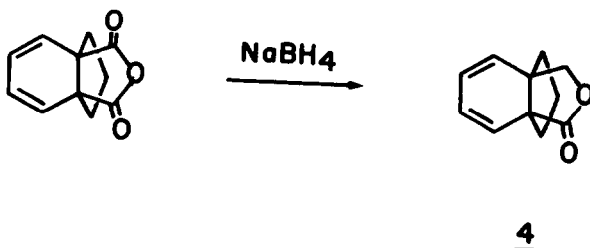
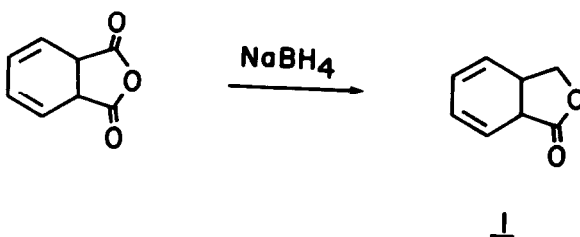


PHOTOCHEMICAL STUDIES¹. IRRADIATION INDUCED
TRANSFORMATIONS OF 1,2-DIHYDROPHthalIDES

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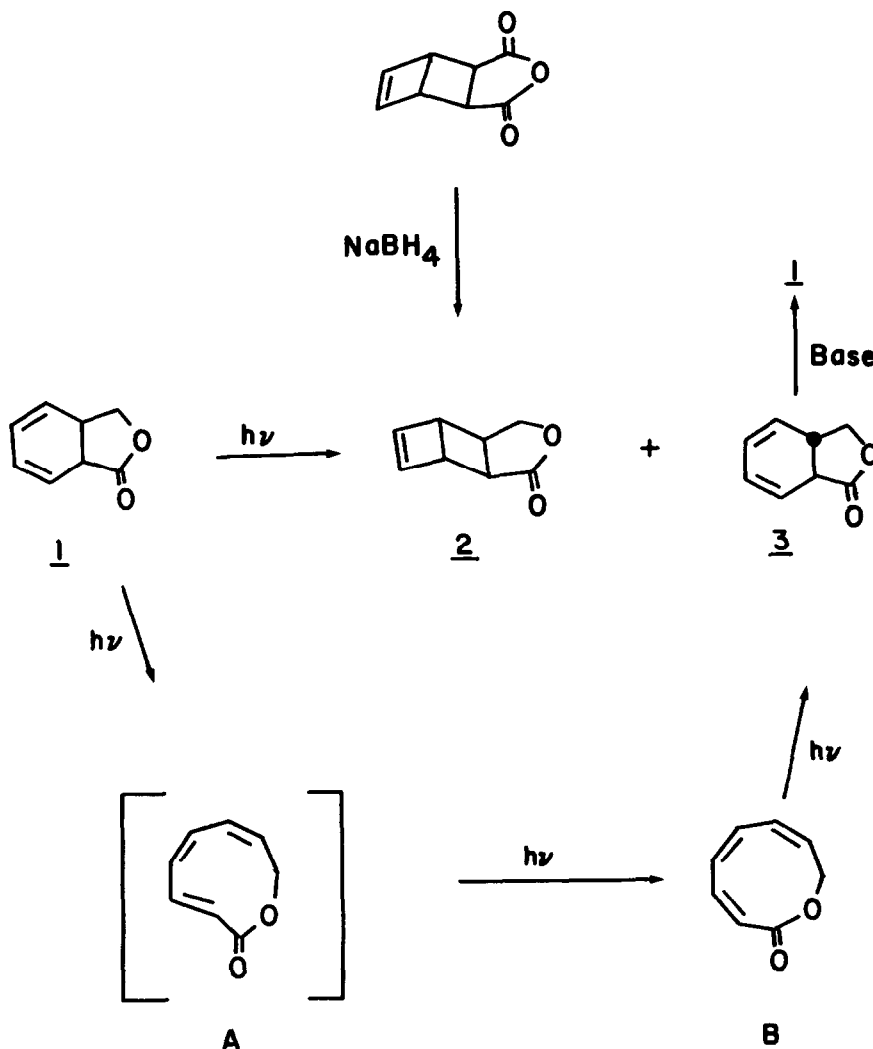
Abstract. The photochemical behavior of cis-1,2-dihydrophthalide (1) and its 1,2-trimethylene derivative (4) was studied. Besides bicyclo[2.2.0]hexene formation in both cases, (1) transforms into its trans isomer (3) whereas (4) undergoes a 1,2-shift to (7).

Our previous studies on the photochemistry of cis-1,2-dihydrophthalic anhydride^{2a}, imide^{2b} and thioanhydride¹, have led to an interesting picture (see ref. 1), wherein α -cleavage followed by partial or total fragmentation is a main photolytic route. One of the most pertinent questions we asked ourselves, was whether the symmetric planar five-membered dicarbonyl grouping plays a crucial role in determining this behavior and when does the electrocyclic cyclohexadiene \rightarrow hexatriene opening^{3,4} become competitive. On our way to investigate the important class of cyclohexa-2,4-dienyl ketones^{4,5} we decided to examine also the photochemistry of 1,2-dihydrophthalide (1) (which is, in fact, the 2-oxa analog of 2,3,8,9-tetrahydroinden-1-one⁴) and its 1,2-trimethylene derivative (4)⁶. To this end, we prepared the two starting compounds (1)⁷ and (4) by NaBH₄ reduction⁸ of the corresponding anhydrides⁹.



Irradiation of 1 (Scheme 1) at 254 nm provided (besides polymer and small amounts of phthalide) two new isolable products: anti-8-oxatricyclo [4.3.0.0^{2,5}]octa-3-ene-7-one (2) in 5% yield and trans-1,2-dihydrophthalide (3) in 22% yield. No benzene or other fragmentation products were observed.¹⁰ The structures of 2 and 3 were unequivocally proven by (IR, UV, NMR and MS) spectroscopic means as well as by chemical correlation with known compounds (Scheme 2). Thus 2 was also independently obtained by NaBH₄ reduction of bicyclo[2.2.0]hex-5-ene-2,3-dicarboxylic anhydride^{2a} while (3) could be chemically re-isomerised to (1) on basic alumina, although not photochemically so.

Scheme 1

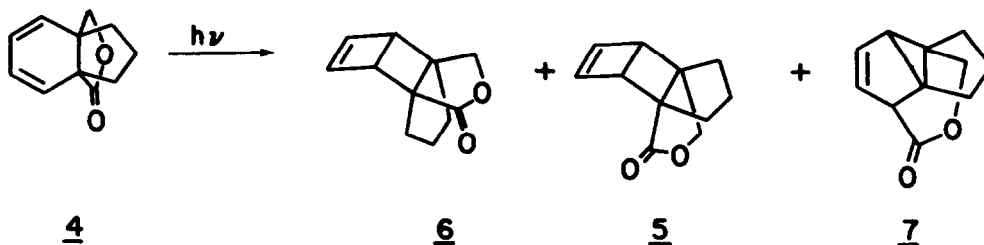


While the electrocyclic closure 1 \rightarrow 2 has no novelty², the cis - trans isomerization 1 \rightarrow 3 is both of preparative importance and mechanistic interest. Our initial thought that 1 undergoes α -cleavage followed by reclosure to 3 had to be abandoned after the results of careful monitoring of the course of photolysis by UV spectroscopy were obtained. Thus (Scheme 2), in the initial stage, an intermediate (which was assigned structure A) with an absorption maximum at 302 nm could be observed, although it defied any isolation attempts. On further irradiation a second intermediate with λ_{max} 287 nm was observed and could be obtained in solution by column chromatography (Silica). This intermediate to which we assign structure B was further irradiated at 254 nm to yield (with an isosbestic point at 268 nm pure trans-1,2-dihydrophthalide (3) λ_{max} 256, 261. These findings suggest the assignment of a cis, cis, cis-triene structure to B, which can then undergo a photochemically allowed electrocyclic closure to 3. It stands to reason that B is formed by double-bond isomerization from A which, as the symmetry-allowed conrotatory photo-opening product of 1, should have a cis, cis, trans-geometry³. The most relevant observation is, however, the fact that photochemical electrocyclic opening of cyclohexadienes 1,2-fused to five-membered rings (and the closure of the corresponding cyclic hexatrienes) becomes important already when one trigonal center occurs in the five-membered ring. This behavior is comparable (although not identical) to that of the bicyclo[4.3.0]-2,4-diene system³ and in contrast to the photochemical behavior of the 1,2-dihydrophthalic anhydride derivatives (cf. ref. 1-3,10) which smoothly undergo α -cleavage due to the steric forbiddenness of the electrocyclic cyclohexadiene \rightleftharpoons hexatriene transformation.

Turning now to 1,2-trimethylene-1,2-dihydrophthalide (4), its photochemistry (Scheme 3) was much cleaner (polymer-free) than that of (1). A typical irradiation (254 nm, 24 hrs) gave three products (at 66% conversion): both syn-(5) and anti-1,6-trimethylene-8-oxatri-cyclo[4.3.0.0.^{2,5}]octa-3-en-7-one (6) in 19% and 28% yield, respectively and the 1,2-acyl shift product (7) in 4% yield. This last product is, evidently, a 1,2-acyl shift (ODPM rearrangement) product, involving the entire diene moiety.^{2b}

It should be mentioned that all the above described processes occur most likely via singlet excited states since none of the products could be obtained by photosensitization. Instead, dimers of 1 and of 4 could be isolated both by their prolonged direct irradiation at 300 nm or by photosensitization with acetone.

Scheme 2



References and Notes

- 1 Part 23. Part 22. T. Baasov and B. Fuchs, preceding communication.
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3. a) W.G. Dauben and M.S. Kellogg, *J. Am. Chem. Soc.*, 102, 4456 (1980)
b) W.G. Dauben and E.G. Olsen, *J. Org. Chem.*, 45, 3377 (1980)
c) W.G. Dauben, R.G. Williams and R.D. McKelvey, *J. Am. Chem. Soc.*, 95, 3932 (1973).
4. S. Abramson and B. Fuchs, *Tetrahedron Letters*, 21, 1165 (1980) and forthcoming publication.
5. J. Zizuashvili and B. Fuchs, submitted for publication.
6. See R.S. Givens and N. Levi in "The Chemistry of Acid Derivatives" (S. Patai, Ed.) Suppl. B. Vol. 1, p. 641, Wiley/Interscience, New York 1979 for a review on the photochemistry of, i.a.l. lactones
7. a) G. Scharf, unpublished results and Ph D. Thesis, Tel-Aviv University, 1977;
b) P. Ashkenazi, D. Ginsburg, G. Scharf and B. Fuchs, *Tetrahedron* 33, 1345 (1977).
8. S. Takano and K. Ogasawara, *Synthesis* 42 (1974).
9. These new compounds were characterized by all spectroscopic means. The dienes underwent also derivation with triazoline-3,5-dione.
10. One should, however, keep in mind that relatively large amounts of polymer are obtained in the irradiation, probably from biradicals formed via α -cleavage.
11. The carbocyclic analog 2,3,8,9-tetrahydroinden-1-one is also able to undergo such an electrocyclic opening but leading to a tricyclo[3.3.0.0^{2,8}]hept-6-en-3-one⁴.

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