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THE PHOTODIMERISATION OF BENZOCYCLOBUTENEDIONE

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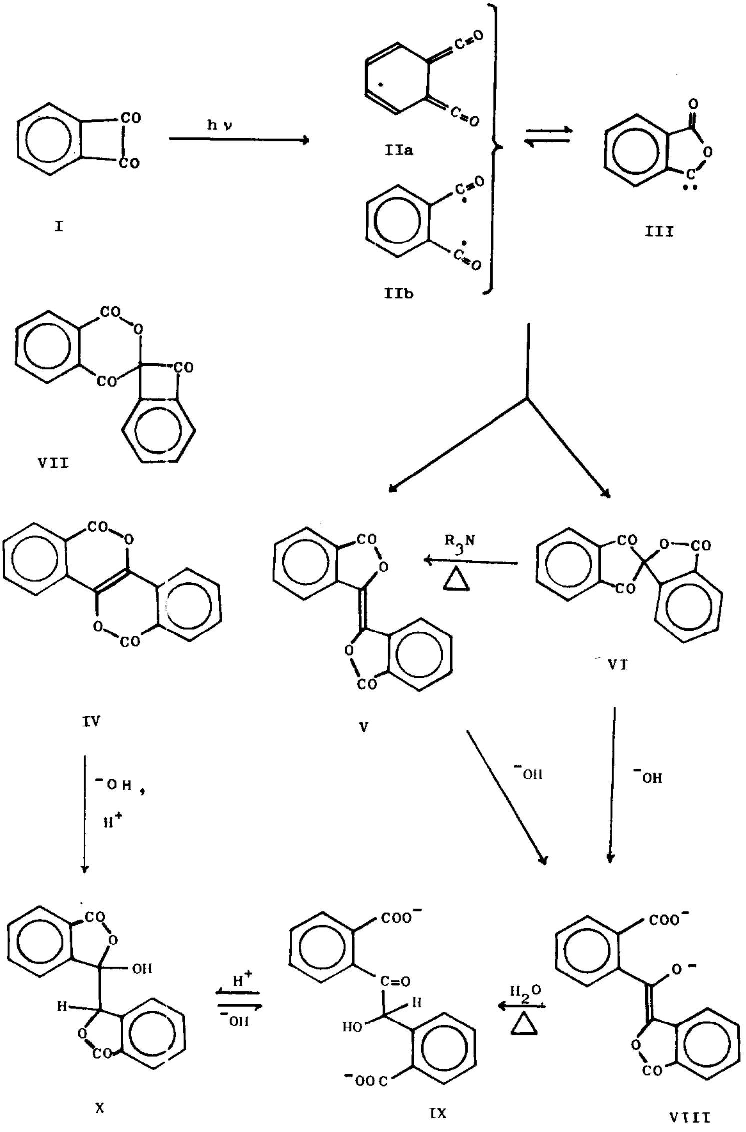
Benzocyclobutenedione (I) was first synthesised by Cava, Napier and Pohl (1) by base-catalysed elimination of nitrite from the dinitrate of benzocyclobutene-1,2-diol. In this synthesis the dione was always accompanied by a small amount of a dimeric compound, m.p. 334-6°, which was assigned structure (IV) on the grounds of its infrared absorption at 1745 cm^{-1} and its hydrolysis with hot alkali to diphthalyl-lactonic acid (X), also obtained on alkaline hydrolysis of biphthalyl (V) (2).

We have taken advantage of the convenient preparation of benzocyclobutenedione by pyrolysis of ninhydrin (3) to examine the photochemistry of this dione. From the nature of the products which we have so far been able to identify we conclude that in cyclohexane the primary process is fission of the CO----CO bond of (I) to produce species (II) and (III) which subsequently combine to form as major products biphthalyl (V) and a new dimer of (I), the spirolactone (VI). We have not detected the presence of dimer (IV).


CO
CO
h ν
I
C=O
C=O
IIa
C=O
C=O
IIb
O
O
C
III
CO
O
CO
CO
VII
CO
O
O
CO
IV
CO
O
O
CO
V
R_3N
Δ
CO
O—CO
CO
VI
$^-$OH ,
H^+
$^-$OH
$^-$OH
CO
O
OH
H
O
CO
X
H^+
$^-$OH
COO$^-$
C=O
H
HO
$^-$OOC
IX
H_2O
Δ
COO$^-$
O$^-$
O
CO
VIII

In a typical experiment benzocyclobutenedione (500 mg.) in degassed cyclohexane (250 ml.) was exposed to bright Canberra sunlight through Pyrex for 10 hr. The almost colourless solution was evaporated and the residue was chromatographed on silica gel. Elution with benzene and recrystallization of the eluate from xylene gave biphthalyl (5.5%), m.p. and mixed m.p. with an authentic sample 352-4°, further identified by comparison of infrared spectra and R_f on thin layer chromatograms (benzene/silica). The column was further eluted with chloroform and then with chloroform containing 10% ethanol to give a fraction containing the sparingly soluble spirolactone (VI) which was recrystallized from hot dimethylformamide to give colourless prisms (38%), m.p. 295-7° (Found: C, 73.1; H, 3.3%. $C_{16}H_8O_4$ requires C, 72.7; H, 3.1%).

The structure (VI) is assigned to this new dimer on the following grounds. Hydrolysis with 1N sodium hydroxide at 100° and acidification gave diphthalyllactonic acid (X, 75%), showing that the carbon skeleton is related to that of the benzoin 2,2'-dicarboxylate anion (IX), while oxidation with hydrogen peroxide/trifluoracetic acid gave phthalic acid. The infrared spectrum (mull) showed two very strong carbonyl bands at 1778 cm^{-1} (broad) and 1715 cm^{-1} (sharp). In a MeCN solution spectrum these appeared at 1788 and 1725 cm^{-1}, but the band shapes were unchanged. A spiro structure was strongly suggested by the ultraviolet spectrum ($\lambda_{max}(CH_2Cl_2)$ 232*, 252 (inflex.), 277, 285.5, 304, and 357 mμ; log ϵ_{max} 4.79*, 4.10,

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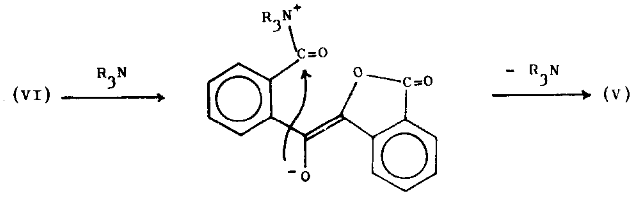
* Uncertain values near the CH_2Cl_2 cut-off. The substance was not sufficiently soluble in ethanol for spectroscopy.

3.36, 3.66, 3.06, and 3.18) which showed the prominent features of the spectra of both phthalide (λ_{max}(EtOH) 227, 273, and 280; log ϵ_{max} 3.99, 3.24, and 3.22) (4) and ninhydrin (λ_{max} (EtOH) 228.5, 248, 278, 287, 302.5 and 353 mμ; log ϵ_{max} 4.70, 4.06, 2.95, 2.90, 2.54, and 1.89). This chemical and spectral evidence is fairly consistent with either of the spiro structures (VI) and (VII), since in hot alkali both should undergo very ready cleavage of their strained and non-enolisable β-diketonic systems to give, ultimately, diphthalyllactonic acid.

A decision between structures (VI) and (VII) was made by further consideration of the reactions of the dimer with bases. In cold aqueous ethanolic NaOH (0.2 - 1.0 N) both biphthalyl (V) and the new dimer dissolved to give a bright yellow solution (λ_{max} 324-7 mμ, $\epsilon \sim$ 8500 and 411 mμ, $\epsilon \sim$ 8500; ϵ values were identical for both substrates but varied with the procedure for preparation of the solution). The yellow solution, which we believe contains the enolate (VIII) derivable from both (V) and (VI), was unstable and on heating or on long standing the spectrum changed to that of the colourless anion (IX). Acidification of either the yellow solution or of a solution decolourized by heating produced the phthalide-like spectrum of diphthalyllactonic acid (X). From this behaviour with alkali it could be predicted that the spiro compound (VI) on vigorous treatment with a tertiary amine would isomerise to the more highly conjugated biphthalyl, whereas the alternative structure (VII) should give the dimer (IV) of Cava, Napier and Pohl. In fact the new dimer when heated for 7 hr. in refluxing anhydrous diisopropylethylamine under nitrogen gave an intractable orange gum, starting material (24%), and biphthalyl (26%), from which we conclude that the structure (VI) is correct. This reasoning depends on the assumption of minimum structural change in the rearrangement, which we formulate as involving the recyclization of an intermediate zwitterion (XI).



XI

It appears that the broad band at 1788 cm^{-1} in the infrared spectrum of (VI) in MeCN must represent the carbonyl frequency of the γ-lactone together with the higher of two bands (ca. 1780 and 1725 cm^{-1}) due to the indanedione system. This requires a rather larger separation of frequencies than is found in ninhydrin (ν_{max}(MeCN) 1760 and 1730 cm^{-1}).

Purified biphthalyl and spiro-lactone (VI) account for only 44% of the total product of irradiation of (I), and thin layer chromatography showed the presence of many minor components. However, it seems likely that most products are derived from initial carbon-to-carbon dimerisation of species (II) and (III), since photolysis of the dione (I) followed by alkaline hydrolysis of the total product gave crystalline diphthalyllactonic acid in 70% yield. A synthesis of the dione (I) by generation of species (IIa) has been attempted by Cava (1) without success, while species (III) has been proposed as one possible intermediate in the reductive dimerisation of phthalic anhydride to biphthalyl in boiling triethyl phosphite (2).

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