavarnos and N.J.Turro, Chem.Rev., 86, 401 (1986), and references therein.

2) H.D.Roth, M.L.M.Schilling, and F.C.Schilling, J.Am.Chem.Soc., 107, 4152 (1985).

3) P.C.Wong and D.R.Arnold, Tetrahedron Lett., 23, 2101 (1979); V.R.Rao and S.S.Hixson, J.Am.Chem.Soc., 101, 6458 (1979); K.Mizuno, J.Ogawa, and Y.Otsuji, Chem.Lett., 1981, 741.

4) K.Maruyama, T.Otsuki, and S.Tai, J.Org.Chem., 50, 52 (1985).

5) K.Maruyama, T.Otsuki, and S.Tai, Chem.Lett., 1984, 371.

6) K.Maruyama, S.Tai, and H.Imahori, Bull.Chem.Soc.Jpn., 59, 1777 (1986).

7) K.Maruyama and H.Imahori, Bull.Chem.Soc.Jpn., 62, 816 (1989).

8) K.Maruyama and H.Imahori, J.Org.Chem., 54, 2692 (1989).

9) Compound 3b: colorless cubics, mp 143-145 ℃ from acetonitrile. MS; m/z 420, 422, 424 (M^+). Found: C, 71.27; H, 4.15; Cl, 16.85%. Calcd for $C_{25}H_{18}O_2Cl_2$: C, 71.27; H, 4.31; Cl, 16.83%. IR; (KBr) 1670 cm^{-1} (C=O). ^1H NMR ($CDCl_3$) δ 3.39 (1H, m), 3.78 (1H, m), 4.87 (2H, m), 6.76 (1H, d, J=7.9 Hz), 6.9-7.0 (6H, m), 7.1-7.3 (6H, m), 8.09 (1H, dd, J=7.0, 1.2 Hz).

10) Crystal data are as follows: monoclinic, space group $P2_1/a$, a=17.469(7), b=8.532(2), c=13.866(5) Å , β =109.20(4)° , V=1952(1) $Å^3$, Z=4, Dc=1.434 g cm^{-3}, R=0.041 (for 2891 independent reflections).

11) The free energy changes (Δ G) in the electron transfer from 1,1-diphenylcyclopropane to the excited triplet quinone were estimated to be negative. Spin density and steric bulkiness around the reaction center may play an important role for the photocyclization.

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