Stereochemistry of Benzodihydrofuran-2-carboxylic Acid Ester Photorearrangement

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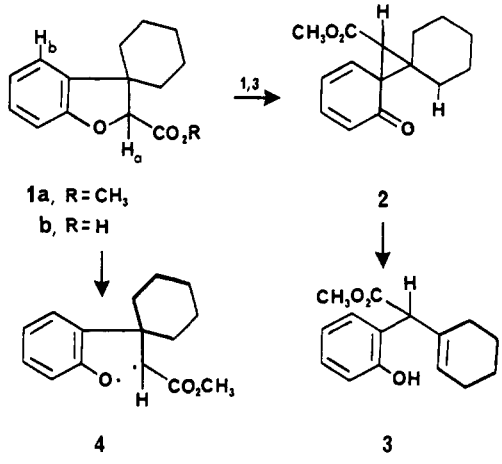
Abstract: The stereoselectivity of the photorearrangement of benzodihydrofuran **1a** to give phenol **3** is determined by preparation and irradiation of optically active **1a**. Chiral shift reagent NMR analysis of recovered **1a** and derivatized **3** (in the form of spirocyclic selenide **22**) indicates that configuration is not lost during the irradiation. A mechanism involving concerted photorearrangement of **1a** to spiro[cyclopropane-2',4'-cyclohexadien-1'-one] **2** followed by intramolecular hydrogen atom transfer in **2** to give **3** is proposed. The diastereoselectivity of spiro[cyclopropane-2',4'-cyclohexadien-1'-one] formation is examined with C(2) alkyl derivatives **28a** and **28b**, which produce only **29a** and **29b**, respectively, with no **30a** or **30b** detected. These results suggest that the effective diastereoisomeric intermediate is type **26** with the ester and cyclohexadienone carbonyl groups syn oriented, rather than **27**. A more sensitive test of diastereoselectivity with the same mechanistic conclusion involves the cyclohexane ring methyl group derivatives **38** and **39**. Factors that may affect diastereoselectivity are discussed.

In a preliminary communication, we described the photorearrangement of 2-carbomethoxybenzodihydrofuran **1a** to olefinic phenol **3** and suggested that spiro[cyclopropane-2',4'-cyclohexadien-1'-one] **2** is an intermediate in this reaction.[1,2] Irradiation of optically active **1** resulted in retention of enantiomeric purity in **3**, suggesting that intermediate **2** is formed by a concerted rearrangement from **1a** rather than by a long-lived diradical (e.g., **4**).[3] Hydrogen transfer in **2** would give phenol **3**.

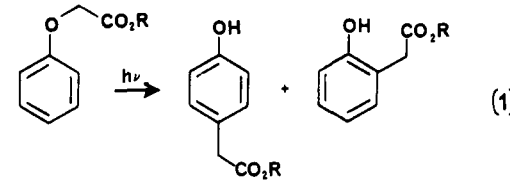


The possible involvement of 2,4-cyclohexadienones of type **2** in benzodihydrofuran photorearrangements is of synthetic as well as mechanistic interest. The interception of photochemically generated 2,4-cyclohexadienones by intramolecular cycloaddition reactions could result in the development of potentially useful methodology for the construction of multicyclic ring systems. However, before attempting to use this photoreaction in a synthetic context, it is clear that the mechanistic requirements of the rearrangement must be elucidated.

In the conversion of **1** into **2**, two diastereoisomers may, in principle, be formed. Both diastereoisomers would be expected to rearrange to phenol **3**. In order to examine this aspect of stereoselectivity in the primary photochemical step, we developed an indirect method for determining the diastereomeric composition of **2**. In this paper, we present complete experimental details of our study of the stereochemistry associated with photorearrangement of type **1** → **3**.

Background

The UV-active chromophore in **1a** is essentially that of a phenoxyacetic acid. (Aryloxy)acetic acid like photochemistry has received considerable attention in recent years.[4-14] 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 (eq 1). (Aryloxy)-



(1)

acetic acid photorearrangements to 2- and 4-substituted phenols have been suggested to occur by a solvent-caged radical mechanism,[6] similar to that proposed for the photo-Fries reaction.[15]

There has been a good deal of work in the general area of phenyl ether photochemistry.[16-18] As with (aryloxy)acetic acids, pho-

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(2) For a report of related photochemistry, see: Schultz, A. G.; Ranganathan, R.; Kulkarni, Y. S. *Tetrahedron Lett.* **1982**, *23*, 4527.
(3) 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**; manuscript in preparation.
(4) Kelly, D. P.; Pinhey, J. T. *Tetrahedron Lett.* **1964**, 3427.
(5) Pinhey, J. T.; Rigby, R. D. G. *Tetrahedron Lett.* **1969**, 1267.
(6) Kelly, D. P.; Pinhey, J. T.; Rigby, R. D. G. *Aust. J. Chem.* **1969**, *22*, 977.
(7) Aly, O. M.; Faust, S. D. *J. Agric. Food Chem.* **1964**, *12*, 541.
(8) Chiamovich, H.; Vaughan, R. J.; Westheimer, F. H. *J. Am. Chem. Soc.* **1968**, *90*, 4088.
(9) Crosby, D. G.; Tutlass, H. O. *J. Agric. Food Chem.* **1966**, *14*, 596.
(10) Crosby, D. G.; Wong, A. S. *J. Agric. Food Chem.* **1973**, *21*, 1049, 1052.
(11) Bell, G. R. *Bot. Gaz. (Chicago)* **1956**, *1138*, 133.
(12) Aandres, C. R.; Dairo, R. J. *Rev. Dep. Quim., Univ. Nac. Colomb.* **1969**, *4*, 26; *Chem. Abstr.* **1971**, *74*, 124481*e*.
(13) Binkley, R. W.; Oakes, T. R. *J. Org. Chem.* **1974**, *39*, 83.
(14) The generality of this process is noted by reports of analogous photorearrangements of *N*-(alkylanilino)acetates and (aryloxy)acetonitriles (Arora, K. J. S.; Dirania, M. K. M.; Hill, J. *J. Chem. Soc. C* **1971**, 2865), of α-*N*-alkylanilino ketones (Hill, J.; Townend, J. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1210; *Tetrahedron Lett.* **1970**, 4607), of (aryloxy)acetamides (Godtfredsen, W. O.; von Daehne, W.; Vangedel, S. *Experientia* **1967**, *23*, 280. Yonemitsu, O.; Naruto, S. *Tetrahedron Lett.* **1969**, 2387), and of allyloxy ketones (Hill, J. *Chem. Commun.* **1966**, 260. Dirania, M. K. M.; Hill, J. *J. Chem. Soc. C* **1968**, 1311. Crollier, J. R.; Dirania, M. K. M.; Hill, J. *Ibid.* **1971**, 155. Arora, K. J. S.; Dirania, M. K. M.; Hill, J. *Ibid.* **1971**, 2865. Saburi, Y.; Yoshimoto, T.; Minami, K. *Nippon Kagaku Zasshi* **1967**, *88*, 1326; **1968**, *89*, 1248).
(15) Kobsha, H. *J. Org. Chem.* **1962**, *27*, 2293. More recent studies of the photo-Fries rearrangement, which establish that the mechanism involve sbond homolysis in the excited state followed by recombination of the radical pair in the solvent cage, include: Adam, W. *J. Chem. Soc., Chem. Commun.* **1974**, 289. Kalmus, C. E.; Hercules, D. M. *J. Am. Chem. Soc.* **1974**, *96*, 449. Meyer, J. W.; Hammond, G. S. *Ibid.* **1970**, *92*, 2189. Humphrey, J. S.; Roller, R. S. *Mol. Photochem.* **1971**, *3*, 35 and references cited therein.

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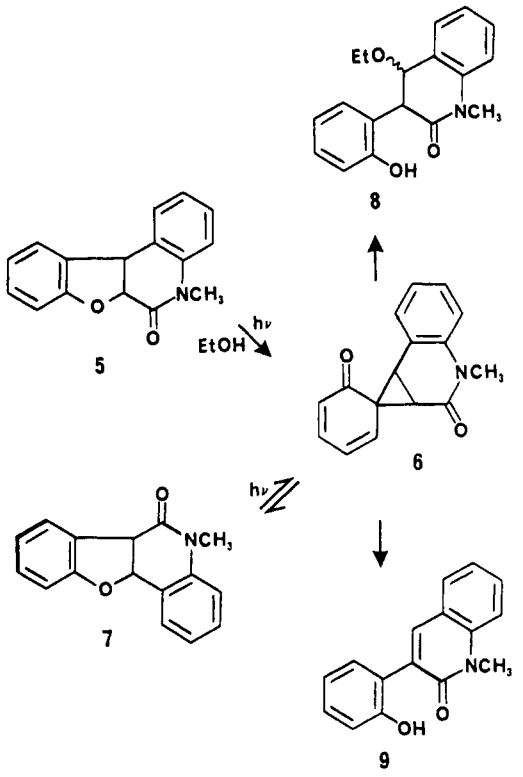
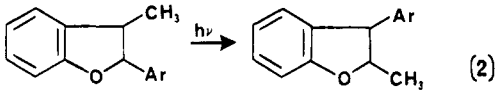
Scheme I



torearrangement results in the production of 2- and 4-substituted phenols. Woodward and Hoffmann suggested that phenyl allyl ether might undergo a [3,5] rearrangement to give 4-allylphenol.[16] However, Hammond and Carroll determined product composition resulting from 254-nm irradiation of 3-methyl-1-phenoxybut-2-ene and suggested the radical recombination mechanism.[17] They do not exclude the concerted mechanism, but point out that the observed product distribution would require five different concerted processes including the supposedly forbidden [3,3] rearrangement.

The photochemistry of benzodihydrofurans has received only limited attention. Spiro[cyclopropane-2′,4′-cyclohexadien-1′-ones] have been postulated to be intermediates in the conversion of 2-aryl-3-methylbenzodihydrofurans to 3-aryl-2-methylbenzodihydrofurans (eq 2).[19] A primary photoprocess involving homolytic

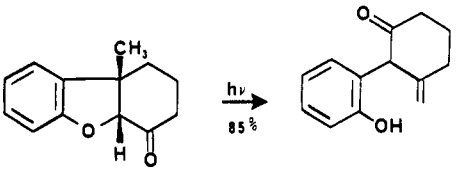


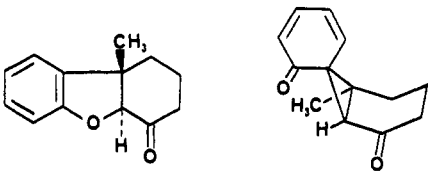
(2)

cleavage of the carbon(2)–oxygen bond was suggested because the rearrangement was found to be nonstereospecific. It is noteworthy that formation of an olefinic phenol analogous to **3** was not reported.

Recently, Kanaska and San-nohe have described the photorearrangement of benzodihydrofuran **5** to **7**, **8**, and **9** (Scheme I).[20] Rearranged benzodihydrofuran **7** also undergoes photorearrangement in ethanol to give phenols **8** and **9**. Spiro[cyclopropane-2′,4′-cyclohexadien-1′-one] **6** was proposed to be an intermediate in the formation of **7**, **8**, and **9**. Significantly, the trans isomer of **5** failed to undergo the photorearrangement.

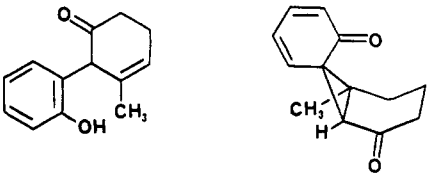
In a preliminary communication, we have reported the photoconversion of **10** to **11** in preparatively useful yield.[2] Under the same reaction conditions trans-fused epimer **12** remains unchanged. While the photorearrangement of **1a** to **3** cannot be





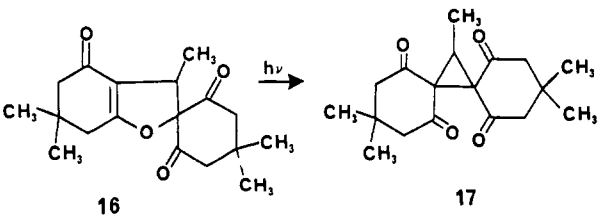
carried to completion using direct irradiation from a mercury arc lamp and Pyrex glassware, that with **10** is complete in several hours. Phenol **11** is isolated (and presumably exists during irradiation) as the internal hemiketal, which no longer bears an effective chromophore when Pyrex filters are used. Thus, potential photodecomposition is averted, and **11** cannot act as a light filter. We have studied the scope of rearrangements of type **10** → **11** from a preparative and mechanistic (flash photolysis) perspective and details of this work will be reported in due course.

The exclusive formation of **11** from **10**, with no endocyclic β,γ-enone **14** being detected, suggested that rearrangement oc-



curred via spiro[cyclopropane-2′,4′-cyclohexadien-1′-one] **13** rather than **15**. Intramolecular hydrogen atom transfer in **13** can occur only from the methyl substituent to give, after rearrangement, olefinic phenol **11**. The discovery of high regioselectivity (and, by implication, high stereoselectivity) for the photoreaction of **10** directly led to the supposition that photorearrangements of benzodihydrofurans of type **1** also might undergo highly stereoselective rearrangements to spiro[cyclohexadienones].

Cyclopropanes have been isolated from photoreactions of dihydrofurans.[21-25] For example, Ohkata and co-workers[21] have described the high-yield photorearrangement of dihydrofuran **16** to cyclopropane **17**.

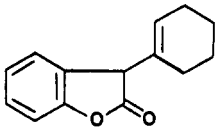


(16) Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 2511.
(17) Carroll, F. A.; Hammond, G. S. *Isr. J. Chem.* **1972**, *10*, 613; *J. Am. Chem. Soc.* **1972**, *94*, 7151.
(18) For a further representative selection from the literature of phenyl ether photochemistry, see: Pinhey, J. T.; Schaffner, K. *Aust. J. Chem.* **1968**, *21*, 2265. Schmid, K.; Schmid, H. *Helv. Chim. Acta* **1953**, *36*, 687. Houser, J. J.; Chen, M.-C.; Wang, S. S. *J. Org. Chem.* **1974**, *39*, 1387 and references cited therein. In the last paper, the photoisomerization of anisole to the three isomeric cresols is discussed. The formation of *m*-cresol is presumed to occur by photoisomerization of the intermediate 4-methyl-2,5-cyclohexadien-1-one.
(19) Schmid, E.; Frater, Gy.; Hansen, H.-J.; Schmid, H. *Helv. Chim. Acta* **1972**, *55*, 1625 and references cited therein.
(20) Kanaska, Y.; San-nohe, K. *Tetrahedron Lett.* **1980**, *21*, 3893.
(21) Ohkata, K.; Sakai, T.; Kubo, Y.; Hanafusa, T. *J. Org. Chem.* **1978**, *43*, 3070.
(22) McGreen, D. E.; Vinjie, M. G.; McDaniel, R. S. *Can. J. Chem.* **1965**, *43*, 1417.
(23) Scribe, P.; Nouet, C.; Wiemann, J. *Tetrahedron Lett.* **1970**, 4375.
(24) Scribe, P.; Wieman, J. *Bull. Soc. Chim. Fr.* **1971**, 2268.
(25) For related photorearrangements, see: Giezendanner, H.; Rosenkranz, H. J.; Hansen, H.-J.; Schmid, H. *Helv. Chim. Acta* **1973**, *56*, 2588. Burns, J. M.; Ashley, M. E.; Crockett, G. C.; Koch, T. H. *J. Am. Chem. Soc.* **1977**, *99*, 6924.

If spiro[cyclopropane] **2** is to be considered as an actual intermediate in the photoconversion of **1a** into **3** then the mechanism of rearrangement to **3** also must be elucidated. We have experimental evidence to support a thermal hydrogen atom transfer step.[26,27] Flash photolysis studies with **1** and a deuterium-labeled derivative have provided activation parameters and a deuterium isotope effect for the rearrangement **2** → **3**. The background and experimental data for this investigation will be described elsewhere.[3] For the purposes of this discussion, we will assume that rearrangements of type **2** → **3** occur by a thermal intramolecular hydrogen atom transfer from the cyclohexane ring to the cyclohexadienone oxygen atom.

Results and Discussion

Irradiation of benzodihydrofuran **1a**[28] in ether solution gives recovered **1a** and phenol **3**. The photoreaction mixture is separated by silica gel chromatography and crystalline **3** (mp 100–102 °C) is isolated in 73–84% yield based on recovered phenol. The structural assignment for **3** is based on IR, ^{1}H NMR, and mass spectral data and the conversion of **3** into lactone **18**.



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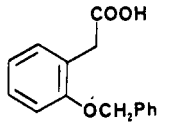

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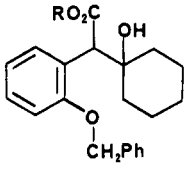
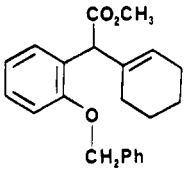


20a, R = H
b, R = CH_3



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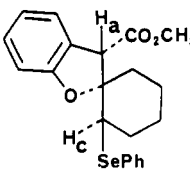
Proof of structure for **3** was obtained by unambiguous synthesis. The sodium salt of carboxylic acid **19**[29] on treatment with isopropyl magnesium bromide gives a dianion, which undergoes condensation with cyclohexanone to give alcohol **20a**. Esterification with diazomethane gives **20b**, and **20b** is converted to olefinic ester **21** by regiospecific dehydration with phosphorous pentoxide and Celite[30] in benzene. Catalytic hydrogenolysis of **21** gives phenol **3**, which is identical with **3** prepared by photorearrangement of **1a**.

Two mechanistic extremes can be considered for the photorearrangement of **1a** to spiro[cyclopropanecyclohexadienone] **2**. A long-lived diradical **4** formed by homolytic cleavage of the carbon(2)–oxygen atom bond in **1a** might be expected to lose stereochemistry at C(2) during the time required for radical recombination to give **2**. On the other hand, a concerted [1,3]-sigmatropic rearrangement from the photoexcited state of **1a** also would give **2**. While both suprafacial and antarafacial rearrangements of C(2) are possible, obvious geometric constraints in the respective transition states for rearrangement would seem to exclude the antarafacial process from further consideration. Thus, a concerted rearrangement of **1a** to **2** should occur with retention of C(2) stereochemistry. Hydrogen atom transfer in **2** to give **3** should occur with retention of stereochemistry at C(2). Optically active **1a** was prepared in order to determine the stereochemical fate of C(2) during the photorearrangement.

Ester **1a** is converted to the crystalline carboxylic acid **1b**[28] and resolution is performed with (*S*)-(−)-α-methyl-*p*-nitrobenzylamine.[31] Three crystallizations of the salt formed by mixing **1b** with the resolving agent followed by acidification and esterification of the resulting carboxylic acid gives resolved ester **1b**. The progress of the resolution is monitored by observing the ^{1}H NMR absorption of H_a, which appears as a distinct singlet for each of the two diastereoisomers of the salt of **1b**. The enantiomeric purity of the resolved ester is determined by use of the chiral NMR shift reagent tris[3-((heptafluoropropyl)hydroxymethylene)-*d*-camphorato]europium(III), i.e., Eu(hfc)$_3$.[32] ^{1}H NMR analysis of the racemate of **1a** with Eu(hfc)$_3$ reveals two singlets of equal intensity for H_a, while partially resolved **1a** shows these two singlets in a ratio of 8.3:1.

Irradiation of optically enriched **1a** in ether followed by chromatography gives recovered **1a** (43% isolated yield) and phenol **3** [41%, $[\alpha]^{24}_D$ −14.0° (*c* 2.9% in ether)]. ^{1}H NMR analysis of recovered **1a** with Eu(hfc)$_3$ reveals an enantiomeric ratio of 8.2:1 indicating that racemization of **1a** does not occur during irradiation. Because of an inability to separate ^{1}H NMR signals arising from enantiomers of **3**, we were not able to measure the enantiomeric purity of **3** directly. Instead, **3** was reacted with benzeneselenenyl chloride to give **22** in 70% yield. The structural



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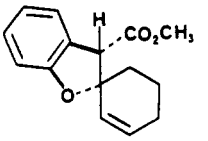

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assignment for **22** follows from the chemical shift for H_c (δ 3.58–3.37, multiplet), which is in accord with a hydrogen atom geminal to a selenium atom.[33] Furthermore, treatment of **22** with hydrogen peroxide gives olefin **23** in 94% isolated yield.

That **22** is indeed a single diastereoisomer was demonstrated by the observation that adding the achiral shift reagent tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium(III) to racemic **22** caused no line broadening. The enantiomeric purity of **22** generated from resolved **1a** was determined by use of the chiral reagent Eu(hfc)$_3$ and was found to be 8:1.

Thus, benzodihydrofuran **1a** undergoes photorearrangement to **3** with retention of optical activity. We presume that this rearrangement occurs with *retention* of C(2) chirality. Clearly, a long-lived diradical such as **4** is incompatible with these experimental results.

The unsensitized Pyrex-filtered irradiation of **1a** is of marginal preparative value in that the photoconversion into **3** cannot be carried to >50% completion. This limitation must be a result of the similarity of chromophores in **1a** and **3**. For this reason, the sensitized photorearrangement of **1a** was attempted in photo-

(26) The thermal hydrogen atom transfer in **2** to give phenol **3** is an example of an intermediate step in the well-known abnormal Claisen rearrangement of ortho-allylic phenols. For studies of the abnormal Claisen rearrangement, see: Marvell, E. N.; Anderson, R. D.; Ong, J. *J. Org. Chem.* **1962**, *27*, 1109. Habich, A.; Barner, R.; Roberts, R. M.; Schmid, H. *Helv. Chim. Acta* **1962**, *45*, 1943. Laver, W. M.; Johnson, T. A. *J. Org. Chem.* **1963**, *28*, 2913. Habich, A.; Barner, R.; von Philipsborn, W.; Schmid, H. *Helv. Chim. Acta* **1965**, *48*, 2281. Roberts, R. M.; Landolt, R. G. *J. Am. Chem. Soc.* **1965**, *87*, 2281; Roberts, R. M.; Greene, R. N.; Landolt, R. G.; Heyer, E. W. *Ibid.* **1965**, *87*, 2282. For a review of the "Abnormal Claisen Rearrangement and Related Sigmatropic Rearrangements", see: Hansen, H.-J. In "Mechanisms of Molecular Migrations"; Thyagarajan, B. S., Ed.; Wiley: New York, 1971; Vol. 3, p 177.

(27) For the possible involvement of a spiro[cyclopropane-2′,4′-cyclohexandien-1′-one] in the photochemistry of 2-*tert*-butyl-1,4-benzoquinone, see: Farid, S. *J. Chem. Soc., Chem. Commun.* **1970**, 303. An abnormal Claisen rearrangement is proposed for the conversion of the cyclohexadienone to an allylic hydroquinone. For a related photoreaction, see: Marvyama, K.; Kozuka, T. *Chem. Lett.* **1980**, 341.

(28) Schultz, A. G.; Napier, J. J.; Ravichandran, R. *J. Org. Chem.* **1983**, *48*, 3408.

(29) Schwenk, E.; Bloch, E. *J. Am. Chem. Soc.* **1942**, *64*, 3051.

(30) Phalnikar, N. L.; Nargund, K. S. *Ind. J. Chem.* **1963**, *14*, 736.

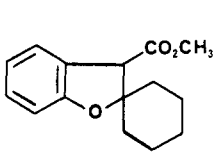
(31) Perry, C. W.; Brossi, A.; Deitcher, K. H.; Tautz, W.; Teitel, S. *Synthesis* **1977**, 492.

(32) Kainosho, M.; Ajisaka, K.; Pirkle, W. H.; Beare, S. D. *J. Am. Chem. Soc.* **1972**, *94*, 5924. Eu(hfc)$_3$ and Eu(fod)$_3$ are available from Aldrich Chemical Co., Inc.

(33) For a discussion of the factors that operate to control stereochemistry in conversions of type **3** → **22**, see: Schultz, A. G.; Sundararaman, P. *J. Org. Chem.*, in press.

chemically active solvent systems. Pyrex-filtered irradiation of **1a** in 20% freshly distilled anisole in ether for 84 h results in complete conversion of **1a** into phenol **3** in >90% yield. We believe that under these reaction conditions the light of highest energy transmitted by the Pyrex glass is absorbed mainly by anisole and that anisole functions as a sensitizer (either singlet or triplet state) for the conversion of **1a** → **3**.

Irradiation of **1a** in benzene containing 25% by weight of acetone results in formation of phenol **3** and rearranged dihydrofuran **24**. Dihydrofuran **24** is identical with the product



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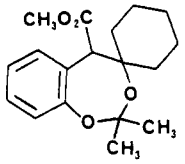
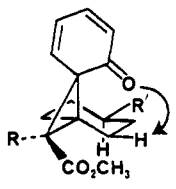


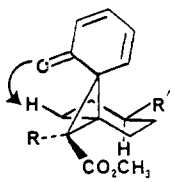
25

of Raney nickel hydrogenolysis of selenide **22**. That dihydrofuran **24** is formed from phenol **3** rather than **1a** was demonstrated by irradiation of phenol **3** in benzene–acetone to give **24** and a small quantity of a new compound, tentatively assigned as the acetone–phenolic olefin **3** addition product **25**. Interestingly, rearranged dihydrofuran **24** is stable to these and direct irradiation conditions.

Resolved **1a** was irradiated in benzene–acetone solution. ^{1}H NMR analysis of the photoreaction mixture revealed that unreacted **1a**, phenol **3**, rearranged benzodihydrofuran **24**, and the acetone addition product **25** were present. Phenol **3** could be obtained by silica gel chromatography; conversion of **3** to selenide **22** and ^{1}H NMR analysis of **22** with Eu(hfc)$_3$ demonstrated that optical activity is retained. If the conversion of **1a** into **3** using these conditions involves triplet sensitization by acetone ($E_T \sim$ 78 kcal/mol),[34] then rearrangement of **1a** from the triplet manifold must be as stereoselective as that occurring from direct irradiation of **1a**. A more meaningful study of the effect of triplet sensitization on the photochemistry of **1a** was considered to be technically difficult because of the anticipated high E_T for **1a**.

Diastereoselectivity of Spiro[cyclopropane-2′,4′-cyclohexadien-1′-one] Formation. It has already been noted that two diastereoisomers can, in principle, be formed during the photoconversion of **1a** into **2**. These diastereoisomers are represented in structures **26a** and **27a**. In **26**, the ester and cyclohexadienone

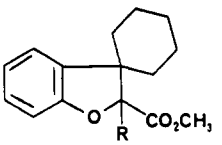




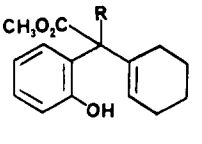
26a, R = R′ = H — **27**
b, R = CH$_3$; R′ = H
c, R = C$_2$H$_5$; R′ = H
d, R = H; R′ = CH$_3$

carbonyl groups are syn oriented; in **27**, these groups are anti oriented. Both **26a** and **27a** may undergo hydrogen atom transfer to give the same phenolic olefin **3**. Thus, the observation of diastereoselection in formation of **2** (i.e., **26a** or **27a**) by way of product formation is not possible in this parent system.

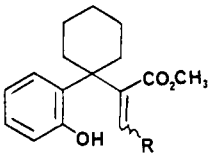
The C(2) alkyl substituted derivatives **28a** and **28b** provide a simple test of the involvement of diastereoisomer type **27**. Hydrogen atom transfer in the intermediates **26b** and **26c** would be expected to give only **29a** and **29b**, respectively, while **27b** and **27c** could rearrange to **30a** and **30b** (by involvement of the methyl and ethyl substituents), as well as **29a** and **29b**. Generation of photoproduct type **30** would be highly suggestive of the involvement of intermediate spiro[cyclopropane-2′,4′-cyclohexadien-1′-one] type **27**.



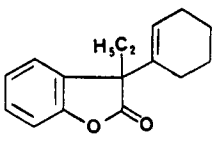
28a, R = CH$_3$
b, R = C$_2$H$_5$



29a, R = CH$_3$
b, R = C$_2$H$_5$



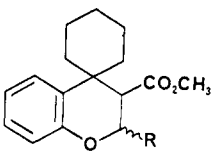
30a, R = H
b, R = CH$_3$



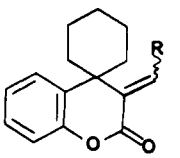
31

Reaction of carboxylic acid **1b** with lithium tetramethylpiperidide (2 equiv) in THF gives a dianion that is alkylated with methyl iodide or ethyl iodide in excellent yield.[28] The alkylated carboxylic acids are converted into methyl esters **28a** and **28b** by esterification with diazomethane. Irradiation of **28a** in ether for 72 h gives crystalline phenol **29a** in 70% yield along with recovered **28a**. Irradiation of **28b** gives an approximately equimolar mixture of **29b** and **28b**. Isolation of **29b** is complicated by partial cyclization to lactone **31** during silica gel chromatographic separation of reaction components. Treatment of the mixture of **29b** and **28b** with *p*-toluenesulfonic acid in methylene chloride gives lactone **31** in excellent yield.

Acrylic esters **30** are very clearly absent from photoreactions of **28a** and **28b**. Furthermore, pyrans **32** and δ-lactones **33**, which



32a, R = H
b, R = CH$_3$



33a, R = H
b, R = CH$_3$

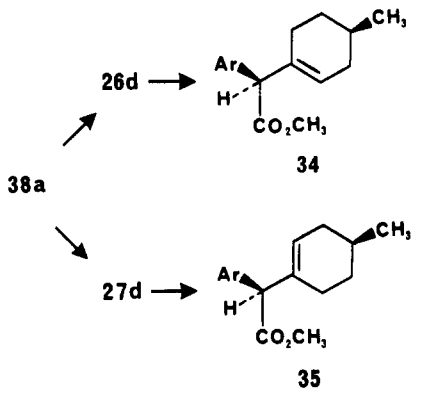
are potentially derivable from **28a** and **28b**, also are not observed. It should be noted, however, that conversion of **30** back to the starting benzodihydrofuran **28** by photochemical intramolecular phenol–olefin addition (cf. **3** → **24**) cannot be ruled out.

The substituent study just presented is not a particularly rigorous test of the involvement of spiro[cyclopropane-2′,4′-cyclohexadien-1′-ones] of type **27**. Besides the caveat already noted, it could be argued that orientational factors for hydrogen atom rearrangement in **27b** and **27c** might lead to exclusive conversion of **27b** and **27c** into **29**, rather than **30**.[35] We, therefore, sought a more sensitive test of diastereoselectivity.

The C(4) methyl substituted derivatives **38** and **39** provide such a test system. Formation of **26d** or **27d** from benzodihydrofuran **38** and subsequent hydrogen atom transfer would generate a diastereoisomerically different phenolic olefin from each spiro[cyclopropane-2′,4′-cyclohexadien-1′-one]; e.g., **26d** would give **34** and **27d** would give **35**. Thus, a preference for photorearrangement to one or the other spirocyclopropyl intermediate would be revealed by the observation of a preference for formation of one or the other phenolic olefin product. It follows that if there is a preference for product formation with **38a**, then irradiation of the other diastereoisomer, **39a**, should result in a preference

(34) Gordon, A. J.; Ford, R. A. "The Chemist's Companion" Wiley-Interscience: New York, 1972; p 351.

(35) The experimentally determined entropy of activation for the conversion **2** → **3** substantiates the supposition drawn from the observation of molecular models, that little reorganization of **2** is required to reach the transition state for hydrogen atom transfer; see ref 3. This may not be the case for hydrogen atom transfer from the freely rotating methyl or ethyl groups in **27b** and **27c**.



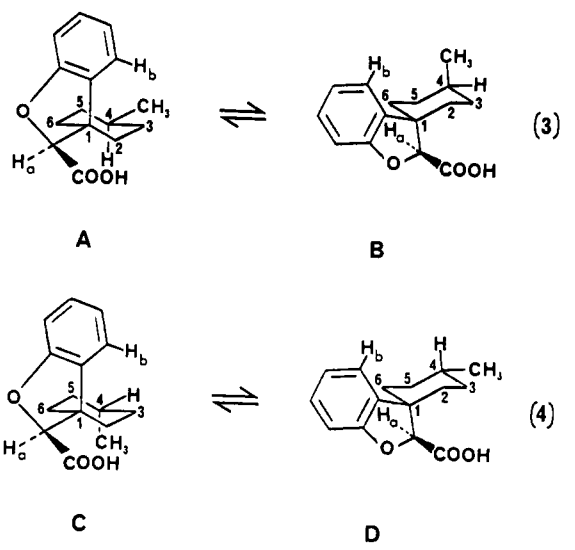
for formation of the other diastereoisomeric phenolic olefin.

The preparation of benzodihydrofurans **38a** and **39a** is outlined in Scheme II. Condensation of a slight excess of the sodium salt of phosphonate **36**[28] with 4-methylcyclohexanone gives aryl vinyl ether **37** in quantitative crude yield (based on starting 4-methylcyclohexanone). Without purification, **37** is irradiated with Pyrex-filtered light in benzene–methanol solution to give an equimolar mixture of **38a** and **39a** in 89% isolated yield. Separation of the two diastereoisomers is carried out by preparative HPLC. The more mobile isomer, **38a**, is crystalline (mp 93–94 °C), while the less mobile isomer, **39a**, is isolated as a colorless oil. Both compounds are converted into highly crystalline carboxylic acids [e.g., **38b** (mp 151–152 °C) and **39b** (mp 127–129 °C)] for purposes of (1) purification for further photochemical study and (2) configurational assignment by ^{1}H NMR spectroscopy.

Assignment of configuration in **38** and **39** is based on well-defined anisotropic effects of the C–C bonding electrons in cyclohexane rings.[36a] The shielding and deshielding zones for the C–C bond are such that protons within an equatorial region of a cyclohexane ring are consistently found further downfield than protons located within an axial region.

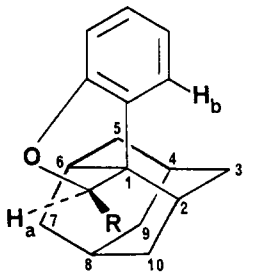
The underlying assumption in the argument for assignment of configuration by ^{1}H NMR spectroscopy is that the C(4) methyl substituent in **38b** and **39b** will alter the equilibrium population of chair conformers with respect to that equilibrium for **1b**.[36b] That is, for the configurational isomer **38b**, in which the aryl group is cis to the C(4) methyl group, there should be relatively more of the conformer type A (eq 3) than there is in the parent system **1b** (e.g., the conformer with an axial aryl group). Conversely, for the corresponding trans isomer **39b**, there should be relatively more of the conformer type D (eq 4) with equatorial methyl and aryl groups. As can be appreciated in the structural representations A–D, H_b in A and C is in an axial zone while H_a is in an equatorial zone. In B and D, the spatial environment of H_a and H_b is opposite to that in A and C; e.g., H_a is in an axial zone and H_b is in an equatorial zone.

Chemical shift data for H_a and H_b in **1b**, **38b**, and **39b** are shown in Table I. Also recorded are chemical shifts for these protons in the 2-adamantanone derivative **40**[2] and the unsubstituted benzodihydrofuran-2-carboxylic acid **41**.[2] The chemical shift of δ 5.25 for H_a in **41** serves as a reference point, from which the anisotropic effects of the spiro[cyclohexane] ring can be examined. In **1b**, **38b**, **39b**, and **40**, the bond to H_a eclipses the cyclohexane ring C(1)–C(6) bond, which results in the placement of H_a within

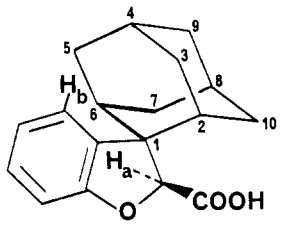


a shielding zone of the C(1)–C(6) bond. This produces an important anisotropic effect as demonstrated by the fact that H_a absorbs at higher field in **1b**, **38b**, and **39b** than in **41**. However, H_a also experiences anisotropic effects from other cyclohexane ring bonds, especially the C(5)–C(6) bond. In conformation type A and C, H_a is located within the deshielding zone of the C(5)–C(6) bond, while, in B and D, H_a is nearer the shielding zone of this bond. The rationale based on the effect of the C(4) methyl substituent on chair–chair equilibria accounts for the observed variation in chemical shift for H_a in the series **1b**, **38b**, and **39b**.

The rigid adamantane derivative **40** serves as a composite structure containing both cyclohexane ring conformer types A/C and B/D; cf. representations **40** and **40′**. To a first approximation,



40, R = COOH



40′

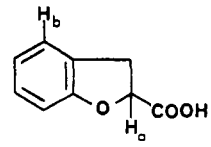
this system represents a static model of **1b**, **38b**, and **39b**, in which the chair–chair equilibrium distribution is 1:1. The chemical shift for H_a in **40** occurs at much lower field than that for **1b**, **38b**, and **39b**. This observation suggests that the major equilibrium conformer for the cyclohexane derivatives is the B/D type, in which the aryl group is in an equatorial position. This conformational preference seems entirely reasonable in light of the high *A* value (~2.6 kcal/mol) measured for a freely rotating phenyl substituent.[37] This "steric effect" should be magnified in **1b**, **38b**, and **39b** because the rigid spiro-ring fusion in these derivatives results in intensified 1,3-diaxial interactions between the phenyl substituent and C(3) and C(5) in conformers A/C.

It is noteworthy that the relative chemical shifts for the C(4) methyl substituent in **38b** and **39b** are consistent[36a] with the configurational assignment and our conformational analysis. Thus, the C(4) methyl group appears at δ 0.95 for **38b** (mainly the axial methyl conformer B) and 1.03 for **39b** (mainly the equatorial conformer D).

Turning to H_b, we note that the anisotropic effects of the cyclohexane ring C(1)–C(6) and C(1)–C(2) bonds are constant for any conformer in the series **1b**, **38b**, and **39b**. However, in conformer type B/D, H_b is located in the deshielding zones of the

(36) (a) For example, see: Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectroscopic Identification of Organic Compounds 4th Ed"; Wiley: New York, 1981; pp 189–190. However, there are special exceptions to this rule, e.g.: Williamson, K. L.; Johnson, W. S. *J. Am. Chem. Soc.* **1961**, *83*, 4623. For examples of the anisotropic effect of the cyclohexane ring on the chemical shifts of rigidly positioned methyl substituents, see: Zürcher, R. F. *Helv. Chim. Acta* **1963**, *46*, 2054. (b) Lemieux, R. V.; Kullnig, R. K.; Burnstein, H. J.; Schneider, W. G. *J. Am. Chem. Soc.* **1958**, *80*, 6098. For a discussion of the application of ^{1}H NMR techniques to configurational and conformational assignments in cyclohexane ring systems, see: Anet, F. A. L.; Anet, R. "Determination of Organic Structures by Physical Methods"; Nachod, F. C., Zuckerman, J. J., Eds.; Academic Press: New York, 1971; Vol. 3, Chapter 7.

(37) Eliel, E. L.; Rerick, M. N. *J. Am. Chem. Soc.* **1960**, *82*, 1367.



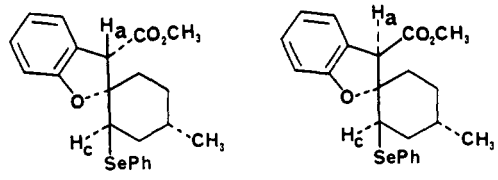
41

C(2)–C(3) and C(4)–C(5) bonds, while H_b in conformer type A/C resides in a shielding zone described by the C(2)–C(3), C(3)–C(4), and C(4)–C(5) bonds. Again, the chemical shifts observed for H_b in the conformationally mobile series **1b**, **38b**, and **39b** are fully in accord with these stereochemical observations.

Interestingly, the chemical shift for H_b in **40** occurs at very low field, as a result of deshielding by the adamantane ring C(4)–C(9) bond. This kind of anisotropy has no counterpart in conformers A, B, and D. However, the C(4)–C(methyl group) bond in C is equivalent to the C(4)–C(9) bond in **40**. The large downfield shift for H_b in **39b** relative to **1b** presumably is a result of deshielding by the C(4)–C(methyl group) bond.

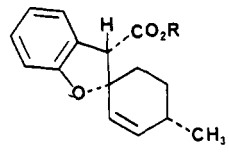
With the configurational assignment for **38** and **39** secure, we were able to examine the diastereoselectivity of the benzodihydrofuran photorearrangement. Pyrex-filtered irradiation of **38a** carried to partial completion gives mainly phenolic olefin **34**, which is isolated by preparative use of analytical HPLC. Irradiation of **39a** under identical conditions gives the isomeric phenolic olefin **35**. While ^1H and ^{13}C NMR spectra for **34** and **35** are very similar, a particularly revealing feature is the resonance for the phenolic hydrogen atom absorbing as a sharp singlet at δ 7.51 for **34** and 7.56 for **35**. These signals disappear on addition of D_2O; both singlets can be clearly observed in mixtures of **34** and **35**. We can set the minimum level of isomer detectability at ~5%; remarkably, the degree of diastereoselection in photorearrangement of **38a** and **39a** must be ≥95%.

The assignment of configuration of **34** and **35** follows from a consideration of the benzeneselenenyl chloride cyclofunctionalization of these phenolic olefins.[33] Treatment of **34** with benzeneselenenyl chloride at −78 °C gives a mixture of selenides **43** and **42** and starting material **34** in a ratio of 18:1:1. Selenide **43**

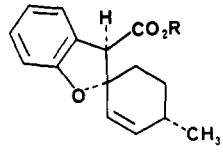


42

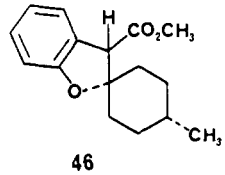
43



44a, R=CH₃
b, R=H



45a, R=CH₃
b, R=H



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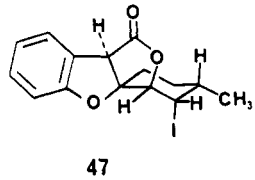
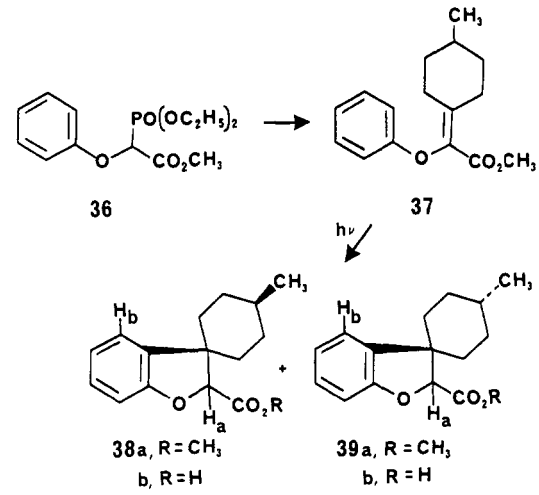


47

(mp 84 °C) is isolated in 80% yield. Similar treatment of **35** gives a mixture of selenides **42** and **43** in a ratio of 20:1, as determined by ^1H NMR analysis. Selenide **42** (mp 69 °C) is isolated in 94% yield by silica gel flash chromatography. Both **42** and **43** are cleanly converted to the same benzodihydrofuran **46** on treatment with Raney nickel. Furthermore, selenides **42** and **43** are converted to olefinic esters **44a** and **45a**, respectively, on oxidation with 30% hydrogen peroxide. Saponification of each ester **44a** and **45a**

Scheme II



36 37

38a, R=CH₃
b, R=H

39a, R=CH₃
b, R=H

Table I. ^1H NMR Chemical Shifts for Benzodihydrofurans

compd	chemical shift, δ	
	H_a	H_b
1b	4.88	7.16
38b	4.99	7.10
39b	4.76	7.47
40	5.36	7.68
41	5.25	7.24

produces the same equilibrium mixture of carboxylic acids **44b** and **45b** in a ratio of 2:5. This carboxylic acid mixture gives a single iodo lactone **47** along with an ca. equimolar mixture of recovered carboxylic acids. The crystalline iodo lactone **47** returns carboxylic acid **45b** (92% yield) on reductive–elimination with zinc dust in ethanol. This recovered carboxylic acid is converted into methyl ester **45a** on esterification with diazomethane.

It is clear that the olefinic carboxylic acid **45b** regenerated from iodo lactone **47** must have the carboxylic acid group syn oriented to the C–C double bond.[33] This, in turn, demands that the selenide **43** (the precursor to olefin **45a**) must have the carbonyl group syn to the phenylselenyl group. Thus, the diastereoselectivity of the photorearrangement **38a** → **34** and **39a** → **35** is demonstrated; the quantitative analysis associated with the phenylselenylation of **34** and **35** establishes the degree of diastereoselectivity as ~95%.

The ^1H NMR chemical shifts of the ester methyl group in selenide **42** at δ 3.73 and selenide **43** at δ 3.36 are consistent with the chemically based configurational assignments. In **42** the carbomethoxy group is anti to the phenylselenyl group and absorbs at a normal position for methyl esters. In **43**, the carbomethoxy group is shielded by the phenylselenyl group, which results in a large upfield shift for the ester methyl resonance. Chemical shifts for the ester methyl group (as well as shifts for H_a and H_c; see Experimental Section) in **42** and **43** may now be used as diagnostic tools for characterization of stereocontrol in related benzodihydrofuran photorearrangements.

Conclusion

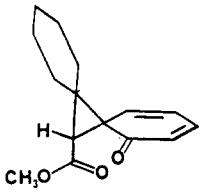
We have demonstrated that benzodihydrofuran-2-carboxylic acid ester **1a** undergoes a highly stereoselective (stereospecific within the error limits of analysis by ^1H NMR spectroscopy) photorearrangement to phenol **3**. The primary photochemical step is best described as a concerted 1,3-migration of C(2) to give the spiro[cyclopropane-2′,4′-cyclohexadien-1′-one] **2**. A thermal hydrogen atom transfer in **2** generates phenol **3**.

Labeling studies with derivatives of **1** (e.g., **38a** and **39a**) demonstrate that primarily one of two possible diastereoisomeric spiro[cyclopropanecyclohexadienones] is involved in the hydrogen atom transfer step. The effective intermediate has been identified as type **26** with the ester and cyclohexadienone carbonyl groups syn oriented. Significantly, this orientation is identical with that suggested by regiospecific conversions **28a** → **29a** and **28b** → **29b**

but opposite to that implied by the conversion of the related benzodihydrofuran **10** into **11**, via the proposed intermediate **13**.

The origins of the diastereoselectivity are not completely understood at present.[38] Possibly, both diastereoisomeric spiro[cyclopropane-2′,4′-cyclohexadien-1′-ones] form in a reversible manner. If so, then hydrogen transfer in **13** might occur with reasonable efficiency, while the diasteroisomer **15** might revert to starting material. This explanation seems reasonable in light of orientational differences for hydrogen atom transfer in **13** and its diastereoisomer. However, large differences in rates of hydrogen atom transfer in **26d** and **27d** are difficult to explain by this kind of rationale.

Alternatively, it is possible that there is a kinetic preference for formation of spiro[cyclopropane-2′,4′-cyclohexadienone] of type **26**, rather than **27**. It may be significant that **26** has conformation **48** available. In **48**, the cyclopropyl ring is orthogonal



48

to the plane containing the two carbonyl groups. Perhaps there is some nonbonded electronic stabilization of this electronic array, which is reflected in the transition state for formation of **26**. Attractive nonbonded interactions have been used to explain the stabilities of *cis*-difluoroethylene and related six-electron systems.[39] It is perhaps significant that this kind of conformer is not available to intermediates generated by rearrangement of ketone **10**. Experiments designed to answer some of the questions raised by the present study are in progress.

Experimental Section

Instrumentation, Solvents, and General Procedures.[40] **Irradiation of Spiro[benzofuran-2(3*H*),1′-cyclohexane]-2-carboxylic Acid Methyl Ester (1a).**[28] A solution of benzodihydrofuran **1a** (2.10 g, 8.6 mmol) in ether (250 mL, 0.034 M) was purged with argon for 30 min and irradiated with Pyrex-filtered light for 72 h. Removal of solvent gave an oil, ^{1}H NMR analysis of which showed it to be a mixture of **1a** and **3**. Column chromatography (silica gel, methylene chloride–hexanes 1:10, then methylene chloride–hexanes 1:3) gave two components. The more mobile fraction was the starting benzodihydrofuran **1a** (1.4 g, 67%). The less mobile fraction was crystallized from ethyl acetate–hexanes to give α-(1-cyclohexenyl)-2-hydroxybenzeneacetic acid methyl ester (**3**) (0.52 g, 24%, mp 100–101 °C): IR ($CHCl_3$) 2.95, 3.44, 5.88, 6.78, 7.01, 8.36 μm; UV (ether) λ_{max} (ε) 282 nm (2000), 276 (2200); ^{1}H NMR δ 1.00–1.80 (m, 4 H), 2.30–1.80 (m, 4 H), 3.73 (s, 3 H), 4.24 (s, 1 H), 5.53 (br s, 1 H), 6.70–7.30 (m, 4 H), 7.57 (s, 1 H); mass spectrum, *m/e* (relative intensity) 246 (M^+, 64), 214 (69), 157 (100).

Anal. Calcd for $C_{15}H_{18}O_3$: an acceptable analysis could not be obtained.

3-(1-Cyclohexenyl)-2-oxo-3*H*-benzofuran (18). A mixture of **3** (10 mg, 0.04 mmol) and *p*-toluenesulfonic acid (2 mg) in benzene (0.3 mL) was stirred at room temperature for 22 h. The reaction mixture was poured into ether (30 mL), washed with 1 N $NaHCO_3$ (2 × 10 mL) and brine (10 mL), and dried ($MgSO_4$). Removal of solvent gave lactone **18** (9 mg, 100%), homogeneous by TLC (silica gel, methylene chloride, R_f 0.62): IR (neat) 3.40, 5.51, 6.19, 6.79, 6.89, 9.45 μm; ^{1}H NMR δ 1.60–2.40 (m, 8 H), 4.23 (s, 1 H), 5.77 (br s, 1 H), 7.00–7.40 (m, 4 H).

α-(1-Hydroxycyclohexyl)-2-(benzyloxy)benzeneacetic Acid (20a). To a solution of 2-(benzyloxy)benzeneacetic acid (**19**)[29] (242 mg, 1.0 mmol) in methanol (1.0 mL) was added $NaHCO_3$ (84 mg, 1.0 mmol), and the mixture was stirred at room temperature for 48 h. Removal of solvent and vacuum drying at room temperature for 6 h gave the sodium salt of the carboxylic acid **19** as a white solid. The sodium salt was added to a solution of isopropyl magnesium bromide (1 mmol) in ether (0.5 mL) at room temperature. The resulting solution was refluxed for 30 min and cooled to 0 °C. A solution of cyclohexanone (87.4 mg, 0.095 mL, 0.91 mmol) in ether (0.5 mL) was added, and a white precipitate formed. The mixture was stirred at 0 °C for 3 h and at room temperature for 12 h. The reaction was quenched at 0 °C by the addition of 2 N hydrochloric acid (2 mL). Water (20 mL) was added and the mixture was extracted with ether (2 × 30 mL). The combined ether layers were extracted with 2 N $NaHCO_3$ (3 × 15 mL). The combined base washes were acidified with 1 N HCl and extracted with ether (3 × 30 mL). The combined ether extracts were washed with brine and dried ($MgSO_4$). Removal of solvent and ^{1}H NMR spectral analysis of the residual yellow oil (235 mg) indicated that a mixture of **19** and **20a** was present. The oil was dissolved in methanol (10 mL) and H_2SO_4 (2 drops). The reaction was stirred at room temperature for 6 h, after which the resulting solution was diluted with ether (30 mL), washed with 1 N $NaHCO_3$ (3 × 15 mL) and brine (15 mL), and dried ($MgSO_4$). Removal of solvent under reduced pressure gave the methyl ester of **19** (89 mg, 35%; ^{1}H NMR δ 3.57 (s, 3 H), 3.63 (s, 2 H), 7.28 (s, 5 H), 6.70–7.50 (m, 4 H)). The base washes were acidified with 2 N HCl and extracted with ether (3 × 30 mL). The combined ether extracts were washed with brine and dried ($MgSO_4$). Removal of solvent gave **20a** (99 mg, 29%): IR (neat) 3.00–4.00, 3.40, 5.88, 6.26, 6.73, 6.94 μm; ^{1}H NMR δ 0.9–1.90 (m, 11 H), 4.37 (s, 1 H), 5.02 (s, 2 H), 7.25 (s, 5 H), 6.75–7.60 (m, 4 H).

α-(1-Hydroxycyclohexyl)-2-(benzyloxy)benzeneacetic Acid Methyl Ester (20b). To a solution of **20a** (99 mg, 0.29 mmol) in ether (2 mL) was added excess diazomethane in ether. After 15 min the excess diazomethane was consumed by the additon of acetic acid. Ether (30 mL) was added, and the solution was washed with 1 N $NaHCO_3$ (3 × 10 mL) and brine (10 mL) and dried ($MgSO_4$). Removal of solvent gave **20b** (98 mg, 95%): IR (neat) 2.90, 5.85, 6.24, 6.73, 6.92 μm; ^{1}H NMR δ 0.9–1.90 (m, 11 H), 3.60 (s, 3 H), 4.38 (s, 1 H), 5.05 (s, 2 H), 7.30 (s, 5 H), 6.70–7.70 (m, 4 H).

α-(1-Cyclohexenyl)-2-(benzyloxy)benzeneacetic Acid Methyl Ester (21). Celite (200 mg) and phosphorous pentoxide (110 mg, 0.77 mmol) were added to a solution of **20b** (48 mg, 0.14 mmol), and the mixture was stirred under N_2 for 2 h. Anhydrous ether (30 mL) was added and the solids were removed by filtration. The filtrate was washed with 1 N $NaHCO_3$ (2 × 10 mL) and brine (10 mL) and dried ($MgSO_4$). Evaporation of solvent gave an oil (47 mg), which was chromatographed (silica gel, ethyl acetate) to afford pure **21** (34 mg, 75%, R_f 0.64): IR (neat) 3.40, 5.78, 6.21, 6.73, 6.89, 8.07 μm; ^{1}H NMR δ 1.10–1.80 (m, 4 H), 1.80–2.20 (m, 4 H), 3.60 (s, 3 H), 4.69 (s, 1 H), 5.05 (s, 2 H), 5.57 (br s, 1 H), 6.70–7.60 (m, with sharp peak at 7.30, 9 H).

α-(1-Cyclohexenyl)-2-hydroxybenzeneacetic Acid Methyl Ester (3). A mixture of **21** (15 mg, 0.045 mmol) and palladium on carbon (5%, 10 mg) in methanol (1 mL) was stirred under 1 atm of hydrogen for 45 min. The mixture was diluted with ether and filtered through Celite. Concentration of the filtrate and chromatography (silica gel, methylene chloride) of the residue (12 mg) afforded **3** (10 mg, 91%, R_f 0.35). Crystallization from ethyl acetate–hexanes gave a crystalline solid, whose melting point (100–101 °C) was not depressed when mixed with **3** obtained from photorearrangement of **1a** (vide supra). This material also was identical (IR, NMR, TLC) with that obtained from photolysis of **1a**.

Resolution of 1b. To a solution of (S)-(−)-α-methyl-*p*-nitrobenzylamine[31] (455 mg, 2.81 mmol) in ether (10 mL) was added **1b**[28] (637 mg, 2.75 mmol). The mixture was heated on a steam bath and a minimum amount of methylene chloride was added. The solution was cooled to room temperature and after 4 h the crystalline salt was isolated by filtration (866 mg, 80%, mp 147–164 °C). Recrystallization from methylene chloride at room temperature (3 h) returned 619 mg of the salt. A second recrystallization gave 302 mg of the salt; ^{1}H NMR analysis revealed that the salt was a mixture of two diastereomers by integration of the furan methine (H_a) signals at δ 4.52 and 4.47 (8:1). The salt was dissolved in 6 N hydrochloric acid (30 mL), and the solution was extracted with ether (3 × 30 mL). The combined organic solution was washed with brine (30 mL) and dried ($MgSO_4$). Removal of solvent under vacuum gave **1b** (110 mg, 17%).

Preparation of Optically Active 1a. Resolved acid **1b** (110 mg, 0.46 mmol) was esterified with diazomethane. The crude ester **1a** was suitable for further operations (116 mg, 100%), $[\alpha]^{24}_D$ −40.1° (*c* 1.4% in ether).

Irradiation of (−)-1a in Ether. A solution of (−)-**1a** (48 mg, 0.20 mmol) in ether (15 mL, 0.013 M) in four sealed tubes was irradiated for 72 h. Removal of solvent gave an oil, which was shown by ^{1}H NMR analysis to be an ca. equimolar mixture of **1a** and **3**. Chromatography (silica gel, methylene chloride) gave **1a** (21 mg, 44%, R_f 0.73) and **3** (20 mg, 42%, R_f 0.43), $[\alpha]^{24}_D$ −14.0° (*c* 2.9% in ether).

NMR Chemical Shift Experiment with 1a (Recovered from Photolysis of (−)-1a in Ether). To **1a** (21 mg, 0.085 mmol) in $CDCl_3$ (0.5 mL) was added $Eu(hfc)_3$[32] (10 mg, 0.0084 mmol). ^{1}H NMR showed the furan

(38) For some related hydrogen atom rearrangements, see: Croce, P. A. *J. Heterocycl. Chem.* **1976**, *13*, 1109. Chiericato, M.; Croce, P. A.; Licandro, E. *J. Chem. Soc., Perkin Trans. 1* **1979**, 211. Tsuge, O.; Noguchi, M.; Moriyama, H. *Heterocycles* **1981**, *16*, 209; **1982**, *19*, 1823.

(39) Epiotis, N. D. *J. Am. Chem. Soc.* **1973**, *95*, 3087.

(40) For this information, see ref 33.

methine (H_a) resonance as two singlets at δ 5.81 and 5.76 in a ratio of 1:8.2 by repetitive integration.

NMR Chemical Shift Experiment with Racemic 1a. To racemic **1a** (15 mg, 0.061 mmol) in $CDCl_3$ (0.5 mL) was added $Eu(hfc)_3$[32] (20 mg, 0.017 mmol). ^1H NMR showed the furan methine resonance as two singlets at δ 6.42 and 6.33 in a ratio of 1:1.

NMR Chemical Shift Experiment with (−)-1a. To (−)-**1a** (14 mg, 0.057 mmol) in $CDCl_3$ (0.5 mL) was added $Eu(hfc)_3$[32] (10 mg, 0.0084 mmol). ^1H NMR showed the furan methine (H_a) resonance as two singlets at δ 5.94 and 5.88 in a ratio of 1:8.3 by repetitive integration.

Spiro[benzofuran-2(3*H*),1′-(2′-phenylseleno)cyclohexane]-3-carboxylic Acid Methyl Ester (22). To a solution of **3** (25 mg, 0.10 mmol) in methylene chloride (1 mL) at −78 °C was added a solution of benzeneselenenyl chloride (22 mg, 0.12 mmol) in methylene chloride (1 mL) over 6 min. The solution was stirred at −78 °C for 1 h, and 1 N $NaHCO_3$ (1 mL) was added. The mixture was warmed to room temperature and poured into methylene chloride (30 mL). The methylene chloride layer was washed with water (10 mL) and brine (10 mL) and dried ($MgSO_4$). Removal of solvent and chromatography (silica gel, methylene chloride) gave **22** as a yellow oil (23 mg, 70%): IR (neat) 3.40, 5.72, 6.19, 6.78, 6.82, 6.95, 8.02 μm; ^1H NMR δ 1.30–2.50 (m, 8 H), 3.37–3.58 (m, 1 H), 3.73 (s, 3 H), 4.62 (s, 1 H), 6.60–7.40 (m, 7 H), 7.40–7.60 (m, 2 H); mass spectrum, *m/e* (relative intensity) 404 (0.7), 403 (0.7), 402 (2.9), 400 (1.5), 399 (0.7), 398 (0.5), 185 (100).

NMR Chemical Shift Experiment with Racemic 22. To a solution of **22** (12 mg, 0.03 mmol) in $CDCl_3$ was added $Eu(hfc)_3$[32] (18 mg, 0.015 mmol). ^1H NMR showed the furan methine (H_a) resonance as two singlets at δ 5.73 and 5.60 in a ratio of 1:1 and the carbomethoxy resonance as two singlets at δ 4.33 and 4.27 in a ratio of 1:1. To a separate solution of **22** (14 mg, 0.034 mmol) in $CDCl_3$ was added $Eu(fod)_3$[32] in portions, and the ^1H NMR spectrum was observed after each addition. In all spectra the furan methine (H_a) and the carbomethoxy resonances were singlets. The results are present below:

$Eu(fod)_3$ added, mg	δ (H_a)	δ OCH_3
0	4.62	3.73
6	5.80	4.20
12	6.08	4.72
24	6.99	5.36
36	7.59	5.72
46	8.22	6.18
57	8.72	6.50

Preparation of (−)-22. Prepared from (−)-**3** as described for the preparation of the racemate (70%), $[\alpha]^{24}_D$ −69° (*c* 0.8% in CH_2Cl_2).

NMR Chemical Shift Experiment with (−)-22. To a solution of (−)-**22** (18 mg, 0.045 mmol) in $CDCl_3$ was added $Eu(hfc)_3$[32] (40 mg, 0.034 mmol). ^1H NMR showed the carbomethoxy resonance as two singlets at δ 4.64 and 4.58 in a ratio of 8:1 and the furan methine resonance as two singlets at δ 6.40 and 6.13 in a ratio of 8:1 by repetitive integration.

Spiro[benzofuran-2(3*H*),1′-cyclohex-2′-ene]-3-carboxylic Acid Methyl Ester (23). To a solution of **22** (26 mg, 0.065 mmol) in THF (0.2 mL) at 0 °C was added hydrogen peroxide (30%, 0.050 mL). The resulting solution was stirred at room temperature for 20 h and then poured into ether (30 mL) and 1 N $NaHCO_3$ (10 mL). The ether layer was washed with brine (10 mL) and dried ($MgSO_4$). Removal of solvent and chromatography (silica gel, methylene chloride) gave **23** as a colorless oil (15 mg, 94%, R_f 0.70): IR (neat) 3.42, 5.73, 6.12 μm; ^1H NMR δ 1.40–2.30 (m, 6 H), 3.73 (s, 3 H), 4.15 (s, 1 H), 5.68–6.19 (m, 2 H), 6.70–7.60 (m, 4 H); decoupling experiment, irradiation of the signal at δ 2.08 causes the olefinic region to collapse to a quartet (δ 6.06, 5.82, J = 10 Hz); mass spectrum, *m/e* (relative intensity) 244 (M^+, 24), 212 (100), 185 (43).

Spiro[benzofuran-2(3*H*),1′-cyclohexane]-3-carboxylic Acid Methyl Ester (24). To a suspension of Raney nickel[41] (470 mg) in THF (2 mL) was added a solution of **22** (47 mg, 0.11 mmol) in THF (2.3 mL). The solution was stirred at room temperature for 50 min, filtered through Celite with ethanol (2 × 25 mL), and evaporated to give **24** as a colorless oil (29 mg, 100%). Chromatography (silica gel, ethyl acetate–hexane, 1:4) gave **24** as a colorless oil, which exhibited a single peak by VPC (6 ft × $^1/_8$ in., 10% SE-30 on Chromasorb W, 175 °C) at R_t = 11.7 min (24 mg, 83%, R_f 0.48): IR (neat) 3.40, 5.78, 6.22, 6.78, 6.89 μm; UV (ether) λ_{max} (ϵ) 287 nm (2420), 281 (2870), 217 (5700); ^1H NMR δ 1.10–2.10 (m, 10 H), 3.73 (s, 3 H), 3.97 (s, 1 H), 6.70–7.30 (m, 4 H); chemical ionization mass spectrum, *m/e* (relative intensity) 247 (M + 1, 9.8), 215 (11), 188 (12), 187 (100), 153 (1.2).

Irradiation of 1a in Ether–Anisole. A solution of **1a** (35 mg, 0.14 mmol) in ether–anisole (5 mL, 4:1) in a sealed tube was irradiated for 84 h. Removal of solvent under vacuum gave a colorless oil (35 mg, 100%), which by ^1H NMR spectral analysis was >90% **3** and contained no **1a**.

Irradiation of 1a in Benzene–Acetone. (1) A solution of **1a** (30 mg, 0.12 mmol) in benzene–acetone (4 mL, 3:1) in a sealed tube was irradiated for 5.5 h. Removal of solvent and chromatography (silica gel, methylene chloride) gave two fractions. The more mobile fraction was a mixture of **1a** and **24** in a ratio of 2.5:1 (6 mg, 20%); the less mobile fraction was **3** (18 mg, 60%).

(2) The reaction was repeated as described above except that irradiation was continued for 17 h. Chromatography gave **24** (30%) and **3** (38%).

(3) In some experiments a small amount of a fourth component was detected in the fraction containing **1a** and **24**. This component had IR and ^1H NMR spectral properties consistent with the structure **25**.

Irradiation of 3 in Benzene-Acetone. A solution of **3** (62 mg, 0.25 mmol) in benzene–acetone (7 mL, 3:4) in two sealed tubes was irradiated for 7 h. Removal of solvent and chromatography (silica gel, ethyl acetate–hexane, 1:4) gave two fractions. The more mobile fraction was a 1:4 mixture of **24** and **25** (11 mg, 15%). The less mobile component was **24** (25 mg, 40%). **25**: IR (neat) 3.40, 5.79 μm; ^1H NMR δ 1.10–2.10 (m, 10 H), 1.50 (s, 3 H), 1.73 (s, 3 H), 3.75 (s, 3 H), 4.49 (s, 1 H), 6.80–7.40 (m, 4 H).

Irradiation of 24. (1) A solution of **24** (24 mg, 0.10 mmol) in benzene–acetone (3.5 mL, 3:4) was irradiated for 7 h. ^1H NMR and VPC analysis indicated that **24** and other uncharacterized material was present.

(2) A solution of **24** (22 mg, 0.09 mmol) in benzene (3 mL, 0.03 M) was irradiated for 7 h. ^1H NMR and VPC analysis indicated that only **24** was present.

(3) A solution of **24** (27 mg, 0.11 mmol) in ether (3.0 mL, 0.04 M) was irradiated for 15 h. ^1H NMR and VPC analysis indicated that only **24** was present.

Irradiation of (−)-1a in Benzene–Acetone. A solution of (−)-**1a** (32 mg, 0.13 mmol) in benzene (4.1 mL) and acetone (0.9 mL) in two sealed tubes was irradiated for 3 h. Removal of solvent under vacuum and chromatography (silica gel, methylene chloride) gave two fractions. The more mobile fraction was a mixture of **1a**, **24**, and **25** in a ratio of 8:2:2 (14 mg, 44%). The less mobile fraction was **3** (9 mg, 28%). To the mixture of **1a**, **24**, and **25** (14 mg) in $CDCl_3$ (0.5 mL) was added $Eu(hfc)_3$[32] (30 mg). The ^1H NMR spectrum showed resonance for H_a in enantiomers of **1a** at δ 6.63 and 6.55 in a ratio of 1:8 by repetitive integration. This sample of **3** was converted to **22** (69%). To a solution of **22** (8 mg, 0.02 mmol) in $CDCl_3$ (0.5 mL) was added $Eu(hfc)_3$[32] (40 mg, 0.034 mmol). The ^1H NMR spectrum showed the furan methine (H_a) resonance as two singlets at δ 6.08 and 5.91 in a ratio of ~8:1, and the carbomethoxy resonance as two singlets at δ 5.43 and 5.28 in a ratio of 8:1 by repetitive integration.

Irradiation of 3 in Ether. A solution of **3** (25 mg, 0.10 mmol) in ether (3 mL, 0.03 M) was irradiated in a sealed tube for 48 h. Removal of solvent gave an oil (25 mg), which by ^1H NMR spectral analysis was essentially pure **3**.

Irradiation of 3 in Benzene. A solution of **3** (30 mg, 0.12 mmol) in benzene (4 mL, 0.03 M) was photostable after irradiation for 18 h.

2-Methylspiro[benzofuran-3(2*H*),1′-cyclohexane]-2-carboxylic Acid. To a solution of tetramethylpiperidine (0.390 mL, 2.2 mmol) in THF (1 mL) at 0 °C was added *n*-butyllithium (1.00 mL of 2.20 M in hexane, 2.2 mmol). After 30 min the solution was cooled to −78 °C and a solution of **1b**[28] (232 mg, 1.0 mmol) in THF (1.5 mL) was added. The solution was stirred at −78 °C for 10 min and 0 °C for 30 min and cooled to −78 °C. Methyl iodide (0.093 mL, 1.5 mmol) was added and the solution was stirred at −78 °C for 6 h and room temperature overnight. The solution was poured into ether (30 mL) and 0.5 N HCl (25 mL). The aqueous layer was extracted again with ether (25 mL). The combined organic solution was washed with brine (20 mL) and dried ($MgSO_4$). Removal of solvent gave a yellow crystalline solid (242 mg, 98%). Recrystallization from ether–hexane gave the title compound (216 mg, 89%, mp 168–175 °C dec): IR ($CHCl_3$) 3.00–4.00, 3.45, 5.84, 6.24 μm; ^1H NMR δ 1.2–2.20 (m, 10 H), 1.53 (s, 3 H), 6.70–7.60 (m, 4 H), 10.92 (s, 1 H).

2-Methylspiro[benzofuran-3(2*H*),1′-cyclohexane]-3-carboxylic Acid Methyl Ester 28a. Prepared from the parent acid (see above) as described for **20b**. Chromatography (silica gel, hexane–methylene chloride, 2:3) gave **28a** (95%, R_f 0.23): IR (neat) 3.44, 5.81, 6.83, 8.93, 9.04 μm; ^1H NMR δ 1.00–2.10 (m, 10 H), 1.53 (s, 3 H), 3.80 (s, 3 H), 6.70–7.50 (m, 4 H); chemical ionization mass spectrum, *m/e* (relative intensity) 261 (M + 1, 26), 241 (2.8), 229 (14), 201 (100), 181 (8.3), 167 (5.5), 153 (8.2).

α-Methyl-α-(1-cyclohexenyl)-2-hydroxybenzeneacetic Acid Methyl Ester (29a). A solution of **28a** (102 mg, 0.39 mmol) in ether (15 mL,

(41) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 192.

0.26 M) in four sealed tubes was irradiated for 70 h. Removal of solvent gave a yellow solid, which by ^{1}H NMR analysis was a mixture of **29a** and **28a** (4:1). Crystallization from hexanes gave **29a** (71 mg, 70%, mp 130–131 °C): IR ($CHCl_3$) 3.01, 3.40, 5.88, 6.92, 7.98 μm; ^{1}H NMR δ 1.70 (s, 3 H), 1.20–2.10 (m, 8 H), 3.73 (s, 3 H), 5.63 (br s, 1 H), 6.70–7.30 (m, 4 H), 7.36 (s, 1 H); chemical ionization mass spectrum, *m/e* (relative intensity) 261 (M + 1, 25), 241 (2.9), 229 (11), 202 (14), 201 (100), 167 (2.4), 145 (2.4). Chromatography (silica gel, methyflene chloride–hexanes, 1:1) of the mother liquor gave **28a** (17 mg, 17%).

2-Ethylspiro[benzofuran-3(2*H*),1′-cyclohexane]-2-carboxylic Acid and Its Methyl Ester (28b). The carboxylic acid was obtained from **1b** and ethyl iodide as described for the preparation of the methyl analogue. Filtration of the crude product through a short column (silica gel, ether) gave the acid as a yellow oil (93%, R_f 0.48): IR (neat) 3.00–4.10, 3.40, 5.82, 6.81, 6.92, 13.93 μm; ^{1}H NMR δ 0.97 (t, *J* = 7 Hz, 3 H), 1.10–2.20 (m, 2 H), 6.80–7.60 (m, 4 H), 9.06 (s, 1 H); chemical ionization mass spectrum, *m/e* (relative intensity) 261 (M + 1, 38), 231 (8.2), 227 (3.3), 215 (19), 187 (100), 181 (17), 167 (3.8), 153 (2.2), 135 (6.0). Methyl ester (**28b**) was prepared from the acid; chromatography (silica gel, methylene chloride) gave pure **28b** as a colorless oil (87%): IR (neat) 3.45, 5.79, 6.21 μm; ^{1}H NMR δ 0.93 (t, *J* = 8 Hz, 3 H), 1.10–2.20 (m, 12 H), 3.83 (s, 3 H), 6.70–7.60 (m, 4 H).

α-Ethyl-α-(1-Cyclohexenyl)-2-hydroxybenzeneacetic Acid Methyl Ester (29b). A solution of **28b** (113 mg, 0.41 mmol) in ether (15 mL, 0.027 M) in four sealed tubes was irradiated for 70 h. Removal of solvent and chromatography (silica gel, methylene chloride–hexane, 1:1) gave three fractions. Fraction 1 (R_f 0.59) was a mixture of **28b** and **31** in a ratio of 3.6:4.0 (8 mg, 7%). Fraction 2 (R_f 0.50) was **28b** (45 mg, 40%). Fraction 3 (R_f 0.33) was a mixture of **29b** and **31** in a ratio of 4:3 (42 mg, 37%). **29b**: IR (neat) 2.98, 3.42, 5.85 μm; ^{1}H NMR δ 0.83 (t, *J* = 10 Hz, 3 H), 1.10–2.20 (m, 10 H), 3.70 (s, 3 H), 5.77 (br s, 1 H), 6.70–7.50 (m, 4 H); gas chromatography–chemical ionization mass spectrum, *m/e* (relative intensity) 275 (M + 1, 24); 243 (13), 216 (14), 215 (100), 181 (4.0).

3-Ethyl-3-(1-cyclohexenyl)-2-oxobenzodihydrofuran (31). To a mixture of **29b** and **31** (10 mg, 0.04 mmol) in methylene chloride (0.5 mL) was added *p*-toluenesulfonic acid (2 mg). The solution was refluxed for 1 h and cooled to room temperature. Methylene chloride (30 mL) was added and the resulting solution was washed with 1 N $NaHCO_3$ (2 × 10 mL) and brine (10 mL) and dried ($MgSO_4$). Removal of solvent under vacuum gave **31** as a colorless oil (9 mg, 100%): IR (neat) 3.42, 5.54, 6.90, 9.63, 13.22 μm; ^{1}H NMR δ 0.70 (t, *J* = 10 Hz, 3 H), 1.10–2.10 (m, 10 H), 5.75 (br s, 1 H), 6.90–7.30 (m, 4 H); chemical ionization mass spectrum, *m/e* (relative intensity) 231 (M + 1, 12), 215 (1.8), 203 (100), 175 (18).

(4-Methylcyclohexylidine)phenoxyacetic Acid Methyl Ester (37). A solution of methyl (diethylphosphono)phenoxyacetate (22.0 g, 0.073 mol) in DME (40 mL) was added to a suspension of sodium hydride (99%, 1.75 g, 0.073 mol) in DME (20 mL) over a period of 30 min. The mixture was warmed to 70 °C for 45 min. After cooling to room temperature, 4-methylcyclohexanone (7.94 g, 0.071 mol) was added, and the mixture was heated to reflux for 12 h. The reaction was cooled, poured into water (240 mL), and extracted with ether (4 × 100 mL). The combined ether extracts were washed with 1 N NaOH (2 × 40 mL) and brine and dried ($MgSO_4$). Removal of solvent gave the aryl vinyl ether **37** as a yellow oil (18.6 g, 100%): IR ($CHCl_3$) 3.44, 5.90, 6.25, 6.33, 6.80, 7.00, 7.09, 7.89, 8.20, 9.09, 9.80, 10.87, 11.50 μm; ^{1}H NMR δ 0.98 (d, *J* = 6 Hz, 3 H), 1.5–1.8 (m, 5 H), 2.2–2.4 (m, 2 H), 2.7–2.9 (m, 2 H), 3.61 (s, 3 H), 6.8–7.4 (m, 5 H); chemical ionization mass spectrum, *m/e* (relative intensity) 261 (M + 1, 40), 229 (18), 201 (100), 167 (16), 135 (2.7).

Irradiation of 37. An argon purged solution of **37** (18.6 g, 0.71 mol) in benzene–methanol (400 mL, 1:1) was irradiated for 120 h. The solution was concentrated in vacuo, and the residue was dissolved in ether (100 mL), washed with 1 N NaOH (3 × 30 mL) and water (2 × 30 mL), and dried ($MgSO_4$). Removal of solvent afforded a light yellow oil (16.5 g). TLC analysis (ethyl acetate–hexanes, 1:9) of this material showed two spots at R_f 0.35 and 0.29. VPC analysis (T_1 = 150, T_2 = 250 °C, 16 °C/min) showed two peaks of equal intensity at R_t = 3.7 and 4.1 min: ^{1}H NMR δ/relative intensity ratio 0.96 (d, *J* = 6 Hz), 1.03 (d, *J* = 5.2 Hz), 1.12–2.20 (m), 3.73 (s), 3.84 (s), 4.74 (s), 5.00 (s), 6.6–7.6 (m)/1:1:18:3:3:1:1:8. A small portion (2.0 g) of the product mixture was chromatographed (HPLC, ethyl acetate–hexanes, 1:20) to afford the following:

(A) Benzodihydrofuran **38a** (280 mg, R_f 0.33), crystallized from ethanol, mp 93–94 °C: IR ($CHCl_3$) 3.44, 5.75, 6.25, 6.87, 6.97, 7.25, 8.55, 9.52, 9.80, 10.31, 11.90 μm; ^{1}H NMR δ 0.96 (d, *J* = 6 Hz, 3 H), 1.1–2.0 (m, 9 H), 3.73 (s, 3 H, ester methyl), 5.00 (s, 1 H, C_2 proton), 6.85–7.25 (m, 4 H); ^{13}C NMR δ 22.2 (q), 31.59 (d, C(4′)), 31.17, 31.30, 31.73 (three overlapping t), 38.95 (t), 49.80 (s, C(3)), 51.74 (q, ester methyl), 87.50 (d, C(2)), 109.61 (d), 121.08 (d), 122.30 (d), 128.37 (d), 134.92 (s), 158.44 (s), 170.55 (s, C=O).

Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.73; H, 7.63.

(B) Benzodihydrofuran **39a** (410 mg, oil, R_f 0.29): IR (neat) 3.42, 5.71, 6.21, 6.31, 6.76, 6.85, 8.33, 9.52, 11.76 μm; ^{1}H NMR δ 1.02 (d, *J* = 3 Hz, 3 H), 1.2–2.05 (m, 9 H), 3.82 (s, 3 H, ester methyl), 4.74 (s, 1 H, C(2) proton), 6.86–7.56 (m, 4 H); ^{13}C NMR δ 22.11 (q), 29.60 (t), 30.38 (t), 31.49 (d, C(4′)), 32.01 (t), 36.04 (t), 48.47 (s, C(3)), 51.99 (q, ester methyl), 90.16 (d, C(2)), 110.31 (d), 120.73 (d), 125.55 (d), 128.36 (d), 133.75 (s), 158.38 (s), 169.94 (s, C=O).

Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 74.05; H, 7.75.

(C) A fraction containing both **38a** and **39a** (1.06 g) also was isolated.

Spiro[benzofuran-3(2*H*),1′-(4′-methyl)cyclohexane]-3-carboxylic Acid. Diastereomer 38b. To a solution of **38a** (280 mg, 1.08 mmol) in methanol (5 mL) was added 1 N NaOH (5 mL), and the mixture was stirred at room temperature under N_2 for 12 h. Saturated NH_4Cl (10 mL) was added and, after cooling to 5 °C, the mixture was acidified to pH 2–3 with 1 N H_2SO_4. The cold reaction mixture was extracted with ether (3 × 20 mL). The combined organic extract was washed with brine, dried, and concentrated to give the carboxylic acid **38b** (260 mg, 98%) as a crystalline solid (ether–hexanes, mp 153 °C): IR ($CHCl_3$) 2.94–3.33 (br), 5.78 μm; ^{1}H NMR δ 0.95 (d, *J* = 6 Hz, 3 H), 1.1–2.0 (m, 9 H), 4.98 (s, 1 H, C(2) proton), 6.85–7.25 (m, 4 H); ^{13}C NMR δ 22.16 (q), 31.24, 31.39, 31.46 (three overlapping t), 31.59 (d, C(4′)), 38.93 (t), 50.04 (s, C(3)), 86.91 (d, C(2)), 109.69 (d), 121.4 (d), 122.38 (d), 128.55 (d), 134.71 (s), 158.21 (s), 175.92 (s).

Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.15. Found: C, 73.26; H, 7.31.

Diastereomer 39b. Prepared from **39a** (150 mg, 0.58 mmol). Recrystallized from ether–hexanes (135 mg, 90%, mp 127 °C): IR ($CHCl_3$) 2.94–3.33 (br), 5.8 μm; ^{1}H NMR δ 1.03 (d, *J* = 5.4 Hz, 3 H), 1.1–2.0 (m, 9 H), 4.76 (s, 1 H, C(2) proton), 6.80–7.56 (m, 4 H); ^{13}C NMR δ 22.11 (q), 29.6 (t), 30.38 (t), 31.49 (d, C(4′)), 32.01 (t), 36.04 (t), 48.47 (s, C(3)), 90.16 (d, C(2)), 110.31 (d), 120.73 (d), 125.55 (d), 128.36 (d), 133.75 (s), 158.38 (s), 169.94 (s, C=O).

Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.24; H, 7.33.

Esterification of **38b** and **39b** with diazomethane afforded **38a** and **39a**, respectively (100%, IR, ^{1}H NMR, mp).

Irradiation of 38a and 39a. α-(4-Methylcyclohex-1-enyl)-2-hydroxybenzeneacetic Acid Methyl Ester. Diastereomer 34. An argon-purged solution of **38a** (200 mg, 0.77 mmol) in ether (20 mL) was irradiated for 80 h. Removal of solvent gave an oil. TLC analysis (ethyl acetate–hexanes, 1:9) of this material showed two spots R_f 0.3 (**38a**) and 0.1 (**34**); a ratio of **38a**:**34** = 3:1 was determined by ^{1}H NMR analysis. Chromatographic fractionation of this mixture by preparative utilization of analytical HPLC (ethyl acetate–isooctane, 1:9, flow rate 2 mL/min) afforded **38a** (150 mg, 75%, R_t = 2.4 min) and **34** (45 mg, 22.5%, R_t = 5.2 min): IR ($CHCl_3$) 2.94, 5.78 μm; ^{1}H NMR δ 0.93 (d, *J* = 6 H, 3 H), 1.0–2.2 (m, 7 H), 3.79 (s, 3 H, ester methyl), 4.28 (br s, 1 H, benzylic proton), 5.51 (br m, 1 H, vinylic proton), 6.84–7.26 (m, 4 H), 7.51 (s, exchangeable with D_2O, 1 H, phenolic OH); ^{13}C NMR δ 21.52 (q), 27.37 (t), 27.95 (d), 30.88 (t), 33.76 (t), 52.66 (q, ester methyl), 56.97 (d, C(α)), 117.86 (d), 120.42 (d), 122.22 (s), 124.41 (d), 129.29 (d), 131.49 (d), 132.21 (s), 155.40 (s), 175.46 (s, C=O).

Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.44; H, 7.57.

Diastereomer 35. Irradiation of **39a** (220 mg, 0.85 mmol) in ether (11 mL) and chromatographic fractionation by preparative utilization of analytical HPLC (ethyl acetate–isooctane, 1:9, flow rate 2 mL/min) afforded **39a** (165 mg, 75%, R_f 0.29, R_t = 3.2 min) and **35** (45 mg, 21%, R_f 0.07, R_t = 6.4 min): IR ($CHCl_3$) 2.94, 5.78 μm; ^{1}H NMR δ 0.93 (d, *J* = 6 Hz, 3 H), 1.0–2.0 (m, 7 H), 3.77 (s, 3 H, ester methyl), 4.29 (br s, 1 H, benzylic proton), 5.53 (br m, 1 H, vinylic proton), 6.84–7.26 (m, 4 H), 7.56 (s, exchangeable with D_2O, 1 H, phenolic OH); ^{13}C NMR δ 21.30 (q), 27.65 (t), 27.90 (d), 30.86 (t), 33.76 (t), 52.67 (q, ester methyl), 57.31 (d, C(α)), 117.89 (d), 120.38 (d), 122.12 (s), 124.36 (d), 129.33 (d), 131.47 (d), 132.35 (s), 155.44 (s), 175.61 (s).

Anal. Calcd for $C_{20}H_{16}O_3$: C, 73.82; H, 7.74. Found: C, 73.66; H, 7.60.

Reactions of 34 with Benzeneselenenyl Chloride. A solution of **34** (≥95% pure by ^{1}H NMR, 30 mg, 0.12 mmol) in methylene chloride (5 mL) was cooled to −78 °C under N_2, and a solution of benzeneselenenyl chloride (28 mg, 0.15 mmol) in methylene chloride (2 mL) was added over 5 min. The reaction mixture was stirred for 1 h, 1 N $NaHCO_3$ (5 mL) was added at −78 °C and the mixture was allowed to warm to room temperature. The organic layer was separated, washed with brine, dried ($MgSO_4$), and concentrated to give a yellow oil (55 mg), the TLC

analysis (silica gel, methylene chloride) of which showed three spots R_f 0.8, 0.7, and 0.2. ^{1}H NMR analysis of this mixture clearly indicated the presence of **43**, **42**, and **34** (18:1:1). Flash chromatography on silica gel (methylene chloride–hexanes, 3:2) afforded spiro[benzofuran-2(3*H*),1′-4′-methyl-2′-(phenylseleno)cyclohexane]-3-carboxylic acid methyl ester **43** (R_f 0.8, 38 mg, 80%, mp 83.5–84 °C): IR ($CHCl_3$) 3.42, 5.75, 6.25, 6.33, 6.78, 6.85, 6.99, 7.46, 8.70, 10.31, 12.05, 15.38 μm; ^{1}H NMR δ 0.98 (d, J = 6 Hz, 3 H), 1.25 (m, 1 H), 1.5 (m, 2 H), 2.0 (m, 4 H), 3.36 (s, 3 H, ester methyl), 3.94 (s, 1 H, C(2′) proton), 4.37 (br s, 1 H, C(3) proton), 6.8–7.6 (m, 9 H, aromatic protons); ^{13}C NMR δ 21.70 (q), 27.08 (d, C(4′)), 29.5 (t), 33.69 (t), 37.42 (t), 47.49 (d, C(2′)), 51.897 (q, ester methyl), 57.26 (d, C(3)), 90.86 (s, C(2)), 110.79 (d), 120.51 (d), 124.95 (d), 126.40 (s), 129.05 (d), 129.55 (d), 130.49 (s), 132.59 (d), 158.73 (s), 170.97 (s, C=O).

Anal. Calcd for $C_{22}H_{26}O_3Se$: C, 63.61; H, 5.82; Se, 19.01. Found: C, 63.71; H, 5.73; Se, 18.88.

A second fraction containing a mixture of **42** and **34** (13 mg, ~1:1 by ^{1}H NMR, vide infra) also was isolated.

Reaction of 35 with Benzeneselenenyl Chloride. 35 (30 mg, 0.12 mmol) was treated with phenylselenenyl chloride (28 mg, 0.15 mmol) as described for **34**. Reaction workup gave a yellow oil (58 gm), the TLC analysis (methylene chloride) of which showed it to be mixture of two products, with R_f 0.8 and 0.68. ^{1}H NMR analysis of this mixture indicated the presence of the two selenides **42** and **43** (20:1). Silica gel flash chromatography (methylene chloride–hexanes, 3:2) afforded spiro[benzofuran-2(3*H*),1′-4′-methyl-2′-(phenylseleno)cyclohexane]-3-carboxylic acid methyl ester diastereomer **42** (45 mg, 94%; R_f 0.68; needles from ethanol, mp 69 °C): IR ($CHCl_3$) 3.42, 5.78, 6.25, 6.33, 6.76, 6.85, 7.0, 8.67, 9.80, 10.30, 11.11, 14.5 μm; ^{1}H NMR δ 0.93 (d, J = 6 Hz, 3 H), 1.05–2.20 (m, 7 H), 3.46 (br s, 1 H, C(2′) proton), 3.73 (s, 3 H, ester methyl), 4.66 (s, 1 H, C(3) proton), 6.8–7.6 (m, 9 H, aromatic protons); ^{13}C NMR δ 21.73 (q), 27.21 (d, C(4′)), 29.51 (t), 30.11 (t), 37.38 (t), 52.04 (q, ester methyl), 52.80 (d, C(2′)), 56.11 (d, C(3)), 91.73 (s, C(2)), 110.22 (d), 120.75 (d), 125.25 (s), 125.53 (d), 127.46 (d), 129.23 (d), 130.68 (s), 133.52 (d), 158.50 (s), 171.36 (s, C=O).

Anal. Calcd for $C_{22}H_{26}O_3Se$: C, 63.61; H, 5.82; Se, 19.01. Found: C, 63.63; H, 5.82; Se, 19.11.

Diastereomer **43** (R_f 0.8; 1.3 mg, 2.7%) also was obtained.

Spiro[benzofuran-2(3*H*),1′-4′-methylcyclohex-2′-ene]-3-carboxylic Acid Methyl Esters. Diastereomer 44a. Hydrogen peroxide (30%, 0.01 mL, ~0.75 mmol) was added to a stirred solution of **42** (20.75 mg, 0.5 mmol) at 0 °C under N_2. After 1 h the mixture was allowed to warm to room temperature and stirring was continued for 15 h. VPC analysis (T_1 = 150, T_2 = 250 °C, 16 °C/min) indicated that the reaction was complete with formation of a single peak (R_t = 3.8 min). Workup as described for **23** and silica gel flash chromatography (methylene chloride) afforded the olefinic ester **44a** (11.2 mg, 86.8%) as a colorless oil: IR ($CHCl_3$) 3.4, 5.75, 6.06, 6.17, 6.25, 6.76, 6.85, 6.97, 8.0, 8.97, 9.85, 10.36 μm; ^{1}H NMR δ 1.08 (d, J = 7 Hz, 3 H), 1.4–1.9 (m, 3 H), 2.15 (m, 2 H, C(4′) proton), 3.74 (s, 3 H, ester methyl), 4.15 (s, 1 H, C(3) proton), 5.82 (br q, J = 12 Hz, 2 H, vinylic protons), 6.86 (m, 2 H, aromatic protons), 7.22 (m, 2 H, aromatic protons); irradiation of resonance centered at δ 2.15 resulted in the collapse of the broadened quartet at δ 5.82 into a sharp quartet with J = 10 Hz as well as of the doublet at δ 1.08 into a sharp singlet; ^{13}C NMR δ 20.91 (q), 27.13 (t), 30.09 (t), 30.61 (d, C(4′)), 52.11 (q, ester methyl), 57.78 (d, C(3)), 86.36 (s, C(2)), 110.16 (d), 120.63 (d), 125.03 (s), 125.8 (d), 127.91 (d), 129.34 (d), 139.19 (d), 158.69 (s), 171.01 (s, C=O); chemical ionization mass spectrum, m/e (relative intensity) 259 (M + 1, 100), 227 (76), 199 (57), 183 (2.7), 165 (37), 149 (3.4), 135 (21).

Anal. Calcd for $C_{16}H_{18}O_3$: an acceptable analysis could ot be obtained.

Diastereomer 45a. 43 (10.4 mg, 0.025 mmol) was treated with hydrogen peroxide (30%, 0.01 mL). VPC analysis (T_1 = 150, T_2 = 250 °C, 16 °C/min) indicated that the reaction was complete after 30 h with formation of a single peak (R_t = 4.1 min). Reaction workup and silica gel flash chromatography (methylene chloride) gave the carboxylic acid **45a** (5.2 mg, 84%) as a colorless oil; IR ($CHCl_3$) 3.4, 5.75, 6.17, 6.25, 6.76, 6.99, 7.46, 7.57, 8.0, 10.31, 11.3, 13.33 μm; ^{1}H NMR δ 1.07 (d, J = 7 Hz, 3 H), 1.4–1.65 (m, 1 H), 1.75–2.1 (m, 2 H), 2.20 (m, 2 H), 3.72 (s, 3 H, ester methyl), 4.10 (s, 1 H, C(3) proton), 5.77 (br q, J = 10 Hz, 2 H, vinylic protons), 6.86 (m, 2 H, aromatic protons), 7.22 (m, 2 H, aromatic protons); irradiation of resonance centered at δ 2.20 resulted in the collapse of the quartet at δ 5.77 into a sharp quartet, J = 12 Hz, as well as the doublet at δ 1.07 into a sharp singlet; ^{13}C NMR δ 20.76 (q), 27.76 (t), 30.15 (d), 35.11 (t), 52.11 (q, ester methyl), 57.92 (d, C(3)), 86.59 (s, C(2)), 110.02 (d), 120.56 (d), 123.99 (d), 124.55 (s), 126.04 (d), 129.33 (d), 139.67 (d), 158.85 (s), 170.85 (s, C=O); chemical ionization mass spectrum, m/e (relative intensity) 259 (M + 1, 100), 227 (60), 205 (2.0), 200 (7.7), 199 (43), 183 (2.0), 165 (28), 149 (2.4), 145 (3.0), 135 (16).

Anal. Calcd for $C_{16}H_{18}O_3$: an acceptable analysis could not be obtained.

Spiro[benzofuran-2(3*H*),1′-4′-methylcyclohexane]-3-carboxylic Acid Methyl Ester (46). 42 (5.2 mg, 0.012 mmol) and **43** (5.2 mg, 0.012 mmol) were each separately treated with Raney nickel in the THF (2 mL) for 1 h to give **46** (3 mg, 97%) in each case: IR ($CHCl_3$) 3.42, 5.78, 6.25, 6.76, 6.87, 6.97, 8.13, 8.58, 10.31, 11.11 μm; ^{1}H NMR δ 1.0–2.05 (m, 9 H), 3.74 (s, 3 H, ester methyl), 3.96 (s, 1 H, C(3) proton), 6.85 (m, 2 H, aromatic protons), 7.19 (m, 2 H, aromatic protons); chemical ionizataion mass spectrum, m/e (relative intensity) 261 (M + 1, 45), 245 (2.1), 229 (8.5), 201 (70), 167 (100).

Anal. Calcd for $C_{16}H_{20}O_3$: an acceptable analysis could not be obtained.

Saponification of 44a and 45a. To a solution of **44a** (15 mg, 0.058 mmol) in MeOH (2 mL) was added 1 M NaOH (2 mL), and the mixture was stirred at room temperature for 24 h. The mixture was acidified to pH 3–4 with 2 M H_2SO_4 after the addition of saturated NH_4Cl (5 mL) and extracted with ether (3 × 15 mL). The combined ether extracts were washed with brine, dried ($MgSO_4$), and evaporated to give a thick gum (14 mg, 98%). ^{1}H NMR analysis of this material indicated the presence of **44b** and **45b** (2:5), based on integration of the C(3) proton resonance at δ 4.16 and 4.12, respectively: ^{1}H NMR δ 1.08 (d, J = 7 Hz, 3 H), 1.75–2.4 (m, 5 H), 4.12, 4.16 (two s in the ratio 5:2, 1 H), 5.83 (q, J = 13 Hz, vinylic protons), 6.8–7.4 (m, 4 H, aromatic protons). A portion of this mixture (4 mg) was re-esterified with diazomethane to afford a mixture of isomeric esters **44a** and **45a** (2:5).

Saponification of **45a** (24 mg, 0.093 mmol) in water–methanol (1:1, 4 mL) with NaOH also gave a gum (23 mg, 100%). This material was a mixture of **44b** and **45b** (2:5) as determined by ^{1}H NMR analysis. Re-esterification with diazomethane afforded a mixture of the isomeric esters **44a** and **45a** (2:5).

Iodo Lactonization of the Mixture of Acids 44b and 45b (2:5). The mixture of carboxylic acids **44b** and **45b** (23 mg, 0.093 mmol) was dissolved in 1 M $NaHCO_3$ (2 mL). After 15 min, a solution of potassium iodide (800 mg, 4.7 mmol) and iodine (220 mg, 0.86 mmol) in water (2 mL) was added and the mixture was stirred under N_2 in the dark for 2 h. The reaction mixture was transferred to a separatory funnel and extracted with chloroform (4 × 5 mL). The combined chloroform extracts were washed with 10% $Na_2S_2O_3$ (2 × 5 mL) and brine and dried ($MgSO_4$). Removal of solvents and crystallization of the residue (ethyl acetate–hexanes) gave the iodo lactone **47** (15.2 mg, 41%; needles, mp 140 °C): IR ($CHCl_3$) 5.60 μm; ^{1}H NMR δ 1.14 (d, J = 8 Hz, 3 H), 1.40 (m, 1 H, C(4′) proton), 1.71 (six-line m, 2 H, C(6′) proton), 2.02, 2.46 (two m, 1 H each, C(5′) protons), 4.04 (s, 1 H, C(3) proton), 4.34 (t, J = 4 Hz, 1 H, C(3′) proton), 5.08 (d, J = 4 Hz, 1 H C(2′) proton), 6.85–7.50 (m, 4 H, aromatic protons); irradiation of the doublet at δ 5.08 resulted in the collapse of the triplet at δ 4.34 into a singlet and vice versa; irradiation of the six-line multiplet centered at δ 1.71 collapsed the multiplet centered at δ 2.02 and 2.46 into two doublets, J = 16 Hz; irradiation of the resonance centered at δ 1.40 collapsed (a) the doublet at δ 1.14 into a singlet, (b) the six-line multiplet at δ 1.71 into a triplet, J = 6 Hz, and (c) the triplet at δ 4.34 into a doublet, J = 4 Hz.

Anal. Calcd for $C_{15}H_{15}O_3I$: C, 48.67; H, 4.09; I, 34.28. Found: C, 48.59; H, 4.03; I, 34.31.

The basic aqueous layers were combined, decolorized with solid $Na_2S_2O_3$, acifidied with 10% HCl, and extracted with chloroform (4 × 15 mL). The combined extracts were washed with brine, dried ($MgSO_4$), and concentrated in vacuo to afford a 1:1 mixture of the isomeric acids **44b** and **45b** (12.7 mg, 55%) as determined by ^{1}H NMR analysis. The composition of this mixture was confirmed (^{1}H NMR) by esterification with diazomethane to afford a 1:1 mixture of **44a**/**45a**.

Spiro[benzofuran-2(3*H*),1′-4′-methylcyclohex-2′-ene]-3-carboxylic Acid. Diastereomer 45b. The iodo lactone **47** (10 mg, 0.027 mmol) was added to a suspension of Zn dust (20 mg) in ethanol (1 mL). The mixture was heated to reflux under N_2 for 12 h, cooled, and filtered to remove solids. The filtrate was concentrated in vacuo, and the residue was partitioned between ether (5 mL) and 1 N HCl (1 mL). The organic layer was separated, washed with brine, dried ($MgSO_4$) and concentrated to give **45b** (6.1 mg, 92%): IR ($CHCl_3$) 3.03–3.45 (br), 5.85, 6.17, 6.25, 6.76, 6.85, 8.0, 8.81, 10.20 μm; ^{1}H NMR δ 1.07 (d, J = 7 Hz, 3 H), 1.4–1.65 (m, 1 H), 1.75–2.1 (m, 2 H), 2.20 (m, 2 H), 4.12 (s, 1 H, C(3) proton), 5.83 (m, 2 H, vinylic protons), 6.80–7.40 (m, 4 H, aromatic protons).

The acid (6 mg) was esterified with diazomethane to afford an ester (6 mg, ~100%), the IR and ^{1}H NMR spectra of which were totally superimposable on **45a** obtained by treatment of the selenide **43** with Raney nickel.

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Registry No. (±)-**1a**, 89908-35-0; (−)-**1a**, 69515-17-9; (±)-**1b**, 89908-41-8; (*R*)-**1b**·(*S*)-α-methyl-*p*-nitrobenzylamine, 90024-32-1; (*S*)-**1b**·(*S*)-α-methyl-*p*-nitrobenzylamine, 90024-31-0; (±)-**3**, 89908-36-1; (±)-**18**, 89908-37-2; **19**, 22047-88-7; (±)-**20a**, 89908-38-3; (±)-**20b**, 89908-39-4; (±)-**21**, 89908-40-7; (±)-**22**, 89955-26-0; (−)-**22**, 89955-27-1; (±)-**23**, 89908-42-9; (±)-**24**, 89908-43-0; (±)-**25**, 89908-44-1; (±)-**28a**, 89908-46-3; (±)-**28a** (acid), 89908-45-2; (±)-**28b**, 89908-47-4; (±)-**29a**, 89908-48-5; (±)-**29b**, 89908-49-6; (±)-**31**, 89908-50-9; **34**, 89908-56-5; **35**, 89908-57-6; **36**, 86728-17-8; **37**, 89908-51-0; **38a**, 89908-52-1; **38b**, 89908-54-3; **39a**, 89908-53-2; **39b**, 89908-55-4; **42**, 89955-28-2; **43**, 89908-58-7; **44a**, 89908-59-8; **44b**, 89908-61-2; **45a**, 89955-29-3; **45b**, 89955-30-6; **46**, 89908-60-1; **47**, 89908-62-3; PhSeCl, 5707-04-0; cyclohexanone, 108-94-1; 4-methylcyclohexanone, 589-92-4; (*S*)-(−)-α-methyl-*p*-nitrobenzylamine, 4187-53-5.

Energy-Transfer Study of a Triplet Exciplex of Cyclohexanone and Mesitylene

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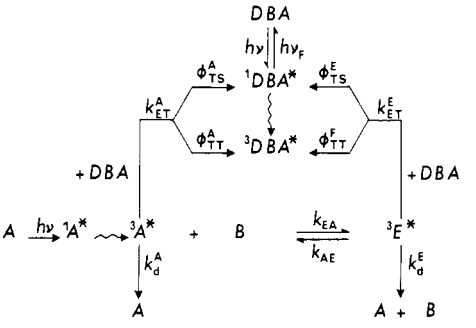
Abstract: Triplet cyclohexanone associates ($k_{EA} \sim 10^7$ M^{-1} s^{-1}) with mesitylene to form a triplet exciplex, E*, with a lifetime of ~0.3 μs in cyclohexane at 20 °C, i.e. half that of the uncomplexed triplet ketone. This conclusion rests on evidence obtained from energy-trasnfer experiments with 9,10-dibromoanthracene (DBA) as energy acceptor in a formal triplet–singlet energy-transfer process which populates DBA (S_1). In degassed cyclohexane solutions of cyclohexanone (0.077 M), DBA ($0.5–5.0 \times 10^{-4}$ M), and mesitylene (0.07–1.0 M), both E* and the uncomplexed triplet alkanone sensitize the fluorescence of DBA; its intensity decay is studied by the time-correlated single-photon counting method following pulse excitation at 305 nm where both cyclohexanone and DBA absorb. In the presence of mesitylene, the DBA fluorescence decay profiles reveal the buildup of an excited transient, which is postulated to be the triplet exciplex. The decay curves can be fitted to triple-exponential functions, as predicted by a kinetic scheme based on the reversible formation of E*. Kinetic expressions derived from this scheme allow the calculation of *all* the rate constants of the scheme. At 20 °C, the equilibrium constant favors the exciplex ($K_E \sim 13$). The efficiency ϕ_{TS}^E of the overall triplet–singlet energy transfer from E* to DBA is ~7 times higher than from the triplet alkanone; this result is in line with an earlier finding in the case of the less stable triplet exciplex of acetone and benzene. Work is in progress to ascertain the origin of the low k_{EA}, to investigate the effects of solvent and substitution on this rate and on K_E, and to investigate the mechanism of TS transfer to DBA.

In contrast to singlet exciplexes, triplet exciplexes in fluid solution have remained largely elusive.[1] Like any other triplet species, they can be expected to be poor emitters at best; thus, only indirect arguments are, by and large, available for proposing their likely intermediacy in reactions.[2] It has recently been shown[3] that exciplexes of triplet alkanones and benzene or methyl-substituted derivatives can be intercepted by 9,10-dibromoanthracene (DBA), which acts as a unique fluorescence probe.[4] Energy transfer from the triplet donors populates DBA (S_1) of 2-ns lifetime, possibly via a higher triplet state of DBA. Consequently, the intensity decay profile of the resulting fluorescence of DBA contains information on the triplet donors. The fluorescence of DBA has a maximum at ~430 nm and is easily monitored as a function of time by the single-photon counting technique.[4b] This DBA method first revealed the presence of an exciplex of triplet acetone in benzene in dynamic equilibrium with its components, in solutions irradiated at 305 nm.[3a] This result showed conclusively that the much reduced lifetime of triplet acetone in benzene, which is 10 times shorter than in cyclohexane and 1000 times shorter than in acetonitrile, can be regarded as the result of weak complexation. The triplet exciplex which results from the association of a more substituted alkanone such as cyclohexanone with *o*-xylene, for example, was shown to be significantly more stable at room temperature, judging by the three-component fluorescence decay of DBA in this system.[3b]

The present paper describes a study of the cyclohexanone/mesitylene system, in cyclohexane at 20 °C. As in the previous work, solutions of the ketone, the aromatic, and DBA were submitted to pulse excitation at a wavelength absorbed by both the

Scheme I



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(2) See, for example: Gupta, A.; Hammond, G. S. *J. Am. Chem. Soc.* **1976**, *98*, 1218. Farid, S.; Hartman, S. E.; Doty, J. C.; Williams, J. L. R. *Ibid.* **1975**, *97*, 3697. Caldwell, R. A.; Creed, D. *Acc. Chem. Res.* **1980**, *13*, 45. Cohen, S. G.; Parola, A.; Parsons, G. H. *Chem. Rev.* **1973**, *73*, 141. Loufty, R. O.; Yip, R. W. *Can. J. Chem.* **1973**, *51*, 1881. Scaiano, J. C.; Perkins, M. J.; Sheppard, J. W. *J. Photochem.* **1983**, *21*, 137. Ulrich, T.; Steiner, U. E.; Föll, R. E. *J. Phys. Chem.* **1983**, *87*, 1873 and references therein.

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