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EVIDENCE FOR OZONIDE REARRANGEMENT IN THE PHOTOOXIDATION OF PHENYL-SUBSTITUTED ISOBENZOFURANS[1]

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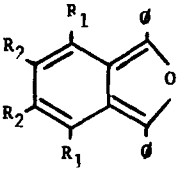
It is well known that 1,3-diphenylisobenzofuran (1a) undergoes photooxidation via the singlet oxygen addition product (2a) to give o-dibenzoylbenzene (3a)[3] Diketone formation has also been reported from photooxidation of 1,3,4,7-tetraphenylisobenzofuran (1b)[4] and hexaphenylisobenzofuran (1c)[5]



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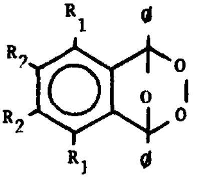

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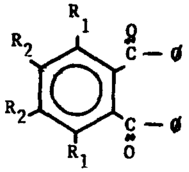

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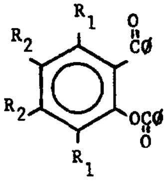
a $R_1 = R_2 = H$, b $R_1 = \phi$, $R_2 = H$; c $R_1 = R_2 = \phi$

We have now found that keto-ester (4a) is also formed as a minor product of photolysis of 1a using either a mercury lamp or sunlight as the ultraviolet source Typically, exposure of a solution of 1g. of 1a in 25 ml of benzene in Pyrex glassware fot 2 days in moderate to strong sunlight results in a 31% yield of insoluble dimer (5)[3] and 15% yield of keto-ester (4a) (based on amount of 1a not converted to 5), the remainder being diketone (3a)[6].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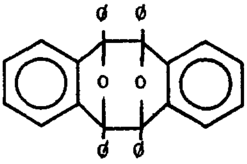
a $R_1 = R_2 = H$
b $R_1 = Ø$; $R_2 = H$
c $R_1 = R_2 = Ø$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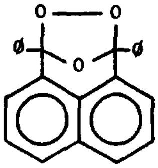
In view of the fact that intermediate 2a is, in effect, the ozonide of 1,2-diphenyl-3,4-benzocyclobutadiene, it is reasonable to assume that keto-ester 4a is formed by a Wieland-type rearrangement analogous to that reported recently for diphenylacenaphthalene ozonide (6)[8] and thioozonide (7).[9]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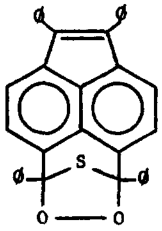
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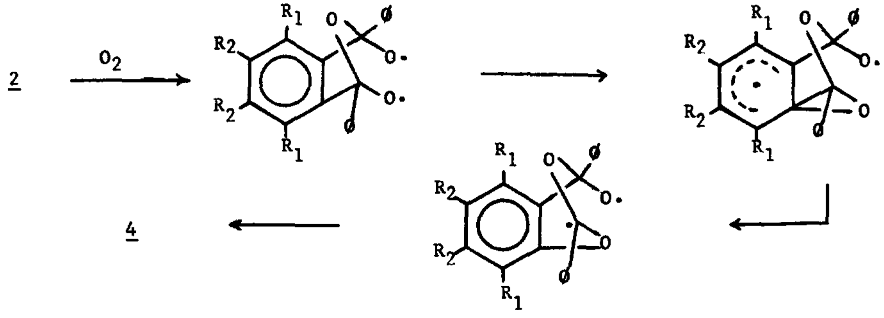
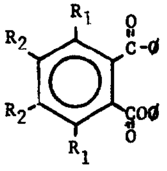
Accordingly a mechanism of rearrangement may be formulated as follows:



In conformity with this mechanism, tetraphenyl-[4] and hexaphenylisobenzofuran[10] (1b and 1c, respectively) should give more keto-ester upon photooxidation since greater resonance stabilization of the intermediate allylic radical would be allowed. This was, in fact, realized Both 1b and 1c gave yields of approximately 30% of keto-ester (4b and 4c, respectively) under the same conditions as determined by isolation of benzoic acid from the reaction mixture hydrolyzate.[11,12]

Interestingly, gas chromatographic analysis of the hydrolyzate of the products from photolysis of 1a, 1b, and 1c with the mercury lamp and of 1b with sunlight showed the presence of small amounts of phenol as well as benzoic acid. This indicates that keto-ester 8 may also be formed as a thermal rearrangement product together with diketone (3), in view of the fact that Hoffman and Schlessinger prepared the corresponding diketone and keto-ester by heating thioozonide (7) in the dark [9]



a $R_1 = R_2 = H$

b $R_1 = Ø; R_2 = H$

c $R_1 = R_2 = Ø$

8

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References and Footnotes

1. Presented in part at the 4th Northeast Regional Meeting of the American Chemical Society, Hartford, Connecticut, U. S. A., October 1972
2. Address correspondence to M P Stevens at the University of Hartford
3. For a discussion of this reaction, see K. Gollnick and G. O. Schenck in "1,4-Cycloaddition Reactions," (J. Hamer, ed.), Academic Press, New York, 1967, pp. 319-320.
4. E. D Bergmann, Sh Blumberg, P. Bracha, and Sh Epstein, Tetrahedron, **20**, 195 (1964)
5. F. Razmara, M. S. Thesis, American University of Beirut, 1970.
6. Diketone (3a) is isolated by filtering off dimer (5), evaporating off the solvent, and adding ether to the residue. Diketone (3a) is insoluble and can be removed by filtration Evaporation of the ether results in an oil having an infrared spectrum identical to that of an authentic sample of keto-ester (4a) (prepared from o-hydroxybenzophenone and benzoyl chloride) apart from a small OH peak. (Possibly some photo-Fries rearrangement) Hydrolysis of the oil gives benzoic acid and o-hydroxybenzophenone.
7. H Wieland, Ber., **44**, 2553 (1911)
8. P R. Story, W H. Morrison, III, and J. M. Butler, J. Am. Chem Soc., **91**, 2398 (1969).

9 J. M. Hoffman, Jr , and R. H. Schlessinger, *Tetrahedron Lett* , 797 (1970)

10. W. Ried and K. H Bonnighausen, *Ann* , **639**, 61 (1960)

11. Infrared spectra of the residue from photooxidation after evaporation of solvent display ester and aromatic ketone carbonyl absorptions at 1740 and 1670 cm^{-1}, respectively No dimer was observed.

12. Yields are approximate since very small samples were used, and no attempt was made to optimize formation of keto-ester. Yields did, however, vary according to photolysis conditions and concentration of both isobenzofuran derivative and oxygen