

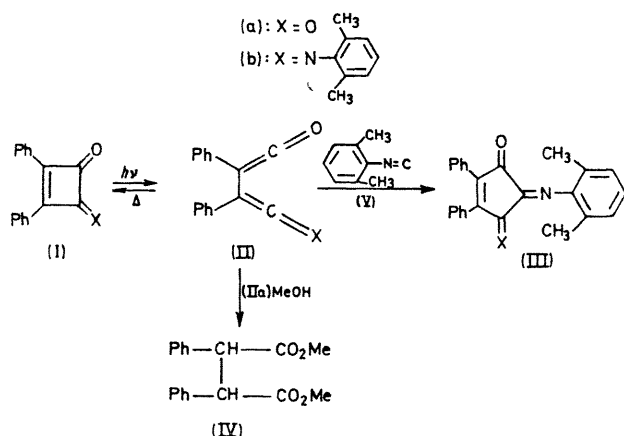
Direct Observation of Conjugated Bis-ketene and Ketene-Ketenimine Intermediates in the Photolysis of Diphenylcyclobutenedione Derivatives

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Summary The photolysis of diphenylcyclobutenedione (Ia) and its imine derivative (Ib) in the presence of an isonitrile gives ring-expanded products (IIIa) and (IIIb) *via* conjugated bis-ketene (IIa) and ketene-ketenimine (IIb) intermediates, which were confirmed by the photolysis of (I) in methanol to give succinate (IV) and directly by i.r. spectroscopy during low temperature photolysis.

BIS-KETENE has previously only been considered as an intermediate in some photochemical reactions of cyclobutenedione derivatives.^{1,2} We have observed that photolysis of diphenylcyclobutenedione (Ia) and also its imine derivative (Ib)³ in the presence of isonitrile (V) or ethanol gave photoproducts *via* conjugated bis-ketene (IIa) and ketene-ketenimine (IIb) intermediates.



SCHEME

In addition to the photochemical reactions, direct observation of the intermediates (IIa) and (IIb) by i.r. spectroscopy during low temperature photolysis is presented.

Irradiation of a benzene solution (under nitrogen) of (Ia) (1.3 mmol) and 2,6-dimethylphenylisonitrile (V) (1.3 mmol) with a 500 W high-pressure mercury lamp for 1.5 h gave the imino-dione (IIIa) m.p. 142–143° (n-hexane-benzene)

in 86% yield. The structure of (IIIa) was established by elemental analysis, molecular weight determination, and its spectra: i.r. ν C=O and ν C=N 1780, 1770sh, 1745, and 1700 cm^{-1} , u.v. (CH_3CN) 230sh ($\log \epsilon$ 4.39), 280 (4.00), 332 (4.23), and 535 nm (2.84), and n.m.r. (CCl_4) 2.65 (m, 10H), 3.10 (s, 3H), and 8.00 τ (s, 6H). The i.r. and u.v. spectra were similar to those of triketones, *e.g.*, diphenylcyclopentenetrione.⁴ The structure of (IIIa) was further confirmed by HCl-hydrolysis and diazotization with toluene-*p*-sulphonylhydrazine which gave 2,2-dihydroxy-4,5-diphenylcyclopentene-1,3-dione and 2-diazo-4,5-diphenylcyclopentene-1,3-dione respectively.

The photolysis of (Ib) in the presence of isonitrile (V) was carried out under similar conditions as used previously. 4,5-Bis-(2,6-dimethylphenylimino)-2,3-diphenylcyclopenten-1-one (IIIb) in 80% yield was obtained, the structure of which was established by comparison with an authentic

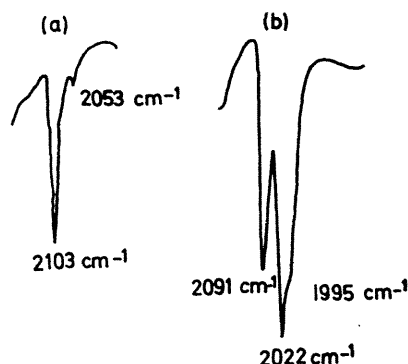


FIGURE. I.r. spectra (tetrahydrofuran solution) of (a) (IIa), -50° and (b) (IIb), -46° .

sample.⁵ Ring-expanded photoproducts, (IIIa) and (IIIb), could be formed by 1,4-cycloaddition of isonitrile (V) to bis-ketene (IIa) or ketene-ketenimine (IIb) intermediates.

When a solution of (Ia) (1.3 mmol) in dry methanol was irradiated for 40 min (under N_2), dimethyl diphenylsuccinate (IV) [*meso*-form (67%) and *DL*-form (17%)] were obtained. The structure of these succinates was confirmed by direct comparison with authentic samples.⁶ These

results indicate that (IIa) and (IIb) could be intermediates in the photochemical reactions of (I).†

A tetrahydrofuran solution of (I) (under nitrogen) was irradiated using a 500 W high-pressure mercury lamp at -78° [(Ia) 2 h, (Ib) 10 h]. The addition of isonitrile (V) or methanol to this solution, corresponding to (IIa) or (IIb), at -78° in the dark gave (III) or (IV) in good yield. Their i.r. spectra were determined using a Nihonbunko DS-403G i.r. spectrometer equipped with a low temperature solution cell [(IIa) -50° , (IIb) -46°] (Figure).

The band at 2103 cm^{-1} for (IIa) is readily assigned to the $\nu\text{C}=\text{O}$ frequency of the ketene.⁷ It follows that the 2091

and 2022 cm^{-1} bands of (IIb) are attributable to ketene $\text{C}=\text{O}$ and ketenimine $\text{C}=\text{N}$. Although (IIa) and (IIb) were stable in the dark for several days at -78° , after raising the temperature of (IIa) slowly (1 h) above 0° , the characteristic peak at 2103 cm^{-1} disappeared. The relation between conformation of (IIa) and (IIb) and their i.r. spectra is not yet well defined.

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† Irradiation of a benzene solution of (Ia) under O_2 gave diphenylmaleic anhydride and phenanthrene-9,10-dicarboxylic acid anhydride; *N*-(2,6-dimethylphenyl)iminodiphenylisomaleimide was obtained in the photolysis of (Ib) in good yield. These photochemical reactions could also proceed *via* intermediates (IIa) and (IIb).

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² For 3-phenylcyclobutene-1,2-dione and pyracloquinone: F. M. Beringer and R. E. K. Winter, *Tetrahedron Letters*, 1968, 6183.

³ N. Obata and T. Takizawa, *Tetrahedron Letters*, 1970, 2231.

⁴ Unpublished results.

⁵ N. Obata and T. Takizawa, *Tetrahedron Letters*, 1969, 3403.

⁶ H. Wren and C. J. Still, *J. Chem. Soc.*, 1915, 107, 444.

⁷ O. L. Chapman and J. D. Lassild, *J. Amer. Chem. Soc.* 1968, 90, 2449.