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The Synthesis of 2-(Diphenylcyclopropenylidene)cyclobutane-1,3-dione (1,2-Diphenylbutatriafulvalene-3,5-dione)[1)]

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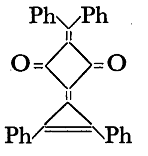
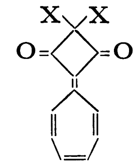
Recently, 4-diphenylmethylene-1,2-diphenylbutatriafulvalene-3,5-dione (**1**)[2)] and heptabutafulvalenedione derivatives (*e.g.*, **2**)[3)] have been synthesized, and their spectral data have been discussed.



(**1**)



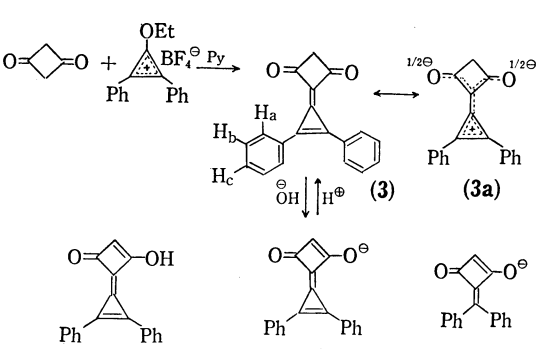
(**2**) X=Cl, Me

In the course of synthetic studies of fulvalenes, we have prepared 2-(diphenylcyclopropenylidene)cyclobutane-1,3-dione (1,2-diphenylbutatriafulvalene-3,5-dione); the results will be reported herein.

The reaction of cyclobutane-1,3-dione and 1,2-diphenyl-3-ethoxycyclopropenylium tetrafluoroborate in methylene chloride in the presence of a minute amount of pyridine afforded pale yellow needles (**3**) (mp 225—230°C (decomp.)) in a 14% yield; the structure of 2-(diphenylcyclopropenylidene)cyclobutane-1,3-dione was inferred from the following spectroscopic data as well as from the results of elemental analyses.

Compound **3** exhibits the mass-spectral parent ion at *m/e* 272 (relative intensity 69), and fragment ions at 257 (14), 230 (100), 216 (18), 215 (19), 202 (88), 178 (23), and 165 (27); IR (KBr) 1840 (m) (methylenecyclopropene), 1660 (s) (C=O), 1600 (w), and 1510 (s) cm^{-1}; UV λ_{max}^{EtOH} 225^{sh} (log ε 4.23), 266 (4.28), and 325 nm (4.65); NMR (CDCl$_3$) δ 3.5 (2H, s, methylene protons), 7.6—7.8 (6H, m, Hb and Hc), and 8.35—8.55 (4H, m, Ha).

The strong deshielding of Ha by the diamagnetic anisotropy of the carbonyl group is similarly observed in compound **1**[2)] and diphenylpentatriafulvalenedione derivatives.[4)]



(**3**) (**3a**)

(**4**) (**5**) (**6**)

From the facts that the C=O stretching frequency appears at 1660 cm^{-1}, and that methylene protons in NMR appear at δ 3.5 as a singlet, compound **3** must be stabilized by a contribution of a dipolar structure **3a**; it seems that an enol structure **4** does not contribute to the structure.

Compound **3** is not soluble in aqueous sodium hydrogen carbonate, but it is soluble in NaOH-EtOH. The ultraviolet absorption curve in a dilute acidic medium does not change from that in ethanol. However, in an alkaline solution, the curve shows absorption maxima at 265 (log ε 4.12), 328 (4.39), and 342 nm (4.37); this curve is reversibly backed to the original curve by the addition of an acid. From these data, an enolate

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[1)] Presented at the 24th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1971.

[2)] F. Toda, *Chem. Lett.*, **1972**, 621.

[3)] N. Morita, T. Asao, and Y. Kitahara, *ibid.*, **1972**, 927.

[4)] I. Agranat, R. M. J. Loewenstein, and E. D. Bergmann, *J. Amer. Chem. Soc.*, **90**, 3278 (1968).

anion **5** may be assigned for compound **3** in an alkaline solution. A similar anion **6** has been assigned for 2-diphenylmethylenecyclobutane-1,3-dione.[2)]

Experimental

2-(Diphenylcyclopropenylidene)cyclobutane-1,3-dione (**3**). To a stirred solution of cyclobutane-1,3-dione (42 mg) and diphenylethoxycyclopropenylium tetrafluoroborate (320 mg) in anhydrous methylene chloride (6 ml), 3 drops of pyridine were added at room temperature. After 30 min, the color of the solution turned red. Water was added, and the solution was extracted with methylene chloride and dried over anhydrous magnesium sulfate, the subsequent removal of the solvent left an oil, which was chromatographed on silica gel to give pale yellow crystals (225 mg). An ether-insoluble part of the crystals was recrystallized from a mixture of methanol and methylene chloride to give 18 mg (14%) of pale yellow needles (**3**) (mp 225—230°C (decomp.)). From the ether-soluble part diphenylcyclopropenone was obtained.

Found: C, 83.42; H, 4.28%. Calcd for $C_{19}H_{12}O_2$: C, 83.80; H, 4.44%.