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ON THE PHOTOREACTIVITY OF BENZODIHYDROFURANS AND 2,4-CYCLOHEXADIEN-1-ONES

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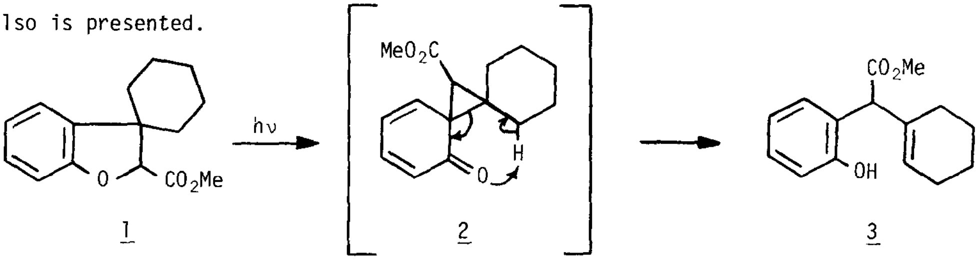
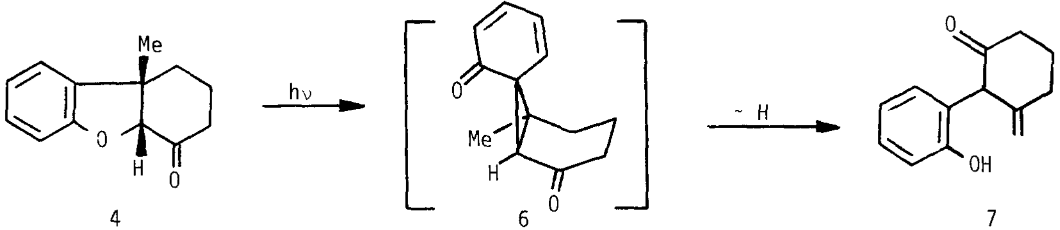
Stereochemical and structural effects on the photoconversion of benzodihydrofurans to spirocyclopropyl-2,4-cyclohexadien-1-ones are presented.

We have described[1a] the photochemical rearrangement of 2-carbomethoxybenzodihydrofuran 1 to olefinic phenol 3 (84% isolated yield ~ 50% conversion).[1b] Related aryloxyacetic acid photorearrangements have been suggested to occur by a "solvent-caged radical mechanism" for *ortho*- and *para*-substituted phenol formation.[1c] However, irradiation of optically active 1 results in complete retention of optical activity in phenol 3, suggesting a concerted rearrangement rather than one involving a long-lived diradical. Spirocyclopropyl-2,4-cyclohexadien-1-one 2 is a likely intermediate in this reaction;[2] hydrogen transfer in 2 by an abnormal Claisen rearrangement[3] would give phenol 3. We now report photochemistry of several benzodihydrofurans, for which important stereochemical requirements of the photorearrangement are noted. Information bearing on the photoreactivity of intermediate 2,4-cyclohexadien-1-ones also is presented.



Pyrex-filtered irradiation of *cis*-fused benzodihydrofuran 4[4] in benzene or methanol solution gives phenol 7 in ~ 85% isolated yield. Under the same reaction conditions, *trans*-fused epimer 5[4] remains unchanged. Photoproduct 7 is readily observed by ^{1}H NMR and silica gel tlc analyses, but none is detected in photoreactions of 5. On extended irradiation, 5 gradually undergoes photodecomposition.



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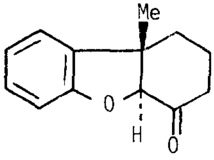

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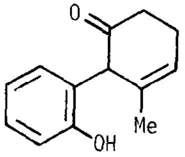

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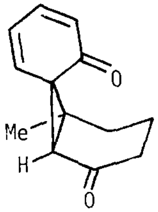

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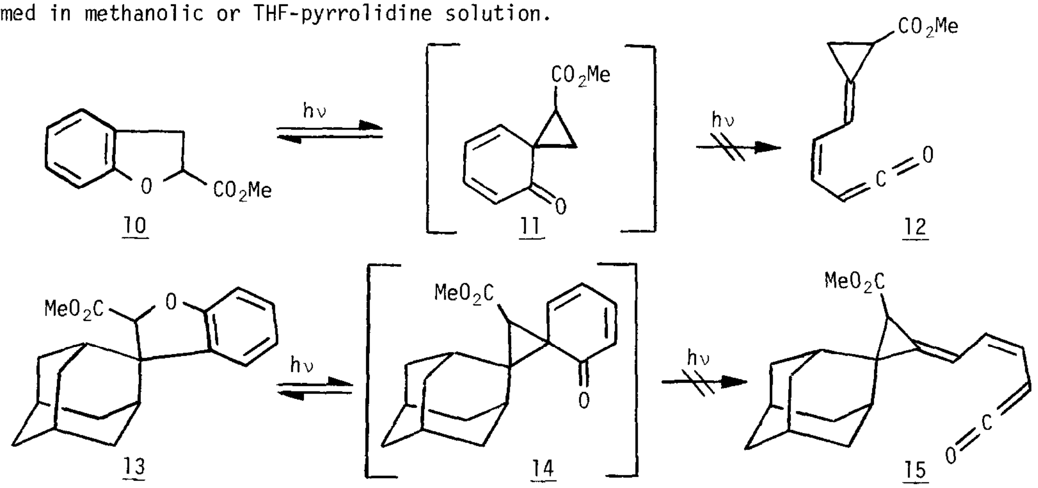
While the photorearrangement of 1 to 3 cannot be carried to completion, that with 4 is complete in several hours. Phenol 7 is isolated (and presumably exists during irradiation) as the internal hemiketal, which no longer bears an effective chromophore when Pyrex filters are used. Thus, potential photodecomposition of phenol 7 is averted and 7 cannot act as a light filter.

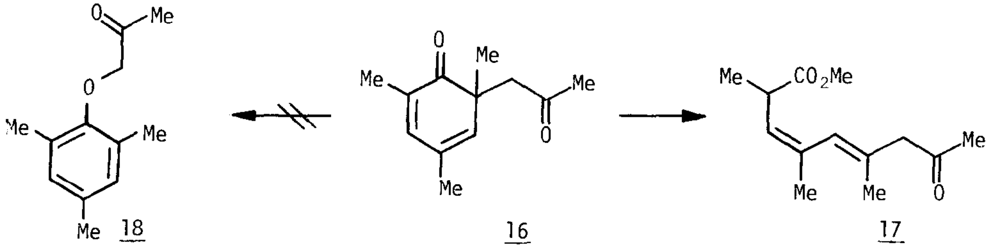
The failure of 5 to undergo photorearrangement may be a result of conformational requirements for either (or both) the diradical or (and) concerted reaction mechanism. The cyclohexanone ring in 5 is very rigid, with the dihydrofuran oxygen atom constrained to occupy an equitorial conformation ~ coplanar with the carbonyl group. The reactive, *cis*-fused isomer 4 is considerably more flexible and can readily adopt a conformation in which the dihydrofuran oxygen atom is perpendicular to the plane of the carbonyl group. We also note that a 1,3-suprafacial rearrangement in 5 would produce a diastereoisomer of 6 with a strained *trans*-fused bicyclo[4.1.0]heptane ring system.[5]

The exclusive formation of 7 from 4, with no endocyclic β,γ-enone 8 detected may be a result of high stereoselectivity for photorearrangement of 4 to give intermediate cyclohexadienone 6 rather than isomeric cyclohexadienone 9. Intramolecular hydrogen atom transf in 6 can occur only from the methyl substituent. Experiments designed to examine the stereochemical questions raised by studies with 4 and 5 are in progress.

In order to obtain information relating to the possible photoreactivity of 2,4-cyclo hexadienones generated by benzodihydrofuran photorearrangement, we prepared 10[6] and 13.[7] By analogy to the conversion 1 → 3, photorearrangement of 10 and 13 would be expected to produce intermediate 2,4-cyclohexadienones 11 and 14, respectively. Abnormal Claisen-type hydrogen atom transfer is precluded for 11, and 14 should be reluctant to undergo H atom transfer because a bridgehead olefin would result. Both 10 and 13 in ether or methanol or THF-pyrrolidine (~ 2:1) solution are photostable to irradiation conditions used for the photoconversion of 1 (450 W mercury arc lamp with Pyrex- or Vycor-filter). We assume that 11 and 14 are being formed,[2] but they photorevert to starting dihydrofurans. A remarkable observation is that 11 and 14 apparently do not undergo ring-opening to ketenes 12 and 15,[8] because no ketene derived methyl esters or amides are ever observed in photoreactions of 10 and 13 performed in methanolic or THF-pyrrolidine solution.



We wondered if the ester carbonyl was an important factor in directing the photoreversion of 11 and 14 to 10 and 13, rather than ring opening to a ketene. This does not seem to be the case, because Pyrex-filtered irradiation of 16[9] in dry, freshly distilled methanol results in rapid, near quantitative conversion to ring-opened keto ester 17;[10] no rearrangement to aryl



ether 18 is observed. Incidentally, Corex-filtered irradiation of 18 in methanolic solution cleanly gives 2,4,6-trimethylphenol and no 16 or 17. This result is consistent with the homolytic cleavage mechanism proposed for simple aryloxyacetic acid derivatives.[1c]

Thus, it appears that the spirocyclopropyl ring in 11 and 14 (and, of course, 2 and 6) is the structural factor which prevents photochemical cyclohexadienone ring opening. Clearly, there would be relatively more angle strain in an exo-methylenecyclopropane[11] such as 12 than the isomeric spirocyclopropane or benzodihydrofuran; e.g., 11 or 10. This observation is of importance in the context of experiments designed to intercept photochemically generated 2,4-cycloxexadien-1-ones by intramolecular cycloaddition reactions.

Acknowledgement. This work was supported by the National Science Foundation (CHE 79-23640).

References and Notes

1. (a) A. G. Schultz, J. J. Napier and R. Lee, J. Org. Chem., 44, 663 (1979); (b) For a related benzodihydrofuran photorearrangement, see Y. Kanaoka and K. San-nohe, Tetrahedron Letters, 21, 3893 (1980); (c) D. P. Kelly, J. T. Pinhey and R. D. G. Rigby, Aust. J. Chem., 22, 977 (1969).
2. Flash photolysis studies in collaboration with R. L. Strong and K. Wisniewski support the assignment of 2 as an intermediate in the photoconversion 1 → 3. A complete report of this and related (e.g., studies with 4, 5, 10, 13 and derivatives) will be published in due course.
3. E. N. Marvell, D. R. Anderson and J. Ong, J. Org. Chem., 27, 1109 (1962).
4. For the method of preparation of 4 (mp 98-99°C) and 5 (mp 126-127°C), see the Ph.D. Dissertation of J. J. Napier, Cornell University, 1981 or the generalized procedures found in A. G. Schultz, R. D. Lucci, W. Y. Fu, M. H. Berger, J. Erhardt and W. K. Hagmann, J. Am. Chem. Soc., 100, 2150 (1978). Compounds 4, 5, 7, 13 and 17 gave satisfactory elemental analyses.
5. For synthesis of a highly strained trans-bicyclo[4.1.0]heptane, see J. V. Paukstelis and J. Kao, J. Am. Chem. Soc., 94, 4783 (1972).
6. W. B. Lawson, J. Biol. Chem., 242, 3397 (1967); we thank L. Moonan for the preparation of 10.
7. Benzodihydrofuran 13 is prepared from 2-adamantanone and the dilithium dianion of phenoxyacetic acid, as described by W. Adam and H.-H. Fick, J. Org. Chem., 43, 4574 (1978) to give a β-hydroxycarboxylic acid, followed by esterification with ethereal diazomethane and dehydration (trimethylamine, thionyl chloride in CH_2Cl_2) to give the 2-phenoxyacrylic ester derivative (mp 94°C, satisfactory elemental analysis) and photocyclization by the method described in references 1 and 4.
8. For examples of this well-known photoreaction of 2,4-cyclohexadien-1-ones, see G. Quinkert, Angew. Chem., Int. Ed. Eng., 4, 211 (1965). For further examples and characterization of another important photoreaction of 2,4-cyclohexadien-1-ones (e.g., bicyclo[3.1.0]hex-3-en-2-one formation) see H. Hart, P. M. Collins and A. J. Waring, J. Am. Chem. Soc., 88, 1005 (1966).
9. M. Nitta, A. Omata and H. Sugiyama, Chemistry Letters, 1615 (1980).
10. Keto ester 17 (colorless oil) displays ^{1}H NMR resonance ($CDCl_3$, 200 MHz) at δ 1.20 (d, J = 6.0 Hz, 3H), 1.63 (d, J = 1.5 Hz, 3H), 1.79 (broad s, 3H), 2.19 (s, 3H), 3.15 (broad s, 2H), 3.27 (dq, J = 8.0 Hz and J = 6.0 Hz, 1H), 3.67 (s, 3H), 5.36 (broad d, J = 8.0 Hz, 1H), 5.78 (m, 1H), and IR absorption (neat) at 5.8, 5.9, 7.0, 7.4, 8.6, and 9.5 μ.
11. E. F. Ullman and W. J. Fanshawe, J. Am. Chem. Soc., 83, 2379 (1961); J. F. Pazos and F. D. Greene, ibid., 89, 1030 (1967).

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