Primary Photochemistry of Cyclobutenediones and Benzocyclobutenediones

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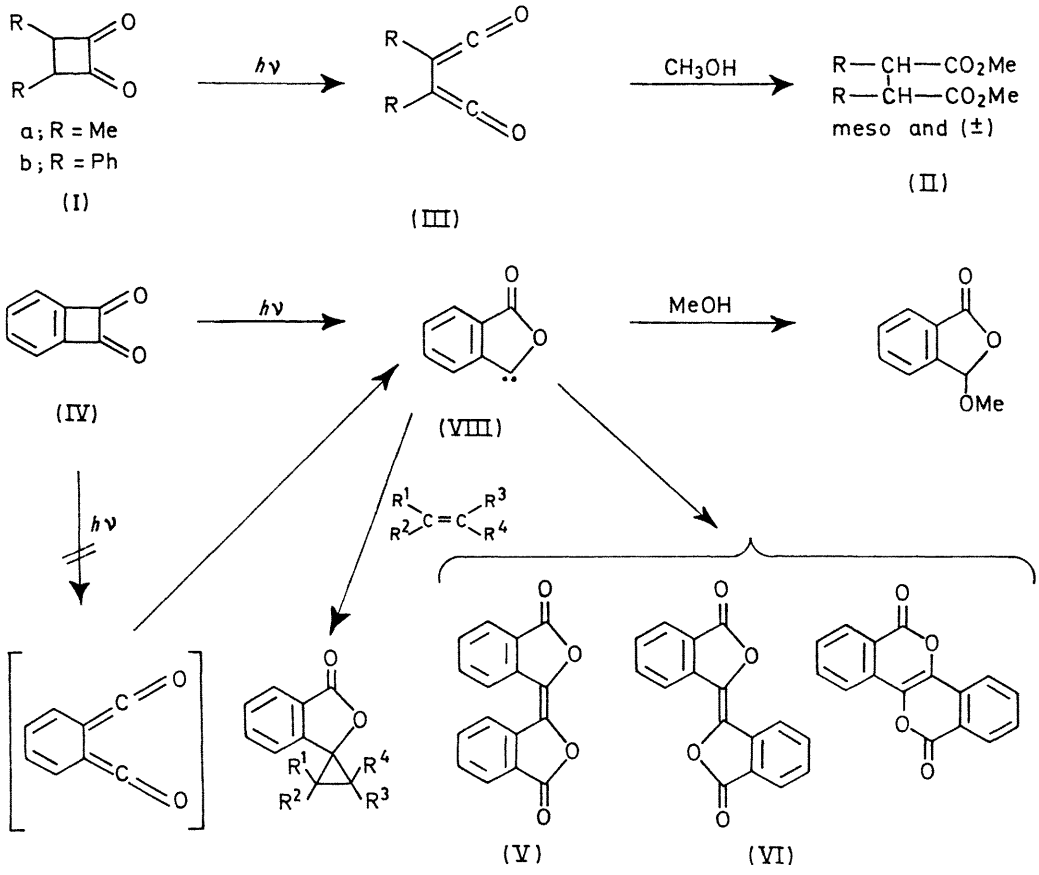
Summary Studies at low temperature show that cyclobutenediones, but not benzocyclobutenediones, give bis-ketens as primary products

WE report the direct observation of bis-ketens and note a significant difference between the photochemistry of cyclobutenediones and benzocyclobutenediones

Bis-ketens have been considered as possible intermediates in the photochemistry of cyclobutenediones and benzocyclobutenediones [1,2] In the latter case, trapping experiments and dimer formation also implicate a carbene [2] We have examined the photochemistry of 3,4-dimethylcyclobutenedione, 3,4-diphenylcyclobutenedione, and benzocyclobutenedione at −196° Irradiation of 3,4-dimethylcyclobutenedione at −196° in methanol gives rise to three new i r absorption bands in the carbonyl region, two strong bands at 2096 and 2117 cm^{-1} and one weak band at 2138 cm^{-1} [3] On warming to −130°, the weak band at 2138 cm^{-1} disappears with no change in other regions of the spectrum This band is tentatively ascribed to carbon monoxide[8] Above −80°, the bands at 2096 and 2117 cm^{-1} disappear at the same rate with concurrent appearance of an ester carbonyl absorption The products formed are the *meso*- and (±)-esters (IIa) The 2096 and 2117 cm^{-1} bands can thus be assigned to the bis-keten (IIIa) Irradiation of (Ib) as a neat film at −196° gives rise to intense new bands at 2100 and 2112 cm^{-1} which can be assigned to (IIIb) [4] Irradiation of (Ib) in methanol at room temperature gives *meso*- and (±)-dimethyl 2,3-diphenylsuccinate (IIb) Irradiation of benzocyclobutenedione (IV) as a thin film at −196° gave no absorption which could be attributed to a keten but did give rise to new bands characteristic of dimers (V) and (VI) It is thus clear that either the bis-keten (VII) is not formed or that it has a half-life too short at −196° to permit observation The high molar extinction coefficient (*ca* 1.5×10^3) of keten stretching vibrations and the short time (*ca* 10 s) between irradiation and scanning make it unlikely that the bis-keten is an inter-



mediate. It is far more likely that the benzocyclobutenedione (IV) goes directly to the carbene (VIII) which is the source of the dimers.

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[1] F. B. Mallory and J. D. Roberts, *J. Amer. Chem. Soc.*, 1961, **83**, 393.
[2] H. A. Staab and J. Ipaktschi, *Chem. Ber.*, 1968, **101**, 1457 and references cited therein.
[3] L. L. Barber, Ph.D. Thesis, Iowa State University, Ames, Iowa, 1969, p. 37.
[4] N. Obata and T. Takizawa, *Chem. Comm.*, 1971, 587.