

## Photoreaction of *p*-Benzoquinone with Unsymmetrical Keten Dimers

By KENJI OGINO, TAKAHARU MATSUMOTO, TAKESHI KAWAI, and SEIZI KOZUKA

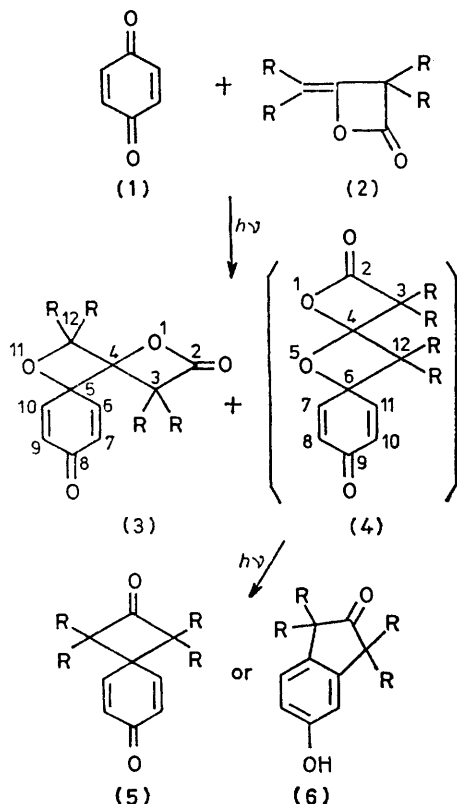
(*Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Osaka 558, Japan*)

**Summary** Photocycloaddition of *p*-benzoquinone to 4-methyleneoxetan-2-one derivatives affords non-regio-specific adducts: the 1,11-dioxadispiro[3.0.5.2]dodeca-6,9-diene-2,8-diones (**3**) and the (undetected) 1,5-dioxadispiro[3.1.5.1]dodeca-7,10-diene-2,9-diones (**4**) which decompose to give spiro[3.5]nona-5,8-diene-2,7-dione or 5-hydroxyindan-2-one.

PHOTOREACTIONS of *p*-benzoquinone with unsymmetrical keten dimers were examined in a Pyrex vessel by external irradiation with a high pressure mercury lamp. After irradiation, the photo-products were isolated by preparative t.l.c. or column chromatography.

Irradiation of *p*-benzoquinone with 4-methyleneoxetan-2-one (**2a**) in CH<sub>2</sub>Cl<sub>2</sub> afforded two different cyclohexadienone

derivatives: the spiro-compound (**5a**, m.p. 77–78 °C, 11% yield, based on quinone) and the dispiro-compound (**3a**, oil, 12%). The structure of (**5a**), reported as an oil,<sup>1</sup> is supported by its <sup>13</sup>C n.m.r. spectrum;  $\delta$  (CDCl<sub>3</sub>) 200.6 (s, C-2), 185.0 (s, C-7), 151.1 (d, C-5,9), 128.7 (d, C-6,8), 57.2 (t, C-1,3), and 33.5 (s, C-4) p.p.m. The product (**3a**) has a cyclohexadienone unit [ $\nu$  1660 and 1625 cm<sup>-1</sup>;  $\delta$  6.25 (d,  $J$  10.5 Hz, 2H) and 7.10 (d,  $J$  10.5, 2H)], and highly strained lactone [ $\nu$  1845 cm<sup>-1</sup>;  $\delta$  3.23<sub>s</sub> (s, 2H)] and oxetan functions [ $\delta$  5.03 (s, 2H)].



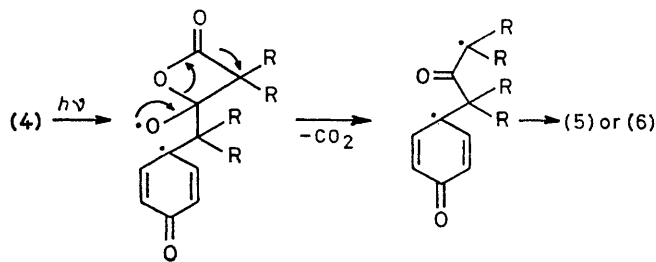
SCHEME 1. a; R = H  
b; R = Me  
c; R = Ph

Similar treatment of (1) with compound (2b) afforded two isolable compounds: (**3b**); m.p. 142–144 °C, 21% yield,  $\nu$  1840, 1670, and 1630 cm<sup>-1</sup>,  $\delta$  1.23, 1.40, 1.56, and 1.73

(each s, Me), 6.18 (d,  $J$  10.5 Hz, 2H), and 7.05 (d,  $J$  10.5 Hz 2H) with fine splitting due to the asymmetric C-4, and (**6b**),<sup>2</sup> m.p. 242–244 °C, 21%. Assignment of structure (**3b**) is also supported by <sup>13</sup>C n.m.r. data:  $\delta$  (CDCl<sub>3</sub>) 184.2 (s, C-8), 172.2 (s, C-2), 144.6 (d) and 144.4 (d, C-6,10), 130.3 (d) and 129.7 (d, C-7,9), 93.1 (s, C-5), 88.1 (s, C-12), 79.6 (s, C-4), 56.8 (s, C-3), 26.9 (q, Me), 25.9 (q, Me), and 20.4 (q, 2Me) p.p.m. The linear dispiro structure (**4b**) could be excluded because of the absence of a signal corresponding to the 1,3-dioxo carbon (C-4).

The reaction of (1) with (2c) proceeded very slowly and the starting materials were recovered even after prolonged irradiation. The only isolable compounds, probably derived from the adducts (**3c**) and (**4c**) by photo-decomposition, were benzophenone and quinone diphenylmethide and these were obtained in poor yields.

Wilson and Wunderly have reported that the photochemical reactions of *p*-benzoquinone in the presence of sulphur dioxide and vinyl acetate give non-regiospecific adducts.<sup>3</sup> Thus, the first stage of the photo-induced cycloadditions of (1) to the ketenimines (2) should be considered to afford two different dispiro-oxetans (3) and (4), although (4) could not be detected. Photo-induced cleavage of oxygen-carbon bonds of spiro-oxetans or spiro-2-imino-oxetans, which are derived from cycloadditions of *p*-quinones to allenes<sup>3</sup> or ketenimines,<sup>4</sup> are well known. The most plausible mechanism for the formation of the spirobutanone (**5a**) and the indanone (**6b**) may be formulated as in Scheme 2.



SCHEME 2

We thank Dr. Takamasa Kinoshita of Osaka City University for helpful discussions on assignment of the <sup>13</sup>C n.m.r. spectra of the photo-products.

(Received, 12th March 1979; Com. 245.)

<sup>1</sup> D. J. Beames and L. N. Mander, *Austral. J. Chem.*, 1974, **27**, 1257.

<sup>2</sup> N. Ishibe and I. Taniguchi, *Tetrahedron*, 1971, **27**, 4883; N. Ishibe, K. Hashimoto, and Y. Yamaguchi, *J.C.S. Perkin*, 1975, 318.

<sup>3</sup> R. M. Wilson and S. W. Wunderly, *J. Amer. Chem. Soc.*, 1974, **96**, 7350.

<sup>4</sup> K. Ogino, S. Yamashina, T. Matsumoto, and S. Kozuka, *J.C.S. Perkin I*, in the press.