and P. J. Derrick, *Org. Mass Spectrom.*, in press.

(33) The time-window for metastable decomposition in the first field-free region extends to shorter times (10^{-7} sec) with FI than with EI. However, the differences in metastable abundances are not due to the wider time-window since the same differences between FI and EI are observed with the second field-free metastables for which the time-windows with FI and EI are more similar to each other.

(34) For an excellent discussion of the relevant aspects of unimolecular reaction theory, see W. Forst, "Theory of Unimolecular Reactions", Academic Press, New York, N.Y. 1973.

(35) These two statements are to some extent synonymous. Decomposition of isolated electronic states do not compete, and internal energy is not randomized over all vibronic states; whereas decompositions of noninterconverting isomeric structures also do not compete, but this is generally not regarded as a failure to achieve energy randomization.

(36) Metastable intensities at electron energies below nominal 12 eV were too low for meaningful measurement. We confirmed, however, the report of Green et al.[13] that loss of water involving the cis-4 hydrogen does rise in importance in the EI mass spectrum relative to processes involving C-3 (C-5) hydrogens as the electron energy is taken below 20 eV.

(37) M. A. Baldwin, A. Kirkien-Konasiewicz, A. Maccoll, and B. Saville, *Chem. Ind.* (*London*), 286 (1966).

(38) F. P. Lossing, private communication, 1974.

Rotational Deactivation, Energy Localization, and Reactivity in the Photochemistry of 1-Methylene-4-phenyl-4-vinylcyclohex-2-ene

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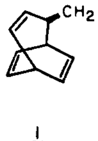
Abstract: The singlet and triplet photochemistry of 1-methylene-4-phenyl-4-vinylcyclohex-2-ene (**5**) has been studied. Triplet sensitized irradiation of **5** gives exclusively vinyl migration to produce *trans*-1-methylene-5-phenyl-6-vinylbicyclo[3.1.0] hexane (**13**) in good yield (83%) but low efficiency [$\Phi = 0.006$]. However, direct excitation of **5** at 253.7 nm affords phenyl migration yielding *trans*-1-methylene-6-phenyl-5-vinylbicyclo[3.1.0]hexane ($\Phi = 0.08$). The contrasting products from direct and sensitized irradiation are attributed to energy localization in the singlet and triplet states of the molecule. The observation of triplet reactivity in an exocyclic methylene system such as **5** is discussed with reference to the concept of rotational deactivation of excited states.

The establishment of the general structural factors which influence excited state reactivity is one of the prime goals of organic photochemistry. One such factor is the alteration of reactivity arising from geometric change about atoms having much lower bond orders in the excited state vs. the ground state. To date rotational deactivation effects[2] have important consequences on the multiplicity and reactivity of di-π-methane[3] and oxa-di-π-methane[4] systems, of olefins in photoaddition processes,[5] and of photocycloaddition processes of enones[6] and imines.[7] The presence of rotational deactivation may likewise contribute to the low emission yields of many acyclic olefin systems.[8]

Since our initial work in establishing the importance of rotational deactivation in the di-π-methane system,[3a] several compounds have been reported which still undergo this rearrangement despite the presence of a potential rotational deactivation process.[3c] In view of the general significance of rotational freedom in altering excited state reactivity, we were interested in establishing those structural features of a molecule which permit efficient triplet reactivity even when rotational deactivation mechanisms can be operative. Especially interesting were molecules such as **1**[9] and **2**[10] which had been reported to undergo efficient triplet di-π-methane rearrangements. These two systems are in marked contrast to the acyclic diene–phenyl system **3**[11] and the diphenyl system **4**[12] which show very low triplet di-π-methane reactivity. Two structural features differ in these two sets of compounds. First, for compounds **1** and **2** the initial bridging process could involve bonding between two olefinic moieties,[13] while for **3** and **4** diene–phenyl bonding would be necessarily involved in the initial phase of the reaction. Since the former would reasonably correspond to a lower energy situation, the dichotomy would then be explained by a more facile bridging process in **1** and **2** vs. **3** and **4**. Second, in molecules such as **1** and **2**, the extensive π interaction in the excited state forced by the rigid bicyclic system could seriously alter the energetics of twisting about the exocyclic methylene group. Thus, in these systems rotational deactivation could be less effective than in compounds **3** and **4**.



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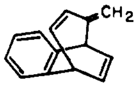

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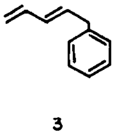

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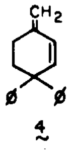

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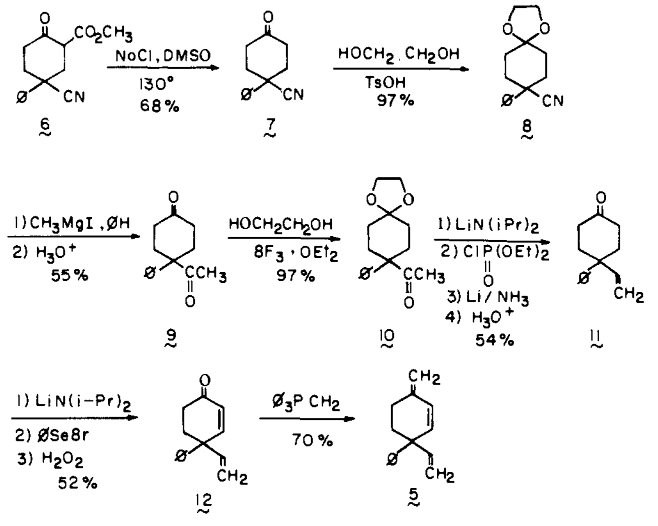
A system which we felt would focus attention on this problem was 1-methylene-4-phenyl-4-vinylcyclohex-2-ene (**5**). This molecule would possess the low energy diene-olefin interaction of **1** and **2**, yet the potentially strong bicyclic conjugation present in the excited state of these molecules would be absent. We wish to present here a study of the singlet and triplet photochemistry of **5**.

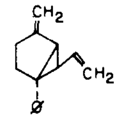
Synthesis of 1-Methylene-4-phenyl-4-vinylcyclohex-2-ene (5). The synthesis of **5** began with the known 2-carbomethoxy-4-cyano-4-phenylcyclohexane[14] (**6**) and is outlined in Scheme I. The steps, except for the formation of **12** from **11**, proceeded smoothly and reproducibly. However, yields for the **11** → **12** sequence were somewhat variable (20–50%); in addition, **12** was contaminated with 5–20% of the difficultly separable **11**.[15]

Sensitized Irradiation of 5. Preparative sensitized irradiation of **5** using 2-acetonaphthone ($E_T = 59.5$ kcal mol^{-1}) as sensitizer at 3500 Å resulted in disappearance of **5** and formation of one product in 83% yield. The photoproduct was separated from the sensitizer by silica gel chromatography and was shown to be isomeric with starting material by mass spectral and combustion analyses. By analogy with

Scheme I. Synthesis of 4-Phenyl-4-vinylcyclohex-2-ene (5)



previous work[3a] the product could be **13**, **14**, **15**, or **16**. While the NMR of the vinyl region suggested that the monosubstituted double bond in the product was coupled to a hydrogen (i.e., **13** or **14**) the spectrum was not sufficiently unique for a rigorous structure assignment. Thus degradation of the photoproduct was undertaken.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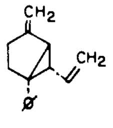
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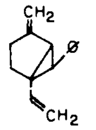
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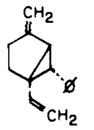
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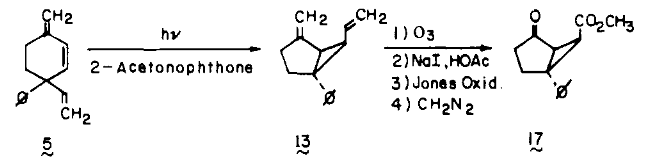
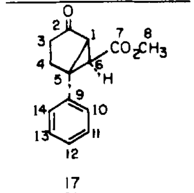
Ozonolysis of **13** followed by Jones oxidation and esterification afforded a 67% yield of the ketoester **17**. While the proton NMR spectrum of **17** was deceptively simple, showing only three signals at τ 2.79 (s, 5 H), 6.29 (s, 3 H), and 7.60 (d, separation of 1.5 Hz, 6 H), the ^{13}C NMR spectrum showed 12 unique absorptions indicative of a more complex structure. Since the spectroscopic data had been so inconclusive in structure assignment and since we wished to rule out any unprecedented rearrangement in this unusual *cis*-divinylcyclopropane derivative, the photochemistry of the ketone **12** was examined.



C^{14} Nmr Spectrum of 5

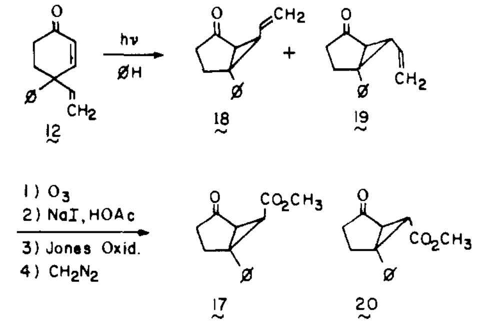


17

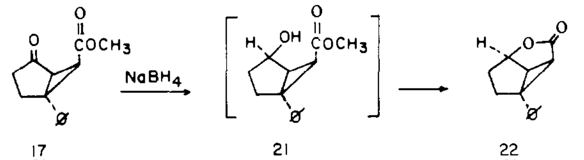
Chemical shift (multiplicity from off-resonanance decoupling) assignment

210.28 (s), C_2; 169.00 (s), C_7; 141.66 (s), C_9; 128.76, 127.44, 126.93, C_{10}-C_{14}; 51.97 (q) C_8; 45.07 (s) C_5; 40.18 (d), C_1 or C_6; 37.99 (t) C_3; 35.13 (d), C_1 or C_6; 27.57 (t) C_4 ppm

The photochemistry of cyclohexenones has been thoroughly investigated[16] and for **12** the vinyl migration should afford **18** as the photoproduct. This material should yield the same ketoester as formed by **13** in the ozonolysis-oxidation esterification sequence. Indeed, irradiation of **12** yielded a photoproduct mixture (as seen by NMR) in 95% distilled yield which could not be separated by a variety of methods. However, ozonization-oxidation-esterification of this photoproduct mixture led to the isolation of a major product (51%) identical with **17** and a minor product (3%) which we tentatively assigned as **20**. While we cannot exclude products other than **18** and **19** being formed in the irradiation of **12**, it appears reasonable that **18** is by far the major product.



While the preceding experiments established the gross structure of the photoproduct as either **13** or **14**, NMR was of no value in establishing the stereochemistry of the vinyl vs. the phenyl moieties. An alternate procedure for establishment of stereochemistry would be to demonstrate lactone formation between the C_2 hydroxyl and the C_7 carboxyl groups. Reduction of the carbonyl group of **17** should afford reduction from the least hindered side to yield alcohol **21** which upon lactonization would yield **22**. This indeed was the case as reduction followed by lactonization in the work-up afforded the lactone **22** in 80% yield. This then rigorously establishes **13** as the product for sensitized irradiation of **5**.



Direct Irradiation of 5. Having established the course of the triplet rearrangement, the direct irradiation of **5** at 253.7 nm was studied. Irradiation of **5** in cyclohexane using tetradecane as internal standard afforded at 67% conversion of **5**, one major product (39%), and two minor products as ascertained by VPC analysis. Longer irradiations resulted in consumption of both starting material and product, with the formation of noticeable polymeric material. The ir of the photoproduct indicated the presence of an exocyclic methylene group (11.25 μ) and a monosubstituted double bond (10.15 and 11.20 μ). The NMR spectrum (100 MHz) of the photoproduct showed: τ 2.76 (s, 5H), 4.12 (d of d, J = 10.2, 17.5 Hz, 1 H), 4.96 (d of d, J = 17.5, 1.5 Hz, 1 H), 5.02 (d of d, J = 10.2, 1.5 Hz, 1 H), 5.01 (part obscured br s, 1 H), 5.12 (br s, 1 H), 7.58 (center of AB d, J = 10.0 Hz, 1 H), 7.81 (center of AB d, J = 10.0 Hz), and 7.85-8.5 (m, 4 H). Especially diagnostic was the appearance of H_5 as a clean doublet of doublets, indicating that the vinyl double bond was bound to a tertiary position, and the appearance of the two cyclopropyl hydrogens as an AB doublet with J = 10.0 Hz. The large coupling constant is indicative of two cis hydrogens on a cyclopropane ring.[17] Thus, on the basis of these spectroscopic data, the structure of the direct exci-

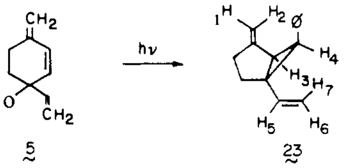


Table I. Quantum Yields for Direct and Sensitized Irradiation of **5**

Run	Irradiation	Concn of **5**, *M*	Φ_5	Φ_{13}	Φ_{23}	% conv
1	Direct, 253.7 nm[a]	6.5×10^{-3}	0.11		0.084	13
2	Direct, 253.7 nm[a]	6.5×10^{-3}	0.11		0.078	12
3	Sensitized,[b] 350 nm[c]	1.02×10^{-2}		0.0060		
4	Sensitized,[b] 350 nm[c]	1.02×10^{-2}		0.0057		

[a] Cyclohexane solvent. [b] Benzene solvent. [c] 2-Acetonaphthone sensitizer (1.8×10^{-2} *M*).

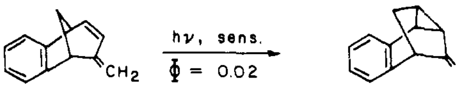
tation product of **5** is assigned as **23**.

Quantum Yields for Irradiation of 5. In order to compare the efficiencies of the excited state processes of **5** with other di-π-methane systems, quantum yield measurements were made and are recorded in Table I. In the case of direct excitation the efficiency of phenyl migration to produce **23** is modest ($\Phi = 0.082$) and this accounts for the major amount of starting material disappearance. For the 2-acetonaphthone ($E_T = 59.5$ kcal mol^{-1}) sensitized reaction, the difficulty in product analysis at low conversion and the low efficiency of the reaction itself make the quantum yields of Table I subject to appreciable error. However, there is no doubt that the reaction is extremely inefficient. To ensure that this inefficiency was not partly due to inadequate exothermicity in the energy transfer step, *m*-methoxyacetophenone ($E_T \approx 72.4$ kcal mol^{-1}) sensitization was briefly studied. In comparative irradiations at 350 nm, it was established that *m*-methoxyacetophenone sensitization is of the same efficiency as the reaction utilizing 2-acetonaphthone as sensitizer. Thus, while **5** does show triplet reactivity chemical reaction to produce **13** accounts for only a small fraction of the triplet excitation.

Discussion

In discussing the photochemistry of **5** it is perhaps prudent to briefly comment on its electronic make-up. Compound **5** may be considered as possessing three separate olefin, diene, and phenyl chromophores or as a composite system in which there is some degree of interaction between the π systems. For the ground state the former condition would appear to best describe **5** while in the excited state we feel there may be interaction between these systems (obviously the di-π-methane reaction is a consequence of this interaction). Thus, throughout this discussion we will refer to the energy as localized in a particular π moiety, cognizant of the fact that for an initially formed excited state the degree of interaction between the chromophores is unknown.

An initial point for discussion is the contrasting efficiency of di-π-methane rearrangement of the triplet state of **5** as compared to the bicyclic system **2**. The difference between the value of 0.006 for **5** and the quantum yield of 0.30 noted for **2** suggests factors in addition to the lower energy vinyl–vinyl bonding process distinguish **2** from other diene systems which have been studied. A very recent study by Goldschmidt and Gutman further supports this conclusion since **24**, which possesses only diene–phenyl bonding possibilities gives **25** with a quantum efficiency of 0.02.[18]

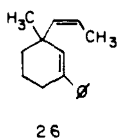


24 **25**

This higher reactivity of the bicyclic systems **2** and **24** reasonably reflects the rigid framework in which these chromophores are held. Whether the higher reactivity is due to the rigidity of the system per se or to possible bicyclic conjugation derived from the fixed geometric relationship of the chromophores in **2** and **24** cannot be answered from the available data. However, the occurrence of nearly exclusive vinyl migration in the triplet state of **5** suggests that diene–vinyl bonding is of lower energy than phenyl–vinyl bonding. If this is the case, then the presence of initial vinyl–vinyl bonding in deactivated triplet states should enhance the reaction efficiency.

A second point is the dramatic change in product between the singlet and the triplet excited states of diene. This appears as one of the few examples wherein two competing di-π-methane processes arise from excited states of different multiplicity.[19,20] The results are conveniently rationalized by considering that there is some degree of energy localization in the excited singlet and triplet states of **5**. In the triplet state, energy is localized in the diene portion of the molecule (E_T(diene) = 60, E_T(olefin) > 75, and E_T(phenyl) = 84 kcal/mol),[21] and the lowest energy pathway is diene–vinyl interaction ultimately producing **13**. In the singlet state the excitation is localized in the aromatic ring (E_S(phenyl) = 108,[22a] E_S(diene) = 124,[22b] E_S(olefin) = 140 kcal/mol[22c]), and the more favorable phenyl–diene bonding affords **23** as the product.[23] The observation of phenyl migration in the case of **5** may have relevance in explaining the singlet di-π-methane reactivity of molecules such as **3** and **4**. As was noted earlier,[3a] the singlet states of dienes should also be subject to rotational deactivation, yet **3** and **4** exhibit modest photochemical reactivity. While the reactions of the systems have been pictured as arising from the excited diene portion, it is perhaps more correct to consider the reaction as arising from the phenyl moiety. As discussed below the reactivity of the system is then as expected (i.e., no rotational deactivation of the phenyl excitation energy would be anticipated).

Since the appearance of the work[3a–c] attributing the low triplet reactivity of acyclic systems and molecules containing exocyclic methylene groups to rotational deactivation of the excited state, several exceptions to this general picture have now appeared. As the majority of these papers have appeared in the last year and have a bearing on the results presented here, they will be briefly discussed. The formal exceptions can be conveniently divided into two classes. The first comprises compounds **26**[24a] and **27**[24b] of Mariano and Hixson which undergo triplet reactivity in spite of the presence of an acyclic vinyl linkage. For these molecules rotational deactivation mechanisms should not be especially important since the excitation energy would be initially localized in the styryl and naphthyl portions of the molecule, and any reduction in the triplet reactivity of such systems should not derive from a lower reactivity in step 1 of Scheme II. Thus, in systems such as **26** and **27** the triplet reactivity of these molecules need not be considered as an exception to the general idea of rotational deactivation of



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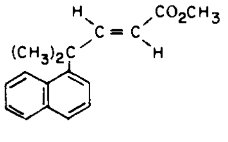

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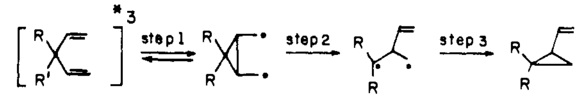
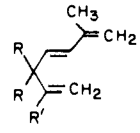
Scheme II. Zimmerman's General Scheme for the Di-π-methane Reaction

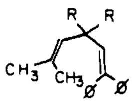


an initially formed excited triplet state.

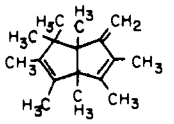
On the other hand, a second group of compounds as illustrated by **28a**,[25] **29a**,[26] **30**,[27] and **31**[28] does constitute clear



28a, R = CH$_3$, R' = H
b, R = H, R' = CH$_3$



29a, R = ϕ
b, R = CH$_3$



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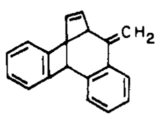

31

exceptions to the concept of facile rotational deactivation of a triplet excited state. Thus, for these molecules the triplet excitation energy should be localized in a chromophore subject to rotational deactivation, yet reaction still occurs. Furthermore, in the case of **29a** the process is of good efficiency (Φ = 0.25).[26] Two factors would appear to be of importance in these systems. First, in each case the bonding process (step 1) is to a vinyl moiety, and the present results demonstrate this to be of substantially lower energy than bonding to an aromatic ring. Examples of the latter type were less appropriately used in illustrating the unreactivity of unconstrained diene triplets. Second, for reactions in these acyclic systems which apparently are less reactive than constrained systems, radical stabilizing groups at the central carbon are important for facile triplet rearrangement.[25,26,30,31] Thus, **28b** and **29b** having less stabilization at this center do not undergo the triplet di-π-methane reaction.[32] Undoubtedly, there is an interplay of both factors in determining triplet reactivity in these molecules capable of rotational deactivation.

Conclusion

As first noted by Goldschmidt and Kende[10] limitations do exist to the rotational deactivation mechanism proposed earlier. In this work it has been demonstrated that the nature of the initial bonding process can enhance the reactivity of less reactive triplet states. From other work cited it is also apparent that the degree and type of substitution at the central carbon can influence the efficiency of the di-π-methane reaction. Thus, while rigidity certainly enhances reactivity in the triplet state, suitably substituted acyclic systems are also capable of reasonably efficient, synthetically useful di-π-methane reactions.

Experimental Section[33]

4-Cyano-4-phenylcyclohexanone (7). A solution of 85.5 g (0.333 mol) of 2-carbomethoxy-4-cyano-4-phenylcyclohexanone, 18.5 ml water, and 20.97 g (0.36 mol) of sodium chloride in 300 ml of DMSO was quickly heated to 130° in a high-temperature (160°) bath.[34] After evolution of carbon dioxide ceased (ca. 2 hr), the reaction mixture was poured into 500 ml of water and extracted with benzene (5 × 100 ml). The combined extracts were washed with water (100 ml) and saturated brine solution (100 ml) and dried over calcium sulfate, and the solvent was removed in vacuo. Recrystallization from ethanol yielded 45.2 g (68%) of 4-cyano-4-phenylcyclohexanone, mp 115–117° (lit.[14] mp 114–115°).

4-Cyano-4-phenylcyclohexanone Ethylene Ketal (8). A solution of 11.0 g (0.055 mol) of 4-cyano-4-phenylcyclohexanone, 30 ml of ethylene glycol, 0.5 g of *p*-toluene sulfonic acid, and 250 ml of toluene was refluxed for 12 hr, the water formed during the reaction being removed via a Dean-Stark trap. The reaction mixture was poured into water (200 ml) and extracted with ethyl ether (3 × 100 ml). The organic phase was washed successively with 10% sodium bicarbonate (100 ml), water (100 ml), and saturated brine solution (100 ml). After drying over calcium sulfate, the ether was removed in vacuo, yielding 13.6 g (97%) of a white solid, mp 111–114°. VPC analysis (column A at 200°) showed greater than 98% purity and this crude material was utilized for the next step: NMR (CCl$_4$, 60 MHz) τ 2.4–2.8 (m, 5 H), 6.10 (s, 4 H), and 7.8–8.4 (m, 8 H); ir (KBr) 3.35 (m), 3.42 (m), 4.41 (w), 9.05 (s), 13.25 (s), and 14.5 μ (s).

4-Acetyl-4-phenylcyclohexanone (9). To a 1000-ml round-bottom flask containing 500 ml of dry ethyl ether (distilled from methyl magnesium iodide) was added 7.2 g (0.30 mol) of magnesium turnings followed by the slow addition (via dropping funnel) of 43.0 g (0.31 mol) of methyl iodide. After the vigorous refluxing subsided, 300 ml of benzene was introduced, followed by distillation of the solvent from the reaction mixture until a head temperature of 74° was reached. Next 22.0 g (0.095 mol) of **8** was added and the reaction mixture was stirred at 74° for 24 hr. To this cooled solution was added hydrochloric acid (39 ml of concentrated hydrochloric acid and 100 ml of water) dropwise followed by refluxing the mixture for 5 hr. The organic layer was separated and the aqueous layer was extracted with benzene (4 × 100 ml). The combined organic phase was washed successively with 10% sodium bicarbonate (200 ml), water (100 ml), and saturated brine solution (100 ml). After drying over calcium sulfate the solvent was removed in vacuo, yielding 18.0 g of a yellow oil. The oil was fractionally distilled through a 6 in. vigreux column and the following fractions were obtained: 45–124° (0.2 mm), 2.2 g of impurities and product; 124–128° (0.2 mm), 11.0 g of product; and 128–135° (0.2 mm), 4.0 g of higher boiling impurities. Recrystallization of the first two fractions from ether yielded 11.4 g (55%) of pure **9**: mp 76.5–78°; ir (KBr) 5.76 (s), 5.88 (s), 6.99 (s), 7.38 (m), 7.50 (m), 8.18 (m), 8.32 (m), 8.60 (m), 9.1 (m), 10.55 (w), 13.18 (s), and 14.4 μ (s); NMR (CDCl$_3$, 60 MHz) τ 2.62 (s, 5 H), 7.52 (br s, 8 H), and 8.02 (s, 3 H); exact mass analysis (70 eV), calcd *m/e* 216.1150218, obsd *m/e* 216.11523919, difference 0.0002. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.80; H, 7.74. Found: C, 77.55; H, 7.44.

4-Phenyl-4-vinylcyclohexanone (11)[35]. A solution of 5.2 g (0.024 mol) of **9** in 50 ml of methylene chloride and 50 ml of freshly distilled ethylene glycol was cooled to −9° by an ice–isopropyl alcohol bath. To this solution, 11.0 ml of boron trifluoride etherate was added slowly via a syringe. The reaction mixture was allowed to stir for 25 min, poured into water (200 ml), and extracted with methylene chloride (3 × 100 ml). The organic layer was successively washed with 50 ml of 10% sodium bicarbonate, 50 ml of water, and 50 ml of a saturated brine solution. After drying over calcium sulfate, the solvent was removed in vacuo, yielding 5.8 g (99%) of **10** as a clear oil. VPC analysis (column A at 180°) showed the product to be sufficiently pure (97%) for use in the next reaction: ir (neat) 3.39 (m), 3.48 (w), 5.87 (s), 6.7 (m), 6.95 (m), 7.4 (m), 8.21 (m), 8.5 (m), 9.10 (s), 9.62 (s), 10.75 (s) 11.9 (m), 13.3 (s), and 14.3 μ (s); NMR (CCl$_4$ 60 MHz) τ 2.78 (s, 5 H), 6.16 (s, 4 H), 7.4–8.5 (m, 8 H), and 8.12 (s, 3 H).

To a solution of 50 ml of dry tetrahydrofuran and 2.64 g (0.026 mol) of diisopropylamine cooled by a Dry Ice–isopropyl alcohol bath was added 14.3 ml of methyllithium (1.82 *M*). After stirring for 30 min, 5.8 g (0.024 mol) of **10** in 5 ml of tetrahydrofuran was introduced. After stirring for 30 min, 6 ml of tetramethylethylene diamine followed by 4.52 g (0.026 mol) of chlorodiethyl phosphate was added to the reaction mixture and the solution was stirred at room temperature for 7 hr. After addition of 10 ml of water the solvent was removed in vacuo affording a brown residue which was extracted with ethyl ether (3 × 100 ml). The organic phase was washed repeatedly with 50-ml portions of water until neutral to pH paper, followed by washing with 50 ml of a saturated brine solution. After drying over calcium sulfate the ethyl ether was removed in vacuo, yielding 8.02 g of a yellow oil. The oil was added to a solution of 100 ml of ethyl ether and 150 ml of liquid ammonia, followed by addition of 0.315 g (0.045 mol) of lithium over a period of 1 hr. After complete reaction of the lithium, 20 ml of a saturated ammonium chloride solution was added slowly to the reaction mixture and the reaction mixture was stirred at room temperature for 2 hr. The solution was then poured into a saturated ammonium chloride solution (100 ml) and extracted with ethyl ether (3 × 100 ml). The organic phase was washed with 100 ml of water and 100 ml of a saturated brine solution. After drying over calcium sulfate the ethyl ether was removed in vacuo, yielding 4.8 g of a yellow oil, which was refluxed for 2 hr with 30 ml of tetrahydrofuran, 10 ml of water, and 2 ml of concentrated hydrochloric acid. The tetrahydrofuran was removed in vacuo, and the residue was extracted with ethyl ether (3 × 100 ml). The organic phase was washed successively with 100 ml of 10% sodium bicarbonate, 100 ml of water, and 100 ml of a saturated brine solution. After drying over calcium sulfate the ethyl ether was removed in vacuo, yielding 3.9 g of a yellow oil which was chromatographed on silica gel (100 g, 60 × 1.5 cm column). Elution proceeded as follows: 20% ether in hexane, 200 ml, nil; 20% ether in hexane, 150 ml, 0.150 g of unknown impurity; 20% ether in hexane, 370 ml, 2.7 g of pure product; 50% ether in hexane, 300 ml, 1.0 g (20%) of the recovered diketone **10**. Recrystallization of product from a 3:1 mixture of ether–hexane yielded 2.5 g (54%) of pure **11:** mp 54–56°; ir (KBr) 3.25 (w), 3.28 (w), 3.31 (w), 3.38 (w), 3.42 (w), 5.87 (s), 6.1 (w), 6.68 (m), 6.92 (m), 7.09 (m), 7.5 (m), 8.8 (m), 9.91 (m), 10.8 (s), 13,0 (s), 14.2 (s), and 15.0 μ (w); NMR (CCl_4, 60 MHz) τ 2.70 (m, 5 H), 4.08 (q, J = 11.0, 16.5 Hz, 1 H), 4.91 (d of d, J = 11.0, 2.0 Hz, 1 H), 5.1 (d of d, J = 16.5, 2.0 Hz, 1 H), and 7.72 (m, 8 H); exact mass analysis, calcd *m/e* 200.12077, obsd *m/e* 200.12027839, difference 0.0005. Anal. Calcd for $C_{14}H_{16}O$: C, 84.00; H, 8.00. Found: C, 83.70; H, 8.01.

4-Phenyl-4-vinylcyclohex-2-enone (12). To a three-necked 250-ml flask fitted for constant nitrogen pressure was added 10 ml of dry tetrahydrofuran (distilled from sodium–benzophenone) and 0.42 ml (3.0 mmol) of diisopropylamine. The solution was cooled to −78°, and 1.67 ml of methyllithium (1.8 *M*) was introduced via a syringe. After stirring for 30 min, 0.500 g (2.5 mmol) of the ketone was introduced as a solid. The solution was stirred for 30 min and a solution of phenylselenium bromide [prepared from 0.082 ml (1.5 mmol) of bromine, 0.467 g (1.5 mmol) of diphenyl diselenide in 5 ml of tetrahydrofuran] was added rapidly. This was followed immediately by a solution of 1.5 ml of water, 0.3 ml of acetic acid, and 1.5 ml of 30% hydrogen peroxide. The cooling bath was removed, and a vigorous bubbling was noted after ca. 5 min. The reaction mixture was allowed to stir at 25° for 30 min, then poured into 100 ml of saturated sodium bicarbonate. The bicarbonate solution was extracted with a 50:50 mixture of diethyl ether–pentane (3 × 100 ml). The organic layer was washed with water (50 ml), 5% hydrochloric acid (50 ml), water (50 ml), and saturated brine solution (50 ml) and then dried over calcium sulfate. Removal of the solvent in vacuo yielded 0.510 g of brown oil which was chromatographed on silica gel (60 g, 30 × 2 cm column). Elution proceeded as follows: 50% methylene chloride in petroleum ether, 160 ml, nil; 50% methylene chloride in petroleum ether (30–60°), 240 ml, 0.120 g of a major side product; 50% methylene chloride in petroleum ether, 500 ml, 0.310 g of product.[36] Molecular distillation at 60° (0.2 mm) yielded 0.260 g (52%) of **12**: ir (neat) 5.95 (s), 6.18 (w), 6.27 (w), 6.71 (m), 6.91 (m), 7.09 (m), 7.24 (m), 10.8 (m), 12.6 (m), 13.2 (s), and 14.28 μ (s); NMR (CCl_4, 60 MHz) τ 2.75 (s, 5 H), 3.17 (d of AB, J = 10.0 Hz, 1 H,), 3.91 (q of an ABX, J = 17.0, 10.5 Hz, 1 H), 3.94 (d of an AB, J = 10.0 Hz, 1 H), 4.72 (d of d of an ABX, J = 10.5, 2.0 Hz, 1 H), 4.83 (d of d of an ABX, J = 17.0, 2.0 Hz, 1 H), and 7.7 (s, 4 H); exact mass analysis, calcd *m/e* 198.10445850, obsd *m/e* 198.10474874, difference 0.0003. Anal. Calcd for $C_{14}H_{14}O$: C, 84.85; H, 7.07. Found: C, 84.49; H, 7.14.

1-Methylene-4-phenyl-4-vinylcyclohex-2-ene (5). To a solution of 0.722 g (2.0 mmol) of methyltriphenylphosphonium bromide in 50 ml of dry ethyl ether (distilled from sodium/benzophenone) under a nitrogen atmosphere, 1.03 ml of *n*-butyllithium (1.97 *M*) was syringed in slowly. The solution turned dark yellow and after 15 min 0.400 g (2.0 mmol) of 4-phenyl-4-vinylcyclohex-2-en-1-one was added dropwise in 20 ml of ethyl ether. The color disappeared instantaneously and the solution was refluxed for 45 min. The reaction mixture was filtered through Celite filter aid and the filter cake was washed with 50 ml of petroleum ether (30–60°). Removal of the solvent in vacuo yielded 0.500 g of a yellow oil. The oil was placed on a short silica gel column (1.5 × 30 cm) and elution with 400 ml of petroleum ether yielded 0.300 g of diene. Molecular distillation at 40° (0.2 mm) yielded 0.280 g (70%) of product. VPC analysis (Column D at 140°) showed one impurity (ca. 5%) which was found to be 1-methylene-4-phenyl-4-vinylcyclohexane. Further purification was achieved on a high-pressure liquid chromatography column (1.5 × 90 cm) packed with TLC grade silica gel: ir (neat) 6.12 (m), 6.25 (m), 6.7 (m), 6.92 (m), 11.0 (s), 11.25 (s), 11.4 (s), 12.6 (m), 13.25 (s), and 14.30 μ (s); NMR (CCl_4, 60 MHz) τ 2.60–3.00 (m, 5 H), 3.66 (d, J = 10.0 Hz, 1 H), 3.93 (q, J = 11.0, 7.0 Hz, 1 H), 4.20 (br d, J = 10.0 Hz, 1 H), 4.80 (d of d, J = 11.0, 2.0 Hz, 1 H), 4.90 (d of d, J = 17.0, 2.0 Hz, 1 H), 5.25 (br s, 2 H), and 7.5–7.82 (m, 4 H); ^{13}C NMR ($CDCl_3$) 146.43, 144.43, 142.56, 134.45, 129.92, 128.19, 127.28, 126.20, 113.84, 47.16 35.23, 26.87; exact mass analysis, calcd *m/e* 196.1251936, obsd *m/e* 196.12538269, difference 0.0002. Anal. Calcd for $C_{15}H_{16}$: C, 91.84; H, 8.16. Found: C, 91.60; H, 8.40.

Sensitized Irradiation of 1-Methylene-4-phenyl-4-vinylcyclohex-2-ene (5). A mixture of 0.115 g (0.576 mmol) of **5** and 0.115 g of 2-acetonaphthone in 12 ml of benzene was placed in a Pyrex test tube and degassed by a nitrogen stream for 15 min. The solution was irradiated for 10.5 hr with 16 RPR-3500 Å lamps. VPC analysis (column B at 170°) showed only one photoproduct and complete disappearence of **5**. The solvent was removed in vacuo yielding a yellow oil which was chromatographed on a silica gel column (1.5 × 30 cm). Elution proceeded as follows: 100% petroleum ether (30–60°), 400 ml, 96 mg of a clear oil. Molecular distillation of the oil at 40° (0.2 mm) yielded 90 mg (78%) (VPC yield, 83%) of pure photoproduct **13**: ir (neat) 3.22 (m), 3.27 (m), 3.30 (w), 3.38 (m), 3.45 (w), 6.03 (m), 6.09 (m), 6.18 (m), 6.60 (m), 6.75 (w), 6.82 (m), 6.88 (w), 10.80 (s), 11.5 (s), 12.9 (s), and 14.1 μ (s); NMR (CCl_4, 100 MHz) τ 2.87 (s, 5 H), 4.26 (overlapping d of q, J = 18.0, 10.0, 6.8 Hz, 1 H), 4.6–4.97 (m, 2 H), 5.02 (br s, 1 H), 5.17 (br s, 1 H), and 7.4–8.3 (m, 6 H); ^{13}C NMR ($CDCl_3$) 151.39, 145.14, 133.48, 128.41, 126.68, 125.93, 118.05, 105.86, 42.84, 39.49, 36.26, 32.48, 30.54; exact mass analysis, calcd *m/e* 196.12519, obsd *m/e* 196.12555, difference 0.0004. Anal. Calcd for $C_{15}H_{16}$: C, 91.84; H, 8.16. Found: C, 91.48; H, 8.48.

Direct Irradiation of 5 at 2537 Å. A solution of 40 mg (0.204 mmol) of **5** and 18.6 mg of tetradecane in 12 ml of cyclohexane was degassed via nitrogen stream for 15 min. The solution was irradiated at 2537 Å for 1.5 hr. VPC analysis (column C at 150°) showed one major product (39%), two minor products (<2%), and unreacted starting material (33%). Longer irradiation times gave only disappearance of both products and starting material. The major product was isolated via preparative VPC (column E at 150°): ir (neat) 6.1 (m), 6.7 (m), 6.95 (m), 9.75 (2), 10.15 (m), 11.25 (s), 11.55 (s), 12.8 (s), 13.5 (s), 13.8 (s), and 14.35 μ (s); NMR (CCl_4, 100 MHz) τ 2.76 (s, 5 H), 4.12 (q, J = 10.2, 17.5 Hz, 1 H), 4.96 (d of d, J = 17.5, 1.5 Hz, 1 H), 5.02 (d of d, J = 10.2, 1.5 Hz, 1 H), 5.01 (partially obscured br s, 1 H), 5.12 (br s, 1 H), 7.58 (half of AB q, J = 10.0 Hz, pH), 7.81 (half of AB q, J = 10.0 Hz, 1 H), and 7.85–8.5 (m, 4 H); ^{13}C NMR (90 MHz, $CDCl_3$) τ 151.34, 142.98, 137.20, 129.17, 128.25, 126.36, 111.31, 105.59, 40.79, 39.71, 33.88, 31.24, 27.35; exact mass analysis, calcd *m/e*, 196.1251936, obsd *m/e* 196.12555168, difference 0.0004. Anal. Calcd for $C_{15}H_{14}$: C, 91.84; H, 8.16. Found: C, 91.36; H, 8.32.

Ozonolysis–Oxidation of *trans*-2-Methylene-5-phenyl-6-vinylbicyclo[3.1.0]hexane (13). Ozone (generated by a Welsbach T-408 Ozonizer) was passed through a Dry Ice–isopropyl alcohol cooled solution of 0.140 g (0.715 mmol) of photoproduct in 50 ml of methanol for 2.5 min. The cold solution was poured into a mixture of 1.0 g of sodium iodide, 2 ml of acetic acid, and 50 ml of methanol. After stirring at ca. 25° for 1 hr the solution was treated with saturated sodium thiosulfate to give a colorless solution. The methanol was concentrated in vacuo to 20 ml, and 100 ml of water was added. This mixture was then extracted with methylene chloride (3 × 75 ml) and the organic layer was washed with 10% sodium bicarbonate (100 ml), water (100 ml), and a saturated brine solution (50 ml). After drying over calcium sulfate, the solvent was removed in vacuo, yielding 150 mg of a clear oil.

To an ice bath cooled solution of 0.150 g of the crude aldehyde in 20 ml of acetone was added 1 ml of Jones reagent (2.67 g of chromium trioxide, 2.3 ml of concentrated sulfuric acid made up to 10 ml with water) and the reaction mixture was stirred at 25° for 2.5 hr. The solution was poured into water (100 ml) and extracted with ethyl ether (3 × 75 ml). The ether layer was extracted with a 10% sodium hydroxide solution (2 × 50 ml). The neutral and basic layers were separated, and upon removing the solvent in vacuo from the neutral layer 30 mg of an oil was obtained. The basic layer was acidified with concentrated hydrochloric acid and extracted with ethyl ether. The ether layer was washed with water (50 ml) and saturated brine solution (50 ml) and concentrated to 20 ml, and then the crude acid esterified with diazomethane. Removal of the ether in vacuo yielded 112 mg of a yellow oil. The yellow oil was distilled onto a Dry Ice–isopropyl alcohol cold finger at 60° (0.2 mm) giving 108 mg (67%) of a clear oil. This oil was crystallized from a 4:1 mixture of ether–petroleum ether to yield white crystals: mp 49–50°; ir (KBr) 5.74 (s), 5.78 (s), 6.88 (m), 7.04

Table II. Quantum Yield Data for the Triplet and Singlet Reaction of **5**

Sensitizer (× 10^2)	Light absorbed, mEinsteins	Concn, $M \times 10^{-3}$	% conversion	Φ^a	Φ_{13}	Φ_{22}
1.23 *M* 2-acetonaphthone	2.20	10.35	10.5		0.0060	
1.23 *M* 2-acetonaphthone	2.15	10.35	9.7		0.0057	
None	0.125	6.4	13.7	0.110		0.084
None	0.122	6.4	12.0	0.110		0.078

[a] Φ of disappearance.

(w), 7.40 (m), 8.35 (s), 8.48 (s), 8.55 (s), 12.8 (s), and 13.9 μ (s); NMR (CCl_4, 60 MHz) τ 2.79 (s, 5 H), 6.29 (s, 3 H), and 7.60 (d, *J* = 1.5 Hz, 6 H). Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.05; H, 6.09. Found: C, 73.14; H, 6.20.

Irradiation of 4-Phenyl-4-vinylcyclohex-2-en-1-one (12). A solution of 236 mg (1.19 mmol) of 4-phenyl-4-vinylcyclohex-2-enone in 50 ml of dry benzene (stored over sodium) was degassed by passing dry nitrogen through it for 30 min. The solution was irradiated for 75 min using a Rayonet Reactor equipped with RPR-3500 Å lamps. The solvent was then removed in vacuo and the 236 mg of a slightly yellow oil was molecularly distilled [(55° (0.15 mm)] to yield 223 mg (94.5%) of the photoproduct as a clear oil. The NMR indicated the material to be primarily one component: ir (neat) 3.17 (w), 3.30 (w), 5.76 (s), 6.07 (w), 6.18 (w), 6.65 (w), 6.90 (w), 7.20 (w), 7.72 (w), 8.00 (w), 8.16 (w), 8.47 (m), 9.34 (w), 9.82 (w), 10.22 (w), 11.07 (m), 12.95 (w), 13.24 (s), and 14.37 μ (s); NMR (CCl_4) τ 2.82 (s, 5 H), 4.53 (comp m, 3 H), and 7.92 (comp m, 6 H). Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.45; H, 7.30.

Oxidative Ozonolysis of Photoproducts from 4-Phenyl-4-vinylcyclohex-2-en-1-one. A solution of 236 mg (1.19 mmol) of photoproduct(s) in 50 ml of methanol was cooled to −78° and ozone was passed through the solution for 4 min using a Welsbach T408 ozonolysis apparatus. The reaction mixture was then poured into 50 ml of methanol containing sodium iodide (1 g) and acetic acid (2 ml) and stirred at room temperature for 1 hr. The liberated iodine was reacted with saturated sodium thiosulfate and then the solution was concentrated to ca. 20 ml in vacuo. Water (50 ml) was added and the solution was extracted with ether (2 × 100 ml). The combined extracts were washed with 10% sodium bicarbonate (50 ml) and water (50 ml) and evaporated in vacuo. The residue was dissolved in 50 ml of acetone and cooled to 0°. To this cooled, stirred solution 1 ml of Jones reagent was added dropwise. The reaction mixture was stirred at 0° for 15 min and at room temperature for 2 hr. Water (50 ml) was added to dissolve the chromate salts and the organic material was extracted with ether (3 × 100 ml). This solution was divided into a neutral and acid fraction by extraction with 10% sodium hydroxide (2 × 50 ml). The neutral fraction yielded 50 mg of a clear oil upon evaporation in vacuo. The sodium hydroxide portion was acidified with concentrated hydrochloric acid to pH 2 and extracted with ether (3 × 100 ml). The volume was reduced in vacuo to about 20 ml and an ethereal solution of diazomethane was added until the yellow color persisted. Excess diazomethane was removed by warming on a steam bath (hood!) and the solution was washed with saturated brine solution (50 ml) and dried over calcium sulfate and the solvent was removed in vacuo to yield 167 mg of a colorless oil. Preparative TLC eluting with 20% ether–petroleum ether (30–60°) yielded 138 mg (51%) of the major endo isomer and 8 mg (3%) of a minor compound. The major product showed ir and NMR spectra identical with those of previously obtained **17**. The minor product isolated has been tentatively assigned as *cis*-6-carbomethoxy-5-phenylbicyclo[3.1.0]hexan-2-one on the basis of the following spectroscopic data: ir (KBr) 5.82 (s), 6.22 (w), 6.71 (w) 6.92 (m), 7.24 (w), 7.37 (m), 7.74 (w), 8.24 (s), 8.54 (s), 11.01 (w), 13.14 (s), and 14.41 μ (s); NMR [CCl_4 $CDCl_3$ (50:50), 90 MHz] τ 2.74 (s, 5 H), 6.55 (s, 3 H), 7.16 (d, *J* = 2.8 Hz, 1 H), 7.40–7.75 (m, 5 H), and 8.75 (s, solvent impurity); exact mass analysis (70 eV), calcd *m/e* 230.09428; obsd *m/e* 230.09476, difference 0.0005.

Sodium Borohydride Reduction of 17. To a stirred solution of *trans*-6-carbomethoxy-5-phenylbicyclo[3.1.0]hexan-2-one (**17**) (41 mg, 0.18 mmol) in 19 ml of methanol, sodium borohydride (6.8 mg, 0.18 mmol) was added in one portion. The reaction mixture was allowed to stir at room temperature for 1 hr and then refluxed for 15 min. The methanol was removed in vacuo and the residue was extracted into ether (50 ml). The organic layer was washed with saturated brine solution (15 ml) and dried over calcium sulfate. Removal of the solvent in vacuo yielded 35 mg of a cloudy oil. Preparative TLC (20% ether–petroleum ether, 30–60°) yielded 29 mg (81%) of a nearly colorless liquid which turned yellow on standing. The material showed: ir (neat) 3.34 (w), 5.65 (s), 6.22 (w), 6.68 (w), 6.93 (w), 7.52 (m), 7.86 (w), 8.01 (w), 8.47 (m), 8.59 (s), 9.36 (w), 9.50 (w), 9.73 (w), 9.96 (m), 10.17 (m), 10.46 (m), 10.93 (w), 11.51 (w), 12.09 (w), 12.75 (w), 13.21 (m), and 14.40 μ (m); NMR (CCl_4, 60 MHz) τ 2.82 (s, 5 H), 4.98 (br m, 1 H), 6.75 (q, *J* = 6.0, 4.0 Hz, 1 H), and 7.73 (comp m, 5 H). Irradiation of the multiplet at τ 4.98 collapses the quartet at τ 6.75 to a clean doublet, *J* = 6 Hz. Thus, this coupling would reasonably be attributed to W coupling between the hydrogens at C_2 and C_6. Exact mass analysis, calcd *m/e* 200.08371, obsd *m/e* 200.08392, difference 0.0002; mass spectrum (70 eV) 200 (2.6%) 156 (loss of CO_2, 100%).

Quantum Yield Determinations. The sensitized quantum yields were measured as previously described.[37] Due to the low output of the high-pressure lamp at 253.7 nm, the quantum yields for the singlet reaction were determined using light from an RPR-2537 Å source and the previously described double compartment cell. The procedures were those previously described.[35] The results of these determinations are given in Table II.

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References and Notes

(1) (a) Alfred P. Sloan Fellow, 1971–1973; Camille and Henry Dreyfus Teacher–Scholar, 1972–1977; (b) American Oil Fellow, 1973–1974.

(2) While this has been termed the "free rotor effect" by Zimmerman, we prefer the more general term "rotational deactivation". The former terminology implies free rotation about such bonds in the excited state while the latter simply indicates relaxation of the high energy Franck-Condon geometry of an excited state to a lower energy geometric configuration.

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(33) General procedures: melting points were taken in open capillaries in a Thomas-Hoover "Unimelt" apparatus and are uncorrected. Infrared spectra were taken in the indicated phase on Perkin-Elmer Model 137 or 467 spectrophotometers. Nuclear magnetic resonance spectra were recorded in the indicated solvent at 60 mHz on Varian A60-A. Jeolco MH-100, or Bruker XL-90 instruments; spectra are reported in ppm τ units with reference to internal tetramethylsilane. Mass spectra were obtained with an AEI-MS9 spectrometer using an ionizing potential of 70 eV. VPC analyses were performed on a Varian Model 1200 or 1400 flame ionization gas chromatograph, and preparative VPC work was conducted on a Varian Model 700 thermal conductivity instrument using the following columns: column A, 5 ft × $\frac{1}{8}$ in., 3% SE-30 on 60–80 mesh DMCS treated Chromosorb G; column B, 25 ft × $\frac{1}{8}$ in., 5% SE-30 on 60–80 mesh DMCS treated Chromosorb G; column C, 13 ft × $\frac{1}{8}$ in., 5% SE-30 on 60–80 mesh DMCS treated Chromosorb G; column D, 10 ft × $\frac{1}{8}$ in., 3% Carbowax 20 M on 60–80 mesh DMCS treated Chromosorb G; column E, 10 ft × 0.25 in., 10% SE-30 on 60–80 Chromosorb W; and column F, 25 ft × 0.25 in., 5% SE-30 on 60–80 Chromosorb W. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark.
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Mechanistic Studies on the Photocyclization of γ,δ-Unsaturated Ketones[1]

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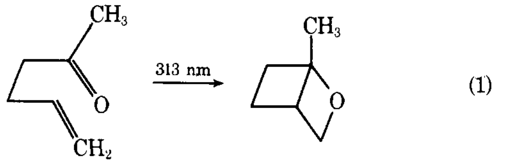
Abstract: Quantum yield studies of the photocyclizations of a series of aliphatic derivatives of *endo*-5-acylnorbornenes have shown that the efficiency of oxetane formation (eq 2) is a function of the steric bulk of the substituent. From an analysis of quenching and sensitization data, it is concluded that singlet states of the carbonyl groups are the reactive excited states. Similar studies with naphthoylnorbornenyl ketones have been interpreted in terms of two reactive states, $(n,\pi^*)_{S_1}$ and $(\pi,\pi^*)_{T_1}$. Although typical triplet state quenchers did not affect the photocyclization of 5-*endo*-benzoylnorbornene, it was concluded that the reaction proceeded via a very short-lived triplet state.

The first example of an intramolecular photocycloaddition of a carbonyl group to an olefin was reported by Srinivasan[2] in 1960 (eq 1). Yang[3] and Morrison[4] and their coworkers subsequently provided additional examples of this reaction with acyclic systems. Since that time, the reaction has found applications in ever more complex molecules with the production of some remarkable oxetanes.[5-21] Our early results with 5-acylnorbornenes[8] (eq 2) included the first examples of intramolecular photocycloadditions of phenyl and naphthyl ketones. The fact that high chemical yields of oxetanes were obtained from a wide variety of acylnorbornenes stimulated our interest in undertaking a more systematic study of this reaction.



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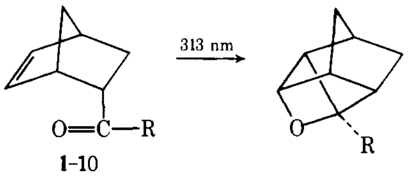

1-10

(2)

Our first objective was to assess the importance of the nature of the acyl group on the quantum efficiencies of these reactions in an effort to delineate the overall importance of steric and electronic factors. In addition, we wished to obtain information on the nature and lifetimes of the reactive state(s) for comparison with the analogous intermolecular reactions. We report here our studies with an extended series of acylnorbornenes and some derivatives of acylbicyclo[2.2.2]octenes.

Results

Syntheses. The following series of R-substituted norbornenyl ketones was prepared by direct Diels–Alder reactions

Sauers et al. / Photocyclization of γ, δ-Unsaturated Ketones