electrostatic interaction between the ground states of $C_{11}PN^+$ and PMA at pH 8. It is also noted that the absorption spectrum is significantly and abruptly changed on the addition of $C_{10}TAB$ above the CAC. Spectra c and d show blue shifts compared to a and b but still show a red shift compared to that in water. It is also noted that there is a narrowing of all 0–0 transition bonds in the systems above the CAC, giving rise to an increase in the absorbance maxima. These trends are similar to the spectral charges observed in hydrophobic media such as compact PMA coils at pH 2 (spectrum e). None of the changes stated above for $C_{11}PN^+$ were observed in the case of pyrene.

Summary

This study shows that a conformational transition of PMA is induced by C_nTAB. The stretched PMA chain at pH 8 collapses on addition of the cationic surfactants, i.e., the cationic surfactants caused neutralized PMA chain refolding, thus providing a hydrophobic host place for fluorescent probes pyrene and/or its derivatives.

The hydrophobic aggregates are formed in cooperative processes once the surfactant concentration exceeds a certain concentration called the critical aggregation concentration, CAC, which is 1.4–1.7 orders of magnitude lower than the cmc of the C_nTAB micelle. The CAC is chain length dependent and also depends on the PMA concentration. On the basis of the measurements of the average aggregation number, decay rate constants, bimolecular quenching constants, and polarization studies, it is suggested that the aggregates of PMA–$C_{10}TAB$ are large structures consisting of about 100 $C_{10}TAB$ molecules and 1 coiled polymer chain. This is depicted as a hydrophobic but a loosely assembled structure with a surface of low-charge density. The interior of the aggregate has a hydrophobicity that is similar to that of micelle. However, the bromide ions are only in bulk aqueous phase and not close to the surface of the aggregate.

Studies using $C_{11}PN^+$ provide further information about the effect of positive charge on the interaction of the fluorescent probe with PMA chains (pH 8) and on the aggregate of PMA–$C_{10}TAB$. Both emission and absorption spectra show that the nature of the interaction and environment of $C_{11}PN^+$ are abruptly changed at concentrations of $C_{10}TAB$ above the CAC, i.e., from an electrostatic bonding with PMA chains in the water phase to solubilization in a hydrophobic aggregate.

This study also shows that the fluorescence probing technique is a very useful and powerful tool for investigations of conformational transition of polyelectrolytes as induced by cationic surfactants, pH, or other means.

Acknowledgment. We thank the National Science Foundation for support of this work via Grant CHE-01226-02.

Registry No. $C_{10}TAB$, 2082-84-0; $C_{12}TAB$, 1119-94-4; $C_{16}TAB$, 57-09-0; C_6TAB, 2650-53-5; C_8TAB, 2083-68-3; $C_{16}TAC$, 112-02-7; $C_{12}TAC$, 112-00-5; C_4PN^+, 81341-11-9; $C_{11}PN^+$, 103692-03-1; PyC_9COOH, 64701-47-9; $PySO_3Na$, 59323-54-5; $Ru(bpy)_3^{2+}2Cl^-$, 14323-06-9; $TlNO_3$, 10102-45-1; O_2, 7782-44-7; CH_3NO_2, 75-52-5; NaI, 7681-82-5; Py, 129-00-0; PyC_3COOH, 3443-45-6; poly(methacrylic acid), 25087-26-7.

A Photochemical Reaction Leading from Cyclohexenones to Cyclobutanones; Mechanistic and Exploratory Organic Photochemistry[1,2]

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Abstract: In previous studies vinylcyclobutanones were encountered as minor products of the photochemistry of cyclohexenones. In the present investigation the structural features required for this reaction were explored. It was found that increased phenyl substitution at carbon five of the cyclohexenone enhanced cyclobutanone formation. Thus, in this study the photochemistry of 4,5,5-triphenylcyclohex-2-en-1-one and 4-methyl-5,5-diphenylcyclohex-2-en-1-one was investigated. In the triphenyl enone photochemistry, cyclobutanone formation reached 20% while in the methyl diphenyl enone case, cyclobutanone formation was the only process observed. The photolysis of 4,5,5-triphenylcyclohex-2-en-1-one led to 60% of 3,5,5-triphenylcyclohex-2-en-1-one, 16% of *exo*-4,4,6-triphenylbicyclo[3.1.0]hexan-2-one, 16% of 2-*trans*-styryl-3,3-diphenylcyclobutanone, and 4% of the *cis*-styryl cyclobutanone. The total quantum yield was 0.15. In the instance of the photochemistry of 4-methyl-5,5-diphenylcyclohex-2-en-1-one only 2-*trans*-propenyl-3,3-diphenylcyclobutanone was formed. The quantum yield in this case was 0.012. Acetophenone sensitization of the two enones led to the same products and efficiencies as observed for the direct irradiations. Triplet rates were measured. A test was devised to determine if a diradical mechanism or, alternatively, a 1,3-sigmatropic process was responsible for cyclobutanone formation. For this purpose the methyl diphenyl enone and its propenyl cyclobutanone product were resolved. Photolysis of the cyclohexenone afforded primarily racemic diphenyl propenyl cyclobutanone with residual 6% enantiomeric excess. Unreacted diphenyl cyclohexenone showed no racemization. Control runs showed vinyl cyclobutanone product was not racemizing under either photolysis or isolation conditions. This evidence suggested a mechanism involving fission of bond 4–5 to afford a diradical stabilized by the two C-5 phenyl groups. Attack of the diphenylmethyl radical center on C-2 then leads to cyclobutanone product. The slight residual chirality is attributed to a rate of diradical conformational equilibration not quite rapid enough to give complete racemization. A concerted 1,3-sigmatropic rearrangement mechanism, with benzhydryl migrating with equal probability on the two π-faces, is excluded by the exclusive formation of *trans*-propenyl product. The photochemistry of the triphenyl enone is also discussed from a mechanistic viewpoint. Finally, the ethylvinyloxy diradical is noted to be involved in a number of photochemical reactions.

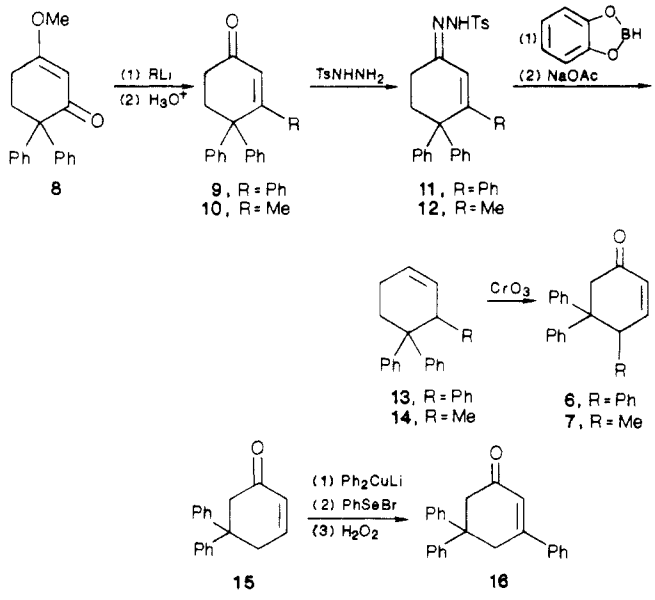
The photochemistry of 4-aryl-substituted cyclohexenones has been a subject of considerable interest. The initial report[3a] revealed that irradiation of 4,4-diphenylcyclohexenone (**1**) led to *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**2**) as the major product.

(1) This is Paper 149 of our photochemical series and Paper 207 of our general series.

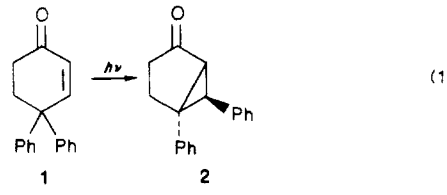
(2) For Paper 148 see: Zimmerman, H. E.; Binkley, R. W. *Tetrahedron Lett.* **1985**, 5859–5862.

0002-7863/86/1508-6276$01.50/0

Scheme I. Synthesis of Photochemical Reactants and One Potential Photoproduct

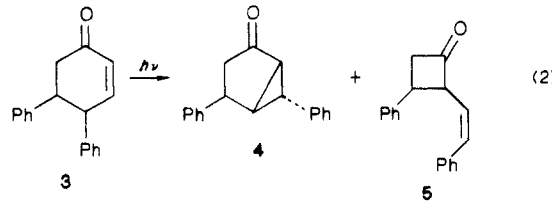


Subsequent studies were directed at the reaction mechanism, multiplicity, migratory aptitudes, and excited state rates.[3b-e,4,5] Note eq 1 as an example of the reaction.



(1)

Interestingly, as minor products in some of these studies of monocyclic cyclohexenones, those having C-5 phenyl groups, 2,3-substituted cyclobutanones were observed. One example[4] is presented in eq 2. Additionally, two related examples[5,6] are known, namely the cases of 4,4,5-triphenylcyclohexenone[5] and verbenone.[6]



(2)

Since one plausible mechanism for cyclobutanone formation involved a diradical engendered by fission of bond-4,5 with C-5 bearing an odd electron, it was of interest to investigate cyclohexenones bearing two C-5 phenyl groups which might further stabilize such diradicals. For this study 4,5,5-triphenylcyclohex-2-en-1-one (**6**) and 4-methyl-5,5-diphenylcyclohex-2-en-1-one (**7**) were selected.

Results

Synthesis of Photochemical Reactants and Potential Photoproducts. The syntheses of the desired 4,5,5-triphenylcyclohex-2-en-1-one (**6**) and 4-methyl-5,5-diphenylcyclohex-2-en-1-one (**7**) both began with the known[7] 6,6-diphenyl-3-methoxycyclohex-2-en-1-one (**8**). The synthesis required a 1,2-carbonyl transposition in converting triphenyl enone **9** to the isomeric triphenyl enone **6** as well as the methyl diphenyl enone **10** to enone **7**. Although the individual steps involved known reactions,[8,9] the sequence appears not to have been used for carbonyl transposition. The advantage of this sequence is its brevity. The overall chemistry, along with a synthesis of triphenyl enone **16**, is outlined in Scheme I.

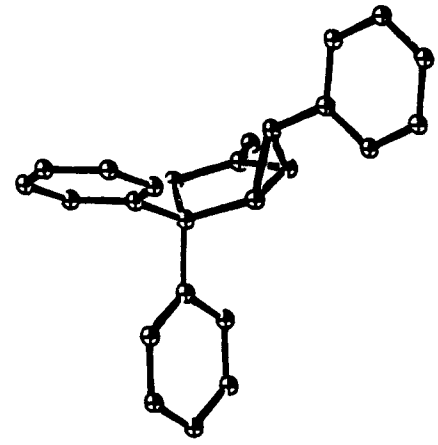
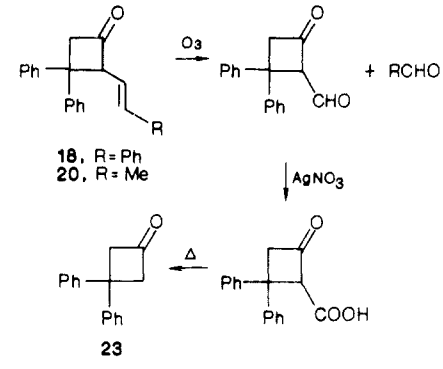


Figure 1. Ortep drawing of bicyclo[3.1.0] photoproduct **17**.

Scheme II. Degradation of the Vinyl Cyclobutanone Photoproducts



Exploratory Photochemical Efforts and Photoproduct Identification in the Case of Triphenyl Enone 6. Direct irradiation of the triphenyl cyclohexenone **6** led to four photoproducts: A, B, C, and D. Product A, mp 117–117.5 °C and formed in 60% yield, proved identical with the synthetic 3,5,5-triphenylcyclohex-2-en-1-one **16**. Photoproduct B (16%), mp 146–147.5 °C, was identified as *exo*-4,4,6-triphenylbicyclo[3.1.0]hexan-2-one (**17**) by X-ray structure determination. Note the Ortep drawing in Figure 1. Photoproducts C, mp 95–96 °C (16%), and D, mp 63–64 °C (4%), were identified as 2-(*trans*-styryl)-3,3-diphenylcyclobutanone (**18**) and its cis stereoisomer **19**, respectively. In the case of the *trans*-styryl cyclobutanone **18** the four-ring structure was suggested by the infrared carbonyl absorption at 1778 cm^{-1}. The precise structure was then elaborated by degradation as depicted in Scheme II, and the stereochemistry of the styryl moiety was established as trans by the typical[10] J = 17 Hz vinyl–vinyl coupling (vs. ca. 10 Hz for cis).

In the case of photoproduct D, the cyclobutanone structure was indicated by the infrared peak at 1782 cm^{-1}. The proton NMR spectrum revealed an AB quartet attributed to an aliphatic CH_2 moiety and a complex ABC pattern ascribable to the CH—CH=CHPh group comprising a ring methine and the styryl

(3) (a) Zimmerman, H. E.; Wilson, J. W. *J. Am. Chem. Soc.* **1964**, *86*, 4036–4042. (b) Zimmerman, H. E.; Hancock, K. G. *J. Am. Chem. Soc.* **1968**, *90*, 3749–3760. (c) Zimmerman, H. E.; Rieke, R. D.; Scheffer, J. R., *J. Amer. Chem. Soc.* **1967**, *89*, 2033–2047. (d) Zimmerman, H. E.; Lewin, N., *J. Amer. Chem. Soc.* **1969**, *91*, 879–886. (e) Zimmerman, H. E.; Elser, W. R. *J. Amer. Chem. Soc.* **1969**, *91*, 887–896.

(4) Zimmerman, H. E.; Sam, D. J. *J. Am. Chem. Soc.* **1966**, *88*, 4905–4914.

(5) Zimmerman, H. E.; Morse, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 954–966.

(6) (a) Hurst, J. J.; Whitham, G. H. *J. Chem. Soc.* **1960**, 2864–2869. (b) Erman, W. F. *J. Am. Chem. Soc.* **1967**, *89*, 3828–3841. (c) Shaffer, G. W.; Pesaro, M. *J. Org. Chem.* **1974**, *39*, 2489–2492.

(7) Zimmerman, H. E.; Pasteris, R. J. *J. Org. Chem.* **1980**, *45*, 4876–4891.

(8) Kabalka, G. W.; Baker, J. D.; Neal, G. W. *J. Org. Chem.* **1977**, *42*, 512–517.

(9) Dauben, W. G.; Lorber, M.; Fullerton, D. S. *J. Org. Chem.* **1969**, *34*, 3587–3592.

(10) Abraham, R. J.; Loftus, P. *Proton and Carbon 13 NMR Spectroscopy*; Heyden & Sons Ltd.: London, 1980; p 41.

Table I. Reaction Quantum Yields[a]

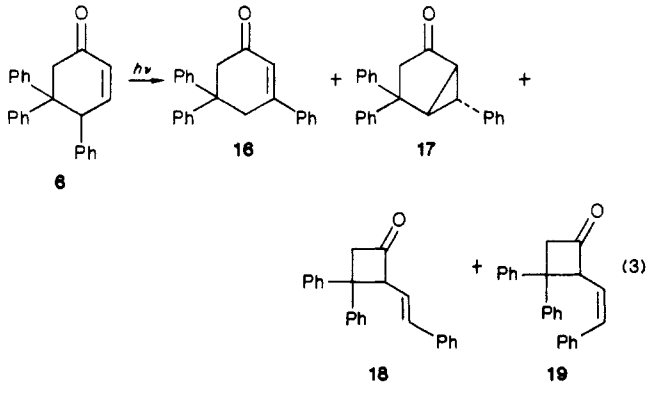
reactant	product	ϕ(DIR)	ϕ(SENS)[b]
4,5,5-triphenyl enone	3,5,5-cyclohexenone **16**	0.087	0.084
	exo-bicyclo[3.1.0] **17**	0.031	0.032
	trans-cyclobutanone **18**	0.029	0.026
	cis-cyclobutanone **19**	0.008_4	0.009_3
methyl diphenyl enone	cyclobutanone **20**	0.012	0.011

[a] Solvent benzene. [b] Acetophenone sensitizer employed.

side chain. The ^{13}C NMR was helpful in confirming the presence of the carbonyl carbon and three saturated (i.e., the ring) carbons. Note the Experimental Section for details. Hence the presence of four ring atoms—one carbonyl carbon and three additional carbons—was apparent. An INEPT experiment[11] provided evidence for the CH_2, CPh_2, C=O, and CH ring carbons as well as ruling out structures having a terminal olefinic $=CH_2$ as in structures of the types $CH{=}CH_2$ and $CPh{=}CH_2$. The evidence thus supports the presence of the C_2H_2Ph side chain.

Finally, the mass spectra of photoproducts C and D afforded peaks at 144.0575 and 180.0939, corresponding to the $Ph_2C{=}CH_2$ and the Ph—CH=CH—CH=C=O fragments which would be anticipated from a reverse $\pi^2_s + \pi^2_s$ fission of the four-membered ring.

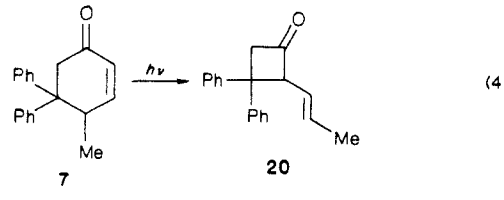
Thus the photochemistry of 4,5,5-triphenylcyclohex-2-en-1-one (**6**) may be depicted as outlined in eq 3.



Exploratory Photochemical Efforts and Photoproduct Identification in the Case of Methyl Diphenyl Enone 7. Irradiation of 4-methyl-5,5-diphenylcyclohex-2-en-1-one (**7**) led to a single photoproduct, mp 71–72 °C, in excellent (93–97%) yield. Again, the infrared spectrum was suggestive of a cyclobutanone structure. The NMR spectrum was analogous to that of the *trans*-styryl cyclobutanone (i.e., **18**) obtained from the parallel triphenyl cyclohexenone irradiations. These NMR data, summarized in the Experimental Section, pointed toward 2-*trans*-propenyl-3,3-diphenylcyclobutanone (**20**) as the structure of the photoproduct.

Confirmation of this assignment of structure derived from a degradative scheme parallel to that utilized previously in the triphenyl cyclohexenone photochemistry. This degradation is included in Scheme II.

Hence the photochemistry of the methyl diphenyl cyclohexenone **7** may be outlined as in eq 4.



Multiplicity and Quantum Yield Studies. We turned next to determining the reaction quantum yields and to elucidating the multiplicity of the cyclohexenone to cyclobutanone reaction. For both enones—the triphenyl cyclohexenone **6** and the methyl diphenyl enone **7**—the same products were observed from sensitized as from direct irradiations, with identical distributions and efficiencies. Note Table I. The "fingerprint method"[3b,c,12] then suggests that the same triplet excited state is utilized in both direct and sensitized photolyses. In the case of the methyl diphenyl cyclohexenone **7**, the fingerprint identification is weaker since only a single product is formed. However, the identity of the quantum efficiencies provides an independent check.

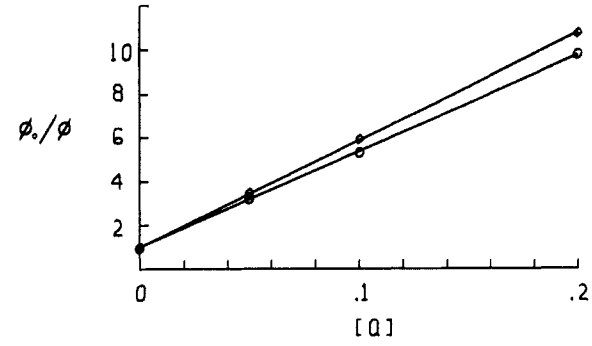


Figure 2. Stern–Volmer plot of ϕ_0/ϕ vs. cyclohexadiene concentration. Circles correspond to quenching of **6**, diamonds correspond to quenching of **7**, and the solid mark refers to both plots.

Still another point of interest is that the reaction efficiency proved independent of solvent polarity, that is, whether acetonitrile or benzene was employed; note the Experimental Section for details.

Linear Stern–Volmer quenching by cyclohexadiene was observed for both cyclohexenones with the quencher concentration in the range of 10^{-1} to 10^{-3} M. This provides further convincing evidence for the triplets being the reactive species (vide infra).

Determination of Excited State Rate Constants. Stern–Volmer treatment of the quenching data, plotting ϕ_0/ϕ vs. cyclohexadiene quencher concentration, led to $k_q\tau$ values for the slopes. The quenching rate used for k_q was the bimolecular rate of diffusion in benzene, namely 6.0×10^9 s^{-1}.[13] This choice is intimately tied to the assumption that the reacting cyclohexenone triplet has a 69-kcal/mol energy.[14] A 61–63 kcal/mol twisted cyclohexenone triplet has recently been reported by Schuster, Bonneau, and Joussot-Dubien[15a,b] and also Pienta.[15c] This low-energy triplet, which is quenched appreciably more slowly than the rate of diffusion, is not quenched by cyclohexadiene.

In contrast, the cyclohexenones of the present study are quenched by cyclohexadiene; hence, the relaxed triplet seems not to be responsible for the observed photochemistry. Therefore the rate of quenching of the vertically excited triplet[13] was used in the Stern–Volmer studies.

The Stern–Volmer plots are given in Figure 2. The derived lifetimes and rates of triplet decay and reaction are listed in Table III.

Check for Possible Ketene Formation. Since the formally related photochemistry of verbenone is known[6] to proceed in part via a fragmentation process affording a ketene intermediate, it seemed

(11) Doddrell, D. M.; Pegg, D. T. *J. Am. Chem. Soc.* **1980**, *102*, 6388–6390.

(12) (a) Zimmerman, H. E.; Lewis, R. G.; McCullough, J. J.; A. Padwa, A.; Staley, S.; Semmelhack, M. *J. Am. Chem. Soc.* **1966**, *88*, 159–161. (b) Zimmerman, H. E.; Hancock, K. G.; Licke, G. *J. Am. Chem. Soc.* **1968**, *90*, 4892–4911.

(13) (a) Wagner, P. J.; Kochevar, I. *J. Am. Chem. Soc.* **1968**, *90*, 2232–2238. (b) Wagner, P. J.; Spoerke, R. W. *J. Am. Chem. Soc.* **1969**, *91*, 4437–4440. (c) Scaiano, Lissi, and Stewart (Scaiano, J. C.; Lissi, E. A.; Stewart, L. C. *J. Am. Chem. Soc.* **1984**, *106*, 1539–1542) have reported a value of 6.0×10^9 $L \cdot M^{-1} \cdot s^{-1}$ for the quenching of *p*-methoxyacetophenone by oxygen in benzene and similar values for analogous quenching of various ketones by dienes in this solvent.

(14) (a) Note the discussion of this point in some recent publications.[13b-d] (b) Zimmerman, H. E.; Jian-hua, Xu; King, R. K.; Caufield, C. E. *J. Am. Chem. Soc.* **1985**, *107*, 7724–7732. (c) Zimmerman, H. E.; Caufield, C. E.; King, R. K. *J. Am. Chem. Soc.* **1985**, *107*, 7732–7744. (d) Zimmerman, H. E.; Lynch, D. C. *J. Am. Chem. Soc.* **1985**, *107*, 7745–7756.

(15) (a) Schuster, D. I.; Bonneau, R.; Dunn, D. A.; Rao, J. M.; Joussot-Dubien, J. *J. Am. Chem. Soc.* **1984**, *106*, 2706–2707. (b) Chan, C. B.; Schuster, D. I. *J. Am. Chem. Soc.* **1982**, *104*, 2928–2929. (c) Pienta, N. J. *J. Am. Chem. Soc.* **1984**, *106*, 2704–2705.

Table II. Summary of Stereochemical Reaction Course Observed[a]

(A) Photolysis of Optically Active Enone

run no.	% conv	rel amt of cyclobutanone added (mol ratio)[b]	opt activity of recovered cyclohexenone,[c] %	stereospecificity of cyclobutanone formation, %	mass balance
1	13.7	none	98.8	7.14	94.7
2	17.8	none	97.9	6.37	96.9
3	23.1	none	98.4	8.68	96.6
4	38.2	none	99.1	7.88	98.6

(B) Control Runs; Admixture of Optically Active Enone and Optically Active Cyclobutanone

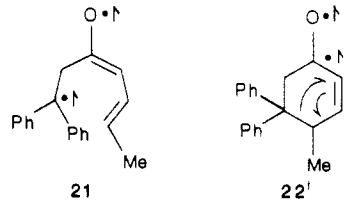
run no.	% conv	rel amt of cyclobutanone added (mol ratio)[b]	opt activity of recovered cyclohexenone,[c] %	stereospecificity of cyclobutanone formation,[d] %	racemization of added cyclobutanone,[e] %	mass balance
5	4.1	18:1	98.2	6.84	0.1	96.7
6	6.8	11:1	99.3	6.24	0.2	93.8
7	8.5	43:1	99.5	5.87	0.5	94.7
8	10.8	20:1	98.7	4.49	1.6	95.7

[a] Entries derived from average for 5 wavelengths. [b] Ratio of cyclohexenone to cyclobutanone. [c] Ratio of final rotation to initial rotation. [d] Calculated assuming no racemization of added cyclobutanone. [e] Calculated assuming the average stereospecificity observed from cyclohexanone.

important to check for the presence of such intermediates. Photolysis in ethanol or in benzene containing cyclohexylamine led only to the usual product distribution. No evidence for ester or amide formation was observed. To the extent that a ketene intermediate were present, it would be anticipated[16] that the ethanol and cyclohexylamine additives would trap the ketene and inhibit the reaction.

Nevertheless, an even more definitive test[16d] was employed. Thus, the ketene mechanism, discussed in detail below, involves dissociation of diradical **21** into 1,1-diphenylethylene and the ketene intermediate under discussion (i.e., **27**). Hence, in a crossover experiment, the photolysis was run with 1 equiv of 1,1-di(*p*-tolyl)ethylene present. However, only the usual photoproduct **20** and unreacted 1,1-di(*p*-tolyl)ethylene were observed.

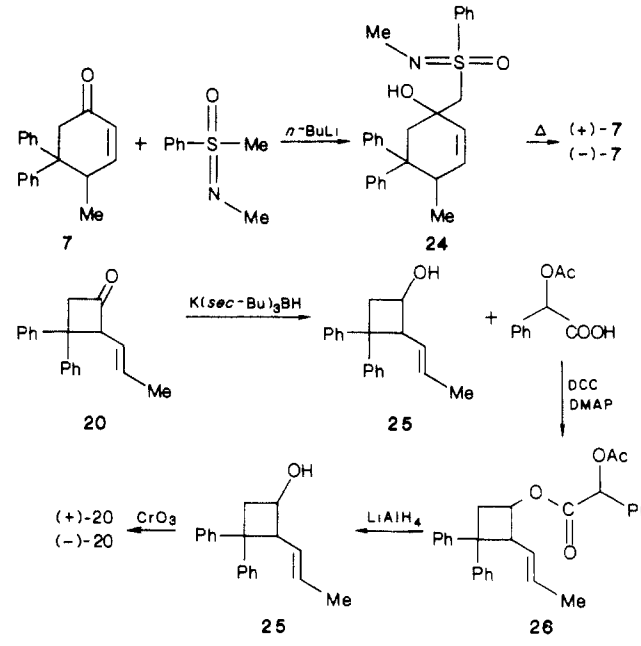
Stereochemical Studies; Resolution of Optically Active Cyclohexenone. In the introduction above, mention was made of a mechanism involving the diradical **21**. An alternative mechanism considered (vide infra) involved a 1,3-sigmatropic ring contraction of the cyclohexenone triplet **22** to afford a cyclobutanone (note structure **22'**). Detailed discussion of these species and mechanisms is delayed for the Interpretative Discussion section. However, it did seem that, starting with one enantiomer of methyl diphenyl cyclohexenone **7**, the diradical mechanism could afford racemic cyclobutanone product while the concerted 1,3-sigmatropic ring contraction should not. Hence it was of interest to study the reaction stereochemistry.



21 **22'**

The resolution of cyclohexenone **7** reactant was effected by use of the Johnson sulfoximine method[17] as outlined in Scheme III. For convenience, material of 90% enantiomeric excess was utilized. The same method was attempted in the resolution of the vinyl cyclobutanone. However, although the vinyl cyclobutanone product **20** readily formed a sulfoximine adduct, the thermal reversion of this adduct to the cyclobutanone did not occur at

Scheme III. Resolution of Methyl Triphenyl Cyclohexenone Reactant and Cyclobutanone Product



temperatures under which **20** was stable. This doubtlessly is due to an I-Strain effect[18] wherein the circa sp^3 hybridized carbon of the four-ring resists conversion to the sp^2 hybridization of the cyclobutanone carbonyl carbon.

Resolution of cyclobutanone **20** was accomplished via the mandelate ester, and this is included in Scheme III.

Assay of Enantiomeric Excesses. Both in the resolutions and in inspection of the activity of the photoproducts, optical rotations were taken at five wavelengths to ensure that errors due to adventitious impurities were avoided. Thus the ratio of rotations at the different wavelengths remained constant from run to run. This procedure was used to obtain relative enantiomeric excesses. Absolute enantiomeric excesses were obtained by use of NMR with a chiral shift reagent, namely tris(3-(heptafluoropropylhydroxymethylene)-*d*-camphorato)europium(III).[19]

The Reaction Stereochemistry. Irradiation of optically active methyl diphenyl cyclohexenone **7** led to vinyl cyclobutanone **20** which was almost completely racemic. In Table II a summary of the results derived from these runs is presented. Inspection of this table reveals that the recovered methyl diphenyl cyclohexenone **7** was unracemized while the cyclobutanone product

(16) (a) For example, in some very pretty studies of the photochemistry of linearly conjugated dienones by Quinkert, intermediate ketenes were trapped. (b) For a recent reference note: Quinkert, G.; Englert, H.; Cech, F.; Stegk, A.; Haupt, E.; Leibfritz, D.; Rehm, D. *Chem. Ber.* **1979**, *112*, 310–348. (c) For an early, pioneering study note: Barton, D. H. R.; Quinkert, G. *J. Chem. Soc.* **1960**, 1–9. (d) Relative rates of ketenes reacting with amines, alcohols, and alkenes seem unreported and lead to a present uncertainty. However, since the ketene cycloaddition with alkenes is electrophilic in nature, it is certain that the di-*p*-tolylethylene will react more rapidly than the diphenyl one.

(17) Johnson, C. R.; Zeller, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 4021–4023.

(18) (a) Brown, H. C.; Gerstein, M. *J. Am. Chem. Soc.* **1950**, *72*, 2926–2933. (b) Brown, H. C.; Fletcher, R. S.; Johannessen, R. B. *J. Am. Chem. Soc.* **1951**, *73*, 212–221.

(19) Goering, H. L.; Eikenberry, J. N.; Koermer, G. S. *J. Am. Chem. Soc.* **1971**, *93*, 5913–5915.

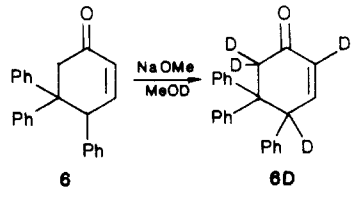
20 had lost 93.3 (±2.0)% of its optical activity, thus being formed with 6.7 (±2.0)% residual enantiomeric excess (standard deviation ±1.0).

We were concerned that the nearly racemic photoproduct might have been racemized during the photolysis or during workup, especially since the chiral center is α to the carbonyl group, and enolization at any stage would racemize this compound. Therefore a series of control runs was carried out. First, optically active vinyl cyclobutanone **20** proved stable to the HPLC separation employed for photoproduct isolation. Second, irradiation of the cyclobutanone photoproduct **20** at wavelengths above 300 nm, the wavelengths used for the photoisomerization, led to no loss of activity. However, most convincing were experiments in which vinyl cyclobutanone **20** of varying optical activities was photolyzed admixed with methyl diphenyl cyclohexenone **7**; note Table II. In each case, the rotation of the reisolated vinyl cyclobutanone was that anticipated on the basis of 93% loss of activity in the vinyl cyclobutanone formed by rearrangement and no loss of activity by the vinyl cyclobutanone which had been added at the outset of the control run. This information is given in two forms in Table II. Thus columns five and six of Part B of Table II are mutually dependent. First we calculate the reaction stereospecificity with the assumption of no racemization of the added active cyclobutanone; here we note that the stereospecificity is the same as in the runs in Part A where no cyclobutanone was added. Second, we calculate the extent of racemization of added cyclobutanone with the assumption that the portion of this compound formed by rearrangement was formed with the usual, low stereospecificity. Here we find negligible racemization of the added cyclobutanone. These are just two useful, but not independent, ways of looking at the data.

We thus conclude that the photoisomerization of the methyl diphenyl cyclohexenone **7** to afford vinyl cyclobutanone **20** occurs with almost complete loss of memory of its initial chirality.

Deuterium Labeling Determination of Mechanism of Formation of the Triphenyl Bicyclic Ketone 17. A final point facing us was the realization that, in the photochemistry of the triphenyl cyclohexenone **6**, the formation of 4,4,6-triphenylbicyclo[3.1.0]-hexan-2-one (**17**) might, a priori, result from a phenyl migration[3] or instead from a type A rearrangement[4] in which the original carbon skeleton had rearranged. Both processes had precedent in phenyl-substituted cyclohexenone photochemistry.

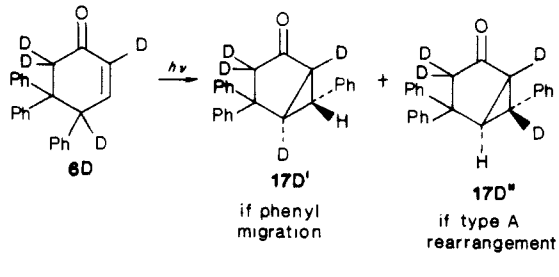
A solution was most accessible by deuterium labeling of the skeleton as outlined in eq 5. Equation 6 shows the two possible



6 **6D** (5)

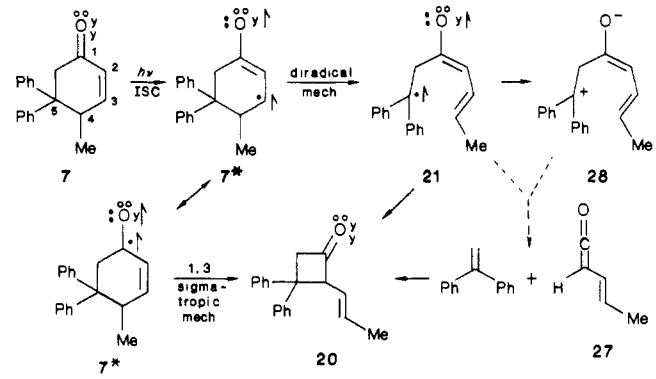
labelings anticipated on the basis of either (i) a phenyl migration mechanism or (ii) a type A mechanism.

Photolysis of the labeled triphenyl cyclohexenone **6D** led to triphenyl bicyclic ketone **17D** in which the carbon-6 benzylic position bore only hydrogen (i.e., **17D'**). Also, the extent of deuterium labeling at C-5 in the triphenyl bicyclic product **17D** was the same as that at carbon-4 in the triphenyl cyclohexenone reactant **6D**. These data indicated that the formation of this photoproduct had resulted from a phenyl migration mechanism (vide infra).



6D **17D'** if phenyl migration **17D"** if type A rearrangement (6)

Scheme IV. Possible Overall Mechanisms of Cyclobutanone Formation



Interpretative Discussion

Since cyclobutanone formation is the focus of this paper, this mechanism is considered first. However, also requiring discussion are the phenyl migration reactions.

Molecular Aspects of the Reaction Mechanism Leading to Cyclobutanones. The n–π* triplet excited state seems accepted as responsible for a variety of cyclohexenone photochemical reactions. Quite some years ago, a useful two-dimensional mode of depicting such excited states was suggested in which the p_y (i.e., n) electrons are shown as small y's, sp-hybridized electrons as small o's, and π-system electrons as solid dots or in pairs by single lines.[20] Using this notation we can readily depict, understand, and often predict many ketone reactions using ordinary organic mechanisms.

Applying this approach to the cyclohexenone to vinylcyclobutanone reaction being studied, we consider one possible mechanism, namely a 1,3-sigmatropic rearrangement. While 1,3-sigmatropic rearrangements are known,[22] nevertheless, using the mechanistic reasoning of n–π* excited states, there seems to be no feature in enone excited **7*** which leads to expectation of such a rearrangement.[23] Thus, the π-system of n–π* excited state **7*** has one extra, antibonding electron, and the rearrangement is forbidden.

In contrast, a second mechanistic pathway is explicable in terms of this n–π* reasoning. Refer to Scheme IV.[23] This begins with 4,5-bond fission to give diradical **21**. It has been noted[20,21] that the reactivity of n–π* excited states can be categorized into two types: (i) that resulting from behavior of the singly occupied p_y orbital (e.g., hydrogen abstraction, disengagement of an alkyl group as in the Norrish type I reaction), and (ii) that resulting from the influence of the antibonding electron of the π-system. In the present instance, it is the antibonding electron density which leads to fission of bond-4,5 and formation of diradical **21**. Two variations of this mechanism might be considered. Referring to Scheme IV, we note that diradical **21**, or its zwitterionic counterpart **28**, may close directly to afford the observed vinyl cyclobutanone product **20**.

Alternatively, it is observed that species **21** is a 1,4-diradical and these commonly undergo a 1,4(2,3)-fragmentation,[21] a process closely related to the Grob fragmentation.[24] Such a fragmentation

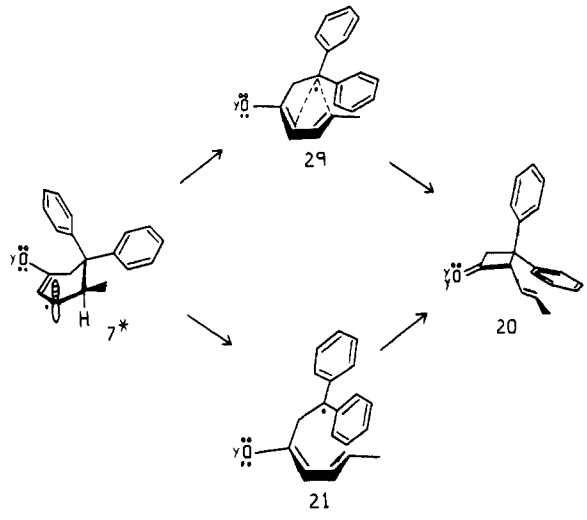
(20) (a) Zimmerman, H. E. *Seventeenth National Organic Symposium of the American Chemical Society*; Bloomington: Indiana, 1961, pp 31–41. (b) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1962**, *84*, 4527–4540. (c) Zimmerman, H. E. In *Advances in Photochemistry*; Noyes, A., Jr., Hammond, G. S., Pitts, J. N., Jr., Eds.; Interscience: New York, 1963; Vol. 1, pp 183–208.

(21) "Topics in Photochemistry," *Zimmerman*, H. E. *Top. Current Chem.* **1982**, *100*, 45–73.

(22) Woodward, R. B.; Hoffmann, R. *Conservation of Orbital Symmetry*; Academic Press: New York, 1970; pp 117–121.

(23) It is recognized that the 1,3-diradical mechanism alternative is effectively a 1,3-sigmatropic process. However, dissociation–recombination is a limiting case, and we reserve the "1,3-sigmatropic" label for mechanisms in which the migrating group begins bonding with the migration terminus before it is totally lost from its initial site.

Scheme V



would lead to ketene **27**. Also, radiationless decay of the n–π^* diradical **21** affords zwitterion **28** which on Grob fragmentation would afford the same ketene **27**. This ketene, then, could react intermolecularly to afford the observed vinyl cyclobutanone **20**. Note Scheme IV again. However, the ketene pathway is ruled out by the evidence presented in the Results section, wherein ketene traps—ethanol solvent and cyclohexylamine—neither detect any ketene intermediate nor inhibit cyclobutanone formation. Ketene scavenging by ethanol or cyclohexylamine should be rapid. Still, some ambiguity remains, since inhibition of cyclobutanone formation does depend on the rate being faster than that with diphenylethylene.

However, the failure to observe any crossover in the presence of 1,1-di(*p*-tolyl)ethylene is unambiguous, since its rate of reaction with ketene **27** should be close to, or faster,[16d] than that of diphenylethylene.

The ketene dissociation–recombination mechanism having been excluded, two mechanisms remained. Hence an experimental means of distinguishing between the direct 1,3-sigmatropic rearrangment mechanism and the diradical alternative was needed.

The Reaction Stereochemistry as a Mechanistic Probe Distinguishing between 1,3-Sigmatropic and Diradical Pathways. As noted in the Results section, the reaction stereochemistry was used to distinguish between the 1,3-sigmatropic and diradical mechanisms. Thus the observation of 93% loss of optical activity argues against a direct 1,3-sigmatropic rearrangement. Perusal of Scheme IV shows that reactant methyl diphenyl cyclohexenone **7** has a chiral center at C-4 while vinyl cyclobutanone product **20** has a chiral center at C-2. Any transition state involving a concerted 1,3-migration is diastereomeric. Thus, if we consider one enantiomer, we begin with one asymmetric center at C-4 in starting material **7***. The reaction at completion again has only one asymmetric center, this at C-2. However, at intermediate points along the reaction coordinate, there are two centers of asymmetry and hence the potential existence of two diastereoisomers. One of the two optically active diastereomers should, except by fortuity, be preferred and lead preferentially to one enantiomer of cyclobutanone product. The possibility of such fortuity is discussed below.

Reference to Scheme V is helpful. Here we depict three dimensionally cyclohexenone reactant **7** and cyclobutanone product **20** as well as two alternative half-reacted species, namely the 1,3-sigmatropic transition state **29** and the open vinyl diradical **21**. The cyclohexenone reactant **7** is shown in a conformation with a pseudoequatorial methyl group. Dreiding models suggest a small preference for this conformation and molecular mechanics calculations[25] are in agreement, although only a 1.0-kcal/mol preference is found.[25i] Note the Experimental Section.

With this in mind, we note that methyl diphenyl cyclohexenone triplet **7*** has bond 4–5 above the plane of the π-system of the enone moiety. Overlap of bond 4–5 with the excited state π-system results in bond weakening. Fission of this bond—either completely to form enoloxy diradical **21** or at the onset of the 1,3-sigmatropic rearrangement mechanism—occurs with continuous overlap of the orbitals of bond 4–5 with the π-system, at no point becoming orthogonal (i.e., never 90°). A species having the methyl group trans on the π-system at atom C-4 is then formed. This twisting mode also occurs with least motion. Cis product cannot result from the equatorial methyl conformer nor trans product from the axial. Interestingly, this is exactly the stereochemistry observed in the photochemical reaction of methyl diphenyl cyclohexenone **7** which affords the *trans*-propenyl cyclobutanone **20** as the kinetic product.

Importantly, exactly the same stereochemical arguments given above for the diradical mechanism apply to the 1,3-sigmatropic rearrangement, except that here the benzhydryl group is bonded to one π face or the other. Also, migration on one face leads to one enantiomer while migration on the second face leads to the other enantiomer. Scheme V depicts only the alternative derived from the pseudoequatorial reactant; and, migration on this face leads to trans product. Migration on the other face would lead to the unobserved cis product. Trans product is observed, which is important since a superficial analysis might suggest that racemic product could result from 1,3-migration of the benzhydryl group equally on the two π-faces.

The observation of nearly racemic vinyl cyclobutanone photoproduct therefore is not consistent with a concerted 1,3-sigmatropic ring contraction mechanism, and we turn to consideration of diradical pathways.

With reference to Scheme IV, diradical **21** closes to the observed vinyl cyclobutanone **20** by bonding of odd-electron centers, namely the benzhydryl carbon and C-2. This mechanism does account for the predominant loss of optical activity. The residual enantiomeric excess encountered most likely arises from incomplete conformational equilibration prior to ring closure; earlier it was noted that the benzhydryl group is initially generated on one face of the π-system. It is, however, conceivable that there is minor competition by the 1,3-sigmatropic rearrangement or from an incompletely disengaged diradical.

Also interesting is the lack of starting material racemization in the reaction of methyl diphenyl cyclohexenone **7**. We can conclude that once bond 4–5 opens to afford triplet diradical **21** there is an overwhelming preference for closure to form the four-ring rather than the original six-membered ring. Any return to cyclohexenone must occur more rapidly than conformational equilibration. Entropy considerations do favor closure to form the four-membered ring.

The same, diradical mechanism accounts for formation of vinyl cyclobutanones **18** and **19** from the triphenyl cyclohexenone **6**. However, in addition to less efficient cyclobutanone formation, we note formation of some cis isomer. Since this cis isomer **19** appears in low conversion runs and hence does not arise from secondary photolysis, its source is of interest. Most likely it arises from cis–trans equilibration of the triphenyl diradicals **30c** and **30t** as depicted in eq 7. Diradical **30** could be expected to have

(24) Grob, C. A. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 535–546.

(25) (a) A VAX molecular mechanics programming package, NOTROUBLE,[24h] was developed which permitted facile construction of three-dimensional molecules, running of a variety of molecular mechanics programs, screen display and plotting of these, geometric manipulation, and interchange of different formats employed. A VAX/750 was used for running molecular mechanics. Previously, we have used TRIBBLE.[25c] (b) Zimmerman, H. E.; Moore, J. M.; Weber, A. W., to be published. (c) Pensak, D. *Ind. Res. Dev.* **1983**, *25*, 74–78. (d) A molecular mechanics modification[25e] incorporating Allinger's MM2[25h] and R. D. Brown's SCF treatment[25f] as found in MMPI.[24h] (e) Gilbert, K. E.; Gajewski, J. J., available for nominal charges from the Sarena Software Co., Indiana University, Bloomington, IN. We thank these authors for sending a program copy. (f) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893–3907. (g) Brown, R. D.; Heffernan, M. L. *Aust. J. Chem.* **1959**, 319–334. (h) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127–8134. (i) In our experience, molecular mechanics energy differences of less than 1 kcal/mol are not meaningful.

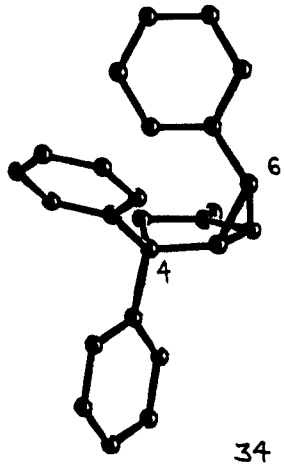
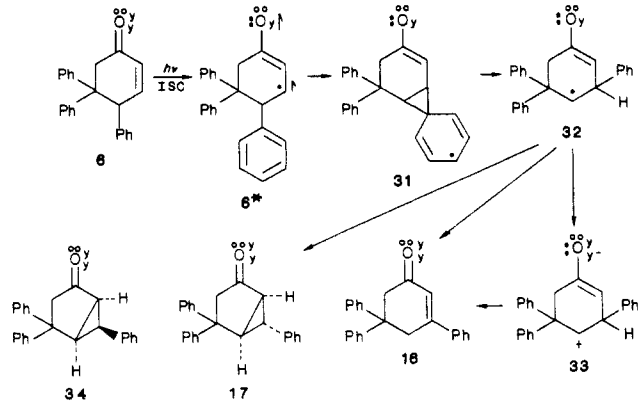
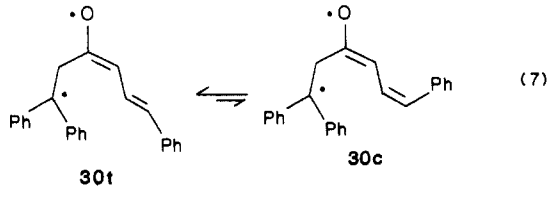


Figure 3. An Ortep drawing of *endo*-4,4,6-triphenylbicyclo[3.1.0]hexan-2-one derived from molecular mechanics.

Scheme VI. Phenyl Migration Mechanisms



a lower styryl π bond order than its methyl analogue **21** as well as a possible longer lifetime; both of these effects should derive from delocalization of electron density into the styryl phenyl ring.



(7)

Phenyl Migration Processes in the Photochemistry of Triphenyl Cyclohexenone 6. The photochemistry of triphenyl cyclohexenone **6** contrasts with the highly selective methyl diphenyl analogue in affording four products. This behavior can be ascribed to the tendency of the C-4 phenyl group to migrate in competition with cyclobutanone formation. The overall mechanisms involved in the phenyl migration processes are outlined in Scheme VI.

Several mechanistic aspects are of interest. The most striking result observed is the formation of the *exo*-phenyl bicyclic product **17** to the exclusion of any *endo*-phenyl bicyclic ketone **34**. In virtually every other known example of the aryl migration reaction,[3-5,14b,c,26,27] a rather large kinetic preference for formation of the *endo*-6-aryl bicyclic photoproduct has been observed. This stereochemistry involves inversion of configuration at C-4 as has been noted.[3] In the present instance, however, the *endo*-phenyl stereoisomer **34** has severe phenyl–phenyl (i.e., C4:C6) steric interactions and its formation is understandably inhibited. Molecular mechanics indicated that this *endo*-phenyl isomer is 4.3 kcal/mol higher in energy than the exo isomer. This molecule, **34**, is drawn in Figure 3 with use of the geometry of the exo-stereoisomer **17** except for the changed stereochemistry at carbon-6; contrast Figures 1 and 3. Previously we have suggested that formation of the *exo*-aryl stereoisomer, resulting from net retention of C-4 configuration, arises via bridging of an open diradical such as **32**. Such an open diradical seems to be a necessary intermediate species when concerted aryl migration and three-ring formation is not possible as in the present instance. In addition, intersystem crossing of this diradical affords zwitterion **33**, which on pinacolic rearrangement with a shift of a hydrogen atom leads to the 3,5,5-triphenylcyclohexenone photoproduct **16**. Although one might consider the alternative of hydrogen migration in the diradical-like n–π^* excited species, the π-system is that of a radical anion and hydrogen migration is then without analogy. We note that hydrogen migration in this species concerted with π^* to n radiationless decay is effectively equivalent to the zwitterion process suggested. Indeed, zwitterion **33** also accounts for formation of exo-bicyclic [3.1.0] ketone **17**.

One aspect not yet discussed is the observation of the phenyl migration process in the triphenyl cyclohexenone **6** contrasted with the overwhelming preference for a type A skeletal rearrangement in the case of the 4,5-diphenylcyclohexenone **3** (note eq 2) studied earlier.[4] Additionally, there is the example of the photochemistry of 4,4,5-triphenylcyclohexenone (**35**) where only phenyl migration was observed.[5]

An understanding of these differences comes with the realization that for migration of a C-4 phenyl group to C-3, the phenyl group must assume a pseudoaxial conformation. In an equatorial conformation the C-4 phenyl's π-system cannot overlap with the π-system at C-3.

In the molecule presently studied, namely the triphenyl cyclohexenone **6**, the reactive conformer has one extra axial phenyl group. Similarly, in the case of 4,4,5-triphenylcyclohexenone (**35**), the same is true. However, in the case of the 4,5-diphenylcyclohexenone **3** which undergoes a type A rearrangement rather than a phenyl migration, the stereoisomer studied[4] was trans, and there, for a phenyl migration, two equatorial phenyl groups need to become axial—a much more energetically demanding requirement.

Reaction Efficiencies and Multiplicity. The reaction efficiency for cyclobutanone formation is of the order of 0.01–0.03. Reactions with quantum yields of the order of 0.001 or above tend to be synthetically practical.[28] Hence the main limitation in the synthetic utility of cyclobutanone formation from cyclohexenones becomes the selectivity of product formation. In the case of the methyl diphenyl cyclohexenone **7** this selectivity is ideal, and we are exploring to ascertain what other substitution leads to similar high selectivity.

Another matter pertains to the reaction multiplicity. In fact, virtually all of cyclohexenone rearrangement photochemistry derives from triplets as in the present case. Rapid intersystem crossing of ketones, effected by spin–orbit coupling, tends to be

Table III. Rate Data for Enones **6** and **7**

reactant	slope	τ, ns	$k_{d(tot)}$	k_r	k_d
triphenyl enone	44.13	7.4	1.4×10^8	2.1×10^7 [a] 5.0×10^6 [b] 1.6×10^7 [c]	1.2×10^8
methyl diphenyl enone	48.37	8.1	1.2×10^8	1.5×10^6	1.2×10^8
4,4-diphenyl enone[d]		1.9	5.3×10^8	2.3×10^7	5.1×10^8

[a] Total of all rates utilized by enone excited triplet. [b] Rate of cyclobutanone (cis + trans) formation. [c] Total rate of phenyl migration reactions. [d] Recalculated in ref 14b with use of rates of diffusion common to that in the present study.

(26) (a) Nobs, F.; Burger, U.; Schaffner, K. *Helv. Chim. Acta* **1977**, *60*, 1607–1628. (b) Swenton, J. S.; Blankenship, R. M.; Sanitra, *J. Am. Chem. Soc.* **1975**, *97*, 4941–4947.

(27) Hahn, R. C.; Kurtz, D. W. *J. Am. Chem. Soc.* **1973**, *95*, 6723–6727.

(28) (a) Previously we had suggested a higher quantum yield being needed for synthetic utility. However, this lower limit is a more reasonable value. (b) Zimmerman, H. E.; Flechtner, T. W. *J. Am. Chem. Soc.* **1970**, *92*, 7178–7183. (c) This was based both on general observation and on the idea that the usual solvents utilized are sufficiently stable for reactions with efficiencies in this range.

more rapid than any competing singlet reactions. Thus, that cyclobutanone formation in the present research derives from the triplet, while not safely predictable, is reasonable.

Triplet Lifetimes and Rates. The triplet lifetimes and rates, summarized in Table III, include those obtained earlier[3b,14b] for the rearrangement of 4,4-diphenylcyclohexenone (**1**). The first observation we note is that lifetimes of the presently studied 5,5-diphenyl enones **6** and **7** are considerably longer than that of the 4,4-diphenylcyclohexenone.[3b] It has been argued that the lifetime of many of the n–π^* cyclohexenones having aryl groups at C-4 is determined by interaction of the enone π-system with the C-4 aryl groups, probably by bridging to give a partially migrated diradical. Such diradicals have especially small T_1–S_0 energy separations, and intersystem crossing to ground state with reversion to reactant becomes facile.

However, in the case of methyl diphenyl enone **7** currently studied, this rapid relaxation mechanism is unavailable due to absence of a C-4 phenyl substituent. In the case of the triphenyl cyclohexenone **6** there is a phenyl at C-4; however, the single phenyl is equatorial in the more stable conformation. Accordingly, a more accurate specification for rapid decay is availability of an axial phenyl group.

A second noteworthy point is the threefold more rapid rate of cyclobutanone formation from the triphenyl cyclohexenone **6** compared with the methyl diphenyl cyclohexenone **7**; note Table III. Since the triplet lifetimes are very similar for the two cyclohexenones, **6** and **7**, this rate difference is reflected in the quantum efficiencies of cyclobutanone formation with cyclobutanone formation from the triphenyl cyclohexenone being, again, about threefold that of the methyl diphenyl reactant.

The larger rate for the triphenyl enone **6** seems likely to derive from having three, vicinal phenyl groups with consequent relief of steric repulsions on scission of bond-4,5. Also the C-4 phenyl group can conjugate with the π-system of the resulting diradical **30**.

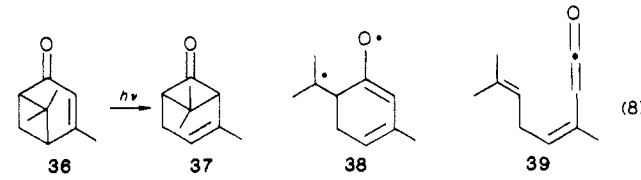
We also note that the rate of phenyl migration in the case of the triphenyl cyclohexenone **6** is about two-thirds that of the previously studied[3b] 4,4-diphenylcyclohexenone. One might have anticipated a rate retardation due to the need for the reactant's equatorial phenyl moiety acquiring an axial conformation prior to bridging and rearranging. Also, as has been noted above, the usual C-4 inversion mechanism is precluded for steric reasons. That the rate of triplet reaction to afford phenyl migrated products is not greatly diminished may arise from the relief of C-4:C-5 phenyl–phenyl van der Waals repulsions as a phenyl begins to migrate.

Nature of the Diradical Species. The proposed diradical intermediate **21** is of intrinsic interest. The expectation is that this diradical is generated as a triplet by the mechanism in Scheme IV. Additionally, MNDO[29] treatment of this species, with four-state configuration interaction, suggests that the triplet **21** should be very close in energy to the corresponding singlet. Since three configurations are admixed for the singlet and only one used for the triplet, it is likely that more extensive CI will tend to lower the triplet energy selectively relative to the singlet.

These calculations indicate that the lowest singlet (i.e., S_0) is a zwitterionic type diradical (i.e., **28**) while an upper singlet (S_1) is better described as a traditional diradical with odd electron densities. The results of the calculations are summarized in the section on calculations in the Experimental Section (vide infra). It seems likely that this zwitterion **28** is formed by intersystem crossing just prior to closure of triplet diradical **21** to afford the cyclobutanone photoproducts. Spin pairing is requisite for bonding, and the singlet–triplet energy gap is small.

Relation of the Present Results to the Previous Examples of Cyclobutanone Formation. We now should consider the relationship of the present cyclohexenone to cyclobutanone rearrangement to the systems previously studied. The example[4] in eq 2 led to 7% of cyclobutanone. Similarly, the photochemistry[5] of 4,4,5-triphenylcyclohexenone afforded 0.3% of cyclobutanone product. Hence, one difference is that the systems now studied give more efficient conversion to cyclobutanone product, and this difference is readily understood as arising from diradical stabilization by the additional C-5 phenyl groups.

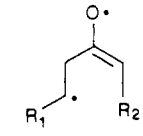
Another example of interest is the rearrangement[6] of verbenone **36** to chrysanthenone **37** as depicted in eq 8. This example contrasts with the current results in competitive (20%) fragmentation of the analogous diradical **38** to give rise to ketene **39**. In this case, however, it is seen that the diradical intermediate **38** is chiral and cannot racemize. Nevertheless, in an elegant study



36 37 38 39 (8)

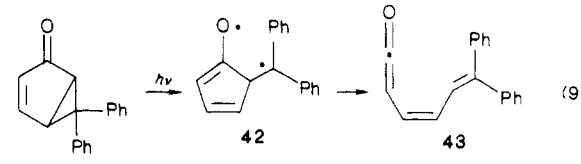
Schaffer has shown[6c] the diradical to have a detectable lifetime. This may result merely from a more difficult and slower ring closure to cyclobutanone in the verbenone case where a more strained system results. A slower closure affords the diradical intermediate a greater chance to fragment to the ketene.

Commonality of the Triplet Ethylvinyloxy Diradical in Organic Photochemistry. It is interesting that a number of literature examples from photochemistry proceed via structurally analogous ethylvinyloxy diradicals (i.e., **40**).



40

For example, the type B rearrangement of bicyclo[3.1.0]hex-3-en-2-ones[20b,30] proceeds via such a triplet ethylvinyloxy diradical followed by fragmentation to afford a ketene (note eq 9). Similarly, in the case of 4,4-diphenylcyclopentenone photochemistry,[31,32] the ethylvinyloxy type of diradical, again, plays the same role (note eq 10).



41 42 43 (9)

The same species appears to account for a further number of varied triplet reactions leading to ketenes via the same basic process.[33] Finally, one needs to note that in none of these systems are cyclobutanones observed although, a priori, one might anticipate such products. Inspection of each case reveals that any cyclobutanone formed in these examples would be especially strained, thus explaining the difference between the current results and the cases cited.

Relationship of the Present Studies to the Type A Cyclohexenone Rearrangement. It is of particular interest that the ethylvinyloxy diradical mechanism advanced for cyclobutanone formation from the 5,5-diphenylcyclohexenones was originally suggested for the type A rearrangement of cyclohexenones, such as $\Delta^{1,9}$-10-methyl-2-octalone **47** and the related phenanthrone **48**, to afford bicyclo[3.1.0]hexanones.[12a] In that study it was noted that the

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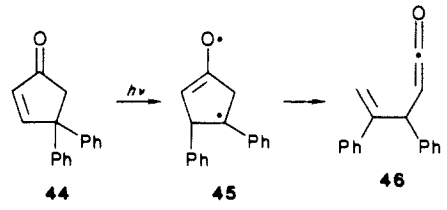
(33) Chapman, O. L.; Clardy, J. C.; McDowell, T. L.; Wright, H. E. *J. Am. Chem. Soc.* **1973**, *95*, 5086–5087.



(10)

odd-electron carbon would tend to be bonded to the vinyloxy π-system. More recently, the rearrangement of the same compounds, however resolved, has been found to lead to product which, at most, had lost only 5% of its optical activity.[33] From these rearrangements no cyclobutanones were encountered.[12a]

It is clear that the type A cyclohexenone rearrangement and presently observed cyclobutanone formation are closely structurally related. However, cyclobutanone formation appears to occur primarily in those cases where the ethylvinyloxy diradical is stabilized sufficiently that it has time for conformational equilibration and energetics permitting the odd-electron carbon center to disengage itself from the vinyloxy π-system. The type A enone rearrangement and cyclobutanone formation seem to be limiting cases of a spectrum of mechanistic gradations.

Conclusion. One aim of organic photochemistry is to expand the scope of known excited state reactivity which is still limited relative to ground state chemistry. The cyclohexenone to cyclobutanone rearrangement is one contribution in this direction. It is our aim now to explore the generality of this reaction.

Experimental Section[34]

3,4,4-Triphenylcyclohex-2-en-1-one. To a −78 °C solution of 10.0 g (36.0 mmol) of 6,6-diphenyl-3-methoxycyclohex-2-en-1-one[7] in 125 mL of tetrahydrofuran was added 37.6 mL (41.4 mmol) of 1.1 M phenyllithium dropwise over 30 min; the solution was then stirred for another 15 min and quenched at −78 °C with 50 mL of water. The hydroxy enol ether was then treated at room temperature with 80 mL of 6 N hydrochloric acid and stirred for 1 h. Neutral workup afforded 7.73 g (66.3%) of a yellow oily solid. Recrystallization from ethanol gave 7.06 g (60.5%) of 3,4,4-triphenylcyclohex-2-en-1-one as a white solid, mp 146.0–147.0 °C (lit.[5] mp 147.0–147.5 °C). The spectral data were the following: IR ($CHCl_3$) 3020, 3010, 2990, 2890, 1670, 1600, 1490, 1440, 1385, 1320, 1175, 1105, 1080, 1030, 985, 700 cm^{-1}; H NMR ($CDCl_3$, 200 MHz) δ 6.9–7.4 (m, 15 H, phenyls), 6.60 (s, 1 H, =CH), 2.84 (t, 2 H, CH_2), 2.20 (t, 2 H, CH_2). The spectral data were identical with that reported[5] for 3,4,4-triphenylcyclohex-2-en-1-one.

3,4,4-Triphenylcyclohex-2-en-1-one Tosylhydrazone. A solution of 20.0 g (61.7 mmol) of 3,4,4-triphenylcyclohex-2-en-1-one, 11.2 g (61.7 mmol) of *p*-toluenesulfonylhydrazide, and 0.10 mL of concentrated hydrochloric acid in 110 mL of ethanol was warmed to 50 °C for 5 min and then stored at −20 °C for 14 h. The resulting solid was filtered to give 27.7 g (91.1%) of the 3,4,4-triphenylcyclohex-2-en-1-one tosylhydrazone, mp 198.0–206.0 °C. Recrystallization from ethanol gave 27.1 g (89.2%) of the tosylhydrazone as a white solid, mp 205.0–206.0 °C. The spectral data were the following: IR ($CHCl_3$) 3220, 3200, 3030, 3010, 2970, 1600, 1490, 1440, 1395, 1355, 1330, 1210, 1160, 1105, 980, 945, 900, 875, 700, 660 cm^{-1}; H NMR ($CDCl_3$, 200 MHz) δ 7.8 (m, 2 H tolyl), 7.0–7.5 (m, 17 H, phenyls), 6.60 (s, 1 H, =CH), 2.42 (t, 2 H, CH_2), 2.30 (s, 3 H, *p*-tolyl-CH_3), 1.90 (t, 2 H, CH_2); MS, *m/e* 492.1873 (calcd for $C_{31}H_{28}N_2O_2S_2$, *m/e* 492.1865).

Anal. Calcd for $C_{31}H_{28}N_2O_2S_2$: C, 75.50; H, 5.85; N, 5.48. Found C, 75.58; H, 5.73; N, 5.68.

3,4,4-Triphenylcyclohexene. The general method of Kabalka, Baker, and Neal[8] was adapted. To a solution of 3.67 g (7.46 mmol) of 3,4,4-triphenylcyclohex-2-en-1-one tosylhydrazone in 40 mL of chloroform at 0 °C was added 2.5 mL (8.12 mmol) of 1,3,2-benzodioxaborole.[35] The resulting orange solution was stirred for 1 h, then 2.20 g (16.2 mmol) of sodium acetate was added, and the solution was refluxed for 1 h. Neutral workup gave 1.68 g of a yellow oil which was chromatographed on a 2.0 × 200 cm silica gel column packed and eluted with 5% ether in hexane, and collection in 500-mL fractions gave fractions 2–3, 1.36 g (76.6%) of 3,4,4-triphenylcyclohexene, mp 103.0–104.0 °C. Recrystallization from ethanol gave 1.28 g (72.3%) of the cyclohexene as a white solid, mp 103.0–104.0 °C. The spectral data were the following: IR ($CHCl_3$) 3030, 3010, 2960, 1600, 1485, 1440, 1030, 750, 700 cm^{-1}; H NMR ($CDCl_3$, 200 MHz) δ 6.8–7.4 (m, 15 H, phenyls), 5.95 (br m, 1 H, =CH), 5.83 (br m, 1 H, =CH), 4.07 (br m, 1 H, CH), 2.50–2.68 (m, 2 H, CH_2), 1.95–2.20 (m, 2 H, CH_2); MS, *m/e* 310.1723 (Calcd for $C_{24}H_{22}$, *m/e* 310.1722).

Anal. Calcd for $C_{24}H_{22}$: C, 92.85; H, 7.15. Found: C, 92.45; H, 7.50.

4,5,5-Triphenylcyclohex-2-en-1-one. The general reaction of Dauben, Lorber, and Fullerton[9] was used. To a 0 °C dry flask containing 50 mL of dichloromethane and 1.0 mL of pyridine was added 3.2 g (32.0 mmol) of chromium trioxide. The solution was stirred at this temperature for 20 min, and to this was added dropwise 0.50 g (1.6 mmol) of 3,4,4-triphenylcyclohexene in 5.0 mL of dichloromethane, followed by stirring at room temperature for 36 h. The solution was decanted and the residue washed thoroughly with ether. Basic–acidic workup gave 485 mg of a yellow oil which was chromatographed on a 2.5 × 600 cm silica gel column packed with use of 10% ether in hexane and 500-mL fractions were collected: fraction 2, 48.3 mg (9.3%) of 3,4,4-triphenylcyclohexene, mp 103.0–104.0 °C; fractions 3–4, 291 mg (56.0%) of 4,4,5-triphenylcyclohex-2-en-1-one, mp 209.0–216.0 °C. Recrystallization from ethyl acetate gave 244 mg (47.1%) of the enone as a white solid, mp 215.0–216.0 °C. The spectral data were the following: IR ($CHCl_3$) 3030, 3010, 2950, 1670, 1490, 1440, 900, 760, 700 cm^{-1}; H NMR ($CDCl_3$, 270 MHz) δ 6.7–7.2 (m, 16 H, phenyls and =CH), 6.15 (d, 1 H, J = 14 Hz, =CH), 4.48 (d, 1 H, J = 10 Hz, CH), 3.48 (d, 1 H, J = 16 Hz, C*H*H), 2.96 (d, 1 H, J = 16 Hz, C*H*H); UV (ethanol) 252 (ϵ 6150), 270 (3200), 290 (841), 320 (36); MS, *m/e* 324.1514 (calcd for $C_{20}H_{24}O$, *m/e* 324.1509).

Anal. Calcd for $C_{20}H_{24}O$: C, 88.85; H, 6.22. Found: C, 88.72; H, 6.36.

Exploratory Direct Photolysis of 4,5,5-Triphenylcyclohex-2-en-1-one. A solution of 150 mg (0.61 mmol) of 4,5,5-triphenylcyclohex-2-en-1-one in 150 mL of photograde benzene was irradiated with a 450-W Hanovia medium pressure mercury lamp through a Pyrex filter for 30 min under purified nitrogen.[34,36] The photolysate was concentrated in vacuo to 150 mg of a colorless oil which was chromatographed on a 20 × 20 cm preparative thick layer chromatography plate, eluting twice with 10% ether in hexane and twice with 15% ether in hexane. The most rapidly moving band, band 1, contained 4.29 mg (2.9%) of 2-*cis*-styryl-3,3-diphenylcyclobutanone, mp 60.0–64.0 °C. Recrystallization from ethanol yielded 3.5 mg (2.3%) of the cyclobutanone as a white solid, mp 63.0–64.0 °C. Band 2 contained 18.1 mg (12.1%) of 2-*trans*-styryl-3,3-diphenylcyclobutanone, mp 94.0–95.0 °C. Recrystallization from ethanol gave 15.3 mg (10.2%) of the cyclobutanone as a white solid, mp 95.0–95.5 °C. Band 3 contained 19.1 mg (12.7%) of *exo*-4,4,6-tri-

(34) Melting points were determined by using a calibrated hot-stage apparatus. Elemental analyses were performed by Galbraith Laboratories, Inc. Knoxville, TN 37921. All reactions were run under dry nitrogen and all photolyses were purged with deoxygenated nitrogen[36] for 1 h before and during photolysis. Anhydrous magnesium sulfate or sodium sulfate were used as drying agents. Column chromatography was performed on silica gel (Matheson, Coleman, and Bell, grade 62, 60–200 mesh) mixed Sylvania 2282 phosphor and slurry packed into quartz columns permitting monitoring by a hand held ultraviolet lamp. Preparative thick-layer chromatography was carried out with MN-Kieselgel G/UV 254 silica gel. High-pressure liquid chromatography (HPLC) was done by using a liquid chromatograph with an LDC 254 nm detector and LDC 5000 psi minipump. Analyses were done on a 0.55 × 25 cm polished stainless steel column packed with 5–12 μm porous silica beads. Preparative separations were performed with a 0.95 × 50 cm column packed with 10–20 μm porous silica beads.[51] Neutral workup refers to diluting with ether, washing with water and brine, drying, filtering, and concentrating in vacuo. Acidic workup involved dilution with ether and washing with 2 N hydrochloric acid followed by neutral workup. Basic workup involved dilution with ether and washing with 5% sodium hydroxide followed by neutral workup. Acidic–basic workup used sequential acid and base washes after dilution. Basic–acidic workup used sequential base and acid washes after dilution. Benzene used for photolysis was purified by washing with concentrated sulfuric acid and potassium permanganate followed by distillation from calcium hydride. Tetrahydrofuran was purified by storage over potassium hydroxide, followed by successive distillations under nitrogen atmosphere from calcium hydride, lithium aluminum hydride, and sodium benzophenone ketyl. Dichloromethane was purified by distillation from phosphorus pentoxide. 95% ethanol was purified by distillation from magnesium metal and a catalytic amount of iodine. The following filter solution systems were used. Filter solution A: cell 1, 2.0 M nickel sulfate in 10% sulfuric acid; cell 2, 1.0 M cobalt sulfate in 10% sulfuric acid; cell 3, 0.01 M sodium vanadate in 10% sodium hydroxide. The transmission was 0% below 330 nm, 36.2% at 366 nm, and 0% above 400 nm. Filter solution B: cell 1, 0.5 M nickel sulfate in 10% sulfuric acid; cell 2, 0.1 M cobalt sulfate in 10% sulfuric acid; cell 3, 0.1 M copper sulfate in 10% sulfuric acid. The transmission was 0% below 290 nm, 40.2% at 322 nm, and 0% above 360 nm. Filter system C was a 0.1 M copper sulfate filter solution. The transmission of this filter solution was 0% below 300 nm, 14% at 310 nm, 32% at 320 nm, and 42% at 330 nm.

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phenylbicyclo[3.1.0]hexan-2-one, mp 145.0–146.0 °C. Recrystallization from hexane gave 16.4 mg (10.9%) of the bicyclic ketone as a white solid, mp 146.0–147.0 °C. Band 4 afforded 35.2 mg (23.4%) of recovered 4,5,5-triphenylcyclohex-2-en-1-one starting material, mp 215.0–216.0 °C. Band 5 was 69.8 mg (46.5%) of 3,5,5-triphenylcyclohex-2-en-1-one, mp 115.0–116.0 °C. Recrystallization from ethanol gave 66.7 (44.4%) mg of the enone as a white solid, mp 117.0–117.5 °C.

The spectral data for 2-*cis*-styryl-3,3-diphenylcyclobutanone were the following: IR ($CHCl_3$) 3010, 2928, 2830, 1782, 1610, 1500, 1450, 1235, 1132, 1080, 710 cm^{-1}; H NMR ($CDCl_3$, 270 MHz) δ 7.0–7.4 (m, 15 H, phenyls), 6.62 (m, 1 H, =CH), 5.03 (m, 2 H, =CH and CH), 3.88 (q, 2 H, CH_2); C NMR ($CDCl_3$, 500 MHz) δ 205.6 (carbonyl), 147.5, 136.5, 133.9, 128.49, 128.47, 128.39, 128.37, 127.73, 127.59, 127.23, 126.70, 126.62, 123.8 (phenyl and vinyl carbons), 69.4 (aliphatic 4-ring carbon), 57.9 (aliphatic 4-ring carbon), 46.8 (aliphatic 4-ring carbon); C NMR INEPT ($CDCl_3$, 500 MHz) δ 136.5 (+), 133.9 (+), 128.49 (+), 128.47 (+), 127.73 (+), 127.59 (+), 127.23 (+), 126.70 (+), 123.8 (+), 69.4 (+), 57.9 (−); UV (ethanol) 258 (ϵ 4550), 288 (1100), 296 (700); MS, *m/e* 324.1485 (calcd for $C_{24}H_{20}O$, *m/e* 324.1509).

Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.22. Found: C, 88.65; H, 6.27.

The spectral data for 2-*trans*-styryl-3,3-diphenylcyclobutanone were the following: IR ($CHCl_3$) 3028, 1788, 1610, 1508, 1460, 1238, 1150, 1129, 1090, 980, 710 cm^{-1}; H NMR ($CDCl_3$, 270 MHz) δ 7.0–7.5 (m, 15 H, phenyls), 6.65 (d, 1 H, J = 17 Hz, =CH), 5.64 (dd, 1 H, J = 9, 17 Hz, =CH), 4.77 (d, 1 H, J = 9 Hz, CH), 3.75 (q, 2 H, CH_2); UV (ethanol) 260 (ϵ 4880), 290 (1200), 296 (700); MS, *m/e* 324.1513 (calcd for $C_{24}H_{20}O$, *m/e* 324.1509).

Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.22. Found: C, 88.54, H, 6.51.

The spectral data for *exo*-4,4,6-triphenylbicyclo[3.1.0]hexan-2-one were the following: IR ($CHCl_3$) 2990, 1720, 1600, 1490, 1440, 1360, 1070, 965, 700 cm^{-1}; H NMR ($CDCl_3$, 270 MHz) δ 7.0–7.5 (m, 15 H, phenyls), 2.97–3.05 (d, 1 H, C*H*H), 2.77–2.84 (m, 2 H, C*H*H and C-5 cyclopropyl H), 2.54 (m, 1 H, C-6 cyclopropyl H), 2.42 (m, 1 H, C-1 cyclopropyl H); UV (ethanol) 270 (ϵ 925), 280 (610), 313 (280); MS, *m/e* 324.1514 (calcd for $C_{24}H_{20}O$, *m/e* 324.1509).

Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.22. Found: C, 88.72; H, 6.32.

The spectral data for 3,5,5-triphenylcyclohex-2-en-1-one were the following: IR ($CHCl_3$) 2990, 1670, 1600, 1490, 1440, 1360, 1270, 900, 700 cm^{-1}; H NMR ($CDCl_3$, 270 MHz) δ 6.9–7.4 (m, 15 H, phenyls), 6.30 (s, 1 H, =CH), 3.48 (s, 2 H, CH_2), 3.24 (s, 2 H, CH_2); UV (ethanol) 270 (ϵ 11 600), 290 (17 000), 310 (10 900); MS, *m/e* 324.1514 (calcd for $C_{24}H_{20}O$, *m/e* 324.1509).

Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.22. Found: C, 88.62; H, 6.28.

Exploratory Sensitized Photolysis of 4,5,5-Triphenylcyclohex-2-en-1-one. A solution of 229 mg (0.71 mmol) of 4,5,5-triphenylcyclohex-2-en-1-one and 5.8 mL (49.9 mmol) of freshly distilled acetophenone in 250 mL of photograde benzene under purified nitrogen[34,36] was photolyzed on the "Wisconsin Black Box"[37] apparatus with filter solution system A.[34] The light output was measured by a digital electronic actinometer[38] calibrated by ferrioxalate actinometry[39] and indicated that the sample absorbed 0.45 mEinsteins of light. The acetophenone was removed by bulb (30 °C) to bulb (dry ice cooled) distillation at 0.2 mm to give 224 mg (97.8%) of crude photolysate. Preparative thick layer chromatography, eluting twice with 5% ether in hexane and twice with 10% ether in hexane, gave the following bands: band 1, 3.30 mg (1.8%) of 2-*cis*-styryl-3,3-diphenylcyclobutanone, mp 63.0–64.0 °C; band 2, 20.6 mg (9.0%) of 2-*trans*-styryl-3,3-diphenylcyclobutanone, mp 95.0–95.5 °C; band 3, 21.4 mg (9.3%) of 4,4,6-triphenylbicyclo[3.1.0]hexan-2-one, mp 145.0–146.0 °C; band 4, 86.1 mg (37.6%) of recovered 4,5,5-triphenylcyclohex-2-en-1-one, mp 215.0–216.0 °C; band 5, 91.3 mg (39.8%) of 3,5,5-triphenylcyclohex-2-en-1-one, mp 117.0–117.5 °C.

3,5,5-Triphenylcyclohex-2-en-1-one. The general method of Reich, Renga, and Reich[40] was used. To a −40 °C solution of 476 mg (2.51 mmol) of cuprous iodide in ether was added 2.08 mL (2.51 mmol) of 1.2 M phenyllithium. After the solution was stirred for 10 min, 500 mg (2.04 mmol) of 5,5-diphenylcyclohex-2-en-1-one[41] in 10 mL of tetrahydrofuran was added rapidly followed by the addition of 780 mg (2.51 mmol) of diphenyl diselenide and 90 μL (1.70 mmol) of bromine in 5.0 mL of tetrahydrofuran. The reaction mixture was then added to 40 mL of ether and 20 mL of saturated ammonium chloride. Neutral workup of the organic layer gave 600 mg of a red oil which was chromatographed on a 2.5 × 200 cm silica gel column packed and eluted with 5% ether in hexane, and 200 mL fractions were collected: fraction 2, 154 mg of diphenyl diselenide; fraction 3, 223 mg (22.9%) of *cis*-2-(phenylseleno)-3,5,5-triphenylcyclohexanone, mp 123.0–125.0 °C. The spectral data were the following: IR ($CHCl_3$) 3030, 3010, 2990, 1710, 1600, 1500, 1440, 1390, 1080, 1030, 910, 760, 700 cm^{-1}; H NMR ($CDCl_3$, 100 MHz) δ 7.2–7.4 (m, 20 H, aromatics), 4.70 (m, 1 H, CH), 3.8 (d, 1 H, J = 12 Hz, CH), 2.8 (m, 2 H, CH_2), 2.2 (m, 2 H, CH_2). Fraction 4 gave 259 mg (26.7%) of *trans*-2-(phenylseleno)-3,5,5-triphenylcyclohexanone, mp 109.0–111.0 °C. The spectral data were the following: IR ($CHCl_3$) 3030, 3000, 2980, 2930, 1710, 1600, 1490, 1440, 1380, 1180, 1080, 1030, 910, 760, 700 cm^{-1}; H NMR ($CDCl_3$, 100 MHz) δ 7.2–7.4 (m, 20 H, aromatics), 4.1 (m, 1 H, CH), 3.5 (d, J = 15 Hz, 1 H, CH), 2.80 (m, 2 H, CH_2), 2.4 (m, 2 H, CH_2). Fraction 5 contained 130 mg (14.1%) of 5,5-diphenylcyclohex-2-en-1-one, mp 115.0–116.0 °C.[41]

To a 0 °C solution of 250.0 mg (0.52 mmol) of *trans*-2-(phenylseleno)-3,5,5-triphenylcyclohexanone and 0.20 mL (24.0 mmol) of pyridine in 5.0 mL of dichloromethane was added 1.0 mL of 30% aqueous hydrogen peroxide. The reaction was stirred at room temperature for 30 min, and basic–acidic workup gave 138 mg (82.1%) of a white solid, mp 104.0–115.0 °C. Recrystallization from ethanol gave 120 mg (71.4%) of 3,5,5-triphenylcyclohex-2-en-1-one, mp 117.0–117.5 °C. The spectral data were identical with the major photoproduct.

Single-Crystal X-ray Structure of *exo*-4,4,6-Triphenylbicyclo[3.1.0]-hexan-2-one.[42] Crystals of *exo*-4,4,6-triphenylbicyclo[3.1.0]hexan-2-one were prepared by slow crystallization from hexane. Preliminary examinations and collection of diffraction data were carried out on a Syntex-Nicolet P_1 diffractometer equipped with a graphite monochromated Mo Kα radiation source. The structures were solved by direct methods with use of the MULTAN80[43a,b] package and refined by full-matrix least-squares refinement. The final cycles of least-squares refinement[43c] assumed the non-hydrogen atoms to vibrate anisotropically and the hydrogen atoms to vibrate isotropically. Results and structural parameters are summarized in the supplementary material.

Ozonolysis of 2-*trans*-Styryl-3,3-diphenylcyclobutanone. To a −20 °C solution of 40.0 mg (0.12 mmol) of 2-*trans*-styryl-3,3-diphenylcyclobutanone in 6.0 mL of ethyl acetate was bubbled 0.14 mmol of ozone. The reaction mixture was purged with nitrogen for 2 min and was left to stand for 5 min, and then the reaction mixture was warmed to room temperature; 3.0 mL of water and 1.0 mL of 40% peroxyacetic acid were added, followed by stirring at room temperature for 8 h. Dilution with 20 mL of ether and basic workup gave 12.3 mg of a colorless oily solid. Bulb (30 °C) to bulb (dry ice cooled) distillation at 0.1 mm gave 9.42 mg (74.2%) of benzaldehyde as a colorless oil identified by infrared and 200-MHz H NMR. Treatment with 0.70 mL (0.91 mmol) of phenylhydrazine and 10 μL of acetic acid in 3.0 mL of ethanol afforded 12.0 mg (69.1%) of the benzaldehyde phenyl hydrazone, mp 154.0–156.0 °C (lit.[4] mp 155.0–156.0 °C).

The basic extract was acidified with 6 N hydrochloric acid and ether extracted. Neutral workup gave 28.1 mg (91.3%) of 3,3-diphenylcyclobutanone-2-carboxaldehyde as a white solid, mp 99.0–101.0 °C. Recrystallization from ethanol afforded 25.1 mg (81.5%) of the cyclobutanone, mp 100.0–101.0 °C. The spectral data were the following: IR ($CHCl_3$) 3030, 3010, 2920, 1780, 1700, 1600, 1580, 1450, 1420, 1280, 1060, 1040, 700 cm^{-1}; H NMR ($CDCl_3$, 200 MHz) δ 9.20 (d, J = 2 Hz, 2 H, HCO), 7.0–7.4 (m, 10 H, phenyls), 5.56 (d, J = 2 Hz, 1 H, CH), 3.52 (d, 1 H, J = 12 Hz, C*H*H), 3.11 (d, 1 H, J = 12 Hz, C*H*H); MS, *m/e* 250.0990 (calcd for $C_{17}H_{14}O_2$, *m/e* 250.0994).

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.97; H, 5.49.

3,3-Diphenylcyclobutanone-2-carboxylic Acid. A solution of 32.0 mg (0.19 mmol) of silver nitrate in 2.0 mL of water was treated with 40.0 mg (1.0 mmol) of sodium hydroxide in 5.0 mL of water and shaken for 5 min. The solid silver oxide was filtered, washed with cold water, and transferred wet to a flask containing 60.0 mg (1.5 mmol) of sodium hydroxide in 5.0 mL of water. The mixture was heated to 55–60 °C and

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added to 25 mg (0.10 mmol) of 3,3-diphenylcyclobutanone-2-carboxaldehyde in 10 mL of ethanol and 1.0 mL of ether to dissolve the aldehyde. The mixture was stirred and refluxed for 1 h and then poured into 25 mL of ether, and acidic workup gave 15.0 mg (56.4%) of 3,3-diphenylcyclobutanone-2-carboxylic acid, mp 108.0–111.0 °C. Recrystallization from pentane gave 12.8 mg (48.1%) of the acid as a white solid, mp 110.0–111.0 °C. The spectral data were the following: IR ($CHCl_3$) 3500–2500 (broad stretch), 3030, 2960, 2940, 1790, 1720, 1600, 1490, 1440, 1410, 1260, 1150, 1100, 1080, 1050, 1010, 880, 800, 700 cm^{-1}; H NMR ($CDCl_3$, 200 MHz) δ 10.80 (br s, 1 H, COO*H*), 7.0–7.5 (m, 10 H, phenyls), 5.65 (s, 1 H, CH), 3.80 (d, 1 H, J = 12 Hz, C*H*H), 2.85 (d, 1 H, J = 12 Hz, CH*H*), MS, m/e 266.0933 (calcd for $C_{17}H_{14}O_3$, m/e 266.0898).

Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found: C, 76.49, H, 5.41.

3,3-Diphenylcyclobutanone. A solution of 12.8 mg (0.050 mmol) of 3,3-diphenylcyclobutanone-2-carboxylic acid in 15 mL of benzene was refluxed for 2.25 h. The solution was concentrated in vacuo, and neutral workup gave 6.8 mg (64.1%) of 3,3-diphenylcyclobutanone as a white solid, mp 83.0–85.0 °C. Recrystallization from ethanol gave 5.9 mg (54.7%) of the cyclobutanone as a white solid, mp 85.0–86.0 °C (lit.[44] mp 85.0–86.0 °C).

3-Methyl-4,4-diphenylcyclohex-2-en-1-one. To a −78 °C solution of 10.0 g (36.0 mmol) of 6,6-diphenyl-3-methoxycyclohex-2-en-1-one[7] in 125 mL of tetrahydrofuran was added 49.3 mL (41.4 mmol) of 0.85 M methyllithium dropwise over 30 min. This solution was stirred for another 15 min and quenched with 50 mL of water. The solution was hydrolyzed by the dropwise addition of 80 mL of 6 N hydrochloric acid, stirred for 1 h, and ether extracted. Basic workup gave 7.19 g of a yellow oily solid. Recrystallization from ethanol yielded 6.30 g (66.9%) of 3-methyl-4,4-diphenylcyclohex-2-en-1-one as a white solid, mp 105.0–107.0 °C. The spectral data were the following: IR ($CHCl_3$) 3030, 3010, 2980, 1670, 1600, 1490, 1440, 1370, 1180, 1080, 1030, 780, 700 cm^{-1}; H NMR ($CDCl_3$, 200 MHz) δ 7.0–7.4 (m, 10 H, phenyls), 6.22 (s, 1 H, =CH), 2.70 (t, 2 H, CH_2), 2.15 (t, 2 H, CH_2), 1.60 (s, 3 H, CH_3); MS, m/e 262.1359 (calcd for $C_{19}H_{18}O$, m/e 262.1353).

Anal. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.91. Found: C, 86.69; H, 6.88.

3-Methyl-4,4-diphenylcyclohex-2-en-1-one Tosylhydrazone. To a solution of 2.0 g (7.63 mmol) of 3-methyl-4,4-diphenylcyclohex-2-en-1-one in 25 mL of ethanol was added a solution of 1.42 g (7.63 mmol) of *p*-toluenesulfonylhydrazide in 20 mL of ethanol and 0.10 mL of concentrated hydrochloric acid. The solution was warmed to 50 °C and then stored at −20 °C for 18 h, and the solution was filtered to give 2.95 g (89.1%) of 3-methyl-4,4-diphenylcyclohex-2-en-1-one tosylhydrazone as a white solid, mp 102.0–107.0 °C. Recrystallization from chloroform gave 2.80 g (85.4%) of the tosylhydrazone as a white solid, mp 107.0–108.0 °C. The spectral data were the following: IR (CH_2Cl_2) 3240, 3200, 3030, 2960, 1600, 1490, 1440, 1390, 1350, 1330, 1210, 1160, 1100, 1040, 980, 950, 920, 820, 660 cm^{-1}; H NMR (C_6D_6, 200 MHz) δ 8.0 (d, 2 H, tolyl), 7.0–7.5 (m, 14 H, aromatics), 6.2 (s, 1 H, =CH), 1.9 (t, 2 H, CH_2), 1.8 (s, 3 H, *p*-tolyl CH_3), 1.4 (t, 2 H, CH_2), 1.2 (s, 3 H, CH_3); MS, m/e 431.1787 (calcd for $C_{26}H_{26}N_2O_2S$, m/e 431.1778).

Anal. Calcd for $C_{26}H_{26}N_2O_2S$: C, 72.51; H, 6.08; N, 6.51. Found: C, 72.88; H, 6.09, N, 6.51.

3-Methyl-4,4-diphenylcyclohexene. To a solution of 1.00 g (23.2 mmol) of 3-methyl-4,4-diphenylcyclohex-2-en-1-one tosylhydrazone in 25 mL of dichloromethane was added 2.30 mL (24.5 mmol) of 1,3,2-benzodioxaborole.[35] After the solution was stirred at 0 °C for 1 h, 4.76 g (35.0 mmol) of sodium acetate was added, and the mixture was refluxed for 1.5 h and then poured into 50 mL of dichloromethane. Neutral workup gave 270 mg of yellow oil which was purified on a 2.5 × 600 cm silica gel column packed in 5% ether in hexane, and 250-mL fractions were collected: fractions 2–3, 162 mg (56.3%) of 3-methyl-4,4-diphenylcyclohexene as a white solid, mp 60.0–62.0 °C. Recrystallization from ethanol gave 160 mg (55.6%) of the cyclohexene as a white solid, mp 60.0–62.0 °C. The spectral data were the following: IR ($CHCl_3$) 3030, 2970, 1600, 1490, 1440, 760, 740, 700 cm^{-1}; H NMR ($CDCl_3$, 270 MHz) δ 7.0–7.4 (m, 10 H, phenyls), 6.03 (br m, 1 H, =CH), 5.65 (br m, 1 H, =CH), 3.05 (m, 1 H, CH), 1.90–2.3 (m, 4 H, CH_2–CH_2), 0.60 (s, 3 H, CH_3); MS, m/e 248.1564 (calcd for $C_{19}H_{20}$, m/e 248.1560).

Anal. Calcd for $C_{19}H_{20}$: C, 91.66; H, 8.31. Found: C, 91.88; H, 8.12.

4-Methyl-5,5-diphenylcyclohex-2-en-1-one. To 4.88 g (48.8 mmol) of chromium trioxide in 75 mL of dichloromethane and 6.0 mL of pyridine at 0 °C was added 600 mg (2.44 mmol) of 3-methyl-4,4-diphenylcyclohexene. After 40 h the solution was decanted, and the residue was washed with ether. Basic–acidic workup gave 586 mg of a yellow oil which was purified on a 2.5 × 100 cm silica gel column packed and eluted with 10% ether in hexane; and 150-mL fractions were collected: fraction 2, 232.4 mg (38.7%) of unreacted 3-methyl-4,4-diphenylcyclohexene, mp 60.0–62.0 °C; fractions 4–5, 118.2 mg (19.8%) of 4-methyl 5,5-diphenylcyclohex-2-en-1-one, mp 143.0–147.0 °C; fraction 6, 46.0 mg (7.7%) of 4-methyl-5,5-diphenylcyclohex-2-en-1-one and 3-methyl-4,4-diphenylcyclohex-2-en-1-one; fractions 7–8, 16.4 mg (10.9%) of 3-methyl-4,4-diphenylcyclohex-2-en-1-one, mp 105.0–107.0 °C. Recrystallization of fractions 4–5 from ethanol gave 107.2 mg (17.9%) of the enone as a white solid, mp 147.0–148.5 °C. The spectral data for 4-methyl-5,5-diphenylcyclohex-2-en-1-one were the following: IR ($CHCl_3$) 3020, 2990, 2920, 1670, 1600, 1490, 1440, 1380, 1180, 1080, 1035, 990, 940, 700 cm^{-1}; H NMR ($CDCl_3$, 270 MHz) δ 7.0–7.4 (m, 11 H, phenyls and =CH), 5.9 (d, 1 H, J = 12 Hz, =CH), 3.3–3.6 (m and q, 3 H, CH and CH_2), 0.9 (d, J = 8 Hz, 3 H, CH_3); UV (ethanol) 250 (ϵ 4990), 272 (2870), 290 (500), 320 (28); MS, m/e 262.1359 (calcd for $C_{19}H_{18}O$, m/e 262.1353).

Anal. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.91. Found: C, 86.72; H, 7.04.

Exploratory Direct Photolysis of 4-Methyl-5,5-diphenylcyclohex-2-en-1-one in Benzene. A solution of 100.0 mg (0.38 mmol) of 4,5,5-triphenylcyclohex-2-en-1-one in 150 mL of photograde benzene was irradiated with a 450-W Hanovia medium pressure mercury lamp through a Pyrex filter for 3 h under purified nitrogen.[34,36] The photolysate was concentrated in vacuo to 100 mg of a colorless oil and subjected to preparative HPLC, eluting with 1% ether in dichloromethane: fraction 1, 57.2 mg (57.2%) of 2-*trans*-propenyl-3,3-diphenylcyclobutanone, mp 71.0–72.0 °C, retention time 12 min; fraction 2, 37.7 mg (37.7%) of recovered starting enone, mp 147.0–148.5 °C, retention time 36 min. Recrystallization of fraction 1 from ethanol gave 54.6 mg (54.6%) of the cyclobutanone as a white solid, mp 71.0–72.0 °C. No other products were observed. The spectral data for 2-*trans*-propenyl-3,3-diphenylcyclobutanone were the following: IR ($CHCl_3$) 3040, 3020, 2990, 2960, 1778, 1600, 1490, 1440, 1330, 1305, 1280, 1215, 1125, 1070, 700 cm^{-1}; H NMR ($CDCl_3$, 270 MHz) δ 6.95–7.45 (m, 15 H, phenyls), 6.75 (m, 1 H, =CH), 5.94 (dd, 1 H, J = 13, 18 Hz, =CH), 4.55 (d, 1 H, J = 13 Hz, CH), 3.8 (d, 1 H, J = 21 Hz, C*H*H), 3.65 (dd, 1 H, J = 1.5, 21 Hz, CH*H*); UV (ethanol) 250 (ϵ 355), 256 (590), 261 (580), 272 (240), 290 (64), 310 (20); MS, m/e 262.1357 (calcd for $C_{19}H_{18}O$, m/e 262.1353).

Anal. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.91. Found: C, 86.70; H, 7.02.

Exploratory Direct Photolysis of 4-Methyl-5,5-diphenylcyclohex-2-en-1-one in Acetonitrile. A solution of 100.0 mg (0.38) of 4,5,5-triphenylcyclohex-2-en-1-one in 150 mL of photograde acetonitrile was irradiated under nitrogen[34,36] with a 450-W Hanovia medium-pressure mercury lamp through a Pyrex filter for 3 h. The photolysate was concentrated in vacuo to 99.1 mg of a colorless oil subjected to preparative HPLC; eluting with 1% ether in dichloromethane gave fraction 1 (51.5 mg (51.5%) of 2-*trans*-propenyl-3,3-diphenylcyclobutanone, identical in all respects with the material obtained in the benzene photolysis, mp 71.0–72.0 °C) and fraction 2 (43.1 mg (43.1%) of recovered starting enone, mp 147.0–148.5 °C).

Exploratory Sensitized Photolysis of 4-Methyl-5,5-diphenylcyclohex-2-en-1-one. A solution of 186 mg (0.71 mmol) of 4-methyl-5,5-diphenylcyclohex-2-en-1-one and 5.8 mL (49.9 mmol) of freshly distilled acetophenone in 250 mL of photograde benzene under purified nitrogen[34,36] was irradiated on the "Wisconsin Black Box"[37] apparatus with use of the filter solution system A.[34] The digital electronic actinometry[38] calibrated by ferrioxalate actinometry[39] indicated absorption of 1.55 mEinsteins of light. Concentration in vacuo and removal of acetophenone by bulb (30 °C) to bulb (dry ice cooled) distillation at 0.2 mm gave 179.1 mg (97.0%) of residue. Preparative HPLC, eluting with 1% ether in dichloromethane, gave fraction 1 (54.3 mg (30.4%) of 2-*trans*-propenyl-3,3-diphenylcyclobutanone, mp 71.0–72.0 °C) and fraction 2 (119.4 mg (64.1%) of starting enone, mp 147.0–148.5 °C).

Ozonolysis of 2-*trans*-Propenyl-3,3-diphenylcyclobutanone. To a −20 °C solution of 50.0 mg (0.19 mmol) of 2-*trans*-propenyl-3,3-diphenylcyclobutanone in 6.0 mL of ethyl acetate was bubbled 0.24 mmol of ozone. The reaction mixture was purged with nitrogen and warmed to room temperature, 3.0 mL of water and 1.0 mL of 40% peroxyacetic acid were added, and the reaction mixture was stirred at room temperature for 8 h. Dilution with 20 mL of ether and basic workup gave 11.4 mg of a colorless oil. Bulb (30 °C) to bulb (dry ice cooled) distillation at 0.1 mm gave 4.5 mg (83.3%) of acetaldehyde as a colorless oil identified by infrared and 200-MHz NMR. Treatment with 15.5 mg (0.10 mmol) of *p*-nitrophenylhydrazine and 10 μL of acetic acid in 3.0 mL of ethanol gave 9.3 mg (51.9%) of acetaldehyde *p*-nitrophenylhydrazone, mp 125.0–129.0 °C. Recrystallization from ethanol gave 8.8 mg (49.1%), mp 128.0–129.0 °C (lit.[45] mp 129.0 °C).

(44) Michejda, C. J.; Comnick, R. W. *J. Org. Chem.* **1975**, *40*, 1046–1054.

The original basic extract was acidified with 6 N hydrochloric acid and ether extracted. Neutral workup gave 28.7 mg (59.8%) of 2-carboxaldehyde-3,3-diphenylcyclobutanone, mp 99.0–101.0 °C. Recrystallization from ethanol gave 24.9 mg (51.9%) of the ketoaldehyde, mp 100.0–101.0 °C. The spectral data were identical with 3,3-diphenylcyclobutanone-2-carboxaldehyde.

Exploratory Direct Photolysis of 4-Methyl-5,5-diphenylcyclohex-2-en-1-one in 95% Ethanol. A solution of 75.2 mg (0.29) of 4-methyl-5,5-diphenylcyclohex-2-en-1-one in 150 mL of distilled ethanol was irradiated under nitrogen[34,36] with a 450-W Hanovia medium-pressure mercury lamp through a Pyrex filter for 2 h. Concentration in vacuo gave 74.8 mg (99.5%) of a colorless oil which when subjected to preparative HPLC, eluting with 1% ether in dichloromethane, gave fraction 1 (14.5 mg (19.3%) of 2-*trans*-3,3-diphenylcyclobutanone, mp 71.0–72.0 °C) and fraction 2 (59.3 mg (78.8%) of recovered starting enone, mp 147.0–148.5 °C). No other products were obtained.

Exploratory Direct Photolysis of 4-Methyl-5,5-diphenylcyclohex-2-en-1-one and Cyclohexylamine in Benzene. A solution of 90.0 mg (0.34 mmol) of 4-methyl-5,5-diphenylcyclohex-2-en-1-one and 0.100 mL (0.86 mmol) of freshly distilled cyclohexylamine in 150 mL of photograde benzene was irradiated under nitrogen[34,36] with a 450-W Hanovia medium pressure mercury lamp through a Pyrex filter for 2 h. Concentration in vacuo gave 88.9 mg of a colorless oil which was dissolved in ether and washed thoroughly with water, dried, and concentrated in vacuo to a yellow solid. Preparative HPLC, eluting with 1% ether in dichloromethane, gave fraction 1 (17.8 mg (19.8%) of 2-*trans*-propenyl-3,3-diphenylcyclobutanone, mp 71.0–72.0 °C) and fraction 2 (69.4 mg (77.1%) of recovered starting enone, mp 147.0–148.5 °C). No other products were obtained.

Exploratory Direct Photolysis of 4-Methyl-5,5-diphenylcyclohex-2-en-1-one and 1,1-Di(*p*-tolyl)ethylene in Benzene. A solution of 80.1 mg (0.31 mmol) of 4-methyl-5,5-diphenylcyclohex-2-en-1-one and 63.5 mg (0.31 mmol) of 1,1-di(*p*-tolyl)ethylene in 150 mL of photograde benzene was irradiated under nitrogen[34,36] with a 450-W Hanovia medium-pressure mercury lamp through a Pyrex filter for 3 h. Concentration in vacuo gave 143.0 mg of a clear oily solid. Preparative HPLC, eluting with 1% ether in dichloromethane, gave fraction 1 (62.4 mg (98.3%) of recovered 1,1-di(*p*-tolyl)ethylene), fraction 2 (28.8 mg (36.0%) of 2-*trans*-propenyl-3,3-diphenylcyclobutanone, mp 71.0–72.0 °C), and fraction 3 (48.9 mg (61.1%) of recovered starting enone, mp 147.0–148.5 °C). No crossover products were obtained.

Resolution of 4-Methyl-5,5-diphenylcyclohex-2-en-1-one. The procedure of Johnson and Zeller[17] was modified and applied. To a −23 °C solution of 774 mg (4.58 mmol) of (+)-(*S*)-*N*,*S*-dimethyl-*S*-phenylsulfoximine[46] in 15 mL of tetrahydrofuran was added 3.06 mL of 1.5 M n-butyllithium (4.58 mmol). The resulting deep yellow solution was stirred for 15 min, and to this was added 800 mg (3.06 mmol) of 4-methyl-5,5-diphenylcyclohex-2-en-1-one in 10 mL of tetrahydrofuran dropwise over 10 min. The reaction was stirred at −23 °C for 90 min and then poured into saturated ammonium chloride. Neutral workup gave 875 mg of a white oily solid. This was chromatographed on a 2.5 × 1000 cm silica gel column packed and eluted with 10% ethyl acetate in hexane and 500-mL fractions were collected: fraction 3, 96.2 mg (12.0%) of starting enone, mp 147.0–148.5 °C; fraction 5, 22.7 mg (2.8%) of diastereomer A, mp 132.0–136.0 °C; fraction 6, 14.5 mg (1.8%) of a mixture of two diastereomers, A and B; fraction 7, 22.5 mg (2.8%) of diastereomer B, mp 154.0–158.0 °C; fractions 9–11, 256 mg (32.0%) of diastereomer C, mp 128.0–131.0 °C; fraction 12, 64.2 mg (8.0%) of a mixture of diastereomers C and D; fractions 13–15, 314 mg (39.3%) of diastereomer D, mp 147.0–150.0 °C.

Recrystallization of diastereomer A from ethanol gave 20.5 mg (2.6%) of the adduct as a white solid, mp 136.0–137.0 °C. The spectral data for diastereomer A were the following: IR ($CHCl_3$) 3560, 3210, 3010, 2970, 2900, 2810, 1655, 1600, 1490, 1440, 1245, 1110, 1080, 700 cm^{-1}; H NMR ($CDCl_3$, 270 MHz) δ 7.1–7.6 (m, 15 H, phenyls), 6.25 (m, 2 H, =CH and =CH), 3.40 (d, 1 H, J = 16 Hz, C*H*H), 3.05 (m, 1 H, CH), 2.55–2.85 (m, 3 H, CH_2 and C*H*H), 2.58 (s, 3 H, N–CH_3), 0.65 (d, 3 H, J = 9 Hz, CH_3); MS, m/e 431.1918 (calcd for $C_{27}H_{28}NO_2S$, m/e 431.1919).

Anal. Calcd for $C_{27}H_{28}NO_2S$: C, 75.14; H, 6.77. Found: C, 74.99; H, 6.97.

Recrystallization of diastereomer B from ethanol gave 19.3 mg (2.4%) of the adduct as a white solid, mp 157.0–158.0 °C. The spectral data for diastereomer B were the following: IR ($CHCl_3$) 3540, 3210, 3010, 2970, 2900, 2800, 1650, 1600, 1490, 1440, 1245, 1185, 1145, 1080, 700 cm^{-1}; H NMR ($CDCl_3$, 270 MHz) δ 7.1–7.7 (m, 15 H, phenyls), 6.05 (d, 1 H, J = 14 Hz, =CH), 6.05 (q, 1 H, =CH), 3.30 (d, 1 H, J = 12 Hz, C*H*H), 3.01 (m, 1 H, CH), 2.54–2.88 (m, 3 H, CH_2 and C*H*H), 2.56 (s, 3 H, N–CH_3), 0.67 (d, 3 H, J = 10 Hz, CH_3); MS, m/e 431.1914 (calcd for $C_{27}H_{28}NO_2S$, m/e 431.1919).

Anal. Calcd for $C_{27}H_{28}NO_2S$: C, 75.14; H, 6.77. Found: C, 75.20; H, 7.07.

Recrystallization of diastereomer C from ethanol gave 247 mg (30.1%) of the adduct as a white solid, mp 130.0–131.0 °C. The spectral data for diastereomer C were the following: IR ($CHCl_3$) 3560, 3210, 3010, 2970, 2900, 2810, 1650, 1600, 1490, 1440, 1245, 1140, 1110, 1080, 700 cm^{-1}; H NMR ($CDCl_3$, 270 MHz) δ 7.1–7.8 (m, 15 H, phenyls), 6.21 (m, 2 H, =CH and =CH), 3.45 (d, 1 H, J = 16 Hz, C*H*H), 3.10 (m, 1 H, CH), 2.82 (d, 1 H, J = 16 Hz, C*H*H), 2.60 (s, 3 H, N–CH_3), 2.54–2.60 (d, 1 H, C*H*H), 0.71 (d, 3 H, J = 9 Hz, CH_3); MS, m/e 431.1915 (calcd for $C_{27}H_{28}NO_2S$, m/e 431.1919).

Anal. Calcd for $C_{27}H_{28}NO_2S$: C, 75.14; H, 6.77. Found: C, 75.27; H, 6.97.

Recrystallization of diastereomer D from ethanol gave 295 mg (36.9%) of the adduct as a white solid, mp 151.0–152.0 °C. The spectral data for diastereomer D were the following: IR ($CHCl_3$) 3555, 3200, 3010, 2980, 2900, 2800, 1650, 1600, 1490, 1440, 1240, 1180, 1145, 1110, 1080, 700 cm^{-1}; H NMR ($CDCl_3$, 270 MHz) δ 7.0–7.8 (m, 15 H, phenyls), 6.1 (q, 1 H, =CH), 5.45 (d, 1 H, J = 12 Hz, =CH), 2.92–3.45 (m, 5 H, C*H*H, CH_2, and CH_2), 2.60 (s, 3 H, N–CH_3), 0.66 (d, 3 H, J = 10 Hz, CH_3); MS, m/e 431.1909 (calcd for $C_{27}H_{28}NO_2S$, m/e 431.1919).

Anal. Calcd for $C_{27}H_{28}NO_2S$: C, 75.14; H, 6.77. Found: C, 75.52; H, 6.93.

Optically Active (−)-4-Methyl-5,5-diphenylcyclohex-2-en-1-one. The procedure of Johnson and Zeller[17] was modified and used. A solution of 384 mg (0.89 mmol) of sulfoximine adduct diastereomer C in 15 mL of toluene was refluxed for 14 h. Concentration in vacuo gave 380 mg (99.0%) of a white solid, which was dissolved in ether and washed with 10% cuprous nitrate to remove the sulfoximine. Neutral workup of the ether layer gave 192 mg (86.8%) of (−)-4-methyl-5,5-diphenylcyclohex-2-en-1-one, mp 153.0–156.0 °C. Recrystallization from ethanol gave 177 mg (79.8%) of the resolved enone as a white solid, mp 158.0–159.0 °C. The specific rotations were the following: (λ) (589) −356.3° (±0.1°), (578) −393.1°, (546) −449.8°, (436) −819.4°, (365) −813.8° (c 0.050, $CHCl_3$, 25 °C). MS, m/e 262.1346 (calcd for $C_{19}H_{18}O$, m/e 262.1353).

Anal. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.91. Found: C, 86.68; H, 6.88.

Optically Active (+)-4-Methyl-5,5-diphenylcyclohex-2-en-1-one. A solution of 400 mg (0.93 mmol) of sulfoximine adduct diastereomer D in 25 mL of toluene was refluxed for 16 h. Concentration in vacuo gave 392 mg of a white solid, which was taken up in ether and washed with 10% cuprous nitrate. Neutral workup gave 213 mg (87.6%) of (+)-4-methyl-5,5-diphenylcyclohex-2-en-1-one, mp 150.0–157.5 °C. Recrystallization from ethanol gave 194 mg (75.7%) of the resolved enone as a white solid, mp 158.0–159.0 °C. The specific rotations were the following: (λ) (589) 355.2° (±0.1°), (578) 392.8°, (546) 448.6°, (436) 817.9°, (365) 813.8° (c 0.050, $CHCl_3$, 25 °C). MS, m/e 262.1340 (calcd for $C_{19}H_{18}O$, m/e 262.1353).

Anal. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.91. Found: C, 86.87; H, 6.96.

Chiral Shift Study of Resolved 4-Methyl-5,5-diphenylcyclohex-2-en-1-one. A 270-MHz NMR spectrum was taken of 5.4 mg (0.02 mmol) of (−)-4-methyl-5,5-diphenylcyclohex-2-en-1-one dissolved in 600 μL of deuteriochloroform; then 20 μL (0.010 mmol) of 0.20 M tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III) was added. The α proton vinyl doublet was now a pair of vinyl doublets. The $\Delta\Delta\delta$ shift difference was 0.34 ppm for the vinyl proton. Integration showed the ratio of the peaks to be 18.9:1.0, indicating the enantiomeric excess was 90.0 ± 2.0%. A chiral shift experiment was done under the same conditions for the (+)-4-methyl-5,5-diphenylcyclohex-2-en-1-one enantiomer. Integration of the separated peaks showed the ratio to be 19.1:1.0, indicating the enantiomeric excess was 90.0 ± 2.0%.

2-*trans*-Propenyl-3,3-diphenylcyclobutanol. To a solution of 50.0 mg (0.19 mmol) of 2-*trans*-propenyl-3,3-diphenylcyclobutanone in 5.0 mL of tetrahydrofuran at −78 °C was added 0.26 mL (0.26 mmol) of potassium tri-*sec*-butylborohydride.[47] The resulting yellow solution was stirred for 3 h, warmed to room temperature, and quenched by addition of 1.0 mL of water, 0.50 mL of ethanol, 1.0 mL of 6 N sodium hydroxide, and 0.50 mL of 30% hydrogen peroxide. Neutral workup gave 44.3 mg (88.6%) of 2-*trans*-propenyl-3,3-diphenylcyclobutanol, mp 104.0–105.0

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°C. Recrystallization from hexane gave 40.9 mg (81.8%) of the alcohol as a white solid, mp 104.0–105.0 °C. The spectral data were the following: IR ($CHCl_3$) 3400, 3030, 3010, 2910, 1650, 1600, 1440, 1380, 1310, 1280, 1260, 1100, 1040, 960, 890, 750, 700 cm^{-1}; H NMR ($CDCl_3$, 270 MHz) δ 7.05–7.50 (m, 10 H, phenyls), 6.75 (m, 1 H, =CH), 6.25 (dd, 1 H, J = 8, 15 Hz, =CH), 4.27 (dd, 1 H, J = 8 Hz, CH), 3.97 (m, 1 H, C*H*-OH), 3.1 (m, 1 H, C*H*H), 2.8 (dd, 1 H, J = 7, 9 Hz, C*H*H), 1.65 (dd, 3 H, J = 1, 7 Hz, CH_3); MS, m/e 264.1514 (calcd for $C_{19}H_{20}O$, m/e 264.1512).

Anal. Calcd for $C_{19}H_{20}O$: C, 86.38; H, 7.43. Found: C, 86.23; H, 7.43.

2-*trans*-Propenyl-3,3-diphenylcyclobutyl Mandelate. The Whitesell and Reynolds esterification[48] was used. To a solution of 64.6 mg (0.33 mmol) of D-(−)-*O*-acetylmandelic acid,[49] 80 mg (0.30 mmol) of 2-*trans*-propenyl-3,3-diphenylcyclobutanol, and 3.6 mg (0.030 mmol) of 4-(dimethylamino)pyridine in 6.0 mL of dichloromethane at 0 °C was added 65.6 mg (0.318 mmol) of dicyclohexylcarbodiimide in 5.0 mL of dichloromethane. A white precipitate immediately formed, and the suspension was stirred at room temperature for 20 h. The urea precipitate was filtered, and acidic–basic workup gave 120 mg (92.6%) of a crude diastereomeric mixture of esters. The esters were separated by preparative HPLC, eluting with 7% ethyl acetate in hexane: fraction 1, 20.1 mg (25.1%) of diastereomer A of 2-*trans*-propenyl-3,3-diphenylcyclobutyl mandelate, mp 168.0–169.0 °C, retention time 44 min. Recrystallization from pentane gave 18.5 mg (23.1%) of the ester as a white solid, mp 168.0–169.0 °C; fraction 2, 18.8 mg (23.4%) of diastereomer B of 2-*trans*-propenyl-3,3-diphenylcyclobutyl mandelate, mp 152.0–153.0 °C, retention time 51 min. Recrystallization from pentane gave 15.4 mg (19.3%) of the ester as a white solid, mp 152.0–153.0 °C. The spectral data for fraction 1 were the following: IR ($CHCl_3$) 3020, 2980, 2920, 1735, 1600, 1510, 1430, 1380, 1310, 1240, 1100, 1050, 1000, 955, 890, 740, 700 cm^{-1}; H NMR ($CDCl_3$, 270 MHz) δ 7.0–7.5 (m, 15 H, phenyls), 5.90 (s, 1 H, C*H*-OAc), 5.60 (m, 1 H, =CH), 5.10 (dd, 1 H, J = 7, 15 Hz, =CH), 4.78 (dd, 1 H, J = 7, 12 Hz, CH), 4.12 (m, 1 H, C*H*–O–mandelate), 3.08 (m, 2 H, CH_2), 1.60 (d, 3 H, J = 8 Hz, CH_3); MS, m/e 440.5545 (calcd for $C_{29}H_{28}O_4$, m/e 440.5547).

Anal. Calcd for $C_{29}H_{28}O_4$: C, 79.07; H, 6.41. Found: C, 79.24; H, 6.35.

The spectral data for fraction 2 were the following: IR ($CHCl_3$) 3020, 2990, 2920, 1735, 1600, 1510, 1430, 1380, 1310, 1240, 1100, 1050, 1000, 945, 890, 700 cm^{-1}; H NMR ($CDCl_3$, 270 MHz) δ 7.0–7.5 (m, 15 H, phenyls), 6.88 (s, 1 H, C*H*–OAc), 5.45 (m, 1 H, =CH), 5.15 (dd, 1 H, J = 7, 15 Hz, =CH), 4.75 (dd, 1 H, J = 7, 12 Hz, CH), 4.05 (m, 1 H, C*H*–O–mandelate), 3.05 (m, 2 H, C*H*H), 1.56 (d, 3 H, J = 8 Hz, CH_3); MS, m/e 440.5543 (calcd for $C_{29}H_{28}O_4$, m/e 440.5547).

Anal. Calcd for $C_{29}H_{28}O_4$: C, 79.07; H, 6.35. Found: C, 79.41; H, 6.25.

Optically Active (−)-2-*trans*-Propenyl-3,3-diphenylcyclobutanol. A solution of 13.0 mg (0.030 mmol) of diastereomer B of 2-*trans*-propenyl-3,3-diphenylcyclobutyl mandelate and 4.55 mg (0.12 mmol) of lithium aluminum hydride in 5.0 mL of tetrahydrofuran was stirred at room temperature for 12 h. Neutral workup gave 14.1 mg of a clear oil. Preparative HPLC, eluting with 7% ethyl acetate in hexane, gave fraction 1 (3.2 mg of an unidentified oil, retention time 5 min), fraction 2 (6.1 mg, (80.2%) of (−)-2-*trans*-propenyl-3,3-diphenylcyclobutanol, mp 113.0–114.0 °C, retention time of 40 min), and fraction 3 (4.8 mg of an unidentified oil, retention time 49 min). Recrystallization of fraction 2 from hexane gave 5.6 mg (73.3%) of the alcohol as a white solid, mp 113.0–114.0 °C. The spectral data of fraction 2 were identical with those of the racemic alcohol. NMR spectra with tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III) showed the material was 100% optically pure. The specific rotations were the following: (λ) (589) −109.4° (±1°), (578), −114.1°, (546) −132.0°, (436) −232.6°, (365) −344.6° (c 0.0045, $CHCl_3$, 25 °C).

Optically Active (+)-2-*trans*-Propenyl-3,3-diphenylcyclobutanol. A solution of 28.6 mg (0.070 mmol) of diastereomer A of 2-*trans*-propenyl-3,3-diphenylcyclobutyl mandelate and 9.87 mg (0.26 mmol) of lithium aluminum hydride in 5.0 mL of tetrahydrofuran was stirred for 12 h. Neutral workup gave 30.0 mg of a clear oil. Preparative HPLC, eluting with 7% ethyl acetate in hexane, gave fraction 1 (3.2 mg of an unidentified oil, retention time 5 min), fraction 2 (11.6 mg (67.9%) of (+)-2-*trans*-propenyl-3,3-diphenylcyclobutanol, mp 112.5–114.0 °C, retention time 40 min), and fraction 3 (5.1 mg of an unidentified oil, retention time 51 min). Recrystallization of fraction 2 from pentane gave 10.7 mg (67.9%) of the alcohol as a white solid, mp 112.5–114.0 °C. The spectral data of fraction 2 were identical with those of the racemic alcohol. The optical purity was determined by NMR spectra with tris-[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III) to be 100%. The specific rotations were the following: (λ) (589) 109.4° (±1°), (578) 114.6°, (546) 131.8°, (436) 233.1°, (365) 341.0° (c 0.0079, $CHCl_3$, 25 °C).

Optically Active (−)-2-*trans*-Propenyl-3,3-diphenylcyclobutanone. To a solution of 0.50 mL of dichloromethane and 25.7 μL (0.32 mmol) of pyridine was added 15.9 mg (0.16 mmol) of chromium trioxide. After 15 min, 7.0 mg (0.030 mmol) of (−)-2-*trans*-propenyl-3,3-diphenylcyclobutanol in 0.30 mL of dichloromethane was added and the mixture was stirred for 20 min. Basic workup gave 7.4 mg of a solid purified by HPLC, eluting with 1% ether in dichloromethane to give 5.2 mg (75.3%) of (−)-2-*trans*-propenyl-3,3-diphenylcyclobutanone, mp 78.0–79.0 °C, retention time 8 min, identical with all spectral data of the racemic material. Recrystallization from ethanol gave 4.7 mg (68.1%) of the cyclobutanone as a white solid, mp 78.0–79.0 °C. NMR spectra with tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium-(III) showed the material was 100% optically pure. The specific rotations were the following: (λ) (589) −86.8° (±0.5°), (578) −92.3°, (546) −106.5°, (436) −206.7°, (365) −402.1° (c 0.0047, $CHCl_3$, 25 °C). MS, m/e 262.1357 (calcd for $C_{19}H_{18}O$, m/e 262.1353).

Anal. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.91. Found: C, 86.70; H, 6.86.

Optically Active (+)-2-*trans*-Propenyl-3,3-diphenylcyclobutanone. To a solution of 1.0 mL of dichloromethane and 33.1 μL (0.41 mmol) of pyridine was added 20.5 mg (0.21 mmol) of chromium trioxide. After 15 min, 9.3 mg (0.030 mmol) of (+)-2-*trans*-propenyl-3,3-diphenylcyclobutanol in 0.40 mL of dichloromethane was added. After 20 min of stirring, basic workup gave a yellow-white solid purified by HPLC, eluting with 1% ether in dichloromethane yielding 6.8 mg (65.1%) (+)-2-*trans*-propenyl-3,3-diphenylcyclobutanone, mp 78.0–79.0 °C, retention time 8 min, identical with all spectral data of the racemic material. Recrystallization from ethanol gave 5.8 mg (55.5%) of the cyclobutanone as a white solid, 78.0–79.0 °C. NMR spectra with tris-[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III) showed the material to be 100% optically pure. The specific rotations were the following: (λ) (589) 86.8° (±0.5°), (578) 92.5°, (546) 106.5°, (436) 206.7°, (365) 402.1° (c 0.0058, $CHCl_3$, 25 °C). MS, m/e 262.1357 (calcd for $C_{19}H_{18}O$, m/e 262.1353).

Anal. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.91. Found: C, 86.84; H, 6.87.

Photolysis of Optically Active 4-Methyl-5,5-diphenylcyclohex-2-en-1-one. A solution of 100 mg (0.38 mmol) of (−)-4-methyl-5,5-diphenylcyclohex-2-en-1-one (90% ee) in 150 mL of photograde benzene was photolyzed under nitrogen[34,36] with a 450-W Hanovia medium-pressure mercury lamp through filter solution C[34] for 3 h. Concentration in vacuo gave a yellow oily solid and separation by HPLC, eluting with 1% ether in dichloromethane, gave fraction 1 (38.2 mg (38.2%) of (−)-2-*trans*-propenyl-3,3-diphenylcyclobutanone, mp 72.0–73.0 °C) and fraction 2 (58.4 mg (58.4%) of recovered starting enone, mp 158.0–159.0 °C). The cyclobutanone photoproduct possessed spectral data identical with those of racemic material. The specific rotations were the following: (λ) (589) −5.51° (±0.1°), (578) −7.50°, (546) −8.03°, (436) −16.83°, (365) −31.17° (c 0.0058, $CHCl_3$, 25 °C). The data for these experiments are summarized in Tables 1 and 2 in the supplementary material.

Chiral Shift Study of 2-Propenyl-3,3-diphenylcyclobutanone. A 7.8-mg (0.030 mmol) sample of (−)-2-*trans*-propenyl-3,3-diphenylcyclobutanone generated from the photolysis of optically active 4-methyl-5,5-diphenylcyclohex-2-en-1-one was dissolved in a minimum of deuteriochloroform and a NMR spectrum taken before and after the addition of 15 μL (0.01 mmol) of 0.2 M tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III). The α methylene proton AB quartet was transformed into a pair of AB quartets with a $\Delta\Delta\delta$ value for the pair of quartets of 0.28 ppm. Integration showed the ratio of the peaks to be 10:9, indicating a 5.3 ± 2% enantiomeric excess.

Control Photolysis of Optically Active 4-Methyl-5,5-diphenylcyclohex-2-en-1-one. A solution of 100 mg (0.381 mmol) of optically active (−)-4-methyl-5,5-diphenylcyclohex-2-en-1-one (90% ee) and 5.0 mg (0.019 mmol) of optically active (−)-2-*trans*-propenyl-3,3-diphenylcyclobutanone (100% ee) in 150 mL of photograde benzene was photolyzed under nitrogen[34,36] with a 450-W Hanovia medium-pressure mercury lamp with filter solution C[34] for 1.5 h. Concentration in vacuo gave 105 mg of a solid. Preparative HPLC, eluting with 1% ether in dichloromethane, gave fraction 1 (15.8 mg (10.8%, 10.8 mg formed via photolysis and the 5.0 mg originally added cyclobutanone) of cyclobutanone) and fraction 2 (86.5 mg (86.5%) of starting enone with optical activity retained, mp 158.0–159.0 °C). The spectral data for the cyclobutanone were identical with those of the racemic material. The specific rotations were the following: (λ) (589) −31.08° (±0.2°), (578) −31.90°, (546) 36.90°, (436) 70.06°, (365) 137.49° (c 0.0158, $CHCl_3$,

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(49) Breitholle, E. G.; Stammer, C. H. *J. Org. Chem.* **1974**, *39*, 1311–1313.

25 °C). The cyclobutanone generated from the photolysis had only a 4.49 ± 0.93% enantiomeric excess.

Control Photolysis of Optically Active 2-*trans*-Propenyl-3,3-diphenylcyclobutanone. A solution of 98.3 mg (0.38 mmol) of racemic 4-methyl-5,5-diphenylcyclohex-2-en-1-one and 7.8 mg (0.030 mmol) of optically active (−)-2-*trans*-propenyl-3,3-diphenylcyclobutanone (100% ee) in 150 mL of photograde benzene was photolyzed under nitrogen[34,36] with a 450-W Hanovia medium-pressure mercury lamp with filter solution C[34] for 0.75 h. Concentration in vacuo and separation by HPLC, eluting with 1% ether in dichloromethane, gave fraction 1 (13.1 mg (5.4%, 5.3 mg formed via photolysis and the 7.8 mg originally added cyclobutanone photoproduct)) and fraction 2 (90.1 mg (91.7%) of recovered starting enone, mp 158.0–159.0 °C). The specific rotations were the following: (λ) (589) −49.9° (±0.4°), (578) −53.1°, (546) −63.3°, (436) −122.0°, (365) −237.2° (*c* 0.0131, $CHCl_3$, 25 °C).

Lanthanide Shift Study of *exo*-4,4,6-Triphenylbicyclo[3.1.0]hexan-2-one. A 4.0-mg (0.012 mmol) sample of *exo*-4,4,6-triphenylbicyclo-[3.1.0]hexan-2-one was dissolved in 600 μL of deuteriochloroform. A 270-MHz H NMR spectrum was taken. To this were added incremental amounts of a standard deuteriochloroform solution of tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione)europium(III) (Eu-fod). The spectral data for the shifted cyclopropyl protons are shown in Table 8 of the supplementary material, and proton assignments were made in conjunction with X-ray bond distance data. The slopes of the plots of $\Delta\delta$ vs. mole ratio were 0.579 (for C-1, δ 2.42), 0.318 (for C-6, δ 2.54), and 0.246 (for C-5, δ 2.78).

2,4,6,6-Tetradeuterio-4,5,5-triphenylcyclohex-2-en-1-one. The general procedure of Hart, Collins, and Waring[50] was used. To a 10-mg (0.44 g-atom) pellet of sodium was added 8.0 mL of methyl alcohol-*d*. This was stirred under nitrogen at room temperature for 20 min, then 50 mg (0.191 mmol) of 4,5,5-triphenylcyclohex-2-en-1-one in 4.0 mL of tetrahydrofuran was added. The yellow solution was stirred for 30 min and poured into 10 mL of deuterium oxide. Neutral workup gave 50 mg of a yellow oil. Several runs were combined and 250 mg were separated by preparative HPLC, eluting with 1% ether in dichloromethane to give fraction 1 (137.6 mg (55.0%) of 2,2,6,6-tetradeuterio-4,5,5-triphenylcyclohex-3-en-1-one as a white solid, mp 156.0–160.0 °C, retention time 56 min) and fraction 2 (96.4 mg (38.6%) of 2,4,6,6-tetradeuterio-4,5,5-triphenylcyclohex-2-en-1-one as a white solid, mp 204.0–210.0 °C, retention time 72 min). The spectral data were the following: IR ($CHCl_3$) 3040, 3020, 2920, 2850, 2210, 2190, 1670, 1600, 1490, 1440, 1355, 1230, 1085, 1035, 965, 910, 700 cm^{-1}; H NMR ($CDCl_3$, 270 MHz) δ 6.7–7.4 (m, 16 H, phenyls and C-3 =CH), 6.15 (d, 0.2 H, C-2 =CH), 4.48 (d, 0.2 H, C-4 CH); UV (ethanol) 252 (ϵ 5320), 270 (3300), 290 (800), 320 (30); MS, *m/e* 328.1774 (calcd for $C_{24}H_{16}OD_4$, 328.1765), 60.1% d_4; 327.1733 (calcd for $C_{24}H_{17}OD_3$, 327.1740), 27.2% d_3; 326.1669 (calcd for $C_{24}H_{18}OD_2$, 326.1602), 12.7% d_2.

Exploratory Direct Photolysis of 2,4,6,6-Tetradeuterio-4,5,5-triphenylcyclohex-2-en-1-one. A solution of 93.0 mg (0.28 mmol) of 2,4,6,6-tetradeuterio-4,5,5-triphenylcyclohex-2-en-1-one in 150 mL of photograde benzene was irradiated under nitrogen[34,36] with a 450-W Hanovia medium-pressure mercury lamp through a Pyrex filter for 30 min. Concentration in vacuo gave 91.0 mg (97.8%) of a colorless oil. Preparative HPLC, eluting with 1% ether in dichloromethane, gave fraction 1 (7.8 mg (8.38%) of a mixture of deuterated cyclobutanones), fraction 2 (9.8 mg (10.5%) of 1,3,3,5-tetradeuterio-4,4,6-triphenylbicyclo[3.1.0]hexan-2-one as a white solid, mp 138–145 °C), fraction 3 (27.1 mg (29.1%) of starting tetradeuterated enone, mp 204.0–210.0 °C), and fraction 4 (42.0 mg (45.2%) of 2,4,6,6-tetradeuterio-3,5,5-triphenylcyclohex-2-en-1-one). The spectral data for 1,3,3,5-tetradeuterio-4,6,6-triphenylbicyclo[3.1.0]hexan-2-one were the following: IR ($CHCl_3$) 3030, 3010, 2940, 2840, 1715, 1600, 1490, 1440, 1260, 1240, 1075, 1040, 755, 735, 700 cm^{-1}; H NMR ($CDCl_3$, 270 MHz) δ 7.0–7.5 (m, 15 H, phenyls), 2.78 (br s, 0.2 H, C-5 cyclopropyl), 2.54 (s, 1 H, C-6 cyclopropyl), 2.42 (br s, 0.2 H, C-1 cyclopropyl); MS, *m/e* 328.1762 (calcd for $C_{24}H_{16}OD_4$, 328.1765), 68.4% d_4; 327.1737 (calcd for $C_{24}H_{17}OD_3$, 327.1740), 20.5% d_3; 326.1666 (calcd for $C_{24}H_{18}OD_2$, 326.1602).

(50) Hart, H.; Collins, P. M.; Waring, A. J. *J. Am. Chem. Soc.* **1966**, *88*, 1005–1014.

(51) Zimmerman, H. E.; Welter, T. R.; Tartler, D.; Bunce, R. A.; Ramsden, W. D.; King, R. K., unpublished results.

Summary of Quantum Yield Results for 4,5,5-Triphenylcyclohex-2-en-1-one. All direct, sensitized, and quenched quantum yields were determined with use of the microbench apparatus.[37] Photolyses employed an Osram HBO 200-W high-pressure mercury lamp, and a Bausch and Lomb Model 33-86-79 monochromator having a 5.4 mm entrance slit and a 3.0 mm exit slit. Light output was measured by using digital electronic actinometry,[38] and all runs were calibrated with ferrioxalate actinometry.[39] The direct and sensitized runs were purged with purified nitrogen[34,36] for 1 h prior to and during photolysis; however, the quenched runs were only purged for 1 h prior to photolysis due to the volatility of 1,3-cyclohexadiene. Analysis was done by HPLC eluting with 1% ether in dichloromethane with purified triphenylmethane as a standard. The runs are summarized in Table 9 of the supplementary material.

Summary of Quantum Yield Results for 4-Methyl-5,5-diphenylcyclohex-2-en-1-one. All direct, sensitized, and quenched quantum yields were determined with the "Wisconsin Black Box"[37] apparatus. Filter solution B[34] was used in the direct and quenched runs and filter solution A[34] in the sensitized runs; otherwise the procedures cited for the microbench runs were used (vide supra). Analysis was done by 270-MHz NMR with purified triphenylmethane as an internal standard.

Molecular Mechanics Calculations. All molecular mechanics calculations were performed with programming package NOTROUBLE.[25a] The total steric energies obtained for minimized conformations were the following: 4-*ax*-methyl-5,5-diphenylcyclohex-2-en-1-one (16.44 kcal/mol), 4-*eq*-methyl-5,5-diphenylcyclohex-2-en-1-one (15.45 kcal/mol), *exo*-4,4,6-triphenylbicyclo[3.1.0]hexan-2-one (49.39 kcal/mol), and *endo*-4,6,6-triphenylbicyclo[3.1.0]hexan-2-one (53.63 kcal/mol) were calculated.

Quantum Mechanical Calculations. All quantum mechanical calculations were performed with the "MOPAC" program package.[29] The geometry of the intermediate was initially optimized with the MMP[25a] program added to the "NOTROUBLE" package,[25a] and final optimization was done with the "MOPAC" package. The state energies for the proposed diradical intermediate calculated from the multielectron configurational interaction are T_1 (−3.635 121 eV), S_1 (−3.632 303 eV), and S_2 (−0.052 354 eV).

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Registry No. (±)-**6**, 103367-50-6; (±)-**6D**, 103367-70-0; (±)-**7**, 103367-61-9; (−)-**7**, 103367-64-2; (+)-**7**, 103367-65-3; **8**, 75010-96-7; **9**, 103367-47-1; **10**, 17429-38-8; **11**, 103367-48-2; **12**, 103367-59-5; (±)-**13**, 103367-49-3; (±)-**14**, 103367-60-8; **15**, 40529-24-6; **16**, 103367-54-0; (±)-*exo*-**17**, 103367-53-9; (±)-*exo*-**17D'**, 103367-71-1; (±)-**18**, 103367-52-8; (±)-**19**, 103367-51-7; (±)-**20**, 103367-62-0; (−)-**20**, 103367-68-6; (+)-**20**, 103367-69-7; (±)-**21**, 103367-57-3; (±)-**22**, 103367-58-4; **23**, 54166-20-0; **24** (diastereomer 1), 103475-75-8; **24** (diastereomer 2), 103475-76-9; **24** (diastereomer 3), 103367-63-1; **24** (diastereomer 4), 103475-77-0; **25**, 103367-66-4; **26**, 103367-67-5; $TsNHNH_2$, 1576-35-8; (*S*)-(+)-PhS(O)Me=NMe, 33993-53-2; (*R*)-(−)-$PhCH(OAc)CO_2H$, 51019-43-3; (±)-*cis*-2-(phenylseleno)-3,5,5-triphenylcyclohexanone, 103367-55-1; (±)-*trans*-2-(phenylseleno)-3,5,5-triphenylcyclohexanone, 103367-56-2; (±)-2,4,6,6-tetradeuterio-3,5,5-triphenylcyclohex-2-en-1-one, 103367-72-2.

Supplementary Material Available: Photolysis data of 4-methyl-5,5-diphenylcyclohex-2-en-1-one and 2-*trans*-propenyl-3,3-diphenylcyclobutanone, tables of atomic coordinates, bond angles, bond distances, and isotropic and anisotropic thermal parameters, and a full scale copy of Figure 1, details and raw data for the photolysis of optically active 4-methyl-5,5-diphenylcyclohex-2-en-1-one, details and raw data for control runs involving the cyclobutanone (21 pages). Ordering information is given on any current masthead page.