Photochemical Fragmentation of 7-Oxonorbornen-2,3-dicarboxylic Anhydride and 1,2-Dihydrophthalic Anhydride

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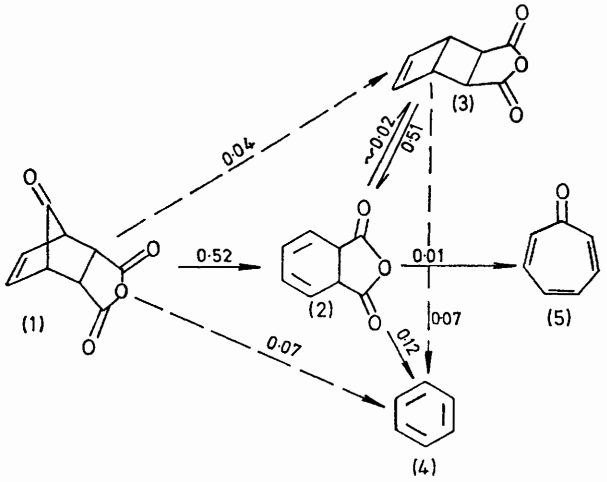
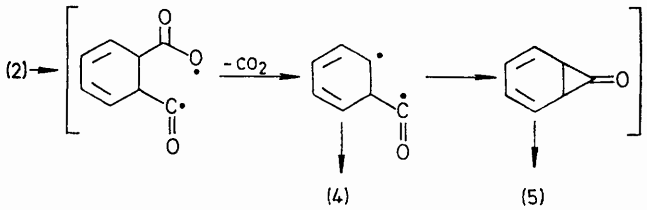
Summary The title compounds (**1**) and (**2**) undergo irradiation-induced decarbonylation and CO + CO_2 fragmentation respectively and consecutively to give benzene, the anhydride (**3**) and tropone (**5**).

We have already reported the photochemical behaviour of various substituted 7-oxonorbornen-2,3-dicarboxylic anhydrides and of the corresponding 1,2-dihydrophthalic anhydrides.[1–3] Earlier, van Tamelen and Pappas had reported that 1,2-dihydrophthalic anhydride (**2**) undergoes photochemical electrocyclic closure to bicyclo[2,2,0]hex-5-ene-2,3-dicarboxylic anhydride (**3**) without mentioning any accompanying fragmentation.[4] Moreover, Warrener and Bremner subsequently contended that the extent of benzene formation is less than 0·1%.[3a] We have therefore undertaken a more careful and mechanistic study of the problem.



Scheme 1. The numbers on the arrows represent quantum yields at 257 nm in MeCN.

Irradiation of the anhydride (**1**) in MeCN with low pressure Hg-lamps (Rayonet) afforded a mixture containing two main products: the bicyclic anhydride (**3**) (14%) and benzene (**4**) (36%). In addition, small amounts of tropone (**5**) were found in the non-carboxylic fraction of the reaction mixture whereas the carboxylic fraction also contained 1,2-dihydrophthalic anhydride (**2**) (10%).



Scheme 2

Direct irradiation (as above) of 1,2-dihydrophthalic anhydride (**2**) gave a nearly photostationary mixture of (**3**) (22%), (**4**) (52%), and (**5**) (3%) and starting material (**2**), as determined by isolation and by n.m.r. analysis.

In a detailed study, each of the three anhydrides (**1**)—(**3**) was irradiated monochromatically at three wavelengths (<300 nm). The quantum yields at 257 nm and low conversion are shown in Scheme 1. The processes (**1**) → (**3**), (**3**) → (**4**) and (**1**) → (**4**) do not take place, or take place to a negligible extent, *i.e.*, the broken arrows are describing artifacts of the actual reactions represented by the full arrows.

The quantum yield for decarbonylation of (**1**) is high for a cyclic ketone in solution[5] and this may be attributed both to the strain in the system and to the $\beta\gamma$-unsaturation.[6] The quantum yield for anhydride fragmentation, although moderate in its absolute value, is high in comparison with saturated anhydrides in solution, for which no photofragmentation was reported and we assert that it is, again, the $\beta\gamma$-unsaturation that promotes allylic bond cleavage, leading to CO + CO_2 extrusion.[7]

Attempted photosensitization with acetone and acetophenone failed and, in the case of (**1**), only a dimer of as yet unknown stereochemistry was isolated. Also, diene triplet quenchers did not affect the decarbonylation nor the anhydride fragmentation. This indicates the possible intermediacy of singlet excited states in these processes.

The detection of tropone in the reaction mixture leads us to formulate the photofragmentation of (**2**) (Scheme 2) involving an initial decarboxylation of (**2**) with the remaining diradical undergoing decarbonylation with benzene formation or, to a lesser extent, recombination and valence tautomerization possibly *via* norcaradienone to tropone. An analogous situation prevails in the recent reported photolyses of substituted cyclobut-3-ene-1,2-dicarboxylic anhydrides, which result mainly in the formation of corresponding substituted cyclopentadienones or their dimers.[8]

(*Received*, 18*th October* 1973; *Com.* 1435.)

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[2] (a) H. Prinzbach, R. Kitzing, E. Druckrey, and H. Achenbach, *Tetrahedron Letters*, 1966, 4625; (b) R. Kitzing and H. Prinzbach, *Helv. Chim. Acta*, 1970, **53**, 158.

[3] R. N. Warrener and J. B. Bremner (a) *Tetrahedron Letters*, 1966, 5691; (b) *Angew. Chem. Internat. Edn*, 1966, **5**, 311.

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[5] (a) J. G. Calvert and J. N. Pitts, jun., 'Photochemistry,' Wiley, New York, 1966, ch. 5; (b) N. C. Yang in 'Reactivity of the Photoexcited Organic Molecule,' Interscience, New York, 1967, p. 145.

[6] See discussion in 1(b) and references cited therein.

[7] A. Zweig, *Pure Appl. Chem.*, 1973, **33**, 389, is to our knowledge the only report dealing with certain quantitative aspects of anhydride photochemistry *in solution*. This author does not mention any electronic or steric effect that may promote photofragmentation although *all* his anhydrides are, in fact, $\beta\gamma$-unsaturated ones.

[8] G. Maier and F. Bosslet, *Tetrahedron Letters*, 1972, 1025 and earlier papers in the series.