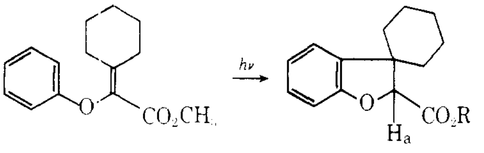
Communications

Stereospecific Benzodihydrofuran Photorearrangement

Summary: Benzodihydrofuran **2a** undergoes a stereospecific photorearrangement to phenol **3**.

Sir: The photochemistry of phenoxyacetic acid derivatives has received considerable attention in recent years.[1-11] A significant portion of this activity has been stimulated by a desire to understand the photochemistry of the chlorinated phenoxyacetic acids, a group of compounds used throughout the world for weed control. Photoreaction products have been characterized and these generally are a result of carbon(2)–oxygen bond cleavage; e.g., simple phenols and 2- and 4-hydroxyphenylacetic acid derivatives. Little mechanistic analysis is available; however, studies by Pinhey and coworkers[3] suggest that rearrangements are intramolecular. These workers favor a solvent-caged radical mechanism similar to that proposed for the photo-Fries reaction.[12] It is interesting to note that experiments designed to detect the existence of free radicals provided no evidence for such intermediates.[3]

Herein, we report the photochemistry of 2-carbomethoxybenzodihydrofuran **2a**. As a consequence of the aromatic ring fusion in **2**, rearrangement is limited to that producing only the 2-hydroxyphenylacetic acid ester **3**. Remarkably, the rearrangement **2a** → **3** is stereospecific and presumably occurs via a [1,3] sigmatropic rearrangement of **2a** to give the cyclopropyl dienone **5** as an intermediate. Clearly, this result should provide an impetus for further study of the mechanism of phenoxyacetic acid photorearrangements.



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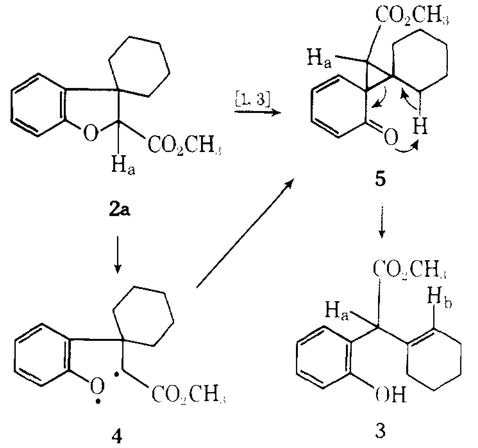
2a, R = CH_3
b, R = H

Benzodihydrofuran **2** is prepared from aryl vinyl ether **1**[13] by the technique of heteroatom directed photoarylation.[14] Pyrex-filtered irradiation of **1** (mp 51.5–53 °C) in degassed benzene–methanol solution, evaporation of solvent, and partition of the reaction components between ether and 1 N sodium carbonate gives dihydrofuran **2a** in the organic layer [88%; bp 140 °C (0.25 mmHg); ^1H NMR δ 4.88 (H_a, sharp singlet); IR (neat) 5.78, 6.25 μm; UV λ_{max} (ether) 279 (ϵ 3620), 285 (ϵ 3350) with tailing to 300 nm].

Acidification of the aqueous layer gives a small amount of phenol **3** [mp 100–101 °C; ^1H NMR δ 4.24 (H_a, broadened singlet), 4.53 (H_b, broadened singlet) and 3.73 (OCH_3, sharp singlet); IR ($CHCl_3$) 2.95, 5.82, 6.20, 6.31 μm; electron impact *m/e* 246]. Appropriate experiments demonstrate that **3** is not formed directly from **1**, but rather arises from a secondary photoreaction of **2a**. In fact, this fascinating rearrangement to phenol **3** occurs in 84% isolated yield (~50% conversion) on extended irradiation of **2a** in ether solution. Under these reaction conditions, **3** is photostable.

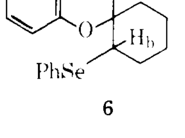
A reasonable mechanism for rearrangement of **2a** assumes the intermediacy of cyclopropyl dienone **5**, from which **3** would form as shown (Scheme I). Homolytic (or heterolytic) carbon–oxygen bond cleavage could occur to give **4** and recombination in **4** would give **5**.[15] On the other hand, a concerted [1,3] sigmatropic rearrangement of **2a** to **5** also must be considered (Scheme I).

Scheme I

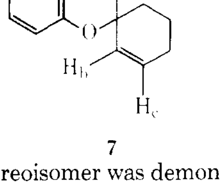


In order to differentiate between the concerted and stepwise mechanism, an enantiomeric resolution of **2b** was performed. Thus, mixing **2b** with (*S*)-(−)-α-methyl-*p*-nitrobenzylamine[16] in ether–methylene chloride followed by three crystallizations from this solvent system and hydrochloric acid wash gives resolved carboxylic acid **2b**; esterification (diazomethane in ether) gives **2a**, $[\alpha]^{24}{}_D$ −40.1° (*c* 1.4% in ether). The enantiomeric purity of **2a** thus resolved was determined by use of the chiral shift reagent $Eu(hfc)_3$ (mole ratio **2a**/shift reagent ~10:1, $\Delta\delta H_a = 0.06$, $CDCl_3$) and by repetitive peak integration was found to be 8.3:1 (upfield/downfield signal, respectively).[17]

Irradiation of resolved **2a** in ether (0.013 M) for 72 h and silica gel chromatography gives recovered **2a** (43% isolated yield) and phenol **3** [41%, $[\alpha]^{24}{}_D$ −14.0° (*c* 2.9% in ether)]. Chiral shift reagent analysis of recovered **2a** (enantiomer ratio found to be 8.2:1) indicates that no racemization of **2a** occurs during irradiation. Because of an inability to separate ^1H NMR signals due to enantiomers of **3**, we were not able to measure the enantiomeric purity of **3** directly. Instead, **3** was reacted with phenylselenyl chloride[18] in methylene chloride at −78 °C to give, after silica gel thick layer chromatography, phenyl selenide **6** [70% yield; $[\alpha]^{24}{}_D$ −69° (*c* 0.8% in CH_2Cl_2); ^1H NMR δ 4.62 (H_a, sharp singlet), 3.73 (OCH_3, sharp singlet), 3.58–3.37 (H_b, multiplet); IR ($CHCl_3$) 5.72 μm]. The structure of **6** follows from the chemical shift noted for H_b, which is in accord with a hydrogen atom geminal to a selenium atom. The observed resonance for H_b is at considerably higher field than that expected for the other possible regioisomer, in which H_b is geminal to an oxygen atom.[18] Furthermore, treatment of **6** with hydrogen peroxide in THF at room temperature gives olefin **7** in 94% isolated yield (electron impact *m/e* 244).[19]



6



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That **6** is indeed a single diastereoisomer was demonstrated by adding the achiral shift reagent tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium [$Eu(fod)_3$]

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to **6** generated from racemic **3** and observing no line broadening (maximum mole ratio **6**/shift reagent 0.63:1; δ 8.72, H_a; 6.50, OCH_3). The enantiomeric purity of **6** generated from resolved **3** was determined by use of the chiral shift reagent $Eu(hfc)_3$ (mole ratio **6**/shift reagent 1.25:1, $\Delta\delta H_a = 0.27$; $\Delta\delta OCH_3 = 0.06$, $CDCl_3$) and was found to be 8:1 (downfield/upfield signal, respectively).

Thus, benzodihydrofuran **2a** undergoes a stereospecific photorearrangement to phenol **3**. Clearly, a long-lived diradical (or zwitterionic) intermediate such as **4** is incompatible with these experimental results. We suggest that photoexcited **2a** undergoes a concerted [1,3] sigmatropic rearrangement to **5**, and **5** rearranges (thermal, photochemical?) as shown.[20] Experiments designed to conclusively establish the intermediacy of cyclopropyl dienones are currently in progress.

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(19) ^1H NMR for **7**: δ 4.15 (H_a, sharp singlet), 6.19–6.68 (H_b, H_c, multiplet); irradiation at δ 2.08 causes a collapse of multiplet to AB quartet, $J_{bc} = 10$ Hz. We were delighted to find the high degree of stereoselectivity in the conversion **3** → **6**; presumably the neighboring carbomethoxy group is of importance in the stereochemical control of this reaction.
(20) The photoconversion of verbenone to chrysanthenone [J. J. Hurst and G. H. Whitham, *J. Chem. Soc.*, 2864 (1960)] involves the [1,3] migration of a quaternary carbon atom; in this case, stereochemical analysis [G. W. Shaffer and M. Pesaro, *J. Org. Chem.*, **39**, 2489 (1974)] demonstrates that a nonconcerted diradical mechanism operates. J. M. Burns, M. E. Ashley, G. C. Crockett, and T. H. Koch, *J. Am. Chem. Soc.*, **99**, 6924 (1977) report a "highly stereospecific" [1,3] rearrangement of 2-ethoxypyrrolin-5-ones to ethoxycyclopropyl isocyanates (98% retention of stereochemistry). These workers favor a mechanism involving "a short-lived singlet diradical intermediate which ring closes by a rate more than an order of magnitude faster than the rate for bond rotation."
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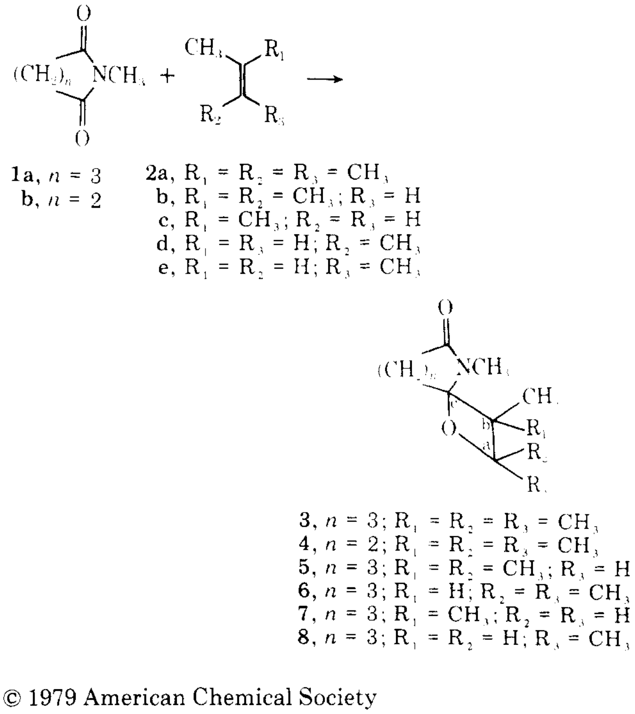
Photoaddition of Olefins to Cyclic Imides: Intermolecular Oxetane Formation and Ring Expansion[1]

Summary: Aliphatic cyclic imides undergo photochemical [2 + 2] addition with olefins to form "imide–oxetanes" whose structures and reactions are elucidated, whereas aromatic cyclic imide gave rise to ring-expanded products.

Sir: The photoreactions of cyclic imides have recently been the subject of considerable study.[2,3] Synthetic work has been concerned with structural variations of the imide substrates, mainly on the basis of the Norrish type II processes, leading to syntheses of a wide variety of nitrogen heterocycles which include even macrocycles.[3,4] Very recently the photoadditions of some olefin and diene systems to the cyclic imides have also been reported and the scope of such reactions involving either the imide carbonyl or the N–C bond is of current interest.[5-7] Earlier it was postulated that the photochemical behavior of the imide carbonyl, at least formally, closely parallels that of the simple ketone system.[3,8] However, this parallelism has been incomplete because the Paterno–Büchi reaction, one of the typical reactions of carbonyl compounds,[9] has not been observed except that intramolecular oxetane formation has recently been described.[5] We now wish to report that the intermolecular photochemical [2 + 2] addition reaction of the aliphatic cyclic imides **1** and olefins **2** lead to isolation of oxetanes, whereas similar reactions of aromatic imide lead to ring expansion as a result of additive incorporation of the olefinic unit.

In a typical run, a solution of **1a** (0.1 M) and 2,3-dimethyl-2-butene (**2a**) (0.5 M) in acetonitrile was irradiated[10] for 10

Scheme I



1a, $n = 3$
b, $n = 2$

2a, $R_1 = R_2 = R_3 = CH_3$
b, $R_1 = R_2 = CH_3$; $R_3 = H$
c, $R_1 = CH_3$; $R_2 = R_3 = H$
d, $R_1 = R_3 = H$; $R_2 = CH_3$
e, $R_1 = R_2 = H$; $R_3 = CH_3$

3, $n = 3$; $R_1 = R_2 = R_3 = CH_3$
4, $n = 2$; $R_1 = R_2 = R_3 = CH_3$
5, $n = 3$; $R_1 = R_2 = CH_3$; $R_3 = H$
6, $n = 3$; $R_1 = H$; $R_2 = R_3 = CH_3$
7, $n = 3$; $R_1 = CH_3$; $R_2 = R_3 = H$
8, $n = 3$; $R_1 = R_2 = H$; $R_3 = CH_3$