JOC Article

Solution and Crystal Lattice Effects on the Photochemistry of 6-Substituted Cyclohexenones[1,2]

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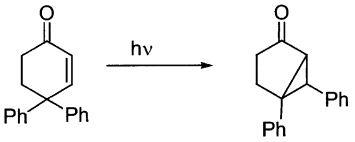
The photochemistry of 13 4,4-diphenylcyclohexenones, substituted at carbon-6, was investigated in solution and in the crystalline state. The stereoselectivity was of particular interest. In the solution photochemistry of C-6 monosubstituted enones in benzene, there was a unique preference for migration of the *cis*-phenyl group with formation of bicyclo[3.1.0]hexanone photoproducts, with the original 6-substituent having an endo configuration at carbon-3 of the product. In methanol the reaction was diverted to afford 3,4-diphenylcyclohex-2-enes understood as arising from a hydrogen-bonded zwitterionic intermediate. The solid-state photochemistry was also investigated. There was a dramatic absence of the 3,4-diphenylcyclohex-2-ene products in accord with the absence of the hydrogen bonding encountered in methanol. Further, the solid-state reactivity correlated with a vector analysis using X-ray atomic coordinates. This established that the migrating phenyl group required an orientation facing the enone β-carbon. While the interesting preference for the cis-endo migration was not intuitively predicted, ab initio computations on the alternative phenyl-bridged triplet intermediates did lead to an understanding of the selectivity.

Introduction

The type B rearrangement is a very general one and potentially of unique synthetic value. Note eq 1. For the limited types of enones previously studied, the overall reaction course can be predicted with certainty.[3] However, in contrast and remarkably, the general reaction stereochemistry is still incomplete and uncertain. This is particularly true for cyclohexenones bearing substituents at C-6 where the solution and solid-state chemistry have not been generalized. One study suggested a preference, still unconfirmed in general, for endo stereochemistry at C-6 in the reaction product.[4] The corresponding solid-state behavior had not been investigated. Hence, it was of particular interest to pursue the chemistry of a series of these photochemical reactants, both in solution and in the crystalline state. As in most of our photochemical investigations, the aim is to develop the reaction to the point where the reaction is understood and may be added to the list of reactions of value.



(1)

Results

Synthetic Aspects. The synthesis of the enones of interest is described in Scheme 1. Diphenylation of enone **1** was accomplished by reaction with diphenyliodonium chloride. Direct monophenylation proved difficult since the monophenyl derivative reacted more rapidly than the reactant enone **1**, but 4,4,6-triphenylcyclohexenone **2a** was obtained by carbomethoxylation of **1**, followed by reaction with diphenyliodonium chloride and then removal of the carbomethoxy group with sodium iodide in DMF−HOAc. The usual direct base or acid removal proved ineffectual. The remaining required 6-subsituted enones were obtained either starting with the known[5] 6-acetoxy enone **2d** or the 6-hydroxy enone **2e**[6] or via the enolate of enone **1** as depicted in Scheme 1.

Solution Photochemistry in Benzene. With the 13 reactants available, we proceeded first to investigate the solution photochemical behavior. One of the most striking observations was the general preference for formation of the endo configuration of single substituents at C-3 in the bicyclic photoproducts (i.e., substituents originally at carbon-6 of the reactant enones). Equation 2 outlines the general reaction course, and Table 1 summarizes the

(1) This is paper 199 of our Photochemical Series and 268 of our General Series.

(2) Papers 198 and 265: Zimmerman, H. E.; Chen, W-S. *Org. Lett.* **2002**, *4*, 1155−1158.

(3) (a) Zimmerman, H. E.; Rieke, R. D.; Scheffer, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 2033−2047. (b) Zimmerman, H. E.; Wilson, J. W. *J. Am. Chem. Soc.* **1964**, *86*, 4036−4042. (c) Zimmerman, H. E.; Hancock, K. G. *J. Am. Chem. Soc.* **1968**, *90*, 3749−3760.

(4) Zimmerman, H. E.; Weber, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 995−1007.

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(6) Vedejs, E.; Engler, D. A.; Telschow, J. E. *J. Org. Chem.* **1978**, *43*, 188−196.

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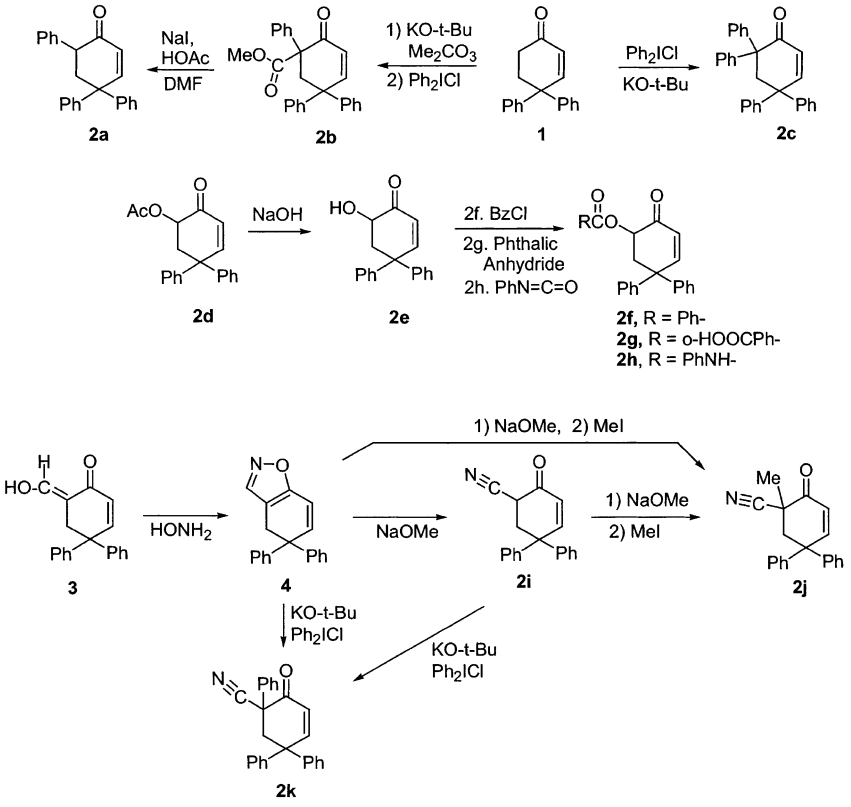
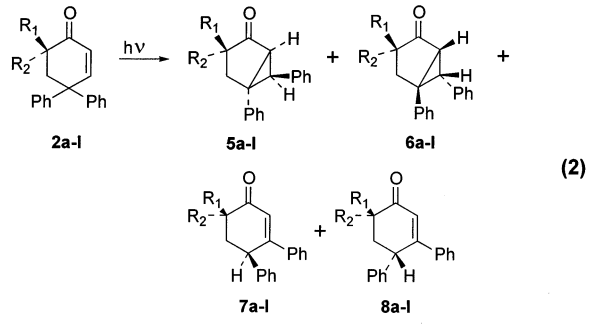
SCHEME 1. Synthesis of Enones



detailed data. Further information on the stereochemical and structural assignments is given in the Supporting Information.



(2)

a R_1=Ph, R_2=H
b R_1=Ph, R_2=$COOCH_3$
c R_1=Ph, R_2=Ph
d R_1=$OCOCH_3$, R_2=H
e R_1=OH, R_2=H
f R_1 =OCOPh, R_2=H
g R_1=OCOPhCOOH-o, R_2=H
h R_1=OCONHPh, R_2=H
i R_1=CN, R_2=H
j R_1=CH_3, R_2=CN
k R_1=Ph, R_2=CN
l R_1=Br, R_2=H
m R_1=CH_3, R_2=H

In view of the solution preferences for formation of the endo stereoisomers **5**, we carried out computations on selected phenyl-bridged intermediates leading to the endo and the exo stereoisomeric photoproducts. Note Table 4.

Solution Photochemistry in Methanol. There was a second exciting set of results. Thus, in the past the type B reaction of 4,4-disubstituted cyclohexenones has led either exclusively or primarily to the bicyclic photoproducts of the type shown in eq 1. Hence, it was of considerable interest when it was found for **2c** that in methanol the major reaction was formation of 3,4-diphenylcyclohexenones **7** and **8**. Note Table 2. These cyclohexenone photoproducts (e.g., **7c**) were encountered in benzene irradiations only in two cases (**2b, 2c**), both disubstituted at carbon-6. Of equal interest was the stereochemistry observed in cyclohexenone formation in methanol. For three of the C-6-monosubstituted reactants, namely, the acetoxy (**2d**), benzoyloxy (**2f**), and hydroxy (**2e**) cases, the preferred course is formation of the C-6-*cis*-cyclohexenones. In the methyl cyano example **2j**, no selectivity was observed. Note Table 2 for bicyclic versus cyclohexenone dependences on solvent—benzene versus methanol.

Solid-State Reactivity. Five of the enones were totally unreactive in the solid state. These were the phenyl enone **2a**, the hydroxy enone **2e,** the phthaloyloxy enone **2g**, the carbamoyloxy enone **2h**, and the cyano enone **2i**.

To better understand the solid-state reactivity, the X-ray structures for the bromo (**2l**), benzoyloxy (**2f**), and hydroxy (**2e**) cyclohexenones were utilized to obtain the atomic coordinates. Note Figure 1. Thus, the two ipso to ortho σ-bonds of the migrating group define two vectors, **V1** and **V2**. Vector multiplication affords a vector, **V3,** which is perpendicular to these two and gives the directionality of the ipso p-orbital. Also, 3,4-σ-bond defines a vector, **V4**, which leads to the p-orbital of the β-carbon of the enone system. The angle θ then obtained between the two vectors **V3** and **V4** gives the orientation between the phenyl and the enone π-systems. When this angle between **V3** and **V4** is 90°, the orientation of the C-4 phenyl group is ideal for overlap with the β-carbon

TABLE 1. Photochemical Product Distribution Ratios in Solution and in the Solid State

				solution stereoselectivity					
				bicyclic product		cyclohexenone		crystal stereoselectivity	
enone	R_1	R_2	solvent	*endo*-R_1 (**5a**−**l**)	*exo*-R_1 (**6a**−**l**)	*cis*-R_1 (**7a**−**l**)	*trans*-R_1 (**8a**−**l**)	*endo*-R_1 (**5a**−**l**)	*exo*-R_1 (**6a**−**l**)
2a	Ph	H	benzene	1.5	1.0	0	0	a	a
2b	Ph	$COOCH_3$	benzene	2.2	1.0		1.1[b]	6.0	1.0
			methanol	1.0	1.5		1.3[b]		
2c	Ph	Ph	benzene	2.0			1	1.0	
			methanol	1.0			2		
2d	CH_3COO	H	benzene	4.5	1.0	0	0	11.0	1.0
			methanol	3.0	1.0	0.7	0		
2e	HO	H	benzene	1.0	0	0	0	a	a
			methanol	3.5	0	1.0	0		
2f	PhCOO	H	benzene	3.0	1.0	0	0	1.0	3.0
			methanol	2.5	1.0	0.3	0		
2g	phthaloyl	H	methanol	3.0	1.0		1.0	a	a
2h	PhNHCOO	H	benzene	3.5	1.0	0	0	a	a
2i	NC	H	benzene	1.4	1	0	0	a	a
			methanol	a	a	a	a		
2j	CH_3	NC	benzene	4.0	1.0	0	0	7.0	1.0
			methanol	3	1	0.5	0.5		
2k	Ph	NC	benzene	1.0	1.8	0	0	2.8	1.0
			methanol	1.0	2.5		1.2[b]		
2l	Br	H	benzene	1.0	6.5	0	0	1.0	0
2m	CH_3	H	benzene	c	c	c	c	3.4	1.0

[a] Product not formed. [b] Stereochemistry unassigned. [c] See ref 4.

TABLE 2. Solvent Dependencies

	ratio of bicyclic to cyclohexenone in two different solvents (conversion, %)			ratio of bicyclic to cyclohexenone in two different solvents (conversion, %)	
reactant	benzene	methanol	reactant	benzene	methanol
2b	2.9:1.0 (34)	1.6:1.0 (50)	**2f**	1.0:0 (54)	11.2:1 (73)
2c	2.0:1.0 (60)	1.0:2.0 (100)	**2j**	1.0:0 (57)	5.5:1 (79)
2d	1.0:0 (60)	5:1 (73)	**2k**	1.0:0 (100)	2.6:1 (50)
2e	1.0:0 (55)	3.1:1.0 (49)			

TABLE 3. Orientation of the C-4 Phenyl p-Orbitals Toward the Enone *β*-Carbon

R_1	stereochemistry of migrating phenyl ring	configuration of the product isomer	orientation, angle θ between **V3** and **V4** (deg)	stereoselectivity of the rearrangement (%)
PhCOO	cis	endo	27	25
PhCOO	trans	exo	60	75
Br	cis	endo	68	100
Br	trans	exo	5	0
OH	cis	endo	29	0
OH	trans	exo	3	0

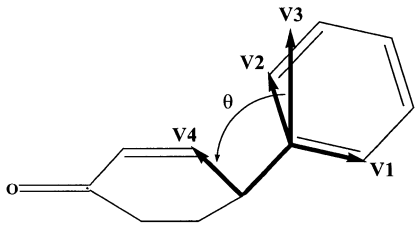


FIGURE 1. A vector analysis of orientation.

p-orbital and requires no twisting for phenyl bridging. This computation was carried out for the two phenyl rings of each of the three representative enones.

The results are listed in Table 3, and more detail is outlined in the Supporting Information.

Host−Guest Complex Chemistry. Interestingly, 6-acetoxy-4,4-diphenylcyclohexenone **2d** interacted with the Seebach−Toda host Taddol[7] **14**. However, two types of crystals could be discerned. One set consisted of a 1:1 complex of the S−T host (i.e., **14**) with one enantiomer of **2d**, while the other proved to be the second enantiomer of **2d**, but uncomplexed. Curiously, the photochemistry of the inclusion compound led to the same product distribution as obtained from pure crystalline **2d** and for one of its enantiomers, **(+)-2d**.

Discussion

General Observations. The first point to be made is the remarkable variation in reactivity depending on substitution at C-6, a site in the reactants respectably

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TABLE 4. Ab Initio Computations for *endo*- and *exo*-Phenyl-Bridged Triplet Species

starting ketone	R_1	R_2	energy of the endo triplet intermediate (au)	energy of the exo triplet intermediate (au)	predicted and obsd stereochem
2a	Ph	H	−995.2352361	−995.2304122	endo (cis migr)
2d	AcO	H	−992.3394893	−992.3363822	endo (cis migr)
2e	OH	H	−840.547001 (H-bonded)	−840.538962	endo (cis migr)
			−840.5366309 (non-H-bonded)		endo (cis migr)
2f	BzO	H	−1182.8515599	−1182.850211	endo (cis migr)
2j	CH_3	CN	−896.4548434	−896.4520566	endo (cis migr)
2l	Br	H	−777.7988962	−777.8007243	exo (trans migr)

[a] Hydrogen bonding obtained with energy minimization, giving a 2.1 Å in-plane distance.

distant from the migrating phenyl group at C-4. A second, equally remarkable, point is the overall preference for migration of the phenyl group cis to the moiety at C-6. The *cis*-phenyl group then becomes endo in the photoproduct. A further point of interest is the remarkable effect of hydroxylic solvents in controlling the partition between bicyclic and enone-type photoproducts.

Photochemistry in Aprotic Solvent Benzene. Several remarkable results were observed in the photochemistry in benzene. The first is that, with two exceptions (**2b** and **2c**), all 6-substituted cyclohexenones (i.e., **2a**−**2m)** proceeded in type B fashion to afford bicyclo[3.1.0]-hexan-2-ones with only traces of the cyclohexenone photoproducts. This result is best discussed in the context of the effect of methanol in leading to the cyclohexenone photoproducts (vide infra).

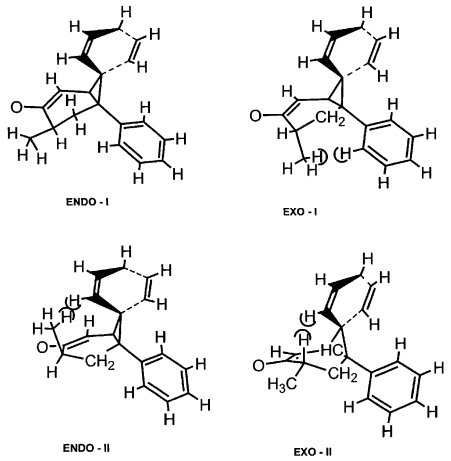
The second exciting result encountered is the preferential formation of the endo stereoisomer observed with one exception (**2l**) from all of the C-6 monosubstituted reactants. The endo isomer arises from migration of the *cis*-phenyl group at C-4. While this does have some suggestive precedent in an earlier study involving the 6-methyl counterpart,[4] we now see the generality of the phenomenon of cis migration. Also we now can determine the source of the selectivity.

In the case of the 6-acetoxy-bridged species **10** (R = AcO, Scheme 3) molecular modeling of the phenyl-bridged intermediate with MacroModel suggests a slight (ca. 0.25 kcal/mol) preference for the endo configuration. However, molecular modeling is really not appropriate in dealing with an excited-state (here triplet) species. Hartree−Fock ROHF/6-31G* computations on six examples of the phenyl-bridged triplets were in agreement with experiment and are summarized in Table 4. Except for the 6-bromo species **2l**, the computations and the experiment favored cis migration. In fact, for this triplet, *trans*-phenyl migration was preferred both by computation and by experiment. Thus, the agreement of the computations with experiment is excellent.

However, one likes to understand the stereoselectivities on a molecular basis. Molecular modeling revealed the source of the preference for *cis*-phenyl migration. Scheme 2 depicts two conformers for *cis*-phenyl migration and two conformers for *trans*-phenyl migration. It is seen that the preferred species is ENDO-**1**, in which the *cis*-phenyl group is migrating.

Photochemistry in Methanol and Solvent Dependence. The role of methanol in the dramatic change in reaction course, from type B bicyclic to cyclohexenone formation, remains to be considered. The overall mechanisms of both rearrangements—type B bicyclic and cyclohexenone formation—are outlined in Scheme 3. The

SCHEME 2. Steric Effects Favoring Cis Migration Leading to Endo Product

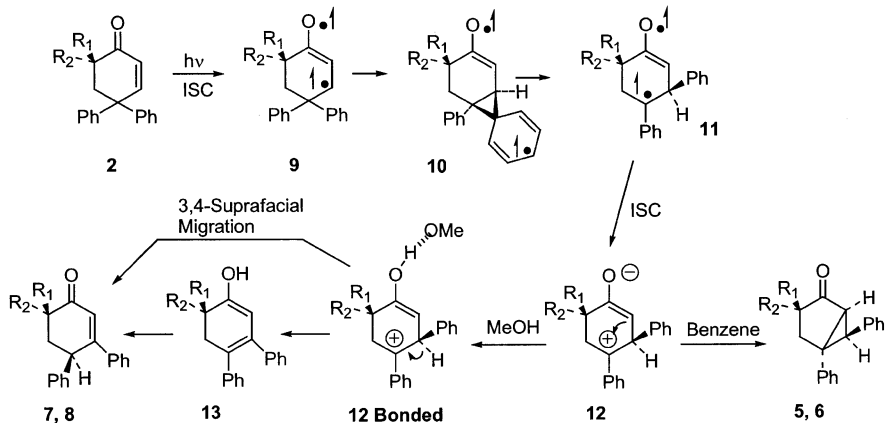


mechanism of formation of these unsaturated photoproducts seems likely to involve intervention of the methanol in hydrogen bonding or protonating the oxygen at a point where three-ring formation normally would occur. The α-carbon of the enolate moiety, or its incipient counterpart formed from the triplet, normally would supply electron density and bond to C-4. But with the enolate density not available in the case of the neutral enol, loss or migration of the C-3 proton is understandable if not predictable.

A final point is that if the mechanism involves loss of a proton rather than a hydride shift, then the product stereochemistry is determined in a γ-protonation of a dienol. Two points are relevant. Protonation of a neutral dienol is, indeed, expected[10] to occur at the γ-carbon, in accord with experimental formation of the conjugated enone product rather than α-protonation as observed for dienolates which afford β,γ-enones. The second point is stereochemical. If a dienol is actually involved, then the stereochemistry must be determined by a preferential attack trans to the C-6 substituent. Hence, it is not surprising that we observed no stereoselectivity for the enone **2j** with two substituents at C-6 of nearly the same size. We note also that cyclohexenone formation did not occur in the solid-state crystal lattice reactions in accord with the absence of protonating species in the crystals.

(8) Zimmerman, H. E. *Acc. Chem. Res.* **1987**, *20*, 263−268.
(9) (a) Zimmerman, H. E. Base-Catalyzed Rearrangements. In *Molecular Rearrangements*; DeMayo, P., Ed.; Interscience: New York, 1963; Chapter 6, pp 345−406. (b) Malhotra, S. K.; Ringold, H. J. *J. Am. Chem. Soc.* **1965**, *87*, 3228−3236.
(10) Zimmerman, H. E.; Hackett, P.; Juers, D. F.; McCall, J. M.; Schroder, B. *J. Am. Chem. Soc.* **1971**, *93*, 3653−3662.

SCHEME 3. Reaction Mechanism and Proton Elimination versus Bicyclic Formation[a]



[a] R_1 is the larger group, and R_2 is the smaller group.

A further finding was that disubstitution at C-6 led to a diminished amount of the bicyclic photoproduct relative to the 3,4-phenylcyclohexenone even in benzene. The extreme case was that of the 6,6-diphenyl derivative **2c**. Here there is inhibition of three-ring closure by phenyl−phenyl repulsion in all four bridged species in Scheme 2.

Solid-State Photochemistry. The Case of Inert Crystal Lattices. Interestingly, crystals of the 6-hydroxy (**2e**), 6-cyano (**2i**), 6-phthaloyloxy (**2g**), 6-phenylcarbamoyloxy (**2h**), and 6-phenyl (**2a**) derivatives proved to be inert. This might have been predicted qualitatively, since in the initial crystal conformation the C-4 phenyl groups have 29° and 3° angles between the π-system of each phenyl group and the 3,4-σ-bond (i.e., the β-carbon p-orbital). And, as noted in the Results, there is a good correlation between the tendency of a phenyl group to migrate and θ. This is the angle between the ipso p-orbital (i.e., **V3**) and the β,γ-σ-bond, which, in turn, is perpendicular to the enone π-system. The correlation holds for the 6-bromo, 6-benzoyloxy, and 6-hydroxy reactants as seen in Table 2.

Conclusion and Take-Home Lessons

This study has dealt with a particularly general and useful organic photochemical reaction, the type B enone rearrangement. What had been lacking was an understanding of the reactivity of the 6-substituted enones, and this study has determined (a) a preference for migration of the C-4 *cis*-phenyl group to give endo stereoselectivity, (b) a quantum mechanical treatment of the triplet intermediate which accounts for the stereochemistry, (c) a dramatic diversion of the reaction course toward formation of isomeric cyclohexenone photoproducts when the reaction is run in hydroxylic solvent and a mechanistic understanding of the solvent effect, and (d) an X-ray study of the solid-state counterparts giving evidence that the reactivity is controlled by the conformation of the migrating phenyl group and also by lack of hydrogen-bonding solvent molecules.

Experimental Section

Compounds 1,[11] **2d,**[5] **2l,**[10] **2m,**[4] **3,**[12] ***N,N′*-Ditritylurea,**[11] **and Diphenyliodonium Chloride.**[13] These compounds were synthesized according to known procedures.

6-Carbomethoxy-4,4,6-triphenylcyclohex-2-en-1-one (2b). To a stirred dimethyl carbonate (5.0 mL) solution of 213 mg (0.86 mmol) of 4,4-diphenylcyclohex-2-en-1-one[11] under nitrogen was added 105 mg of a 60% suspension of sodium hydride (2.63 mmol) in mineral oil. The mixture was refluxed for 30 min, and 537 mg (1.7 mmol) of diphenyliodonium chloride[12] was added. The resulting mixture was refluxed for 1 h, cooled to 25 °C, stirred overnight, diluted with 20 mL of water, acidified with 1 N HCl, and extracted with chloroform. The extract was dried (Na_2SO_4), concentrated, and chromatographed on a silica gel column slurry packed and eluted successively with benzene and 5% ethyl acetate in benzene to give the impure product, which was chromatographed again on a silica gel column, eluted with 20% ether in hexane. It gave 213 mg (65%) of **2b** as white crystals: mp 111−113 °C (hexanes−ether); ^{1}H NMR ($CDCl_3$) δ 7.4−7.1 (m, 16 H), 6.40 (d, 1 H), 3.67 (dd, J = 1.5, 13.5 Hz, 1 H), 3.56 (d, J = 13.5 Hz, 1 H), 3.10 (s, 3H); ^{1}H NMR (CD_3OD) δ 7.5−7.0 (m, 16 H), 6.35 (d, 1 H), 3.60 (s, 2 H), 3.00 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 193.6, 170.8, 153.5, 146.0, 143.8, 137.5, 128.3, 128.0, 127.9, 127.8, 127.7, 127.2, 127.1, 127.0, 126.7, 126.4, 60.2, 51.9, 48.5, 43.1; HRMS *m/z* 405.1456 (405.1467, calcd for $C_{26}H_{22}O_3Na$, M + Na^+).

4,4,6-Triphenylcyclohex-2-en-1-one (2a). Method a. To a stirred solution of 33 mg (0.086 mmol) of **2b** in 3.0 mL of DMSO under nitrogen was added 120 mg (2.14 mmol) of potassium hydroxide. The mixture was stirred for 16 h, acidified with 1 N HCl, extracted with ether, dried (Na_2SO_4), concentrated, and chromatographed on a silica gel column slurry packed and eluted with 20% ether in hexane to give 6 mg (21%) of **2a** as white crystals: mp 145−146 °C (hexanes−ether); ^{1}H NMR ($CDCl_3$) δ 7.5−7.0 (m, 16 H), 6.35 (d, 1 H), 3.65 (dd, 1 H), 3.05 (dd, 1 H), 2.90 (ddd, 1 H); ^{1}H NMR (C_6D_6) δ 7.3−6.9 (m, 15 H), 6.85 (dd, 1 H), 6.15 (d, 1 H), 3.60 (dd, 1H), 2.80 (dd, 1 H), 2.65 (ddd, 1 H); HRMS *m/z* 347.1423 (347.1412, calcd for $C_{24}H_{20}ONa$, M + Na^+).

Method b. A mixture of 50 mg (0.13 mmol) of **2b**, 219 mg of sodium iodide, and 0.50 mL of acetic acid in 3.0 mL of dimethylformamide under nitrogen was refluxed for 4.5 h, cooled to 25 °C, diluted with 30 mL of water, and left overnight.

(11) Ng, K. D.; Hart, H. *Tetrahedron* **1995**, *51*, 7883−7906.
(12) Zimmerman, H. E.; Lamers, P. H. *J. Org. Chem.* **1989**, *54*, 5788−5804.
(13) Beringer, F. M.; Geering, E. J.; Kuntz, I.; Mauser, M. *J. Phys. Chem.* **1956**, *60*, 141−150.

The precipitate formed was filtered off, dried in air, and chromatographed on a silica gel column slurry packed and eluted with 20% ether in hexane to give 30 mg (71%) of **2a**, identical to that described vide supra.

Method c. A mixture of 297 mg (0.77 mmol) of **2b**, 1.3 g of sodium iodide, and 3.0 mL of acetic acid in 18 mL of dimethylformamide under nitrogen was refluxed for 4.5 h, cooled to 25 °C, diluted with 100 mL of water, and left overnight. The precipitate formed was filtered off, dried in air, and chromatographed on a silica gel column slurry packed and eluted with 20% ether in hexane to give 206 mg (83%) of **2a**, identical to that described vide supra.

4,4,6,6-Tetraphenylcyclohex-2-en-1-one (2c). To a stirred solution of 213 mg (0.86 mmol) of 4,4-diphenylcyclohex-2-en-1-one (**1**) and 190 mg (1.7 mmol) of potassium *tert*-butoxide in 3.0 mL of *tert*-butyl alcohol under nitrogen was added 543 mg (1.7 mmol) of diphenyliodonium chloride[12] in portions. The reaction mixture was refluxed for 3 h, cooled to 25 °C, and diluted with 15 mL of water. The mixture was extracted with ether (2 × 20 mL), dried (Na_2SO_4), and evaporated. The residue was chromatographed on a silica gel column slurry packed and eluted with 50% benzene in hexane to give 157 mg (65%) of **2c** as white crystals: mp 136−137 °C (hexanes−ether); ^{1}H NMR ($CDCl_3$) δ 7.3−6.8 (m, 21 H), 6.45 (d, 1 H), 3.75 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 199.75, 153.4, 145.5, 141.7, 128.46, 128.05, 127.54, 127.44, 127.36, 126.20, 126.02, 58.55, 49.17, 45.33; HRMS *m/z* 423.1707 (423.1725, calcd for $C_{30}H_{24}ONa$, M + Na^+).

6-Hydroxy-4,4-diphenylcyclohex-2-en-1-one[6] (2e). To a stirred solution of 398 mg (1.3 mmol) of 6-acetoxy-4,4-diphenylcyclohex-2-en-1-one[5] (**2d**) in 16 mL of THF and 6.0 mL of water under nitrogen was added 267 mg (4.7 mmol) of potassium hydroxide. The mixture was stirred at 25 °C for 50 min, diluted with 50 mL of water, and extracted with ether (3 × 10 mL). The extract was dried (Na_2SO_4), concentrated, and chromatographed on a silica gel column slurry packed and eluted with 5% ethyl acetate in benzene to give 321 mg (94%) of **2e** as white crystals: mp 96−97 °C (hexanes−ether) (lit.[6] mp 182−183 °C); ^{1}H NMR ($CDCl_3$) δ 7.4−7.2 (m, 10 H), 7.15 (d, J = 9 Hz, 1 H), 6.30 (d, J = 9 Hz, 1 H), 4.23 (dd, J = 3, 12 Hz, 1 H), 3.50 (s, 1 H), 3.02 (ddd, 1 H), 2.60 (dd, J = 12, 12 Hz, 1 H); ^{1}H NMR (C_6D_6) δ 7.1−6.7 (m, 10 H), 6.62 (m, 1 H), 5.95 (d, 1 H), 4.10 (dd, 1 H), 3.65 (s, 1 H), 2.90 (m, 1 H), 2.40 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 199.73, 157.36, 146.94, 142.74, 128.75, 128.70, 127.71, 127.26, 127.01, 126.97, 125.74, 70.16, 50.95, 43.86; MS (EI/CI) *m/z* 265.4 (M + 1), 236.4 (M^+ − CO).

6-Benzoyloxy-4,4-diphenylcyclohex-2-en-1-one (2f). To a stirred solution of 0.122 g (0.46 mmol) of **2e** in 0.5 mL of pyridine was added 0.053 mL (0.46 mmol) of benzoyl chloride. The mixture was stirred for 2 h, diluted with water, and acidified with cold 5% H_2SO_4. The precipitated sticky solid was washed with water, dissolved in ether, washed subsequently with 1 N HCl and water, dried (Na_2SO_4), and concentrated. The residue was dissolved in benzene and chromatographed on a silica gel slurry packed and eluted with 5% ethyl acetate in benzene to yield 145 mg (85%) of **2f** as white crystals: mp 144−145 °C (hexanes−ether); ^{1}H NMR ($CDCl_3$) δ 8.10 (m, 2 H), 7.7−7.1 (m, 14 H), 6.30 (d, 1 H), 5.65 (dd, 1 H), 3.15 (ddd, 1 H), 2.90 (d, 1 H); HRMS *m/z* 391.1327 (391.1310, calcd for $C_{25}H_{20}O_3Na$, M + Na^+).

6-Phthaloyloxy-4,4-diphenylcyclohex-2-en-1-one (2g). A mixture of 0.122 g (0.46 mmol) of **2e**, 0.136 g (0.92 mmol) of phthalic anhydride, and 0.50 mL of pyridine under nitrogen was stirred for 4 h, diluted with 5 mL of water, acidified with 1 N HCl, and extracted with chloroform (3 × 5 mL). The extract was dried (Na_2SO_4), concentrated, and chromatographed on a silica gel column slurry packed and eluted with chloroform to yield 14 mg (11%) of the starting **2e** and 136 mg (72%) of **2g** as white crystals: mp 159−162 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.65 (br s, 1 H), 8.0−7.0 (m, 15 H), 6.25 (d, 1 H), 5.70 (dd, 1 H), 3.20 (ddd, 1 H), 2.75 (d, 1 H); HRMS *m/z* 411.1226 (411.1233, calcd for $C_{26}H_{19}O_5$, M − H^-).

6-Phenylcarbamato-4,4-diphenylcycloex-2-en-1-one (2h). A mixture of 198 mg (0.75 mmol) of **2e** and 0.10 mL (110 mg, 0.83 mmol) of phenyl isocyanate in 3.0 mL of dry benzene under nitrogen was refluxed for 3 h, concentrated, and chromatographed on a silica gel column slurry packed and eluted subsequently with benzene and 2.5% ethyl acetate in benzene to give 142 mg (49%) of **2h** as white crystals: mp 167−168 °C; ^{1}H NMR ($CDCl_3$) δ 7.5−7.0 (m, 16 H), 6.80 (br s, 1 H), 6.25 (d, 1 H), 5.45 (dd, 1 H), 3.10 (ddd, 1 H), 2.70 (dd, 1 H); HRMS *m/z* 406.1427 (406.1419, calcd for $C_{25}H_{21}NO_3Na$, M + Na^+).

7,7-Diphenylbicyclo-3-oxa-4-aza[4.3.0]nona-1,4,8-triene (4). To a solution of 589 mg (2.13 mmol) of 6-hydroxymethyleno-4,4-diphenylcyclohex-2-en-1-one[11] (**3**) in 75 mL of acetic acid was added 288 mg (2.13 mmol) of finely ground hydroxylamine hydrochloride. The mixture was refluxed for 10 min, cooled, diluted with 50 mL of water, and extracted with ether (3 × 10 mL). The extract was washed with aqueous saturated sodium bicarbonate, dried (Na_2SO_4), and concentrated to give 507 mg (87%) of **4** as yellow crystals: mp 146−147 °C; ^{1}H NMR ($CDCl_3$) δ 8.10 (s, 1 H), 7.4−7.1 (m, 10 H), 6.70 (d, 1 H), 6.60 (d, 1 H), 3.40 (s, 2 H). HRMS *m/z* 296.1059 (296.1051, calcd for $C_{19}H_{15}NONa$, M + Na^+).

6-Cyano-4,4-diphenylcyclohex-2-en-1-one (2i). A mixture of 74 mg of **4** and 29 mg of sodium methoxide in 3.5 mL of dry methanol was stirred for 2 h at 0 °C. Then 4.0 mL of ether was added, and the mixture was stirred for an additional 3 h at 0 °C and left at this temperature overnight. The reaction mixture was diluted with 25 mL of water, acidified with 1 N HCl, and extracted with ether. The extract was dried (Na_2SO_4), concentrated, and chromatographed on a silica gel column slurry packed and eluted with 16% ether in hexane to give 15 mg (20%) of starting **4** and 25 mg (35%) of **2i** as white crystals: mp 120−121 °C (hexanes−ether); ^{1}H NMR (C_6D_6) δ 7.2−6.5 (m, 10 H), 6.40 (d, 1 H), 5.75 (d, 1 H), 2.95 (dd, 1 H), 2.5−2.3 (m, 2 H); ^{1}H NMR (CD_3OD) δ 7.55 (dd, 1 H), 7.5−6.2 (m, 13 H), 6.90 (d, 0.3 H), 6.25 (d, 1 H), 6.10 (d, 0.3 H), 3.10 (m, 2 H), 2.95 (s, 0.6 H); HRMS *m/z* 296.1062 (296.1051, calcd for $C_{19}H_{15}NONa$, M + Na^+).

6-Cyano-6-methyl-4,4-diphenylcyclohex-2-en-1-one (2j). To a stirred solution of 165 mg (0.6 mmol) of **2i** in 3.5 mL of DMSO was added 50 mg of sodium methoxide. To this mixture was added 0.16 mL (3 mmol) of methyl iodide, and the resulting reaction mixture was stirred for 1 h at 25 °C. Then an additional 0.50 mL of methyl iodide was added, and the mixture was heated for 1 h at 100 °C, cooled, diluted with 5.0 mL of water, acidified with 1 N HCl, and extracted with ether. The extract was dried (Na_2SO_4), concentrated, and chromatographed on a silica gel column slurry packed and eluted with 50% chloroform in hexane to give 47 mg (28%) of **2i** and 30 mg (17%) of **2j** as white crystals: mp 116−117 °C (hexanes−ether); ^{1}H NMR ($CDCl_3$) δ 7.5−7.2 (m, 11 H), 6.35 (d, 1 H), 3.20 (dd, 1 H), 2.90 (d, 1 H), 1.45 (s, 3 H); HRMS *m/z* 310.1199 (310.1208, calcd for $C_{20}H_{17}NONa$, M + Na^+). Also isolated was 10 mg (6%) of 1-cyano-2-methoxy-5,5-diphenylcyclohexadiene-1,3 (**10**) as a clear glassy material: ^{1}H NMR ($CDCl_3$) δ 7.4−7.0 (m, 10 H), 6.80 (d, 1 H), 6.10 (d, 1 H), 3.90 (s, 3 H), 3.05 (s, 2 H). HRMS *m/z* 310.1197 (310.1208, calcd for $C_{10}H_{27}NONa$, M + Na^+).

2i and 2j. To a solution of 685 mg (2.5 mmol) of **4** in 10 mL of *tert*-butyl alcohol under nitrogen was added 650 mg (5.75 mmol) of potassium *tert*-butoxide. After 15 min 0.36 mL (5.75 mmol) of methyl iodide was added. The reaction mixture was stirred under nitrogen for 1 h at 25 °C, additionally refluxed for 30 min, then cooled to 25 °C, diluted with 20 mL of water, and extracted with ether. The extract was chromatographed on a silica gel column slurry packed and eluted with 50% chloroform in hexane to give 256 mg (36%) of **2j**, 366 mg (53%) of **2i**, and 33 mg (5%) of 1-cyano-2-methoxy-5,5-diphenylcyclohexadiene-1,3, identical to those described vide supra.

6-Cyano-4,4,6-triphenylcyclohex-2-en-1-one (2k). Method a. To a stirred solution of 137 mg (0.5 mmol) of **2i** in 2.0

mL of *tert*-butyl alcohol under nitrogen was added 0.13 g (1.15 mmol) of potassium *tert*-butoxide. Then 0.37 g (1.15 mmol) of diphenyliodonium chloride was added, and the mixture was refluxed for 2 h, cooled to 25 °C, diluted with 20 mL of water, and extracted with ether (3 × 5 mL). The extract was dried (Na_2SO_4), concentrated, and chromatographed on a silica gel column slurry packed and eluted with benzene to give 90 mg (52%) of **2k** as white crystals: mp 121−122 °C (hexanes−ether); ^{1}H NMR ($CDCl_3$) δ 7.6−7.0 (m, 16 H), 6.55 (d, 1 H), 3.40 (s, 2 H); ^{1}H NMR (C_6D_6) δ 7.2−6.5 (m, 16 H), 6.05 (d, 1 H), 3.05 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 189.59, 157.02, 144.14, 143.10, 135.64, 128.58, 128.39, 128.13, 127.84, 127.45, 127.01, 126.91, 126.80, 126.76, 117.58, 51.00, 48.43, 46.82; HRMS *m*/*z* 372.1340 (372.1364, calcd for $C_{25}H_{19}NONa$, M + Na^+).

Method b. To a stirred solution of 685 mg (2.5 mmol) of **4** in 10 mL of *tert*-butyl alcohol under nitrogen was added 0.65 g (5.75 mmol) of potassium *tert*-butoxide. After 15 min 1.85 g (5.75 mmol) of diphenyliodonium chloride was added, and the mixture was refluxed for 3 h, cooled to 25 °C, diluted with 20 mL of water, and extracted with ether (3 × 5 mL). The extract was dried (Na_2SO_4), concentrated, and chromatographed on a silica gel column slurry packed and eluted with benzene to give 382 mg (44%) of **2k**, identical to that described vide supra.

Cyclization of 2h in Methanol. A solution of 5.0 mg of **2h** in 1.0 mL of methanol was left for 48 h at 25 °C. The reaction mixture containing by NMR 23% starting **2h** and 77% **10** was chromatographed on a silica gel column slurry packed and eluted with 33% hexane in dichloromethane to give 1 mg (20%) of starting **2h** and 3 mg (60%) of **10** as a white sticky solid: ^{1}H NMR ($CDCl_3$) δ 7.4−7.1 (m, 15 H), 6.40 (dd, 1 H), 5.80 (d, 1 H), 4.45 (dd, 1 H), 3.20 (br s, 1 H), 2.95 (ddd, 1H), 2.45 (dd, 1 H).

(+)-6-Acetoxy-4,4-diphenylcyclohex-2-en-1-one ((+)-2d). Inclusion Compound of (−)-6-Acetoxy-4,4-diphenylcyclohex-2-en-1-one ((−)-2d) and 14. An 80 mg (0.26 mmol) portion of **2d** and 60 mg (0.13 mmol) of **14** were crystallized from ether−hexane until the constant melting point to give 76 mg of an inclusion compound of (−)-**2d** and **14** as white needles: mp 144−145 °C. The host:guest ratio determined by NMR was 1:1.

The initial mother solution also precipitated compact crystals, which were crystallized from ether−hexane until the constant melting point to give (+)-**2d** as compact crystals: mp 130−131 °C; α_{25}(589 nm) = +0.16 (grad·m^2)/mol, α_{25}(578 nm) = +0.17 (grad·m^2)/mol, α_{25}(546 nm) = +0.20 (grad·m^2)/mol, α_{25}(436 nm) = +0.45 (grad·m^2)/mol. The ^{1}H NMR spectrum of (+)-**2d** was identical to that of the racemic **2d**.

(−)-2d. A 63 mg portion of the inclusion compound of (−)-**2d** and **14** was chromatographed on a silica gel column slurry packed and eluted with 15% ether in hexane to give 37 mg (80%) of (−)-**2d** as clear crystals: mp 130−131 °C; α_{25}(589 nm) = −0.16 (grad·m^2)/mol, α_{25}(578 nm) = −0.17 (grad·m^2)/mol, α_{25}(546 nm) = −0.20 (grad·m^2)/mol, α_{25}(436 nm) = −0.45 (grad·m^2)/mol.

Inclusion Compound of 2e with γ-Cyclodextrin. To a solution of 130 mg (0.1 mmol) of γ-cyclodextrin in 0.50 mL of water was added a solution of 26 mg (0.1 mmol) of **2e** in 2.0 mL of ethanol. The mixture was stirred for 17 h. The solid was filtered out, washed subsequently with 0.50 mL portions of ether, water, and ether again, and dried in air. It gave 38 mg of a solid which consisted of **2e** and γ-cyclodextrin in a ratio of 1:1.5 (by NMR).

Inclusion Compound of 2d with γ-Cyclodextrin. To a solution of 130 mg (0.1 mmol) of γ-cyclodextrin in 0.50 mL of water was added a solution of 31 mg (0.1 mmol) of **2d** in 1.5 mL of ethanol. The mixture was stirred for 42 h. The solid was filtered out, washed subsequently with 0.5 portions of ether, water, and ether again, and dried in air. It gave 8.0 mg of a solid which consisted of **2d** and γ-cyclodextrin in a ratio of 2:3.

Photolysis of 2a in C_6D_6 (Typical Procedure). A solution of 20 mg of **2a** in 1.0 mL of C_6D_6 was purged with purified nitrogen for 15 min and photolyzed by a 400 W mercury lamp with a water cooling well through a 2 mm Pyrex filter. The reaction was monitored by NMR and led to mixtures of *trans-endo*-3,5,6-triphenylbicyclo[3.1.0]hexan-2-one (**5a**) and *trans-exo*-3,5,6-triphenylbicyc-lo[3.1.0]hexan-2-one (**6a**).

Photolysis versus Conversion of 2a. After 1 h and 27% conversion, the ratio **5a**:**6a** was 1.4. After 2 h and 46% conversion, the ratio was 1.5.

The reaction mixture was chromatographed on a silica gel column slurry packed and eluted with 33% chloroform in hexane to give 5.0 mg (25%) of **6a** as a clear glassy material: ^{1}H NMR ($CDCl_3$) δ 7.5−7.1 (m, 13 H), 6.90 (m, 2 H), 3.20 (d, 1 H), 3.0−2.8 (dd+d, 2 H), 2.60 (dd, 1 H), 2.35 (dd, 1H); HRMS *m*/*z* 347.1418 (347.1412, calcd for $C_{24}H_{20}ONa$, M + Na^+). Also isolated was 1 mg (5%, purity ca. 80%) of **5a** as a sticky material: ^{1}H NMR ($CDCl_3$) δ 7.5−6.9 (m), 6.30 (m), 3.80 (m), 3.15 (m), 2.90 (m), 2.65 (m).

Photolysis of 2a in the Solid State (Typical Procedure). An 11 mg portion of crystalline **2a** was placed between two glass slides and photolyzed for 13.5 h in a large beaker filled with ice and water with a 400 W mercury lamp through a 2 mm Pyrex filter. Then the reaction mixture was dissolved in $CDCl_3$, dried (Na_2SO_4), and analyzed by ^{1}H NMR. Only the starting material was present.

Photolysis of 2b in C_6D_6. A solution of 30 mg of **2b** in 1.0 mL of C_6D_6 was photolyzed for 10 min following the typical procedure. The reaction led to a mixture of *endo*-3-carbomethoxy-*exo*-3-phenyl-6-*trans*-phenyl-5-phenylbicyclo[3.1.0]-hexan-2 -one (**6b**), *exo*-3-carbomethoxy-*endo*-3-phenyl-6-*trans*-phenyl-5-phenylbicyclo[3.1.0]hexan-2 -one (**5b**), and 6-carbomethoxy-3,4,6-triphenylcyclohex-2-en-1-one **7b** in a ratio of 2.2:1:1.1.

The reaction mixture was chromatographed on a silica gel column slurry packed and eluted with 20% ether in hexane to give 11 mg of a white solid, which was crystallized from hexanes−ether to give 7 mg (23%) of **5b** as white crystals: mp 119−120 °C (hexanes−ether); ^{1}H NMR ($CDCl_3$) δ 7.6−6.7 (m, 15 H), 3.72 (s, 3 H), 3.35 (dd, 1 H), 3.25 (d, 1 H), 3.05 (d, 1 H), 2.95 (d, 1H); ^{1}H NMR (C_6D_6) δ 7.5−6.7 (m, 15 H), 3.40 (d, 1 H), 3.25 (s, 3 H), 2.85 (d, 1 H), 2.75 (s, 2 H); HRMS *m*/*z* 405.1469 (405.1467, calcd for $C_{26}H_{22}O_3Na$, M + Na^+). Another chromatography fraction gave 14 mg of a sticky solid, which was thoroughly washed with hexane to give 8 mg (27%) of **6b** as a clear glassy material: ^{1}H NMR ($CDCl_3$) δ 7.5−7.1 (m, 15 H), 3.70 (d, 1 H), 3.25 (s, 3 H), 3.20 (d, 1 H), 3.05 (d, 1 H), 2.90 (d, 1H); ^{1}H NMR (C_6D_6) δ 7.5−6.9 (m, 15 H), 3.70 (d, 1 H), 2.95, 2.90 (d+s, 4 H), 2.65 (s, 2 H); HRMS *m*/*z* 405.1465 (405.1467, calcd for $C_{26}H_{22}O_3Na$, M + Na^+). The mother solutions were combined and chromatographed on an HPLC instrument, eluted with 25% chloroform in hexane, to give 2 mg (7%) of 6-carbomethoxy-3,4,6-triphenylcyclohex-2-en-1-one **7b** or **8b** as a clear glassy material: ^{1}H NMR ($CDCl_3$) δ 7.5−6.9 (m, 15 H), 6.65 (d, 1 H), 3.95 (m, 1 H), 3.60 (s, 3 H), 3.0 (m, 2 H); ^{1}H NMR (C_6D_6) δ 7.5−6.65 (m, 15 H), 6.60 (d, 1 H), 3.85 (ddd, *J* = 10.0, 4.5, 2.3 Hz, 1H), 3.35 (s, 3 H), 3.23 (dd, *J* = 14.3, 10.0 Hz, 1 H), 2.90 (dd, 1 H); HRMS *m*/*z* 405.1481 (405.1467, calcd for $C_{26}H_{22}O_3Na$, M + Na^+).

Photolysis of 2b in the Crystalline State. A 20 mg portion of **2b** was photolyzed following the typical procedure. The reaction led to mixtures of **6b** and **5b**.

Photolysis versus Conversion of 2b in the Crystalline State. After 5 h and 50% conversion the **5b**:**6b** ratio was 5.8. After 7 h and 75% conversion the ratio was 6.0.

Photolysis of 2b in CD_3OD. A solution of 10 mg of **2b** in 1.0 mL of CD_3OD was photolyzed following the typical procedure. The reaction led to mixtures of **6b**, **5b**, and **7b** or **8b**.

Photolysis versus Conversion of 2b in Solution. After 10 min and 50% conversion, the ratio **6b**:**5b** was 1.2 and the product yield was 19%. After 40 min and a conversion of 87%, the ratio was 1.6 with a 33% yield.

Attempted Photolysis of 6b in CD_3OD. A solution of 10 mg of **6b** in 1.0 mL of CD_3OD was photolyzed following the typical procedure. Only the starting **6b** along with trace amounts of impurities was found in the reaction mixture.

Attempted Photolysis of 5b in CD_3OD. A solution of 10 mg of **5b** in 1.0 mL of CD_3OD was photolyzed following the typical procedure. Only the starting **5b** along with trace amounts of impurities was found in the reaction mixture.

Photolysis of 2c in C_6D_6. A solution of 20 mg of **2c** in 1.0 mL of C_6D_6 was photolyzed following the typical procedure. The reaction led to mixtures of *trans*-3,3,5,6-tetraphenylbicyclo-[3.1.0]hexan-2-one (**5c**) and 4,5,6,6-tetraphenylcyclohex-2-en-1-one (**7c**).

Photolysis versus Conversion of 2c. After 15 min, the conversion was 60% with a 40% yield of **5c** and a 20% yield of **7c**. After 60 min, the conversion was 97% with a 64% yield of **5c** and 33% yield of **7c**.

The reaction mixture was chromatographed on a silica gel column slurry packed and eluted with benzene to give 10 mg (50%) of **5c** and 5 mg (25%) of **7c**. Data for compound **5c**: glassy material; ^{1}H NMR ($CDCl_3$) δ 7.5−6.9 (m, 18 H), 6.60 (m, 2 H), 3.25 (d, 1 H), 3.10, 3.05 (d + s, 3 H); ^{1}H NMR (C_6D_6) δ 7.4−6.8 (m, 20), 3.20 (d, 1 H), 2.95 (d, 1 H), 2.80 (d, 1 H), 2.65 (d, 1 H); HRMS *m/z* 423.1712 (423.1725, calcd for $C_{30}H_{24}$-ONa, M + Na^+). Data for compound **7c**: glassy material; ^{1}H NMR ($CDCl_3$) δ 7.5−7.0 (m, 20 H), 6.70 (d, J = 2.3 Hz, 1 H), 4.10 (dd, 1 H), 3.10 (dd, J = 14.25, 4.5 Hz, 1 H), 2.95 (dd, J = 14.25, 10.5 Hz, 1 H); HRMS *m/z* 400.1827 (400.1827, calcd for $C_{30}H_{24}O$, M^+).

Photolysis of 2c in 10% C_6D_6 in CD_3OD. A solution of 55 mg of **2c** in 2.0 mL of 10% C_6D_6 in CD_3OD was photolyzed following the typical procedure. The reaction led to mixtures of **5c** and **7c**.

Photolysis versus Conversion of 2c in Solution. After 6 h and 97% conversion, the yield of **5c** was 32% and that of **7c** was 64%. After 8.5 h, the conversion was 100%, with a yield of 37% **5c** and 63% **7c**.

Photolysis of 2c in CD_3OD. A solution of 5.0 mg of **2c** in 2.0 mL of CD_3OD was photolyzed following the typical procedure. The reaction led to a mixture of **5c** and **7c** in a ratio of 1:2.

Photolysis of 2c in the Crystalline State. A 10 mg portion of crystalline **2c** was photolyzed following the typical procedure. The reaction led exclusively to **5c**.

Photolysis versus Conversion of 2c Crystals. After 1.5 h the conversion was 54%, and after 4.0 h it was 100%.

Photolysis of 2d in C_6D_6. A solution of 10 mg (0.062 mol) of **2d** in 1.0 mL of C_6D_6 was photolyzed following the typical procedure. The reaction led to mixtures of *endo*-3-acetoxy-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**5d**) and *exo*-3-acetoxy-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**6d**).

Photolysis versus Conversion of 2d in C_6D_6. After times of 5, 15, 30, 60, and 105 min, the conversions were, respectively, 7.5%, 41%, 80%, 97.6%, and 100%. The ratios of **5d** to **6d** were 4.6, 4.4, 4.5, 4.1, and 3.6, respectively.

The reaction mixture was chromatographed on a silica gel column (HPLC), eluted with 25% ether in hexane, to give 5 mg (53%) of the **2d**, 3 mg (32%) of **5d** as colorless needles, and 1 mg (11%) of **6d** as a clear oil. Data for compound **5d**: mp 65−66 °C; ^{1}H NMR ($CDCl_3$) δ 7.5−7.2 (m, 10 H), 5.05 (dd, 1 H), 3.25 (d, 1 H), 3.00 (dd, 1 H), 2.85 (d, 1 H), 2.15 (dd, 1 H), 1.65 (s, 3 H). Data for compound **6d**: ^{1}H NMR ($CDCl_3$) δ 7.5−7.2 (m, 10 H), 3.85 (dd, 1 H), 3.25 (d, 1 H, J = 9 Hz), 2.90 (dd, 1 H), 2.75 (d, 1 H, J = 9 Hz), 2.40 (dd, 1 H), 2.05 (s, 3 H); HRMS *m/z* 329.1153 (329.1154, calcd for $C_{20}H_{18}O_3Na$, M + Na^+).

Photolysis of 2d in CD_3OD. A solution of 40 mg of **2d** in 1.0 mL of CD_3OD was photolyzed for 7 h following the typical procedure. The reaction led to mixtures of **5d**, **6d**, and *cis*-6-acetoxy-3,4-diphenylcyclohex-2-en-1-one (**7d**).

Photolysis versus Conversion of 2d in CD_3OD. At times of 15, 45, 75, and 360 min, the conversions were 28%, 73%, 80%, and 84%, respectively. The ratios of **5d** to **6d** were 3.2, 2.6, 2.9, and 3.2, respectively. The yields of **7d** were 4%, 12%, 13%, and 18% at these times.

The reaction mixture was chromatographed on a silica gel column (HPLC), eluted with 25% ether in hexane, to give 5 mg (12.5%) of the initial **2d**, 20 mg (50%) of **5d**, 7 mg (17.5%) of **6d**, and 4 mg (10%) of **7d** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.3−7.0 (m, 10 H), 6.52 (d, J = 2.2 Hz, 1 H), 5.61 (dd, J = 13.5, 5.3 Hz, 1 H), 4.50 (ddd, 1 H), 2.68 (ddd, J = 13.1, 5.0, 5.0 Hz, 1 H), 2.32 (ddd, J = 13.1, 13.1, 10.6 Hz, 1 H), 2.15 (s, 3 H); HRMS *m/z* 329.1155 (329.1154, calcd for $C_{20}H_{18}O_3Na$, M + Na^+).

Photolysis of 2d in the Crystalline State. A 15 mg (0.049 mol) portion of crystalline **2d** was photolyzed following the typical procedure. The reaction led to mixtures of **5d** and **6d**.

Photolysis versus Conversion of 2d as Crystals. At times of 11.5, 20, and 30 min, the conversions were 30%, 69%, and 82%, respectively. The ratios of **5d** to **6d** were 11.0, 5.5, and 4.6, respectively.

Photolysis of (+)-2d in the Crystalline State. A 15 mg (0.049 mol) portion of crystalline (+)-**2d** was photolyzed following the typical procedure. The reaction led to mixtures of **5d** and **6d**.

Photolysis versus Conversion of (+)-2d as Crystals. At times of 6, 8, and 11.5 h, the conversions were 12%, 22%, and 46%, respectively. The ratios of **5d** to **6d** were 12, 10, and 8.5, respectively.

Photolysis of 2e in C_6D_6. A solution of 22 mg of **2e** in 1.0 mL of C_6D_6 was photolyzed for 1 h following the typical procedure. The reaction mixture was chromatographed on a column slurry packed with octadecylated silica gel and eluted with 20% ether in hexane to give 10 mg (45%) of starting **2e** and 10 mg (45%) of *endo*-3-hydroxy-*trans*-5,6-diphenylbicyclo-[3.1.0]hexan-2-one (**5e**) as a clear oil: ^{1}H NMR ($CDCl_3$) δ 7.5−7.1 (m, 10 H), 4.20 (m, 1 H), 3.20 (d, J = 10.5 Hz, 1 H), 2.85 (m, 2 H), 2.12 (dd, J = 15, 6 Hz, 1 H), 1.40 (d, 1 H); HRMS *m/z* 287.1065 (287.1048, calcd for $C_{18}H_{16}O_2Na$, M + Na^+).

Photolysis of 2e Followed by Acetylation. A solution of 30 mg (0.114 mmol) of **2e** in 1.0 mL of C_6D_6 was photolyzed for 15 min following the typical procedure. The solution was concentrated, and a mixture of pyridine (0.19 mL, 2.29 mmol) and acetic anhydride (0.37 mL, 3.9 mmol) was added. The mixture was kept overnight, diluted with 10 mL of water, and extracted with chloroform (3 × 3 mL). The extract was dried (Na_2SO_4), concentrated, and chromatographed on a silica gel column (HPLC), eluted with 20% ether in hexane, to give 16 mg (53%) of **2d** and 16 mg (47%) of **5d**. A similar procedure of acetylation was applied to a photoproduct of **2e** in methanol and suggested the absence of the hypothetical exo photoproduct **6e** in the reaction mixture.

Photolysis of 2e in CD_3OD. A solution of 20 mg of **2e** in 1.0 mL of CD_3OD was photolyzed following the typical procedure. The reaction led to **5e** and *cis*-6-hydroxy-3,4-diphenylcyclohex-2-en-1-one (**7e**).

Photolysis versus Conversion of 2e. After 60 and 140 min, respectively, the conversions were 49% and 79%. The yields of **7e** at these times were 12% and 21%.

The reaction mixture was chromatographed on a silica gel column slurry packed and eluted with 20% ether in hexane to give 2 mg (10%) of **7e** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.3−7.0 (m, 10 H), 6.55 (d, 1 H), 4.95 (m, 2 H), 3.75 (br s, 1 H), 2.80 (ddd, 1 H), 2.05 (d, 1 H); ^{1}H NMR (C_6D_6) δ 7.0−6.5 (m, 10 H), 6.38 (d, J = 2.5 Hz, 1 H), 4.10 (dd, J = 14.0, 6.3 Hz, 1 H), 3.90 (br s, 1 H), 3.75 (ddd, J = 11.0, 5.5, 2.5 Hz, 1 H), 2.52 (ddd, J = 14.0, 6.3, 5.5 Hz 1 H), 1.90 (ddd, 14, 14, 11 Hz, 1 H); HRMS *m/ z* 287.1042 (287.1048, calcd for $C_{18}H_{16}O_2Na$, M + Na^+).

Attempted Photolysis of 2e in the Solid State. A 21 mg (0.080 mmol) portion of crystalline **2e** was photolyzed for 11.5 h following the typical procedure. After the workup only 20 mg (95%) of the initial **2e** was isolated.

Photolysis of 2f in C_6D_6. A solution of 6 mg of **2f** in 1.0 mL of C_6D_6 was photolyzed following the typical procedure. The reaction led to mixtures of *endo*-3-benzoyloxy-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**5f**) as white crystals and *exo*-3-benzoyloxy-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**6f**) as white crystals.

Irradiations versus Time for 2f. With times of 20, 60, 120, and 180 min, the conversions were 18%, 54%, 83%, and 97%, respectively. The ratios of endo to exo product were >20, 6.7, 4.2, and 3.6, respectively.

Data for compound **5f**: mp 138−140 °C; ^{1}H NMR ($CDCl_3$) δ 7.6−7.2 (m, 15 H), 5.45 (ddd, 1 H), 3.25 (d, 1 H), 3.10 (ddd, 1 H), 2.90 (dd, 1 H), 2.30 (dd, 1 H); HRMS *m*/*z* 391.1329 (391.1310, calcd for $C_{25}H_{20}O_3Na$, M + Na^+). Data for compound **6f**: mp 60−62 °C; ^{1}H NMR ($CDCl_3$) δ 7.95 (m, 2 H) 7.6−7.2 (m, 13 H), 4.10 (dd, 1 H), 3.30 (d, 1 H), 3.00 (dd, 1 H), 2.80 (d, 1 H), 2.55 (dd, 1 H); HRMS *m*/*z* 391.1311 (391.1310, calcd for $C_{25}H_{20}O_3Na$, M + Na^+).

Photolysis of 2f in CD_3OD. A solution of 10 mg of **2f** was photolyzed for 1 h following the typical procedure. By NMR analysis, the reaction mixture contained **5f** (48%), **6f** (19%), and *cis*-4,5-diphenyl-6-benzoyloxycyclohex-2-en-1-one (**7f**) (6%). The conversion was 73%. The reaction mixture was chromatographed on a silica gel column (HPLC), eluted with 15% ether in hexane, to give 4 mg (40%) of **5f**, 1 mg (10%) of **6f**, and 0.5 mg (5%) of **7f** as white crystals: mp 55−57 °C); ^{1}H NMR ($CDCl_3$) δ 8.05 (m, 2 H), 7.6−7.0 (m, 13 H), 6.56 (d, J = 2.5 Hz, 1 H), 5.86 (dd, J = 14.0, 5.0 Hz, 1 H), 4.58 (ddd, 11.0, 5.0, 2.5 Hz, 1 H), 2.81 (ddd, J = 14.0, 5.0, 5.0 Hz, 1 H), 2.46 (ddd, J = 14.0, 14.0, 11.0 Hz, 1 H); HRMS *m*/*z* 391.1320 (391.1310, calcd for $C_{25}H_{20}O_3Na$, M + Na^+).

Photolysis of 2f in the Crystalline State. A 8.0 mg portion of crystalline **2f** was photolyzed for 7 h following the typical procedure. The reaction led to a mixture of the initial **2f** (54%), **5f** (14%), and **6f** (32%).

Photolysis of 2g in CD_3OD. A solution of 5.0 mg of **2g** in 1.0 mL of CD_3OD was photolyzed following the typical procedure. The reaction was monitored by NMR (δ(HCOPhthal) = 5.40 ppm (endo) and 3.95 ppm (exo)) and led to mixtures of *endo*-3-phthaloyloxy-*trans*-5,6-diphenylbicyclo-[3.1.0]hexan-2-one (**5g**), *exo*-3-phthaloyloxy-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**6g**), and 6-phthaloyloxy-4,5-diphenylcyclohex-2-en-1-one **7g** or **8g**.

Photolysis versus Conversion for 2g. With times of 45 and 100 min, the conversions were 23% and 39%, respectively. The ratios of **5g** to **6g** were 2.3 and 3.5, and the unsaturated product yields were 4% and 11%, respectively.

Attempted Photolysis of 2g in the Solid State. An 11 mg portion of crystalline **2g** was photolyzed for 11.0 h following the typical procedure. After the workup only 10 mg (91%) of the initial **2g** was isolated.

Photolysis of 2h in C_6D_6. A solution of 20 mg of **2h** in 1.0 mL of C_6D_6 was photolyzed following the typical procedure. The reaction led to *endo*-3-phenylcarbamato-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**5h**) and *exo*-3-phenylcarbamato-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**6h**).

Photolysis versus Conversion for 2h. After 15 and 45 min, the conversions were 23% and 50% and the ratios of **5h** to **6h** were 3.5 and 3.2, respectively.

The reaction mixture was chromatographed on a silica gel column (HPLC), eluted with 33% hexane in CH_2Cl_2, to give 8 mg (40%) of starting **2h**, 1 mg (5%, purity ca. 90%) of **6h**, and 5 mg (25%) of **5h** as a clear oil: ^{1}H NMR ($CDCl_3$) δ 7.5−6.9 (m, 15 H), 5.80 (br s, 1 H), 5.05 (m, 1 H), 3.25 (d, 1 H), 3.00 (ddd, 1 H), 2.85 (dd, 1 H), 2.30 (dd, 1 H). HRMS *m*/*z* 406.1418 (406.1419, calcd for $C_{25}H_{21}NO_3Na$, M + Na^+) Data for compound **6h**: ^{1}H NMR ($CDCl_3$) δ 7.5−7.2 (m), 6.65 (br s, NH), 3.90 (dd), 3.30 (d), 3.00 (dd), 2.80 (d), 2.50 (d).

Attempted Photolysis of 2h in the Solid State. A 21 mg portion of crystalline **2h** was photolyzed for 10.0 h following the typical procedure. After the workup only 20 mg (95%) of the initial **2h** was isolated.

Photolysis of 2i in C_6D_6. A solution of 20 mg of **2i** in 1.0 mL of C_6D_6 was photolyzed following the typical procedure. The reaction was monitored by NMR in chloroform-*d* (δ-(HCCN) = 3.40 ppm (endo) and 2.20 ppm (exo)) and led to *endo*-3-cyano-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**5i**) and *exo*-3-cyano-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**6i**).

Photolysis versus Conversion of 2i. After times of 20, 40, and 100 min, the conversions were 22%, 33%, and 73% and the ratios of **5i** to **6i** were 1.44, 1.16, and 0.67, respectively.

The reaction mixture was chromatographed on a silica gel column slurry packed and eluted with 15% ether in hexane to give 6 mg (30%) of the initial **2i** and 12 mg (60%) of **6i** as white crystals: mp 143−144 °C; ^{1}H NMR ($CDCl_3$) δ 7.5−7.3 (m, 10 H), 3.30 (d, 1 H), 2.9−2.6 (m, 3 H), 2.19 (dd, 1 H); HRMS *m*/*z* 296.1041 (296.1051, calcd for $C_{19}H_{15}NONa$, M + Na^+).

Kinetic Epimerization of 6i. To a solution of 4 mg of **6i** in 2.0 mL of methanol were added 2.0 mL of water and 20 mg of potassium hydroxide. The clear yellow solution was kept for 5 min at 25 °C, diluted with 3.0 mL of water, acidified with 1 N HCl, and ether extracted (3 × 5 mL). The extract was dried (Na_2SO_4) and concentrated to give 3 mg of a 4:1 mixture of **5i** and **6i**. Data for the mixture of **5i** and **6i**: ^{1}H NMR ($CDCl_3$) δ 7.5−7.3 (m, 10 H), 3.43 (dd, 0.8 H, **5i**), 3.28 (m, 1 H, **5i** + **6i**), 3.0−2.6 (m, 3 H, **5i** + **6i**), 2.20 (dd, 0.2 H, **6i**).

Attempted Photolysis of 2i in the Solid State. A 21 mg (0.08 mmol) portion of crystalline **2i** was photolyzed for 11.5 h following the typical procedure. After the workup only 20 mg (95%) of the initial cyanide **2i** was isolated.

Attempted Photolysis of 2i in CD_3OD. A solution of 4 mg (0.080 mmol) of crystalline **2i** in 1.0 mL of CD_3OD was irradiated following the typical procedure. Only the starting cyanide **2i**, deuterated at the α-position to the cyano group, was isolated (4 mg, 100%).

Photolysis of 2j in C_6D_6. A solution of 5.0 mg of **2j** in 1.0 mL of C_6D_6 was photolyzed following the typical procedure. The reaction led to *endo*-3-methyl-*exo*-3-cyano-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**5j**) and *exo*-3-methyl-*endo*-3-cyano-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**6j**).

Photolysis versus Conversion for 2j. After 10 and 40 min, the conversions were 57% and 100%, respectively. The ratios of **5j** to **6j** were 3.4 and 2.8, respectively.

The reaction mixture was chromatographed on a silica gel column (HPLC), eluted with 33% chloroform in hexane, to give **5j** as white crystals and **6j** as white crystals. Data for compound **5j**: mp 94−95 °C (hexanes−ether); ^{1}H NMR ($CDCl_3$) δ 7.5−7.2 (m, 10 H), 3.30 (d, 1 H), 3.15 (dd) + 2.96 (d), (2 H), 2.40 (d, 1 H), 0.50 (s, 3 H); HRMS *m*/*z* 310.1214 (310.1208, calcd for $C_{20}H_{17}NONa$, M + Na^+). Data for compound **6j**: mp 136−137 °C (hexanes−ether); ^{1}H NMR ($CDCl_3$) δ 7.5−7.2 (m, 10 H), 3.35 (d, 1 H), 2.97 (d) + 2.90 (d), (2 H), 2.40 (dd, 1 H), 1.55 (s, 3 H); HRMS *m*/*z* 310.1200 (310.1208, calcd for $C_{20}H_{17}NONa$, M + Na^+).

Photolysis of 2j in CD_3OD. A solution of 33 mg of **2j** in 2.0 mL of CD_3OD was photolyzed for 100 min following the typical procedure. The reaction mixture was chromatographed on a silica gel column slurry packed and eluted with 20% ether in hexane to give 7 mg (21%) of the starting **2j**, 12 mg (36%) of **5j**, 10 mg (30%) of **6j**, 2 mg (6%) of *cis*-6-cyano-*trans*-6-methyl-3,4-diphenylcyclohex-2-en-1-one (**7j**), and 2 mg (6%) of *trans*-6-cyano-6-*cis*-methyl-3,4-diphenylcyclohex-2-en-1-one (**8j**). Data for compound **7j**: ^{1}H NMR ($CDCl_3$) δ 7.3−7.0 (m, 10 H), 6.57 (d, J = 2.5 Hz, 1 H), 4.68 (ddd, J = 11.0, 5.0, 2.5 Hz, 1 H), 2.72 (dd, 15.0, 5.0 Hz, 1 H), 2.15 (dd, J = 15.0, 11.0 Hz, 1 H), 1.55 (s, 3 H); HRMS *m*/*z* 310.1214 (310.1208, calcd for $C_{20}H_{17}NONa$, M + Na^+). Data for compound **8j**: ^{1}H NMR ($CDCl_3$) δ 7.3−7.0 (m, 10 H), 6.60 (d, J = 1.8 Hz, 1 H), 4.40 (m, 1 H), 2.7−2.6 (m, 2 H), 1.73 (s, 3 H); ^{1}H NMR (C_6D_6) δ 7.0−6.6 (m, 10 H), 6.32 (d, J = 1.8 Hz, 1 H), 3.67 (ddd, J = 9.0, 6.0, 1.8 Hz, 1 H), 2.13 (dd, 14.5, 9.0 Hz, 1 H), 1.86 (dd, J = 14.5, 6.0 Hz, 1 H), 1.20 (s, 3 H); HRMS *m*/*z* 310.1205 (310.1208, calcd for $C_{20}H_{17}NONa$, M + Na^+).

Photolysis of 2j in the Crystalline State. A 7.0 mg portion of crystalline **2j** was photolyzed for 7 h, following the typical procedure. It gave a mixture of 50% starting **2j**, 41.5% **5j**, and 8.5% **6j**.

Photolysis of 2k in C_6D_6. A solution of 20 mg of **2k** in 1.0 mL of C_6D_6 was photolyzed for 2 h, following the typical procedure. The reaction led to the *endo*-phenyl photoproduct **5k** and the *exo*-phenyl photoproduct **6k** in a ratio of 1.8:1. The mixture was chromatographed on a silica gel column slurry packed and eluted with 20% ether in hexane to give 5 mg (25%) of *endo*-3-phenyl-*exo*-3-cyano-6-*trans*-phenyl-5-phenylbicyclo-[3.1.0]hexan-2-one (**5k**) as white crystals and 14 mg (70%) of *endo*-3-cyano-*exo*-3-phenyl-6-*trans*-phenyl-5-phenylbicyclo[3.1.0]-hexan-2-one (**6k**) as white crystals. Data for compound **5k**: mp 149−150 °C; ^{1}H NMR ($CDCl_3$) δ 7.7−7.0 (m, 13 H), 6.55 (m, 2 H), 3.45 (d, 1 H), 3.24 (dd, 1 H), 3.12 (d) + 3.07 (d), (2 H). Data for compound **6k**: mp 146−147 °C; ^{1}H NMR ($CDCl_3$) δ 7.5−7.2 (m, 10 H), 3.27 (d) + 3.26 (d) (2 H), 3.16 (d, 1 H), 3.04 (dd, 1 H).

Photolysis of 2k in the Crystalline State. A 40 mg portion of **2k** was photolyzed for 140 min following the typical procedure. The reaction led to **6k** and **5k** in a ratio of 2.8:1 at 90% conversion.

Photolysis of 2k in CD_3OD. A solution of 10 mg of **2k** in 1.0 mL CD_3OD was photolyzed following the typical procedure. The reaction led to a mixture of **6k**, **5k**, and 6-cyano-3,4,6-triphenylcyclohex-2-en-1-one **7k**.

Photolysis versus Conversion of 2k. After 10 and 30 min, the conversions were 50% and 92%, respectively. The ratios of **6k** to **5k** were 2.9 and 2.0, respectively. The yields of **7k** were 14% and 26% at these times.

The mixture was chromatographed on a silica gel column (HPLC), eluted with 15% ether in hexane, to give 4 mg (40%) of starting **2k**, 1 mg (10%) of **5k**, 1 mg (10%) of **6k**, and 1 mg (10%) of **7k** as white crystals. Data for compound **7k**: mp 195−196 °C; ^{1}H NMR ($CDCl_3$) δ 7.5−6.9 (m, 15 H), 6.75 (d, J = 2.4 Hz, 1 H), 4.29 (ddd, J = 10.0, 4.8, 2.4 Hz, 1 H), 3.13 (dd, J = 14.5, 4.8 Hz, 1 H), 2.80 (dd, J = 14.5, 10.0 Hz, 1 H); HRMS m/z 372.1366 (372.1364, calcd for $C_{25}H_{19}NONa$, M + Na^+).

Photolysis of 6-Bromo-4,4-diphenylcyclohex-2-en-1-one (2l) in the Crystalline State. A 32 mg portion of crystalline **2l** was photolyzed following the typical procedure. The reaction led exclusively to *endo*-3-bromo-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**5l**). The reation mixture was chromatographed on a silica gel column (HPLC), eluted with 5% ether in hexane, to give 5 mg of the initial bromide **2l** and 0.5 mg (1.6%, purity c.a. 80%) of **5l** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.5−7.2 (m, 10 H), 4.45 (dd, 1 H), 3.15 (d + dd), 2.95 (d, 1 H), 2.55 (dd, 1 H).

Photolysis of 2l in C_6D_6. A solution 16 mg (0.114 mmol) of **2l** in 1.0 mL of C_6D_6 was photolyzed following the typical procedure. The reaction was monitored by NMR (δ(CHBr) = 4.45 ppm (endo) and 3.25 ppm (exo)) and led to mixtures of **5l** and *exo*-3-bromo-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**6l**).

Photolysis version Conversion for 2l. After times of 10, 70, and 130 min, the conversions were 7.0%, 25%, and 30% respectively. The ratios of **6l** to **5l** were 6.6, 6.7, and 5.2, respectively.

The reaction mixture was chromatograped on a column filled with octadecylated silica gel and eluted with 10% ether in hexane under a slight pressure of nitrogen to give 8 mg (50%) of the initial **2l** and 3 mg (19%) of **6l** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.2−6.7 (m, 10 H), 3.25 (dd, J = 8.3, 8.3 Hz, 1 H), 2.68 (dd, J = 14.3, 8.3 Hz, 1 H), 2.55 (m, 2 H), 2.34 (d, J = 9 Hz, 1 H). HRMS m/z 349.0204 (349.0204, calcd for $C_{18}H_{15}$-^{79}BrONa, M + Na^+).

Photolysis of 5l in C_6D_6. A solution of 0.50 mg of **5l** in 1.0 mL of C_6D_6 was photolyzed for 1 h following the typical procedure to give a mixture of the starting **5l** and **6l** in a ratio of ca. 1:1.

Photolysis of 6-Methyl-4,4-diphenylcyclohex-2-en-1-one (2m) in the Solid State. A 10 mg portion of crystalline **2m** was photolyzed for 1 h following the typical procedure. The reaction led to a mixture of 69% starting **2m**, 24% *endo*-3-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**5m**), and 7% *exo*-3-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**6m**), which were identical to the known compounds.

Photolysis of the Inclusion Compound of (−)-2d and 14. A 28 mg portion of the Inclusion Compound of (−)-**2d** and **14** was photolyzed for 30 h following the typical procedure. The reaction mixture contained the starting **2d** and **5d** in a ratio of 4.4:1. Only traces amounts of **6d** were observed.

Photolysis of the Inclusion Compound of 2d and γ-Cyclodextrin. A 130 mg portion of the inclusion compound of **2d** and γ-cyclodextrin was photolyzed for 18 h following the typical procedure. The product was treated with 5 mL of water and extracted with ethyl acetate (3 × 3 mL). The extract was dried (Na_2SO_4) and concetrated to give 10 mg (33%) of a mixture 50% starting **2d**, 33% endo photoproduct **5d**, and 17% exo photoproduct **6d**.

Photolysis of 2d in the Solid State in the Presence of γ-Cyclodextrin. A mixture of 130 mg (0.1 mmol) of γ-cyclodextrin and 31 mg (0.1 mmol) of **2d** was ground for 5 min in a mortar, and the product was photolyzed for 18 h following the typical procedure. The product was treated with 5 mL of water and extracted with ethyl acetate (3 × 3 mL). The extract was dried (Na_2SO_4) and concetrated to give 10 mg (33%) of a mixture 50% starting **2d**, 33% endo photoproduct **5d**, and 17% exo photoproduct **6d**.

Photolysis of 2d in the Solid State in the Presence of *N,N′*-Ditritylurea. A mixture of 7.5 mg (0.025 mmol) of **2d** and 13.5 mg (0.025 mmol) of *N,N′*-ditritylurea was melted, cooled to 25 °C, ground in a mortar, and photolyzed following the typical procedure. The reaction led to a mixture of the starting **2d**, the endo photoproduct **5d**, and the exo photoproduct **6d** in a ratio of 1:4:1.3.

Photolysis of the Inclusion Compound of 2e and γ-Cyclodextrin. A 159 mg portion of the inclusion compound of **2e** and γ-cyclodextrin was photolyzed for 18 h following the typical procedure. The product was treated with 10 mL of water and extracted with ethyl acetate (6 × 3 mL). The extract was dried (Na_2SO_4) and concetrated to give 15 mg of a mixture, which was treated with 0.19 mL (2.29 mmol) of pyridine and 0.34 mL (3.9 mmol) of acetic anhydride under nitrogen for 16 h. The mixture was diluted with 5.0 mL of water, acidified with 1 N HCl, and extracted with chloroform. The extract was washed with water, dried (Na_2SO_4), and concentrated. The mixture contained 73% **2d**, 20% **5d**, and 6% **6d**.

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Supporting Information Available: Experimental and X-ray data. This material is available free of charge via the Web at http://pubs.acs.org.

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