Synthesis of Cyclobutenedione

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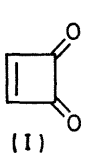
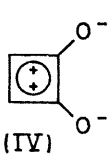
Summary Cyclobutenedione has been synthesized by hydrolysis of the photocycloadduct of acetylene and dichlorovinylene carbonate.

DESPITE continued interest in cyclobutenediones[1] (cyclobutadienequinones), the parent member (I) of the group has, until now, remained unknown.



(I)

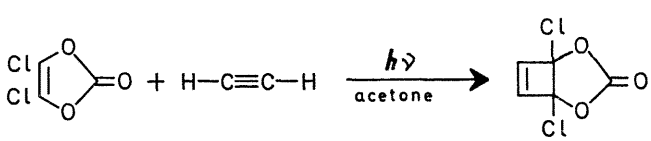


(IV)

We report the synthesis of (I) by a method which may prove to be a useful alternative to the established procedures[1] for the preparation of other members of this class of compounds.

Irradiation† of an acetone solution of dichlorovinylene carbonate[2] (II) in the presence of an excess of acetylene gave the cycloadduct[3] (III) as a rather unstable liquid, b.p. 41—42° at 0·05 Torr, in 10—15% yield; τ (CCl_4) 3·15 (sharp s); λ_{max} (neat) 5·40 μm (C=O).

Hydrolysis of adduct (III) at 60° in 60% acetone/H_2O gives cyclobutenedione (I) as a light yellow solid, m.p. 40—41° (ether–pentane); τ (CCl_4) 0·27. Such a low-field resonance is not completely unexpected for ring hydrogens in cyclobutenediones and may indicate, in part, the contribution of canonical forms such as (IV) to the resonance hybrid.



(II) (III)

The i.r., u.v., and mass spectra were also completely consistent[1] with the structure formulated: λ_{max} (KBr) 5·58 μm (C=O); λ_{max} (ether) 214 (ϵ 3690) and 340 nm (ϵ 21); parent *m/e* 82·0052 (calc. 82·0054).

Compound (I) appears to be stable when stored as a solid at 6° but in the presence of methanol at room temperature it is completely destroyed within 18 h. Thus compound (I) shows stability comparable to that of diphenylcyclobutenedione[1] but is considerably more reactive than the dimethyl derivative.[1]

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† Hanovia 450 W medium-pressure mercury lamp in quartz.

[1] M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, 1967, Ch. 4.
[2] H. D. Scharf, W. Droste, and R. Liebig, *Angew. Chem. Internat. Edn.*, 1968, **7**, 215.
[3] An analogous photocycloaddition of acetylene and vinylene carbonate has very recently been reported. R. H. Grubbs, *J. Amer. Chem. Soc.*, 1970, **92**, 6693.