anediol, 556-48-9; benzoyl chloride, 98-88-1; 4-benzoyloxycyclohexanol, 6308-92-5; 4-benzoyloxycyclohexanone ethylene thioacetal, 54531-77-0; ethane-1,2-dithiol, 540-63-6; 4-hydroxycyclohexanone ethylene thioacetal, 22428-86-0; 4-methylcyclohexanone, 589-92-4.

References and Notes

(1) (a) Fellow of the Alfred P. Sloan Foundation; (b) University Fellow, Rutgers University.
(2) H. E. Simmons, T. L. Cairns, S. A. Vladuchick, and C. M. Hoiness, *Org. React.*, **20,** 1 (1973).
(3) R. A. Moss, "Carbenes", Vol. 1, M. Jones, Jr., and R. A. Moss, Ed., Interscience, New York, N.Y., 1973, p 153 ff.
(4) W. Grimme, J. Reisdorff, W. Jünemann, and E. Vogel, *J. Am. Chem. Soc.*, **92,** 6335 (1970).
(5) D. Seyferth and V. A. Mai, *J. Am. Chem. Soc.*, **92,** 7412 (1970).
(6) M. A. Tobias and B. E. Johnston, *Tetrahedron Lett.*, 2703 (1970).
(7) R. A. Moss, *J. Am. Chem. Soc.*, **94,** 6004 (1972).
(8) See ref 7, p 6008.
(9) L. Tenud, S. Farooq, J. Seibl, and A. Eschenmoser, *Helv. Chim. Acta*, **53,** 2059 (1970), and references cited therein.
(10) R. A. Moss and C. B. Mallon, *Tetrahedron Lett.*, 4481 (1973).
(11) More reactive carbenic species do attack the oxygen atoms of allylic and homoallylic ethers. See ref 10, notes 17–20.
(12) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J. H. Treiber, and S. R. Dowd, *J. Am. Chem. Soc.*, **87,** 4259 (1965).
(13) (a) W. E. Parham and S. H. Groen, *J. Org. Chem.*, **29,** 2214 (1964). (b) A referee has suggested that ". . .the total destruction of **5** does (not) imply that there is a synergistic relation but rather that now one has introduced a Michael acceptor into the system for an alternate intermolecular pathway". The introduction of a Michael acceptor group per se does not cause destructive intermolecular reactions in CCl_2-generating systems (cf. **3b**). The presence of *both* an ethylene thioacetal and a carboethoxyethylene function in the same substrate molecule (e.g., **5**), however, does lead to an alternative, fast (relative to cyclopropanation), presumably intermolecular destructive process. In the sense of "cooperative behavior", this result is an example of synergism because neither the ethylene thioacetal (cf. **4**) nor the carboethoxy function[10] *alone* prevents cyclopropanation or induces destructive intermolecular reactions. Unfortunately, the synergism is not a desirable one.
(14) W. E. Parham and S. H. Groen, *J. Org. Chem.*, **30,** 728 (1965); **31,** 1694 (1966).
(15) W. Ando, Y. Saiki, and T. Migita, *Tetrahedron*, **29,** 3511 (1973); G. Andrews and D. A. Evans, *Tetrahedron Lett.*, 5121 (1972); M. Yoshimoto, S. Ishihara, E. Nakayama, and N. Soma, *ibid.*, 2923 (1972); I. Ojima and K. Kondo, *Bull. Chem. Soc. Jpn.*, **46,** 1539 (1973); K. Kondo and I. Ojima, *J. Chem. Soc., Chem. Commun.*, 62 (1972).
(16) W. Ando, H. Fujii, T. Takeuchi, H. Higuchi, Y. Saiki, and T. Migita, *Tetrahedron Lett.*, 2117 (1973), and references cited therein. Review: A. P. Marchand and N. M. Brockway, *Chem. Rev.*, **74,** 431 (1974). See also M. Numata, Y. Imashiro, I. Minamida, and M. Yamaoka, *Tetrahedron Lett.*, 5097 (1972); M. Yoshimoto, S. Ishihara, E. Nakayama, E. Shoji, H. Kuwano, and N. Soma, *ibid.*, 4387 (1972).
(17) See ref 10. Experimental details for the preparation of **7**-Ox and **8**-Ox will appear in the Ph.D. Thesis of C. B. Mallon, and are available, on request, from the authors.
(18) W. M. Wagner, *Proc. Chem. Soc., London*, 229 (1959).
(19) The σ_I values are 0.23 and 0.27, respectively: S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Prog. Phys. Org. Chem.*, **10,** 1 (1973).
(20) R. A. Moss and C. B. Mallon, unpublished work.
(21) Attempts to construct stabilized allylic sulfonium ylides lead to [2,3] sigmatropic rearrangement products under even extremely mild conditions: J. E. Baldwin and W. F. Erickson, *Chem. Commun.*, 359 (1971).
(22) Boiling points and melting points are uncorrected. NMR spectra were determined in CCl_4 (unless otherwise indicated) with a Varian T-60 spectrometer. Chemical shifts are given in δ units, relative to an internal Me_4Si standard. Exact mass determinations employed an Hitachi Perkin-Elmer RMU-7E mass spectrometer. Exact mass calculations, and exclusion of possible alternative elemental compositions within ±5 mmu, were done using the computer program described by S. R. Shrader, "Introductory Mass Spectrometry", Allyn and Bacon, Boston, Mass., 1971, p 233 ff. Microanalyses were done by Micro-Tech Laboratories, Skokie, Ill.
(23) E. R. H. Jones and F. Sondheimer, *J. Chem. Soc.*, 615 (1949).
(24) T. Reichstein, *Helv. Chim. Acta*, **40,** 1621 (1957), employs a similar method for oxidation of the (oxy) acetal analog.
(25) In benzene solvent, the cyclohexyl "singlet" is a broad multiplet, δ 2.57–1.90.
(26) This procedure was adapted from the work of Corey et al.: E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84,** 866 (1962); **87,** 1345 (1965); R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28,** 1128 (1963).
(27) This procedure was adapted from W. S. Wadsworth, Jr., and W. D. Emmons, *J. Am. Chem. Soc.*, **83,** 1733 (1961).
(28) Conversions of **7**-Ox and **8**-Ox to **7** and **8** were apparently quantitative.

Communications

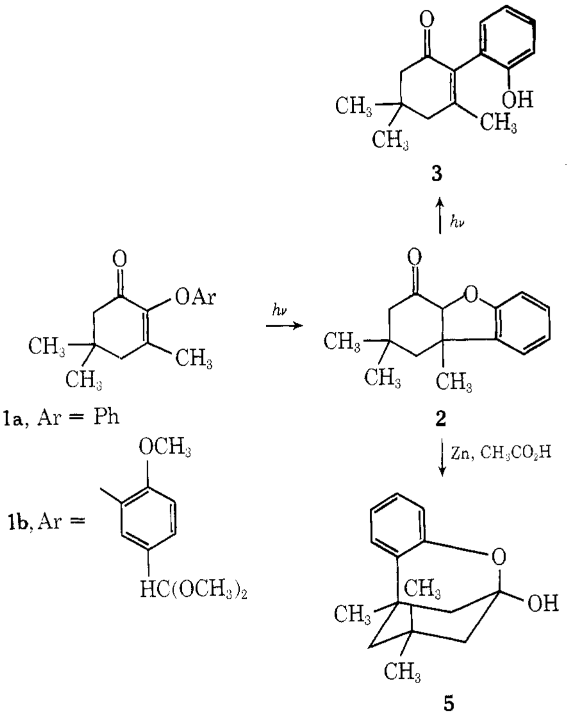
Heteroatom Directed Photoarylation. Photochemistry of Aryloxyenones

Summary: Aryloxyenones **1a** and **1b** undergo photocyclization–rearrangement to give dihydrofurans **2** and **7**, respectively.

Sir: Reported photoreactions of aryl ethers have been limited to (1) cleavage of the ether bond(s) followed by hydrogen abstraction from solvent to give phenols and (2) photorearrangement to give ortho- and para-substituted hydroxybiphenyls.[1] Photocyclization of unsubstituted diaryl ethers or aryl vinyl ethers to annelated dihydrofurans apparently has not been observed;[2,3] however, photocyclization–elimination of *o*-methoxyphenyl phenyl ethers[2] and *o*-chlorophenyl 1-naphthyl ether[3] to annelated furans in low to moderate yield has been reported. Herein, we communicate the photochemistry of 2-phenoxy-3,5,5-trimethylcyclohexen-2-one (**1a**), which represents the first report of nearly exclusive photochemical carbon–carbon bond formation from an unsaturated ether, to give an annelated dihydrofuran.

Aryloxyenone **1a** was prepared by the potassium hydride (0.1 equiv) assisted reaction of isophorone oxide[4] with 1.1 equiv of phenol in refluxing tetrahydrofuran solution containing 0.75 equiv of hexamethylphosphoramide (91% isolated yield, mp 104–105°). Pyrex-filtered photolysis of **1a** (20 g) was performed in benzene–methanol–acetic acid solution (2000 ml, equal portions of each solvent component) while purged with argon. After 23 hr irradiation with a 450-W high-pressure mercury arc lamp, <2% **1a** remained in the nearly colorless reaction mixture; formation of dihydrofuran **2** (95%), rearranged phenol **3** (~2%), and trace amounts of phenol and isophorone was observed (vpc analysis). Evaporation of solvent and partition of the reaction components between ether and 1 *N* sodium hydroxide solution gave nearly pure dihydrofuran **2** (88% yield) in the organic layer. Two crystallizations from ether–petroleum ether produced analytically pure **2** (80% yield, mp 85–87°, *m/e* 230).

Acidification of the sodium hydroxide layer gave, after ether extraction and crystallization from ether–petroleum ether, pure **3** (2% yield, mp 172–175°, *m/e* 230). The nmr spectrum of **3** in $CDCl_3$ above 5 ppm is nearly identical with that of **1** and displays singlets at 1.11 (6 protons, *gem*-dimethyl), 1.83 (3 protons, vinyl methyl), and 2.42 ppm (4 protons, two methylene groups). The phenolic proton in **3** appears as a broadened singlet at 5.8 ppm and exchanges with deuterium oxide, while the four aromatic protons appear as a complex multiplet at 6.8 to 7.4 ppm. Para aromatic substitution in **3** is ruled out on the basis of NMR data. Good evidence for ortho substitution is obtained from the ir spectrum of **3** (Nujol) between 12 and 15 μ; i.e., a single strong absorption appears at 13.3 μ (C–H out-of-plane deformation).



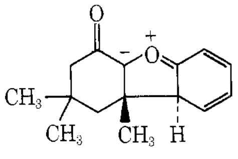
1a, Ar = Ph

1b, Ar =

2

3

5



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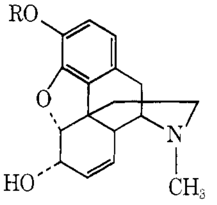
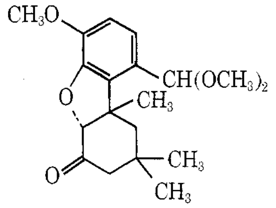
The process **1a** → **2** presumably occurs by conrotatory photocyclization[8] of **1a,** leading to intermediate carbonyl ylide **4**, which undergoes rearrangement to give dihydrofuran **2**. Stereochemistry of the ring junction in **2** is considered to be cis, because this would be the stable configuration for a fused five–six-membered ring system capable of epimerization; on treatment with methanolic sodium hydroxide at room temperature, **2** was recovered unchanged.

Extended irradiation of solutions of **1a** resulted in increased amounts of rearranged phenol **3** at the expense of **2**. Independent photolysis of **2** gave a complex mixture of products, the major component of which was **3**. Thus, **3** is not formed directly from **1a**, but rather arises from a secondary photoreaction involving **2**. The detailed mechanism for this process as well as *o*-hydroxybiphenyl formation from diaryl ethers[1] currently is being investigated.

Photocyclization of aryloxyenones to dihydrofurans may have considerable synthetic importance. For example, approaches toward the synthesis of morphine alkaloids, here represented by morphine (**6a**) and codeine (**6b**), have been long and hence suffer from low overall yields.[9] Our approach toward the synthesis of morphine confronts the difficult task of forming the only carbon–carbon bond possessing a quaternary carbon atom by the technique of heteroatom-directed photoarylation.[6] In this regard, irradiation of model system **1b** resulted in nearly exclusive formation of dihydrofuran **7**.[10]



6a, R = H
b, R = CH$_3$



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It should be noted that **2** undergoes quantitative conversion to an ortho-substituted phenol, isolated in hemiketal form **5** (mp 97–98°, *m/e* 232), on treatment with zinc dust in refluxing acetic acid solution. The method described here for the two step conversion **1** → **5** complements our recently reported method for preparation of complex meta-substituted phenols.[6]

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References and Notes

(1) M. S. Kharasch, G. Stampa, and W. Nadenberg, *Science*, **116**, 309 (1952); D. P. Kelly, J. T. Pinhey, and R. D. G. Rigby, *Tetrahedron Lett.*, 5953 (1966); D. P. Kelly, J. T. Pinhey, and R. D. G. Rigby, *Aust. J. Chem.*, **22**, 977 (1969); Y. Ogata, K. Takagi, and I. Ishino, *Tetrahedron*, **26**, 2703 (1970); H. G. Hageman, H. L. Louwerse, and W. J. Mijs, *ibid.*, **26**, 2045 (1970); and H.-I. Joschek and S. I. Miller, *J. Am. Chem. Soc.*, **88**, 3269 (1966).

(2) J. A. Elix, D. P. H. Murphy, and M. V. Sargent, *Synth. Commun.*, **2**, 427 (1972).

(3) W. A. Henderson and A. Zweig, *Tetrahedron Lett.*, 625 (1969).

(4) E. I. Wasson and H. O. House, *Org. Synth.*, **37**, 58 (1957).

(5) Attempts to prepare **1** from phenol and isophorone oxide by the procedure of Tobias et al. failed; see M. A. Tobias, J. G. Strong, and R. P. Napier, *J. Org. Chem.*, **35**, 1709 (1970).

(6) Assignment of structure for **2** is based on spectral evidence and comparison to products characterized in a related study; see A. G. Schultz, *J. Org. Chem.*, **39**, 3185 (1974).

(7) Compounds **1**, **2**, **3**, and **5** gave correct elemental analysis.

(8) A. G. Schultz and M. B. DeTar, *J. Am. Chem. Soc.*, **96**, 296 (1974).

(9) G. Stork in "The Alkaloids," Vol. VI, R. H. F. Manske, Ed., Academic Press, New York, N.Y., 1960, p 235.

(10) Aryloxyenone **1b** was prepared from isovanillin dimethyl acetal by the method described for the synthesis of **1a**. Both **1b** and photoproduct **7** gave NMR, ir, and mass spectra completely in accord with assigned structures.

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