Photochemistry in a Crystalline Cage. Control of the Type-B Bicyclic Reaction Course: Mechanistic and Exploratory Organic Photochemistry[1,2]

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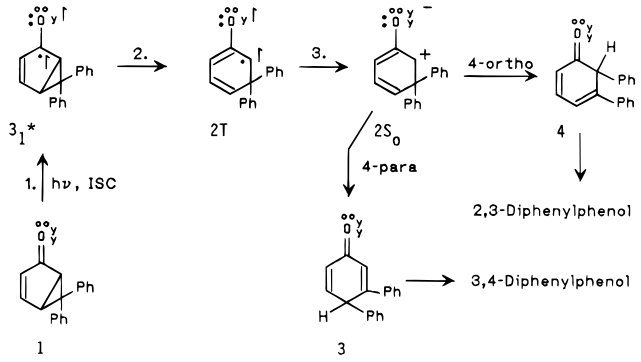
Abstract: Our current theories on crystal lattice control of organic photochemistry were subjected to studies of type-B rearrangement of bicyclo[3.1.0]hex-3-en-2-ones. A first finding was that the solid state photochemistry differed dramatically from that in solution. One of our past observations in this bicyclic photochemistry in solution was that the six-membered ring, type B, zwitterion was a ubiquitous intermediate. This intermediate invariably underwent a preferential migration of an aryl group to carbon-2 relative to carbon-4 with formation of a 2,3-disubstituted phenol, a result deriving from electronic effects. In contrast, the crystal lattice photochemistry revealed a regioselectivity depending on the surrounding lattice rather than electronics. Perhaps an even more dramatic difference was an observation of the dependence of reactant stereochemistry. Thus, in solution, for 6,6-disubstituted bicyclics with two different groups at C-6, a common zwitterion is formed and the same photoproduct is formed independent of reactant stereochemistry. In crystal lattices the endo and exo stereoisomers of the 6,6-disubstituted bicyclics react differently and the group originally endo tends to migrate after three-ring opening to the zwitterion. The experimental results were paralleled with a theoretical analysis. This consisted of generation of a "mini crystal lattice" with sufficient lattice molecules to completely surround a central, reacting electronically excited state molecule. Then computational extraction of the central molecule and replacement by a transition structure afford a model of the reacting excited state inside the crystal lattice. Overlap of this species with the lattice neighbors and energy computations are then possible. These permit prediction and understanding of excited state crystal lattice reactivity on a quantitative basis.

Introduction

One of the most fascinating reactions we have encountered in our photochemical studies has been the type-B[3] rearrangement of bicyclo[3.1.0]hex-3-en-2-ones.[4] The reaction of the n−π* triplet permits two competitive three-membered ring openings. A priori, either the internal bond or an external bond might be severed. Irreversible fission of the internal bond leads to a six-membered ring diradical as shown in Scheme 1. Intersystem crossing affords the type-B zwitterion which then rearranges.[4]

In our previous studies, we have investigated a variety of complex rearrangements which proceed differently in crystalline media than in our earlier solution research. More importantly, we provided a new general theory correlating reactivity with crystal structure.[5,6] Thus, we decided to extend our efforts to the type-B bicyclic rearrangement. The basic philosopy is that, even with minor changes in substituents, not anticipated to have major effects on solution photochemistry, one may expect different crystal packing patterns and different space groups. With different orientations of neighboring molecules in a crystal, any one reacting excited state molecule should have its reactivity modified in a major way by the surrounding lattice.

Scheme 1. Type-B Rearrangement via a Zwitterion Intermediate[4e *a*]



a **2T** is a triplet while $\mathbf{2S_0}$ is a ground state singlet.

Results

Synthesis of Reactants. The syntheses of starting materials are outlined in Schemes 2−4. One basic approach involved the thermal reaction of diaryldiazomethanes with cyclopent-2-

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1997.

(1) This is paper 245 of our general series and 180 of our photochemical papers.

(2) For our last photochemical publication see: Zimmerman, H. E.; Hoffacker, K. D. *J. Org. Chem.* **1996**, *61*, 6526−6534.

(3) This rearrangement originally was termed a "type B" process as it was the reaction of the product of the "type A" lumi rearrangement. However, the migration of a π-group from C-4 to C-3 of the cyclohexenone also has been termed a type B process. Thus, "type-B bicyclic" and "type-B enone" are more appropriate.

(4) (a) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1961**, *83*, 4486−4487. (b) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1962**, *84*, 4527−4540. (c) Zimmerman, H. E.; Grunewald, J. O. *J. Am. Chem. Soc.* **1967**, *89*, 3354−3356. (d) Zimmerman, H. E.; Grunewald, J. O. *J. Am. Chem. Soc.* **1967**, *89*, 5163−5172. (e) Zimmerman, H. E.; Epling, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 3245−3246. (f) Zimmerman, H. E.; Epling, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 7806−7811. (g) The "circle-dot-y" notation was introduced[4a,b] to permit one to write a three-dimensional electronic structure in two dimensions. The o's represent sp hybrid electrons, p_y's the "n" in-plane electrons, solid dots π-system electrons, and double bonds π-system electron pairs.

(5) (a) Zimmerman, H. E.; Zuraw, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 2358−2361. (b) Zimmerman, H. E.; Zuraw, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 7974−7989.

(6) (a) Zimmerman, H. E.; Zhu, Z. *J. Am. Chem. Soc.* **1994**, *116*, 9757−9758. (b) Zimmerman, H. E.; Zhu, Z. *J. Am. Chem. Soc.* **1995**, *117*, 5245−5262.

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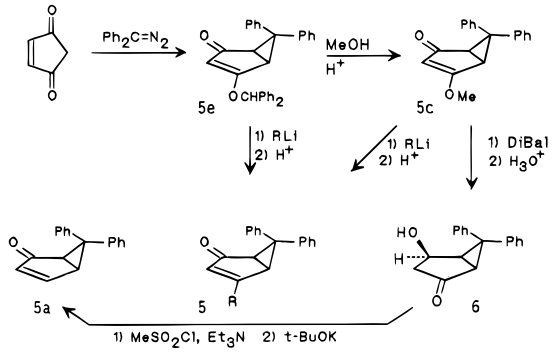
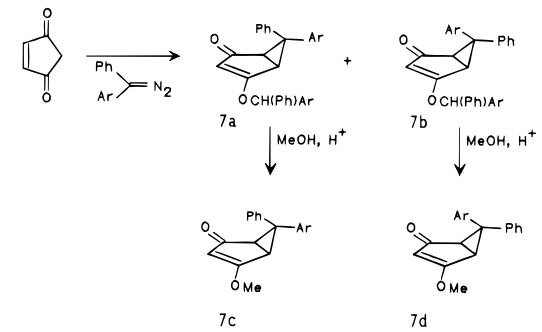
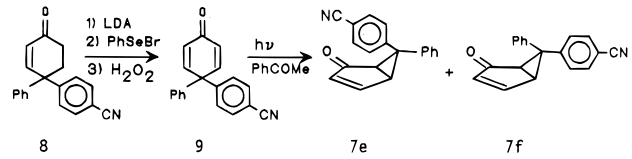
Scheme 2. Synthesis of Diphenyl Reactants



Scheme 3. Synthesis of Stereoisomeric Reactants



Scheme 4. Synthesis of Phenyl, *p*-Cyanophenyl Reactants



ene-1,4-dione to afford a bicyclo[3.1.0]hex-3-en-2-one skeleton. This general approach has proven useful in our earlier research.[7] Presently, the methodology, in leading to the enol ethers of bicyclo[3.1.0]hexane-1,3-diones, had the advantage of permitting the facile introduction of a variety of groups at the β-carbon of the enone moiety. As noted above, such minor variation in structure promised totally different solid-state photochemistry in these closely related reactants.

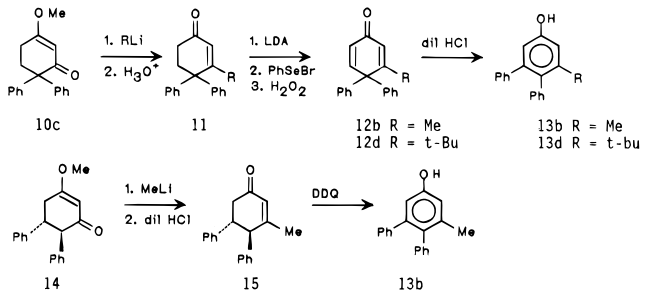
Synthesis of Potential Photoproducts. In addition, with known solution photochemistry in mind and with mechanistic reasoning, some potential photoproducts were selected for independent synthesis. The selection was based as well on structures of photoproducts encountered in the research as it proceeded. We concentrated our synthesis on photoproducts which promised to be elusive and less available for structure elucidation. Independent synthesis of really major photoproducts was less necessary, since these compounds were readily available for X-ray structure determination.

From our previous investigations there was reason to anticipate the formation of both 2,3-diphenyl-substituted and 3,4-diphenyl-substituted phenols. However, in the present study, of course, additional groups were present. Additionally, there was evidence for the role of linearly conjugated cyclohexa-2,4-dienones, and three were synthesized as well. These syntheses are outlined in Schemes 5−7.

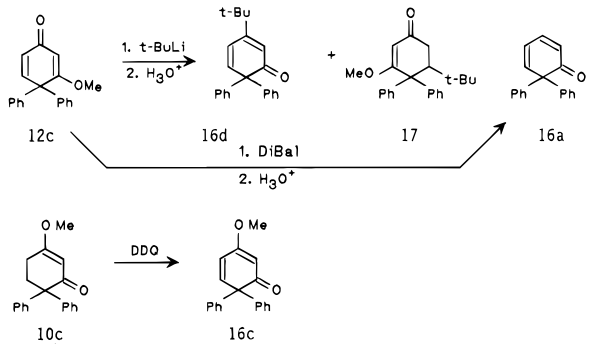
The dienone−phenol rearrangement of **12b** and **12d** to give the 5-methyl- and 5-*tert*-butyl-3,4-diphenylphenols (**13b** and **13d**) (note Scheme 5), respectively, is not totally unambiguous, since there is the possibility of the C-4 phenyl migrating to the

(7) Zimmerman, H. E.; Pasteris, R. J. *J. Org. Chem.* **1980**, *45*, 4864−4876.

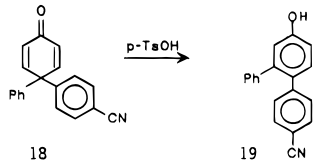
Scheme 5. Synthesis of Some 5-Substituted 3,4-Diphenylphenols



Scheme 6. Synthesis of Two Linearly Conjugated Dienones



Scheme 7. Synthesis of 3-Phenyl-4-(*p*-Cyanophenyl)phenol



substituted β-carbon and then onward to C-2. For this reason the alternative synthesis starting from methoxy diphenyl enone **14** was employed; it did afford the product anticipated from a simple dienone−phenol rearrangement.

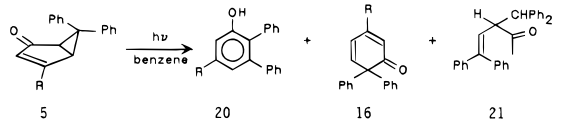
In the case of the dienone−phenol rearrangement of 4-phenyl-4-(*p*-cyanophenyl)cyclohexa-2,5-dienone (**18**), the product structure **19** is deduced from the preference for phenyl over *p*-cyanophenyl migration in cationic rearrangements.

Photochemistry. Solution Behavior. For our study of the effect of crystal lattices on the photochemistry of these bicyclic systems, it was necessary first to determine the behavior in solution. Irradiation in benzene led to three types of photoproducts: (a) substituted phenols, (b) ketenes and their products of nucleophilic addition, and (c) 2,4-cyclohexadienones (i.e., "linear dienones"). From a different perspective, mechanistic in nature, there are several alternative bond-fission processes which are potentially available to the excited state. One is scission of the internal three-ring bond. A second is breaking of an out-of-plane bond. Since here we are concerned with the nature of the products, the mechanistic aspects will be mentioned here only when relevant and delayed for the Discussion of Results section.

Thus, the solution photochemistry was carried out first. Scheme 8 tabulates the course of the reactions and the products obtained. The photoproduct structures in the cases of **20a** and **20c** were known, independently prepared and checked by NMR analysis. Of the remaining structures, **16a**, **16c**, and **16d** were synthesized independently and the structures of **16b**, **20d**, **20e**, and **21** were established by X-ray analysis. The structure of **20b** was derived from NMR analysis (see the Experimental Section).

We note that in Scheme 8 both the 2,3-diphenylphenol derivatives and the linearly conjugated 2,4-cyclohexadienone

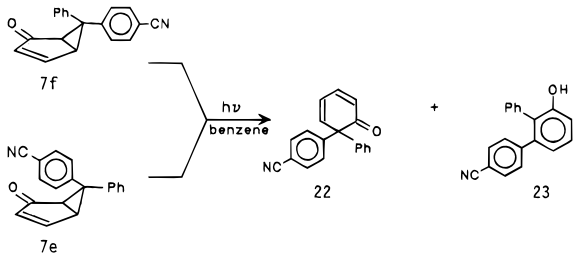
Scheme 8. Solution Photolysis of a Series of Bicyclics



REACTANT		PRODUCT RATIO[a] 20		16		21	CONVERSION[b]
5a	R = H	20	:	80	:	NONE	80 %
5b	R = Me	27	:	73	:	NONE	40 %
5c	R = MeO	43	:	57	:	NONE	10 %
5d	R = t-Bu	37	:	63	:	NONE	35 %
5e	R = Ph_2CHO	38	:	12	:	48	10 %
5e	R = Ph_2CHO	36	:	4	:	60	24 %
5e	R = Ph_2CHO	39	:	0	:	61	44 %
5e	R = Ph_2CHO	40	:	0	:	60	70 %

[a] Ratios by NMR analysis.[b] Maximum conversion studied without variation.

Scheme 9. Irradiation of the Stereoisomeric *p*-Cyanophenyl, Phenyl Bicyclics in Benzene



derivatives **16** are formed in every case. However, with a diphenylmethoxy substituent, a new photoproduct, **21**, an unsaturated ketone, is formed.

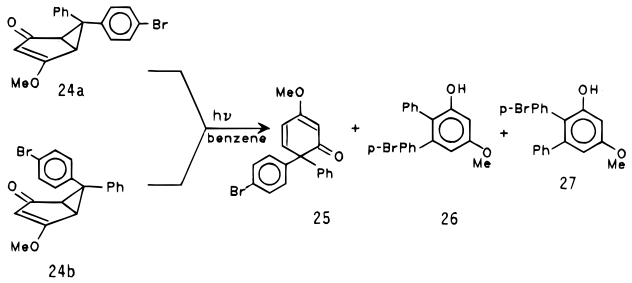
While we defer discussion of the detailed reaction mechanisms, for the present we note differences from our earlier solution studies[4,7−9] in polar solvents. Thus, in contrast, no 3,4-diarylphenols are formed from irradiation in benzene. In polar media the linear cyclohexadienones were not formed. Also, products resulting from a conjugated ketene (Ph_2C═CH−CH═CH−CH═C═O) were encountered in nucleophilic solvents but not presently in benzene. Finally, the formation of the unsaturated ketone **21** is without precedent.

The solution photochemistry of the stereoisomeric 6-(*p*-cyanophenyl)-6-phenylbicyclo[3.1.0]hexenones **7e** and **7f** was of considerable interest not only for comparison with the solid-state chemistry but also because in our earlier studies[4c,d] in polar solvents it had been observed that there was complete regioselectivity with preferential migration of phenyl relative to *p*-cyanophenyl. Additionally, there was a preference for migration to carbon-2 compared to C-4 in a ratio of 3:1. This evidence indicated that the intermediate undergoing aryl migration was the zwitterion $\mathbf{2S_0}$ rather than its triplet counterpart **2T** (note Scheme 1). The reasoning was that, in migrations to an odd-electron center, cyanophenyl should be preferred while in migrations to a cationic center, phenyl should migrate more readily.

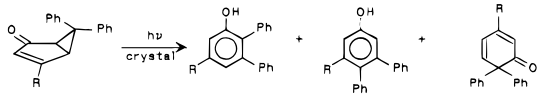
In benzene solvent, the same preference for phenyl migration was observed. However, in contrast to the polar solvent irradiation, independent of reactant stereochemistry, only migration to carbon-2 resulted; note Scheme 9. In this case the 2-phenyl-3-(*p*-cyanophenyl)phenol (**23**) was known from our earlier studies[4c,d] and the structure of the linear dienone **22** was established by its NMR spectrum and its spectroscopic pattern close to that of the other linear dienones. Note Scheme 9 for the reaction course observed in benzene.

The second difference in this benzene photolysis was the formation of the linear dienone **22**. In aqueous nucleophilic solvents, the photoacid of structure Ar_2C═CH−CH═CH−CH_2−COOH was formed instead.

Scheme 10. Photolysis of *p*-Bromophenyl, Phenyl Bicyclics in Benzene



Scheme 11. Crystal Lattice Photolysis of a Series of Bicyclics



REACTANT		PRODUCT RATIO 20		13		16	CONVERSION
5a	R = H	60	:	40	:	NONE	to 15%, a
5b	R = Me	0	:	100	:	NONE	to 70%, b
5c	R = MeO	100	:	0	:	NONE	to 30%, c
5d	R = t-Bu	42	:	8	:	50	to 5%, d

[a] Loss of selectivity beyond 15%.[b] Melting beyond 70% conversion.[c] Not attempted beyond 30%.[d] Loss of selectivity and new products beyond 5% conversion.

Finally, irradiation of each cyanophenyl bicyclic (i.e., **7e** or **7f**) with partial conversion to photoproduct resulted in no interconversion of the reactant with its stereoisomer.

A similar photolysis of the *p*-bromophenyl, phenyl bicyclics **24a** and **24b** (Scheme 10) differed in proceeding with nearly equal extents of phenyl-migrated and bromophenyl-migrated phenols (i.e., **26** and **27**). However, the product ratio was again found to be independent of reactant configuration.

Photochemistry. Crystal Lattice Behavior. In pursuing the crystal lattice counterparts of the solution photochemistry, we began by studying the β-substituted bicyclics (i.e., **5a**, **5b**, **5c**, **5d**, and **5e**). The photochemical methodology utilized was patterned after that which we used in our earlier studies. The results with reactants **5a**, **5b**, **5c**, and **5d** are collected in Scheme 11. The results obtained from **5e** are discussed separately.

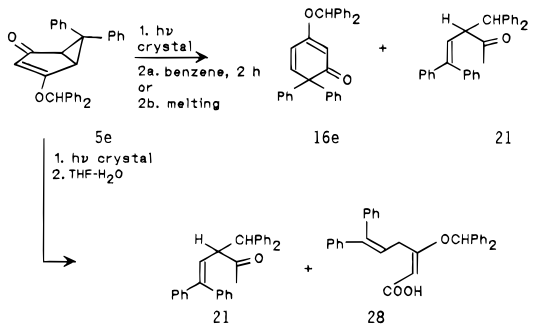
Evidence for those photoproducts also formed in the solution photochemistry has been discussed above. The structure of 3,4-diphenylphenol (**13a**) was known.[4a,b] That of 5-methyl-2,3-diphenylphenol (**13b**) and 5-*tert*-butyl-2,3-diphenylphenol (**13d**) was derived from independent syntheses discussed earlier. Similarly 3-*tert*-butyl-6,6-diphenyl-1,3-cyclohexadienone (**16d**) had been independently prepared (vide supra).

The case of the β-benzhydroxy bicyclic **5e** proceeded differently in that no phenolic photoproducts resulted. In addition, the NMR spectrum of the crystalline photoproduct showed a (diphenylmethoxy)ketene, **37e**, to be the main product. However, after photolysis, dissolving in THF−water the diphenylmethoxy carboxylic acid **28** was formed along with the methyl ketone **21** (Scheme 12). On keeping the photolysis product in dry benzene for 1.5 h or, instead, melting the crystal, the linear dienone **16e** was obtained along with the same methyl ketone **21**. Thus, the crystal lattice photolysis contrasted with the solution photochemistry in affording none of the phenol **20e** but was similar in giving the linear dienone **16e** seen in the solution photochemistry.

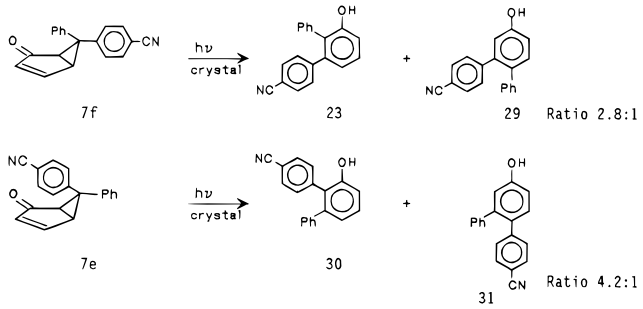
Turning to the stereoisomeric 6-(*p*-cyanophenyl)-6-phenylbicyclo[3.1.0]hex-3-en-2-ones, **7e** and **7f**, crystal lattice

(8) Zimmerman, H. E.; Nasielski, J.; Keese, R.; Swenton, J. S. *J. Am. Chem. Soc.* **1966**, *88*, 4895−4903.
(9) Zimmerman, H. E.; Lynch, D. C. *J. Am. Chem. Soc.* **1985**, *107*, 7745−7756.

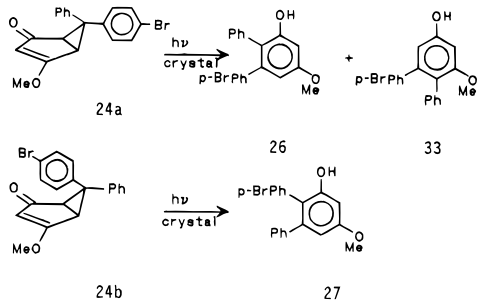
Scheme 12. Crystal Photochemistry of the Diphenylmethoxy Bicyclic **5e**



Scheme 13. Crystal Lattice Photolysis of the *p*-Cyanophenyl, Phenyl Bicyclics



Scheme 14. Crystal Lattice Photochemistry of the *p*-Bromophenyl, Phenyl Bicyclics



conversions were carried out in runs ranging up to 20% in the case of **7e** and 40% in the case of **7f**. This chemistry is outlined in Scheme 13. Unlike the solution photochemistry, the reaction course did depend on the configuration of the reactant bicyclic enone. In the case of the *exo*-cyano stereoisomer **7f**, the normal preference for phenyl vs cyanophenyl migration was observed. Additionally, the usual preference for migration to C-2 compared to C-4 was seen. In dramatic contrast, the endo reactant **7e** led to a preference for cyanophenyl migration, both to C-2 and to C-4, with the former being preferred. Thus, it is the endo group which tends to migrate predominately.

The stereoisomeric 6-(*p*-bromophenyl)-6-phenylbicyclo[3.1.0]-hex-3-en-2-ones **24a** and **24b** were the last to be studied as crystal lattices. The results are given in Scheme 14. In the case of the exo stereoisomer **24a** a 3:1 preference for phenyl migration to C-2 compared with C-4 was encountered; only a minor amount (ca. 3 %) of bromophenyl migration was observed. The endo stereoisomer **24b**, in contrast, afforded bromophenyl migration with the phenyl migration product (i.e., **26**) as a very minor product. Thus, again these results are quite different from those of the solution photochemical counterpart. Firstly, here in the crystal lattice photochemistry, the same product distribution did not result from the two stereoisomers. Secondly, the linear dienone **25** was not formed. Thirdly, the preference for phenyl migration no longer was encountered. And finally, there was a preference for the endo group to migrate.

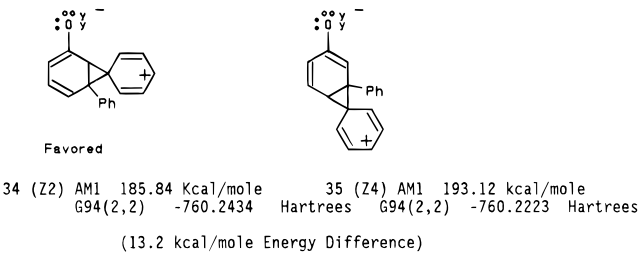
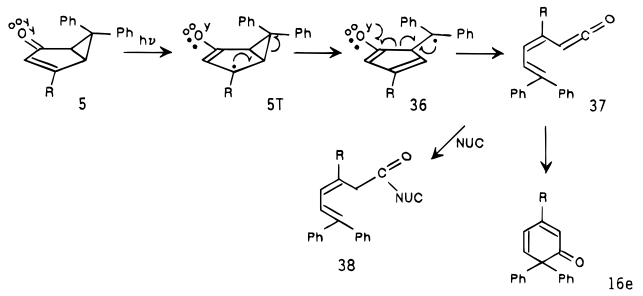


Figure 1. Two alternative pathways for the type-B zwitterion.

Scheme 15. Ketene Formation and Competitive Reactions[a]



[a] **5T** and **36** are triplets.

Interpretative Discussion

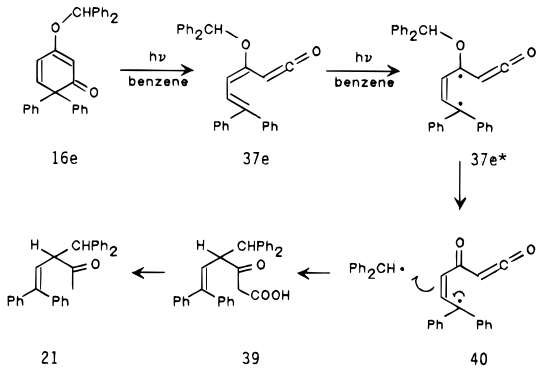
Discussion of the Solution Photochemistry. The preference for the formation of 2,3-diphenylphenols relative to the their 3,4-isomers has been ascribed to lower energy of the bridged zwitterionic species **34** compared with **35**.[4b,8,10] This is the species leading from the type-B zwitterion[4,8] $\mathbf{2S_o}$ in Scheme 1 onward to the two alternative phenols. The selectivity results from extra delocalization of the dienolate **34** compared to the monoenolate **35**. This is the qualitative suggestion we made decades ago. AM1 and ab initio computations now confirm this; an energy difference (AM1, 17.3 kcal/mol; G92 CASSCF(2,2)/3-21G, 13.2 kcal/mol) (see Figure 1) favors the 2,3-zwitterion. As noted above, the selectivities tended to be on the order of 3:1. As the acidity of the medium was increased, migration to C-4 increased relative to C-2.[8] In contrast, however, in benzene only the 2,3-diphenyl isomer was formed. Since this was observed for all cases studied, it appears to be a general phenomenon. The most reasonable rationale seems to be that, in hydroxylic solvents, the negative oxygen becomes hydrogen bonded with inhibition of enolate delocalization, the source of the regioselectivity preferring migration to C-2 (vide supra). This also accounts for the lower selectivity in hydrogen bonding solvents than anticipated from a 13 kcal/mol calculated energy difference.

A second point of interest is the formation of the linear dienones[11a−c] which had not been observed in our earlier solution photochemistry carried out in hydroxylic solvents. While the phenolic photoproducts result from in-plane three-ring fission, the formation of ketenes results from external three-ring bond breaking as outlined in the mechanism in Scheme 15. In the presence of a nucleophile, an acid or acid derivative is formed by trapping[4] while in the absence of a nucleophile, as in benzene solvent, an electrocyclic closure to form linear dienone occurs.

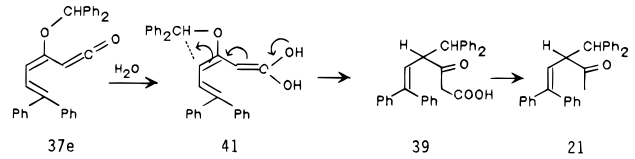
(10) Zimmerman, H. E. In *Advances in Photochemistry*; Noyes, A., Jr., Hammond, G. S., Pitts, J. N., Jr., Eds.; Interscience: New York, 1963; Vol. 1, pp 183−208.

(11) (a) See refs 11b,c for examples and further references on the thermal cyclization of ketones to linear cyclohexadienones. For a discussion see: Schaffner, K. In *Rearrangements in Ground and Excited States*; DeMayo, P., Ed.; Academic Press: New York, 1980; pp 328−330. (b) Quinkert, G. *Angew. Chem.* **1972**, *11*, 1072−1087. (c) Chapman, O. L.; Kane, M.; Lassila, J. D.; Loeschen, R. L.; Wright, H. E. *J. Am. Chem. Soc.* **1969**, *91*, 6856−6858. (d) Allinger, N. L. *MM3*; University of Georgia, December 1990. (e) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902−3909.

Scheme 16. Mechanism Involving Secondary Photolysis of the Ketene



Scheme 17. Alternative Mechanism for Formation of Methyl Ketone



A final point about the competition between the in-plane versus out-of-plane bond scission is that overlap of the π-system with the in-plane bond is not orthogonal as might be surmised. Thus, the Coulson "banana" bonds are close to sp^5 oriented and aim below the five-membered ring.

One particularly interesting case is the photolysis of the β-(diphenylmethoxy)-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**5e**) to afford the methyl ketone **21** in addition to the 2,3-diphenylphenol **20e** and the linear dienone **16e**. Two mechanisms are reasonable possibilities; note Schemes 16 and 17.

The second possible mechanism assumes that the enediol intermediate, formed in the reaction of the ketene, rearranges in a thermal process as depicted in Scheme 17. The driving force for this process is conversion of the unstable enediol to a more stabilized enol of a β-dicarbonyl compound.

Discussion of the Crystal Lattice Photochemistry. The Differences. That the photochemistry observed in crystal lattices differed from the solution counterparts was not surprising, and the differences emphasize the way in which external steric constraints, imposed by the surrounding lattice, may overcome the normal electronic and other intramolecular energetic factors which control a solution reaction. The variations with different lattice constraints, however, are dramatic and informative.

One of the striking results was the observation that the normal preference for formation of the 2,3-diphenylphenols characteristic of the solution photochemistry was no longer general. In the parent bicyclic **5a**, lacking substituents, close to equal amounts of the 2,3-diphenyl- and 3,4-diphenylphenols were found. With a β-methyl substituent, the bicyclic **5b** gave only migration to carbon-4. Thus, the 13 kcal/mol electronic preference (vide supra) was overcome by the crystal lattice cage effect.

Another remarkable difference was the absence of formation of the ketenes and the ketene cyclization products, namely, the linear dienones, in three of the bicyclics studied (i.e., **5a**, **5b**, and **5c**).

In the case of the diphenylmethoxy bicyclic **5e** the ketene photoproduct, along with the methyl ketone **21**, could be observed at the reaction end, thus permitting observation of the reactivity of the ketene.

A particularly remarkable result was found in the *p*-cyanophenyl, phenyl-substituted bicyclics **7e** and **7f**. In contrast to the solution photochemistry, fission of the internal three-ring bond did not lead to a common intermediate with common behavior. What is meant here is that the intermediate zwitterion must be taken as paired with the surrounding lattice which differs for the two reactants. Thus, it was observed that the aryl group which was originally endo was the one which migrates. Qualitatively, this may be understood on the basis that the endo group is "tucked" into a space within the molecule's outer periphery rather than protruding into the lattice space. The endo group hence has more possibility for motion. This is not obvious and emphasizes the importance of quantitative assessment of lattice interference. Preferential migration of the *p*-cyanophenyl group in the case of the endo reactant provides an antithesis to solution mechanistic considerations. A priori, either (i) an electronically reluctant cyanophenyl group is forced to migrate to a somewhat positive center in the type-B zwitterion or, alternatively, (ii) rearrangement of the precursor triplet diradical (of general structure **2T** in Scheme 1) is more rapid than intersystem crossing, and it is the triplet diradical which rearranges in the crystal. In migration of a triplet diradical such as **2T**, cyanophenyl migration should take preference over phenyl migration. It is possible that steric constraints might prevent formation of a conformation favorable to optimal spin−orbit coupling with consequent inhibition of intersystem crossing. But since the endo group is the less hindered one, this possibility seems remote. Hence, aryl migration of the zwitterion seems the more likely mechanism.

The preference for migration of the *endo*-aryl group is confirmed by the same behavior of the *p*-bromophenyl, phenyl-substituted bicyclics **24a** and **24b** where a totally different lattice is present. Another difference observed for the cyanophenyl and bromophenyl reactants is lack of external three-ring fission, leading to a linear dienone and hence a ketene. Intuitively it seems that scission of an out-of-plane bond requires more space than fission of an in-plane bond. Finally, that appreciable migration of aryl groups to C-4 occurred, contrasting with the reactivity in benzene, is only part of the pattern of the a priori unpredictability of crystal lattice behavior.

Quantitative Treatments. We have reported several quantitative treatments of crystal lattice reactivity.[5,6] The basic approach involves computer generation of a "mini crystal lattice" composed of just enough molecules (e.g., 20) to completely surround a central molecule which is then taken as the reacting one. Next, this central molecule is computationally removed from the crystal lattice and replaced by a variety of alternative transition structure models. The most useful structures for the purpose of predicting a reaction course are the "branch points", namely, the alternative species formed from a common precursor which has partitioned itself. Thus, for 2,3-aryl migration relative to 3,4-aryl migration, structures **34** and **35** were used with appropriate substitution and with stereochemistry corresponding to that of its precursor. The electronic state was not defined.

One way of considering this situation is expressed in eqs 1a and 1b. Here we have the energies of the components of the crystal lattice with the included central molecule. This central

$$EL(S) = EL(Empty) + ES(Min) + ES(Deform) + ELS \quad (1a)$$

$$EL(R) = EL(Empty) + ER(Min) + ER(Deform) + ELR \quad (1b)$$

Energy of Lattice With SM or Reacting Species	Energy of Empty Lattice	Energy of Geometry Optimized Guest	Guest Deformation Energy	Lattice-Guest Interaction Energy
		Energy of Extracted Guest		
ΔEL	Zero	Calc'd		By Difference

molecule might be the reactant (eq 1a) or an imbedded transition

Table 1. Calculated Deformation and Interaction Energies (kcal/mol) for the Branch Points for Phenol Formation with Rigid Superpositions

	migration to C-2				migration to C-4			
substrate	obsd	Ed	Ei	sum[d]	obsd	Ed	Ei	sum[d]
H endo	*c*	12.7	−37.1	−24.4	*c*	10.7	−33.7	−23.0
H exo		18.4	−34.0	−15.6		19.1	−21.4	−2.3
Me endo		21.6	−30.1	−8.5	*c*	10.7	−32.1	−21.9
Me exo		16.0	−27.8	−11.8		13.5	−18.7	−5.2
MeO endo	*c*	3.2	−34.8	−31.6		15.0	−24.7	−9.7
MeO exo		17.9	−30.8	−12.9		17.0	−25.1	−8.1
t-Bu endo	*c*	8.8	−51.8	−43.0		8.5	−37.3	−28.8[e]
t-Bu exo		14.7	−48.1	−33.4		15.3	−32.7	−17.4
CNPh endo	*c*	10.6	−41.2	−30.6		10.8	−38.0	−27.2[e]
Ph exo		39.9	−22.5	17.4		19.4	36.9	17.5
Ph endo				X-ray data not available				
CNPh exo								
BrPh endo	*c*	9.2	−39.0	−29.8		30.7	6.1	36.8
Ph exo		26.5	−26.2	0.3		19.9	−32.6	−12.7
Ph[a] endo	*c*	13.0	−42.8	−29.8	*c*	14.0	−39.6	−25.6
BrPh exo		17.7	−24.9	−7.2		16.1	−28.5	−12.4
Ph[b] endo		12.8	−34.6	−21.8		12.3	−39.7	−27.4
BrPh exo		26.2	−30.3	−4.1		20.6	−30.7	−10.1

[a] Molecule 1. [b] Molecule 2. *a* and *b* refer to two conformations in the crystal lattice. [c] Process predicted and in accord with observation. [d] Underlining indicates observed products. [e] Minor product.

Table 2. Calculated Deformation and Interaction Energies (kcal/mol) for the Branch Points for Phenol Formation with Flexible Superpositions

	migration to C-2				migration to C-4			
substrate	obsd	Ed	Ei	sum[d]	obsd	Ed	Ei	sum[d]
H endo	*c*	11.8	−37.0	−25.2	*c*	11.1	−33.3	−22.2
H exo		9.1	−33.8	−14.7		19.1	−22.0	−2.9
Me endo		21.2	−30.0	−8.8	*c*	9.5	−31.8	−22.3
Me exo		15.0	−28.1	−13.1		14.3	−19.7	−5.4
MeO endo	*c*	3.7	−35.3	−31.6		14.1	−25.2	−11.1
MeO exo		16.0	−29.9	−13.9		19.5	−27.2	−7.7
t-Bu endo	*c*	9.7	−51.8	−42.1		9.6	−38.7	−29.1[e]
t-Bu exo		14.5	−47.9	−33.4		19.4	−36.4	−17.0
CNPh endo	*c*	11.5	−41.5	−30.0		10.8	−37.2	−26.2[e]
Ph exo		28.4	−26.7	1.7		20.2	−37.6	17.4
Ph endo				X-ray data not available				
CNPh exo								
BrPh endo	*c*	8.9	−39.6	−30.7		27.7	−36.0	−8.3
Ph exo		29.7	−28.9	0.8		18.5	−32.8	−14.3
Ph[a] endo	*c*	12.1	−38.8	−26.7	*c*	11.7	−38.0	−26.3
BrPh exo		20.6	−33.3	−12.7		16.1	−28.5	−12.4
Ph[b] endo		12.3	−34.5	−22.2		10.4	−39.0	−28.6
BrPh exo		26.9	−31.1	−4.2		20.0	−29.3	−9.3

[a] For conformer I in the crystal lattice. [b] For conformer II in the crystal lattice. [c] See footnote *c* in Table 1. [d] See footnote *d* in Table 1. [e] See footnote *e* in Table 1.

structure, intermediate, or product (eq 1b). EL is the summation of the energy of the empty lattice, plus the energy of the guest (i.e., ER or ES), as it exists in the lattice, plus the energy of interaction of the guest with the lattice (i.e., ELR or ELS). However, since the imbedded guest molecule will be deformed somewhat by inclusion in the lattice, its energy can be further dissected into its optimal energy when isolated outside the lattice plus a deformation energy. All of this is summarized in eqs 1a and 1b.

EL for the mini crystal lattice is measurable using molecular mechanics. After computational extraction of the central, imbedded molecule, EL(empty) is measurable in the same way. The third item calculated is ES (or ER) in eq 1, namely, the energy of the extracted molecule in the conformation it originally had in the crystal. Thus, all terms of either eq 1a or eq 1b are known except for one, ELS or ELR, which is the lattice−guest interaction energy. This is obtained then by difference.

Geometry optimization of the extracted molecule leads to a lowering of its energy, since it had been deformed by the surrounding lattice molecules. The energy decrease on geometry optimization then corresponds to the molecule's deformation energy, the penalty it pays for inclusion in the lattice.

Finally, the subtraction of corresponding terms in eq 1a from eq 1b, we can determine the total energy change ΔEL in having the new molecule in the crystal lattice compared with the reactant. Alternatively, one can determine the guest deformation energy and the energy due to lattice−guest interaction. In placing various molecular species into the mini crystal lattice, we have used a "rigid superposition", wherein the molecule with original geometry is placed so that its atoms are optimally close to the positions of the original, central lattice molecule replaced. Here the injected molecule was subjected to geometry optimization in the crystal cavity, and its deformation energy (Ed) and lattice interaction energy (Ei) were calculated. Table 1 gives results based on this method.

A second approach, "flexible superposition", permitted dihedral rotation about single non-ring bonds in order to obtain the optimal position of each atom relative to the atom of reactant being replaced. Table 2 below gives the energies computed on this basis. We note that electronic effects are not included by either method since MM3[11d] was used to compare final energies.

In our past studies of crystal lattice photochemistry we have attempted to determine different measures of "fit" of the reacting molecule in the crystal lattice[5,6] including the energetic considerations discussed above. However, still another property

Table 3. Calculated Overlap at the Branch Points for Phenol Formation with Rigid Superpositions

	migration to			migration to	
substrate	C-2	C-4	substrate	C-2	C-4
H endo	*18.8	*20.0	Ph endo		
H exo	26.6	31.4	CNPh exo		
Me endo	31.0	*21.2	BrPh endo	*17.3	31.3
Me exo	31.9	36.6	Ph exo	42.9	37.3
MeO endo	*10.1	19.1	Ph[a] endo	*16.7	22.9
MeO exo	33.1	25.2	BrPh exo	31.9	36.0
t-Bu endo	*12.3	*15.4[d]	Ph[b] endo	19.5	20.7
t-Bu exo	32.9	32.9	BrPh exo	31.1	34.7
CNPh endo	*28.0	*27.0[d]			
Ph exo	34.8	35.2			

[a] Molecule 1. [b] Molecule 2. [c] Overlap is in Å3. The asterisk signifies predicted photoproduct. Underlining signifies the observed product. [d] Minor product.

Table 4. Calculated RMS Motion (Å) at the Branch Points for Phenol Formation with Rigid and Flexible Superpositions[c]

	rigid super migration to		flexible super migration to	
substrate	C-2	C-4	C-2	C-4
H endo	1.60	1.26	1.03	0.75
H exo	1.59	1.95	1.04	1.28
Me endo	*1.50	1.09	*0.79	0.73
Me exo	1.48	2.05	1.48	2.05
MeO endo	*1.13	1.31	*0.64	0.81
MeO exo	2.14	1.81	1.33	1.16
t-Bu endo	*1.10	1.40[d]	*0.72	0.76[d]
t-Bu exo	1.41	1.73	0.95	1.20
CNPh endo	1.25	1.28[d]	0.83	0.82[d]
Ph exo	1.84	1.49	1.28	0.95
Ph endo	X-ray data not available			
CNPh exo				
BrPh endo	1.78	1.43	1.13	0.82
Ph exo	1.82	2.15	1.08	1.38
Ph[a] endo	1.78	1.28	1.08	0.75
BrPh exo	1.75	2.17	1.08	1.35
Ph[b] endo	1.78	1.34	1.08	0.72
BrPh exo	1.81	2.26	1.12	1.36

[a] Molecule 1. [b] Molecule 2. [c] The asterisk signifies predicted photoproduct. Underlining signifies the observed product. [d]Minor product.

is the overlap of the van der Waals radii of the reacting molecular species with the atoms of the surrounding crystal lattice. Again the mini crystal lattice with the imbedded intermediate zwitterion was utilized. The overlaps, ΔS values, calculated are listed in Table 3. The agreement with experiment is quite good. One might anticipate that the van der Waals overlap with the crystal lattice corresponds to the reaction molecule−lattice interaction energy, that is, the last term in eq 1.

A final parameter we have used in attempts to quantify the behavior of photochemistry in crystal lattices is the measurement of RMS motion in proceeding from reactant to first intermediate. The premise is that the preferred reaction will be the one which involves the least motion[12] of the reacting molecule. Again, both rigid and flexible superpositions were used to generate the reacting species and thus in determining the RMS motion. Note Table 4. However, inspection of this table reveals a rather poor correlation useful in dealing with previous types of solid-state reactions in the past.

Thus, it seems that the predictive value of the energetics and overlap provide the best approach in correlating the reaction course in a crystal lattice with theory.

Alternative Methodology and Background. The present research results need to be taken in perspective with earlier findings in mind. Thus, the early work of Cohen and Schmidt[13] considered $2\pi + 2\pi$ cycloadditions and put forth the concept of a "reaction cavity".[13a] A more quantitative suggestion made by Schmidt[13b] was that such $2\pi + 2\pi$ cycloadditions will take place when the intermolecular distance between the π bonds is 4.2 Å or less. A particularly interesting approach was described by Gavezzotti[14a] who used the packing potential energy of a dissociating peroxide reactant. This quantity affords the energy of one molecule taken from infinity and inserted into a crystal lattice. Another treatment involved molecular volumes available in cavities of inclusion compounds.[14b] Still another idea was the energy of pyramidalization of a dimethylamino group in an intermolecular methyl transfer reaction, and the packing potential was also used for this reaction.[14c,d] Another quantitative approach, this by Ramamurthy,[15] dealt with the dimerization of coumarin derivatives. The treatment considered local van der Waals attractive and repulsive forces exerted on the photoproducts relative to the reactant pairs. A different approach was employed by McBride[16] using molecular mechanics to ascertain the ease of migration of fragments within the reaction cavity in free radical dissociations. A recent communication describes the use of molecular mechanics to obtain the difference in energy of the most stable conformation of a final product molecule in a crystal lattice and the geometry-optimized conformation outside of the lattice.[17] Scheffer in an elegant study has compared the ease of two dibenzobarrelene esters to twist toward a bridged intermediate; in this he used van der Waals attractive and repulsive forces.[18a] In a more recent study he has suggested control by steric compression effects in a 2 + 2 cycloaddition.[18b] Ohashi[19] has correlated the volumes of cavities of two crystal modifications with the rates of racemization of a cobalt complex. Lahav and coworkers[20] have used packing potentials to correlate with ease of group rotation in considering intermolecular hydrogen abstraction of deoxycholic acid−acetophenone inclusion compounds. Hasegawa[21] studied cinnamate oligomerizations by 2 + 2 cyclization and correlated these with π-bond separations. Finally, Thomas[22] has used van der Waals attractive and repulsive forces to obtain potential energies of a molecule with its adjacent neighbors and related this to 2 + 2 intermolecular

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cyclizations; his finding was that those pairs with higher energies of interaction with six surrounding molecules tend to react.

Interestingly, Gavezzotti has commented[16e] that "the general problem of obtaining information on solid-state reactivity from a theoretical calculation has not yet been tackled in a systematic way". And, indeed, the main weakness of the literature has been the application to a limited number of examples rather than a broad spectrum of test cases. Additionally, the emphasis on either reactant and/or product effects has been a problem. Crystal lattice photochemistry is clearly kinetically controlled in most cases.

Many additional but more qualitative treatments of reactivity have also been described. However, an excellent general review has been edited by Ramamurthy,[18] and this covers both qualitative and quantitative approaches.

Turning to our own earlier studies,[5,6] we note that use was made of volume increase during reaction, least motion in proceeding toward product, and the overlap of the transition structure with the crystal lattice. Additionally, the transition structure deformation energy in the lattice and the energy of replacing a reactant molecule with a transition structure molecule were obtained. Finally, a "lock and key" analysis was devised to determine which points of contact of the reacting molecule were most involved in controlling its reaction course. These studies have utilized a large number of different reactants of widely varying structures rather than single examples and thus provide a sound test of the methodologies employed.

Assessment of Treatments. Firstly, it is clear that for unimolecular rearrangements all methods are not applicable. Secondly, in determining what reaction courses are likely, one needs to select branch points in the reaction, most simply alternative intermediates, each leading to different photoproducts. Although the use of final photoproducts has been successful in cases,[5] it is clear that once the transition state is passed, control by alternative products is not relevant. Theories based on single examples do pose a risk. Finally, one notes that both intramolecular energy deformation and molecule−lattice interaction energies contribute to controlling what species may be formed in the lattice.

Experimental Section

General Procedures. All reactions were performed under an atmosphere of dry nitrogen. Column chromatography was performed on silica gel (Matheson, Coleman and Bell, grade 62, 60−200 mesh) mixed with Sylvania 2282 phosphor and slurry packed into quartz columns to allow monitoring with a hand-held UV lamp. Preparative thick-layer chromatography (TLC) was carried out with MN-Kiesegel G/UV 254 silica gel (40 g of silica gel per plate, 20 cm × 20 cm) unless stated otherwise. Plates were dried for 24 h after preparation at room temperature. Using this kind of TLC plates is important for successful isolation of photoproducts. Chromatography on commercially available column silica gel (see above) leads to their partial or total loss. Deactivated column silica gel was prepared by mixing 300 g of silica gel (see above) with 500 mL of water, subsequent filtration, drying for 12 h at room temperature, and heating at 85 °C for 3 h.

Exploratory solution photolyses were carried out with a Hanovia 450 W medium-pressure mercury lamp or a 400 W Sylvania discharge lamp equipped with a 5 mm filter of circulating solution of 0.025 M sodium metavanadate in 5% sodium hydroxide unless stated otherwise. All solutions were purged with purified[24] nitrogen both prior to and during photolysis. All compounds were subjected to multiple crystallizations until the melting point was constant. Tetrahydrofuran (THF) was purified by successive distillation under a nitrogen atmosphere, from calcium hydride, lithium aluminum hydride, and sodium−benzophenone ketyl. Diethyl ether was dried by distillation from sodium−benzophenone ketyl. Photograde benzene was prepared by washing four times with a mixture of 100 mL of saturated potassium permanganate and 10 mL of sulfuric acid, water, saturated sodium bicarbonate, and brine, drying over calcium chloride, refluxing overnight, and distilling from calcium hydride.

General Procedure for Solid State Photolysis. Large crystals were gently cracked. Crystals were spread over a strip of "Parafilm".[25] Both the photochemical reactor and the strip with crystals were placed in a drybox and purged with nitrogen for 1 h. The film was placed on the cooling well of the photochemical reactor, and the edges were tied up with Teflon tape. The cooling well was placed into the reactor flask filled with water and purged with nitrogen 1 h before and during photolysis. The photoreactor was placed in an ice−water bath. The temperature of the filter solution and water in the photoreactor was kept between 15 and 20 °C. Most of the irradiated crystals were recovered mechanically, and the rest were obtained by a quick washing of the Parafilm strip with a small amount of appropriate solvent.

General Procedure for X-ray Crystallography Analysis. X-ray diffraction data were collected on a Siemens P4/CCD diffractometer for single crystals of each compound. Lorentz and polarization corrections were applied, and each structure was solved under the appropriate space group symmetry by direct methods using SHELXTL and SHELXS86.[26] Hydrogen atom positions were calculated and refined with a rigid model. Full-matrix least-squares refinement on F^2 was carried out employing anisotropic displacement parameters for all non-hydrogen atoms and isotropic displacement parameters for all hydrogen atoms. The coordinates for all compounds studied by X-ray crystallography were deposited with the Cambridge Crystallographic Data Center. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Center, 12 Union Rd., Cambridge, CB2 1EZ, U.K.

***endo*-4-Hydroxy-6,6-diphenylbicyclo[3.1.0]hexan-2-one.** A 2.90 mL (2.90 mmol) solution of 1 M diisobutylaluminum hydride was added dropwise to a stirred solution of 670 mg (2.42 mmol) of 4-methoxy-6,6-diphenylbicyclo[3.2.1]hex-3-en-2-one[7] in 50 mL of benzene at 10 °C, and the mixture was stirred for 15 min. A 10 mL portion of water followed by 3 mL of 1.2 M HCl was added. The mixture was extracted twice with 60 mL of ether. A 20 mL portion of THF and 20 mL of 1.2 M HCl were added to the ether extract, and the mixture was stirred for 30 min at 20 °C. Ether extraction, washing with water, saturated sodium bicarbonate, and water, and drying with magnesium sulfate afforded crude product which was chromatographed on a silica gel 2.5 cm × 30 cm column. Elution with 50% ether in hexane gave 55 mg of a mixture of unidentified products in fraction 1 and 452 mg (71%) of *endo*-4-hydroxy-6,6-diphenylbicyclo[3.1.0]hexan-2-one **6** in fraction 2. Crystallization from benzene gave 412 mg (64%) of colorless crystals, mp 193−194 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.58 (m, 2H), 7.37−7.12 (m, 8H), 5.86 (m, 1H), 3.06 (dd, J = 5.7, 5.7 Hz, 1H), 2.66 (m, 1H), 2.36 (ddd, J = 18.4, 9.5, 1.4 Hz, 1H), 2.05 (d, J = 8.2 Hz, 1H), 1.36 (ddd, J = 18.4, 8.7, 0.8 Hz, 1H). MS *m/e* 264.1168 (calcd for $C_{18}H_{16}O_2$, 264.1150). IR (KBr) 1716 cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_2$: 81.79; H, 6.10. Found: C, 81.83; H, 6.24.

***endo*-6,6-Diphenyl-4-[(methylsulfonyl)oxy]bicyclo[3.1.0]hexan-2-one.** A 0.209 mL (2.70 mmol) portion of methanesulfonyl chloride was added dropwise to a mixture of 650 mg (2.46 mmol) of *endo*-6,6-diphenyl-4-hydroxybicyclo[3.2.1]hexan-2-one (**6**) and 0.514 mL (3.69 mmol) of triethylamine in 65 mL of dry methylene chloride at 0 °C. The reaction mixture was stirred for 1 h and then poured into 20 mL of 1.2 M HCl and extracted with ether. The organic layers were collected, washed with water, sodium bicarbonate, and brine, and dried with magnesium sulfate. Removal of solvent in vacuo afforded oil which crystallized after addition of a small amount of ether to give 796 mg (94%) of crude product. Crystallization from benzene−hexane gave 701 mg (83%) of colorless crystals, mp 113 °C dec.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.61−7.55 (m, 2H), 7.35−7.17 (m, 8H), 5.64 (ddd, J = 9.6, 8.4, 5.8 Hz, 1H), 3.25 (dd, J = 5.8, 5.8 Hz, 1H), 3.03 (s, 3H), 2.81 (brd, J = 5.8 Hz, 1H), 2.48 (ddd, J = 18.4, 9.6, 1.0 Hz, 1H), 1.62 (ddd, J =

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18.4, 8.4, 0.8 Hz, 1H); IR (KBr) 1735, 1348, 1180 cm^{-1}. Anal. Calcd for $C_{19}H_{18}SO_4$: C, 66.65; H, 5.30; S, 9.36. Found: C, 66.92; H, 5.61; S, 9.37.

6,6-Diphenylbicyclo[3.1.0]hex-3-en-2-one (5a). A 1.13 g (3.30 mmol) portion of *endo*-6,6-diphenyl-4-[(methylsulfonyl)oxy]bicyclo-[3.1.0]hexan-2-one was dissolved in 85 mL of dry THF, and 391 mg (3.48 mmol) of *t*-BuOK was added at 20 °C. The reaction mixture was stirred for 30 min and then poured into 100 mL of water and extracted with ether. The combined organic layers were washed with brine, dried with magnesium sulfate, and evaporated under vacuum. Chromatography of crude product on a 3 cm × 25 cm silica gel column eluted with 20% ether in hexane gave 149 mg (18%) of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**5a**). Crystallization from heptane gave 132 mg (16%) of colorless crystals, mp 140−141 °C (lit.[8] mp 140.0−140.2 °C).

4-Methyl-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (5b). To a −78 °C solution of 4.0 g (9.34 mmol) of 4-(diphenylmethoxy)-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**5e**)[7] in 95 mL of THF was added 10.0 mL of 1.4 M methyllithium in ether (14.0 mmol). The solution was stirred at −78 °C for 15 min, and 150 mL of water was added. The mixture was allowed to warm to 5 °C, 65 mL of 6 N HCl was added, and the mixture was stirred at room temperature for 1 h. Ether extraction, washing of the organic phase with saturated sodium bicarbonate, brine, and water, and drying with magnesium sulfate afforded 3.64 g of a white oil. Chromatography on a 4 cm × 30 cm silica gel column eluted with 10% ether in hexane afforded 1.53 g (89%) of diphenylmethanol (pure by NMR) in fraction 1. Fraction 2 gave 1.75 g (72%) of 3-methyl-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**5b**). Crystallization of enone **5b** from heptane gave 1.53 g (63%) of colorless crystals, mp 140−141 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.22−7.14 (m, 10 H), 5.28 (m, 1 H), 3.10 (d, J = 4.7, 1 H), 2.76 (dd, J = 4.7, 1.0 Hz, 1H), 2.12 (d, J = 1.2 Hz, 3H); IR (KBr) 1697, 1612 cm^{-1}. UV (MeCN) λ(max) = 340 nm (ϵ = 176); MS *m/e* 260.1203 (calcd for $C_{19}H_{16}O$, 260.1201). Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: C, 87.38; H, 6.07.

4-*tert*-Butyl-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (5d). To a −78 °C solution of 1.50 g (5.43 mmol) of 4-methoxy-6,6-diphenylbicyclo[3.1.0.]hex-3-en-2-one (**5d**)[7] in 45 mL of THF was added 4.15 mL of 1.7 M *tert*-butyllithium in ether (7.06 mmol). The solution was stirred at −78 °C for 15 min, and 75 mL of water was added. The mixture was allowed to warm to 5 °C, 90 mL of 6 N HCl was added, and the mixture was stirred at room temperature for 1 h. Ether extraction, washing of the organic phase with saturated sodium bicarbonate, brine, and water, and drying with magnesium sulfate afforded crude product. Chromatography on a 3 cm × 40 cm silica gel column eluted with 10% ether in hexane and crystallization from heptane gave 1.27 g (77%) of 4-*tert*-butyl-6,6-diphenylbicyclo[3.1.0]-hex-3-en-2-one (**5d**) as colorless crystals, mp 91−92 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) 7.36−7.15 (m, 10H), 5.39 (m, 1H), 3.28 (d, J = 5.0, 1.0 Hz, 1H), 2.69 (dd, J = 5.0, 1.3 Hz, 1H), 1.18 (s, 9H); IR (KBr) 1691, 1591 cm^{-1}; UV (MeCN) λ(max) = 345 nm (ϵ = 162); MS *m/e* 302.1678 (calcd for $C_{22}H_{22}O$, 302.1671). Anal. Calcd for $C_{22}H_{22}O$: C, 87.38; H, 7.33. Found: C, 87.57 H, 7.21.

4-(*p*-Cyanophenyl)-4-phenylcyclohexa-2,5-dienone (9). The general method of Reich et al.[27] was used. To a −78 °C of LDA (prepared by the addition of 4.77 mL (6.68 mmol) of 1.40 M methyllithium in hexane to 0.936 mL (6.68 mmol) of diisopropylamine in 32 mL of THF) was added a solution of 1.52 g (5.56 mmol) of 4-(*p*-cyanophenyl)-4-phenylcyclohex-2-en-1-one (**8**)[28] in 24 mL of THF. The solution was stirred at −78 °C for 15 min, and a solution of 6.68 mmol of phenylselenyl bromide (prepared by addition of 0.171 mL (3.34 mmol) of bromine to 1.04 g (3.34 mmol) of PhSeSePh in 5 mL of THF) was added in one portion. The reaction mixture was stirred for 5 min and poured into 50 mL of diethyl ether and 50 mL of 0.5 M HCl. Ether extraction, washing with saturated aqueous soduim bicarbonate and brine, drying with anhydrous magnesium sulfate, and concentrating in vacuo gave 2.37 g of crude product which was used without further purification. To a solution of 2.37 g of crude 4-(*p*-cyanophenyl)-4-phenyl-6-(phenylseleno)cyclohex-2-en-1-one in 20 mL of dichloromethane and 1.10 mL of pyridine was added 1.70 mL (15.0 mmol) of 30% H_2O_2. The solution was stirred at room temperature for 2 h, diluted with ether, washed with saturated aqueous sodium bicarbonate, 1.2 N HCl, and brine, dried with magnesium sulfate, and concentrated in vacuo. The crude product, 1.19 g, was chromatographed on a 3 cm × 30 cm silica gel column eluted with 30% ether in hexane. Fraction 1 gave 0.18 g of a mixture of unknown compounds. Fraction 2 gave 0.881 g (57%) of 4-(*p*-cyanophenyl)-4-phenylcyclohexa-2,5-dienone (**9**). Crystallization from hexane afforded 0.675 mg (44%) of colorless crystals, mp 151−153 °C (lit.[4d] mp 152−153 °C).

3-Methyl-4,4-diphenylcyclohexa-2,5-dienone (12b). The general method of Reich et al.[27] was used. To a −78 °C of LDA (prepared by the addition of 1.95 mL (4.57 mmol) of 2.35 M *n*-butyllithium in hexane to 0.671 mL (4.57 mmol) of diisopropylamine in 17 mL of THF) was added a solution of 1.0 g (3.81 mmol) of 3-methyl-4,4-diphenylcyclohex-2-en-1-one (**11b**)[29] in 5 mL of THF. The solution was stirred at −78 °C for 15 min, and a solution of 4.58 mmol of phenylselenyl bromide (prepared by addition of 0.118 mL (2.29 mmol) of bromine to 0.715 g (2.29 mmol) of PhSeSePh in 5 mL of THF) was added in one portion. The reaction mixture was stirred for 5 min and poured into 50 mL of diethyl ether and 50 mL of 0.5 M HCl. Ether extraction, washing with saturated aqueous sodium bicarbonate and brine, drying with anhydrous magnesium sulfate, and concentrating in vacuo gave 0.711 g of oil which was used without further purification. The crude product was dissolved in a mixture of 7 mL of dichloromethane and 0.28 mL of pyridine, and 0.55 mL (4.84 mmol) of 30% H_2O_2 was added. The solution was stirred at room temperature for 2 h, diluted with ether, washed with saturated aqueous sodium bicarbonate, 1.2 N HCl, and brine, dried with magnesium sulfate, and concentrated in vacuo to give 0.411 g (41%) of crude product. Crystallization from hexane afforded 318 mg (32%) of 3-methyl-4,4-diphenylcyclohexa-2,5-dienone (**12b**) as colorless crystals, mp 121−122 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.38−7.08 (m, 10H), 7.10 (d, J = 9.3 Hz, 1H), 6.33 (m, 1H), 6.26 (dd, J = 9.3, 1.5 Hz, 1H), 1.83 (d, J = 1.5 Hz, 3H); MS *m/e* 260.1213 (calcd for $C_{19}H_{16}O$, 260.1201); IR (KBr) 1650, 1617 cm^{-1}. Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: C, 87.50 H; 6.13.

3-Methyl-4,5-diphenylphenol (13b). Acid-Catalyzed Isomerization of 3-Methyl-4,4-diphenylcyclohexa-2,5-dienone (12b). The general procedure of Zimmerman et al.[4b] was used. A mixture of 100 mg (0.38 mmol) of 3-methyl-4,4-diphenylcyclohexa-2,5-dienone (**12b**), 1.5 mL of glacial acetic acid, 0.2 mL of water, and 0.5 mL of concentrated HCl was heated at 120 °C for 2 h. The solution was cooled, diluted with 25 mL of water, and extracted with chloroform. The extract was washed with water and brine, dried with magnesium sulfate, and concentrated under vacuum. Crystallization of the crude product from hexane gave 82 mg (82%) of 3-methyl-4,5-diphenylphenol (**13b**) as colorless crystals, mp 109−110 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.22−6.99 (m, 9H, arom), 6.79 (d br, J = 2.7 Hz, 1H), 6.78 (d br, J = 2.7 Hz, 1H), 6.74 (d br, J = 2.7 Hz, 1H), 4.68 (s, 1H), 2.13 (s, 3H); MS *m/e* 260.1200 (calcd for $C_{19}H_{16}O$, 260.1201); IR (KBr) 3150−3600, 1577, 1469, 1327, 1250, 1176, 1072, 1006 cm^{-1}. Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: C, 87.26; H, 6.19.

3-Methyl-4,5-diphenylphenol (13b). Oxidation of 3-Methyl-4,5-diphenylcyclohex-2-en-1-one (15). A mixture of 100 mg (0.38 mmol) of 3-methyl-4,5-diphenylcyclohex-2-en-1-one (**15**) and 116 mg (0.56 mmol) of DDQ in 10 mL of dioxane was refluxed for 31 h. The mixture was cooled and filtered quickly through a 5 cm × 2 cm silica gel column eluted with diethyl ether, and the solvent was removed in vacuo. Chromatography of the residue on a preparative TLC plate eluted with 7% ether in hexane afforded 24 mg (24%) of 3-methyl-4,5-diphenylphenol (**13b**). Crystallization from hexane gave colorless crystals, mp 107−109 °C.

3-Methyl-4,5-diphenylcyclohex-2-en-1-one (15). To a −78 °C solution of 120 mg (0.43 mmol) of 3-methoxy-5,6-diphenylcyclohex-2-en-1-one (**14**)[30] in 3 mL of THF was added 0.40 mL of 1.4 M

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methyllithium in ether (0.56 mmol). The solution was stirred at −78 °C for 15 min and then 5 mL of water added. The mixture was allowed to warm to 20 °C, 2 mL of 6 N HCl was added, and the mixture was stirred at room temperature for 1 h. Ether extraction, washing of the organic phase with saturated sodium bicarbonate, brine, and water, and drying with magnesium sulfate afforded crude product. Chromatography on a TLC preparative plate eluted with 20% ether in hexane gave 101 mg (90%) of 3-methyl-5,6-diphenylcyclohex-2-en-1-one (**15**). Crystallization from pentane gave 77.2 mg (69%) of colorless crystals, mp 65−67 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.28 −7.12 (m, 6H), 7.06−7.02 (m, 4H), 6.19 (m, 1H), 3.73 (d br, J = 7.7 Hz, 1H), 3.42 (ddd, J = 9.5, 7.7, 5.4 Hz, 1H), 2.77 (dd, J = 16.4, 9.5 Hz, 1H), 2.69 (dd, J = 16.4, 5.4 Hz, 1H), 1.76 (m, 3H); MS *m*/*e* 262.1347 (calcd for $C_{19}H_{18}O$, 262.1361); IR (KBr) 1664, 1629 cm^{-1}. Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92. Found: C, 87.14; H, 7.02.

3-*tert*-Butyl-4,4-diphenylcyclohex-2-en-1-one (11d). To a solution of 1.50 g (5.39 mmol) of 3-methoxy-6,6-diphenylcyclohex-2-en-1-one (**10**)[29] in 45 mL of THF at −78 °C was added 4.12 mL of 1.7 M *tert*-butyllithium in pentane (7.01 mmol). The solution was stirred at −78 °C for 15 min and then 75 mL of water added followed by 90 mL of 6 N HCl. The mixture was allowed to warm to 20 °C and stirred at room temperature for 1 h. Ether extraction, washing of the organic phase with saturated sodium bicarbonate, brine, and water, and drying with magnesium sulfate afforded crude product which after chromatography on a silica gel 3 × 25 cm column eluted with 10% ether in hexane afforded 1.31 g (80%) of 3-*tert*-butyl-4,4-diphenylcyclohex-2-en-1-one (**11d**). Crystallization from heptane gave 1.18 g (72%) of colorless crystals, mp 159−160 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.46−7.25 (m, 10H), 6.53 (s, 1H), 2.64 (m, 2H), 2.03 (m, 2H), 0.96 (s, 9H); MS *m*/*e* 304.1821 (calcd for $C_{22}H_{24}O$, 304.1828); IR (film) 1671, 1579 cm^{-1}. Anal. Calcd $C_{22}H_{24}O$: C, 86.80; H, 7.94. Found: C, 87.17; H, 8.17.

3-*tert*-Butyl-4,4-diphenylcyclohexa-2,5-dienone (12d). The general method of Reich et al.[27] was used. To a −78 °C of LDA (prepared by addition of 0.84 mL (1.97 mmol) of 2.35 M *n*-BuLi in hexane to 0.276 mL (1.97 mmol) of diisopropylamine in 8 mL of THF) was added a solution of 500 mg (1.64 mmol) of 3-*tert*-butyl-4,4-diphenylcyclohex-2-en-1-one (**11d**) in 5 mL of THF. The solution was stirred at −78 °C for 15 min, and a solution of 1.96 mmol of phenylselenyl bromide (prepared by addition of 0.050 mL (0.98 mmol) of bromine to 306 mg (0.98 mmol) of PhSeSePh in 4 mL of THF) was added in one portion. The reaction mixture was stirred for 5 min and poured into 100 mL of diethyl ether and 100 mL of 1.2 M HCl. Ether extraction, washing with saturated aqueous sodium bicarbonate and brine, drying with magnesium sulfate, and concentrating in vacuo gave yellow oil. Column chromatography of the crude product on a 3 cm × 40 cm silica gel column eluted with 5% ether in hexane gave 75 mg of a mixture of unidentified compounds in fraction 1. Fraction 2 afforded 472 mg of an oil. Fraction 3 contained 35 mg (7%) of starting enone **11d**. Fraction 2 was dissolved in a mixture of 4 mL of methylene chloride and 0.20 mL of pyridine, and 0.30 mL (2.64 mmol) of 30% hydrogen peroxide was added. The reaction mixture was stirred for 2 h at 20 °C. The mixture was poured into 100 mL of ether with 100 mL of saturated sodium bicarbonate, extracted with ether, washed with brine and water, dried with magnesium sulfate, and evaporated in vacuo. Chromatography of the crude product on a silica gel 3 × 20 cm column eluted with 10% ether in hexane afforded 51 mg of unidentified compound in fraction 1. Fraction 2 contained 208 mg (42%) of 3-*tert*-butyl-4,4-diphenylcyclohexa-2,5-dienone (**12d**). Crystallization from heptane gave 169 mg (34%) of colorless crystals, mp 142−143 °C.

The spectral characteristics were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.51−7.26 (m, 10H), 6.85 (d, J = 9.7 Hz, 1H), 6.74 (d, J = 1.7 Hz, 1H), 6.02 (dd, J = 9.7, 1.7 Hz, 1H), 0.92 (s, 9 H); MS *m*/*e* 302.1669 (calcd for $C_{22}H_{22}O$, 302.1671); IR (film) 1654, 1619 cm^{-1}. Anal. Calcd for $C_{22}H_{22}O$: C, 87.38; H, 7.33. Found: C, 87.56; H, 7.61.

3-*tert*-Butyl-4,5-diphenylphenol (13d). The general procedure of Zimmerman et al.[4b] was used. A mixture of 70 mg (0.23 mmol) of 3-*tert*-butyl-4,4-diphenylcyclohexa-2,5-dienone (**12d**), 1.0 mL of glacial acetic acid, 0.13 mL of water, and 0.33 mL of concentrated HCl was refluxed for 30 min. The solution was cooled, diluted with 100 mL of water, and extracted with ether. The extract was washed with brine and water, dried with magnesium sulfate, and concentrated under vacuo. Crystallization of the crude product from heptane gave 58.0 mg (83%) of 3-*tert*-butyl-4,5-diphenylphenol (**13d**) as colorless crystals, mp 141−143 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.10−6.91 (m, 11H), 6.67 (d, J = 2.7 Hz, 1H), 4.88 (s, 1H), 1.17 (s, 9H); MS *m*/*e* 302.1675 (calcd for $C_{22}H_{22}O$, 302.1671); IR (film) 3150−3600, 1602, 1583, 1495, 1483, 1440, 1425, 1363, 1319, 1252, 1200, 1178 cm^{-1}. Anal. Calcd for $C_{22}H_{22}O$: C, 87.38; H, 7.33. Found: C, 87.31; H, 7.35.

6,6-Diphenylcyclohexa-2,4-dienone (16a). A 1.30 mL (1.30 mmol) sample of a 1 M solution of diisobutylaluminium hydride in hexane was added dropwise into a solution of 300 mg (1.09 mmol) of 4,4-diphenyl-3-methoxycyclohexa-2,5-dienone[30] in 20 mL of dry benzene at 10 °C, and the mixture was stirred for 15 min. A 100 mL portion of water followed by 3 mL of 1.2 M HCl was added. The mixture was extracted with ether and washed with water, and the solvents were removed in vacuo. The residue was dissolved in 30 mL of THF, 15 mL of 1.2 M HCl was added, and the solution was stirred for 30 min at 20 °C. Ether extraction, washing with water, saturated sodium bicarbonate, and water, and drying with magnesium sulfate afforded 298 mg of oil. Chromatography of the crude mixture on a silica gel 2.5 cm × 36 cm column gave 126 mg (47%) of 6,6-diphenylcyclohexa-2,4-dienone (**16a**). Crystallization of dienone **16a** from hexane gave 106 mg (39%) of colorless crystals, mp 98.0−98.5 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.34−7.16 (m, 10 H), 7.10 (ddd, J = 9.7, 5.8, 1.8 Hz, 1H), 6.75 (ddd, J = 9.4, 1.8, 0.8 Hz, 1H), 6.39 (ddd, J = 9.4, 5.8, 0.8 Hz, 1H), 6.10 (ddd, J = 9.7, 0.8, 0.8, 1H); MS *m*/*e* 246.1055 (calcd for $C_{18}H_{14}O$, 246.1045); IR (film) 1664, 1633 cm^{-1}. Anal. Calcd for $C_{18}H_{14}O$: C, 87.78; H, 5.73. Found: C, 87.65; H, 5.99.

3-*tert*-Butyl-6,6-diphenylcyclohexa-2,4-dienone (16d). A 0.275 mL (0.468 mmol) portion of 1.7 M *t*-BuLi in pentane was added dropwise into a solution of 100 mg (0.36 mmol) of 3-methoxy-4,4-diphenylcyclohexa-2,5-dienone (**12c**)[30] in 4 mL of THF at −78 °C. The solution was stirred for 15 min. A 6 mL portion of water followed by 2 mL of 6 N HCl was added and the mixture allowed to warm to 20 °C and stirred for 1 h. Ether extraction, washing with sodium bicarbonate and water, and drying with magnesium sulfate gave crude product which was purified by chromatography on a silica gel 2.5 cm × 17 cm column. Elution with 5% ether in hexane afforded 34.2 mg (31%) of 3-*tert*-butyl-6,6-diphenylcyclohexa-2,4-dienone (**16d**) in fraction 1. Crystallization from pentane gave 24.5 mg (23%) of colorless crystals, mp 108−109 °C. Fraction 2 contained 36.1 mg (30%) of 5-*tert*-butyl-3-methoxy-4,4-diphenylcyclohex-2-en-1-one (**17**). Crystallization from hexane gave 32.8 mg (27%) of colorless crystals, mp 154−155 °C.

The spectral characteristics of 3-*tert*-butyl-6,6-diphenylcyclohexa-2,4-dienone (**16d**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.32−7.20 (m, 10H), 6.70 (dd, J = 9.8, 0.6 Hz, 1H) 6.52 (dd, J = 9.8, 1.6 Hz, 1H), 6.00 (dd, J = 1.6, 0.6 Hz, 1H), 1.21 (s, 9H, *t*-Bu); MS *m*/*e* 302.1680 (calcd for $C_{22}H_{22}O$, 302.1671); IR (film) 1652, 1564 cm^{-1}. Anal. Calcd for $C_{22}H_{22}O$: C, 87.38; H, 7.33. Found: C, 87.55; H, 7.38.

The spectral characteristics of 5-*tert*-butyl-3-methoxy-4,4-diphenylcyclohex-2-en-1-one (**17**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.63−7.50 (m, 4H), 7.43−7.22 (m, 6H), 5.58 (s, 1H), 3.44 (s, 3H), 3.21 (dd, J = 12.5, 3.3 Hz, 1H), 2.50 (dd, J = 16.4, 3.3 Hz, 1H), 2.40 (dd, J = 16.4, 12.5 Hz, 1H), 0.56 (s, 9H); MS *m*/*e* 334.1937 (calcd for $C_{23}H_{26}O_2$, 334.1933); IR (film) 1649, 1598, 1211 cm^{-1}. Anal. Calcd for $C_{23}H_{26}O_2$: C, 82.60; H, 7.84. Found: C, 82.81; H, 7.58.

3-Methoxy-6,6-diphenylcyclohexa-2,4-dienone (16c). A mixture of 420 mg (1.51 mmol) of 3-methoxy-6,6-diphenylcyclohex-2-en-1-one (**10c**),[30] 411 mg (1.81 mmol) of DDQ, and 1 mg of *p*-toluenesulfonic acid in 15 mL of benzene was refluxed for 97 h. The reaction mixture was cooled and poured into a mixture of 30 mL of ether and 30 mL of water. The organic layer was separated, washed with 10% NaOH, water, and brine, and dried with magnesium sulfate. Chromatography of the crude product on a 18 cm × 3 cm silica gel column eluted with 10% ether in hexane afforded 270 mg (65%) of solid.

Crystallization twice from hexane−benzene gave 178 mg (43%) of 3-methoxy-6,6-diphenylcyclohexa-2,4-dienone (**16c**) as colorless crystals, mp 131−132 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.33−7.16 (m, 10H), 6.76 (d, J = 10.1 Hz, 1H), 6.26 (dd, J = 10.1, 2.1 Hz, 1H), 5.52 (d, J = 2.1 Hz, 1H), 3.81 (s, 3H); MS *m*/*e* 276.1152 (calcd for $C_{19}H_{16}O_2$, 276.1150); IR (film) 1652, 1573, 1240 cm^{-1}. Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.59; H, 5.84. Found: C, 82.60; H, 6.12.

4-(*p*-Cyanophenyl)-3-phenylphenol (19). A mixture of 150 mg (0.552 mmol) of 4-(*p*-cyanophenyl)-4-phenylcyclohexa-2,5-dienone (**18**) and 35 mg (0.18 mmol) of *p*-toluenesulfonic acid monohydrate was stirred at 120 °C for 5 min. Chromatography on a 70 × 1 cm silica gel column eluted with 20% ether in hexane afforded 44.0 mg (29.3%) of 4-(*p*-cyanophenyl)-3-phenylphenol in fraction 1. Crystallization from benzene−heptane gave 33.5 mg (13.4%) of colorless crystals, mp 271−272 °C. Fraction 2 gave 4.3 mg of a mixture of 3-(*p*-cyanophenyl)-4-phenylphenol (**29**) and an unidentified compound (by NMR).

The spectral characteristics of 4-(*p*-cyanophenyl)-3-phenyphenol (**19**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.47 (m, 2H), 7.30−7.21 (m, 4H), 7.18 (m, 2H), 7.12−7.05 (m, 2H), 6.95−6.90 (m, 2H), 5.10 (s, 1H). MS *m*/*e* 271.1009 (calcd for $C_{19}H_{13}NO$, 271.0997); IR (KBr) 3150−3500, 2229, 1602, 1583, 1569, 1483, 1450, 1432, 1309, 1199 cm^{-1}. Anal. Calcd for $C_{19}H_{13}NO$: C, 84.11; H, 4.83; N, 5.16. Found: C, 84.20; H, 5.01; N, 5.04.

(*p*-Bromophenyl)phenyldiazomethane. (*p*-Bromophenyl)phenyldiazomethane was prepared by the general procedure of Miller.[31] A mixture of 40.3 g (0.146 mol) of (*p*-bromophenyl)benzophenone hydrazone, 19.6 g of anhydrous sodium sulfate, 420 mL of ether, 59.0 g (0.272 mol) of yellow mercuric oxide, and 22.5 mL of ethanol saturated with potassium hydroxide was stirred for 24 h. The reaction mixture was filtered and 500 mL of pentane added. The solution was extracted with 200 mL of water and dried with magnesium sulfate. Solvent was removed in vacuo to give 31.2 g (78%) of (*p*-bromophenyl)phenyldiazomethane as a red solid which was used without further purification.

6-*exo*-(*p*-Bromophenyl)-4-methoxy-6-*endo*-phenylbicyclo[3.1.0]-hex-3-en-2-one (24a) and 6-*endo*-(*p*-Bromophenyl)-4-methoxy-6-*exo*-phenylbicyclo[3.1.0]hex-3-en-2-one (24b). A 4.0 g (41.7 mmol) portion of cyclopent-2-ene-1,4-dione[32] was added into a solution of 24.0 g (87.9 mmol) of (*p*-bromophenyl)phenyldiazomethane in 150 mL of dry benzene. The mixture was stirred at room temperature for 12 h and then refluxed for 3 h. The solvent was removed in vacuo and the mixture chromatographed on a 5.5 cm × 50 cm silica gel column eluted with 20% ether in hexane to give 19.8 g of a mixture of enones **7a** (Ar = *p*-bromophenyl) and **7b** (Ar = *p*-bromophenyl) as a yellow oil. The mixture was dissolved in 300 mL of dry methanol, 100 mg of *p*-toluenesulfonic acid was added, and the solution was refluxed for 12 h. Solvent was removed in vacuo and the residue chromatographed on a 4 cm × 90 cm silica gel column eluted with 20% ether in hexane. Fraction 1 afforded 6.3 g of 1-(*p*-bromophenyl)-1-phenylmethyl methyl ether. Fraction 2 gave 3.32 g (22%) of 6-*endo*-(*p*-bromophenyl)-4-methoxy-6-*exo*-phenylbicyclo[3.1.0]hex-3-en-2-one (**24a**). Crystallization from ether yielded 2.94 g (20%) of colorless crystals, 134−135 °C. Fraction 3 gave 0.712 g (5%) of a mixture of enone **24a** and enone **24b**. Fraction 4 afforded 3.98 g (27%) of 6-*exo*-(*p*-bromophenyl)-4-methoxy-6-*endo*-phenylbicyclo[3.1.0]hex-3-en-2-one (**24b**). Crystallization from hexane−benzene afforded 3.40 g (23%) of colorless crystals, mp 139−140 °C.

The spectral characteristics of 6-*exo*-(*p*-bromophenyl)-4-methoxy-6-*endo*-phenylbicyclo[3.1.0]hex-3-en-2-one (**24a**) were the following: NMR (300 MHz, $CDCl_3$) δ 7.43−7.19 (m, 7H), 7.07 (m, 2H), 4.54 (m, 1H), 3.62 (s, 3H), 2.97 (dd, J = 5.3, 0.9 Hz, 1H), 2.79 (dd, J = 5.3, 1.4 Hz, 1H); MS *m*/*e* 356.0226 (calcd for $C_{19}H_{15}O_2Br$, 356.0238); IR (film) 1684, 1587, 1371, 1236 cm^{-1}. Anal. Calcd for $C_{19}H_{15}O_2$-Br: C, 64.24; H, 4.26; Br, 22.49. Found: C, 64.11; H, 4.44; Br, 22.50.

The spectral characteristics of 6-*endo*-(*p*-bromophenyl)-4-methoxy-6-*exo*-phenylbicyclo[3.1.0]hex-3-en-2-one (**24b**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.40 (m, 2H), 7.30−7.14 (m, 7H), 4.57 (m, 1H), 3.65 (s, 3H), 3.01 (dd, J = 5.3, 1.1 Hz, 1H), 2.84 (dd, J = 5.3, 1.3 Hz, 1H); MS *m*/*e* 356.0332 (calcd for $C_{19}H_{15}O_2Br$, 356.0238); IR (film) 1684, 1587, 1371, 1236 cm^{-1}. Anal. Calcd for $C_{19}H_{15}O_2$-Br: C, 64.24; H, 4.26; Br, 22.49. Found: C, 64.26; H, 4.32; Br, 22.90.

Exploratory Solution Photolysis of 6,6-Diphenylbicyclo[3.1.0]hex-3-en-2-one (5a). A solution of 117 mg (0.48 mmol) of 6,6-diphenylbicyclo[3.2.1]hex-3-en-2-one (**5a**) in 120 mL of benzene was irradiated for 40 min. The solvent was removed in vacuo and the crude mixture chromatographed on a preparative silica gel TLC plate eluted with 5% ether in hexane. Band 1 (9.8 mg, 8.4%) contained 2,3-diphenylphenol (**20a**). Crystallization from hexane gave mp 101−102 °C (lit.[8] mp 102.2−103.2 °C). Band 2 (42.8 mg, 36.6%) contained 6,6-diphenylcyclohexa-2,4-dienone (**16a**). Crystallization from heptane gave 29.4 mg (25.1%) of crystals, mp 98−99 °C. The third band gave 15.1 mg (13%) of starting 6,6-diphenylbicyclo[3.2.1]hex-3-en-2-one (**5a**) together with unidentified impurities.

Exploratory Solution Photolysis of 4-Methyl-6,6-diphenylbicyclo-[3.1.0]hex-3-en-2-one (5b). A solution of 250 mg (0.95 mmol) of 4-methyl-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**5b**) in 200 mL of photolysis grade benzene was irradiated for 30 min. The crude mixture was chromatographed on two preparative TLC plates (20 cm × 20 cm, 20 g of TLC silica gel per plate) eluted with 7% ether in hexane. Band 1 (22.0 mg, 8.8%) contained 5-methyl-2,3-diphenylphenol (**20b**). Two-fold crystallization from hexane gave 10.3 mg (4.1%) of colorless crystals, mp 126−127 °C. Band 2 gave 43.9 mg (17.6%) of 3-methyl-6,6-diphenylcyclohexa-2,4-dienone (**16b**) as an oil. Slow evaporation of the hexane solution gave 29.2 mg (11.7%) of colorless crystals, mp 61−62 °C. Band 3 contained 126.6 mg (50.6%) of starting 4-methyl-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**5b**).

The spectral data for 3-methyl-6,6-diphenylcyclohexa-2,4-dienone (**16b**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.36−7.17 (m, 10H), 6.69 (d, J = 9.6 Hz, 1H), 6.24 (dd, J = 9.6, 1.2 Hz, 1H), 5.95 (m, 1H), 2.10 (d, J = 1.2, 3H); MS *m*/*e* 260.1205 (calcd for $C_{19}H_{16}O$, 260.1201); IR (film) 1650, 1570 cm^{-1}. Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: C, 87.83; H, 6.34. The structure assignment was supported by X-ray diffraction (see the Supporting Information). The spectral data for 3-methyl-5,6-diphenylphenol (**20b**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.36−7.22 (m, 4H), 7.19−7.02 (m, 6H), 6.83−6.88 (m, 2H), 5.06 (s, 1H), 2.40 (s, 3H); MS *m*/*e* 260.1206 (calcd for $C_{19}H_{16}O$, 260.1201). Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: C, 87.34; H, 6.29.

Exploratory Solution Photolysis of 4-Methoxy-6,6-diphenylbicyclo-[3.1.0]hex-3-en-2-one (5c). A solution of 250 mg (0.90 mmol) of 4-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**5c**)[7] in 250 mL of photolysis grade benzene was irradiated for 30 min. Solvent was removed in vacuo and the crude mixture separated by preparative chromatography on a TLC plate eluted with 10% ether in hexane. Band 1 (12.9 mg, 5.2%) contained 3-methoxy-5,6-diphenylphenol. Crystallization from hexane afforded 9.1 mg (3.6%) of colorless crystals, mp 115−117 °C (lit.[30] mp 115.5−117 °C). Band 2 (14.7 mg, 5.9%) contained 3-methoxy-6,6-diphenylcyclohexa-2,4-dienone (**16c**). Crystallization from hexane yielded 10.0 mg (4.0%) of colorless crystals, mp 130−132 °C. Band 3 gave 179 mg (71.6%) of starting 4-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**5c**).

Exploratory Solution Photolysis of 4-*tert*-Butyl-6,6-diphenyl-[3.2.1]cyclohex-3-en-2-one (5d). A 150 mg (4.96 mmol) sample of 4-*tert*-butyl-6,6-diphenyl[3.2.1]cyclohex-3-en-2-one (**5d**) in 150 mL of benzene was irradiated for 25 min. Solvent was removed in vacuo and the mixture separated on a preparative TLC silica gel plate eluted with 5% ether in hexane. Band 1 gave 17.9 mg (11.9%) of 3-*tert*-butyl-5,6-diphenylphenol (**20d**). Crystallization from hexane afforded 13.6 mg (9.1%) of colorless crystals, mp 149−150 °C. Band 2 contained 31.1 mg (20.7%) of 3-*tert*-butyl-6,6-diphenylcyclohexa-2,4-dienone (**16d**) as an oil. Slow evaporation of the pentane solution gave 15.2 mg (10.1%) of colorless crystals, mp 105−107 °C. The third band gave 81.9 mg (54.6%) of starting 4-*tert*-butyl-6,6-diphenylbicyclo-[3.2.1]cyclohex-3-en-2-one (**5d**).

The spectral characteristics of 3-*tert*-butyl-5,6-diphenylphenol (**5d**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.34−7.03 (m, 12H), 5.10 (s, 1H), 1.38 (s, 9H); IR (film) 3150−3600, 1616, 1577, 1558, 1479, 1407, 1301, 1186 cm^{-1}; MS *m*/*e* 302.1680 (calcd for $C_{22}H_{22}O$, 302.1671). Anal. Calcd for $C_{22}H_{22}O$: C, 87.38; H, 7.33. Found: C, 87.06; H, 7.10. The structure assignment was supported by X-ray diffraction (see the Supporting Information).

(31) Miller, J. B. *J. Org. Chem.* **1959**, *24*, 560−561.

(32) Rasmussen, G. H.; House, H. O.; Zaweski, E. F.; De Puy, C. H. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, pp 324−332.

Exploratory Solution Photolysis of 6,6-Diphenyl-4-(diphenylmethoxy)bicyclo[3.1.0]hex-3-en-2-one (5e). A solution of 227 mg (0.53 mmol) of 6,6-diphenyl-4-(diphenylmethoxy)bicyclo[3.1.0]hex-3-en-2-one (**5e**)[7] in 200 mL of photolysis grade benzene was irradiated for 100 min. The solvent was removed in vacuo. The reaction mixture contained 5,6-diphenyl-3-(diphenylmethoxy)phenol (**20e**) and 3-oxo-6,6-diphenyl-4-(diphenylmethyl)hex-5-enoic acid (**39**) in a ratio of approximately 45:55 (by NMR). The crude mixture was heated at 130 °C for 3 min and cooled quickly in an ice−water bath. Signals of acid **39** disappeared in the NMR, and ketone **21** was observed instead. The crude mixture was chromatographed on two preparative TLC plates eluted with 10% ether in hexane. Band 1 gave 4.5 mg of a mixture of unknown compounds. Band 2, 55.6 mg (37.2%), afforded 5,5-diphenyl-3-(diphenylmethyl)pent-4-en-2-one (**21**) as an oil. Treatment with hexane and crystallization from heptane gave 32.3 mg (21.6%) of colorless crystals, mp 119−121 °C. Band 3 (5.9 mg) gave a mixture of phenol **20e** with unidentified compound. Band 4, 30.1 mg (18.9%), contained 5,6-diphenyl-3-(diphenylmethoxy)phenol (**20e**) as an oil. Treatment with pentane and crystallization from hexane−benzene gave 15.8 mg (9.9%) of colorless crystals, mp 147−148 °C. Band 5 afforded 68.1 mg (30.0%) of starting 6,6-diphenyl-4-(diphenylmethoxy)bicyclo-[3.1.0]hex-3-en-2-one (**5e**) with traces of unidentified impurities.

The spectral data for 5,5-diphenyl-3-(diphenylmethyl)pent-4-en-2-one (**21**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.39−7.36 (m, 3H), 7.25−7.09 (m, 13H), 7.00−6.96 (m, 2H), 6.87−6.86 (m, 2H), 5.91 (d, J = 10.8 Hz, 1H), 4.45 (d, J = 10.8 Hz, 1H), 4.15 (dd, J = 10.8, 10.8 Hz, 1H), 1.94 (s, 3H); MS *m*/*e* 402.2027 (calcd for $C_{30}H_{26}O$, 402.1985); IR (film) 1712 cm^{-1}. Anal. Calcd for $C_{30}H_{26}O$: C, 89.51; H, 6.51. Found: C, 89.56; H, 6.47. The structure assignment was confirmed by X-ray crystallography (see the Supporting Information).

The spectral data for 5,6-diphenyl-3-(diphenylmethoxy)phenol (**20e**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.48−7.42 (m, 4H), 7.40−7.19 (m, 9H), 7.14−7.06 (m, 5H), 7.02−6.95 (m, 2H), 6.70 (d, J = 2.6 Hz, 1H), 6.63 (d, J = 2.6 Hz, 1H), 6.28 (s, 1H), 5.08 (s, 1H); MS *m*/*e* 428.1768 (calcd for $C_{31}H_{24}O_2$, 428.1777); IR (film) 3200−3600, 1614, 1581, 1495, 1454, 1419, 1340, 1305, 1194, 1146, 1041 cm^{-1}. Anal. Calcd for $C_{31}H_{24}O_2$: C, 86.89; H, 5.65. Found: C, 86.93; H, 5.62. The structural assignment was confirmed by X-ray crystallography (see the Supporting Information).

Exploratory Solution Photolysis of 6-*exo*-(*p*-Cyanophenyl)-6-*endo*-phenylbicyclo[3.1.0]hex-3-en-2-one (7f). A solution of 30 mg (0.11 mmol) of 6-*exo*-(*p*-cyanophenyl)-6-*endo*-phenylbicyclo[3.1.0]hex-3-en-2-one (**7f**) in 17 mL of benzene was irradiated for 35 min to give a mixture of 6-(*p*-cyanophenyl)-6-phenylcyclohexa-2,4-dienone (**22**) and 3-(*p*-cyanophenyl)-2-phenylphenol (**23**). The presence of 3-(*p*-cyanophenyl)-2-phenylphenol (**23**) was confirmed by addition of a standard sample of 3-(*p*-cyanophenyl)-2-phenylphenol (**23**)[4d] to the reaction mixture analyzed by NMR (see the Supporting Information). Solvent was removed in vacuo and the mixture separated on a preparative TLC plate (10 cm × 20 cm, Machery Nagel No. 81638-25 TLC silica gel) eluted with 30% ether in hexane. Separation was achieved with loss of 3-(*p*-cyanophenyl)-2-phenylphenol (**23**). Band 1 gave 16.1 mg (53.7%) of 6-(*p*-cyanophenyl)-6-phenylcyclohexa-2,4-dienone (**22**) as oil. Band 2 afforded 5.4 mg (18.0%) of 6-*exo*-(*p*-cyanophenyl)-6-*endo*-phenylbicyclo[3.1.0]hex-3-en-2-one (**7f**).

The spectral characteristics for 6-(*p*-cyanophenyl)-6-phenylcyclohexa-2,4-dienone (**22**) were the following: ^{1}H NMR (300 MHz, CD_3CN) δ 7.58 (m, 2H), 7.36−7.26 (m, 5H), 7.20−7.10 (m, 3H), 6.68 (ddd, J = 9.4, 1.7, 0.7 Hz, 1H), 6.45 (ddd, J = 9.4, 5.9, 0.7 Hz, 1H), 6.11 (m, 1H); MS *m*/*e* 271.0987 (calcd for $C_{19}H_{13}NO$, 271.0997); IR (film) 3086, 3059, 2919, 2232, 1664, 1631, 1602, 1562, 1493, 1446, 1412, 1369, 1246, 1190, 1134, 1020, 912, 838, 820 cm^{-1}.

Exploratory Solution Photolysis of 6-*endo*-(*p*-Cyanophenyl)-6-*exo*-phenylbicyclo[3.1.0]hex-3-en-2-one (7e). A solution of 30 mg (0.11 mmol) of 6-*endo*-(*p*-cyanophenyl)-6-*exo*-phenylbicyclo[3.1.0]hex-3-en-2-one (**7e**) in 17 mL of benzene was irradiated for 35 min to give a mixture of 6-(*p*-cyanophenyl)-6-phenylcyclohexa-2,4-dienone (**22**) and 3-(*p*-cyanophenyl)-2-phenylphenol (**23**). The presence of 3-(*p*-cyanophenyl)-2-phenylphenol (**23**) was confirmed by addition of a standard sample of 3-(*p*-cyanophenyl)-2-phenylphenol (**23**)[4d] into the reaction mixture analyzed by NMR. Solvent was removed in vacuo and the mixture chromatographed on a preparative TLC plate (10 cm × 20 cm, Machery Nagel No. 81638-25 TLC silica gel). Separation was achieved with loss of 3-(*p*-cyanophenyl)-2-phenylphenol (**23**). Band 1 gave 13.8 mg (30.0%) of 6-(*p*-cyanophenyl)-6-phenylcyclohexa-2,4-dienone (**22**) as an oil. Band 2 afforded 6.1 mg (20.3%) of 6-*endo*-(*p*-cyanophenyl)-6-*exo*-phenylbicyclo[3.1.0]hex-3-en-2-one (**7e**).

Exploratory Solution Photolysis of 6-*exo*-(*p*-Bromophenyl)-4-methoxy-6-*endo*-phenylbicyclo[3.1.0]hex-3-en-2-one (24a). A 150 mg (0.42 mmol) portion of 6-*exo*-(*p*-bromophenyl)-4-methoxy-6-*endo*-phenylbicyclo[3.1.0]hex-3-en-2-one (**24a**) was irradiated in 250 mL of benzene for 75 min. The crude mixture contained 6-(*p*-bromophenyl)-3-methoxy-6-phenylcyclohexa-2,4-dienone (**25**), 5-(*p*-bromophenyl)-3-methoxy-6-phenylphenol (**26**), and 6-(*p*-bromophenyl)-3-methoxy-5-phenylphenol (**27**) in a ratio of 64:20:16 (by NMR). Chromatography on a preparative TLC plate eluted with 10% ether in hexane afforded 11.8 mg (7.9%) of a mixture of phenol **26** and phenol **27** in a ratio of 60:40 (by NMR; see the Supporting Information) in band 1. Band 2 contained 20.9 mg (13.9%) of 6-(*p*-bromophenyl)-3-methoxy-6-phenylcyclohexa-2,4-dienone (−25) as an oil which solidified upon treatment with pentane. Crystallization from hexane−methylene chloride gave 12.1 mg (8.1%) of colorless crsytals, mp 119−120 °C. Band 3 afforded 90.1 mg (60.0%) of starting 6-*exo*-(*p*-bromophenyl)-4-methoxy-6-*endo*-phenylbicyclo[3.1.0]hex-3-en-2-one (**24a**).

The spectral data for 6-(*p*-bromophenyl)-3-methoxy-6-phenylcyclohexa-2,4-dienone (**25**) were the following: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (m, 2H), 7.34−7.25 (m, 3H), 7.21−7.15 (m, 2H), 7.09 (m, 2H), 6.71 (d, J = 10.0 Hz, 1H), 6.27 (dd, J = 10.0, 2.2 Hz, 1H), 5.52 (d, J = 2.2 Hz, 1H); MS *m*/*e* 356.0235 (calcd for $C_{19}H_{15}O_2Br$, 356.0238); IR (film) 1652, 1576 cm^{-1}. Anal. Calcd for $C_{19}H_{15}O_2Br$: C, 64.24; H, 4.26; Br, 22.49. Found: C, 64.19; H, 4.42; Br, 22.44.

Exploratory Solution Photochemistry of 6-*endo*-(*p*-Bromophenyl)-4-methoxy-6-*exo*-phenylbicyclo[3.1.0]hex-3-en-2-one (24b). A 200 mg (0.56 mmol) sample of 6-*endo*-(*p*-bromophenyl)-4-methoxy-6-*exo*-phenylbicyclo[3.1.0]hex-3-en-2-one (**24b**) in 200 mL of benzene was irradiated for 0.5 h. A second identical run was conducted, reaction mixtures were combined, and solvent was removed in vacuo. The crude mixture which contained 6-(*p*-bromophenyl)-3-methoxy-6-phenylcyclohexa-2,4-dienone (**25**), 5-(*p*-bromophenyl)-3-methoxy-6-phenylphenol (**26**), and 6-(*p*-bromophenyl)-3-methoxy-5-phenylphenol (**27**) in a ratio of 64:19:17 (by NMR) was chromatographed on two preparative TLC plates eluted with 10% ether in hexane. Combined bands 1 afforded 13.2 mg (3.3%) of a mixture of phenol **26** and phenol **27** in a ratio of 58:42 (by NMR; see the Supporting Information). Combined bands 2 gave 28.0 mg (7.0%) of 6-(*p*-bromophenyl)-3-methoxy-6-phenylcyclohexa-2,4-dienone (**25**) as an oil. Treatment with pentane and crystallization from hexane−methylene chloride afforded 16.2 mg (4.1%) of colorless crystals, mp 118−120 °C. Combined bands 3 yielded 324 mg (81.0%) of starting enone **24b**.

Solid-State Photolysis of 6,6-Diphenylbicyclo[3.2.1]hex-3-en-2-one (5a). A 100 mg (0.41 mmol) sample of 6,6-diphenylbicyclo[3.2.1]-hex-3-en-2-one (**5a**) was irradiated under standard conditions (see the General Procedures) for 20 min. The reaction mixture contained, besides starting enone **5a**, 2,3-diphenylphenol (**20a**) and 3,4-diphenylphenol (**13a**) in a ratio of 58:42 (by NMR and comparison of NMR spectra with those of independently prepared[4b,8] samples; see the Supporting Information).

Exploratory Solid-State Photolysis of 4-Methyl-6,6-diphenylbicyclo-[3.1.0]hex-3-en-2-one (5b). A 40 mg (0.15 mmol) portion of 4-methyl-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**5b**) was irradiated under conditions described in the General Procedures for 10 min through a 5 mm filter solution of 10^{-3} M sodium metavanadate in 5% sodium hydroxide. The mixture was chromatographed on preparative TLC plate eluted with 7% ether in hexane. Band 1 (28.0 mg, 70%) contained 3-methyl-4,5-diphenylphenol (**13b**). Crystallization from hexane gave 14.1 mg (35%) of colorless crystals, mp 109−110 °C. Band 2 gave 7.0 (17.5%) of starting 4-methyl-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**5b**).

Exploratory Solid-State Photolysis of 4-Methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (5c). A 100 mg (0.36 mmol) portion of crystals of 4-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**5c**)[7] was irradiated under conditions described in the General Procedures for 5 h. The crude mixture was chromatographed on a TLC plate eluted with 15% ether in hexane. Band 1 (26.6 mg, 26.6%) contained 3-methoxy-5,6-diphenylphenol (**20c**). Crystallization from hexane gave

19.4 mg (19.4%) of colorless crystals, mp 114−116 °C (lit.[7] mp 115.5−117 °C). Band 2 afforded 60.2 mg (60.2%) of starting 4-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**5c**).

Exploratory Solid-State Photolysis of 4-*tert*-Butyl-6,6-diphenylbicyclo[3.2.1]hex-3-en-2-one (5d). A 50 mg (0.17 mmol) portion of 4-*tert*-butyl-6,6-diphenylbicyclo[3.2.1]hex-3-en-2-one (**5d**) was placed in an NMR tube and irradiated for 1.5 h. The same procedure was repeated 17 times. The overall amount taken into reaction was 850 mg, and conversion reached approximately 5%. Crystals in each NMR tube were dissolved in 0.2 mL of dry benzene under a dry argon atmosphere and kept for 2 h. Individual portions were collected, and the solvent was removed in vacuo. Crude product was crystallized from hexane. Crystals were filtered off, the filtrate was evaporated, and the residue was crystallized again from hexane. The combined crystalline portions gave 640 mg (75.2%) of starting enone **5d**. The filtrate was evaporated. The residue contained, besides starting enone **5d**, phenol **20d**, phenol **13d**, and dienone **16d** in a ratio of 42:8:50 (by NMR). The mixture was separated on a preparative TLC silica gel plate eluted with 5% ether in hexane. Band 1 (11.7 mg, 1.4%) gave 3-*tert*-butyl-5,6-diphenylphenol (**20d**), mp 149−150 °C, from hexane. Band 2 (13.2 mg, 1.6%) contained 3-*tert*-butyl-6,6-diphenylcyclohexa-2,4-dienone (**16d**) which solidified from pentane, mp 105−107 °C. Band 3 gave 121 mg (14.2%) of a mixture of starting 4-*tert*-butyl-6,6-diphenylbicyclo[3.2.1]hex-3-en-2-one (**5d**) and 3-*tert*-butyl-4,5-diphenylphenol (**13d**) in a ratio of 100:2 (by NMR) with other minor impurities.

Exploratory Solid-State Photolysis of 6,6-Diphenyl-4-(diphenylmethoxy)bicyclo[3.1.0]hex-3-en-2-one (5e). Final Treatment with Water. A 200 mg (0.47 mmol) portion of crystals of 6,6-diphenyl-4-(diphenylmethoxy)bicyclo[3.1.0]hex-3-en-2-one (**5e**)[7] was irradiated under conditions described in the General Procedures for 1.5 h with a Hanovia 450 W medium-pressure mercury lamp (conversion approximately 20% by NMR). The crystals were dissolved in a mixture of 5 mL of THF and 0.5 mL of water. The mixture was kept for 12 h at 20 °C. Solvent was removed in vacuo. The procedure was repeated four times. The mixture contained, besides starting enone **5e**, 5,5-diphenyl-3-(diphenylmethyl)pent-4-en-2-one (**21**) and 2-(*E*)-6,6-diphenyl-3-(diphenylmethoxy)hexa-2,5-dienoic acid (**28**) in a ratio of 20:80 (by NMR). The combined crude mixtures were chromatographed on a 3 cm × 25 cm silica gel column. Elution with 10% ether in hexane afforded 22.2 mg (10.3%) of 5,5-diphenyl-3-(diphenylmethyl)-pent-4-en-2-one (**21**) in fraction 1. Crystallization of ketone **21** from heptane gave 18.6 mg (8.6%) of colorless crystals, mp 119−121 °C. Subsequent elution of the column with 30% of ether in hexane afforded 572.8 mg (71.6%) of starting 6,6-diphenyl-4-(diphenylmethoxy)bicyclo-[3.1.0]hex-3-en-2-one (**5e**) in fraction 2. Fraction 3 gave 38.2 mg (16.0%) of 2-(*E*)-6,6-diphenyl-3-(diphenylmethoxy)hexa-2,5-dienoic acid (**28**). Crystallization from heptane−ether gave 25.5 mg (10.7%) of colorless crystals, mp 151−152 °C.

The spectral data for 2-(*E*)-6,6-diphenyl-3-(diphenylmethoxy)hexa-2,5-dienoic acid (**28**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.33−7.18 (m, 20H), 6.16 (t, J = 7.3 Hz, 1H), 6.06 (s, 1H), 5.04 (s, 1H), 3.69 (d, J = 7.3 Hz, 2H); MS *m*/*e* 402.1985 ($M^+ - CO_2$, calcd for $C_{30}H_{26}O$ 402.1985); IR (film) 1685, 1600 cm^{-1}. Anal. Calcd for $C_{31}H_{26}O_3$: C, 83.38; H, 5.87. Found: C, 82.99; H, 6.51. The structure was assigned using X-ray crystallography (see the Supporting Information).

Control Experiment of the Stability of 2-(*E*)-6,6-Diphenyl-3-(diphenylmethoxy)hexa-2,5-dienoic Acid (28). A 2 mg (4.5×10^{-3} mmol) sample of 2-(*E*)-6,6-diphenyl-3-(diphenylmethoxy)hexa-2,5-dienoic acid (**28**) was dissolved in a mixture of 100 μL of THF and 10 μL of water, and the solution was kept for 24 h in the dark at 20 °C. Solvent was removed in vacuo, and the NMR spectrum showed no presence of 5,5-diphenyl-3-(diphenylmethyl)pent-4-en-2-one (**21**).

Exploratory Solid-State Photolysis of 6,6-Diphenyl-4-(diphenylmethoxy)bicyclo[3.1.0]hex-3-en-2-one (5e). Final Isomerization in Benzene. A 200 mg (0.47 mmol) portion of crystals of 6,6-diphenyl-4-(diphenylmethoxy)bicyclo[3.1.0]hex-3-en-2-one (**5e**)[7] was irradiated under conditions described in the General Procedures with a 400 W Sylvania discharge lamp for 1.5 h without external cooling with water (conversion approximately 10% by NMR). The same procedure was repeated three times. The crystals were dissolved in 600 mL of photolysis grade benzene and kept under dry nitrogen for 1.5 h at 20 °C. Solvent was evaporated under vacuum. Chromatography on a TLC preparative silica gel plate eluted with 5% ether in hexane afforded 2.6 mg of a mixture of unidentified compounds in band 1. Band 2 (4.8 mg, 4.3%) gave 5,5-diphenyl-3-(diphenylmethyl)pent-4-en-2-one (**21**). Band 3 gave a mixture of 6,6-diphenyl-3-(diphenylmethoxy)-cyclohexa-2,4-dienone (**16e**) and starting 6,6-diphenyl-4-(diphenylmethoxy)bicyclo[3.1.0]hex-3-en-2-one (**5e**). Flash chromatography on a 2 cm × 30 cm silica gel column eluted with 20% ether in hexane gave 44.1 mg (37.1%) of 6,6-diphenyl-3-(diphenylmethoxy)cyclohexa-2,4-dienone (**16e**) in fraction 1. Crystallization from heptane−chloroform yielded 32.6 mg (27.4%) of colorless crystals, mp 178−180 °C. Subsequent elution of the column with 40% ether in hexane afforded 481 mg (80.2%) of bicyclic enone **5e** in fraction 2.

The spectral data for 6,6-diphenyl-3-(diphenylmethoxy)cyclohexa-2,4-dienone (**16e**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.40−7.14 (m, 20H), 6.78 (d, J = 10.1 Hz, 1H), 6.41 (dd, J = 10.1, 2.1 Hz, 1H), 6.22 (s, 1H), 5.50 (d, J = 2.1 Hz, 1H); MS *m*/*e* 428.1773 (calcd for $C_{31}H_{24}O_2$ 428.1776); IR (film) 1647, 1569, 1226 cm^{-1}. Anal. Calcd for $C_{31}H_{24}O_2$: C, 86.89; H, 5.65. Found: C, 86.90; H, 5.71.

Exploratory Solid-State Photolysis of 6,6-Diphenyl-4-(diphenylmethoxy)bicyclo[3.1.0]hex-3-en-2-one (5e). Final Isomerization by Melting of Crystals. A 200 mg (0.47 mmol) sample of crystals of 6,6-diphenyl-4-(diphenylmethoxy)bicyclo[3.1.0]hex-3-en-2-one (**5e**) was irradiated under conditions described in the General Procedures for 1.5 h with a 400 W Sylvania discharge lamp without external cooling with water (conversion approximately 10% by NMR). Identical runs were done 10 times. Individual portions were collected and put into 5 mL round bottom flasks and heated under an argon atmosphere at 170 °C until melted. The reaction mixture was quickly cooled in an ice−water bath. Flash chromatography on a 2.5 cm × 30 cm column eluted with 15% ether in hexane gave 26.0 mg (6.5%) of 5,5-diphenyl-3-(diphenylmethyl)pent-4-en-2-one (**21**) together with minor impurities in fraction 1. The second fraction afforded 131 mg (31.6%) of 6,6-diphenyl-3-(diphenylmethoxy)cyclohexa-2,4-dienone (**16e**). Subsequent elution of the column with 40% ether in hexane afforded 1.585 g (79.3%) of starting 6,6-diphenyl-4-(diphenylmethoxy)bicyclo[3.1.0]hex-3-en-2-one (**5e**). Fraction 2 was crystallized from heptane−chloroform to give 99.9 mg (24.1%) of 6,6-diphenyl-3-(diphenylmethoxy)cyclohexa-2,4-dienone (**16e**), mp 179−180 °C.

Exploratory Solid-State Photolysis of 6-*endo*(*p*-Cyanophenyl)-6-*exo*-phenylbicyclo[3.1.0]hex-3-en-2-one (7e). Two separate runs of irradiation of 200 mg (0.74 mmol) of 6-*endo*-(*p*-cyanophenyl)-6-*exo*-phenylbicyclo[3.1.0]hex-3-en-2-one (**7e**)[4d] were conducted. Each sample was irradiated for 1.5 h under conditions described in the General Procedures. Both portions were combined and crystallized from acetonitrile to give 246 mg (61.5%) of starting 6-*endo*-(*p*-cyanophenyl)-6-*exo*-phenylbicyclo[3.1.0]hex-3-en-2-one (**7e**) with traces of phenol **30**. The acetonitrile solution was evaporated in vacuo and the residue chromatographed on two TLC silica gel plates eluted with 5% ether in hexane. Bands 1, 61.6 mg (15.4%), contained a mixture of 2-(*p*-cyanophenyl)-3-phenylphenol (**30**) and 4-(*p*-cyanophenyl)-3-phenylphenol (**31**) in a ratio of 10:1 (by NMR). Combined bands 2 afforded 50.0 mg (13%) of starting enone **7e**. Crystallization of fraction 1 from acetonitrile gave 43.0 mg (10.8%) of 2-(*p*-cyanophenyl)-3-phenylphenol (**30**) with traces of 4-(*p*-cyanophenyl)-3-phenylphenol (**31**). Evaporation of the acetonitrile solution afforded 18.3 mg (4.6%) of a mixture of 2-(*p*-cyanophenyl)-3-phenylphenol (**30**) and 4-(*p*-cyanophenyl)-3-phenylphenol (**31**) in a ratio of approximately 1:1 (see the Supporting Information). Crystallization of 2-(*p*-cyanophenyl)-3-phenylphenol (**30**) from acetonitrile gave 34.0 mg (8.5%) of colorless crystals, mp 214−215 °C.

The spectral characteristics of 2-(*p*-cyanophenyl)-3-phenylphenol (**30**) were the following: ^{1}H NMR (300 MHz, CD_3CN) δ 7.54 (m, 2H), 7.34−7.21 (m, 3H), 7.20−7.12 (m, 3H), 7.07−7.00 (m, 2H), 6.97 (dd, J = 5.4, 1.2 Hz, 1H), 6.93 (dd, J = 4.9, 1.1 Hz, 1H); MS *m*/*e* 271.0974 (calcd for $C_{19}H_{13}NO$, 271.0997). Anal. Calcd for $C_{19}H_{13}NO$: C, 84.11; H, 4.83; N, 5.16. Found: C, 84.10; H, 4.68; N, 5.26. The structure assignment was confirmed by X-ray crystallography (see the Supporting Information).

Solid-State Photolysis of 6-*exo*-(*p*-Cyanophenyl)-6-*endo*-phenylbicyclo[3.1.0]hex-3-en-2-one (7f). A 100 mg (0.37 mmol) sample of 6-*exo*-(*p*-cyanophenyl)-6-*endo*-phenylbicyclo[3.1.0]hex-3-en-2-one (**7f**)[4d] was divided in five NMR tubes and irradiated under a nitrogen

atmosphere in an ice−water bath for 9 h. The crystals were shaken every 30 min. Reaction mixtures were connected and chromatographed on a preparative TLC plate eluted with 10% ether in hexane. Band 1 (21.8 mg, 21.8%) contained 3-(*p*-cyanophenyl)-2-phenylphenol (**23**), mp 189−190 °C, from hexane−methylene chloride (lit.[4d] mp 189.5−190.5 °C). Band 2 (7.9 mg, 7.9%) contained 3-(*p*-cyanophenyl)-4-phenylphenol (**29**), mp 227−229 °C, from acetonitrile (lit.[4d] mp 222.8−225.4 °C). The structure assignment was supported by X-ray crystallography (see the Supporting Information). Band 3 yielded starting enone **7f** (42.1 mg, 42.1%).

Exploratory Solid-State Photolysis of 6-*exo*-(*p*-Bromophenyl)-4-methoxy-6-*endo*-phenylbicyclo[3.1.0]hex-3-en-2-one (24a). A 300 mg (0.84 mmol) sample of 6-*exo*-(*p*-bromophenyl)-4-methoxy-6-*endo*-phenylbicyclo[3.1.0]hex-3-en-2-one (**24a**) was irradiated under standard conditions (see the General Procedures) for 7 h. Identical runs were done five times, and individual portions were connected. The crude reaction mixture contained 5-(*p*-bromophenyl)-3-methoxy-6-phenylphenol (**26**), 6-(*p*-bromophenyl)-3-methoxy-5-phenylphenol (**27**), and 5-(*p*-bromophenyl)-3-methoxy-4-phenylphenol (**33**) in a ratio of 72:3:24 (by NMR). Chromatography on a 2.5 × 75 cm column of deactivated silica gel eluted with 5% ether in hexane gave 66.0 mg (4.4%) of 5-(*p*-bromophenyl)-3-methoxy-6-phenylphenol (**26**) with traces of phenol **27** in fraction 1. Fraction 2 contained 15.0 mg (1.0%) of a mixture of phenol **26** and phenol **27** in a ratio of 98:2. Fraction 3 contained 15.0 mg (1.0%) of a mixture of phenol **26** and phenol **27** in a ratio of 91:9. Subsequent elution of the column with 35% ether in hexane gave 42.8 mg (3.5%) of 5-(*p*-bromophenyl)-3-methoxy-4-phenylphenol (**33**) in fraction 4. Fraction 5 afforded 860 mg (57.3%) of starting 6-*exo*-(*p*-bromophenyl)-4-methoxy-6-*endo*-phenylbicyclo[3.1.0]hex-3-en-2-one (**24a**). Fraction 1 was crystallized twice from heptane to give 47.8 mg (3.2%) of 6-(*p*-bromophenyl)-3-methoxy-5-phenylphenol (**26**) as colorless crystals, mp 170−171 °C. Fraction 4 was crystallized twice from hexane−methylene chloride to give 18.2 mg (1.2%) of 5-(*p*-bromophenyl)-3-methoxy-4-phenylphenol (**33**) as colorless crystals, mp 144−145 °C.

The spectral characteristics of 5-(*p*-bromophenyl)-3-methoxy-6-phenylphenol (**26**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.38−7.22 (m, 5H), 7.15−7.06 (m, 2H), 6.94 (m, 2H), 6.61 (d, J = 2.5 Hz, 1H), 6.55 (d, J = 2.5 Hz, 1H), 5.16 (s, 1H), 3.85 (s, 3H); MS *m*/*e* 356.0242 (calcd for $C_{19}H_{15}O_2Br$, 356.0238); IR (CCl_4) 2843, 1616, 1574, 1475, 1425, 1346, 1304, 1205, 1147, 1055 cm^{-1}. Anal. Calcd for $C_{19}H_{15}O_2Br$: C, 64.24; H, 4.26; Br, 22.49. Found: C, 63.93; H, 4.16. The structure was confirmed by X-ray crystallography (see the Supporting Information).

The spectral characteristics of 5-(*p*-bromophenyl)-3-methoxy-4-phenylphenol (**33**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.29−7.12 (m, 5H), 7.00−7.08 (m, 2H), 6.90 (m, 2H), 6.53 (d, J = 2.5 Hz, 1H), 6.45 (d, J = 2.5 Hz, 1H), 4.83 (s, 1H), 3.74 (s, 3H); MS *m*/*e* 356.0242 (calcd for $C_{19}H_{15}O_2Br$, 356.0238); IR (CCl_4) 3575, 3356, 3059, 3016, 2940, 2839, 1598, 1464, 1429, 1346, 1246, 1167, 1136, 1049, 1009, 974 cm^{-1}. Anal. Calcd for $C_{19}H_{15}O_2Br$: C, 64.24; H, 4.26; Br, 22.49. Found: C, 63.84, H, 4.33.

Exploratory Solid-State Photolysis of 6-*endo*-(*p*-Bromophenyl)-4-methoxy-6-*exo*-phenylbicyclo[3.1.0]hex-3-en-2-one (24b). A 250 mg (0.70 mmol) sample of 6-*endo*-(*p*-bromophenyl)-4-methoxy-6-*exo*-phenylbicyclo[3.1.0]hex-3-en-2-one (**24b**) was irradiated under standard conditions (see the General Procedures) for 8 h. The reaction mixture contained, besides starting enone **24b**, 6-(*p*-bromophenyl)-3-methoxy-5-phenylphenol (**27**), 5-(*p*-bromophenyl)-3-methoxy-6-phenylphenol (**26**), and an unknown isomeric phenol in a ratio of 93:2:5 (by NMR). Identical runs were done six times, and individual portions were connected. Chromatography on a 2.5 × 60 cm deactivated silica gel column eluted with 5% ether in hexane gave 30.1 mg (2.0%) of a mixture of phenol **27** and phenol **26** in a ratio of 92:8 in fraction 1. Fraction 2 contained 40.3 mg (2.7%) of a mixture of phenol **27** and phenol **26** in a ratio of 97:3. Fraction 3 afforded 89.0 mg (5.9%) of 6-(*p*-bromophenyl)-3-methoxy-5-phenylphenol (**27**) with traces of phenol **26**. Double crystallization from heptane−chloroform gave 41.8 mg (2.8%) of colorless crystals, mp 130−131 °C. Fraction 4 gave 4.8 mg (0.3%) of an unknown phenol with molecular weight identical with that of 6-(*p*-bromophenol)-3-methoxy-5-phenylphenol (**27**), mp 64−65 °C, from hexane−ether. Subsequent elution of the column with 40% ether in hexane yielded 730 mg (48.7%) of starting enone **24b** in fraction 5.

The spectral characteristics of 6-(*p*-bromophenyl)-3-methoxy-5-phenylphenol (**27**) were the following: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.38 (m, 2H), 7.15−7.20 (m, 3H), 7.03−7.09 (m, 2H), 7.00 (m, 2H), 6.58 (m, 2H), 4.99 (s, 1H), 3.85 (s, 3H); MS *m*/*e* 356.0242 (calcd for $C_{19}H_{15}O_2Br$, 356.0238); IR (film) 2838, 1612, 1579, 1471, 1342, 1304, 1207, 1153, 1055 cm^{-1}. Anal. Calcd for $C_{19}H_{15}O_2Br$: C, 64.24; H, 4.26; Br, 22.49. Found: C, 63.86; H, 4.11; Br, 22.12. The structure was confirmed by X-ray diffraction (see the Supporting Information).

The spectral characteristics for the unknown phenol were the following: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.29 (m, 2H), 7.19−7.13 (m, 3H), 7.06−6.98 (m, 2H), 6.92 (m, 2H), 6.52 (d, J = 2.4 Hz, 1H), 6.49 (d, J = 2.4 Hz, 1H), 5.02 (s, 1H), 3.75 (s, 3H); MS *m*/*e* 356.0223 (calcd for $C_{19}H_{15}O_2Br$, 356.0238).

Crystal Packing from the X-ray Crystallography Results. Mini crystal lattices composing 15−30 molecules were built using SmartPac.[6b]

MM3 Calculations. Molecular mechanics calculations were performed with MM3(92).[11d] Reaction intermediates were included in the "reaction cavity" using flexible or rigid superposition. The central molecule was than optimized in fixed crystal lattice. Electron positive and negative centers in zwitterionic intermediates were treated as sp^2 carbons.

Flexible and Rigid Superpositions. Geometry analyses were performed using Macromodel 4.0[33] and Flexit.[34] RMS distances between corresponding atoms of the starting material in its X-ray conformation and the appropriate intermediate were evaluated. In flexible superpositions all non-ring dihedral angles in the molecule of the intermediate were allowed to alter.

Overlap Calculations of Reaction Intermediates in Their Crystal Lattice. Intermediates optimized by MM3 were inserted into the reaction cavity using rigid superposition. CrystLap[6b] was used to evaluate their overlap with the surrounding crystal lattice.

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Supporting Information Available: Summary of X-ray determinations, tables giving detailed steric energies from MM3, and a description of the programming used (9 pages). See any current masthead page for ordering and Internet access instructions.

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