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PHOTOCHEMICAL AND THERMAL TRANSFORMATIONS OF PHTHALOYL DIXANTHATE

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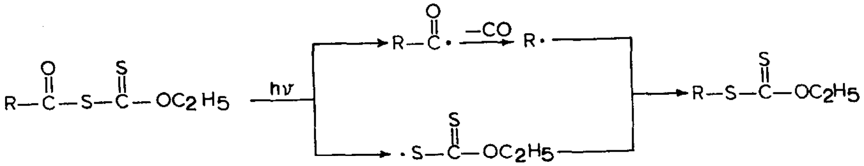
Acyl xanthates are reported to undergo CO-S bond fission on photolysis, giving rise to acyl and xanthate radicals and these acyl radicals are decarbonylated at appropriate temperatures to give alkyl radicals, which combine with xanthate radicals to furnish S-alkyl xanthates (Chart I).[2,3] The primary alkanecarbonyl radicals, in general, decarbonylate slowly and hence the recombination of the carbonyl fraction has also been observed in such cases.

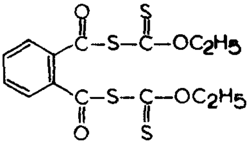
CHART I



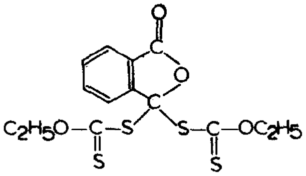
The object of the present investigation was to study the photolysis of a symmetrical aroyl dixanthate like di-O-ethyl S,S-phthaloyl dixanthate (I) and to see whether this procedure could be used in preparing benzocyclobutenedione (III).[4]

Acyl and aroyl xanthates are conveniently prepared by the treatment of potassium O-ethyl xanthate with the corresponding acid chlorides,[2] but our attempts at preparing I by this procedure were unsuccessful. The only product that could be isolated (86%) from the treatment of potassium O-ethyl xanthate with a solution of phthaloyl dichloride in acetone at -50°, was an unsymmetrical dixanthate II, m.p. 143-4°, (Found: C, 44.99; H, 3.64. $C_{14}H_{14}O_4S_4$ requires: C, 44.9; H, 3.74%). UV spectrum (ethanol) λ_{max}: 209 (ϵ, 48,500) 233 (27,200), 288 (27,200) and 365 $m\mu$ (1,400). IR spectrum (KBr) ν_{max}: 1790 (C = O) and 1032 cm^{-1} (C = S). The high carbonyl frequency is in agreement with structure II for the dixanthate.[5]

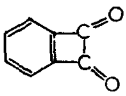
Further evidence for structure II was derived from the NMR spectrum of the dixanthate which showed a characteristic ABCD pattern for the aromatic protons with the most intense absorption at 2.2 τ down field from tetramethylsilane.[6]



I



II

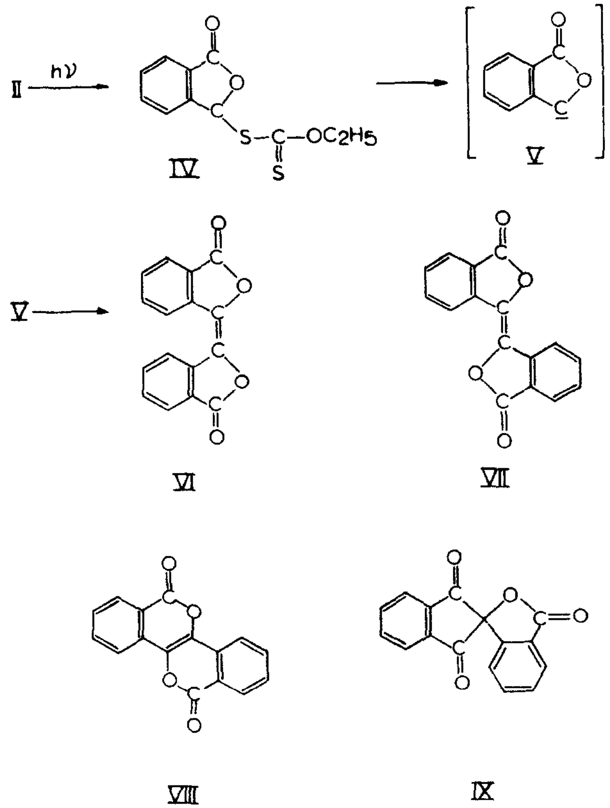


III

When the reaction of potassium O-ethyl xanthate with symmetrical phthaloyl dichloride was carried out in acetone around 0°, the major product obtained was phthalic thioanhydride, m.p. 110° (mixture m.p.). IR spectrum (KBr) ν_{max}: 1805, 1745 and 1712 cm^{-1}.

The photolysis of II gave a mixture of cis-biphthalyl (VI) (9%), m.p. 290-5° and trans-biphthalyl (VII) (16%), m.p. 352-4°. The formation of products like VI and VII suggests

CHART II



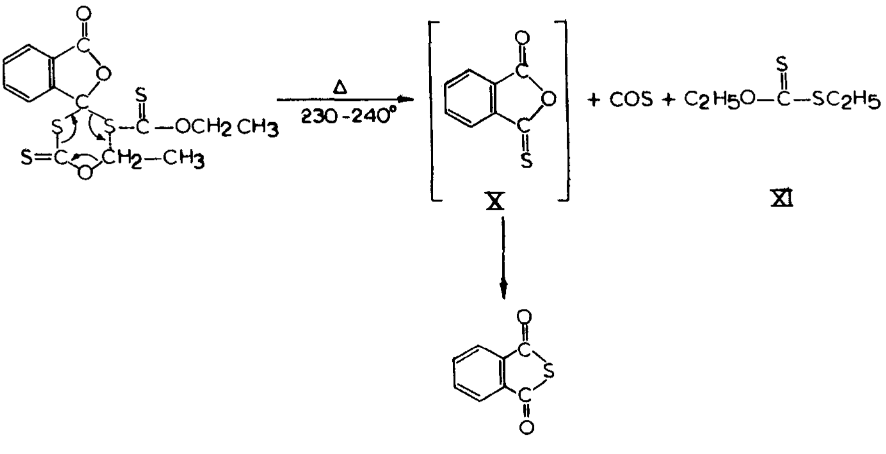
that the photolysis of II may be proceeding through a C-S bond fission giving rise to the radical intermediate IV which then undergoes a second C-S bond fission giving rise to the carbene intermediate V. A similar type of C-S bond fission is reported in the photolysis of 9,9-dixanthogenyl xanthene.[7] Dimerization of V leads to both VI and VII (Chart II). It has not been possible, however, to isolate dimeric products like VIII and IX which have been reported to be formed from the photolysis of III and involving intermediates such as V.[8,9]

The structure of VI was further confirmed by its isomerization to VII, on heating to 230° under vacuum.[9]

Thermal decomposition of acyl xanthates are reported to give rise to a mixture of products.[2,10,11] We have examined the decomposition of II by heating it around 230-40° under a stream of nitrogen for 20 minutes. The products formed in this reaction were carbonyl sulphide (55%), as identified through its piperidinium salt, m.p. 112° (mixture m.p.),[12] trans biphthalyl (VII) (2.7%), thiophthalic anhydride (60%) and O-ethyl S-ethyl xanthate (XI) (35%).

The formation of VII from the thermal decomposition of II suggests that a small portion of II may be undergoing decomposition to the intermediate V, which finally dimerizes to VII. The exact nature of the pyrolytic decomposition is still unclear. A probable mechanism which accounts for the formation of products such as thiophthalic anhydride, carbonyl sulphide and O-ethyl S-ethyl xanthate is one which involves a cyclic concerted process, as indicated in Chart III. The formation of thiophthalic anhydride may be due to the rearrangement of the intermediate thionphthalic anhydride.[13]

CHART III



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