

**Photoreactions of Dispiro{naphthalene-1,2'-naphtho[2,1-b]pyran-3',1''-naphthalene}-2(1*H*),2''(1''*H*)-dione. A Novel Case of  $\beta$ -C-C Cleavage in an Enone**

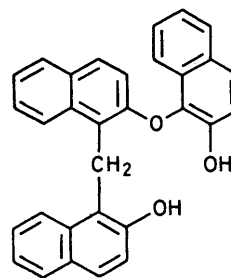
By TIRUMALAI R. KASTURI,\* GONIBELLA J. RAJU, and VAIDHYANATHAN RAMAMURTHY  
(Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012, India)

*Summary* Irradiation of the title compound (**2**) gave a wide range of products, identified as compounds (**3**)—(**7**) on the basis of spectroscopic data and chemical evidence, which result from  $\beta$ -cleavages and intramolecular cycloaddition.

An X-ray crystallographic investigation<sup>1</sup> of the title compound (**2**) revealed that the 2',3'-carbon-carbon bond is unusually long (1.632 Å) and that the two olefinic  $\pi$ -bonds of the enones are fairly well oriented for intramolecular cycloaddition. Consistent with the former observation, hydrogenation of compound (**2**) readily gave<sup>1</sup> the dihydroxy-compound (**1**) *via* cleavage of the C(2')-C(3') bond. It was therefore thought that compound (**2**) could be a useful model for observing the less known photochemical  $\beta$ -C-C cleavage in enones as well as the intramolecular cycloaddition to form a novel cage compound. This was con-

firmed;  $\beta$ -C-C cleavage products were the predominant compounds obtained on irradiation of compound (**2**), along with a cage compound and a  $\beta$ -C-O cleavage product.

The lowest excited-state energy ( $S_1$ ) of compound (**2**) is

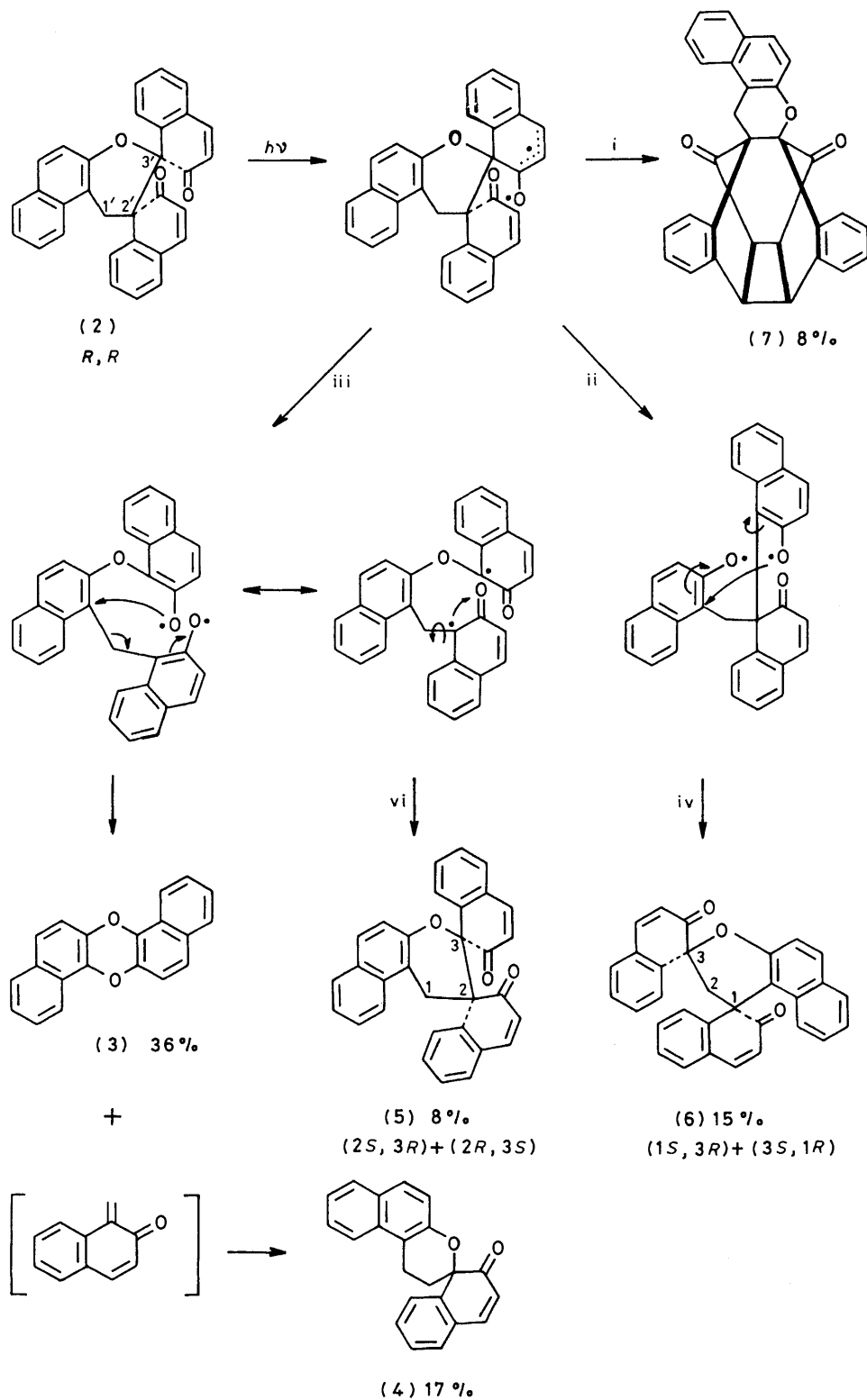


(1)

estimated to be  $332 \text{ kJ mol}^{-1}$ , based on absorption and emission spectra. Compound (2) shows a highly structured emission in the region  $360\text{--}520 \text{ nm}$  on excitation to  $S_1$  or

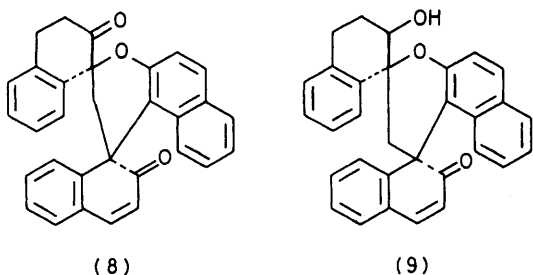
$S_2$  states. No emission attributable to an intramolecular exciplex is seen.

Irradiation of compound (2) for about 6 h in benzene



SCHEME i, Cycloaddition; ii,  $\beta\text{-C-O}$  cleavage; iii,  $\beta\text{-C-C}$  cleavage; iv, rotation and recoupling.

(0.01M), using a 450 W medium-pressure mercury lamp with a Pyrex filter, gave a mixture of products. The five products, separated by column chromatography and t.l.c. (silica gel; chloroform-hexane as eluant, 4:1) followed by crystallisation, were tentatively identified as (3)—(7), based on their spectral data.† The identities of compounds (3) and (4) were confirmed by comparison with authentic samples.<sup>1,2</sup> In the case of compound (5), a diastereoisomer of (2), the structure was confirmed by its hydrogenation to the aforementioned dihydroxy-compound (1). The configuration of the racemic (5) is 2'R, 3'S and 2'S, 3'R, as the X-ray study indicates the configuration of (2) (racemic) to be 2'R, 3'R and 2'S, 3'S. The behaviour of compound (6), which on hydrogenation gave only the compounds (8) and



(9),‡ was quite different from that of (2), clearly showing that the two spiro-carbon atoms in (6) are not directly linked.§

Compounds (3)—(7) are believed to arise from the lowest

excited state of compound (2) via  $\beta$ -C-C cleavage [compounds (3)—(5)],  $\beta$ -C-O cleavage [compound (6)], and intramolecular cycloaddition [compound (7)] as illustrated in the Scheme [given for only one enantiomer of (2), namely RR]. Salient features are: (i) compound (2) in the excited state undergoes at least three primary photochemical processes, namely  $\beta$ -C-C cleavage,  $\beta$ -C-O cleavage, and intramolecular cycloaddition; (ii) of the three processes, the  $\beta$ -C-C cleavage is the predominant pathway, and (iii) although the naphthalenone system is known to undergo easy photocycloaddition (both inter-<sup>3</sup> as well as intramolecular<sup>4</sup>) in compound (2), the enone cycloaddition is the least preferred pathway.

Although photochemical  $\beta$ -cleavage in carbonyl compounds has been reported ready cleavage of  $\beta$ -C-C and  $\beta$ -C-O bonds in enones has not been reported. It is interesting to note that the  $\beta$ -C-O bond in compound (2), which does not exhibit any unusual characteristics in the X-ray crystal structure analysis, also undergoes cleavage. This may be due to the stability of the resultant diradical.

As a search for selectivity, crystals of compound (2) were exposed to u.v. radiation (pyrex filter). Unfortunately, this also resulted in the formation of compounds (3)—(7) in almost the same yields as in solution. This is understandable, as even the most probable intramolecular cycloaddition requires sufficient distortion of various atoms to bring the two reactive  $\pi$ -bonds parallel to each other.

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† Satisfactory elemental analyses were obtained for all new compounds. Physical constants and spectroscopic data of compounds (3)—(9) given below. <sup>1</sup>H n.m.r. were taken in CDCl<sub>3</sub> with tetramethylsilane as internal standard on a Bruker 270 MHz Fourier-transform instrument. Compound (3), white needles (CHCl<sub>3</sub>), m.p. 216 °C; compound (4), yellow solid (benzene-hexane), m.p. 139—141 °C; compound (5), yellow needles (CHCl<sub>3</sub>-hexane), m.p. 171 °C; *m/e* 440;  $\nu_{\max}$  (Nujol) 1680 and 1660 cm<sup>-1</sup>;  $\lambda_{\max}$  (CHCl<sub>3</sub>) 245 ( $\epsilon$  23,600), 268 (8000), 280 (7555), 290 (6330), 316 (6000), 334 (4660), and 360 (1100) nm; <sup>1</sup>H n.m.r. 'AB quartet' centred at  $\delta$  3.61 ( $\Delta\nu_{AB}$  35.7,  $J_{AB}$  17.3 Hz), 5.57 (d,  $J$  10.0 Hz, 1 H), 5.64 (d,  $J$  9.7 Hz, 1 H), 6.69 (d,  $J$  10.0 Hz, 1 H), 6.77 (d,  $J$  9.7 Hz, 1 H), and 7.02—7.90 (m, 14 H) [cf. physical data of compound (2) in ref. 1]; compound (6), pale yellow needles (CHCl<sub>3</sub>-hexane), m.p. 266 °C; *m/e* 440;  $\nu_{\max}$  (Nujol) 1700 and 1680 cm<sup>-1</sup>;  $\lambda_{\max}$  (CHCl<sub>3</sub>) 245 ( $\epsilon$  15,000), 265 (7000), 276 (7370), 289 (7870), 313 (10,300), and 360 (560) nm; <sup>1</sup>H n.m.r. 'AB quartet' centred at  $\delta$  2.74 ( $\Delta\nu_{AB}$  81.0,  $J_{AB}$  14.3 Hz), 5.47 (d,  $J$  10.3 Hz, 1 H), 6.17 (d,  $J$  9.7 Hz, 1 H), 6.39 (d,  $J$  7.6 Hz, 1 H), 6.56 (d,  $J$  7.6 Hz, 1 H), 6.98 (d,  $J$  9.7 Hz, 1 H), and 7.04—7.92 (m, 13 H); compound (7), white needles (CHCl<sub>3</sub>-hexane), m.p. > 300 °C; *m/e* 440;  $\nu_{\max}$  (CHCl<sub>3</sub>) 1742 and 1725 cm<sup>-1</sup>;  $\lambda_{\max}$  (CHCl<sub>3</sub>) 244 ( $\epsilon$  11,640), 267 (3210), 278 (2280), 318 (1210), and 333 (1500) nm; <sup>1</sup>H n.m.r. 'AB quartet' centred at  $\delta$  3.61 ( $\Delta\nu_{AB}$  13.2,  $J_{AB}$  18.1 Hz), 4.05—4.18 (m, 4 H), 6.78 (d,  $J$  7.6 Hz, 1 H), and 6.98—8.10 (m, 13 H); compound (8), pale yellow needles (CHCl<sub>3</sub>-hexane), m.p. 252 °C;  $\nu_{\max}$  (Nujol) 1730 and 1675 cm<sup>-1</sup>;  $\lambda_{\max}$  (CHCl<sub>3</sub>) 246 ( $\epsilon$  17,000), 266 (7930), 276 (9260), 288 (9400), 314 (9800), and 330 (5000) nm; <sup>1</sup>H n.m.r. 'AB quartet' centred at  $\delta$  2.80 ( $\Delta\nu_{AB}$  20.8,  $J_{AB}$  13.5 Hz), 1.62—1.75 (m, 1 H), 2.17—2.30 (m, 1 H), 2.87—3.15 (m, 2 H), 6.26 (d,  $J$  9.5 Hz, 1 H), 6.40 (d,  $J$  8.1 Hz, 1 H), 6.62 (d,  $J$  7.6, 1 H), and 7.03—7.92 (m, 13 H); compound (9), white solid (benzene-hexane), m.p. 140—142 °C;  $\nu_{\max}$  (CHCl<sub>3</sub>) 3575 and 1670 cm<sup>-1</sup>;  $\lambda_{\max}$  (CHCl<sub>3</sub>) 243 ( $\epsilon$  17,500), 268 (3800), 278 (4630), 290 (5000), 305 (4680), and 330 (2540) nm; <sup>1</sup>H n.m.r. 1.76—1.85 (m, 2 H, 1 H exchangeable), 2.13—2.23 (m, 1 H), 2.69—3.03 (m, 4 H), 4.12—4.18 (m, 1 H), 6.09 (d,  $J$  10.0 Hz, 1 H), 6.47 (d,  $J$  8.6 Hz, 1 H), 6.80 (d,  $J$  8.1 Hz, 1 H), and 7.04—7.87 (m, 13 H).

‡ The alternative structures for compounds (8) and (9) in which the other enone system is reduced are ruled out on the grounds of hindrance (Drieding models).

§ A structure with the two spiro-carbons linked by oxygen is ruled out on mechanistic grounds as well as from <sup>13</sup>C spectral data. The isomeric structure of compound (6) with *cis*-carbonyl groups is ruled out as it will involve severe interactions especially between carbonyl groups (Drieding models).

<sup>1</sup> T. R. Kasturi, R. Rajasekar, G. J. Raju, R. Sivaramakrishnan, N. Ramasubbu, and K. Venkatesan, *J. Chem. Soc., Chem. Commun.*, 1980, 1087.

<sup>2</sup> An authentic sample of (3) was prepared by the reported procedure of J. Van Alphon and G. Drost, *Recl. Trav. Chim.*, 1948, **67**, 623, with slight modification.

<sup>3</sup> T. Mukai, T. Oine, and H. Sukawa, *Chem. Commun.*, 1970, 271.

<sup>4</sup> Y. Nakamura, J. Zsindoly, and H. Schmid, *Heterocycles*, 1976, **5**, 427.