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Photo-induced Reaction of 2-Bromo-3-methoxy-1,4-naphthoquinone with 1,1-Dicyclopropylethylenes

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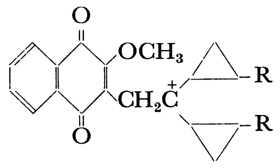
Synopsis. 2-(2,2-Dicyclopropylethenyl)-3-methoxy-1,4-naphthoquinone was isolated as a major product, accompanied by 2,2-dicyclopropyl-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione in the photochemical reaction of 2-bromo-3-methoxy-1,4-naphthoquinone with 1,1-dicyclopropylethylene. An ionic pathway to lead these products was suggested.

Photochemical reaction of 2-bromo-3-methoxy-1,4-naphthoquinone with a variety of 1,1-diarylethylenes was found to yield polycyclic aromatic *p*-quinones such as 5-arylbenz[*a*]anthracene-7,12-diones *via* 2-(2,2-diarylethenyl)-3-methoxy-1,4-naphthoquinone as their precursor (see an example in Scheme 1).[1]

To see a profound insight into the mechanistic aspects of the photochemical reaction —radical process or not— the photochemical reactivity of 1,1-dicyclopropylethylenes (**2**) with 2-bromo-3-methoxy-1,4-naphthoquinone (**1**) was examined here, because the radical generated at the α-position of cyclopropyl group was reported to cause the ring-opening reaction of cyclopropane, resulting in the isomerization to substituted 3-pentenyl radical in good yield (Scheme 2).[2]

When 2-bromo-3-methoxy-1,4-naphthoquinone (**1**) (1 mmol) and 1,1-dicyclopropylethylene (**2a**) (2 mmol) dissolved in benzene (25 ml) were irradiated by a high pressure Hg arc lamp (300 W), 2-(2,2-dicyclopropylethenyl)-3-methoxy-1,4-naphthoquinone (**3a**) (25%) and 2,2-dicyclopropyl-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (**4a**) (5%) were isolated from the reaction mixture, accompanied by 4-cyclopropyl-3-pentenyl bromide (**5a**) (30% as a mixture of *E*- and *Z*-isomers) (Scheme 3). Moreover, 1,1-bis(2-methylcyclopropyl)ethylene (**2b**) gave the similar mixture of products **3b** (25%) and **5b** (30%) in its reaction with **1**. **5** may be produced *via* the acid-catalyzed ring-opening reaction by hydrogen bromide liberated during the formation of **3** and/or **4**.

Although the present evidences are not conclusive because of the rather poor yield of the products isolated from the reaction mixture,[3] no products which are originated from the radical ring-opening reaction of 1,1-dicyclopropylethylenes can be identified so far. By analogy to the photochemical reaction of 1,1-diaryethylene with **1**, the charge transfer interaction between quinone **1** and 1,1-dicyclopropylethylene (**2**) may play a role in the initial stages of the reaction, leading to the formation of intermediate **6** *via* **7** by eliminating bromide ion.[4] **6** is a possible intermediate which could be stabilized finally as **3** or **4**. Thus, the ionic pathway including radical ions may be dominant at least in the photochemical reaction of 1,1-dicyclopropylethylenes (**2**) with 2-bromo-3-methoxy-1,4-naphthoquinone (**1**).



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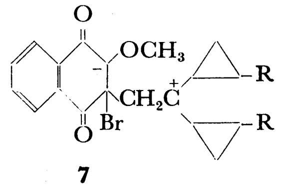

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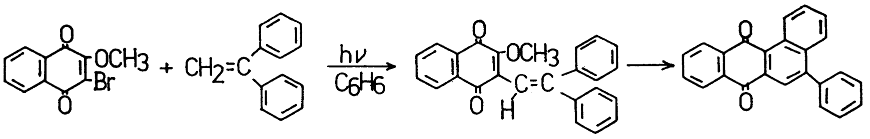
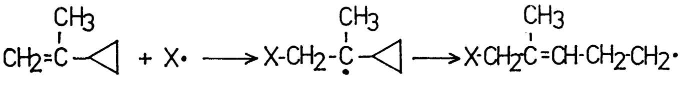
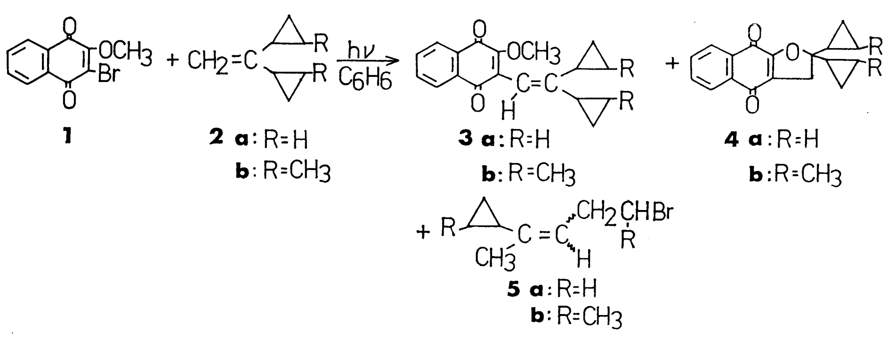


Scheme 1.



Scheme 2.



Scheme 3.

Experimental

Starting Materials. The synthesis of 2-bromo-3-methoxy-1,4-naphthoquinone (**1**) was described in the previous report.[1b] 1,1-Dicyclopropylethylene (**2a**) and 1,1-bis(2-methylcyclopropyl)ethylene (**2b**) were synthesized by the Wittig reaction[5] of the corresponding dicyclopropyl ketones.[6] 1,1-Dicyclopropylethylene (**2a**): colorless oil, bp 36—38 °C/22 mmHg. NMR (CCl_4): δ: 0.3—0.8 ppm (8H, m), 1.0—1.5 (2H, m), 4.41 (2H, s). IR (liq. film): 3100, 890 cm^{-1}. 1,1-Bis(2-methylcyclopropyl)ethylene (**2b**); colorless oil, bp 79—80 °C/62 mmHg. NMR (CCl_4): δ; 0.2—0.4 ppm (2H, m), 0.6—1.4 (4H, m), 1.10 (6H, d, J=5 Hz), 1.6—2.1 (2H, m), 4.36 (2H, s). IR (liq. film): 3100, 890 cm^{-1}.

Photochemical Reaction. A benzene solution (25 ml) of 2-bromo-3-methoxy-1,4-naphthoquinone (**1**) (1 mmol) and 1,1-dicylopropylethylene (**2**) (2 mmol) was irradiated by a high pressure Hg arc lamp (300 W). A half amount of quinone was consumed on irradiating the reaction mixture for 10 h at room temperature. After concentrated *in vacuo*, the reaction mixture was further purified by column chromatography on silica gel. The physical properties of the products were as follows. 2-(2,2-Dicyclopropylethenyl)-3-methoxy-1,4-naphthoquinone (**3a**): orange yellow needles, mp 84—86 °C. NMR ($CDCl_3$): δ; 0.6—0.8 ppm (8H, m), 1.2 (2H, m), 4.07 (3H, s), 5.97 (1H, s), 7.5—7.8 (2H, m), 7.9—8.2 (2H, m). IR (KBr): 3100, 1675 cm^{-1}. UV (C_2H_5OH): 424 nm (log ε: 3.15), 327 (3.34), 272 (4.11), 255 (sh) (4.06). MS: *m/e* (relative intensity); 294 (M^+, 36), 279 (M^+-15, 13), 266 (M^+-28, 57), 251 (M^+-43, 100). 2-[2,2-Bis(2-methylcyclopropyl)-ethenyl]-3-methoxy-1,4-naphthoquinone (**3b**): orange yellow needles, mp 98—100 °C. NMR ($CDCl_3$): δ; 0.4—1.4 ppm (14H, m), 3.92 (3H, s), 5.71 (1H, s), 7.3—7.6 (2H, m), 7.7—8.0 (2H, m). IR (KBr): 3100, 1670 cm^{-1}. UV (C_2H_5OH): 427 nm (log ε: 3.18), 326 (3.32), 274 (4.13), 256 (sh) (4.04). MS: *m/e* (relative intensity): 322 (M^+, 14), 280 (M^+-42, 100), 266 (M^+-56, 53). 2,2-Dicyclopropyl-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (**4a**): yellow needles, mp 134—135 °C. NMR ($CDCl_3$): δ; 0.5—0.7 ppm (8H, m), 1.3 (2H, m), 2.85 (2H, s), 7.5—7.8 (2H, m), 7.9—8.2 (2H, m). IR (KBr): 3100, 1680 cm^{-1}. UV (C_2H_5OH): 397 nm (log ε: 2.94), 334 (3.30), 287 (3.95), 254 (4.23), 249 (sh) (4.21). MS *m/e*: (relative intensity); 280 (M^+, 26), 252 (M^+-28, 100), 224 (M^+-56, 28). 4-Cyclopropyl-3-pentenyl bromide (**5a**) as a mixture of *E*- and *Z*-isomers (the relative ratio of the two isomers, 40/60 (A/B),[7] was estimated on the basis of their NMR signals): colorless oil. NMR (CCl_4): δ; 0.5 ppm (4H, m), 1.46 (3H, s), 1.5 (1H, m), 2.6 (2H, m), 3.40 (2H, t, J=1.7 Hz), 5.2 (1H, m) for an isomer A. 0.5 ppm (4H, m), 1.56 (3H, s), 1.5 (1H, m), 2.6 (2H, m), 3.34 (2H, t, J=1.7 Hz), 5.2 (1H, m) for another isomer B. IR (liq. film): 3100 cm^{-1}. MS: *m/e* (relative intensity); 190 (M^+, 27), 188 (M^+, 27), 109 (M^+-Br, 100). 5-Bromo-2-(2-methylcyclopropyl)-2-hexene (**5b**) as a mixture of *E*- and *Z*-isomers (the relative ratio of the two isomers, 40/60 (A/B),[7] was estimated on the basis of their NMR signals): colorless oil. NMR (CCl_4): δ; 0.2—1.8 ppm (7H, m), 1.46 (3H, s), 1.72 (3H, d, J=4 Hz), 2.4—2.8 (2H, m), 3.8—4.2 (1H, m), 4.9—5.3 (1H, m) for an isomer A. 0.2—1.8 ppm (7H, m), 1.56 (3H, s), 1.66 (3H, d, J=4 Hz), 2.4—2.8 (2H, m), 3.8—4.2 (1H, m), 4.9—5.3 (1H, m) for another isomer B. IR (liq. film): 3100 cm^{-1}.

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1) a) K. Maruyama and T. Otsuki, *Chem. Lett.*, **1975**, 87; b) K. Maruyama, T. Otsuki, and K. Mitsui, *Bull. Chem. Soc. Jpn.*, **49**, 3361 (1976); c) K. Maruyama, K. Mitsui, and T. Otsuki, *Chem. Lett.*, **1977**, 853; d) K. Maruyama, K. Mitsui, and K. Mitsui, *ibid.*, **1978**, 323; e) K. Maruyama, T. Otsuki, and K. Mitsui, *J. Org. Chem.* in press.; f) K. Maruyama, T. Otsuki, K. Mitsui, and M. Tojo, *J. Heterocyclic Chem.*, in press.

2) E. S. Heyser and T. D. Taliaferro, *J. Org. Chem.*, **28**, 3442 (1963).

3) The poor yields of the products could be partly due to the trivial reactions such as the demethylation of the starting quinone caused by hydrogen bromide liberated during the course of the reaction.

4) When 1,1-diarylethylene such as 1-(*p*-chlorophenyl)-1-phenylethylene, 1-phenyl-1-(2-thienyl)ethylene or 1-phenyl-1-(2-*N*-methylpyrrolyl)ethylene was submitted to the reaction (*cf.* Scheme 1), one of two aryl groups donating highly its π-electrons cyclizes preponderantly to give polycyclic aromatic *p*-quinone (see Refs. (1b), (1c), and (1d)). By inspection of molecular model it is clear that the isomeric distribution of the final products can be determined by the configuration of the intermediate, 2-(2,2-diarylethenyl)-3-methoxy-1,4-naphthoquinone. Therefore, these results indicate that the charge-transfer interactions between quinone and the aryl group of reacting ethylene in the initial stages are playing a role for determining the isomeric distribution of final products.

In addition, an important contribution of the similar charge-transfer interactions has been confirmed in the photosubstitution reaction of halogenated 1,4-naphthoquinones. (see K. Maruyama and T. Otsuki, *Chem. Lett.*, **1977**, 851, *Bull. Chem. Soc. Jpn.*, **50**, 3249 (1977)).

5) T. Teraji, I. Moritani, E. Tsuda, and S. Nishida, *J. Chem. Soc., C*, **1971**, 3252.

6) *Org. Synth.*, Coll. Vol. IV, 278 (1963).

7) The assignment of an isomeric mixture of A and B to that of *E*- and *Z*-isomers was not completed yet.