1,3-Bis(diphenylmethylene)cyclobutane-2,4-dione

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ALTHOUGH ketens have been known for nearly seventy years, the only reported examples of compounds containing a longer cumulative unsaturated system terminating in a carbonyl group are carbon suboxide (Ia), triphenylphosphoranylideneketen (Ib),[1] and pentacarbon dioxide,[2] the last being of doubtful authenticity.† Unsuccessful attempts to prepare (Ic) by pyrolysis of the mixed anhydride (IIa) have been described.[3] This Communication reports the formation of the title compound (III) during the catalysed decomposition of the mixed anhydride (IIb), apparently by dimerisation of the transient intermediate diphenylpropadienone (Id).

On heating a solution of (IIb) in ethyl acetate with a small amount of potassium carbonate, a gas was evolved and the mixture turned dark red. Work-up gave a compound, $C_{30}H_{20}O_2$, as crimson plates, m.p. 295°; its n.m.r. spectrum consisted solely of a sharp singlet at τ 2·54, the i.r. spectrum showed absorption at 1692 cm.$^{-1}$ (KBr disc), and the visible and u.v. spectrum showed absorption at 462, 437 sh, 347, and 311 mμ (log ϵ 4·73, 4·55, 3·91, and 4·01). Prolonged acidic hydrolysis gave the keto-acid (IVa), m.p. 182° (decomp), τ ($CDCl_3$) 3·95 (1H, s), 2·4—3·6 (20H, m), 0·30 br (1H, s) removed by treatment with D_2O), ν_{max} (KBr disc) 1698 and 1620 cm.$^{-1}$. Pyrolysis of (IVa) decarboxylated the acid giving the ketone (IVb), m.p. 151°, τ ($CDCl_3$) 3·85 (2H, s), 2·4—3·5 (20H, m), ν_{max} (KBr disc) 1625 cm.$^{-1}$. Ozonolysis of the red compound gave a low yield of benzophenone, identified as the dinitrophenylhydrazone. The red compound dissolved in sodium methoxide and methanol or alcoholic potassium hydroxide to give a colourless solution; acidification quantitatively regenerated the starting material. On the basis of these observations, the structure (III) is suggested for the red compound. The possible alternative (V) is ruled out by the absence of allenic absorption in the i.r. spectrum, and the behaviour with sodium methoxide and methanol. It is thought that the colourless solution formed from (III) and sodium methoxide arises by reversible formation of (VI), a vinylogous carboxylate anion.

The conversion of (IIb) into the postulated monomer (Id) is similar to the well known formation of ketens on pyrolysis of mixed anhydrides of substituted malonic acids.[4] Attempts to trap the intermediate (Id) have so far been unsuccessful.

A compound, assigned the structure (III), was reported[5] to be obtained by controlled ozonolysis of the photo-dimer of tetraphenylbutatriene, but the evidence adduced for the assigned structure was far from conclusive. The reported properties of this substance differ widely from those of the compound obtained from the mixed anhydride (IIb).

Satisfactory analytical data have been obtained for all new compounds reported.

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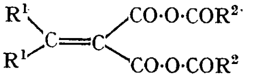
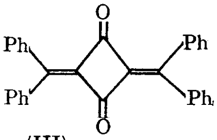
$X{=}C{=}C{=}O$

(Ia) $X{=}CO$
(Ib) $X{=}Ph_3P$
(Ic) $X{=}Me_2C$
(Id) $X{=}Ph_2C$

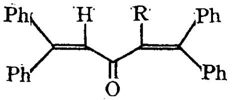


$R^1_2C{=}C(CO{\cdot}O{\cdot}COR^2)_2$

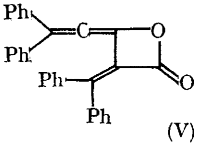
(IIa) $R^1{=}Me$, $R^2{=}Ph_2CH$
(IIb) $R^1{=}Ph$, $R^2{=}Me$



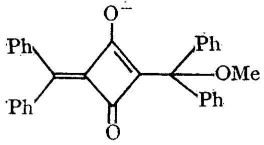
(III)



(IVa) $R{=}CO_2H$
(IVb) $R{=}H$



(V)



(VI)

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† Since the submission of this communication, a paper by G. H. Birnum and C. N. Matthews, *J. Amer. Chem. Soc.*, 1968, **90**, 3842, reports the formation of heterocumulenes analogous to (Id) by the reaction of carbonyl compounds with (Ib).

[1] C. N. Matthews and G. H. Birnum, *Tetrahedron Letters*, 1966, 5707.
[2] A. Klemenc and A. Wagner, *Ber.*, 1937, **70**, 1880.
[3] H. Staudinger, E. Anthes and H. Schneider, *Ber.*, 1913, **46**, 3539; H. Staudinger, and H. Schneider, *Helv. Chim. Acta*, 1923, **6**, 316.
[4] W. E. Hanford and J. C. Sauer, *Org. Reactions*, 1946, **3**, 108.
[5] R. O. Uhler, H. Schechter and G. V. D. Tiers, *J. Amer. Chem. Soc.*, 1962, **84**, 3397.