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General Theoretical Treatments of Solid-State Photochemical Rearrangements and a Variety of Contrasting Crystal versus Solution Photochemistry[1,2]

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Abstract: In continuing our investigations of control of excited state reactivity by inclusion in crystal lattices, we have encountered a variety of new examples of differing reactivity resulting from lattice restraints. Different theoretical treatments were tested and several proved applicable. Not only could the course of reactions imposed by the crystal lattice be predicted but also the ability to react versus lack of reactivity. For cyclohexenones with C-2 and C-5 substitution, either of two aryl groups at C-4 are available for migration; which one migrates depends on the lattice. One C-2 substituted and seven C-5 substituted cyclohexenones were investigated. Additionally some cyclopentenone photochemistry was investigated. Throughout, programming was developed to generate a "mini crystal lattice" having the appropriate space group symmetry and X-ray coordinates and with a central molecule surrounded by reactant molecules. Replacement of the central molecule with a transition state molecule provided a new "mini-lattice". Generally, the first diradical intermediate was used to simulate the reaction transition state. The mini-lattice was then subject to study. Overlap of the central, partially reacted species with the surrounding molecules provided one criterion. Molecular motion of the reactant excited state in forming the partially reacted species provided a test of least motion as a second criterion. A third test utilizing MM3 geometry optimization of the reacting species imbedded in the rigid mini-lattice, provided a measure of the increase in intra- and intermolecular energy of this molecule. A final approach determined the points of nearest molecule–lattice approach and mapped these in the form of a "lock and key"; this has the advantage of indicating which interactions result in inhibition or lack thereof of a particular reaction route. Predicting ability to react proved important since reactivity falls into three categories: (1) no reaction in the lattice, (2) differing reactivity compared to solution, (3) the same behavior in solution. Perturbing an intermediate geometry toward that of the reactant and then determining the deformation energy provided a reactivity measure.

Introduction

One of our group's main interests has been the ability of the course of a reaction to be diverted by environmental constraints. Thus our previous studies have dealt with photochemistry in crystalline[3] and polymeric media.[4] The present paper focusses on the photochemical reactivity in crystal lattices.

One can envisage a reacting molecule in a lattice cavity as originally suggested by Cohen.[5] However, except for a generalization that two π-bonds would undergo a $[2\pi + 2\pi]$ cycloaddition when the double bond separation is less than 4.2 Å, the cavity concept has been only qualitative.

Our objective has been the development of theoretical and quantitative treatments of crystal state reactions in general. Additionally, we wished to uncover a broad spectrum of unimolecular rearrangements in crystal lattices.[6] Our initial efforts described[3] a number of such reactions and some quantitative indices correlated with reactivity. For the present study we selected a group of γ,γ-diarylcyclohexenones, so substituted that one can determine which of the aryl groups migrates to the β-carbon of the excited state enone moiety.

Results

Synthesis of Enone Reactants. Five 4,4-diphenyl enones (i.e. **2–6**) substituted at carbon-5 were desired and were obtained by conjugate addition of the appropriate organometallic reagent to 4,4-diphenyl-2,5-cyclohexadienone (**1**) as depicted in eq 1. One of these (i.e. **6**) was known[7] from our earlier research. Additionally, we planned the study of *cis-* and *trans*-4,5-diphenyl-4-(*p*-cyanophenyl)cyclohexenone (**9c** and **9t**), and the preparation of these is outlined in Scheme 1. In Scheme 1 the preparation of 6-(3,3-diphenylpropyl)cyclohexenone (**13**) is also described. The syntheses of 4-phenyl-4-biphenylcyclohexenone (**16**) and 4-phenyl-4-(*p*-ethynylphenyl)cyclohexenone (**18**) are described in Scheme 2.

® Abstract published in *Advance ACS Abstracts*, April 15, 1995.

[1] (a) This is Paper 173 of our photochemical series and 236 of our general papers. (b) For Paper 233 see Zimmerman, H. E.; Kutateladze, A. G.; Maekawa, Y.; Mangette, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 9795–9796. (c) For Publication 235 See Zimmerman, H. E.; Wilson, D. W. *J. Org. Chem.* **1994**, *59*, 1809.

[2] For a preliminary publication describing a portion of the present results see Zimmerman, H. E.; Zhu Zhaoning. *J. Am. Chem. Soc.* **1994**, *116*, 9757–9758.

[3] (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.

[4] Zimmerman, H. E.; O'Brien, M. E. *J. Org. Chem.* **1994**, *59*, 1809–1816.

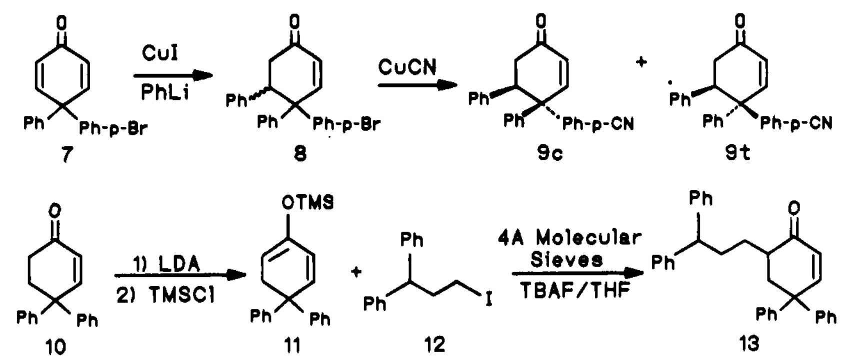
[5] (a) Cohen, M. D. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 386. (b) Cohen, M. D.; Schmidt, G. M. J. *J. Chem. Soc.* **1964**, 1996–2000.

[6] Some unimolecular rearrangements, mainly of barrelene derivatives, have been described in elegant studies by Scheffer. (a) Gudmundsdottir, A. D.; Scheffer, J. R. *Photochem. Photobiol.* **1991**, *54*, 535–538. (b) Chen, J.; Pokkuluri, P. R.; Scheffer, J. R.; Trotter, J. *Photochem. Photobiol. A* **1991**, *57*, 21–26. (c) Pokkuluri, P. R.; Scheffer, J. R.; Trotter, J. *Acta Crystallogr.* **1993**, *B49*, 754–760. (d) Fu, T.-Y.; Liu, Z.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1993**, *115*, 12202–12203. (e) Schultz, A. G.; Taveras, A. G.; Taylor, R. E.; Tham, F. S.; Kullnig, R. K. *J. Am. Chem. Soc.* **1992**, *114*, 8725–8727. (f) Roughtonk, A. L.; Muneer, M.; Demuth, M. *J. Am. Chem. Soc.* **1993**, *115*, 2085–2087. (g) Angermund, K.; Klopp, I.; Kruger, C.; Nolte, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1354–1356.

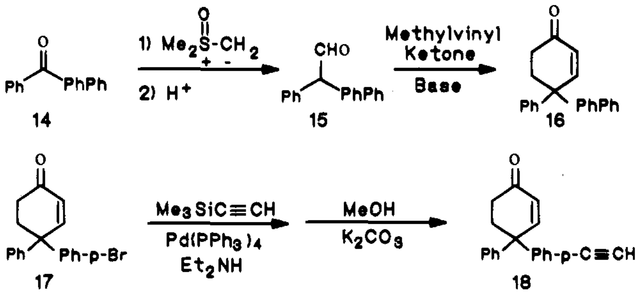
[7] Zimmerman, H. E.; Morse, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 954–966.

0002-7863/95/1517-5245$09.00/0

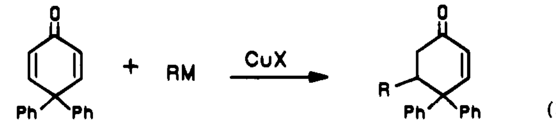
Scheme 1. Syntheses of Selected Cyclohexenones **9c**, **9t**, and **13** for Study



Scheme 2. Syntheses of Selected Enones **16** and **18**



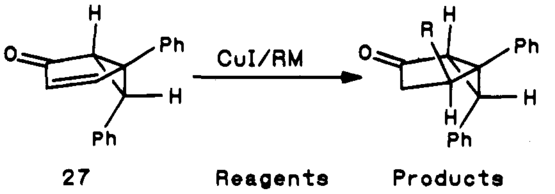
2-Methyl-4,4-diphenylcyclohexenone (**26**) was synthesized according to a known procedure.[8] Additionally, two cyclopentenones were required, **23** and **25**. These preparations are given in Scheme 3.



(1)

Reagents	Products
MeLi, CuCN	2
EtMgBr, CuCN	3
i-PrMgBr, CuCN	4
t-BuLi, CuCN	5
PhLi, CuI	6

Synthesis of Potential Photoproducts. With the photochemical reactants in hand, we turned next to the synthesis of some of the most likely photoproducts. Note eq 2. The common reactant **27** was known from our earlier studies.[7] We note that, *a priori*, there are two possible stereoisomers for each of the bicyclic [3.1.0] ketones **28**–**31**. In the cuprate reaction, one would anticipate an approach of the various organometallic species from the less hindered, exo side of the enone moiety. This assumption was confirmed with an X-ray analysis of bicyclic ketone **31** (see the supplementary section). X-ray analysis of the other three bicyclics was precluded by their being oils. However, we note that the *trans*-5,6-diphenyl configurations are in accord with the generalization[9] that in such systems cyclopropyl H–H NMR trans coupling constants are close to 3–4 Hz while the cis are circa 10 Hz.

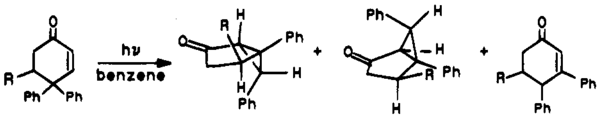


(2)

Reagents	Products
MeLi	28
EtMgBr	29
i-PrMgBr	30
PhLi	31

Solution Photochemistry of the 5-Substituted 4,4-Diphenylcyclohexenones. Each of the five 5-substituted cyclohexenones in eq 1 was irradiated in benzene. In each case two bicyclic stereoisomers were obtained differing in configuration at C-4 (bicyclic numbering); this corresponds to C-5 of the reactants. In the methyl and ethyl cases, 5-substituted 3,4-diphenylcyclohexenones were also formed. The 4-*exo-trans*-diphenyl bicyclic [3.1.0] photoproduct structures were established by independent synthesis and X-ray analysis in two cases (**31** and **32**). The structure of the 4-endo stereoisomers (**33**–**36**) was established by the characteristic cis-5,6-hydrogen coupling, the typical ABX pattern of the CH-CH$_2$ moiety (see Experimental for NMR detail), and comparison to the known structure of **37**.[7] For cyclohexenone **38** an X-ray structure was obtained. The structure of the very minor cyclohexenone **39** was derived from its NMR spectrum and comparison with **38**.

The photochemistry is summarized in eq 3. The endo versus exo configuration of each of these products is controlled by which original C-4 aryl group has migrated. Thus photoproducts with a C-4 endo configuration arise from migration of the *cis*-phenyl group while bicyclic products with a C-4 exo configuration result from migration of the *trans*-phenyl group. We note that for C-5 methyl and ethyl reactants it is the *cis*-phenyl group which migrates preferentially while for the remaining cyclohexenones it is the *trans*-phenyl. This point is discussed subsequently.



(3)

	R			enone 2,3 only
2	Me	28 (1.0)	33 (2.5)	38 (0.5)
3	Et	29 (1.0)	34 (2.0)	39 (0.4)
4	i-Pr	30 (1.4)	35 (1.0)	
5	t-Bu	32 (10.0)	36 (1.0)	
6	Ph	31 (1.2)	37 (1.0)	

Solution Photochemistry of 4-(*p*-Cyanophenyl)-4,5-diphenylcyclohexenone. One especially interesting case was that of the *cis*- and *trans*-4,5-diphenylcyclohexenones having a *p*-cyanophenyl moiety at carbon-4 (i.e. **9c** and **9t**), respectively. As anticipated, the photoproducts consisted of *trans*-5,6-diarylbicyclo[3.1.0]hexan-2-ones. However, from the *cis*-diphenyl isomer **9c** photolysis afforded a 7.3:1 ratio of *exo*-4,5-diphenyl-6-(*p*-cyanophenyl)bicyclo[3.1.0]hexan-2-one (**40**) and *endo*-4,6-diphenyl-5-(*p*-cyanophenyl)bicyclo[3.1.0]hexan-2-one (**41**). From the *trans*-diphenyl isomer **9t** a 1:1 ratio of phenyl to cyanophenyl migration occurred to afford *exo*-4,6-

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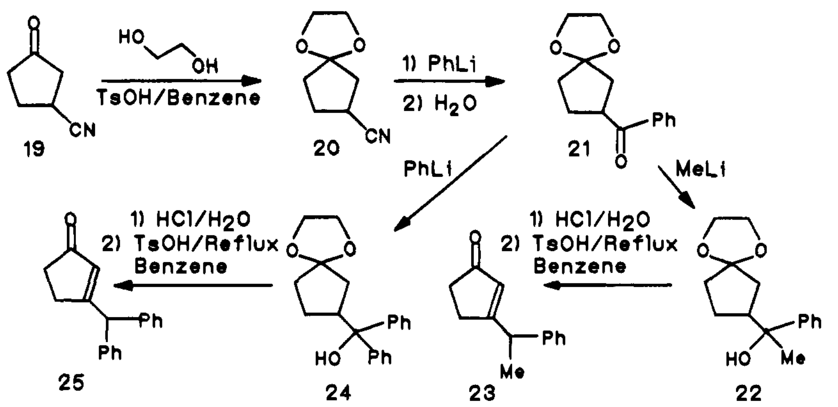
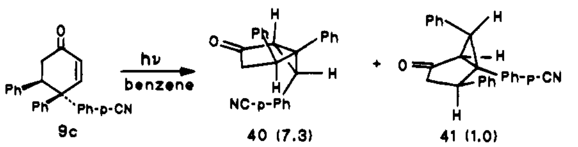
[8] (a) Frimer, A. A.; Marks, V.; Sprecher, M.; Gilinsky-Sharon, P. *J. Org. Chem.* **1994**, *59*, 1831–1834. (b) Lee, H. S.; Namgung, K. S.; Sung, J. K.; Chae, W. K. *Bull. Kor. Chem. Soc.* **1991**, *12*, 247–249.

[9] Zimmerman, H. E.; Rieke, R. D.; Scheffer, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 2033–2047.

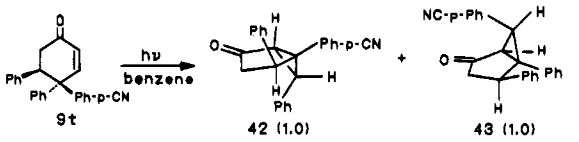
Scheme 3. Syntheses of Two Cyclopentenones **23** and **25**



diphenyl-5-(*p*-cyanophenyl)bicyclo[3.1.0]hexan-2-one (**42**) and *endo*-4,5-diphenyl-6-(*p*-cyanophenyl)bicyclo[3.1.0]hexan-2-one (**43**). The structures of **40** and **42** were established by X-ray analysis. Again, the structures of the 4-endo stereoisomers were obtained by NMR analysis and comparison with the other 4-endo photoproducts. These transformations are outlined in eqs 4a and 4b.



(4a)

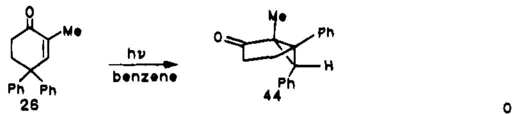


(4b)

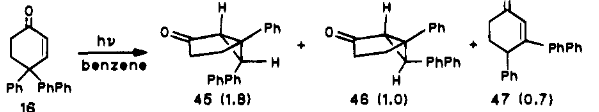
Solution Photochemistry of Cyclohexenone Reactants Lacking C-5 Substitution. 2-Methyl-4,4-diphenylcyclohexenone (**26**)[8] led to 1-methyl-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**44**) as one might anticipate from standard 4-aryl-substituted cyclohexenone reactivity. Similarly, 4-phenyl-4-biphenylylcyclohexenone (**16**) and 4-(*p*-ethynylphenyl)-4-phenylcyclohexenone (**18**) reacted with preferential rearrangement of the para-substituted phenyl groups. Bicyclic photoproducts **44**, **45**, **48**, and **49** were subjected to X-ray analysis. The structure of cis photoproduct **46** was obtained by its facile photoequilibration with **45** following the known bicyclic stereoisomerization. In these equilibrations cyclohexenone **47** was also obtained, paralleling our earlier findings.[11] The three cyclohexenone rearrangements are shown in eqs 5a–c while the equilibration of the photoproducts are given in eq 6.

Solution Photochemistry of 3-Benzhydryl and 3-Phenethyl Cyclopentenones. From each of these a bicyclic photoproduct was obtained. Despite the five-membered ring-structure of the reactants, the same 5,6-substituted bicyclo[3.1.0]hexanones were obtained as originating from 4,4-disubstituted cyclohexenones. However, the reaction stereochemistry proved different.

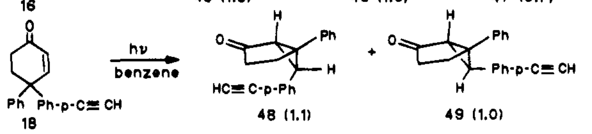
From 3-benzhydrylcyclopentenone (**25**), *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**52** and **53**) were obtained in a 3.7:1 ratio. From 3-phenethylcyclopentenone **23**, *trans*- and *cis*-6-methyl-5-phenylbicyclo[3.1.0]hexan-2-one (**50** and **51**) were formed in a 4.2:1 ratio. The product ratio of the *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones (**52** and **53**) differs from that obtained from 4,4-diphenylcyclohexenone and thus is useful if it is the cis stereoisomer which is desired. In the case of the photolysis of the 3-phenethylcyclopentenone **23** in benzene, the photoproduct has the phenyl and methyl groups transposed compared with the product of the photolysis of 4-methyl-4-phenylcyclohexenone observed by Dauben.[10]



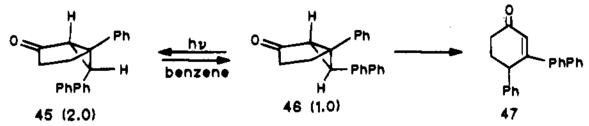
(5a)



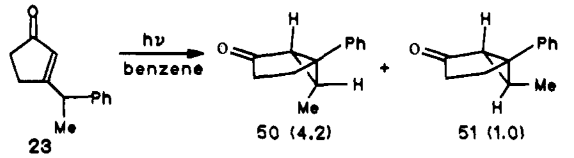
(5b)



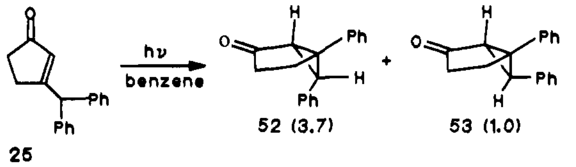
(5c)



(6)



(7a)



(7b)

X-ray Analysis. The details of the X-ray determinations are given in the Experimental and Supplementary Sections. Of the twelve compounds analyzed, two (enones **2** and **5**) crystallized in chiral space groups. The remaining eight crystallized as racemates and in centrosymmetric space groups. One other facet is that for four of the enones (**2**, **3**, **4**, and **25**), the analyses revealed two conformationally distinct molecules in the ordered crystal. In these cases, we applied our theoretical analyses to both of the conformers. In one instance, two crystal modifications of the same enone were obtained, each with its own reactivity. The list of crystals, their space groups, and the number of different conformations are given in Table 1. Finally, it is of interest to note that for all seven 5-substituted enones the C-5 substituent is pseudoequatorial in the crystal.

Crystal Lattice Photochemistry of the Seven 5-Substituted Cyclohexenones. Corresponding to the solution phase photo-

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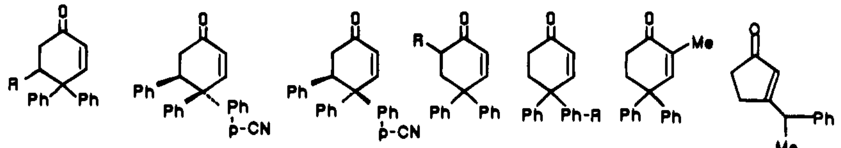
(10) (a) Dauben, W. G.; Spitzer, W. A.; Kellogg, M. S. *J. Am. Chem. Soc.* **1971**, *93*, 3674–3679. (b) In *tert*-butyl alcohol a more complex product distribution was observed with formation of both **52** and **53** as very minor products.

(11) Zimmerman, H. E.; Hancock, K. G.; Licke, G. *J. Am. Chem. Soc.* **1968**, *90*, 4892–4911.

Table 1. Crystal Lattices Obtained



2 R = Me
3 R = Et
4 R = i-Pr
5 R = t-Bu
6 R = Ph

9c

9t

13
R = Pr

16
R = Ph
18
R = Ethynyl

26

25

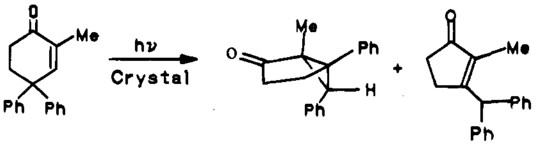
enone	space group	conformations	enone	space group	conformations
5-Me-enone **2**	$P2_1$	2	6-Pr-enone **13**	Cc	1
5-Et-enone **3**	$P2_1/c$	2	4-biph-enone **16**	$P\bar{1}$	1
5-i-Pr-enone **4**	Cc	2	4-biph-enone **16**	$Pbca$	1
5-t-Bu-enone **5**	$P2_12_12_1$	1	hexenone **18**	$P2_1/c$	1
5-Ph-enone **6**	$P2_1/c$	1	2-Me-enone **26**	$P2_1/c$	1
t-5-Ph-enone **9t**	$P2_1/c$	1	pentenone **25**	$P2_1/n$	2
c-5-Ph-enone **9c**	$Fdd2$	1			

chemistry described above, the seven cyclohexenones with C-5 substituents were subjected to irradiation in crystalline form. In contrast to the solution behavior, the 4,4-diphenylcyclohexenones (**2**–**6**) all led exclusively to the 4-exo stereoisomer (note bicyclic numbering) with the exception of the 5-methylcyclohexenone **2** which led to a 6.3:1 ratio of exo to endo stereoisomers. These results are included, along with contrasting solution results, in Table II at the end of the section.

For the moment it is sufficient to note that for the C-5 methyl and ethyl examples, **2** and **3**, the reaction stereochemistry in the crystal lattice is reversed from that in solution. In the remaining cases, the lattice photochemistry led to single stereoisomers while the solution photochemistry afforded both endo and exo photoproducts.

The case of the stereoisomeric 4-(*p*-cyanophenyl)-4,5-diphenylcyclohexenones **9c** and **9t** proved particularly interesting. We know that for 4-(*p*-cyanophenyl)-4-phenylcyclohexenone (**54**) there is a preference for *p*-cyanophenyl migration to the β-enone carbon.[9] While for the cis-isomer **9c** no appreciable difference was seen compared to the solution photochemistry (i.e. a 7.2:1.0 ratio), for the trans-isomer **9t** there was a dramatic difference with only phenyl migration being observed to afford exo photoproduct **42**. Hence the crystal lattice has led to complete reversal of the normal preferential cyanophenyl migration.

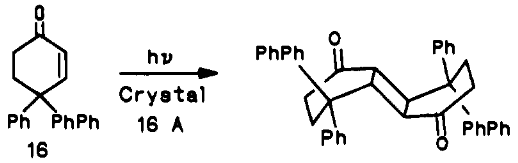
Crystal Lattice Photochemistry of the 2-Methylcyclohexenone 26. The solid-state photochemistry in this case led to totally different behavior from solution chemistry in which 2-methyl-3-benzhydrylcyclopentenone (**55**) was formed along with 1-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**44**) in a 1:1 ratio. As the conversion reached ca. 15 percent, the photochemistry changed and led to increasing formation of bicyclic photoproduct **44** at the expense of one primary photoproduct **55**. The primary lattice photochemistry is shown in eq 8 (see Table 2). This secondary photochemistry is discussed below.



26 44 (1.0) 55 (1.0) (8)

Crystal Lattice Behavior of Two Crystal Morphologies of 4-Phenyl-4-biphenylcyclohexenone and Three Photoinert Crystals; Crystal Defects. One interesting case was that of phenyl-biphenylyl cyclohexenone **16**. Recrystallization from ether afforded one crystal modification, mp 103–104 °C; We term this "crystal 16A". From ethanol, a crystal form, mp 109–110 °C, resulted; this we term "crystal 16B". The X-ray of "16A" revealed a $P\bar{1}$ space group with the biphenylyl group pseudoequatorial. The X-ray of "16B" had a space group of P_{bca}; in this case the biphenylyl group was pseudoaxial.

Only "crystal 16A" exhibited photoreactivity and led to a dimeric product, the X-ray structure of which showed head-to-tail dimerization with cis-anti stereochemistry. In contrast "crystal 16B" was essentially inert. The reaction of **16A** is depicted in eq 9. Interestingly the crystal lattices were in accord with observed reactivities with "crystal 16A" having its parallel π-bonds separated by 3.847 Å and the molecules oriented as in the product. Conversely, in "crystal 16B" the double bonds of neighboring molecules were separated by a center to center distance of 4.89 Å and twisted about a center to center intermolecular axis by 37.2°. In this case, the reactivity difference was predictable on the basis of the "topochemical principle" of Cohen and Schmidt.[5b,12]



16 56 (9)

Both 6-(3,3-diphenylpropyl)-4,4-diphenylcyclohexenone (**13**) and 4-(*p*-ethynylphenyl)-4-phenylcyclohexenone (**18**) were unreactive as crystal lattices. This is discussed below in the context of prediction of reactivity.

3-Benzhydrylcyclopentenone **25** also proved exceptionally unreactive. While the reactive crystal lattices had reached 10–20% conversion in 30 min, this cyclopentenone was essentially unreactive under these conditions but did finally lead to a 5% conversion to *cis*- and *trans*-5,6-diphenylbicyclo[3.1.0]hexanones **50** and **51** after 12 h.

The lack of reactivity of 3-benzhydrylcyclopentenone **25** proved understandable (vide infra). However, the formation of two stereoisomers was less subject to our quantitative treatment. Therefore, we looked more closely at this unreactive enone and compared it with our reactive enones. The plot of conversion versus extent of irradiation is shown in Figure 1. It

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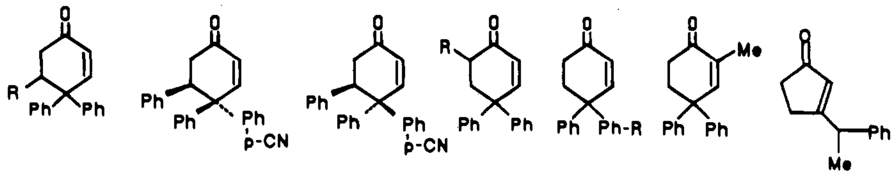
(12) Schmidt, G. M. J. *Solid State Photochemistry*; Ginsberg, D., Ed.; Verlag Chemie: New York, 1976.

Table 2. The Product Ratios in Solution And in Crystalline State



2 R = Me
3 R = Et
4 R = i-Pr
5 R = t-Bu
6 R = Ph
9c
9t
13 R = Pr
16 R = Ph
18 R = Ethynyl
26
25

enone	solution product	solution ratio	solid state product	solid state ratio
5-Me-enone **2**	*exo*-**28**:*endo*-**33**:**38**	1.0:2.5:0.5	*exo*-**28**:*endo*-**33**	6.3:1.0
5-Et-enone **3**	*exo*-**29**:*endo*-**34**:**39**	1.0:2.0:0.4	*exo*-**29**	only
5-i-Pr **4**	*exo*-**30**:*endo*-**35**	1.4:1.0	*exo*-**30**	only
5-*tert*-Bu **5**	*exo*-**32**:*endo*-**36**	10.0:1.0	*exo*-**32**	only
5-Ph **6**	*exo*-**31**:*endo*-**37**	1.2:1.0	*exo*-**31**	only
c-4,5-diPh **9c**	*exo*-**40**:*endo*-**41**	7.3:1.0	*exo*-**40**:*endo*-**41**	7.2:1.0
t-4,5-diPh **9t**	*exo*-**42**:*endo*-**43**	1.0:1.0	*exo*-**42**	only
2-Me **26**	**44** only	–	**44**:**55**	1.0:1.0
2-ethynyl **18**	*trans*-**48**:*cis*-**49**	1.1:1.0	inert	–
4-biph **16**	*trans*-**45**:*cis*-**48**:**47**	1.8:1.0:0.7	**56** (crystal 16A)	
			inert (crystal 16B)	–
pentenone **25**	*trans*-**52**:*cis*-**53**	3.7:1.0	inert	–
6-Pr **13**	–	–	inert	–

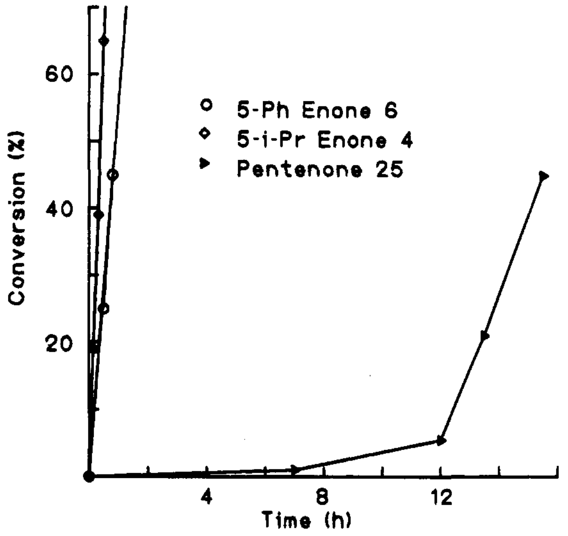


Figure 1. Test of nonlinearity in conversions as a test of crystal defects.

is seen that there is an induction period and then an upwards slope for this relatively unreactive enone while the more reactive enones exhibited linearity of conversion with extent of irradiation. Such nonlinearity has been considered[13] diagnostic for reactions at crystal defects. This suggests that 3-benzhydrylcyclopentenone **25** falls into a different category of lattice control than the more reactive examples.

Interpretative Discussion

Theoretical Considerations and Useful Quantitative Parameters. A main objective of this research was to obtain a generalized theory capable of rationalizing, if not predicting, crystal lattice reactivity. Invariably, reports of solid state photochemistry have been discussed on an ad hoc basis in which each case has been rationalized with some molecular group being too close to the surrounding lattice for normal, solution reactivity. One exception to this deficiency has been the work of Cohen and Schmidt[12] in which the special case of [$2\pi + 2\pi$] cycloadditions have been considered with their topological rule that when separated by less than 4.2 Å, cycloaddition of two parallel double bonds will be successful. Also, Cohen[5] suggested the important qualitative idea that solid-state photochemical reactions can be pictured as occurring within a "reaction cavity". But, the reaction cavity concept has not been used except qualitatively. Similarly, least motion was suggested by Cohen and Schmidt[5b] from a qualitative viewpoint.

For organic reactions in general, including unimolecular processes, what has been lacking are systematic studies of series of different molecules in varying crystal lattices and quantitative theory correlating with reactivity.

To some extent in our previous studies[3] we have advanced several quantitative reaction parameters which proved quite successful in correlating prediction with the actual solid-state reaction course. However, further testing and refining of these parameters and finding new ones were our aims. Furthermore, in the past, either a crystal proved reactive or unreactive, which had not been predictable. Hence we had another objective. The approaches of use are discussed in order: (a) least motion is possible with several variations, (b) overlap of the reacting molecule with the crystal lattice provides a guide, (c) monitoring of the intramolecular and molecule-lattice energies during reaction, and (d) relaxation energy of the molecule in emerging from the excited reactant and forming the first reaction intermediate. Each provides an estimate of reactivity in a solid-state reaction.

Crystal Lattice Reactions of the 5-Substituted Cyclohexenones. First we turn to a consideration of least motion which we have treated quantitatively in our previous study.[3] We note that the concept of least motion as utilized for solution reactivity is an old one. Thus, the idea seems to have been originated by Rice and Teller.[14a] The idea has been applied to solution

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[13] (a) Studies on behavior of free radical pairs at crystal defects, as measured spectroscopically, has been related to stress as determined by molecular mechanics, have been carried out by McBride.[13b] (b) Kearsley, S. K.; McBride, M. *Mol. Cryst. Liq. Inc. Nonlin. Opt.* **1988**, *156*, 109–122 and references cited therein. (c) Murthy, G. S.; Arjunan, P.; Venkatesan, K.; Ramamurthy, V. *Tetrahedron* **1987**, *43*, 1225–1240. (d) Bhadbhade, M. M.; Murthy, G. S.; Venkatesan, K.; Ramamurthy, V. *Chem. Phys. Lett.* **1984**, *109*, 259–263. (e) Gnanaguru, K.; Ramasubbu, N.; Venkatesan, K.; Ramamurthy. *J. Org. Chem.* **1985**, *50*, 2337–2346.

Scheme 4. The Stereochemical Pathways of the 5-Substituted Enones

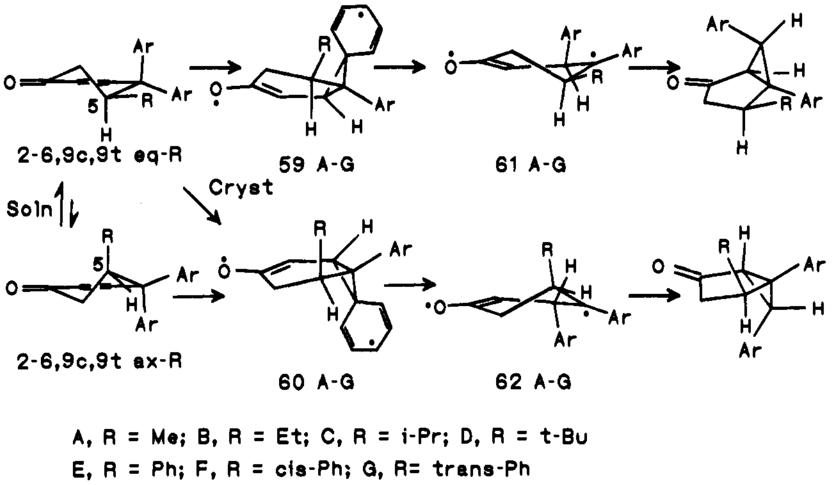


Table 3. RMS Motions from Crystal Conformations of Starting Enones to Their Different Diradicals I

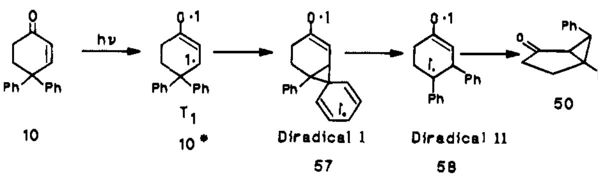
		rigid superposition		flexible superposition[a]	
enones		*cis*-Ph migration **59** A-G	*trans*-Ph migration **60** A-G	*cis*-Ph migration **59** A-G	*trans*-Ph migration **60** A-G
5-Me-enone **2**	Ind. Mol1[b]	1.40	0.74[c]	0.66	0.56[c]
	Ind. Mol2	1.56	0.78[c]	0.70	0.58[c]
5-Et-enone **3**	Ind. Mol1	1.48	0.71[c]	0.71	0.52[c]
	Ind Mol2	1.45	0.68[c]	0.67	0.51[c]
5-i-Pr-enone **4**	Ind Mol1	1.46	0.70[c]	0.68	0.55[c]
	Ind. Mol2	1.37	0.78[c]	0.70	0.72[c]
5-t-Bu-enone **5**		1.05	0.46[c]	0.63	0.43[c]
5-Ph-enone **6**		1.81	0.84[c]	0.75	0.65[c]
t-5-Ph-enone **9t**		1.77	0.70[c]	0.77	0.54[c]
c-5-Ph-enone **9c**		1.83	0.85[c]	0.75	0.66[c]

[a] Terminal atoms were not considered. [b] Refers to different conformations in the crystal lattice. [c] Intermediate Leading to Observed (Major) Photoproduct.

chemistry by several researchers,[14] both qualitatively and quantitatively.

In applying least motion to reactions in crystal lattices[3] we used an approach different from that of the literature which had considered only motion in proceeding from reactant all the way to product. Rather, we included consideration of the amount of molecular motion in going from reactant to the first reaction intermediate, using the latter as an approximation to the transition structure. In the present study we used RMS motion as obtained from the square root of the sum of squares of displacements of the various atoms of reactant, whereas in our earlier work we considered the sum of atomic motions.

For the cyclohexenone rearrangements, the commonly accepted reaction mechanism[9,11,15] is given in eq 10. As an approximation to the transition structure we used "diradical I". To obtain the desired RMS motion index, we performed a superposition of each "diradical I" on the corresponding reactant (i.e. enones **2**–**6**, **9c**, and **9t**). The superposition process involved computationally superimposing the reaction transition structures (i.e. diradical I) so that the RMS displacements between corresponding atoms was minimized. We note that two types of superposition were utilized. In a rigid position, diradical I was kept in a fixed conformation during the superposition process. In a "flexible superposition", nonring dihedral angles were permitted to change while bond lengths and valence angles were kept fixed during the superposition process. The flexible superposition process utilized both Macromodel[16] and Flexit[17] with the same results.



(10)

The various molecular structures required were obtained from X-ray analysis for the reactants and from MM3[18a] and AM1[18b] computations for the first intermediate species (here diradicals I) encountered in proceeding from a reactant toward a given possible photoproduct. Depending on which phenyl group migrates, one obtains one of two diastereomeric diradicals I. This is clearly seen in Scheme 4.

For the reaction of each enone, independent of the mode of superposition, it was found that the molecular motion required to proceed from reactant to transition structure (diradical I) was less for the observed reaction. These results are given in Table 3. We note that least motion does not take into account interactions of the reacting molecule with the surrounding crystal lattice. This point is considered below in connection with our alternative predictors.

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(14) (a) Rice, F. O.; Teller, E. *J. Chem. Phys.* **1938**, *6*, 489–496. (b) Hine, J. *J. Org. Chem.* **1966**, *31*, 1236–1244. (c) Hine, J. *J. Am. Chem. Soc.* **1966**, *88*, 5525–5528. (d) Tee, O. S. *J. Am. Chem. Soc.* **1969**, *91*, 7144–7149. (e) Altman, J. A.; Tee, O. S.; Yates, K. *J. Am. Chem. Soc.* **1976**, *98*, 7132–7138.

(15) Zimmerman, H. E.; Wilson, J. W. *J. Am. Chem. Soc.* **1964**, *86*, 4036–4042.

(16) Still, W. C.; Mohamadi, F.; Richards, N. G. J.; Guida, W. C.; Lipton, M.; Liskamp, R.; Chang, G.; Hendrickson, T.; Degunst, F.; Hasel, W. *MacroModel*, V3.5, Department of Chemistry, Columbia University, New York, NY 10027.

(17) Zimmerman, H. E.; St. Clair, J. "Flexit", Program to do flexible superposition, determine RMS variations and related geometric operations.

(18) (a) Allinger, N. L. *MM3*, University of Georgia, Dec. 1990. (b) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909.

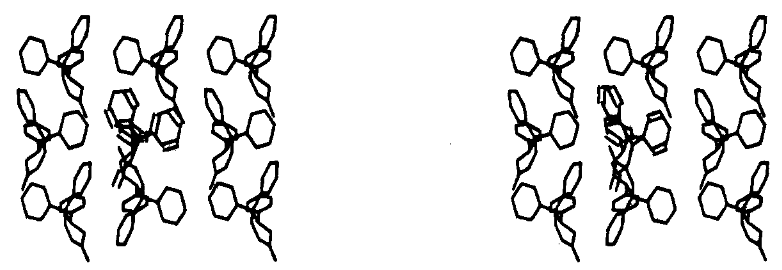

Figure 2. Alternative diradicals I in a mini-crystal lattice; equatorial migration left, axial migration right.

Table 4. Van der Waals Overlaps of Alternative Diradicals I from Each Enone

enones		overlap with lattice ΔS (Å^3) of	
		cis-Ph migration diradical I **59** A-G	*trans*-Ph migration diradicals I **60** A-G
5-Me-enone **2**	Ind. Mol1[a]	20.4	13.8[b]
	Ind. Mol2	28.0	12.5[b]
5-Et-enone **3**	Ind. Mol1	23.2	14.2[b]
	Ind. Mol2	24.2	14.6[b]
5-i-Pr-enone **4**	Ind. Mol1	17.3	11.4[b]
	Ind. Mol2	18.6	13.5[b]
5-t-Bu-enone **5**		16.9	7.7[b]
5-Ph-enone **6**		29.4	15.1[b]
t-5-Ph-enone **9t**		27.8	5.6[b]
c-5-Ph-enone **9c**		26.9	16.5[b]

[a] Refers to different conformations in the crystal lattice. [b] Intermediate leading to observed (major) photoproduct.

Our second mode of prediction does consider interactions of the reacting molecule with the crystal lattice. This measures the van der Waals overlap of our approximation to the transition structure, namely diradical I, with the surrounding crystal lattice. Clearly, a transition structure which doesn't fit is not going to lead to an observed product.

Figure 2 shows a cross-section of the mini-lattices (see below) for the equatorial phenyl migration versus the axial phenyl migration in 4,4,5-triphenylcyclohexenone (**6**) with the alternative diradicals I imbedded in the center of the lattice. Inspection of such lattices is difficult due to the multiplicity of interactions and the complexity of the lattice. This illustrates the importance of not relying on qualitative ad hoc assessments of the fit of alternative reacting species in a crystal lattice.

In order to obtain the desired quantitative measure of overlap, as well as confinement energies discussed subsequently, we needed an appreciable but manageable section of crystal lattice as derived from our X-ray analysis. Ortep[19] can construct a small aggregate of molecules (e.g. one unit cell). However, in this truncation of the entire crystal lattice, the periphery of the unit cell is composed of partial structures.

Thus we devised programming, "SmartPac", which builds up a "mini-crystal lattice" composed of (e.g.) 18−36 complete molecules. From this mini-crystal lattice, we computationally extract the central molecule. This leaves a cavity into which our transition structure (generally diradical I) was inserted by rigid superposition of this species on the corresponding coordinates of the extracted reactant molecule. A second program, "CrystaLap", was utilized to determine the overlap of the inserted species with the crystal lattice environment. The transition structure inserted was one obtained from MM3 and/or AM1 computation. Table 4 lists the van der Waals overlaps for each alternative pair of diradicals I formed from each enone reactant.

The third assessment was based on MM3 geometry optimization of the alternative transition structures (i.e. diradicals I) in the rigid, surrounding crystal lattice. MM3 geometry optimization was used to minimize the total energy of the lattice containing the transition structure. In this optimization process, the lattice was kept fixed and only the included diradical I was modified in the process. One practical point is that the same energy should be obtained after the optimization process independent of the starting diradical I geometry. In most cases this assumption proved correct. However, it was found that use of starting structures flexibly superimposed on reactant X-ray coordinates tended to avoid local minima in the geometry optimization process.

The optimized energy of the new lattice, E'(lattice), containing the transition structure (diradical I) was compared with the original mini-crystal lattice energy, E_0(lattice). The difference ΔE(replace) then is a measure of the energy of replacement of a reactant molecule by a transition structure one. Note eq 11. ΔE(replace) is independent of mini-lattice size while E'(lattice) and E_0(lattice) are not. ΔE(replace) includes intermolecular effects arising from interaction of the transition structure with the lattice as well as intramolecular effects arising from the transition structure deformation. There also are contributions due to removal of the reactant molecule from the lattice, but these are constant in comparisons of two alternative reaction modes (i.e. forming alternative transition structures). Thus it is important to consider only the relative values of ΔE(replace) for a given starting crystal; one should not compare these energies with different crystalline reactants. The values of these replacements energies are given in Table 5.

$$\Delta E(\text{replace}) = E'(\text{lattice}) - E_0(\text{lattice}) \qquad (11)$$

A second piece of information is obtained by extracting the transition structure optimized in the crystal lattice and determining the unimolecular MM3 energy of this molecule without any relaxation. Clearly the conformation will have been deformed by its previous inclusion in the lattice. We may term the energy of this unrelaxed transition structure E(unimolec,deform); this, too, is included in Table 5.

Comparison of the energy of the unrelaxed transition structure with the geometry optimized energy, E(unimolec,relax), gives us the relaxation (or conversely, the deformation) energy; note eq 12. This is termed ΔE(deform) and also is in Table 5.

$$\Delta E(\text{deform}) = E(\text{unimolec,deform}) - E(\text{unimolec,relax}) \qquad (12)$$

Finally, it is interesting to derive the transition structure−lattice interaction energy ΔE(inter) by subtracting the ΔE(deform), the energy rise due to molecular distortion, from the total replacement energy. See eq 13a. Rearranged, as in eq 13b, this confirms the two-fold source of the replacement energy.

$$\Delta E(\text{inter}) = \Delta E(\text{replace}) - \Delta E(\text{deform}) \qquad (13a)$$

$$\Delta E(\text{replace}) = \Delta E(\text{deform}) + \Delta E(\text{inter}) \qquad (13b)$$

These lattice−molecule interaction energies are also included in Table 5.

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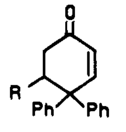
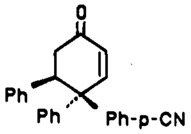
(19) Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, TN.

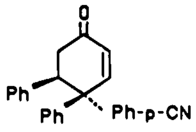
Table 5. Energies of Transition Structures in Mini-Crystal Lattices



2-6



9c



9t

	cis-Ph (ax) migration diradical I **59** A-G			*trans*-Ph (eq) migration[b] diradicals I **60** A-G		
enones	Δ*E*(replace)	Δ*E*(deform)	Δ*E*(inter)	Δ*E*(replace)	Δ*E*(deform)	Δ*E*(inter)
5-Me-enone **2**						
Mol1[a]	33.92	14.17	19.65	27.12	6.95	20.16
Mol2	45.54	27.62	17.92	23.10	4.78	18.32
5-Et-enone **3**						
Mol1	42.67	22.78	19.89	27.24	8.24	19.00
Mol2	36.67	16.72	19.95	23.57	5.24	18.33
5-i-Pr-enone **4**						
Mol1	38.68	22.40	16.28	24.05	7.18	16.87
Mol2	38.90	19.55	19.35	26.25	7.71	18.54
5-t-Bu-enone **5**	30.83	10.80	20.03	12.05	1.95	10.10
5-Ph-enone **6**	45.78	16.33	29.45	29.75	7.37	22.38
t-5-Ph-enone **9t**	34.18	7.10	27.08	14.08	2.13	11.95
c-5-Ph-enone **9c**	16.93	4.09	12.84	17.70	3.76	13.94

[a] Refers to different conformations in the crystal lattice. [b] Intermediate leading to observed (major) photoproduct.

Table 6. Energies of Flexibly Superimposed Transition Structures in the Mini-Crystal Lattices

enones		*cis*-Ph (ax) migration diradical I **59** A-G Δ*E*(super) (kcal/mol)	*trans*-Ph (eq) migration diradicals I **60** A-G Δ*E*(super) (kcal/mol)
5-Me-enone **2**	Mol1	41.64	0.06[b]
	Mol2	66.29	0.69[b]
5-Et-enone **3**	Mol1	46.41	2.89[b]
	Mol2	52.62	3.16[b]
5-i-Pr-enone **4**	Mol1	72.96	0.51[b]
	Mol2	130.70	2.25[b]
5-t-Bu-enone **5**		57.84	1.22[b]
5-Ph-enone **6**		20.58	0.04[b]
t-5-Ph-enone **9t**		19.78	4.40[b]
c-5-Ph-enone **9c**		27.24	2.04[b]
2-methyl-enone **26**		1.6[b]	13.5[b]
p-biph-enone **16A**		51.64	7.69
p-biph-enone **16B**		9.31	38.36
p-ethynyl-enone **18**		7.07	5.00
6-propyl-enone **13**		23.29	10.0
cyclopentenone	Mol1	29.81	34.6
	Mol2	29.0	34.0

[a] The diradicals I for pentenones **25** were the species of phenyl half migrating from benzhydryl to the β carbon of the enone. They are different from those of the 5-substituted enones. [b] Observed major reaction.

Reference to Table 5 shows that the preferred reaction is predicted correctly by the minimum replacement energy Δ*E*(replace). The reaction course correlates with the unimolecular deformation energy Δ*E*(deform) of the transition structure as deformed by the lattice and with the replacement energy Δ*E*(replace) but not with the molecule–lattice interaction energy. Correlation with Δ*E*(replace) seems theoretically most justified.

One other approach is to take the reaction intermediates (i.e. diradicals I), which have been geometry optimized in the mini-crystal lattice, and then subject these to a flexible superposition onto the reactant structures. Thus these structures have been distorted toward their reactants and hence toward the transition states affording the diradical I. The differences in the two diradical I MM3 energies, Δ*E*(super), are listed in Table 6. It is seen that these also correlate nicely with the observed stereoselectivity. These values are also of use in predicting overall ability to react in a given crystal lattice.

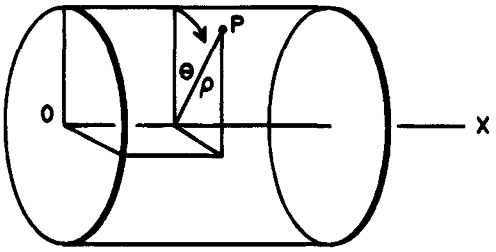


Figure 3. Cylindrical coordinate system for the lock and key determinations.

A particularly informative approach proved applicable to all of the various methods for determining reactivity or lack thereof. Thus one major problem in cavity control is the need for ascertaining just what interactions between the transition structure and the surrounding cavity are most serious and thus controlling. For these we developed programming ("Lock_Key"). Our approach involved computationally determining the long axis of the transition structure imbedded in the cavity. The most suitable orientation was obtained by a rigid superposition upon the coordinates of the lattice molecule removed to provide the cavity. This long axis was taken as x, and the atom of the imbedded molecule most distant from the x-axis was used to define the origin of the theta (θ) angle of a cylindrical coordinate system. Note Figure 3. Then the distance ϱ from the x-axis to each peripheral atom's most distant surface and the corresponding θ were taken in conjunction with the x-value to define the location of the various atoms. The x, θ, and ϱ values for the ten atoms having the largest overlap with lattice atoms were recorded. The vector, or list, of ϱ values was taken as a "key". The overlap distance of each of the ten atoms from its nearest neighbor, afforded the "fit", was subtracted from ϱ to give corresponding ϱ' values. The ϱ' vector is characteristic of the cavity and is termed the "lock". With no overlap the key (ϱ) and the lock (ϱ') are identical. With overlap at some point x along the long molecular axis, the key is seen to be too large for the lock and the "fit" is positive. The advantage of this description is that one can locate the sites of difficulty in fitting a transition structure into a given cavity. Table 6 gives one such example and the rest are in our supplementary section. For simplicity, in Table 7 only the ϱ,

Table 7. Lock (ϱ') and Key (ϱ) Representation of Three Molecules in Crystal Lattice of 5-*tert*-Butyl Enone: (a) Enone **5**; (b) Diradical I of Axial Ph Migration 59d; (c) Diradical I of Equatorial Ph Migration 60d (observed product)[a]

(a) atom	C44	C36	H37	C 5	H 6	H43	C27	H28	C31	C29
key:										
ϱ	6.50	4.35	3.54	4.70	3.64	6.38	2.94	2.90	3.81	2.90
lock:										
ϱ'	7.01	5.03	3.91	5.05	4.12	6.63	3.45	3.26	4.30	3.58
fit:	0.31	0.41	0.22	0.21	0.29	0.15	0.31	0.22	0.29	0.41

(b) atom	C18	C20	H21	C22	C25	C33	C27	C31	H28	H32
key:										
ϱ	2.52	2.16	2.89	1.92	2.69	4.94	2.26	4.49	0.91	4.62
lock:										
ϱ'	2.27	1.53	2.48	1.45	2.42	4.68	1.96	4.13	0.53	4.22
fit:	0.58	1.49	0.95	1.09	0.62	0.60	0.71	0.83	0.89	0.93

(c) atom	C14	C44	O 1	H 4	C 3	C22	H23	H 6	C29	H30
key:										
ϱ	3.36	7.12	7.05	5.80	5.87	2.47	1.97	3.99	3.16	2.76
lock:										
ϱ'	3.36	7.12	7.05	5.80	5.87	2.47	1.97	3.99	3.16	2.76
fit:	0.38	0.36	0.69	0.39	0.42	0.41	0.39	0.39	0.64	0.45

[a] The fit values are unnormalized.

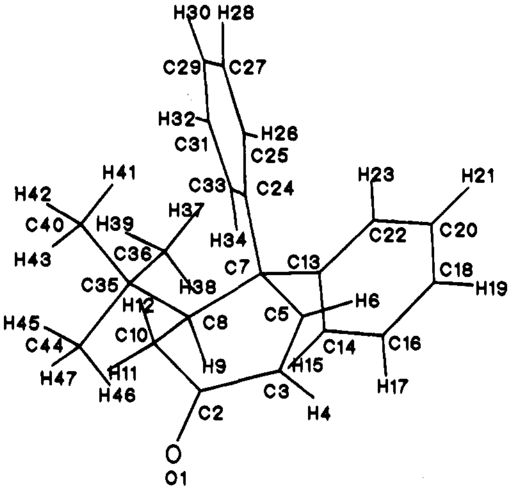


Figure 4. 5-*tert*-Butyl-4,4-diphenylcyclohexenone with numbering for lock and key.

ϱ', and unnormalized "fit" values are given. The atom numbers given in the heading correspond to the drawing in Figure 4.

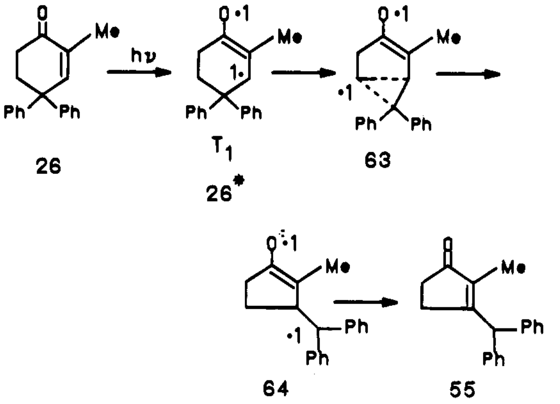
Inspection of Table 7 reveals that the key corresponding to the transition structure for migration of the equatorial phenyl group (note part c) has a perfect "fit" (i.e. set of ϱ values matching the lock's values (ϱ'). The precise fit derives from our normalizing[20] the best "key". But then inspection of the "fit" of the transition structure for axial migration reveals seriously large ϱ values with appreciable "fit" values. The points of worst interference of the axial transition structure with the cavity are seen (note Figure 4) to be with transition structure atoms C-20, H-21, C-27, H-28, and H-32 which interfere with their lattice neighbors.

Crystal Lattice Reactions of 2-Methylcyclohexenone. In the crystal lattice the 2-methylcyclohexenone (**26**) afforded two photoproducts. The bicyclic [3.1.0] ketone (i.e. **44**) is formed via the clearly defined mechanism involving bridging of a 4-phenyl group to the β-carbon of the enone. The basic mechanism is outlined in eq 10. The second photoproduct, 2-methyl-3-benzhydryl-2-cyclopentenone (**55**) has literature precedent in solution chemistry.[7,10,21] This mechanism is outlined in eq 14. It is seen that the reaction has afforded

Table 8. RMS Motion, Overlap, and ΔE(replace) Parameters for All of the Rest of the Enones Studied

enone	diradical[a] intermediates	RMS motion[b] rigid	RMS motion[b] flexible	overlap	ΔE-(replace)
2-Me-enone **26**	**64**(**R**)	1.13	0.56	20.1	31.4
	64(**S**)	1.22	0.78	9.9	30.4
	diradical I-a	1.46	0.88	24.9	49.4
	diradical I-e	0.85	0.61	11.6	34.6
pentenone **25**	independent Mol 1				
	diradical A	1.23	0.86	20.7	53.7
	diradical B	1.47	0.68	33.7	47.9
	independent Mol 2				
	diradical A	1.25	0.62	24.6	53.1
	diradical B	1.32	0.72	22.2	38.7
biph-enone **16A**	diradical I-a	1.47	0.72	29.0	12.1
	diradical I-e	1.04	0.56	24.2	10.6
biph-enone **16B**	diradical I-a	0.89	0.56	14.9	11.4
	diradical I-e	1.29	0.74	28.6	17.2
ethynyl-enone **18**	diradical I-a	1.01	0.66	19.0	40.1
	diradical I-e	0.98	0.60	19.6	30.0

[a] Except for diradical **64**(**R**) and **64**(**S**), all the other intermediates were taken as diradical I species. diradical I-a denotes diradical I originated from the axial phenyl migration and diradical I-e equatorial phenyl migration. [b] "Rigid" and "flexible" refer to rigid and flexible superposition operations, respectively.



(14)

benzhydrylcyclopentenone **55** in addition to the solution photoproduct, bicyclo[3.1.0]hexanone **44**; the product ratio was 1:1. This was one case which was not readily subject to our various criteria for several reasons. First, the reaction mechanism of the type A ring contraction of saturated cyclohexenones is subject to uncertainty.[21] Secondly, if we assume the half-ring-contracted species **63** is the transition structure for the reaction, its precise geometry is not readily obtained. Use of the diradical II structure **64** brings us too far beyond the transition state. Nevertheless, use of diradical II (**64**) affords overlap and geometry optimized energies which suggest the type A process to be competitive with the phenyl migration process. Still, the various reactivity parameters we have used are included for reactant **26** in Table 8.

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(20) In each case the larger key is normalized to the size of the smaller key using

$$\varrho(\text{key},j) = \varrho_0(\text{key\_o},j) - [\varrho'(\text{lock},j) - \varrho(\text{key\_o},j)]\sum_j[\varrho'(\text{lock},j) - \varrho(\text{key\_ref},j)]/\sum_j[\varrho'(\text{lock},j) - \varrho(\text{key\_o},j)]$$

where j is the value along the x-axis, key_o designates the unnormalized key, key_ref designates the reference key, and lock indicates the lattice or lock.

(21) (a) Zimmerman, H. E.; Lewis, R. G.; McCullough, J. J.; Padwa, A.; Staley, S.; Semmelhack, M. *J. Am. Chem. Soc.* **1966**, *88*, 159–161. (b) Zimmerman, H. E.; Lewis, R. G.; McCullough, J. J.; Padwa, A.; Staley, S.; Semmelhack, M. *J. Am. Chem. Soc.* **1966**, *88*, 1965–1973. (c) Zimmerman, H. E.; Sam, D. J. *J. Am. Chem. Soc.* **1966**, *88*, 4114–4116. (d) Zimmerman, H. E.; Solomon, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 6276–6289. (e) Chapman, O. L.; Rettig, T. A.; Griswold, A. A.; Dutton, A. I.; Fitton, P. *Tetrahedron Lett.* **1963**, 4060. (f) See also ref 6f for a similar pentenone rearrangement.

Table 9. Summary of Parameters

PARAMETER	DEFINITION	COMMENT
Least Motion	$\left[\sum_{r=x,y,z} 1/N\ (r_i^{SM} - r_i^{TS})^2\right]^{1/2}$	RMS Displacement of Nuclei from Reactant to Transition Structure (TS)
Overlap	$\sum_i^n V_i(\text{Overlap})$	Sum of v.d.Waals Overlaps of TS with Lattice
ΔE(replace)	E'(lattice) - E_0(lattice)	Energy of Lattice with Imbedded TS vs Original Lattice
ΔE(deform)	E(unimolec,deform) - E(unimolec,relax)	Energy of TS Optimized in Lattice relative to that Optimized in Space
ΔE(super)	E(flexibly super TS) - E(unimolec,deform)	Energy of TS Flexibly Superimposed on SM Relative to TS Optimized in the Lattice
Key-Lock Analysis	ρ versus ρ', Fit	Distances from Molecular Long Axis for Given Molecule in Lattice (ρ) and Distance to Nearest Lattice Atom (ρ'), Discrepancy in Fit

The Matter of Crystal Lattice Reactivity versus Lack of Crystal Lattice Reactivity. Also the Matter of Crystal Defects. Empirically, photochemical crystal lattice behavior falls into three categories: (a) cases where there is no appreciable reactivity in the solid state, (b) cases where the reactivity is the same in the crystal lattice as in solution, and (c) those cases where the crystal reaction affords different products and/or product distribution than in solution. We have dealt with the last category thus far. Equally challenging is the matter of predicting the first two, namely reactivity and unreactivity.

The Results Section lists four compounds which are unreactive (**13**, **16**, **18**, and **25**). Both crystal morphologies of the second of these were unreactive. The best approach to predicting reactivity proved to be the energy of the reaction intermediate flexibly superimposed on the reactant with values as given in Table 6. It appears that those reactions with energies in the range of more than 4.5 kcal/mol do not occur in our crystal lattices. Further reactivity indices for these compounds are given in Table 8.

In such cases, it is possible that a reaction will take place at a crystal defect created by an initially very slow reaction. This defect is not one originally present in a well-ordered crystal. The net result is that a reaction may eventually occur.

One caveat to be reckoned with in our discussion is that the inherent electronic predisposition of an excited state to react is an added factor which is not included but must be superimposed upon the reactivity preferred by the crystal lattice.

Summary and Conclusion. Table 9 summarizes the parameters described in our continuing investigations to put crystal lattice photochemistry on a more predictable, quantitative, and understandable basis. It is clear that reactivity is predictable from several measures of the fit and energy of the reacting excited state in the lattice cavity. This has proven more useful and satisfying than the previous qualitative assessments and descriptions.

Experimental Section

General Procedures. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN 37950. 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-Kieselgel G/UV 254 silica gel. High pressure liquid chromatography (HPLC) was performed employing a LDC 254-nm detector and a LDC 6000 psi minipump, using a 0.95 × 25 cm polished stainless steel column packed with 3–5 μm silica beads with 5 mg of sample per 10 μL injection.[22] Exploratory solution photolyses were carried out with a Hanovia 450-W medium pressure mercury lamp equipped with the appropriate filter and/or with 5-mm of a recirculating filter solution of 0.07 M sodium metavanadate[23] solution. All photolysis solutions were purged with purified nitrogen[24] both prior to and during photolysis. All solid compounds were subjected to multiple crystallizations until the melting point was constant. Tetrahydrofuran (THF) and dimethoxyethane (DME) were 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. Dimethylformamide (DMF) was distilled from barium oxide. HPLC hexane was prepared by washing with nitric acid and sulfuric acid (1:1), water, saturated aqueous sodium bicarbonate and brine, drying over calcium chloride, passing through alumina, and distilling from calcium hydride. 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, and refluxing overnight with and distilling from calcium hydride.

General Procedure for Crystallization of Photochemical Reactants. Into 20 mL vials each containing 10–20 mg of pure photo starting material was added 10–15 mL of methanol, ethanol, 2-propanol, propanol, acetone, chloroform, dichloromethane, hexane, pentane, cyclohexane, methylcyclohexane, benzene, toluene, ether, THF, dimethoxyethane, pyridine, dioxane, acetonitrile, dimethyl sulfoxide, and *N*,*N*-

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[22] Zimmerman, H. E.; Welter, T. R.; Tartler, D.; Bunce, R. A.; Ramsden, W. D.; King, R. K.; St. Clair, J. D.; Baker, M.; Mangette, J. E.; Wilson, D. W. Unpublished results for HPLC column preparation.

[23] Sodium metavanadate solution was made by dissolving the appropriate amount of sodium metavanadate in 5% sodium hydroxide. A 1 cm thick solution of 0.07 M sodium metavanadate cuts off greater than 99.9% light intensity with wavelengths shorter than 324 nm.

[24] Meites, L.; Meites, T. *Anal. Chem.* **1948**, *20*, 984–985.

dimethylformamide, respectively. The solutions were left with small apertures in the cap and kept in the hood for slow evaporation.

General Procedure for Solid State Photolyses. (a) Single crystal photolyses. Single crystals from the described crystallization procedure were put into a 5 × 200 mm Pyrex NMR tube and purged with dry nitrogen 1 h before and during the photolysis. The NMR tube was placed 2 inches from a 450-W Hg lamp with a water cooling well. The compounds were photolyzed in 30 min intervals in order to follow the photochemical reaction by NMR and prevent over-heating of the samples by the lamp. The crystals were inspected under a microscope to make sure no melting was observable. (b) Bulk solid state photolyses. The crystals from large scale crystallization using the same conditions as the crystallization screening were collected and large crystals were gently cracked. The crystals were suspended and stirred in a water bath cooled with running tap water or low temperature coolant. The mixture was photolyzed with a 450-W mercury lamp through a Pyrex filter. The photolyses were also carried out in 30 min intervals. The compounds were filtered after photolysis and subjected to separation and analysis. Throughout this study, all of the crystal photochemistry for single crystals and large scale water suspension photolysis were consistent.

General Procedure for X-ray Crystallography Analysis. X-ray diffraction data were collected on a Nicolet (Syntax) P-1 diffractometer for single crystals of each compound. Unit cell parameters were determined by least-square refinement of 25 reflections. Data were collected with three check reflections monitored after every 97 reflections. Data having $F > 3\ \sigma(F)$ were rejected. Lorentz and polarization corrections were applied, and each structure was solved under the appropriate space group symmetry by direct methods using SHELXSTL[25] or SHELX93.[26] Hydrogen atoms were calculated and full-matrix least-square refinement was carried out employing anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. Detailed information about X-ray data collection, structure solution and refinement, the final atomic coordinates, and thermal ellipsoid parameters are given in the supplementary material.

5-Methyl-4,4-diphenylcyclohex-2-en-1-one (2). To a mixture of 1.91 g (10.0 mmol) of cuprous iodide in 100 mL of ether at 0 °C was added 14 mL (19.6 mmol) of 1.4 M methyllithium in hexane. The solution was stirred 5 min, and 1.0 g (4.0 mmol) of 4,4-diphenylcyclohex-2,5-dien-1-one[27] (**1**) in 40 mL of ether was added to the mixture over 15 min. It was stirred for 1.5 h, allowed to warm to rt, poured onto ice-saturated ammonium chloride, and stirred for 1 h. The mixture was ether extracted, the combined organic layers were dried over anhydrous magnesium sulfate, and the solvent was removed in vacuo to afford 1.4 g of an oil which was chromatographed on a 150 × 3.5 cm silica gel column, eluted with 3% ether in hexane to yield 1.05 g (99%) of 5-methyl-4,4-diphenylcyclohex-2-en-1-one (**20**) as a colorless oil which solidified upon standing. Recrystallization by slow evaporation from pentane gave 1.0 g (95%) of colorless prism crystals, mp 78.0–80.0 °C.

The spectral data were the following: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.47–7.06 (m, 11 H, arom and β-vinyl), 6.19–6.14 (d, J = 10 Hz, α-vinyl), 3.31–3.19 (m, 1 H, C*H*), 2.50–2.17 (m, 2 H, CH_2), 0.86 (d, J = 6 Hz, 3 H, CH_3); IR (film) 3030, 2965, 2934, 2910, 2878, 1689, 1677, 1598, 1578, 1494, 1445, 1414, 1385, 1329, 1322, 1280, 1254, 1216, 1199, 1174, 1158, 1082, 1034, 1001, 917, 900, 889, 757, 703 cm^{-1}; MS *m/e* 262.1353 (calcd for $C_{19}H_{18}O$, 262.1358); UV (benzene) λ_{max} = 335 nm (ϵ = 31.9). Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.91. Found: C, 87.04; H, 7.11.

Exploratory Solution Photolysis of 5-Methyl-4,4-diphenylcyclohex-2-en-1-one (2). A 250 mL photograde benzene solution of 123.0 mg of 5-methyl-4,4-diphenylcyclohex-2-en-1-one (**2**) was photolyzed through a Pyrex filter and filter solution for 2 h. The solvent was removed in vacuo to afford 126.0 mg of a pale yellow oil which was chromatographed on a 3.0 × 50 cm silica gel column eluted with 2.5–10% ether in hexane. Fraction 1, a mixture (107.0 mg, 87.2%) of 4-*exo*-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**28**) and 4-*endo*-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**33**); fraction 2, 15.0 mg (12.1%) of *cis*-5-methyl-3,4-diphenylcyclohex-2-en-1-one (**38**) as a white solid which was recrystallized from pentane to give 12 mg (9.8%) of colorless prisms (mp 79.0–80.5 °C). The structure of *cis*-5-methyl-3,4-diphenylcyclohex-2-en-1-one (**38**) was verified by X-ray crystallography (see supplementary material). The mixture from fraction 1 containing the endo/exo bicyclo[3.1.0]photoproducts **28** and **33** was separated with repetitive HPLC eluting with 2.0% acetonitrile and 6% ether in pentane. Fraction 1, retention time 97.2 min, 29.1 mg (23.6%) of 4-*exo*-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**28**) as a colorless oil. Fraction 2, retention time 103.2 min, 72.0 mg (58.5%) of 4-*endo*-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**33**) as a colorless oil.

The spectral data for *cis*-5-methyl-3,4-diphenylcyclohex-2-en-1-one (**38**) were the following: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.47–7.20 (m, 10 H, arom), 6.69 (s, 1 H, α-vinyl), 4.10 (d, J = 5 Hz, 1 H, C*H*), 2.74–2.62 (m, 1 H, C*H*Me), 2.34–2.17 (m, 2 H, CH_2), 0.90 (d, J = 7 Hz, 3 H, CH_3); IR (film) 3057, 3027, 2958, 2925, 2872, 2854, 1726, 1662, 1598, 1572, 1492, 1451, 1445, 1280, 1247, 760, 750, 703 cm^{-1}; MS *m/e* 262.1345 (calcd for $C_{19}H_{18}O$, *m/e* 262.1358). Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.91. Found: C, 86.83; H, 6.97.

The spectral data for 4-*endo*-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**33**) were the following: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.54–7.26 (m, 10 H, arom), 3.28 (d, J = 9.5 Hz, 1 H, cyclopropyl-*H*), 2.90–2.77 (m, 1 H, C*H*Me), 2.49 (d, 1 H, J = 9.5 Hz, cyclopropyl-*H*), 2.27 (dd, J = 18, 10 Hz, 1 H, CH_2), 1.45 (dd, J = 18, 10 Hz, 1 H, CH_2), 0.86 (d, 3 H, J = 7.5 Hz, CH_3); IR (film) 3026, 2974, 2960, 2928, 2917, 2877, 2849, 1722, 1601, 1494, 1445, 1412, 1321, 1300, 1229, 1217, 1181, 1167, 1029, 934, 773, 758, 703, 687 cm^{-1}; MS *m/e* 262.1362 (calcd for $C_{19}H_{18}O$, 262.1358). Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.91. Found: C, 86.61; H, 6.93.

The spectral data for 4-*exo*-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**28**) were the following: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.45–7.25 (m, 10 H, arom), 2.97 (d, J = 9.5 Hz, 1 H, cyclopropyl-*H*), 2.72 (d, J = 9.5 Hz, 1 H, cyclopropyl-*H*), 2.67 (m, 1 H, C*H*Me), 1.56 (m, 2 H, CH_2), 0.80 (d, J = 12 Hz, 3 H, CH_3); IR (film) 3083, 3056, 3026, 2956, 2924, 2868, 1724, 1601, 1494, 1445, 1410, 772, 701; MS *m/e* 262.1362 (calcd for $C_{19}H_{18}O$, 262.1358). Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92. Found: C, 87.03; H, 6.97.

Exploratory Solid State Photolysis of 5-Methyl-4,4-diphenylcyclohex-2-en-1-one (2). Low conversion run. A stirred water suspension of 101.6 mg of crystals of 5-methyl-4,4-diphenylcyclohex-2-en-1-one (**2**) (recrystallized from pentane) was irradiated through a Pyrex filter for 2 h. The photolysis mixture was filtered and dried to yield 95.0 mg of a solid which was separated with a 3.5 × 45 cm silica gel column eluted with 2% ether in hexane. Fraction 1, 14.6 mg (14.3%) of a mixture of *exo*/*endo*-4-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones (**28** and **33**). Fraction 2, 83.1 mg (81.8%) of starting material. The photoproduct mixture was further separated by repetitive HPLC eluting with 2.0% acetonitrile and 6% ether in pentane. Fraction 1, retention time 97.2 min, 11.5 mg (11.3%) of 4-*exo*-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**28**). Fraction 2, retention time 103.2 min, 1.8 mg (1.8%) of 4-*endo*-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**33**).

Exploratory Solid State Photolysis of 5-Methyl-4,4-diphenylcyclohex-2-en-1-one (2). High conversion run. A stirred water suspension of 300.0 mg of crystals of 5-methyl-4,4-diphenylcyclohex-2-en-1-one (**2**) was irradiated through a Pyrex filter for 2 h. The mixture was filtered and dried to yield 298.0 mg of a solid which was separated with a 3.5 × 45 cm silica gel column. Fraction 1, 139.2 mg (46.4%) of a mixture of the *exo*/*endo*-4-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones (**28** and **33**). Fraction 2, 135.6 mg (47.3%) of starting material. A 40 mg portion of the photoproduct mixture was separated by HPLC with the same conditions described above. Fraction 1, retention time 97.2 min, 29.3 mg (34%) of 4-*exo*-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**28**). Fraction 2, retention time 103.2 min, 9.7 mg (11.2%) of 4-*endo*-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**33**).

Independent Synthesis of 4-*exo*-Methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (33). To a mixture of 764 mg (4.0 mmol) of cuprous iodide in 50 mL of THF at 0 °C was added 5.7 mL (8.0 mmol) of 1.4 M methyllithium in hexane. The solution was stirred for 5 min and 520 mg (2.1 mmol) of *trans*-5,6-diphenylbicyclo[3,1,0]hex-3-en-

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[25] Sheldrick, G. M. *SHELXTL PLUS*, VERSION 4.2, Siemens Analytical X-Ray Instrumentations, Inc., Madison, WI.

[26] Sheldrick, G. M. *J. Appl. Cryst.*, 1993, in preparation.

[27] (a) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1961**, *83*, 4486. (b) *Ibid.* **1962**, *84*, 4527.

2-one[7] (**27**) in 10 mL of THF was added followed by stirring for 30 min. The reaction mixture was poured onto ice-saturated ammonium chloride, stirred for 2 h, and ether extracted. The combined ether solution was dried with anhydrous magnesium sulfate and concentrated in vacuo to yield 540 mg of a colorless oil which was purified via a 2.5 × 50 cm silica gel column eluted with 2% ether in hexane to yield 0.52 g (94.6%) 4-*exo*-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**28**) as a colorless oil.

5-Ethyl-4,4-diphenylcyclohex-2-en-1-one (3). To a 50 mL ether solution of ethylmagnesium bromide at 0 °C made from 1.0 g (9.2 mmol) of ethyl bromide and 250 mg (10.3 mmol) of magnesium was added 880 mg (4.6 mmol) of cuprous iodide. The resultant solution was stirred for 5 min, and 500 mg (2.0 mmol) of 4,4-diphenylcyclohex-2,5-dien-1-one (**1**)[26] in 15 mL of ether was added. The final mixture was stirred for 5 min. The reaction mixture was poured onto ice-saturated ammonium chloride, stirred for 1 h, and ether extracted. The combined organic layers were dried over anhydrous magnesium sulfate, and the solvent was removed in vacuo to yield 550 mg of a colorless oil which solidified upon standing. The solid was recrystallized from pentane to give 500 mg (90%) of 5-ethyl-4,4-diphenylcyclohex-2-en-1-one (**3**) as colorless prism crystals, mp 85.0–86.0 °C.

The spectral data for 5-ethyl-4,4-diphenylcyclohex-2-en-1-one (**3**) were the following: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.40–7.14 (m, 10 H, arom), 7.05 (d, J = 10 Hz, 1 H, β-vinyl), 6.15 (d, J = 10 Hz, α-vinyl), 2.94–2.84 (m, 1 H, C*H*Et), 2.62 (dd, J = 16.5, 3.5 Hz, 1 H, C*H*$_2$CO), 2.19 (dd, J = 16.5, 11.5 Hz, 1 H, C*H*$_2$CO), 1.77–1.60 (m, 1 H, C*H*$_2$Me), 0.96 (t, J = 7 Hz, 3 H, C*H*$_3$), 0.85–0.66 (m, 1 H, C*H*$_2$Me); IR (film) 3084, 3056, 3030, 2963, 2932, 2901, 2874, 1685, 1598, 1494, 1444, 1384, 1255, 1190, 1033, 889, 771, 757, 703 cm^{-1}; MS *m/e* 276.1507 (calcd for $C_{20}H_{20}O$, 276.1514); UV (benzene) λ_{max} = 338 nm (ϵ = 28.8). Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 87.02; H, 7.19.

Exploratory Solution Photolysis of 5-Ethyl-4,4-diphenylcyclohex-2-en-1-one (3). A solution of 100 mg of 5-ethyl-4,4-diphenylcyclohex-2-en-1-one (**3**) in 250 mL of photograde benzene was photolyzed through a Pyrex filter and filter solution for 2.8 h. The solvent was removed in vacuo to yield 101 mg of a pale yellow oil which was chromatographed on a 2.5 × 75 cm silica gel column eluted with 2% of ether in hexane. Fraction 1, 88 mg of a mixture of *exo*-4-ethyl-*trans*-5,6-diphenyl[3,1,0]hexan-2-one (**29**) and *endo*-4-ethyl-*trans*-5,6-diphenylbicyclo[3,1,0]hexan-2-one (**34**). Fraction 2, 10.7 mg of 5-ethyl-3,4-diphenylcyclohex-2-en-1-one (**39**). Recrystallization of **39** from pentane gave 6.0 mg (6.0%) of a powdery solid (mp 83.0–84.0 °C). The endo/exo bicyclic photoproduct mixture **34** and **29** was repetitively separated with TLC plates eluted with 2% chloroform in hexane. The mixture appeared as a broad band and the fastest fifth contained pure *exo*-4-ethyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**29**); the slowest fifth portion contained pure *endo*-4-ethyl-*trans*-5,6-diphenylbicyclo-[3.1.0]hexan-2-one (**34**). Repetitive separations afforded 25.1 mg (25.1%) of exo photoproduct **29** and 48.0 mg (48.0%) of the endo-photoproduct **34** and 15 mg of an unseparated mixture containing a 1:2 ratio of exo/endo products **29** and **34**.

The spectral data for *exo*-4-ethyl-*trans*-5,6-diphenylbicyclo[3.1.0]-hexan-2-one (**29**) were the following: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.50–7.25 (m, 10 H, arom), 2.93 (d, J = 9.5 Hz, 1 H, cyclopropyl-*H*), 2.73 (d, J = 9.5 Hz, 1 H, cyclopropyl-*H*), 2.45–2.30 (m, 1 H, C*H*Et), 1.83–1.78 (m, 1 H, C*H*$_2$CO), 1.4–0.9 (m, 3 H, C*H*$_2$CO and C*H*$_2$CH$_3$), 0.72–0.64 (t, J = 7 Hz, 3 H, C*H*$_3$); IR (film) 3081, 3055, 3025, 2997, 2960, 2929, 2899, 2875, 2861, 1723, 1600, 1493, 1458, 1445, 1407, 1320, 1202, 1029, 767, 701 cm^{-1}; MS *m/e* 276.1503 (calcd for $C_{20}H_{20}O$, 276.1514). Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 86.73; H, 7.46.

The spectral data for *endo*-4-ethyl-*trans*-5,6-diphenylbicyclo[3.1.0]-hexan-2-one (**34**) were the following: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.50–7.26 (m, 10 H, arom), 3.28 (d, J = 9.5 Hz, 1 H, cyclopropyl-*H*), 2.65–2.55 (m, 1 H, C*H*$_2$CO), 2.46 (d, J = 9.5 Hz, 1 H, cyclopropyl-*H*), 2.32 (dd, J = 18.0, 9.0 Hz, 1 H, C*H*$_2$CO), 1.64–1.59 (m, 1 H, C*H*Et), 1.46–1.25 (m, 2 H, C*H*$_2$Me), 0.64 (t, J = 7.5 Hz, 3 H, C*H*$_3$); IR (film) 3056, 3026, 2959, 2928, 2872, 1722, 1601, 1494, 1457, 1445, 771, 712, 700, 663 cm^{-1}; MS *m/e* 276.1513 (calcd for $C_{20}H_{20}O$ 276.1514). Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 86.92; H, 7.46.

The spectral data for 5-ethyl-3,4-diphenylcyclohex-2-en-1-one (**39**) were the following: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.47–7.22 (m, 10 H, arom), 6.67 (s, 1 H, α-vinyl), 4.19 (d, J = 4 Hz, 1 H, C*H*Ph), 2.5–2.1 (m, 3 H, C*H*$_2$CO and C*H*Et), 1.51–1.35 (m, 1 H, C*H*$_2$Me), 1.05–0.75 (m, 4 H, C*H*$_3$ and C*H*$_2$Me); IR (film) 3080, 3057, 3027, 2960, 2929, 2899, 2873, 1726, 1660, 1598, 1571, 1492, 1451, 1445, 1349, 1329, 1296, 1261, 754, 703, 695 cm^{-1}; MS *m/e* 276.1488 (calcd for $C_{20}H_{20}O$ 276.1514). Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 86.96; H, 7.28.

Exploratory Solid State Photolysis of 5-Ethyl-4,4-diphenylcyclohex-2-en-1-one (3). A water suspension of 50.0 mg of crystals (pentane slow evaporation) of 5-ethyl-4,4-diphenylcyclohex-2-en-1-one (**3**) was photolyzed for 20 min through a Pyrex filter. The mixture was filtered and dried to give 48.2 mg of a solid. The mixture was chromatographed with a 2.5 × 50 cm silica gel column eluted with 2% ether in hexane. Fraction 1, 4.1 mg (8.2%) of 4-*exo*-ethyl-*trans*-5,6-diphenylbicyclo-[3.1.0]hexan-2-one (**29**). Fraction 2, 41.6 mg (83.2%) of starting material.

Independent Synthesis of 5-*exo*-Ethyl-*trans*-5,6-diphenylbicyclo-[3.1.0]hexan-2-one (29). To a suspension of 764 mg (4.0 mmol) of cuprous iodide in 100 mL of ether at 0 °C was added an 8.0 mL (8.8 mmol) of ether solution of 1.1 M ethylmagnesium bromide. The mixture was stirred for 5 min at 0 °C. To this mixture was added 521 mg (2.12 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**27**)[7] in 20 mL of ether. The mixture was stirred for 30 min, poured onto ice-saturated ammonium chloride, stirred for 1 h, and ether extracted. The combined organic layers were dried over anhydrous magnesium sulfate, and the solvent was removed in vacuo to afford 0.59 g of a colorless oil which was chromatographed on a 3.5 × 100 cm silica gel column eluted with 2% ether in hexane to give 0.57 g (96.8%) of 4-*exo*-ethyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**29**) as a clear oil.

5-Isopropyl-4,4-diphenylcyclohex-2-en-1-one (4). To a mixture of 720 mg cuprous cyanide (8.0 mmol) in 50 mL of ether at 0 °C was added 12.3 mL of 1.30 M isopropylmagnesium bromide (16 mmol). The mixture was stirred for 5 min and 1.0 g (4.0 mmol) of 4,4-diphenylcyclohex-2,5-dien-1-one (**1**)[26] in 30 mL of ether was added. The reaction mixture was stirred at 0 °C for 30 min, poured onto ice-saturated ammonium chloride, stirred for 1 h, and ether extracted. The combined organic layers were dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to give 1.10 g of a colorless oil which solidified upon standing. The solid was crystallized by slow evaporation of an ethanol solution to give 0.90 g (76%) of 5-isopropyl-4,4-diphenylcyclohex-2-en-1-one (**4**) as colorless prism crystals (mp 95.0–96.0 °C).

The spectral data for 5-isopropyl-4,4-diphenylcyclohex-2-en-1-one (**4**) were the following: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.37–7.17 (m, 10 H, arom), 6.92 (d, J = 10 Hz, 1 H, β-vinyl), 6.09 (d, J = 10 Hz, 1 H, α-vinyl), 3.05 (dd, J = 9.0, 8.0 Hz, 1 H, C*H*Pr^i), 2.36 (d, J = 8.0 Hz, 1 H, C*H*$_2$CO), 2.36 (d, J = 9.0 Hz, 1 H, C*H*$_2$CO), 2.12–2.02 (septet, J = 7 Hz, 1 H, C*H*Me$_2$), 1.05 (t, J = 7 Hz, 3 H, C*H*$_3$), −0.05 (t, J = 7 Hz, 3 H, C*H*$_3$); IR (film) 2956, 2928, 2909, 2876, 1679, 1647, 1596, 1493, 1465, 1443, 1416, 1391, 1369, 1264, 1214, 1194, 1170, 1159, 1034, 911, 889, 756, 732, 703 cm^{-1}; MS *m/e* 290.1675 (calcd for $C_{21}H_{22}O$, 290.1671); UV (benzene) λ_{max} = 330 nm (ϵ = 38.8). Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 87.15; H, 7.82.

Exploratory Solution Photolysis of 5-Isopropyl-4,4-diphenylcyclohex-2-en-1-one (4). A solution of 210 mg of 5-isopropyl-4,4-diphenylcyclohex-2-en-1-one (**4**) in 250 mL of benzene was photolyzed through a Pyrex filter and filter solution for 2.0 h. The solvent was removed in vacuo to give 215 mg of a pale yellow oil which was separated with a silica gel thick layer chromatography plate eluted with 3% chloroform in hexane. Band 1, 121.6 mg of 4-*exo*-isopropyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**30**). Recrystallization from pentane gave 95.0 mg (45.2%) of **30** as a colorless solid (mp 85.0–85.5 °C). Band 2, 86.1 mg of 4-*endo*-isopropyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**35**). Recrystallization from pentane gave 63 mg (30.0%) of **35** as colorless crystals (mp 102.0–103.0 °C).

The spectral data for 4-*exo*-isopropyl-*trans*-5,6-diphenylbicyclo-[3.1.0]hexan-2-one (**30**) were the following: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.50–7.40 (m, 10 H, arom), 2.92 (d, J = 9.5 Hz, 1 H, cyclopropyl-*H*), 2.70 (d, J = 9.5 Hz, 1 H, cyclopropyl-*H*), 2.57 (d, J = 8.0 Hz, 1 H, C*H*Pr^i), 1.87 (d, J = 19 Hz, 1 H, C*H*$_2$CO), 1.82–1.62 (doublet of septet, J = 7.0, 2.5 Hz, 1 H, C*H*Me$_2$), 1.10 (dd, J = 19.0, 8.0 Hz, 1 H, C*H*CO), 0.59 (d, *J* = 7.0 Hz, 3 H, C*H*$_3$), 0.55 (d, *J* = 7.0 Hz, 3 H, C*H*$_3$); IR (film) 2894, 2873, 2810, 1726, 1684, 1601, 1494, 1464, 1445, 1412, 1387, 1369, 1321, 1285, 1242, 1204, 1164, 1117, 1088, 1076, 1029, 925, 767, 701 cm^{-1}; MS *m/e* 290.1667 (calcd for $C_{21}H_{22}O$, 290.1671). Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 87.21; H, 7.96.

The spectral data for 4-*endo*-isopropyl-*trans*-5,6-diphenylbicyclo-[3.1.0]hexan-2-one (**35**) were the following: ^{1}H-NMR (CDCl$_3$, 200 MHz) δ 7.57–7.26 (m, 10 H, arom), 3.57 (d, *J* = 9.5 Hz, cyclopropyl-*H*), 2.85–2.55 (dd, *J* = 9.5, 9.0 Hz, 1 H, C*H*Pr^i), 2.43 (dd, *J* = 18.0, 9.0 Hz, 1 H, C*H*$_2$CO), 2.26 (d, *J* = 9.5 Hz, 1 H, cyclopropyl-*H*), 1.50 (dd, *J* = 9.0, 18.0 Hz, 1 H, C*H*$_2$CO), 1.75–1.50 (m, 1 H, C*H*Me$_2$), 0.67 (d, *J* = 7 Hz, 3 H, C*H*$_3$), 0.60 (d, *J* = 7 Hz, 3 H, C*H*$_3$); IR (film) 3082, 3056, 3027, 2957, 2921, 2868, 1722, 1601, 1495, 1466, 1445, 1219, 1172, 1078, 1037, 1030, 1019, 975, 927, 774, 762, 713, 700 cm^{-1}; MS *m/e* 290.1683 (calcd for $C_{21}H_{22}$, 290.1671). Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 86.55; H, 7.65.

Exploratory Solid State Photolysis of 5-Isopropyl-4,4-diphenylcyclohex-2-en-1-one (4). A NMR tube containing 30.0 mg of 5-isopropyl-4,4-diphenylcyclohex-2-en-1-one (**4**) (ethanol slow evaporation) was photolyzed for 0.5 h. The mixture was separated on a 2.5 × 50 silica gel thick layer chromatography plate eluted with 2% ether in hexane. Band 1, 17.3 mg (57.3%) of 4-*exo*-isopropyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**30**) as a colorless solid (mp 85.0–86.0 °C). Band 2, 12.1 mg (40.3%) of starting enone (**4**).

Independent Synthesis of 4-*exo*-isopropyl-*trans*-5,6-diphenylbicyclo-[3.1.0]hexan-2-one (30). To a mixture of 276 mg (3.1 mmol) of cuprous cyanide in 50 mL of ether at 0 °C was added 4.8 mL of 1.30 M (6.2 mmol) isopropylmagnesium bromide and stirred for 5 min. A solution of 382.0 mg (1.55 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]-hex-3-en-2-one (**27**) in 20 mL of ether was added. The reaction mixture was stirred for an additional 30 min, poured onto ice-saturated ammonium chloride, stirred for 1 h, and ether extracted. The combined organic layers were dried over anhydrous magnesium sulfate, and the solvent was removed in vacuo to give 450.0 mg of a colorless oil which was purified with 2.5 × 75 cm silica gel column chromatography eluted with 3% ether in hexane to give 434.6 mg (97.3%) of 4-*exo*-isopropyl-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**30**) as a white solid (mp 85.0–86.5 °C).

5-*tert*-Butyl-4,4-diphenylcyclohex-2-en-1-one (5). To a mixture of 360 mg (4.0 mmol) cuprous cyanide in 50 mL of ether at 0 °C was added 4.7 mL (8.0 mmol) of a 1.7 M pentane solution of *tert*-butyllithium. The mixture was stirred for 5 min, and 500 mg (2.0 mmol) of 4,4-diphenylcyclohex-2,5-dien-1-one (**1**) in 20 mL of ether was added. The mixture was stirred for 30 min at 0 °C, poured onto ice-saturated ammonium chloride, stirred for 1 h, and ether extracted. The combined organic layers were dried over anhydrous magnesium sulfate, and the solvent was removed in vacuo to give 617 mg of an oil which was separated with a 2.0 × 50 cm silica gel column eluted with 3% ether in hexane. Fraction 1, 20 mg of an unidentified substance. Fraction 2, 394.4 mg of 5-*tert*-butyl-4,4-diphenylcyclohex-2-en-1-one (**5**) as a colorless oil which solidified upon standing. This was recrystallized by slow evaporation from pentane to give 306 mg (49.6%) of prism crystals of **5** (mp 115.0–116.0 °C). Fraction 3, 210 mg of a mixture of starting material and some unidentified substances.

The spectral data for 5-*tert*-butyl-4,4-diphenylcyclohex-2-en-1-one (**5**) were the following: ^{1}H-NMR (CDCl$_3$, 200 MHz) δ 7.55–7.25 (m, 10 H, arom), 6.94 (d, br, *J* = 10 Hz, 1 H, β-vinyl), 6.05 (d, *J* = 10 Hz, 1 H, α-vinyl), 3.24 (dd, *J* = 8.0, 6.0 Hz, 1 H, C*H*(CH$_3$)$_3$), 2.71–2.67 (m, 2 H, C*H*$_2$CO), 0.68 (s, 9 H, C(C*H*$_3$)$_3$); IR (film) 2998, 2962, 2908, 2873, 1681, 1597, 1493, 1446, 1421, 1399, 1388, 1368, 1279, 1265, 1230, 1214, 1191, 1168, 1159, 1036, 889, 757, 731, 703 cm^{-1}; MS *m/e* 304.1813 (calcd for $C_{22}H_{24}O$, 304.1827); UV (benzene) λ_{max} = 335 nm (ϵ = 29). Anal. Calcd for $C_{22}H_{24}O$: C, 86.80; H, 7.95. Found: C, 86.86; H, 8.25.

Exploratory Solution Photochemistry of 5-*tert*-Butyl-4,4-diphenylcyclohex-2-en-1-one (5). A 250 mL benzene solution of 444 mg of 5-*tert*-butyl-4,4-diphenylcyclohex-2-en-1-one (**5**) was photolyzed for 1.7 h through a 2 mm Pyrex filter and filter solution. The solvent was removed in vacuo to afford 450 mg of a pale yellow oil which was recrystallized in pentane to give 360 mg (81.1%) of 4-*exo*,*tert*-butyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**32**) as colorless prisms (mp 110.0–111.0 °C). The mother liquor was concentrated to give 90 mg of an oil which was separated using a 20 × 20 cm silica gel thick layer chromatography plate eluted with 2% ether in hexane. Band 1, 38.0 mg (8.5%) of *endo*,*tert*-butyl-*trans*-5,6-diphenylbicyclo[3.1.0]-hexan-2-one (**36**) as a colorless oil which solidified upon standing. Recrystallization from pentane yielded 25 mg (5.6%) of needle crystals (mp 103.0–104.0 °C). Band 2, 30.1 mg of 4-*exo*,*tert*-butyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**32**) (combined yield 87.9%). Band 3, 11.2 mg (2.5%) of starting material. The structure of **32** was unambiguously assigned using X-ray crystallography (supplementary material).

The spectral data for 4-*exo*-*tert*-butyl-*trans*-5,6-diphenylbicyclo-[3.1.0]hexan-2-one (**32**) were the following: ^{1}H-NMR (CDCl$_3$, 200 MHz) δ 7.45–7.26 (m, 10 H, arom), 2.80 (d, br, *J* = 9.5 Hz, 1 H, cyclopropyl-*H*), 2.73 (d, *J* = 9.5 Hz, 1 H, cyclopropyl-*H*), 2.43 (dd, *J* = 9.0, 2.0 Hz, 1 H, C*H*(CH$_3$)$_3$), 2.05 (dt, *J* = 19.0, 2.0 Hz, 1 H, C*H*$_2$-CO), 1.26 (dd, *J* = 19.0, 9.0 Hz, 1 H, C*H*$_2$CO), 0.66 (s, 9 H, C(C*H*$_3$)$_3$); IR (film) 2907, 2881, 2875, 1725, 1601, 1494, 1478, 1469, 1445, 1411, 1397, 1367, 1323, 1286, 1213, 1191, 1161, 1077, 1027, 1016, 919, 770, 732, 702 cm^{-1}; MS *m/e* 304.1826 (calcd for $C_{22}H_{24}O$, 304.1827). Anal. Calcd for $C_{22}H_{24}O$: C, 86.80; H, 7.95. Found: C, 86.62; H, 8.03.

The spectral data for 4-*endo*-*tert*-butyl-*trans*-5,6-diphenylbicyclo-[3.1.0]hexan-2-one (**36**) were the following: ^{1}H-NMR (CDCl$_3$, 300 MHz) δ 7.57–7.26 (m, 10 H, arom), 3.45 (d, br, *J* = 9.5 Hz, 1 H, cyclopropyl-*H*), 3.02 (dd, *J* = 11.5, 8.0 Hz, 1 H, C*H*(CH$_3$)$_3$), 2.31 (d, *J* = 9.5 Hz, 1 H, cyclopropyl-*H*), 2.21 (ddd, *J* = 17.5, 8.5, 1.5 Hz, 1 H, C*H*$_2$CO), 2.11 (dd, *J* = 17.5, 11.5 Hz, 1 H, C*H*$_2$CO), 0.56 (s, 9 H, (C*H*$_3$)$_3$); IR (film) 3083, 3056, 3026, 2957, 2905, 2867, 1719, 1600, 1495, 1475, 1446, 1397, 1366, 1233, 1211, 1191, 1165, 1039, 1030, 1020, 768, 703 cm^{-1}; MS 304.1825 (calcd for $C_{22}H_{24}O$, 304.1827). Anal. Calcd for $C_{22}H_{24}O$: C, 86.80; H, 7.95. Found: C, 86.85; H, 8.07.

Exploratory Solid State Photochemistry of 5-*tert*-Butyl-4,4-diphenylcyclohex-2-en-1-one (5). A stirred water suspension of 101 mg of 5-*tert*-butyl-4,4-diphenylcyclohex-2-en-1-one (**5**) was photolyzed for 20 min through a Pyrex filter. The solid was filtered and dried to give 105.0 mg of a pale yellow mixture which was separated with a 20 × 20 cm thick layer silica gel plate eluted with 4% ether in hexane. Band 1, 31.0 mg (31%) of **32** as a colorless solid (mp 110.0–111.5 °C). Band 2, 67.6 mg of starting material.

5-Phenyl-4,4-diphenylcyclohex-2-en-1-one (6). To a mixture of 1.53 g (8.0 mmol) of cuprous iodide in 50 mL of ether at 0 °C was added 18 mL (16.0 mmol) of 0.88 M phenyllithium in ether and stirred for 5 min. A solution of 1.0 g (4.0 mmol) of 4,4-diphenylcyclohex-2,5-dienone (**6**)[26] in 50 mL of ether was added to the mixture, and it was stirred for 30 min at 0 °C, poured onto ice-saturated ammonium chloride, stirred for 1 h, and ether extracted. The combined organic layers were dried over anhydrous magnesium sulfate, and the solvent was removed in vacuo to afford 1.30 g of a solid which was recrystallized from ether/hexane to give 1.20 g (91%) of 5-phenyl-4,4-diphenylcyclohex-2-en-1-one (**6**) as colorless crystals (mp 172–173 °C).

The spectral data were the following: ^{1}H-NMR (CDCl$_3$, 200 MHz) δ 7.5–6.6 (m, 16 H, arom and β-vinyl), 6.29 (d, *J* = 10 Hz, 1 H, α-vinyl), 4.49 (dd, *J* = 10.5, 4.5 Hz, 1 H, C*H*Ph), 2.99–2.61 (m, 2 H, C*H*$_2$); IR (film) 3056, 3031, 1680, 1493, 1447, 770, 765, 754, 699 cm^{-1}; MS *m/e* 324.1528 (calcd for $C_{24}H_{20}O$, 324.1514); UV (benzene) λ_{max} = 340 nm (ϵ = 40). Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 89.12; H, 6.37.

Exploratory Solution Photolysis of 5-Phenyl-4,4-diphenylcyclohex-2-en-1-one (6). A benzene solution of 500 mg of 5-phenyl-4,4-diphenylcyclohex-2-en-1-one was photolyzed for 1.5 h with a Pyrex filter and filter solution. The solvent was removed in vacuo to afford 505.0 mg of an oil which was separated with a 3.5 × 70 cm silica gel column eluted with 2% ether in hexane. Fraction 1, 245.6 mg of 4-*exo*-phenyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**31**) as a white solid. Recrystallization by slow evaporation of its ether solution afforded 204 mg (41.0%) of colorless prism crystals (mp 147.5–150.0 °C). The structure assignment of **31** was supported by X-ray crystallography (supplementary material) and independent synthesis.[7] Fraction 2, 200.1 mg of 4-*endo*-phenyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**37**) as a white solid. Recrystallization from ethane/pentane afforded 152 mg (30.4%) of **37** (mp 136.0−137.5 °C). Fraction 3, 38.8 mg (7.8%) of starting material **6**.

The spectral data for 4-*exo*-phenyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**31**) were the following: ^{1}H-NMR (CDCl$_3$, 200 MHz) δ 7.53−6.91 (m, 15 H, arom), 3.73 (d, J = 8 Hz, 1 H, C*H*Ph), 3.05 (d, J = 9 Hz, 1 H, cyclopropyl-*H*), 2.94 (d, J = 9 Hz, 1 H, cyclopropyl-*H*), 2.20 (d, J = 18 Hz, 1 H, C*H*$_2$CO), 1.70 (dd, J = 18.0, 8.0 Hz, 1 H, C*H*$_2$CO); IR (film) 3105, 3083, 3059, 3028, 3004, 2981, 2926, 2915, 1722, 1601, 1494, 1454, 1445, 1407, 1319, 1158, 1029, 911, 784, 767, 732, 699 cm^{-1}; MS *m/e* 324.1515 (calcd for $C_{24}H_{20}O$, 324.1514). Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.55; H, 6.69.

The spectral data for 4-phenyl-5,6-*trans*-diphenylbicyclo[3.1.0]hexan-2-one (**37**) were the following: ^{1}H-NMR (CDCl$_3$, 200 MHz) δ 7.55−6.45 (m, 15 H, arom), 4.26 (dd, J = 10.5, 9.0 Hz, 1 H, C*H*Ph), 3.42 (d, J = 9.5 Hz, 1 H, cyclopropyl-*H*), 2.56−2.40 (m, 2 H, cyclopropyl-*H* and C*H*$_2$CO), 2.16 (dd, J = 18.0, 10.5 Hz, 1 H, C*H*$_2$CO); IR (film) 3083, 3056, 3028, 3002, 1724, 1600, 1495, 1446, 1215, 772, 753, 730 cm^{-1}; MS *m/e* 324.1518 (calcd for $C_{24}H_{20}O$, 324.1514). Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 89.10; H, 6.18.

Exploratory Solid State Photolysis of 5-Phenyl-4,4-diphenylcyclohex-2-en-1-one (6). A water suspension of 100.0 mg of crystals of 5-phenyl-4,4-diphenylcyclohex-2-en-1-one (**6**) (from ether/hexane) was photolyzed through a Pyrex filter for 45 min. The mixture was filtered to give 99.5 mg of a pale yellow solid which was separated with a 20 × 20 cm silica gel thick layer chromatography plate eluted with 5% ether in hexane. Band 1, 47 mg (47%) of 4-*exo*-phenyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**31**) (mp 150.0−150.5 °C). Band 2, 51.0 mg (51%) of starting material **6**.

***cis*- and *trans*-4,5-Diphenyl-4-(*p*-cyanophenyl)cyclohex-2-en-1-ones (9c and 9t).** To a mixture of 592 mg (3.1 mmol) of cuprous iodide in 100 mL ether at 0 °C was added 6.5 mL of 0.95 M (6.2 mmol) phenyllithium ether solution and stirred for 5 min at 0 °C. A 30 mL ether solution of 500 mg (1.54 mmol) of 4-phenyl-4-(*p*-bromophenyl)cyclohex-2,5-dienone (**7**)[28] was added in 10 min, stirred for 30 min at 0 °C and then poured onto ice-saturated ammonium chloride and ether extracted. The combined ether solution was dried over anhydrous magnesium sulfate, and the solvent was removed in vacuo to give 800 mg of pale yellow oil which was used directly for the next step.

A solution of 800 mg of the above mixture containing 80% of a 1:1 mixture of *cis/trans*-4,5-diphenyl-4-(*p*-bromophenyl)cyclohex-2-en-1-ones (**8**) and 300 mg (3.33 mmol) cuprous cyanide in 20 mL of *N*-methylpyrrolidone was refluxed for 3 h. After cooling to rt, this solution was poured into a mixture of 2.0 g of potassium cyanide in 50 mL of water and 100 mL of benzene. The organic layer was washed with 40 mL of 10% potassium cyanide and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to yield 700 mg of a pale yellow solid which was chromatographed on a 2.5 × 120 cm silica gel column eluted with 20% ether in hexane. Fraction 1, 300 mg unidentified substrates. Fraction 2, 350 mg (65.2%) of a mixture of *cis/trans*-4,5-diphenyl-4-(*p*-cyanophenyl)cyclohex-2-en-1-ones (**9c** and **9t**) which was separated with TLC plates eluted with 20% chloroform in hexane. *trans*-4,5-Diphenyl-4-(*p*-cyanophenyl)cyclohex-2-en-1-one (**9t**) was collected from band 1 (182 mg) as a white solid. Crystallization by slow evaporation of ether afford 150 mg (28.3%) of prism crystals (mp 151.5−153.0 °C). *cis*-4,5-Diphenyl-4-(*p*-cyanophenyl)cyclohex-2-en-1-one (**9c**) was collected from band 2 (170 mg, 32.0%) as colorless crystals (mp 132.0−133.0 °C). X-ray crystallography crystal structures were obtained for both stereoisomers (supplementary material).

The spectral data for *trans*-4,5-diphenyl-4-(*p*-cyanophenyl)cyclohex-2-en-1-one (**9t**) were the following: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.44−6.60 (m, 15 H, arom and β-vinyl), 6.33 (d, J = 10.0 Hz, 1 H, α-vinyl), 4.51 (dd, J = 8.0, 5.5 Hz, 1 H, C*H*Ph), 2.80−2.73 (m, 2 H, C*H*$_2$CO); IR (film) 3087, 3057, 3031, 3005, 2227, 1682, 1604, 1496, 1452, 1444, 1408, 1458, 910, 834, 761, 752, 731, 701 cm^{-1}; MS *m/e* 349.1462 (calcd for $C_{25}H_{19}NO$, 349.1467); UV (benzene) λ_{max} = 338 nm (ϵ = 37). Anal. Calcd for $C_{25}H_{19}O$: C, 85.93; H, 5.48; N, 4.00. Found: C, 85.91; H, 5.49; N, 3.97.

The spectral data for *cis*-4,5-diphenyl-4-(*p*-cyanophenyl)cyclohex-2-en-1-one (**9c**) were the following: ^{1}H-NMR (CDCl$_3$, 200 MHz) δ 7.65−6.57 (m, 15 H, arom and β-vinyl), 6.35 (d, J = 10 Hz, 1 H, α-vinyl), 4.45 (dd, J = 9.0, 4.0 Hz, 1 H, C*H*Ph), 2.81 (dd, J = 16.5, 11.0 Hz, 1 H, C*H*$_2$CO), 2.62 (dd, J = 16.5, 4.0 Hz, 1 H, C*H*$_2$CO); IR (film) 3058, 3032, 2957, 2922, 2902, 2228, 1682, 1603, 1501, 1446, 1402, 1384, 1258, 1189, 1159, 1035, 1020, 911, 898, 837, 772, 760, 731, 700 cm^{-1}; MS *m/e* 349.1475 (calcd for $C_{25}H_{19}NO$, 349.1467); UV (benzene) λ_{max} = 342 nm (ϵ = 33.9). Anal. Calcd for $C_{25}H_{19}O$: C, 85.93; H, 5.48; N, 4.00. Found: C, 85.78; H, 5.61; N, 4.01.

Exploratory Solution Photochemistry of *trans*-4,5-Diphenyl-4-(*p*-cyanophenyl)cyclohex-2-en-1-one (9t). A 200 mL benzene solution of 100 mg (0.29 mmol) of *trans*-4,5-diphenyl-4-(*p*-cyanophenyl)cyclohex-2-en-1-one (**9t**) was photolyzed through a 2.0-mm Pyrex filter and filter solution for 0.5 h. The solvent was removed to yield 101 mg of a colorless oil which was separated with a 2.5 × 74 cm silica gel column eluted with 20% ether in hexane. Fraction 1, 42.1 mg (42.1%) of photoproducts as a colorless oil; fraction 2, 59.7 mg (59.7%) of starting material. The photoproduct mixture was further separated with a 20 × 20 cm silica gel thick layer chromatography plate repeatedly eluted with 20% chloroform in hexane. Band 1, 20.4 mg of *exo,endo*-4,6-diphenyl-5-(*p*-cyanophenyl)bicyclo[3.1.0]hexan-2-one (**42**) as a white solid. Recrystallization by slow evaporation of its ether solution yielded 15.1 mg (15.1%) of prism crystals (mp 191.0−191.5 °C). The structural assignment of photoketone **42** was supported by X-ray crystallography (see supplementary material). Band 2, 19.8 mg of *endo*-4,5-diphenyl-*endo*-6-(*p*-cyanophenyl)bicyclo[3.1.0]hexan-2-one (**43**) as a colorless oil which solidified upon standing. The solid was recrystallized from ether/hexane to give 11.0 mg (11.0%) of crystals (mp 142.0−143.0 °C).

The spectral data for *exo,endo*-4,6-diphenyl-5-(*p*-cyanophenyl)bicyclo[3.1.0]hexan-2-one (**42**) were the following: ^{1}H-NMR (C$_6$D$_6$, 200 MHz) δ 7.27−6.44 (m, 14 H, arom), 3.37 (d, J = 8.0 Hz, 1 H, C*H*Ph), 2.58 (d, J = 9.5 Hz, 1 H, cyclopropyl-*H*), 2.32 (d, J = 9.5 Hz, 1 H, cyclopropyl-*H*), 2.03 (d, J = 19.0 Hz, 1 H, C*H*$_2$CO), 1.64−1.50 (dd, J = 19.0, 8.0 Hz, 1 H, C*H*$_2$CO); IR (film) 3082, 3058, 3029, 3007, 3002, 2994, 2975, 2967, 2948, 2921, 2226, 1725, 1607, 1508, 1495, 1454, 1445, 1407, 1319, 1275, 1235, 1221, 1205, 1193, 1179, 1159, 1111, 1078, 1036, 1027, 1020, 1002, 966, 852, 830, 767, 701 cm^{-1}; MS *m/e* 349.1457 (calcd for $C_{25}H_{19}NO$, 349.1467). Anal. Calcd for $C_{25}H_{19}O$: C, 85.93; H, 5.48; N, 4.00. Found: C, 85.82; H, 5.71; N, 3.88.

The spectral data for *endo*-4,5-diphenyl-*endo*-6-(*p*-cyanophenyl)bicyclo[3.1.0]hexan-2-one (**43**) were the following: ^{1}H-NMR (C$_6$D$_6$, 200 MHz) δ 7.16−6.29 (m, 14 H, arom), 3.88 (t, J = 10 Hz, 1 H, C*H*Ph), 2.66 (d, J = 9.0 Hz, 1 H, cyclopropyl-*H*), 2.23 (dd, J = 18.0, 10.0 Hz, 1 H, C*H*$_2$CO), 2.09 (d, J = 9.0 Hz, 1 H, cyclopropyl-*H*), 1.75 (dd, J = 18.0, 10.0 Hz, 1 H, C*H*$_2$CO); IR (film) 3056, 3029, 2925, 2921, 2227, 1724, 1497, 1446, 1415, 1408, 1321, 1310, 1213, 1180, 1156, 1114, 1080, 1034, 1020, 1010, 1001, 976, 950, 920, 865, 831, 784, 769, 757, 699 cm^{-1}; MS *m/e* 249.1480 (calcd for $C_{25}H_{19}NO$, 249.1467). Anal. Calcd for $C_{25}H_{19}O$: C, 85.93; H, 5.48; N, 4.00. Found: C, 85.71; H, 5.62; N, 3.88.

Exploratory Solid State Photochemistry of *trans*-4,5-Diphenyl-4-(*p*-cyanophenyl)cyclohex-2-en-1-one (9t). Single crystals (ether slow evaporation) of *trans*-4,5-diphenyl-4-(*p*-cyanophenyl)cyclohex-2-en-1-one (**9t**) (20.4 mg) in an NMR tube were photolyzed through a Pyrex filter for 0.5 h. The photolysis mixture was separated with a 20 × 20 cm thick layer silica gel plate eluted with 25% ether in hexane. Band 1, 12.4 mg (60.8%) of *exo,endo*-4,6-diphenyl-5-(*p*-cyanophenyl)bicyclo[3.1.0]hexan-2-one (**42**) as a white solid (mp 191.0−192.0 °C). The structure assignment was supported by X-ray crystallography (see supplementary material). Band 2, 7.6 mg (37.2%) of starting material as a white solid.

Exploratory Solution Photochemistry of *cis*-4,5-Diphenyl-4-(*p*-cyanophenyl)cyclohex-2-en-1-one (9c). A 220 mL benzene solution of 110 mg (0.315 mmol) *cis*-4,5-diphenyl-4-(*p*-cyanophenyl)cyclohex-2-en-1-one (**9c**) was photolyzed through a 2.0 mm Pyrex filter and filter solution for 0.5 h. The solvent was removed to yield 111.3 mg of a colorless oil which was separated with a 20 × 20 cm silica gel thick layer chromatography repeatedly eluted with 5% ethyl acetate in hexane. Band 1, 33.0 mg of *exo*-4-phenyl-5-phenyl-*endo*-6-(*p*-cyanophenyl)bicyclo[3.1.0]hexan-2-one (**40**) as a white solid. Recrys-

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[28] Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434−5447.

tallization by slow evaporation of its ether solution yielded 25.1 mg (22.8%) of prism crystals (mp 210.0−211.0 °C). The structure assignment of photoketone **40** was supported by X-ray crystallography (see supplementary material). Band 2, 4.5 mg (4.1%) of *endo,endo*-4,6-diphenyl-5-(*p*-cyanophenyl)bicyclo[3.1.0]hexan-2-one (**41**) as a colorless oil which solidified upon standing. The solid was recrystallized from ether/hexane to give 2.1 mg (1.9%) of crystals (mp 181.0−182.0 °C). Band 3, 69.7 mg (63.4%) of starting material.

The spectral data for *exo*-4,5-diphenyl-*endo*-6-(*p*-cyanophenyl)-bicyclo[3.1.0]hexan-2-one (**40**) were the following: ^{1}H-NMR (C_6D_6, 200 MHz) δ 7.16−6.68 (m, 14 H, arom), 3.28 (d, *J* = 8.5 Hz, 1 H, C*H*Ph), 2.62 (d, *J* = 9.5 Hz, 1 H, cyclopropyl-*H*), 2.26 (d, *J* = 9.5 Hz, 1 H, cyclopropyl-*H*), 2.09 (d, *J* = 19.0 Hz, 1 H, C*H*$_2$CO), 1.30 (dd, *J* = 19.0, 8.5 Hz, 1 H, C*H*$_2$CO); IR (film) 3062, 3026, 2996, 2979, 2966, 2946, 2918, 2230, 1720, 1605, 1507, 1497, 1454, 1447, 1406, 1316, 1307, 1194, 1181, 1155, 1034, 864, 829, 698 cm^{-1}; MS *m*/*e* 349.1461 (calcd for $C_{25}H_{19}NO$, 349.1467). Anal. Calcd for $C_{25}H_{19}O$: C, 85.93; H, 5.48; N, 4.00. Found: C, 85.61; H, 5.55; N, 3.86.

The spectral data of *endo,endo*-4,6-diphenyl-5-(*p*-cyanophenyl)-bicyclo[3.1.0]hexan-2-one (**41**) were the following: ^{1}H-NMR (C_6D_6, 300 MHz) δ 7.15−6.29 (m, 14 H, arom), 3.63 (t, *J* = 10 Hz, 1 H, C*H*Ph), 2.70 (d, *J* = 9.5 Hz, 1 H, cyclopropyl-*H*), 2.25 (ddd, *J* = 18, 10, 2 Hz, 1 H, COC*H*$_2$), 2.02 (dd, *J* = 18, 11 Hz, 1 H, COC*H*$_2$), 2.04 (d, *J* = 9.5 Hz, 1 H, cyclopropyl-*H*); IR (film) 3057, 3029, 2956, 2923, 2852, 2226, 1723, 1682, 1603, 1496, 1462, 1454, 1445, 1406, 1378, 1167, 873, 769, 699 cm^{-1}; MS *m*/*e* 349.1467 (calcd for $C_{25}H_{19}NO$, 349.1467). Anal. Calcd for $C_{25}H_{19}O$: C, 85.93; H, 5.48; N, 4.00. Found: C, 85.71; H, 5.58; N, 3.91.

Exploratory Solid State Photochemistry of *cis*-4,5-Diphenyl-4-(*p*-cyanophenyl)cyclohex-2-en-1-one (9c). Single crystals (pentane slow evaporation) of *cis*-4,5-diphenyl-4-(*p*-cyanophenyl)cyclohex-2-en-1-one (**9c**) (35.2 mg) in a NMR tube was photolyzed through a Pyrex filter for 0.5 h. The photolysis mixture was separated with a 20 × 20 cm thick layer silica gel plate eluted with 10% ethyl acetate in hexane. Band 1, 17.4 mg of *exo*-4-phenyl-5-phenyl-*endo*-6-(*p*-cyanophenyl)-bicyclo[3.1.0]hexan-2-one (**40**) as a white solid. Recrystallization by slow evaporation of its ether/pentane solution yielded 13.4 mg (38.0%) of prism crystals (mp 210.0−211.0 °C). Band 2, 2.4 mg of *endo,endo*-4,6-diphenyl-5-(*p*-cyanophenyl)bicyclo[3.1.0]hexan-2-one (**41**) as a colorless oil which solidified upon standing. The solid was recrystallized from ether/pentane to give 2.1 mg (6.0%) of crystalline **41** (mp 181.5−182.0 °C). Band 3, 15.0 mg of starting material (43.8%) as a white solid.

Exploratory Solution Photolysis of 2-Methyl-4,4-diphenylcyclohex-2-en-1-one (26). A benzene solution of 450 mg (1.72 mmol) of 2-methyl-4,4-diphenylcyclohex-2-en-1-one (**26**) was photolyzed through a Pyrex filter for 2.5 h. The solvent was removed in vacuo to give 451 mg of a white solid. Recrystallization from ether/hexane yielded 425 mg (94.4%) of 1-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hex-2-one (**44**) as colorless prisms (mp 140.0−141.0 °C). The structure assignment was supported by X-ray crystallography (see supplementary material).

The spectral data were the following: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.42−7.25 (m, 10 H, arom), 2.99 (s, 1 H, cyclopropyl-*H*), 2.32−2.25 (m, 2 H, C*H*$_2$CO), 2.13−1.98 (m, 1 H, C*H*$_2$), 1.21−1.00 (m, 1 H, C*H*$_2$), 1.21 (s, 3 H, C*H*$_3$); IR (film) 3030, 3010, 2915, 1720, 1650, 1575, 1475, 1430, 1340, 1080, 800, 775, 751, 710 cm^{-1}; MS *m*/*e* 262.1365 (calcd for $C_{19}H_{18}O$, 262.1358). Anal. Calcd for $C_{19}H_{18}O$: C, 87.12; H, 6.58. Found: C, 86.99; H, 6.92.

Exploratory Solid State Photolysis of 2-Methyl-4,4-diphenylcyclohex-2-en-1-one (26). A water suspension of 202.0 mg of crystals of 2-methyl-4,4-diphenylcyclohex-2-en-1-one (**26**) (ethanol slow cooling) was photolyzed through a Pyrex filter for 12 h. The mixture was filtered to give 200 mg of a solid mixture which was chromatographed on a 2.0 × 50 cm silica gel column eluted with 2% ether in hexane. Fraction 1, 180 mg of a mixture of starting material and 1-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**44**); fraction 2, 8.0 mg of 2-methyl-3-benzhydrylcyclopent-2-en-1-one (**55**) as a colorless oil. Recrystallization from slow evaporation of pentane solution yielded 5 mg (2.5%) of **44** as colorless prisms (mp 66.0−67.5 °C). The structure of photoketone **55** was confirmed by X-ray crystallography (see supplementary material).

The mixture of the starting material and the bicyclic photoproduct **44** was further separated with HPLC eluted with 5% ether in hexane. Fraction 1, retention time 42.7 min, 20.5 mg of (10.1%) 1-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**44**); fraction 2, retention time 47.7 min, 160 mg of (79.2%) starting material.

The spectral data for 2-methyl-3-(diphenylmethyl)cyclopent-2-en-1-one (**55**) were the following: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.38−7.11 (m, 10 H, arom), 5.44 (s, 1 H, C*H*Ph$_2$), 2.43 (m, 4 H, C*H*$_2$), 1.69 (s, 3 H, C*H*$_3$); IR (film) 3065, 3010, 2890, 2830, 1700, 1630, 1605, 1475, 1455, 1375, 1325, 1090, 1030, 790, 750, 705 cm^{-1}; MS *m*/*e* 262.1368 (calcd for $C_{19}H_{18}O$, 262.1358). Anal. Calcd for $C_{19}H_{18}O$: C, 87.12; H, 6.58. Found: C, 87.15; H, 6.67.

Exploratory Solid State Photolysis of 2-Methyl-4,4-diphenylcyclohex-2-en-1-one (26). An NMR tube containing 60 mg of 2-methyl-4,4-diphenylcyclohex-2-en-1-one (**26**) was photolyzed through a Pyrex filter, and 5 mg of the solid was taken up for a NMR spectrum for a given time to determine the conversion of the photochemical reaction. After 12 h the conversion was 5% to a 1:1 ratio of 2-methyl-3-(diphenylmethyl)cyclopent-2-en-1-one (**55**) and 1-methyl-*trans*-5,6-diphenylbicyclo[3.1.0]hex-2-one (**44**). After 15 h the conversion increased to 20% to a 1:3 ratio of **55** and **44**. After 18 h the conversion increased to 36% to a single photoproduct **44**. Photoketone **26** was consumed completely.

3-Cyanocyclopentanone Ethylene Ketal (20). A mixture of 4.6 g (42.2 mmol) of 3-cyanocyclopentanone (**19**), 4.6 mg (100 mmol) of ethylene glycol, and 500 mg of toluenesulfonic acid monohydrate in 100 mL of anhydrous benzene was refluxed for 48 h with a Dean−Stark trap. After the solution cooled to rt, 2 mL of 40% triton B in methanol and 10 g of anhydrous sodium sulfate were added. The mixture was filtered, and the solid was washed with 200 mL of ether. The solvent was removed, and the residue was distilled (bp 102.5−103.5 °C/1.75 mmHg) to give 6.4 g (99.2%) of 3-cyanocyclopentanone ethylene ketal (**20**) as a colorless oil.

The spectral data for 3-cyanocyclopentanone ethylene ketal (**20**) were the following: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 3.97−3.85 (m, 4 H, OC*H*$_2$C*H*$_2$O), 2.91 (quint, *J* = 6.0 Hz, 1 H, C*H*CN), 2.26−1.76 (m, 6 H, C*H*$_2$); IR (film) 2980, 2955, 2888, 2239, 1435, 1337, 1326, 1201, 1118, 1061, 1026, 1005, 966, 947 cm^{-1}; MS *m*/*e* 153.0788 (calcd for $C_8H_{11}O_2N$, 153.0790). Anal. Calcd for $C_8H_{11}NO_2$: C, 62.73; H, 7.24; N, 9.14. Found: C, 62.55; H, 7.22; N, 9.02.

3-Benzoylcyclopentanone Ethylene Ketal (21). To a mixture of 1.0 g (8.3 mmol) of 3-cyanocyclopentanone ethylene ketal (**20**) and 80 mg of (0.44 mmol) cuprous iodide in 100 mL of THF was added 8.3 mL of (16.6 mmol) 2 M phenylmagnesium bromide ether solution. After refluxing overnight, the mixture was poured onto ice-saturated ammonium chloride and ether extracted and the combined organic layers were dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to yield 2.0 g of an oil which was purified with a 2.5 × 50 cm silica gel column eluted with 2% ether in hexane to give 1.7 g of (88%) 3-benzoylcyclopentanone ethylene ketal (**21**) as a colorless oil.

The spectral data were the following: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.98−7.41 (m, 5 H, arom), 3.90 (s, 4 H, OC*H*$_2$C*H*$_2$O), 3.97−3.83 (m, 1 H, C*H*COPh), 2.32−1.87 (m, 6 H, C*H*$_2$); IR (film) 2972, 2948, 2881, 1681, 1596, 1579, 1447, 1332, 1221, 1179, 1114, 1073, 1033, 1004, 973, 946, 698 cm^{-1}; MS *m*/*e* 232.1074 (calcd for $C_{14}H_{16}O_3$, 232.1099). Anal. Calcd for $C_{14}H_{16}O$: C, 72.39; H, 6.94. Found: C, 72.35; H, 6.93.

3-(Diphenylhydroxymethyl)cyclopentanone Ethylene Ketal (24). To a 100 mL THF solution of 1.7 g (7.3 mmol) of 3-benzoylcyclopentanone ethylene ketal (**21**) at −78 °C was added 9 mL (18 mmol) of 2 M phenylmagnesium bromide ether solution. The solution was stirred overnight and then poured onto ice-saturated ammonium chloride and ether extracted. The combined organic layers were dried over anhydrous magnesium sulfate, and the solvent was removed in vacuo to give 2.5 g of an oil which solidified upon standing. The solid was recrystallized in ether/hexane to give 2.1 g (92.5%) of 3-(diphenylhydroxymethyl)cyclopentanone ethylene ketal (**24**) as a colorless solid (mp 124.5−125.5 °C).

The spectral data for 3-(diphenylhydroxymethyl)cyclopentanone ethylene ketal (**24**) were the following: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.51−7.17 (m, 10 H, arom), 3.93−3.84 (m, 4 H, OC*H*$_2$C*H*$_2$O), 3.45 (quint, *J* = 8 Hz, 1 H, C*H*), 3.28 (s, 1 H, O*H*), 1.98−1.57 (m, 6 H, C*H*$_2$); IR (film) 3469, 3057, 3024, 2969, 2959, 2946, 2882, 1596, 1491, 1474, 1447, 1336, 1267, 1206, 1170, 1164, 1157, 1118, 1076, 1063, 1032, 1013, 960, 947, 892, 749, 701, 669 cm^{-1}; MS *m/e* 310.1578 (calcd for $C_{20}H_{22}O_3$, 310.1569). Anal. Calcd for $C_{20}H_{22}O_3$: C, 72.39; H, 6.94. Found: C, 72.35; H, 6.93.

3-Benzhydrylcyclopent-2-en-1-one (25). A mixture of 0.5 g (5.6 mmol) of oxalic acid in 35 mL of water and 1.2 g (3.9 mmol) of 3-(diphenylhydroxymethyl)cyclopentan-2-one ethylene ketal **24** in 50 mL of ether and 100 mL of hexane was refluxed for 30 min. The mixture was ether extracted and the combined organic layers were washed with 5% sodium bicarbonate and dried over anhydrous magnesium sulfate, and the solvent was removed in vacuo to yield 1.0 g of an oil which was refluxed with 0.5 g of toluenesulfonic acid monohydrate in 200 mL of toluene for 12 h with a Dean–Stark trap. The solution was cooled to rt and washed with saturated sodium bicarbonate and brine and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to yield 850 mg (88%) of an oil which solidified upon standing. Recrystallization in pentane gave 800 mg (83%) of 3-benzhydrylcyclopent-2-en-1-one (**25**) as colorless crystals (mp 68.5–69.5 °C).

The spectral data for 3-benzhydrylcyclopent-2-en-1-one (**25**) were the following: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.38–7.05 (m, 10 H, arom), 5.79 (s, 1 H, α-vinyl), 5.01 (s, 1 H, C*H*Ph$_2$), 2.63–2.36 (m, 4 H, C*H*$_2$); IR (film) 3083, 3059, 3027, 3002, 2920, 1708, 1680, 1611, 1600, 1494, 1451, 1232, 1179, 746, 703 cm^{-1}; MS *m/e* 248.1209 (calcd for $C_{18}H_{16}O$, 248.1201); UV (benzene) λ_{max} = 334 nm (ϵ = 60). Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.49. Found: C, 86.70; H, 6.62.

Solution Photolysis of 3-Benzhydrylcyclopent-2-en-1-one (25). A 250 mL benzene solution of 380 mg of 3-benzhydrylcyclopent-2-en-1-one (**25**) was photolyzed through a Pyrex filter and filter solution for 3 h. The solvent was removed in vacuo to give 384 mg of pale yellow oil which was chromatographed with a 3.5 × 50 cm silica gel column. Fraction 1, 302.0 mg of *trans*-5,6-diphenylbicyclo[3.1.0]-hexan-2-one (**52**) as a colorless solid. Recrystallization from ether/hexane yielded 280 mg (73.7%) of colorless prism crystals (mp 74.0–75.5 °C), (lit.[15,29] 73–74 °C). Fraction 2, 81.7 mg of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**51**) as a colorless solid. Recrystallization from ether/hexane yielded 71 mg of (18.7%) of colorless crystals (mp 116.0–117.0 °C), (lit.[9] 114–116 °C).

3-Phenethylcyclopent-2-en-1-one (23). To a 100 mL THF solution of 2.3 g (10 mmol) of 3-benzoylcyclopentanone ethylene ketal (**21**) at −78 °C was added 16.7 mL of (20 mmol) 1.2 M methyllithium. The solution was stirred for 4 h, allowed to warm to rt, and poured into a mixture of ice–ammonium chloride. To the solution was added 50 mL of 10% hydrochloric acid. The mixture was heated on a steam bath for 30 min, cooled to rt and ether extracted. The combined organic layers were combined, washed with 100 mL of 5% sodium carbonate, and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the residue was refluxed with 1.0 g of toluenesulfonic acid monohydrate in benzene for 2 h. The solution was cooled to rt, washed with saturated sodium bicarbonate, and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to give 1.4 g of a dark oil which was purified with a 3.5 × 50 cm silica gel column (with one inch of 1:1 Norite/silica gel on top) eluted with 5% ether in hexane. Fraction 1, 1.1 g (63%) of phenethylcyclopent-2-en-1-one (**23**) as a colorless oil.

The spectral data of 3-phenethylcyclopent-2-en-1-one (**23**) were the following: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.36–7.05 (m, 10 H, arom), 6.05 (s, 1 H, α-vinyl), 3.75 (q, *J* = 7 Hz, 1 H, C*H*Me), 2.48–2.25 (m, 4 H, C*H*$_2$), 1.53 (d, *J* = 7 Hz, 3 H, C*H*$_3$); IR (film) 3083, 3060, 3027, 2968, 2924, 2874, 2853, 1705, 1676, 1610, 1493, 1452, 1437, 1261, 1235, 1181, 864, 766, 702 cm^{-1}; MS *m/e* 186.1044 (calcd for $C_{18}H_{16}O$, 186.1045); UV (benzene) λ_{max} = 334 nm (ϵ = 47). Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.40; H, 7.67.

Solution Photolysis of Phenethylcyclopent-2-en-1-one (23). A solution of 615 mg of phenethylcyclopent-2-en-1-one (**23**) in 500 mL of benzene was photolyzed through a Pyrex filter for 2.5 h. The solvent was removed in vacuo to yield 613.7 mg of a pale yellow oil which was separated with a 2.5 × 50 cm silica gel column eluted with 1% ethyl acetate in hexane. Fraction 1, 109.6 mg of *endo*-6-methyl-5-phenylbicyclo[3.1.0]hexan-2-one (**50**) as a colorless oil; fraction 2, 401.0 mg of a mixture of *endo*/*exo*-6-methyl-5-phenylbicyclo[3.1.0]hexan-2-one (**50** and **51**); fraction 3, 86.5 mg of *exo*-6-methyl-5-phenylbicyclo-[3.1.0]hexan-2-one (**51**).[10] The mixture from fraction 2 was further separated with repetitive chromatography. The total amount of *endo*-6-methyl-5-phenylbicyclo[3.1.0]hexan-2-one (**50**) is 464.0 mg (75.4%). The total amount of *exo*-6-methyl-5-phenylbicyclo[3.1.0]hexan-2-one (**51**) was 110.9 mg (18.0%).

The spectral data for *endo*-6-methyl-5-phenylbicyclo[3.1.0]hexan-2-one (**50**) were the following: ^{1}H-NMR ($CDCl_3$, 200 MHz0 δ 7.36–7.17 (m, 15 H, arom), 2.59–2.38 (m, 2 H, C*H*$_2$CO), 2.28 (d, *J* = 10 Hz, 1 H, cyclopropyl-*H*), 2.18–1.99 (m, 1 H, C*H*$_2$), 1.80 (dq, *J* = 10.0, 6.5 Hz, 1 H, C*H*Me), 1.30 (d, *J* = 6.5 Hz, 3 H, C*H*$_3$); IR (film) 3056, 3027, 3002, 2958, 2952, 2935, 2911, 2891, 2872, 1719, 1601, 1499, 1462, 1446, 1412, 1297, 1230, 1188, 1131, 1088, 1033, 892, 763, 732 cm^{-1}; MS *m/e* 186.1047 (calcd for $C_{13}H_{14}O$, 186.1045). Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.81; H, 7.65.

The spectral data for *exo*-6-methyl-5-phenylbicyclo[3.1.0]hexan-2-one (**51**) were the following: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.82–7.21 (m, 5 H, arom), 2.62–2.08 (m, 4 H, C*H*$_2$), 1.92 (d, *J* = 3 Hz, 1 H, cyclopropyl-*H*), 1.73 (dq, *J* = 6.0, 3.0 Hz, 1 H, C*H*CH$_3$), 0.93 (d, *J* = 6.0 Hz, 3 H, C*H*$_3$); IR (film) 3079, 3056, 3027, 2989, 2958, 2930, 2872, 1724, 1683, 1669, 1602, 1497, 1460, 1457, 1446, 1417, 1369, 1356, 1296, 1239, 1204, 1177, 1128, 1093, 1079, 1064, 1027, 1002, 973, 953, 946, 922, 897, 761, 701 cm^{-1}; MS *m/e* 186.1035 (calcd for $C_{13}H_{14}O$, 186.1045). Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.68; H, 7.82.

2-Biphenylyl-2-phenylacetaldehyde (15). A procedure similar to that described by Corey and Chaykovsky[9,30] was employed. Trimethyloxosulfonium iodide (2.42 g, 11 mmol) prepared by the method of Kuhn and Trischmann[31] was dissolved in 30 mL of dimethyl sulfoxide under nitrogen. To the solution was slowly added 300 mg (12.5 mmol) of sodium hydride, obtained from 0.5 g of a 60% suspension in mineral oil and washed free of oil, during 15 min. A solution of 2.6 g (10 mmol) of *p*-benzoylbiphenyl in 10 mL of dimethyl sulfoxide was added to the dimethyloxosulfonium methylide during 10 min. The dark solution was stirred at rt for 1 h and then heated to 50–55 °C for 2 h. The hot reaction mixture was poured into ice–water and extracted with ether, washed with sodium bicarbonate and brine, and dried with anhydrous magnesium sulfate. The solvent was removed in vacuo to give 2.7 g (99%) of 1-phenyl-1-biphenylylethylene oxide as a light yellow oil. The IR spectrum showed no trace of starting material: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.58–7.33 (m, 14 H, arom), 3.31 (s, 2 H, epoxide C*H*$_2$). This material was used directly without further purification.

To a solution of 2.7 g (9.9 mmol) of 1-phenyl-1-*p*-biphenylylethylene oxide in a 30 mL benzene solution was added 1.4 g of boron trifluoride etherate (10 mmol). The solution was stirred for 2 min and then poured into a mixture of ether and saturated sodium bicarbonate. The mixture was shaken vigorously, and the organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to afford 2.7 g of a colorless oil which was chromatographed with a 2.5 × 50 cm silica gel column eluted with 3% ether in hexane to give 2.5 g (92%) of 2-*p*-biphenylyl-2-phenylacetaldehyde (**15**) as a colorless oil.

The spectral data were the following: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 8.97 (d, *J* = 2.0 Hz, 1 H, C*H*O), 6.66–6.22 (m, 14 H, arom), 3.93 (d, *J* = 2.0 Hz, 1 H, C*H*Ph$_2$); IR (film) 3065, 3030, 2820, 2725, 1735, 1605, 1500, 1460, 1430, 1075, 1030, 765, 748, 705 cm^{-1}; MS *m/e* 272.1203 (calcd for $C_{20}H_{16}O$, 272.1201). Anal. Calcd for $C_{24}H_{20}O$: C, 88.00; H, 5.83. Found: C, 88.33; H, 5.86.

4-Biphenylyl-4-phenylcyclohex-2-en-1-one (16). To a solution of 2.5 g (9.2 mmol) 2-*p*-biphenylyl-2-phenylacetaldehyde (**15**) and 0.64 g (9.2 mmol) of methyl vinyl ketone in 100 mL of anhydrous ether at 0 °C was added 0.5 mL of 3 N potassium hydroxide in anhydrous ethanol. The mixture was stirred at 0 °C for 1 h and at rt for 2 h. The final mixture was washed with 50 mL of 10% hydrochloric acid, water, and saturated sodium bicarbonate and dried over anhydrous magnesium sulfate. The organic solvent was removed in vacuo to afford 2.7 g of a colorless oil which solidified upon standing. The solid was

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(30) (a) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1962**, *84*, 867. (b) *Ibid.* **1965**, *87*, 1353.

(31) Kuhn, R.; Trischmann, H. *Ann.* **1958**, *611*, 117.

recrystallized in ether/hexane to afford 2.0 g (67.1%) of 4-phenyl-4-biphenylylcyclohex-2-en-1-one (**16**) as prism crystals (mp 101.0−102.0 °C).

The spectral data were the following: ^{1}H-NMR (CDCl$_3$, 200 MHz) δ 7.60−7.25 (m, 15 H, arom and β-vinyl), 6.24 (d, J = 10 Hz, 1 H, α-vinyl), 2.80−2.40 (m, 4 H, CH_2); IR (film) 3030, 3025, 2910, 1680, 1493, 1450, 1010, 765, 701 cm^{-1}; MS *m/e* 324.1506 (calcd for $C_{24}H_{20}O$, *m/e* 324.1514); UV (benzene) λ_{max} = 338 nm (ϵ = 43). Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.71; H, 6.25.

Exploratory Solution Photolysis of 4-Biphenylyl-4-phenylcyclohex-2-en-1-one (16). A solution of 410 mg (1.26 mmol) of 4-biphenylyl-4-phenylcyclohex-2-en-1-one (**16**) in 250 mL of benzene was photolyzed through a Pyrex filter for 1 h. The solvent was removed in vacuo to afford 415.6 mg of a pale yellow oil which was separated with a 2.5 × 50 cm silica gel column eluted with 2% ether in hexane. Fraction 1, 266.6 mg of 5-phenyl-*endo*-6-biphenylylbicyclo[3.1.0]hexan-2-one (**45**) as white solid. Recrystallization from ether gave 194 mg (47.3%) of prism crystals (mp 182.0−184.0 °C). X-ray crystallography supported the structure assignment (see supplementary material). Fraction 2, 139.8 mg of 5-phenyl-*exo*-6-biphenylylbicyclo[3.1.0]hexan-2-one (**46**) as a white solid. Recrystallization from ether gave 110 mg (26.8%) of **46** as a powderous solid (mp 132.5−133.0 °C). Fraction 3, 1.0 mg (0.24%) of 3-biphenylyl-4-phenylcyclohex-2-en-1-one (**47**) as a white solid (mp 149−151 °C).

The spectral data for 5-phenyl-*endo*-6-biphenylylbicyclo[3.1.0]hex-2-one (**45**) were the following: ^{1}H-NMR (CDCl$_3$, 200 MHz) δ 7.62−7.26 (m, 14 H, arom), 3.15 (d, J = 9.5 Hz, 1 H, cyclopropyl-*H*), 2.71 (d, J = 9.5 Hz, 1 H, cyclopropyl-*H*), 2.50−2.35 (m, 2 H, CH_2CO), 2.20−2.02 (m, 1 H, CH_2CPh), 1.35−1.12 (m, 1 H, CH_2CPh); IR (film) 3056, 3027, 2963, 2938, 1722, 1684, 1600, 1497, 1487, 1456, 1446, 1405, 1299, 1171, 1013, 1007, 835, 771, 761, 739, 698 cm^{-1}; MS *m/e* 324.1518 (calcd for $C_{24}H_{20}O$, *m/e* 324.1514). Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.97; H, 6.28.

The spectral data for 5-phenyl-*exo*-6-biphenylylbicyclo[3.1.0]hexan-2-one (**46**) were the following: ^{1}H-NMR (CDCl$_3$, 200 MHz) δ 7.60−6.80 (m, 14 H, arom), 2.86 (d, J = 3 Hz, 1 H, cyclopropyl-*H*), 2.86 (d, J = 3.0 Hz, 1 H, cyclopropyl-*H*), 2.73−2.30 (m, 4 H, CH_2); IR (film) 3051, 3026, 3004, 2954, 2937, 2929, 1715, 1600, 1487, 1445, 1416, 1235, 1212, 1194, 1167, 1122, 1073, 1037, 1025, 1005, 900, 845, 763, 730, 700, 692 cm^{-1}; MS *m/e* 324.1531 (calcd for $C_{24}H_{20}O$, 324.1514). Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.51; H, 5.96.

The spectral data for 3-biphenylyl-4-phenylcyclohex-2-en-1-one (**47**) were the following: ^{1}H-NMR (CDCl$_3$, 200 MHz) δ 7.60−7.15 (m, 14 H, arom), 5.84 (m, 1 H, C*H*Ph), 5.05 (s, 1 H, α-vinyl), 2.7−2.4 (m, 4 H, CH_2); IR (film) 2957, 2926, 2869, 1707, 1683, 1609, 1582, 1487, 1451, 1435, 1407, 1282, 1270, 1231, 1178, 1120, 1075, 1007, 840, 761, 739, 722, 698 cm^{-1}; MS *m/e* 324.1511 (calcd for $C_{24}H_{20}O$, 324.1514).

Exploratory Solution Photolysis of 5-Phenyl-*endo*-6-biphenylylbicyclo[3.1.0]hexan-2-one (45). A solution of 20 mg of 5-phenyl-*endo*-6-biphenylylbicyclo[3.1.0]hexan-2-one (**45**) in 2 mL of benzene-d_6 was photolyzed for 3 h through a Pyrex filter, and the solvent was removed in vacuo. The final mixture was separated with a 10 × 20 cm TLC plate eluted with 3% ether in hexane. Band 1, 10.1 mg of (50.5%) 5-phenyl-*endo*-6-biphenylylbicyclo[3.1.0]hexan-2-one (**45**); band 2, 5.1 mg of (25.5%) 5-phenyl-*exo*-6-biphenylylbicyclo[3.1.0]hexan-2-one (**46**), and band 3, 3.9 mg (19.5%) of 4-phenyl-3-biphenylylcyclohex-2-en-1-one (**47**).

Exploratory Solution Photolysis of 5-Phenyl-*exo*-6-biphenylylbicyclo[3.1.0]hexan-2-one (46). A solution of 14.5 mg of 5-phenyl-*exo*-6-biphenylylbicyclo[3.1.0]hexan-2-one (**46**) in 2 mL of benzene-d_6 was photolyzed for 3 h through a Pyrex filter. The final mixture was separated with a TLC plate eluted with 3% ether in hexane. Band 1, 8.5 mg (58.6%) of *endo*-5-phenyl-6-biphenylylbicyclo[3.1.0]hexan-2-one (**45**); band 2, 4.2 mg (29.0%) of 5-phenyl-*exo*-6-biphenylylbicyclo-[3.1.0]hexan-2-one (**46**), and band 3, 1.0 mg (6.9%) of 4-phenyl-3-biphenylylcyclohex-2-en-1-one (**47**).

Crystallization of 4-Biphenylyl-4-phenylcyclohex-2-en-1-one (16). Recrystallization of 4-biphenylyl-4-phenylcyclohex-2-en-1-one (**16**) by slow evaporation of its ether solution afforded a prism crystal of space group *P*-1. Recrystallization by slow evaporation from its methanol solution afforded another crystal modification of space group of P_{bca}.

Exploratory Solid State Photolysis of 4-Biphenylyl-4-phenylcyclohex-2-en-1-one (*P*-1 space group) (16). Single crystals (178 mg) of 4-biphenylyl-4-phenylcyclohex-2-en-1-one (**16**) from ether slow evaporation (*P*-1) were photolyzed in an NMR tube through a Pyrex filter for 48 h. The NMR tube was rotated every 6 h. The photolysis mixture was separated with a 3.0 × 75 cm silica gel column eluted with 5% ether in hexane. Fraction 1, 137 mg of starting material. Fraction 2, 18.8 mg (11.1%) of photodimer **56** as a white powdery solid (mp 392−395 °C dec). The solid was recrystallized from chloroform to give a colorless prism crystal containing solvent which lost chloroform upon standing in air to become a white powder. The structure of the photodimer was determined with X-ray crystallography (see supplementary material).

The spectral data were the following: ^{1}H-NMR (CDCl$_3$, 200 MHz) δ 7.54−7.07 (m, 28 H, arom), 3.75 (m, 2 H), 3.08 (m, 4 H), 2.83−2.37 (m, 4 H), 1.96−1.76 (m, 2 H); IR (film) 3030, 3025, 2910, 1680, 1493, 1450, 1010, 765, 701 cm^{-1}; MS *m/e* 324.1506 (calcd for $C_{24}H_{20}O$, 324.1514). Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.71; H, 6.25.

4-(*p*-Ethynylphenyl)-4-phenylcyclohex-2-en-1-one (18).[32] To a mixture of 10 mg of cuprous iodide (0.05 mmol), 18 mg of (0.1 mmol) bis(triphenylphosphine)palladium dichloride, and 3.27 g (10 mmol) of 4-(*p*-bromophenyl)-4-phenylcyclohex-2-en-1-one (**17**) in 10 mL of diethylamine was added 1.08 g (11 mmol) of (trimethylsilyl)acetylene in 5 mL of diethylamine. The mixture was refluxed for 4 h and stirred overnight at rt during which a white precipitate developed. The final mixture was filtered to give 1.2 g (78%) diethylammonium chloride as a white solid. The filtrate was concentrated in vacuo and the residue was dissolved in hexane and filtered through a thin pad of silica gel. The filter pad was washed with 200 mL of 20% ether in hexane. The solvent was removed in vacuo to afford 2.5 g of a yellow oil which was mixed with 200 mL of methanol and 1.0 g of potassium carbonate and stirred overnight. The mixture was filtered, and the filtrate was concentrated in vacuo to afford a dark brown oil which was purified with a 3.5 × 75 cm silica gel column eluted with 5% ether in hexane to give 2.1 g of 4-(*p*-ethynylphenyl)-4-phenylcyclohex-2-en-1-one (**18**) as a pale yellow oil which solidified upon standing (mp 102.0−103.0 °C). The solid was recrystallized in ethanol to give 1.8 g (66%) of a colorless crystal (mp 102.0−102.5 °C). The structure of the **18** was determined with X-ray crystallography (see supplementary material).

The spectral data were the following: ^{1}H-NMR (CDCl$_3$, 200 Hz) δ 7.47−7.09 (m, 10 H, arom), 6.22 (d, J = 10.0 Hz, 1 H, α-vinyl), 3.07 (s, 1 H, acetylene), 2.71−2.39 (m, 4 H, CH_2); IR (film) 3029, 2954, 2896, 2875, 2107, 1682, 1599, 1494, 1455, 1445, 1412, 1385, 1329, 1257, 1226, 1217, 1189, 1018, 890, 833, 759, 734, 701, 664 cm^{-1}; MS *m/e* 272.1198 (calcd for $C_{20}H_{16}O$, 272.1201); UV (benzene) λ_{max} = 324 nm (ϵ = 79). Anal. Calcd for $C_{20}H_{16}O$: C, 88.15; H, 5.92. Found: C, 88.14; H, 6.02.

Exploratory Solution Photochemistry of 4-(*p*-Ethynylphenyl)-4-phenylcyclohex-2-en-1-one (18). A 250 mL benzene solution of 408.5 mg of 4-phenyl-4-(*p*-ethynylphenyl)cyclohex-2-en-1-one (**18**) was photolyzed through a Pyrex filter for 2 h. The solvent was removed in vacuo to yield 418 mg of a colorless oil which was separated with a 3.5 × 50 cm silica gel column eluted with 3% ether in hexane. Fraction 1, 213.2 mg of *endo*-6-(*p*-ethynylphenyl)-5-phenylbicyclo-[3.1.0]hexan-2-one (**48**) as a colorless solid which was recrystallized from ether/hexane to give 151 mg (37%) of prism crystals (mp 104.0−105.5 °C). Fraction 2, 196.3 mg of *exo*-6-(*p*-ethynylphenyl)-5-phenylbicyclo[3.1.0]hexan-2-one (**49**) as a white solid which was recrystallized from ether/hexane to give 160 mg (39.2%) of prism crystals (mp 126.0−128.0 °C). The structure of photoproducts **48** and **49** were determined with X-ray crystallography (see supplementary material).

The spectral data for *endo*-6-(*p*-ethynylphenyl)-5-phenylbicyclo-[3.1.0]hexan-2-one (**48**) were the following: ^{1}H-NMR (CDCl$_3$, 200 MHz) δ 7.51−7.25 (m, 10 H, arom), 3.10 (s, 1 H, acetylene), 3.08 (d, J = 10.5 Hz, 1 H, cyclopropyl-*H*), 2.68 (d, J = 10.5 Hz, 1 H, cyclopropyl-*H*), 2.47−2.03 (m, 3 H, CH_2CO, CH_2), 1.10 (dt, J = 19.0, 4.5 Hz, 1 H, CH_2); IR (film) 3286, 3058, 3029, 2964, 2941, 2885, 2107, 1722, 1684, 1602, 1506, 1457, 1446, 1406, 1318, 1299, 1260,

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1227, 1202, 1171, 1146, 1108, 1029, 1014, 951, 919, 895, 884, 865, 834, 759, 699 cm^{-1}; MS *m/e* 272.1202 (calcd for $C_{20}H_{16}O$, 272.1201). Anal. Calcd for $C_{20}H_{16}O$: C, 88.15; H, 5.92. Found: C, 88.36; H, 5.96.

The spectral data for *exo*-6-(*p*-ethynylphenyl)-5-phenylbicyclo[3.1.0]-hexan-2-one (**49**) were the following: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.30−6.65 (m, 10 H, arom), 3.01 (s, 1 H, acetylene), 2.80 (d, J = 3.0 Hz, 1 H, cyclopropyl-*H*), 2.64 (d, J = 3.0 Hz, 1 H, cyclopropyl-*H*), 2.46−2.28 (m, 4 H, CH_2); IR (film) 3289, 3258, 3082, 3061, 3025, 2969, 2940, 2870, 2106, 1725, 1605, 1507, 1497, 1458, 1445, 1415, 1388, 1295, 1281, 1259, 1233, 1191, 1168, 1117, 1074, 1061, 1026, 984, 951, 912, 895, 845, 760, 742, 700 cm^{-1}; MS *m/e* 272.1205 (calcd for $C_{20}H_{16}O$, 272.1201). Anal. Calcd for $C_{20}H_{16}O$: C, 88.15; H, 5.92. Found: C, 87.75; H, 5.92.

5,5-Diphenylcyclohex-1,3-dien-2-ol Trimethylsilyl Ether (11).[33] To a 100 mL ether solution of lithium diisopropylamide at −78 °C made from 14.8 mL of 1.5 M (22.2 mmol) butyllithium and 2.04 g (2.82 mL, 20.2 mmol) of diisopropylamine was added 5.0 g (20.2 mmol) of 4,4-diphenylcyclohex-2-en-1-one in 70 mL of ether. After the solution was stirred for 10 min, 5.2 mL (40.2 mmol) of trimethylsilylchloride was added. The final reaction mixture was poured onto ice-saturated ammonium chloride and ether extracted, and the combined organic layers were dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the residue was distilled at reduced pressure (bp 210.0−215.0 °C/2.0 mmHg) to give 5.43 g (84%) of **11** as a colorless oil which solidified upon storage at −10 °C (mp 35.0−36.0 °C).

The spectral data were the following: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.33−7.13 (m, 10 H, arom), 6.33 (d, J = 10.0 Hz, 1 H, α-vinyl), 5.84 (dd, J = 10.0, 2.0 Hz, 1 H, β-vinyl), 4.96 (dt, J = 4.0, 2.0 Hz, 1 H, α-vinyl), 2.88 (d, J = 4.0 Hz, 2 H, CH_2), 0.09 (s, 9 H, CH_3); IR (film) 2894, 2876, 2835, 1685, 1651, 1596, 1576, 1491, 1444, 1396, 1251, 1215, 1190, 1162, 1035, 1005, 935, 911, 902, 886, 845, 768, 752, 698 cm^{-1}; MS *m/e* 320.1591 (calcd for $C_{21}H_{24}OSi$, *m/e* 320.1596).

6-(3,3-Diphenylpropyl)-4,4-diphenylcyclohex-2-en-1-one (13).[34] A mixture of 0.52 g of tetrabutylammonium fluoride (TBAF), 3.0 g of 4 Å molecular sieves, and 4 mL of THF were stirred until the molecular sieves were pulverized (4 h). To the mixture were added 1.0 g (3.1 mmol) of 5,5-diphenylcyclohex-1,3-dien-2-ol trimethylsilyl ether (**11**) and 1.0 g (3.1 mmol) of 3,3-diphenylpropyl iodide in 10 mL of THF. The mixture was stirred overnight and filtered, and the solid was washed with 100 mL of ether. The solvent was removed in vacuo to give an oil which was chromatographed on a 2.5 × 50 cm silica gel column to give 0.6 g (44%) of 6-(3′,3′-diphenylpropyl)cyclohex-2-en-1-one (**13**) as a white solid. The solid was recrystallized in ethanol to give a 0.55 g (40%) of a white solid (mp 119.0−120.0 °C). The structure of enone **13** was determined with X-ray crystallography (see supplementary material).

The spectral data for 6-(3′,3′-diphenylpropyl)cyclohex-2-en-1-one (**13**) were the following: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.40−7.10 (m, 21 H, arom and α-vinyl), 6.15 (d, J = 10 Hz, 1 H, β-vinyl), 3.78 (t, J = 8.0 Hz, 1 H, C*H*), 2.68−2.63 (m, 1 H), 2.48−2.33 (m, 2 H), 2.12−1.96 (m, 2 H), 1.89−1.75 (m, 1 H), 1.44−1.33 (m, 1 H); IR (film) 3083, 3058, 3025, 2927, 2866, 1679, 1598, 1582, 1492, 1447, 1383, 1225, 1218, 1188, 1157, 1090, 1080, 1061, 1031, 1001, 754, 700 cm^{-1}; MS *m/e* 442.2305 (calcd for $C_{33}H_{30}O$, 442.2297); UV (benzene) λ_{max} = 334 nm (ϵ = 32.1). Anal. Calcd for $C_{33}H_{30}O$: C, 89.55; H, 6.83. Found: C, 89.37; H, 7.09.

Crystal Packing from the X-ray Crystallography Results. Computational crystal packing was accomplished by the following algorithm. (i) The lattice coordinates of the independent molecule(s) was (were) read from the X-ray structure output (filename.res) from Shelxtl or Shelx93. (ii) The space group symmetries were applied to the independent molecule(s) to generate symmetry equivalent molecules. (iii) All the molecules generated were translated into a closely packed cluster so that the closest distance between any two molecules was within unit cell dimensions. This is important to insure complete packing. (iv) A large crystal packing was generated with the original independent molecule in the center by displacement of the first cluster in the a, b, and c directions to form a packing 5 × 5 × 5 the original size. (v) The lattice coordinates of the large packing were transformed into Cartesian coordinates using the unit cell parameters. The big crystal lattice was reduced in size by deletion of the outer molecules of the packing whose closest distance to any atom of the central molecule was greater than 5.0 Å. The final reduced crystal lattice was usually composed of more than 18 molecules, depending on the molecular size.

MM3 Calculation. The MM3 (92) force field[18a] was used to generate the reaction intermediates and to obtain the crystal packing energies. The diradical I conformations were generated with molecular mechanics by treating the radical centers as sp^2 carbons. For missing force constants in MM3, corresponding MM2 force constants and closely related force constants were employed. Throughout the study, energies were compared between two geometric isomers so that the systematic errors from the force constants canceled out. The geometries and energies of the triplet states of all the diradicals I of the 5-substituted enones (i.e. **2**−**6**, **9c**, and **9t**) were also obtained with semiempirical AM1 calculations.[18b] The energy differences between the pairs of stereoisomers from MM3 and AM1 were comparable, and the RMS difference between the geometries from these two different methods were less than 0.3 Å.

The energies of the starting molecules in the crystal packings as described above were obtained by geometrically optimizing the central molecule while fixing the rest of the lattice. The energies of the reaction intermediates in the crystal lattice were also obtained similarly by replacing the starting molecule with the appropriate diradical I. All the nitriles were treated as localized systems as recommended in MM3. All the lattice energy calculations were carried out with the block diagonalization minimization method. The reaction intermediates being put into the crystal cavity before minimization were in conformations superimposed onto the starting molecule in its crystal conformation. It has been found that in most cases, the optimized energies of the reaction intermediates were independent of superimposed conformations.

Flexible and Rigid Superpositions. Marcomodel 4.0[16] and Flexit[17] were used for the computation of the superimposed conformations of the reaction intermediates onto corresponding starting material in its crystal conformation. In doing this, the RMS distances between the corresponding atoms from the starting molecule and its diradicals I were minimized. Two slightly different superimposition methods were used (i.e. rigid and flexible). The rigid superpositions were carried out for all the atoms in the molecule with the diradical conformations fixed. The flexible superpositions were carried out for nonterminal atoms by altering all the nonring dihedral angles.

Overlap Calculations of Reaction Intermediates in Their Crystal Lattice. An algorithm for the computation of overlaps between the molecule of interest and the crystal lattice based on a similar program used by Zimmerman and Zuraw[3] was developed. The Van der Waals radii used in the computation were 1.85 Å for carbon, 1.20 Å for hydrogen, 1.50 Å for nitrogen, and 1.40 Å for oxygen.[35]

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Supplementary Material Available: X-ray crystal structure data (193 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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