Photoreactions of *trans*-1-*o*-Hydroxyphenyl-2-phenylcyclopropane

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The photochemistry of *trans*-1-*o*-hydroxyphenyl-2-phenylcyclopropane, *trans*-**1**, was studied under a variety of experimental conditions. Direct irradiation through quartz in cyclohexane gave rise mainly to ring-expanded products, 2-phenyl-3,4-dihydro-2*H*-benzopyran, **2**, 2-benzyl-2,3-dihydrobenzofuran, **3**, and 1-*o*-hydroxyphenylindan, **4**. The major products, **2** and **3**, are rationalized by intramolecular proton transfer. However, a significant fraction of **3** is formed via ring-opening to cinnamylphenol, **5**. An additional product, *o*-(α-cyclohexylmethyl)phenol, **7**, suggests fragmentation of *trans*-**1** and (formal) insertion of *o*-hydroxyphenylcarbene into cyclohexane. Direct irradiation in methanol produced methanol adducts **8** and **9** instead of **2**, **3**, **4**, or **7**. Finally, acetone-sensitized irradiation of *trans*-**1** resulted in geometric isomerization to *cis*-**1**; this result can be rationalized via a biradical intermediate.

Introduction

The photochemistry of cyclopropane and derivatives has been of interest for many years; numerous derivatives have been studied under a variety of reaction conditions.[1−18] Among the many reaction types established are addition/substitution with ring opening,[1−3] geometric isomerization,[1−3,5−7] ring opening generating alkenes,[1] ring enlargement forming indans,[1−3] or fragmentation yielding carbenes.[1−3] The pathways to the various products may be formulated via a range of intermediates, including excited singlet[1−3] or triplet states,[6,7,18] radical cations,[4−17] triplet biradicals,[6,7,18] or zwitterions.

We have studied the photoreactions of *trans*-1-*o*-hydroxyphenyl-2-phenylcyclopropane,[19] *trans*-**1**, a *trans*-1,2-diarylcyclopropane bearing a hydroxyl function in one ortho position. This substrate was of interest because its excited singlet state may react by (excited state) proton transfer (ESPT)[20,21] to the cyclopropane moiety, whereas its radical cation may react by intramolecular nucleophilic capture,[22−27] aside from the wealth of other reactions suggested by the analogy to previous studies.

The photochemistry of the diarylcyclopropane, *trans*-**1**, was studied under a variety of experimental conditions, including (a) direct irradiation in cyclohexane (through quartz), (b) direct irradiation in methanol, (c) acetone-sensitized irradiation (through Pyrex), and (d) direct irradiation in dichloromethane in the presence of oxygen (Pyrex). Under these conditions, a range of interesting products were formed. The observed significantly different structure types require involvement of several different primary excited states and divergent types of intermediates.

Results

Direct irradiation of *trans*-**1** through quartz in cyclohexane gave rise to products of several structure types, including five isomeric products formed with either ring expansion or ring opening. The ring-expansion products are formed in the highest yields, viz., 2-phenyl-3,4-dihydro-2*H*-benzopyran,[28] **2** (∼25%), 2-benzyl-2,3-dihydrobenzofuran,[29] **3** (∼35%), and 1-*o*-hydroxyphenylin-

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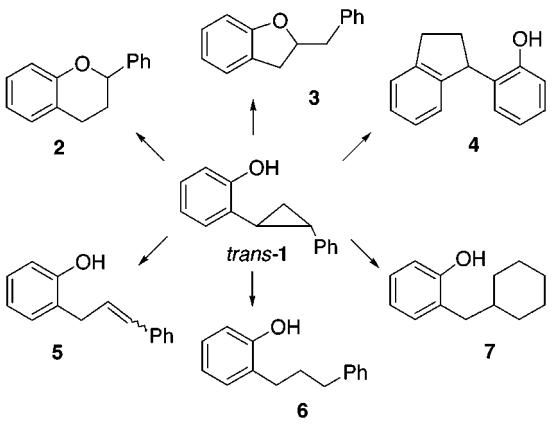
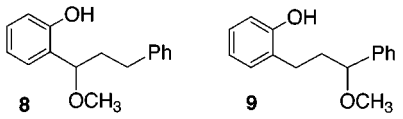
Scheme 1



dan,[30] **4** (~8%). Ring-opened products include *cis*- and *trans*-1,3-diarylpropenes, **5** (~5% each), and a saturated ring-opened diarylpropane, **6** (~5%). Finally, the structure of *o*-(α-cyclohexylmethyl)phenol[31] (~15%), **7**, suggests reaction of a fragment of the starting material with the solvent (Scheme 1). At 30% conversion, the material balance was 72%. Direct irradiation of a mixture, consisting of 90% *cis*-**1** and 10% *trans*-**1**, gave rise to essentially the same product distribution. However, the cis isomer was depleted significantly (~10 times) faster.

Upon direct irradiation (through quartz) in methanol as reagent/solvent, the formation of essentially all intramolecular reaction products was suppressed in favor of two methanol adducts, **8** and **9**[32] (in yields of 55 and 43%, respectively; mass balance 93% at 70% conversion). Only the saturated ring-opened diarylpropane, **6**, was formed in minor yield (~2%).



Acetone-sensitized irradiation of *trans*-**1** (through Pyrex) resulted in geometric isomerization to *cis*-**1**, a very clean reaction with excellent material balance (96% at 40% conversion). Similarly, irradiation of acetone solutions containing *trans*-1-*o*-acetyloxyphenyl-2-phenylcyclopropane (*trans*-**10**) caused geometric isomerization to *cis*-**10**.

Discussion

Direct irradiation of *trans*-**1** generates the excited singlet state, *trans*-^{1}**1***. Phenol excited states are known to show enhanced acidity;[20,21] typically, they react by (intramolecular) proton transfer, if a suitable proton-accepting function is present. This type of reaction generates zwitterionic intermediates that combine to form cyclic ethers. For example, the alkene isomer of *trans*-**1**, 3-(*o*-hydroxyphenyl)-1-phenylpropene (*trans*-**5**), upon irradiation forms the same two cyclic ethers, **2** and **3**, obtained from *trans*-**1**; their formation was rationalized by excitation of two π-complex conformers via two "tight" zwitterions, **11**-zw and **12**-zw (Scheme 2).[21] Substrates lacking an intramolecular hydroxyl function reacted in intermolecular fashion; for example, photoexcited phenylcyclopropanes add methanol.[2] In light of this and other precedence, we expected proton transfer from the phenolic hydroxy function to the three-membered ring. Proton transfer was all the more anticipated, as the FT-IR spectrum of *trans*-**1** showed a narrow "associated" OH band (3604 cm^{-1}), indicating a weak intramolecular complex between the phenolic OH and the cyclopropane ring (Figure 1). A similar association between the OH group and an alkene function was observed for *trans*-**5**.[21]

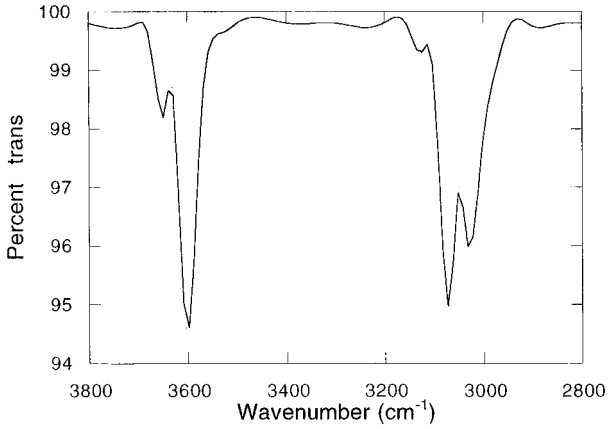
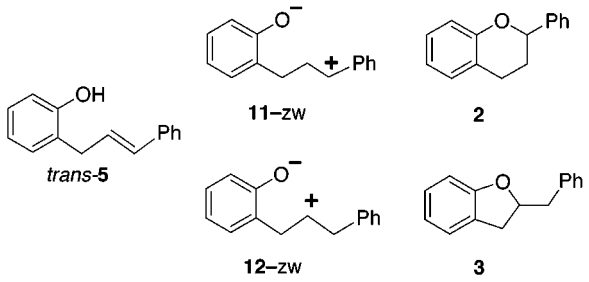


Figure 1. Gas-phase FT-IR spectrum (3800−2800 cm^{-1}) of *trans*-1-*o*-hydroxyphenyl-2-phenylcyclopropane (*trans*-**1**).

Scheme 2



Reactions of *trans*-1 Involving "Addition" of the OH Group. The cyclic ethers, **2** and **3**, obtained in cyclohexane and the open-chain ethers, **8** and **9**, formed in methanol formally are in line with the anticipated reaction. Ethers **8** and **9** are readily explained via methanol addition across the doubly benzylic bond (vide infra). For the cyclic ethers **2** and **3**, protonation at the secondary cyclopropane carbon (C_3) can be excluded as it would generate a methyl group, which is clearly not present. Product **2** is readily explained by protonation at the tertiary benzylic cyclopropane position next to the phenol moiety (C_1) with opening of the doubly benzylic bond; cyclization of zwitterion **11**-zw accounts for the formation of product **2** (Scheme 3) in direct analogy to its formation from *trans*-**5**.[21] In contrast, the formation of cyclic ether **3** was unexpected; it poses an interesting mechanistic problem.

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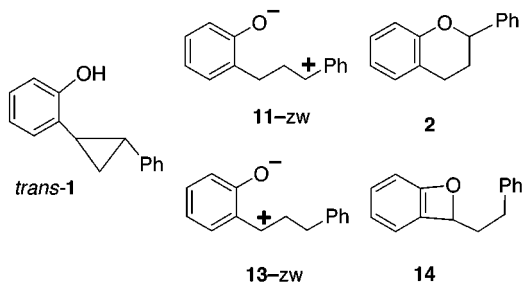
Scheme 3



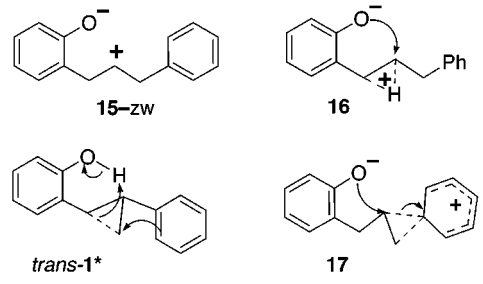
A trivial explanation for its formation involves ring opening of *trans*-**1** to *cis*- or *trans*-**5**, followed by a secondary photoreaction of the cinnamylphenols;[21] however, this cannot be the only pathway to **3**. Irradiation of *trans*-**1** produces **3** as the predominant product (35%), whereas **5** forms larger quantities of **2** (30%) than of **3** (22%).[21] Thus, even if the entire yield of **2** (25% from *trans*-**1**) were formed via **5** (which is unlikely), close to 50% of **3** would have to be formed by a separate pathway not involving **5**.

Potential Pathways to 3. Since cyclic ether **3** has two benzylic methylene groups, its formation must include a rearrangement, either a hydrogen shift or a reorganization of the carbon skeleton. The structure of **3** does not reveal the position to which the proton is transferred. Protonation at the benzylic cyclopropane carbon next to the phenyl ring (C_2) would generate a zwitterion with a benzylic carbocationic site, **13**-zw, but this species cannot explain the formation of **3**; cyclization of **13**-zw (Scheme 3) would form the highly strained benzooxetene, **14**, an unlikely precursor for **3**.

A hydride shift in zwitterion, **13**-zw, would yield a rearranged zwitterion, **15**-zw, which is a reasonable precursor for **3**; however, conversion of a benzylic (**13**-zw) to a secondary carbocation (**15**-zw) is hardly favorable. A hydride shift in concert with the approach of the phenoxyl group (transition state **16**) lacks precedent. Thus, **13**-zw is an unlikely precursor for **3**.

A more appealing alternative involves protonation at C_1 with cleavage of a singly benzylic (C_1–C_3) bond, assisted by the phenyl group forming a phenonium ion, **17**. Capture of the tertiary carbon of **17** by the phenoxyl group would give rise to ether **3** (Scheme 4). The key

Scheme 4



intermediate postulated has ample precedent; phenonium ions have been invoked in various solvolysis reactions, including on primary carbons.[33–35]

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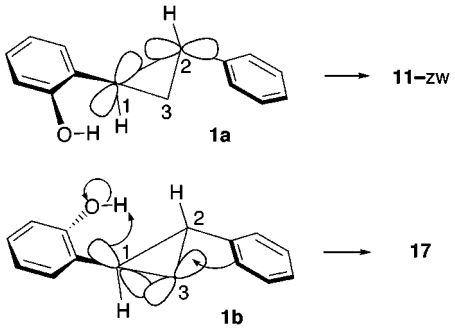
A mechanism involving two different pathways via protonation at the same carbon (C_1) may appear unlikely; however, two conformers with different orientations of the phenol moiety may protonate the cyclopropane ring with different "trajectories", leading to different intermediates. One conformer may cause cleavage of the C_1–C_2 bond, generating the "ordinary" zwitterion, **11**-zw. Another conformer may transfer the proton with cleavage of the C_1–C_3 bond; this attack is feasible only if the phenyl moiety stabilizes the developing primary carbocation, forming the phenonium ion, **17** (Scheme 5).

Scheme 5



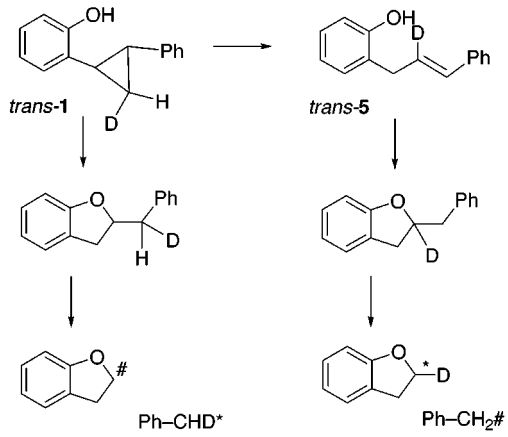
It is a moot point whether these reactions proceed in concerted fashion or involve short-lived intermediates. The key point is the stabilization of a developing primary carbocation by neighboring group participation of the phenyl group. This type of stabilization is in the best tradition of phenonium ion involvement (although these species do not appear to be in fashion currently).[33–35]

If the course of the reaction is determined by two phenol rotamers, the stereochemistry of the phenyl group may be less important; it appears that a phenonium ion can be formed by capturing the back lobe of a Walsh orbital from either face of the ring plane. This would explain why the photochemistry of the cis isomer gives rise to the same product distribution, albeit with enhanced efficiency.

Partition between Ring-Opening and Phenonium Ion Mechanism. The partition between the projected mechanisms leading to **3**, ring-opening to cinnamylphenol, **5**, and excited-state proton-transfer involving the putative phenonium ion, **17**, can be evaluated by analyzing the fate of a deuterium label in the cyclic ether. For this purpose, we synthesized *trans*-1-*o*-hydroxyphenyl-2-phenylcyclopropane-*d* (*trans*-**1**-*d*) from D-exchanged 1-*o*-hydroxyacetophenone in a three-step synthesis via chalcone and pyrazoline. MS analysis indicated a deuterium content of ~50% for *trans*-**1**-*d*. The photoproducts contained similar levels of D; the molecular ions of the cyclic ethers, **2** and **3**, had ~55 and ~45% deuterium, respectively (Scheme 6).

The analysis of the fragment ions derived from **3** indicated the presence of D in both a larger (dihydrobenzofuranyl) and a smaller fragment ion (benzyl). This finding supports two different pathways for the formation of **3**, placing D either into the benzyl or the dihydrofuran moiety. The distribution of the label between the fragments is derived from the intensities of the appropriate peaks. The analysis of the larger fragment ion(s) (F_1, *m*/*e* = 119+, C_8H_7O, dihydrobenzofuranyl, − C_7H_7; F_1 − H, 118+, benzofuran+, H transfer to benzyl via McLafferty rearrangement; − C_7H_8) is complicated by the coincidence

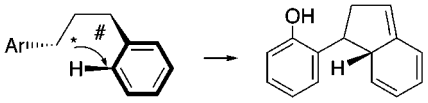
Scheme 6



of F_1-$^{13}C_1$ with F_1-d_1 peaks and of F_1 with (F_1-d_1 − H) peaks. The data suggest an essentially equal distribution of the label between the fragments, ~32% in the larger vs ~33% in the smaller fragment ion. Although the numerical data contain uncertainties, they nevertheless establish unambiguously the existence of two different pathways leading to **3**.

Reactions of *trans*-1 Not Involving the OH Group. The third ring expansion product, the indan derivative, **4**, as well as the ring-opened alkenes (*cis*- and *trans*-**5**), and the ring-opened diarylpropane, **6**, are generated in reactions without involvement of the phenolic hydroxyl group. With the possible exception of **6**, products of these structure types have precedence in photolysis reactions of cyclopropane systems. Indan derivatives are typical photolysis products of diarylcyclopropanes;[1−3] a reaction of this type was first observed in the photolysis of the symmetrical prototype, 1,2-diphenylcyclopropane.[1] The conversion is readily explained via cleavage of the doubly benzylic cyclopropane bond, yielding a 1,3-bifunctional species, **18**, either a biradical (*, # = •) or a zwitterion (* = +, # = −). Addition of one benzylic carbon, a free radical or carbocation, to the second aromatic ring, followed by a 1,3- (or 1,7-) hydrogen shift in the resulting *exo*-methylenecyclohexadiene intermediate, **19**, then gives rise to the observed indan (Scheme 7).

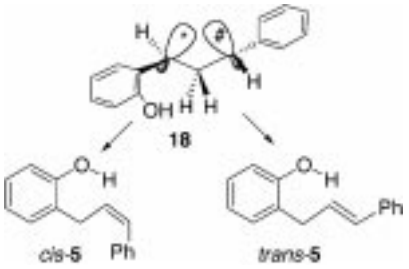
Scheme 7



Unsymmetrical substrates, such as *trans*-**1** in our study, may form two different ring-expansion products via two different methylenecyclohexadiene species. The exclusive formation of indan derivative, **4**, in the photolysis of *trans*-**1** documents an interesting regiochemical preference. It indicates that the *o*-hydroxybenzyl (cationic) site is more reactive than the unsubstituted benzyl function. Conversely, attack on the unsubstituted benzene ring is easier than attack on the phenol ring. This preference can be rationalized as a result of resonance electron donation by the *o*-hydroxy substituent.

The formation of the geometric isomers, *cis*- and *trans*-**5** and of product **6** also require ring opening. The formation of alkenes from cyclopropanes may proceed either in concerted fashion by a [1,3]-sigmatropic shift

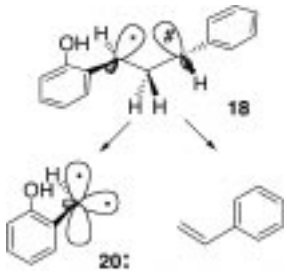
Scheme 8



or via a 1,3-bifunctional intermediate of type **18** and hydrogen migration (Scheme 8). In the case of the ring-opened intermediate, a hydrogen shift in different conformers can explain the formation of the isomeric alkenes; concerning the excited state, a [1,3]-sigmatropic shift can account for the isomeric alkenes, depending on the identity of the migrating hydrogen, the nature of the intermediate, and the stereochemistry of the migration. The ring-opened diarylpropane, **6**, requires a reduction step, in addition to ring opening.

Cyclopropane Fragmentation. One of the products formed upon direct irradiation of *trans*-**1**, *o*-(α-cyclohexylmethyl)phenol, **7**, is significantly different from any other product or the starting material. It consists of two components, suggesting that a fragment of *trans*-**1** reacts with the solvent; product **7** is compatible with fragmentation of an excited state, **1***, generating styrene and *o*-hydroxyphenylmethylene, **20:**. A biradical of the general structure type **18** (*,# = •) is a possible intermediate in the formation of **20:**. The resulting carbene fragment then reacts with the solvent, cyclohexane, by (formal) C−H insertion (Scheme 9).

Scheme 9



The generation of phenylmethylene upon photolysis of diarylcyclopropanes has precedent; irradiation of 1,2-diphenylcyclopropane in methanol generated benzyl methyl ether, which was rationalized via phenylmethylene.[1,3] Similarly, irradiation of 2,3-diphenyloxirane gave rise to insertion and addition products of phenylmethylene. When this reaction was carried out at cryogenic temperatures, a carbonyl ylide was identified as an intermediate based on its optical absorption spectra; upon warming to 140 K, this intermediate underwent thermal fragmentation to phenylmethylene.[36]

Typical arylmethylenes have triplet ground states;[34] the corresponding singlet states, when generated in solution, undergo rapid intersystem crossing. The carbene presumably involved in the current system has not been studied because the acidity of the phenolic OH group is incompatible with the diazo function in the potential

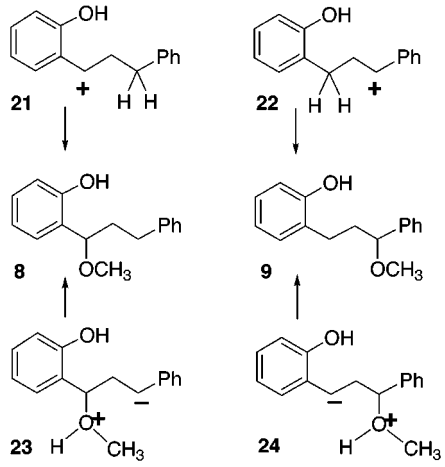
(36) Do-Minh, T.; Trozzolo, A. M.; Griffin, G. W. *J. Am. Chem. Soc.* **1970**, *92*, 1402−1403.

precursor. It is not clear whether the fragmentation proceeds in one or two steps or whether the singlet state, ^{1}**20**, or the triplet state, ^{3}**20**, of the carbene is the primary intermediate generated in this process. Interestingly, the fragmentation generates only one carbene; products derived from phenylmethylene are not observed. Once again, as in the selective formation of the indan, **4**, the precursor shows a pronounced regiochemical preference. In the case of the fragmentation leading to ^{1}**20**, this preference can be rationalized as a result of resonance electron donation by the *o*-hydroxy substituent and, possibly, by a lone pair contribution.

Photolysis in Methanol. Upon direct irradiation through quartz with methanol instead of cyclohexane as solvent, the intramolecular formation of the cyclic ethers **2** and **3** was suppressed in favor of two methanol adducts, **8** and **9**. This observation can be explained by a competition between intramolecular reactions (proton transfer, ring-opening, fragmentation) and intermolecular quenching. The alcohol function of the solvent (~20 M) will fully solvate the phenol function, replacing the weak intramolecular association between the phenolic O−H function and the cyclopropane ring. Accordingly, it is not surprising that the intramolecular proton transfer is efficiently suppressed. On the other hand, the suppression of ring-opening and fragmentation by methanol requires an efficient reaction of the external reagent with the excited singlet state, ^{1}**1***.

This reaction may proceed either by protonation with ring opening, generating benzylic carbocations, **21** and **22**, or by nucleophilic attack with ring opening, giving rise to zwitterions, **23** and **24** (Scheme 10). Because

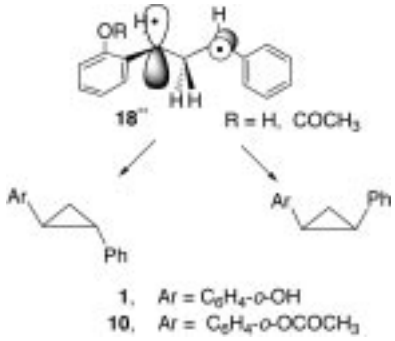
Scheme 10



alcoholic OH functions are less acidic than phenolic ones, the intermolecular proton transfer is not expected to be highly efficient. However, the molar concentration of methanol is very high.

Acetone-Sensitized Irradiation. Irradiating solutions of *trans*-**1** in acetone through Pyrex resulted in geometric (cis,trans) isomerization to *cis*-**1**. Similarly, irradiation of acetone solutions containing *trans*-1-*o*-acetyloxyphenyl-2-phenylcyclopropane (*trans*-**10**) caused clean rearrangement to the cis isomer. Under these conditions, the direct irradiation of *trans*-**1** or *trans*-**10** is precluded, and all incident irradiation is absorbed by acetone. The initially excited singlet state of acetone undergoes rapid intersystem crossing, populating the triplet state. The acetone triplet energy (E_T = 78 kcal/mol) is sufficiently high to allow energy transfer to *trans*-**1** (or *trans*-**10**). This follows from a comparison with the triplet energy assigned to 1,2-diphenylcyclopropane,[38,39] $E_T \approx 53$ kcal/mol or to the corresponding biradical, $E_T \approx 29$ kcal/mol.[18] The resulting triplet state derived from **1** or its acetate, **10**, could be either a biradical or a phosphorescent triplet-state, viz., ^{3}**1***. (Scheme 11). In the potential biradical (structure type

Scheme 11



18, *,# = •), the C_1-C_2 bond is broken, whereas in the phosphorescent triplet-state, ^{3}**1***, the C_1-C_2 bond may be weakened; in either case, the isomerization would be facilitated. These results are similar to other cyclopropane compounds undergoing triplet-sensitized[2,3] or electron-transfer-induced[6,7,18] geometric isomerization.

The electron-transfer-induced geometric isomerization of *cis*- and *trans*-1,2-diphenylcyclopropane[6,7] involves radical cations and triplet species consecutively. The radical cations retain a significant degree of bonding in the doubly benzylic (C_1-C_2) bonds and fail to undergo geometric isomerization. The lifetimes of cis and trans radical cations with respect to isomerization must be greater than their spin lattice relaxation times ($^2T_1$'s typically fall into the microsecond range).[6,7] The failure of the radical cations to isomerize was recently confirmed by fast, time-resolved optical spectroscopy.[18] On the other hand, the triplet intermediates contain the substituents in orthogonal planes; upon deactivation, they may "collapse" to either the cis or trans ground state.[6,7]

Nature of Bifunctional Reaction Intermediates. 1,3-Diarylpropane-1,3-diyl intermediates of the general structure type **18** have been discussed as potential intermediates in the formation of four different product types obtained under different reaction conditions. These product types include the geometric cyclopropane isomer, *cis*-**1**, the (ring-opened) alkenes, *cis*- and *trans*-**5**, the (ring-enlarged) indan, **4**, and the formal carbene insertion product, **7**. Having delineated the various reaction types, we can define the nature of one of these intermediates somewhat more narrowly and define limitations for the others. Because the (acetone) triplet-sensitized reaction of *trans*-**1** shows a highly specific reactivity, limited to the formation of *cis*-**1**, we identify the corresponding intermediate as a triplet biradical, **18••**. This assignment is in keeping with the detailed results of the electron-

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transfer induced geometric isomerization of 1,2-diphenylcyclopropane.[6,7,18]

Given the specific reactivity of **18••**, the (generic) bifunctional species considered as intermediates in the formation of **4**, *cis*- and *trans*-**5**, and **7** cannot have biradical structures. Specifically, the carbene, **20:**, is not likely derived from **18••**, because there is no precedent of carbene formation from 1,2-diphenylcyclopropane triplet biradical.

Conclusion

The photochemistry of the *trans*-diarylcyclopropane, *trans*-**1**, gives rise to an interesting variety of products. The cyclic ethers, **2** and **3**, obtained upon direct irradiation in cyclohexane are rationalized by intramolecular proton transfer, reflecting the enhanced acidity of phenol excited states; however, a significant fraction of **3** is formed via prior ring-opening to cinnamylphenol, **5**. The formation of *o*-(α-cyclohexylmethyl)phenol, **7**, is rationalized via fragmentation of *trans*-**1** yielding *o*-hydroxyphenylcarbene and insertion into cyclohexane. Direct irradiation in methanol produced methanol adducts **8** and **9**; all products formed in cyclohexane were suppressed. Finally, acetone-sensitized irradiation of *trans*-**1** resulted in geometric isomerization to *cis*-**1**; this result is rationalized via a biradical intermediate.

Experimental Section

Materials. Diarylcyclopropane (*trans*-**1**) was prepared by a reaction sequence initiated by Claisen−Schmidt condensation of *o*-hydroxyacetophenone with benzaldehyde; condensation of the resulting chalcone with hydrazine hydrate generated a pyrazoline,[40,41] which was deazetized under basic conditions.[19] A D-labeled sample was prepared from *o*-hydroxyacetophenone-d_3 and benzaldehyde (∼50% D incorporation).

Irradiation Procedures. A. Exploratory experiments were carried out with solutions of 0.02 g of the substrate in 7 mL of solvent; these were irradiated for 1 h in Pyrex or quartz tubes surrounding a central quartz cooling jacket with a 125-W medium-pressure mercury lamp. **B.** For preparative runs, solutions of 1.00 g of the substrate in 400 mL of freshly distilled solvent were irradiated at ambient temperature with a 125-W medium-pressure mercury lamp inside a quartz immersion well.

Isolation. Reaction products were isolated and purified by conventional column chromatography on silica gel Merck 60 (0.063−0.200 mm), by preparative thin layer chromatography on silica gel Merck 60 PF_{254}, using dichloromethane as eluent, or by means of isocratic HPLC equipment provided with a semipreparative Microporasil column, using hexane/ethyl acetate as eluent.

Identification. Products were identified by comparison with authentic samples by GC retention time and MS and FTIR spectra. A sample of 1-*o*-hydroxyphenylindan, **4**, was independently synthesized from indan and phenol according to a literature procedure.[30] IR spectra were recorded on a GC−FTIR instrument; ^1H (^{13}C) NMR spectra ($CDCl_3$) were recorded at 300 (75) MHz; mass spectra were obtained on a commercial low-resolution electron impact mass spectrometer; high-resolution mass spectra were determined at SCSIE with either electron impact or chemical ionization. Combustion analyses were performed at the Instituto de Quimica Bio-Orgánica of the CSIC in Barcelona.

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Supporting Information Available: IR (ν_{max}, cm^{-1}), ^1H NMR (300 MHz, $CDCl_3$, δ, ppm downfield of TMS), ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm downfield of TMS), and mass spectra (*m*/*z*, relative intensities) for compounds *cis*-**1**, **8**, and *cis*- and *trans*-**10**. Synthesis, photoreaction, and mass spectral data of *trans*-**1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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