Cycloaddition Reactions of Strained Ring Systems. Photosensitized [2 + 2] Cycloadditions of 2-(Acyloxy)-Substituted Cyclopropenes

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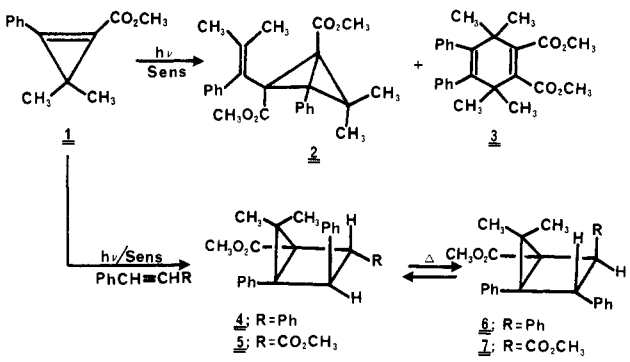
The sensitized [2 + 2] photocycloaddition reaction of 1-phenyl-2-carbomethoxy-3,3-dimethylcyclopropene with a series of phenyl-substituted olefins has been investigated. The photocycloaddition is sensitive to steric factors with the reactants approaching each other in a fashion that minimizes steric interactions. The major product can be explained in terms of an initial bond formation to give the most stable diradical intermediate. Coupling of the diradical to the bicyclo[2.1.0]pentane ring will occur so as to give a cycloadduct with the most stable trans relationship of the substituent groups. The sensitized cycloaddition of 1,2-diphenyl-3,3-dimethylcyclopropene with several aryl olefins was also studied and the results obtained were compared to the reactions in the carbomethoxy series. The intramolecular [2 + 2] cycloaddition of a series of 2-(acyloxy)-substituted cyclopropenes was also investigated. Chemical reactivity in the intramolecular [2 + 2] cycloaddition was found to be significantly affected by the length of the alkenyl side chain and by the substituents attached to the π-bond. The facility with which the internal cycloadditions occur makes this type of approach particularly attractive for the synthesis of some unusual polycyclic ring compounds.

Small-ring organic molecules have fascinated organic chemists since 1883, when Perkin synthesized the first known cyclobutane and cyclopropane derivatives.[1] During the next 100 years experimental and theoretical study of strained ring hydrocarbons has burgeoned.[2,3] Investigations of the behavior of small-ring systems are especially suitable for revealing relationships between structure and reactivity. In ground-state chemistry, it is observed that molecules possessing excessive ring strain quite often undergo unusual and sometimes unexpected chemical transformations to species of lower energy content. Similarly, ring strain would be anticipated to have a pronounced effect upon the reactivity of molecules in an electronically excited state. In an attempt to assess the importance of this effect, we have studied the photochemical transformations of variously substituted cyclopropene derivatives.[4]

Cyclopropene itself was first prepared some 60 years ago,[5] but, despite its unusual structure, the molecule received minimal attention until the late 1950s.[6] Two factors led to a resurgence of interest with this highly strained ring system. First, developments in carbene chemistry led to new and convenient syntheses of cyclopropene derivatives.[7] Secondly, it was realized that the cyclopropenyl cation obeyed the Hückel [$4n$ + 2]-π rule.[8] Owing to their 54.5 kcal/mol intrinsic strain energy,[9] cyclopropene derivatives are thermally labile.[10] Experimentally, the thermal reaction of a cyclopropene consists of dominant ring cleavage leading to a carbenic species.[11] Cycloaddition across the double bond in cyclopropene has been found to proceed quite readily since ring strain is reduced by 26 kcal/mol.[12,13] The transition-state energy for the cycloaddition reaction, however, is very sensitive to steric factors as is indicated by the observation that 3,3-disubstituted cyclopropenes do not readily undergo Diels–Alder reactions.[14] Since chemical reactivity in cycloaddition processes can be significantly modified by the appropriate choice of substituent groups,[15] we have undertaken an investigation of the [2 + 2] cycloaddition behavior of several 3,3-disubstituted cyclopropenes containing a carbonyl substituent on the π-bond.[16] FMO theory predicts that attachment of a carbomethoxy group on the cyclopropene π-bond will lower the energy of the LUMO and thereby enhance the cycloaddition rate.[17] We report here the results of our studies which show that 1-phenyl-2-carbalkoxy-substituted cyclopropenes undergo a ready photosensitized [2 + 2] cycloaddition reaction to give bicyclo[2.1.0]pentanes in high yield.

Results and Discussion

We have previously reported that the thioxanthenone-sensitized photolysis of 1-phenyl-2-carbomethoxy-3,3-dimethylcyclopropene (**1**) in benzene gave rise to a mixture of two dimers (**2** and **3**).[16] In subsequent studies we have



† Alexander von Humboldt Senior Scientist, University of Wurz-'85.

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(2) de Meijere, A. *Angew. Chem., Int. Ed. Eng.* **1979**, *18*, 809.
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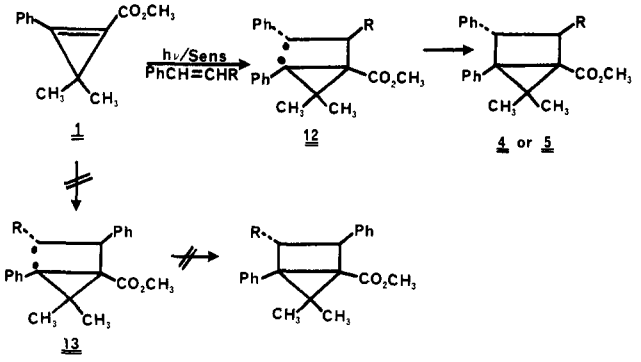
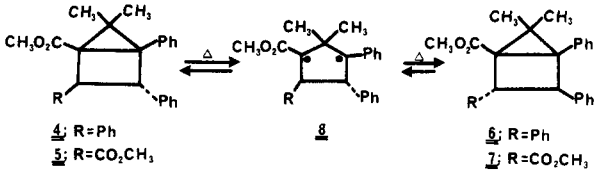
Scheme I

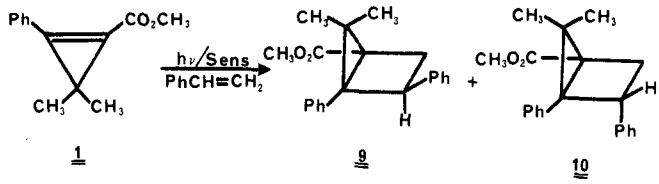


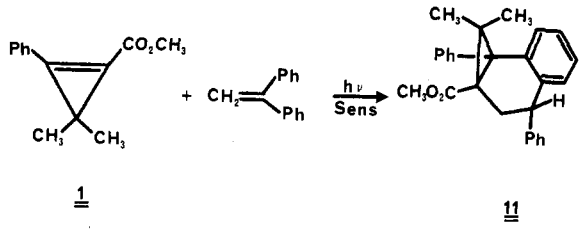
found that cyclopropene 1 can undergo photochemical [2 + 2] cycloaddition to several phenyl-substituted alkenes in high yield. The cycloadditions are carried out by using a slight excess of the olefinic acceptor in the presence of thioxanthenone as the triplet sensitizer. These conditions almost completely suppress the formation of dimers **2** and **3**, which are formed in high yield in the absence of a trapping agent. The photosensitized cycloadditions were reasonably efficient, with quantum yields varying from 0.2 to 0.3 at 40 °C. The triplet-sensitized cycloaddition of 1 and *trans*-stilbene produced a single 1:1 cycloadduct (Φ = 0.31) whose structure was assigned as 1-carbomethoxy-5,5-dimethyl-*exo*,2-*endo*-3,4-triphenylbicyclo[2.1.0]pentane (**4**). Similarly, the thioxanthenone-sensitized photolysis of 1 with methyl cinnamate afforded cycloadduct **5** as the exclusive photoadduct (Φ = 0.22). The structures of the cycloadducts rest largely upon the interpretation of the ^{13}C and ^{1}H NMR spectra (see Experimental Section) and by analogy with the earlier work of Arnold[18,19] and Farid.[20] These authors were the first to obtain a cross-adduct from the photocycloaddition of a cyclopropene with an olefin. Assignment of the trans stereochemistry to the cycloadducts is consistent with the observed 5.0-Hz coupling constant of the cyclobutyl protons. Thermolysis of cycloadducts **4** and **5** at 125 °C resulted in the formation of an isomeric set of cycloadducts (i.e., **6** and **7**) (ratio 1:1). This isomerization undoubtedly involves cleavage of the central bond to give diradical **8**, which undergoes ring-flipping followed by a subsequent ring-closure.[21]



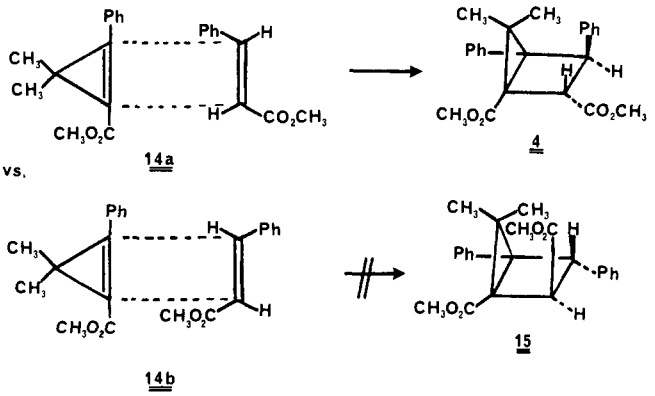
In an effort to establish the regiochemical features of the photocycloaddition, sensitized reactions with several unsymmetrical alkenes were carried out. Addition of styrene to cyclopropene 1 under the conditions described resulted in a mixture of cycloadducts **9** and **10**. These compounds were readily interconverted by heating in benzene at 125 °C.

A somewhat unexpected reaction was encountered in the sensitized irradiation of 1 with 1,1-diphenylethylene. In this case a single 1:1 cycloadduct was isolated in high yield whose structure was assigned as 1-carbomethoxy-3,6-diphenyl-4,5-benzo-7,7-dimethylbicyclo[4.1.0]hept-4-ene (**11**) on the basis of its characteristic NMR spectrum: δ 0.93 (s, 3 H), 1.27 (s, 3 H), 2.35 (dd, 1 H, J = 16.0 and 5.0 Hz), 3.34 (s, 3 H), 3.62 (dd, 1 H, J = 16.0 and 3.0 Hz), 4.13 dd, 1 H, J = 5.0 and 3.0 Hz), and 6.72–7.43 (m, 14 H).





The mechanism by which these reactions proceed is worthy of comment in view of the subtle variations in product distribution. It should be noted that only a single photoadduct is obtained when *trans*-stilbene or methyl cinnamate is used as the trapping agents. The exclusive formation of **4** and **5** from the sensitized irradiation indicates that the photocycloaddition is sensitive to steric factors. The reactants approach each other in a fashion that minimizes steric interactions. Thus, the π-center bearing the R substituent (R = Ph, CO_2CH_3, H) attacks the cyclopropene π-bond from the least hindered exo face. Coupling of the initially produced diradical will occur so as to give a cycloadduct with the most stable (trans) relationship of the substituent groups.[22] This explanation is perfectly consistent with the exclusive formation of cycloadducts **4** and **5** as well as the mixture of stereoisomers (i.e., **9** and **10**) when styrene is used as the trapping agent. The regiochemistry encountered in the cycloaddition can be rationalized (see Scheme I) in terms of a stepwise addition to give the most stable diradical intermediate (i.e., **12** not **13**). Alternatively, if the system stays on the triplet surface until cycloaddition is complete and the triplet product then collapses to its ground-state singlet, the pathway to the observed product **4** (or **5**) will be a [π_2s + π_2a] "allowed" excited-state reaction.[23] Even if collapse to the ground state occurs along the cycloaddition pathway, the [π_2s + π_2s] path will still be substantially favored over the other possible mode of cycloaddition (i.e., [π_2s + π_2a]).[23,24] Of the two possible orientations, **14a** and **14b**,



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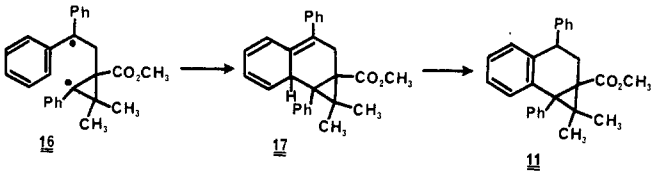
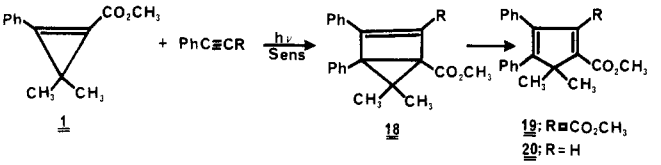
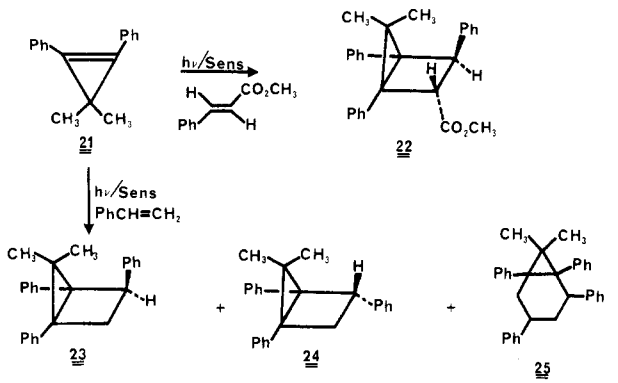
the former would lead to a more stable transition state for concerted cycloaddition than the latter, in which there would be steric repulsion between the phenyl substituents. Thus, the fact that bicyclopentane **4** is formed rather than the alternative isomer **15** is also understandable in terms of a concerted cycloaddition. The formation of the trans cycloadducts does not require the cycloaddition to be concerted. More than likely, the second bond from diradical intermediate **12** is formed faster than bond rotation which would be required for formation of a cis cycloadduct. In fact, the isolation of bicyclo[4.1.0]heptene **11** from the sensitized irradiation of **1** with diphenylethylene is most compatible with the diradical mechanism. In this case the initially formed diradical (i.e., **16**) prefers to cyclize onto the neighboring ortho position to give **17** which then undergoes a subsequent 1,3-hydrogen shift.

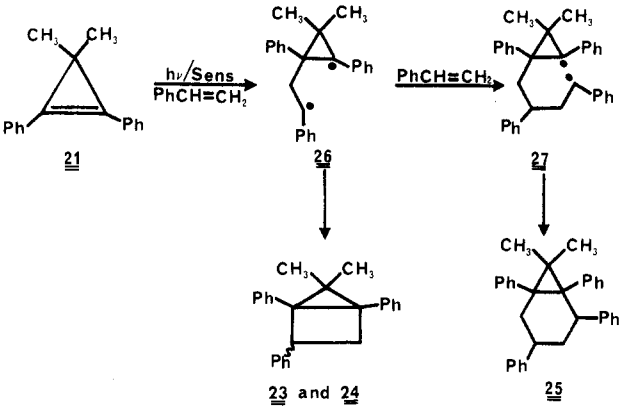


Aryl-substituted alkenes are effective substrates, whereas electron-rich or electron-deficient olefins failed to react with the electronically excited triplet state of **1**. This is probably related to the required stabilization of both diradical centers by the phenyl groups. The triplet-induced photolysis of **1** in the presence of methyl phenylpropiolate or phenylacetylene was also studied and was found to give cyclopentadiene **19** (or **20**) as the exclusive photoproduct. The formation of **19** (or **20**) is most readily accomodated by a [2 + 2] cycloaddition followed by an electrocyclic ring opening of the initially generated bicyclo[2.1.0]pentene intermediate **18**.

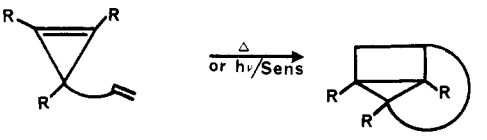


Previous work by DeBoer has shown that trisubstituted cyclopropenes undergo [2 + 2] dimerization to give tricyclo[3.1.0.0^{2,4}]hexanes upon triplet sensitization.[25] Earlier attempts to obtain cross-adducts with these systems were unsuccessful. This was rationalized by assuming that the rate of reaction of the triplet excited cyclopropene with a ground-state molecule is so rapid that observable cross-adduct formation is precluded. DeBoer's studies also showed that there are severe steric constraints associated with the triplet dimerization reaction. Thus, 1,2-diphenylcyclopropenes, where both 3-positions are substituted with alkyl groups, do not dimerize. During the course of our studies we found that 1,2-diphenyl-3,3-dimethylcyclopropene (**21**) also undergoes the triplet-induced [2 + 2] cycloaddition reaction. For example, photolysis of **21** in benzene in the presence of thioxanthenone and methyl cinnamate gave rise to cycloadduct **22**. The structure of **22** was easily assigned on the basis of its characteristic NMR spectrum (see Experimental Section). The sensitized irradiation of **21** with styrene produced a mixture of three compounds whose structures were assigned as **23–25** on the basis of their spectral properties. The formation of **25** (10%) may be most simply interpreted on the basis of a subsequent addition of the initially produced diradical **26** to another molecule of styrene followed by collapse of the resulting diradical **27** to the observed 2:1 adduct.





During the past decade there has been remarkable interest in the development of intramolecular cycloaddition processes.[26-29] Internal cycloadditions have been found to offer a powerful solution to many problems in complex natural product synthesis.[30,31] Converting olefin geometry into the stereochemistry of saturated carbon combined with forming two rings simultaneously from acyclic precursors accounts for the popularity of this approach. Earlier work in our laboratory has established that cyclopropene derivatives containing π-unsaturation at the 3-position of the ring undergo ready intramolecular [2 + 2] cycloadditions.[32-35] The driving force for this reaction



is undoubtedly associated with the considerable relief of bond angle strain of the cyclopropene ring. As a continuation of our investigations in this area, we were particularly interested in determining whether the internal cycloaddition reaction would also occur when the unsaturated

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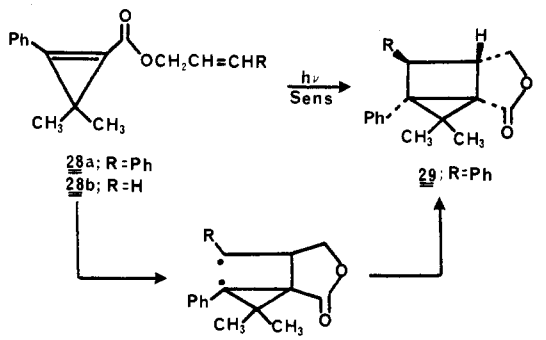
side chain was attached to the 2-position of the cyclopropene ring. In order to probe this possibility, we carried out a photochemical study with a series of unsaturated cyclopropenyl esters.

As our first model we chose to investigate the photosensitized behavior of 3-phenyl-2-propen-1-yl) 2-phenyl-3,3-dimethylcyclopropenecarboxylate (**28a**). This material was prepared by hydrolysis of ester 1 into the corresponding carboxylic acid with potassium hydroxide in isopropyl alcohol. Conversion of the acid into the desired ester(s) was accomplished using triphenylphosphine, diethyl azodicarboxylate, and cinnamyl alcohol.[36] The triplet-sensitized irradiation of **28a** afforded the expected internal cycloadduct **29** in 75% yield (Φ = 0.24). Thermolysis of **28a**, however, did not produce any detectable quantities of **29**.

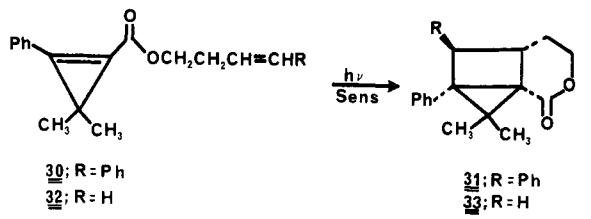
In contrast to the clean reaction which occurred with cyclopropene **28a** the corresponding allyl-substituted ester **28b** failed to undergo the cycloaddition. This result is analogous to that encountered with the bimolecular cycloadditions of cyclopropene 1 where it was found that simple alkenes are ineffective trapping substrates. The reluctance of **28b** to undergo [2 + 2] cycloaddition is probably a result of the high energy associated with the unstabilized diradical intermediate (R = H). Apparently,



radical stabilization of both centers is necessary for the cycloaddition reaction to occur. This would suggest that the reaction proceeds via an initial cyclization through a five-membered transition state to give a diradical which undergoes subsequent ring closure. In fact, this is the normal pattern of closure as predicted by the "rule of five".[37,38]

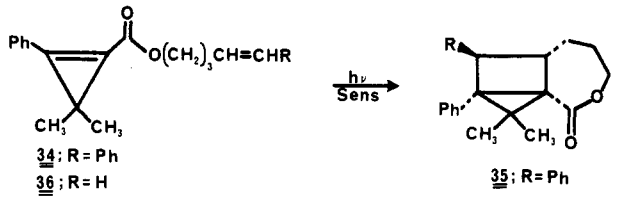
In view of the stringent spatial requirements associated with the intramolecular [2 + 2] cycloaddition of 3-substituted cyclopropenes,[32-35] we thought it worthwhile to consider what effect a variation in the spatial proximity between the cyclopropene and the internal double bond would have on the course of the intramolecular cycloaddition of these 2-(acyloxy)-substituted cyclopropenes. This led us to examine the sensitized behavior of several 3-butenyl-substituted cyclopropene esters so as to compare their behavior with the homologous allyl systems. The sensitized photolysis of cyclopropene **30** (R = Ph) resulted in the formation of the intramolecular [2 + 2] cycloadduct **31** in 50% yield. Most interestingly, the simple butenyl-substituted ester **32** afforded a related cycloadduct (i.e., **33**) in 90% yield. This result stands in dramatic contrast to that encountered with cyclopropene **28b**.

Since the intramolecular [2 + 2] cycloaddition of **32** occurs across a simple alkyl-substituted π-bond, one might inquire why the reaction occurs at all. One possible explanation is that in this case the two interacting π-bonds

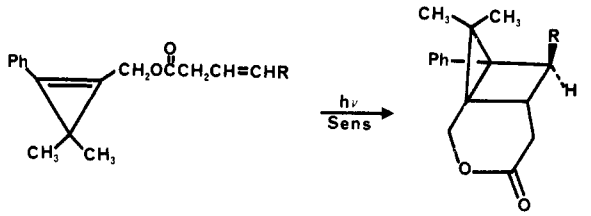


can very easily approach each other in parallel planes. The ease of internal cycloaddition that occurs with **32** reflects an extremely favorable entropy factor that offsets the unfavorable radical stabilization term.

As an extension of our studies in this area we have also examined the sensitized behavior of the next higher homologous series. Irradiation of a sample of 5-phenyl-4-penten-1-yl cyclopropenecarboxylate **34** in benzene in the presence of thioxanthenone afforded cycloadduct **35** in 42% yield. In addition to recovered starting material (25%), it was also possible to isolate a significant amount (28%) of the isomerized *cis*-cyclopropenyl-substituted ester. Thus, the triplet state of this bichromophoric cyclopropene can undergo both cycloaddition and cis–trans isomerization about the π-bond. One additional point worth mentioning deals with the photosensitized behavior of the unsubstituted 4-pentenylcyclopropene ester **36**. In contrast to the butenyl system (i.e., **32**), no signs of an intramolecular cycloadduct could be detected in the crude reaction mixture derived from **36**. Clearly, the spatial relationship of the two π-bonds plays an important role in controlling the facility of the internal [2 + 2] cycloaddition of an unactivated alkene.



This is further borne out from a study of the sensitized behavior of cyclopropenyl esters **37** and **38**. In both cases



an intramolecular 1:1 cycloadduct could be isolated in high yield. Moreover, the facility of the reaction clearly indicates that it is not necessary to have the carbonyl group in conjugation with the cyclopropene π-bond in order for the cycloaddition to occur. Inspection of molecular models indicates that the transition-state geometry associated with the parallel plane approach of π-bonds is very easily attained with this system. The ease with which **38** undergoes internal cycloaddition undoubtedly reflects an extremely favorable entropy factor which offsets the traditional reluctance of the excited triplet state to add to an unactivated alkene. The sensitized irradiation of (3,3-dimethyl-2-phenylcyclopropenyl)methyl cinnamate (**41**), the lower homologue of **37**, failed to undergo cycloaddition. With this system the triplet energy is probably localized on the cinnamate moiety and extended irradiation only leads to cis–trans isomerization about the double bond.

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In conclusion, the facility with which the [2 + 2] photocycloaddition reaction of 2-(acyloxy)-substituted cyclopropenes occurs makes this type of approach particularly attractive for the synthesis of some unusual polycyclic ring compounds. We are continuing to explore the scope and mechanistic details of these cycloadditions and will report additional findings at a later date.

Experimental Section

All melting points and boiling points are uncorrected.

Photosensitized Cycloaddition of 1-Carbomethoxy-3,3-dimethyl-2-phenylcyclopropene (1) with *trans*-Stilbene. A 1.0-g sample of cyclopropene 1 was irradiated in 180 mL of benzene in the presence of 0.90 g of *trans*-stilbene and 100 mg of thioxanthenone using a 450-W Hanovia medium pressure mercury arc lamp equipped with a Uranium filter sleeve for 100 h. The solvent was removed under reduced pressure and the crude residue was subjected to flash chromatography using a 5.5 × 18 cm silica gel column with a 2% acetone–hexane mixture as the eluent. In addition to a small amount (41 mg) of recovered starting material, 0.570 g (31%) of a white solid, mp 125–126 °C, was obtained which was identified as 1-carbomethoxy-5,5-dimethyl-*exo*-2,*endo*-3,4-triphenylbicyclo[2.1.0]pentane (**4**): NMR (90 MHz, $CDCl_3$) δ 1.12 (s, 3 H), 1.28 (s, 3 H), 3.32 (s, 3 H), 3.59 (d, J = 5 Hz, 1 H), 4.08 (d, J = 5 Hz, 1 H), 7.10–7.85 (m, 15, H); IR (KBr) 3075, 2975, 2355, 1730, 1601, 1499, 1439, 1395, 1295, 1265, 1195, 1175, 1100, and 950 cm^{-1}; UV (cyclohexane) 219 nm (ϵ 21 600); MS, m/e 382 (M^+), 215, 202, 178, 167, 143, 128, 115, and 91 (base). Anal. Calcd for $C_{27}H_{26}O_2$: C, 84.78; H, 6.85. Found: C, 84.75; H, 6.85.

A 113-mg sample of bicyclo[2.1.0]pentane **4** was heated in 2 mL of a 4:1 benzene-d_6/pyridine-d_5 mixture in a sealed thick walled NMR tube. The tube was heated for 25 h at 125 °C. The crude reaction mixture consisted of a 1:1 mixture of 1-carbomethoxy-5,5-dimethyl-*exo*-2,*endo*-3,4-triphenylbicyclo[2.1.0]-pentane (**4**) as well as a new isomer which was assigned as 1-carbomethoxy-5,5-dimethyl-*endo*-2,*exo*-3,4-triphenylbicyclo-[2.1.0]pentane (**6**). The two components could be separated via preparative reverse phase HPLC using a Zorbax column with a 75:25 methanol/water mixture as the solvent. The new isomer **6** was assigned on the basis of the following data: NMR (90 MHz, 80:20 benzene-d_6/pyridine-d_5) δ 1.22 (s, 3 H), 1.31 (s, 3 H), 3.58 (s, 3 H), 3.72 (d, J = 5 Hz, 1 H), 4.82 (d, J = 5 Hz, 1 H), 6.80–7.90 (m, 15 H); IR (neat) 2980, 1725, 1601, 1500, 1442, 1199, and 1108 cm^{-1}; UV (cyclohexane) 219 (ϵ 21 600); MS, m/e 382 (M^+), 215, 202, 178, 167, 143, 128, 115, and 91 (base). Anal. Calcd for $C_{27}H_{26}O_2$: C, 84.78; H, 6.85. Found: C, 84.87; H, 6.58.

Photosensitized Cycloaddition of 1-Carbomethoxy-3,3-dimethyl-2-phenylcyclopropene (1) with Methyl Cinnamate. A 1.0-g sample of **1**[16] was irradiated in 180 mL of dry benzene in the presence of 0.9 g of methyl cinnamate and 0.10 g of thioxanthenone with a 450-W Hanovia medium pressure mercury arc lamp equipped with a Uranium filter sleeve for 30 h. The solvent was removed under reduced pressure and the crude product was subjected to flash chromatography using a 5.5 × 18 cm silica gel column with a 2% acetone–hexane mixture as the eluent. The major product obtained contained 931 mg (52%) of a white solid, mp 104–105 °C, whose structure was assigned as *exo*-1,2-dicarbomethoxy-5,5-dimethyl-*endo*-3,4-diphenylbicyclo[2.1.0]pentane (**5**): NMR (90 MHz, $CDCl_3$) δ 1.13 (s, 3 H), 1.18 (s, 3 H), 3.31 (d, J = 5 Hz, 1 H), 3.66 (s, 3 H), 3.91 (s, 3 H)), 4.22 (d, J = 5 Hz, 1 H), 7.10–7.73 (m, 10 H); IR (KBr) 3500, 3070, 2980, 2590, 2350, 1738, 1708, 1601, 1450, 1380, 1360, 1320, 1208, 1170, 1108, 1022, and 960 cm^{-1}; UV (cyclohexane) 218 nm (ϵ 13 600); MS, m/e 364 (M^+), 304 (base), 273, 245, 229, 215, and 91. Anal. Calcd for $C_{23}H_{24}O_4$: C, 75.80; H, 6.64. Found: C, 75.76; H, 6.64.

A 170-mg sample of bicyclo[2.1.0]pentene **5** was thermolyzed at 136 °C for 6 h in 15 mL of benzene in a sealed tube. The solvent was removed under reduced pressure and the crude residue was shown by NMR to contain a 2:1 mixture of *exo*-1,2-dicarbomethoxy-5,5-dimethyl-*endo*-3,4-diphenylbicyclo[2.1.0]pentane (**5**) and *endo*-1,2-dicarbomethoxy-5,5-dimethyl-*exo*-3,4-diphenylbicyclo[2.1.0]pentane (**7**). These two components could be separated by preparative reverse phase HPLC using a Zorbax column and a 75:25 methanol/water mixture as the eluent. Bicyclo-[2.1.0]pentane **7** was assigned on the basis of its spectral properties: NMR (90 MHz, 4:1 benzene-d_6/pyridine-d_5) δ 1.31 (s, 3 H), 1.48 (s, 3 H), 3.42 (s, 3 H), 3.58 (s, 3 H), 3.88 (d, J = 5 Hz, 1 H), 4.27 (d, J = 5 Hz, 1 H), 6.80–7.85 (m, 10 H); IR (neat) 2995, 1735, 1601, 1500, 1440, 1320, 1230, 1200, 1162, 1108, 1078, 1020, and 800 cm^{-1}; UV (cyclohexane)) 218 nm (ϵ 13 600); MS, m/e 364 (M^+), 304 (base), 273, 245, 229, 215, and 91. Anal. Calcd for $C_{23}H_{24}O_4$: C, 75.80; H, 6.64. Found: C, 75.68; H, 6.57.

Photosensitized Cycloaddition of 1-Carbomethoxy-3,3-dimethyl-2-phenylcyclopropene (1) with Styrene. A 1.0-g sample of cyclopropene **1** was irradiated in 180 mL of benzene in the presence of 520 mg of styrene and 100 mg of thioxanthenone using a 450-W Hanovia medium pressure mercury arc lamp equipped with a Uranium filter sleeve for 60 h. The solvent was removed under reduced pressure and the crude residue was percolated through a 2 × 15 cm silica gel column with hexane. The resultant yellow oil was rechromatographed on a 2 × 100 cm silica gel medium pressure column using a 2% acetone–hexane mixture as the eluent. The first component isolated from the column contained 543 mg (36%) of a clear oil which was identified as 1-carbomethoxy-5,5-dimethyl-*endo*-3,4-diphenylbicyclo-[2.1.0]pentane (**9**): NMR (90 MHz, $CDCl_3$) δ 1.08 (s, 3 H), 1.20 (s, 3 H), 2.16 (dd, 1 H, J = 11.5 Hz), 3.12 (dd, 1 H, J = 11 Hz), 3.64 (s, 3 H), 3.97 (dd, 1 H, J = 11.5 Hz), 6.94–7.57 (m, 10 H); IR (neat) 3050, 2975, 1060, 1880, 1715, 1601, 1490, 1435, 1395, 1288, 1225, 1195, 1100, 1064, 1005, and 910 cm^{-1}; MS, m/e 306 (M^+), 247, 231, 215, 202, 178, 156, 128, 115, and 91 (base). Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.17; H, 7.19.

The second component isolated contained 408 mg (27%) of a yellow oil whose structure was assigned as 1-carbomethoxy-5,5-dimethyl-*exo*-3,4-diphenylbicyclo[2.1.0]pentane (**10**): NMR (90 MHz, CCl_4) δ 1.07 (s, 3 H), 1.53 (s, 3 H), 2.24 (dd, 1 H, J = 12.4 Hz), 2.62 (dd, 1 H, J = 12.4 Hz), 3.22 (dd, 1 H, J = 6.4 Hz), 3.75 (s, 3 H), 6.85–7.17 (m, 10 H); IR (neat) 3400, 2975, 2340, 1715, 1601, 1495, 1425, 1220, 1193, and 1098 cm^{-1}; MS, m/e 306 (M^+), 247, 231, 215, 202, 178, 156, 128, 115, and 91 (base). Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.08; H, 6.95.

When the endo-phenyl isomer **9** was subjected to molecular distillation, the resultant oil was found to contain a 1:1 mixture of **9** as well as the exo-phenyl isomer **10**, thereby establishing that the two isomers can be thermally equilibrated. The third fraction that was obtained from the medium pressure chromatography contained 280 mg of the cyclopropene dimer 1,2-dicarbomethoxy-4,4-dimethyl-2-(2-methyl-1-phenyl-1-propenyl)-3-phenylbicyclo[1.1.0]butane (**2**).[16]

Photosensitized Reaction of 1-Carbomethoxy-3,3-dimethyl-2-phenylcyclopropene (1) with 1,1-Diphenylethylene. A 1.0-g sample of cyclopropene **1** was irradiated in 180 mL of benzene in the presence of 900 mg of 1,1-diphenylethylene and 100 mg of thioxanthenone using a 450-W Hanovia lamp equipped with a Uranium filter sleeve for 16 h. The solvent was removed under reduced pressure and the crude residue was chromatographed on a silica gel column using a 1% acetone–1% triethylamine–hexane mixture as the eluent. The major fraction contained 700 mg of a clear oil whose structure was assigned as methyl 7,7-dimethyl-*exo*-3,6-diphenyl-4,5-benzobicyclo[4.1.0]-hept-4-enoate (**11**) on the basis of its characteristic NMR spectrum (360 MHz, $CDCl_3$): δ 0.94 (s, 3 H), 1.29 (s, 3 H), 2.41 (dd, 1 H, J = 16.0 and 3.0 Hz), 3.38 (s, 3 H), 3.65 (dd, 1 H, J = 16.0 and 5.0 Hz), 4.16 (dd, J = 5.0 and 3.0 Hz), and 6.80–7.49 (m, 14 H).

Photosensitized Cycloaddition of 1-Carbomethoxy-3,3-dimethyl-2-phenylcyclopropene (1) with Methyl Phenylpropiolate. A 1.0-g sample of cyclopropene **1** was irradiated in 180 mL of benzene in the presence of 800 mg of methyl phenylpropiolate and 0.100 g of thioxanthenone using a 450-W Hanovia medium pressure mercury arc lamp equipped with a Uranium filter sleeve for 60 h. The solvent was removed under reduced pressure and the crude residue was percolated through a 2.5 × 13 cm silica gel column with a 5% acetone–hexane mixture as the eluent. The resulting yellow oil was rechromatographed on a flash silica gel column using a 5% acetone–hexane mixture as the eluent. The only material that could be isolated contained 604 mg (34%) of a white solid, mp 124–125 °C, which was identified as 1,2-dicarbomethoxy-3,4-diphenyl-5,5-dimethyl-1,3-cyclopentadiene (**19**): NMR (90 MHz, $CDCl_3$) δ 1.40 (s, 6 H), 3.73 (s, 3 H), 3.80 (s, 3 H), 7.0–7.5 (m, 10 H); IR (KBr) 3000, 1740, 1705, 1601, 1550, 1440, 1380, 1335, 1285, 1218, 1180, 1135, and

1065 cm^{-1}; UV (cyclohexane) 241 nm (ϵ 17 030), 307 (5530); MS, m/e 362 (M$^+$), 302, 271 (base), 270, 243, and 228. Anal. Calcd for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12. Found: C, 76.26; H, 6.14.

Photosensitized Cycloaddition of 1-Carbomethoxy-3,3-dimethyl-2-phenylcyclopropene (1) with Phenylacetylene. A 1.0-g sample of cyclopropene 1 was irradiated in 180 mL of benzene in the presence of 510 mg of phenylacetylene and 100 mg of thioxanthenone using a 450-W Hanovia medium pressure mercury arc lamp equipped with a Uranium filter sleeve for 60 h. The solvent was removed under reduced pressure and the crude residue was percolated through a 2.5 × 15 cm silica gel column using hexane as the eluent. The resulting yellow oil was rechromatographed on a 2 × 60 cm silica gel medium pressure column using a 1% acetone–hexane mixture as the eluent. The major fraction isolated from the column contained 834 mg (54%) of a white solid, mp 77–78 °C, whose structure was identified as 1-carbomethoxy-3,4-diphenyl-5,5-dimethyl-1,3-cyclopentadiene (**20**): NMR (90 MHz, $CDCl_3$) δ 1.36 (s, 6 H), 3.84 (s, 3 H), 7.07–7.53 (m, 10 H), and 7.67 (s, 1 H); IR (KBr) 3000, 2600, 2260, 1960, 1815, 1700, 1600, 1545, 1435, 1340, 1250, 1180, 1120, 1060, and 895 cm^{-1}; UV (cyclohexane) 242 nm (ϵ 19 500), 310 (7200); MS, m/e 305, 304 (M$^+$, base), 245, 229, 215, 166, 152, 115, and 91. Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.85; H, 6.64. Found: C, 82.69; H, 6.70.

Photosensitized Cycloaddition of 3,3-Dimethyl-1,2-diphenylcyclopropene (21) with Methyl Cinnamate. A 220-mg sample of **21** was irradiated in 200 mL of benzene in the presence of 180 mg of methyl cinnamate and 20 mg of thioxanthenone using a 450-W Hanovia medium pressure arc lamp equipped with a Uranium filter sleeve for 48 h. The solvent was removed under reduced pressure and the crude residue was chromatographed on a 1.5 × 60 cm silica gel column using hexane as the eluent. The major fraction contained 150 mg of a crystalline solid (42%), mp 126–127 °C, whose structure was assigned as 5,5-dimethyl-*endo*-1,2,4-triphenyl-*exo*-3-carbomethoxybicyclo[2.1.0]pentane (**22**): NMR ($CDCl_3$, 90 MHz) δ 0.87 (s, 3 H), 1.08 (s, 3 H), 3.45 (d, 1 H, J = 5.0 Hz), 3.68 (s, 3 H), 4.65 (d, 1 H, J = 5.0 Hz), and 7.0–7.9 (m, 15 H); IR (KBr) 3500, 3000, 1740, 1599, 1500, 1450, 1395, 1210, 760, and 700 cm^{-1}; UV (cyclohexane) 218 nm (ϵ 20 700); MS, m/e 382 (M$^+$), 367, 322, 307, 277, 229, 215, 105, and 91 (base). Anal. Calcd for $C_{27}H_{26}O_2$: C, 84.78; H, 6.85. Found: C, 84.73; H, 6.82.

Photosensitized Cycloaddition of 3,3-Dimethyl-1,2-diphenylcyclopropene (21) with Styrene. A 300-mg sample of cyclopropene **21** was irradiated in 180 mL of benzene in the presence of 156 mg of styrene and 30 mg of thioxanthenone using a 450-W Hanovia medium pressure mercury arc lamp equipped with a Uranium filter sleeve for 48 h. The solvent was removed under reduced pressure and the crude residue was chromatographed on a 1.5 × 60 cm silica gel medium pressure column using hexane as the eluent. The first component eluted from the column contained 37 mg of recovered starting material. The second component isolated contained 58 mg (11%) of 2,2-dimethyl-1,3,4-*endo*,6-*exo*-tetraphenylbicyclo[4.1.0]heptane (**25**). The structure of this material was assigned on the basis of its spectral properties: NMR (400 MHz, $CDCl_3$) δ 0.98 (s, 3 H), 1.34 (s, 3 H), 1.77 (m, 1 H), 1.88 (dd, 1 H, J = 12 Hz), 2.35 (m, 1 H), 2.62 (m, 1 H), 2.76 (m, 1 H), 3.28 (m, 1 H), 6.89–7.43 (m, 20 H); IR (KBr) 3480, 3075, 2975, 2580, 1601, 1485, 1440, 1380, and 740 cm^{-1}; UV (cyclohexane) 235 nm (ϵ 14 400); MS, m/e 428 (M$^+$, base), 351, 297, 282, 216, and 206. Anal. Calcd for $C_{33}H_{32}$: C, 92.47; H, 7.53. Found: C, 92.41; H, 7.56.

The third component isolated from the column contained 148 mg (32%) of a viscous clear oil whose structure was assigned as 5,5-dimethyl-1,2,4-*endo*-triphenylbicyclo[2.1.0]pentane (**23**): NMR (60 MHz, CCl_4) δ 0.92 (s, 3 H), 1.07 (s, 3 H), 2.43 (dd, 1 H, J = 11.6 Hz), 2.85 (dd, 1 H, J = 11 Hz), 4.10 (dd, 1 H, J = 11.6 Hz), 6.83–7.65 (m, 15 H); IR (neat) 2975, 1755, 1705, 1601, 1500, 1455, 1245, 1130, 1070, and 775 cm^{-1}; UV (cyclohexane) 226 nm (ϵ 7020); MS, m/e 324 (M$^+$), 309, 115, 105, and 91 (base). Anal. Calcd for $C_{25}H_{24}$: C, 92.53; H, 7.47. Found: C, 92.47; H, 7.51.

The fourth component isolated from the column contained 196 mg (42%) of a white solid, mp 91–92 °C, whose structure was assigned as 5,5-dimethyl-1,2,4-*exo*-triphenylbicyclo[2.1.0]pentane (**24**): NMR (60 MHz, CCl_4) δ 0.82 (s, 3 H), 1.57 (s, 3 H), 2.42 (d, 1 H, 5 Hz), 2.44 (d, 1 H, J = 5 Hz), 3.34 (t, 1 H, J = 5 Hz), 6.73–7.55 (m, 15 H); IR (KBr) 3020, 2930, 1601, 1495, 1445, 1385, 1065, 1025, 1018, and 765 cm^{-1}; UV (cyclohexone) 226 nm (ϵ 7020); MS, m/e 324 (M$^+$), 309, 115, 105, and 91 (base). Anal. Calcd for $C_{25}H_{24}$: C, 92.53; H, 7.47; Found: C, 92.47; H, 7.51.

Preparation of 3,3-Dimethyl-2-phenylcyclopropenecarboxylic Acid. A 3.50-g sample of 1-carbomethoxy-3,3-dimethyl-2-phenylcyclopropene (1)[16] was heated at reflux in 120 mL of isopropyl alcohol for 36 h with an equivalent of potassium hydroxide and 15 mL of water. The reaction mixture was concentrated under reduced pressure and 200 mL of a 10% hydrochloric acid solution was added. Concentrated hydrochloric acid was added dropwise until the solution was strongly acidic and then the aqueous mixture was extracted with ether. The ether extracts were combined and dried over magnesium sulfate, and the solvent was removed under reduced pressure. The crude acid was crystallized from petroleum ether to give 2.8 g (88%) of a white solid, mp 123–124 °C, whose structure was assigned as 3,3-dimethyl-2-phenylcyclopropenecarboxylic acid: NMR (90 MHz, CCl_4) δ 1.49 (s, 6 H), 7.35–7.87 (m, 5 H), and 10.08 (br s, 1 H); IR (KBr) 2920, 1800, 1650, 1490, 1455, 1415, 1300, 1215, 1040, 940, 790, and 780 cm^{-1}; UV (95% ethanol) 290 nm (ϵ 16 400); MS, m/e 188 (M$^+$), 145, 143 (base), 129, 128, 115, and 77. Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.41; H, 6.47.

Preparation and Triplet-Sensitized Irradiation of 3-Phenyl-2-propen-1-yl 3,3-Dimethyl-2-phenylcyclopropenecarboxylate (28a). A solution containing 360 mg of cinnamyl alcohol and 711 mg of triphenylphosphine in 20 mL of ether was added dropwise to a stirred solution containing 500 mg of 3,3-dimethyl-2-phenylcyclopropenecarboxylic acid and 0.43 mL of diethyl azodicarboxylate in 30 mL of ether at room temperature. The mixture was stirred for 12 h and the solvent was removed under reduced pressure. The crude residue was percolated through a 2 × 15 cm column of silica gel using hexane as the eluent. The major component isolated contained 383 mg (47%) of a white solid, mp 84–85 °C, whose structure was assigned as 3-phenyl-2-propen-1-yl 3,3-dimethyl-2-phenylcyclopropenecarboxylate (**28a**) on the basis of its spectral properties: NMR (90 MHz, CCl_4) δ 1.43 (s, 6 H), 4.87 (d, J = 7 Hz, 1 H), 6.30 (dt, J = 17 and 7 Hz, 1 H), 6.70 (d, J = 17 Hz, 1 H), and 7.10–7.80 (m, 10 H); UV (95% ethanol) 227 nm (ϵ 13 400), 250 (20 100), 284 (17 000), and 292 (18 700); IR (KBr) 2970, 1810, 1685, 1500, 1460, 1385, 1315, 1290, 1200, 1180, 990, 965, 765, and 710 cm^{-1}; MS, m/e 304 (M$^+$), 187, 117, 115, 105, and 91. Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.85; H, 6.64. Found: C, 82.75; H, 6.67.

A 125-mg sample of **28a** and 25 mg of fluorenone were dissolved in 250 mL of anhydrous benzene, and the mixture was irradiated for 3 h using a 450-W Hanovia medium pressure mercury arc lamp equipped with a Uranium filter sleeve under an argon atmosphere. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel using a 10% acetone–hexane mixture as the eluent. The major fraction contained 88 mg (75%) of a clear oil whose structure was assigned as 6,7-diphenyl-8,8-dimethyl-3-oxatricyclo[3.3.0.0^{1,7}]octan-2-one (**29**) on the basis of its spectral properties: IR (neat) 3060, 3040, 3000, 2960, 1755, 1740, 1605, 1500, 1450, 1420, 1380, 1280, 1255, 1180, 1130, 1110, 1050, 1030, 1000, 985, and 790 cm^{-1}; NMR (360 MHz, $CDCl_3$) δ 1.15 (s, 3 H), 1.29 (s, 3 H), 2.94 (ddd, 1 H, J = 9.6, 6.2, and 3.3 Hz), 3.93 (d, 1 H, J = 3.3 Hz), 4.68 (dd, 1 H, J = 9.6 and 6.2 Hz), 5.06 (t, 1 H, J = 9.6 Hz) and 7.18–7.40 (m, 10 H); UV (95% ethanol) 228 nm (ϵ 15 000); MS, m/e 304 (M$^+$), 179, 178, 117, and 91. Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.85; H, 6.64. Found: C, 82.73; H, 6.67.

Preparation of 4-Phenyl-3-buten-1-yl 3,3-Dimethyl-2-phenylcyclopropenecarboxylate (30). A 4.6-g sample of 4-phenyl-3-butenoic acid was allowed to react with 1.10 g of lithium aluminum hydride in 200 mL of anhydrous ether. The mixture was heated at reflux for 18 h and was then quenched with sodium sulfate. The aluminum salts were filtered and the filtrate was dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude residue was distilled at 100 °C (0.5 mm) to give 3.11 g (75%) of a colorless oil whose structure was assigned as 4-phenyl-3-buten-1-ol on the basis of its spectral properties: NMR (90 MHz, CCl_4) δ 2.31 (q, J = 7 Hz, 2 H), 3.42 (br s, 1 H), 3.58 (t, J = 7 Hz, 2 H), 6.00 (dt, J = 1.6 and 7 Hz, 1 H), 6.33 (d, J = 16 Hz, 1 H), and 7.00–7.30 (m, 5 H); IR (neat) 3325, 2930, 1950, 1880, 1805, 1705, 1655, 1600, 1500, 1460, 1190, 1055, 980, 755, and 705 cm^{-1}.

A solution containing 414 mg of 4-phenyl-3-buten-1-ol and 727 mg of triphenylphosphine in 20 mL of ether was added dropwise to a stirred solution containing 522 mg of 3,3-dimethyl-2-phenylcyclopropenecarboxylic acid and 0.44 mL of diethyl azodicarboxylate in 30 mL of ether at room temperature. The mixture was stirred for 12 h and the solvent was removed under reduced pressure. The crude mixture was percolated through a 2 × 15 cm column of silica gel using a 5% acetone–hexane mixture as the eluent. The major fraction contained 570 mg (64%) of a light yellow oil whose structure was assigned as 4-phenyl-3-buten-1-yl 3,3-dimethyl-2-phenylcyclopropenecarboxylate (**30**): NMR (90 MHz, CCl_4) δ 1.43 (s, 6 H), 2.62 (q, J = 7 Hz, 2 H), 4.33 (t, J = 7 Hz, 2 H), 6.14 (dt, J = 16 and 7 Hz, 1 H), 6.50 (d, J = 16 Hz, 1 H), and 7.10–7.76 (m, 10 H); IR (neat) 2960, 1810, 1700, 1600, 1495, 1455, 1295, 1195, 1050, 980, 760, and 705 cm^{-1}; UV (cyclohexane) 254 nm (ϵ 19900), 283 (12200), and 292 (11900). Anal. Calcd for $C_{22}H_{22}O_2$: C, 82.98; H, 6.96. Found: C, 82.75; H, 6.87.

Triplet-Sensitized Irradiation of 4-Phenyl-3-buten-1-yl 3,3-Dimethyl-2-phenylcyclopropenecarboxylate (30). A solution containing 140 mg of cyclopropene **30** and 20 mg of thioxanthenone in 200 mL of benzene was irradiated for 1.5 h using a 450-W Hanovia medium pressure mercury arc lamp equipped with a Uranium filter sleeve. The solvent was removed under reduced pressure and the crude residue was percolated through a 2 × 11 cm column of silica gel using a 10% acetone–hexane mixture as the eluent. The main fraction was rechromatographed on a 2-mm silica gel chromatotron plate using a 20% acetone–hexane mixture as the eluent. The product contained 80 mg (58%) of a solid, mp 169–170 °C, whose structure was assigned as 9,9-dimethyl-*exo*-7,8-diphenyl-3-oxatricyclo[4.3.0.0^{1,8}]nonan-2-one (**31**): NMR (360 MHz, $CDCl_3$) δ 1.21 (s, 3 H), 1.37 (s, 3 H), 2.15 (dtd, J = 15.6, 10.6, and 3.3 Hz, 1 H), 2.55 (m, 2 H), 3.56 (d, J = 4.0 Hz, 1 H), 4 .27 (td, J = 11.00 and 2 Hz, 1 H), 4.52 (dt, J = 11.0 and 3.7 Hz, 1 H), and 7.18–7.40 (m, 10 H); IR (KBr) 3430, 2930, 1710, 1505, 1455, 1420, 1395, 1290, 1205, 1150, 1095, and 710 cm^{-1}; UV (cyclohexane) 260 nm (ϵ 950); MS, m/e 318 (M^+), 227, 199, 131, 105, 91 (base), and 77; ^{13}C NMR ($CDCl_3$, 50 MHz) δ 20.33 (q), 21.58 (q), 32.20 (t), 35.06 (s), 35.56 (d), 37.09 (s), 51.88 (d), 53.59 (s), 66.91 (t), 125.67 (d), 126.23 (d), 127.45 (d), 128.31 (d), 128.62 (d), 129.96 (d), 137.92 (s), 141.40 (s), and 168.85 (s). Anal. Calcd for $C_{22}H_{22}O_2$: C, 82.98; H, 6.96. Found: C, 83.00; H, 6.97.

Preparation of 3-Buten-1-yl 3,3-Dimethyl-2-phenylcyclopropenecarboxylate (32). A solution containing 195 mg of 3-buten-1-ol and 710 mg of triphenylphosphine in 20 mL of ether was added dropwise to a stirred solution containing 500 mg of 3,3-dimethyl-2-phenylcyclopropenecarboxylic acid and 0.43 mL of diethyl azodicarboxylate in 30 mL of ether at room temperature. The mixture was stirred for 12 h and the solvent was removed under reduced pressure. The crude residue was percolated through a 2 × 15 cm column of silica gel using a 5% acetone–hexane mixture as the eluent. The product was rechromatographed on a 4-mm silica gel chromatotron plate using a 3% acetone–hexane mixture as the eluent. A single component was isolated which contained 406 mg (62%) of a light oil whose structure was assigned as 3-buten-1-yl 3,3-dimethyl-2-phenylcyclopropenecarboxylate (**32**): NMR (90 MHz, CCl_4) δ 1.42 (s, 6 H), 2.48 (q, J = 7 Hz, 2 H), 4.27 (t, J = 7 Hz, 2 H), 5.00–5.28 (m, 2 H), 5.61–6.10 (m, 1 H), and 7.30–7.80 (m, 5 H); IR (neat) 3075, 3960, 1815, 1695, 1640, 1600, 1575, 1490, 1450, 1370, 1290, 1180, 1050, 930, 760, and 700 cm^{-1}; UV (cyclohexane) 272 nm (ϵ 9200), and 286 (9500). Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.08; H, 7.32.

Triplet-Sensitized Irradiation of 3-Buten-1-yl 3,3-Dimethyl-2-phenylcyclopropenecarboxylate (32). A solution containing 200 mg of cyclopropene **32** and 20 mg of thioxanthenone in 200 mL of benzene was irradiated for 2.5 h using a 450-W Hanovia medium pressure mercury arc lamp equipped with a Uranium filter sleeve. The solvent was removed under reduced pressure and the crude product was percolated through a 2 × 10 cm column of silica gel using an acetone–hexane mixture as eluent to give 180 mg of a white solid, mp 112–113 °C, whose structure was assigned as 9,9-dimethyl-8-phenyl-3-oxatricyclo-[4.3.0.0^{1,8}]nonan-2-one (**33**): NMR (360 MHz, $CDCl_3$) δ 1.30 (s, 3 H), 1.45 (s, 3 H), 1.87 (dd, J = 12.04 and 3.26 Hz, 1 H), 1.96 (m, 1 H), 2.27 (m, 2 H), 2.38 (dd, J = 12.04 and 5.46 Hz, 1 H), 4.30 (ddd, J = 11.18, 8.26, and 2.45 Hz, 1 H), 4.48 (ddd, J = 11.18, 6.25, and 2.9 Hz, 1 H), and 7.10–7.35 (m, 5 H); IR (KBr) 2950, 1700, 1490, 1450, 1415, 1295, 1245, 1200, 1130, 1100, 780, and 715 cm^{-1}; MS, m/e 242 (M^+), 227, 199, 155, 128, 115, 105, 91 (base), and 77; ^{13}C NMR (50 MHz, $CDCl_3$) δ 16.40 (q), 20.13 (q), 28.18 (d), 31.01 (t), 33.46 (t), 35.19 (s), 38.49 (s), 49.37 (s), 66.70 (t), 126.81 (d), 127.60 (d), 128.38 (d), 139.11 (s), and 169.56 (s). Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.20; H, 7.52.

Preparation of 5-Phenyl-4-penten-1-yl 3,3-Dimethyl-2-phenylcyclopropenecarboxylate (34). A 5.0-g sample of 5-phenyl-4-pentenoic acid was allowed to react with 1.1 g of lithium aluminum hydride in 120 mL of anhydrous ether. The mixture was refluxed for 18 h and was quenched with an aqueous sodium sulfate solution. The aluminum salt were filtered and the filtrate was dried under reduced pressure, and the crude residue was distilled at 100 °C (0.5 mm) to give 3.16 g (70%) of 5-phenyl-4-penten-1-ol on the basis of its spectral properties: NMR (90 MHz, CCl_4) δ 1.65 (m, 2 H), 2.24 (q, J = 7 Hz, 2 H), 3.60 (t, J = 6 Hz, 2 H), 5.27 (br s, 1 H), 6.07 (dt, J = 16.0 and 7.0 Hz, 1 H), 6.33 (d, J = 16 Hz, 1 H), and 7.02–7.33 (m, 5 H); IR (neat) 3320, 3030, 2940, 1705, 1600, 1495, 1450, 1070, 975, and 750 cm^{-1}.

A solution containing 422 mg of 5-phenyl-4-penten-1-ol and 682 mg of triphenylphosphine in 20 mL of ether was added dropwise to a stirred solution containing 488 mg of 3,3-dimethyl-2-phenylcyclopropenecarboxylic acid and 0.41 mL of diethyl azodicarboxylate in 30 mL of ether at room temperature. The mixture was stirred for 12 h, the solvent was removed under reduced pressure, and the crude residue was percolated through a 2 × 15 cm silica gel column using a 5% acetone–hexane mixture as the eluent. The resulting product was rechromatographed on a 2-mm silica gel chromatotron plate using a 3% acetone–hexane mixture as the eluent. The major component contained 356 mg (42%) of a light oil, whose structure was assigned as 5-phenyl-4-penten-1-yl 3,3-dimethyl-2-phenylcyclopropenecarboxylate (**34**): NMR (90 MHz, CCl_4) δ 1.43 (s, 6 H), 1.90 (m, 2 H), 2.35 (q, J = 7 Hz, 2 H), 4.27 (t, J = 7 Hz, 2 H), 6.13 (dt, J = 15 and 6 Hz, 1 H), 6.42 (d, J = 15 Hz, 1 H), and 7.40–7.85 (m, 10 H); IR (neat) 2950, 1810, 1710, 1600, 1495, 1450, 1370, 1295, 1230, 1195, 1050, 760, and 700 cm^{-1}; UV (cyclohexane) 250 nm (ϵ 15800), 284 (11700), and 292 (11μtc800). Anal. Calcd for $C_{23}H_{24}O_2$: C, 83.08; H, 7.29. Found: C, 82.89; H, 6.98.

Triplet-Sensitized Irradiation of 5-Phenyl-4-penten-1-yl 3,3-Dimethyl-2-phenylcyclopropenecarboxylate (34). A solution containing 178 mg of cyclopropene **34** and 18 mg of thioxanthenone in 200 mL of dry benzene was irradiated for 45 min using a 450-W Hanovia medium pressure mercury arc lamp equipped with a Uranium filter sleeve. The solvent was removed under reduced pressure, and the crude mixture was percolated through a 2 × 12 cm column of silica gel using a 5% acetone–hexane mixture as the eluent. The residue was rechromatographed on a 2-mm silica gel chromatotron plate using a 5% acetone–hexane mixture as the eluent. The first component isolated from the plate contained 93 mg of recovered starting material although the 4-phenylpentenyl side chain had partially isomerized to a mixture of cis and trans isomers. The second component isolated contained 36 mg (42%) of a crystalline product, mp 144–145 °C, whose structure was assigned as 10,10-dimethyl-*exo*-8,9-diphenyl-3-oxatricyclo[5.3.0.0^{1,9}]decan-2-one (**35**): NMR (360 MHz, $CDCl_3$) δ 1.00 (s, 3 H), 1.70 (m, 1 H), 1.78 (s, 3 H), 1.86 (m, 2 H), 2.00 (m, 1 H), 2.86 (dt, J = 12.64 and 5.06 Hz, 1 H), 3.39 (d, J = 5.06), 4.28 (dd, J = 12.64, 9.93 Hz, 1 H), 4.38 (dd, J = 12.64 and 4.88 Hz, 1 H), and 6.97–7.15 (m, 10 H); UV (cyclohexane) 255 nm (ϵ 900); IR (CCl_4) 3060, 3030, 2950, 1735, 1495, 1465, 1450, 1420, 1395, 1355, 1290, 1195, 1150, 1110, 1075, 1040, 965, 925, and 705 cm^{-1}; MS, m/e 273, 241.47, 215, 128, 115, 105, 91 (base), and 77. Anal. Calcd for $C_{23}H_{24}O_2$: C, 83.08; H, 7.29. Found: C, 82.80; H, 7.34.

Preparation of (3,3-Dimethyl-2-phenylcyclopropenyl)methyl 4-Phenyl-3-butenecarboxylate (37). To a solution containing 400 mg of 3,3-dimethyl-2-phenyl-1-(hydroxymethyl)cyclopropene,[16] 373 mg of 4-phenyl-3-butenoic acid and 60 mg of *N,N*-dimethyl-4-aminopyridine[39] in 35 mL of methylene chloride at 0 °C was added 474 mg of *N,N*-dicyclohexylcarbo-

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diimide. The mixture was stirred at 0 °C for 5 min and then at room temperature for 3 h. The precipitated urea was filtered, and the solvent was removed under reduced pressure. Fresh methylene chloride was added, and the remaining urea was precipitated and filtered. The filtrate was washed twice with a 10% hydrochloric acid solution and once with a saturated sodium bicarbonate solution. The organic phase was separated and dried over magnesium sulfate, and the solvent was removed under reduced pressure. The crude reddish oil was percolated through a 2 × 15 cm column of silica gel using hexane as the eluent. The product contained 560 mg (76%) of a light yellow oil whose structure was assigned as (3,3-dimethyl-2-phenylcyclopropenyl)methyl 4-phenyl-3-butenecarboxylate (**37**): NMR (90 MHz, CCl_4) δ 1.30 (s, 6 H), 3.27 (d, J = 6 Hz, 2 H), 5.20 (s, 2 H), 6.23 (dt, J = 16 and 6 Hz, 1 H), 6.47 (d, J = 16 Hz, 1 H), and 7.08–7.48 (m, 10 H); UV (cyclohexane) 252 nm (ε 24300); IR (neat) 3450, 3030, 2940, 2870, 1840, 1740, 1600, 1500, 1455, 1375, 1300, 1250, 1165, 1085, 980, 775, and 710. Anal. Calcd for $C_{22}H_{22}O_2$: C, 82.98; H, 6.96. Found: C, 82.71; H, 6.84.

Triplet-Sensitized Irradiation of (3,3-Dimethyl-2-phenylcyclopropenyl)methyl 4-Phenyl-3-butenecarboxylate (37). A solution containing 280 mg of cyclopropane **37** and 30 mg of thioxanthenone in 200 mL of benzene was irradiated for 4 h using a 450-W Hanovia medium pressure mercury arc lamp equipped with a Uranium filter sleeve. The solvent was removed under reduced pressure and the crude residue was chromatographed on a 2 × 15 cm silica gel column using a 10% acetone–hexane mixture as the eluent. The major fraction was rechromatographed on a 2-mm silica gel chromatotron plate using a 10% acetone–hexane mixture as the eluent. The major component isolated contained 200 mg (72%) of a white solid, mp 164–165 °C, whose structure was assigned as 9,9-dimethyl-*exo*-7,8-diphenyl-3-oxatricyclo[4.3.0.0^{1,8}]nonan-4-one (**39**): NMR (360 MHz, $CDCl_3$) δ 1.02 (s, 3 H), 1.14 (s, 3 H), 2.66 (ddd, J = 7.79, 4.0, and 1.82 Hz, 1 H), 3.06 (dd, J = 15.87 and 7.79 Hz, 1 H), 3.16 (dd, J = 15.87 and 1.82 Hz, 1 H), 3.65 (d, J = 4 Hz, 1 H), 4.24 (d, J = 12.68 Hz, 1 H), 4.02 (d, J = 12.68 Hz, 1 H), and 7.10–7.56 (m, 10 H); IR (CCl_4) 2975, 1750, 1500, 1455, 1430, 1375, 1330, 1170, 1070, 1010, and 705 cm^{-1}; UV (cyclohexane) 255 nm (ε 3900). Anal. Calcd for $C_{22}H_{22}O_2$: C, 82.98; H, 6.96. Found: C, 83.02; H, 7.12.

Preparation of (3,3-Dimethyl-2-phenylcyclopropenyl)-methyl 3-Butenecarboxylate (38). To a solution containing 1.0 g of 3,3-dimethyl-2-phenyl-1-hydroxymethylcyclopropene,[16] 495 mg of 3-butenoic acid, and 60 mg of *N,N*-dimethyl-4-aminopyridine[39] in 25 mL of methylene chloride at 0 °C was added 1.18 g of *N,N*-dicyclohexylcarbodiimide. The mixture was stirred at 0 °C for 5 min and then at room temperature for 3 h. The precipitated urea was removed by filtration and the solvent was removed under reduced pressure. Fresh methylene chloride was added, and the remaining urea was precipitated and filtered. The filtrate was washed twice with a 10% hydrochloric acid solution and once with a saturated sodium bicarbonate solution. The organic phase was separated and dried over magnesium sulfate, and the solvent was removed under reduced pressure. The crude product was percolated through a 2 × 15 cm column of silica gel using hexane as the eluent. The product contained 1.04 g (76%) of a light yellow oil whose structure was assigned as (3,3-dimethyl-2-phenylcyclopropenyl)methyl 3-butenecarboxylate (**38**): NMR (90 MHz, CCl_4) δ 1.31 (s, 6 H), 3.12 (dt, J = 7.0 and 1.5 Hz), 5.16 (s, 2 H), 5.03–5.30 (m, 2 H), 5.68–6.18 (m, 1 H), and 7.12–7.48 (m, 5 H); UV (cyclohexane) 222 nm (ε 9200), 252 (11300), 266 (11300), and 270 (11300); IR (neat) 3075, 3030, 2940, 2860, 1840, 1740, 1645, 1600, 1495, 1450, 1370, 1330, 1300, 1260, 1165, 1005, 935, 775, and 705 cm^{-1}. Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.18; H, 7.60.

Triplet-Sensitized Irradiation of (3,3-Dimethyl-2-phenylcyclopropenyl)methyl 3-Butenecarboxylate (38). A solution containing 178 mg of cyclopropene **38** and 20 mg of thioxanthenone in 200 mL of benzene was irradiated for 2 h using a 450-W Hanovia medium pressure mercury arc lamp equipped with a Uranium filter sleeve. The solvent was removed under reduced pressure and the crude residue was percolated through a 2 × 13 cm column of silica gel using a 5% acetone–hexane mixture as the eluent. The major product isolated from the column was rechromatographed on a 2-mm silica gel chromatotron plate using a 5% acetone–hexane mixture as the eluent. The major product contained 123 mg (69%) of a white solid, mp 86–87 °C, whose structure was assigned as 9,9-dimethyl-8-phenyl-3-oxatricyclo[4.3.0.0^{1,8}]nonan-4-one (**40**): NMR (360 MHz, $CDCl_3$) δ 0.91 (s, 3 H), 1.41 (s, 3 H), 1.85 (dd, 8.39 and 2.38 Hz, 1 H), 2.28 (dd, J = 8.12 and 5.27 Hz, 1 H), 2.30 (m, 1 H), 2.77 (dd, J = 15.94 and 1.86 Hz, 1 H), 2.87 (dd, J = 15.94 and 8.19 Hz, 1 H), 4.29 (d, J = 12.66 Hz, 1 H), 4.85 (d, J = 12.66 Hz, 1 H), and 7.19–7.26 (m, 5 H); UV (cyclohexane) 221 nm (ε 7400); IR (CCl_4) 2940, 2880, 1750, 1465, 1450, 1430, 1370, 1355, 1215, 1160, 1135, 1070, 1020, and 920 cm^{-1}; MS, m/e calcd (M^+) 242.1307, found 242.1305.

Quantum Yield Determinations. Quantum yields were determined by using a "merry-go-round" apparatus[40] equipped with a 450-W Hanovia lamp housed in a quartz well at the center of the carriage. Samples in 13-mm Pyrex test tubes were degassed to 5 × 10^{-3} mm in 5 freeze–thaw cycles and then sealed. Benzophenone–benzhydrol actinometry was used for quantum yield determinations. An actinometer yield of 0.69 was used when the concentration of benzophenone and benzhydrol in benzene was 0.1 M.[41] For the sensitized runs a filter solution of potassium dichromate in aqueous potassium carbonate was circulated through the well, and the entire unit allowed to run for 1 h prior to use.[42] A Uranium glass filter sleeve and Corning 7-54 filters were also used in conjunction with the filter solution. The concentrations were adjusted so that the sensitizer absorbed more than 98% of the light. The conversions were run to 25% or less. The mass balance in these runs was generally better than 98%.

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Supplementary Material Available: Experimental details are given for the preparation of allyl 3,3-dimethyl-2-phenylcyclopropenecarboxylate (**28b**), 4-penten-1-yl 3,3-dimethyl-2-phenylcyclopropenecarboxylate (**36**), and (3,3-dimethyl-2-phenylcyclopropenyl)methyl cinnamate (**41**) (2 pages). Ordering information is given on any current masthead page.

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