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The Mechanism of the Photochemical Cycloaddition Reaction between 2-Cyclopentenone and Polar Alkenes: Trapping of Triplet 1,4-Biradical Intermediates with Hydrogen Selenide[1]

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Abstract: The regiochemistry of the photochemical cycloaddition reaction between 2-cyclopentenone and the polar alkenes 1,1-difluoroethene and methyl acrylate has been investigated. With 1,1-difluoroethene the major cycloaddition product is a cyclobutane adduct possessing head-to-tail regiochemistry; with methyl acrylate the reaction is non-regioselective and a 46.5:53.5 ratio of head-to-head and head-to-tail cyclobutane regioisomers is obtained. These regiochemical outcomes are not those predicted by the Corey–de Mayo mechanism conventionally used to describe the enone–alkene photocycloaddition reaction. The triplet 1,4-biradicals implicated as intermediates in the photocycloaddition reaction between 2-cyclopentenone and the polar alkenes methyl acrylate and ethyl vinyl ether have been trapped quantitatively using hydrogen selenide as a hydrogen atom donor. The structures of the trapped products have been determined and hence the structures of their biradical precursors have been inferred. The yields of the trapped biradicals indicate that in both reactions the product distribution is controlled by the extent to which each of the isomeric biradical intermediates closes to products in competition with fragmentation to its ground state precursors. The product distribution does not reflect the relative rates of formation (and hence the relative amounts) of the isomeric biradical intermediates formed in each reaction. This conclusion is inconsistent with the long held idea that an oriented exciplex intermediate controls the reaction regiochemistry by favoring the formation of some biradicals over others. The structures of the biradical intermediates also reveal that both the 2-position and the 3-position of the enone are involved in forming the first bond to the alkene; with ethyl vinyl ether this bond is to the less substituted end of the alkene exclusively, while with methyl acrylate no selectivity in the site of initial bonding is observed.

Introduction

The addition of alkenes to the triplet excited state of cyclic enones to produce cyclobutane adducts is a reaction that has been extensively applied by synthetic organic chemists and has been investigated from a mechanistic viewpoint for over 30 years.[2] One aspect of the reaction that received early attention is the regiochemistry of the cyclobutane products formed when monosubstituted ethenes are utilized as the alkene partner.[3] Corey and co-workers found that when the ethene is substituted at one terminus with an electron-donating group (EDG in Scheme 1), such as an ethoxy group, then the reaction with 2-cyclohexenone is directed toward the formation of cyclobutane products that exhibit so-called head-to-tail regiochemistry; however, alkenes bearing an electron-withdrawing group (EWG in Scheme 1) at one terminus were found to react photochemically with 2-cyclohexenone to form cyclobutane adducts with head-to-head regiochemisty.[3]

The regioselectivity observed by Corey is conventionally explained in terms of the Corey–de Mayo mechanism.[2,4] This mechanism (Scheme 1) includes two types of intermediates: an oriented triplet excited state complex between the enone and alkene (an exciplex), and triplet 1,4-biradical intermediates that are formed from the exciplex. A major reason for including the exciplex in the reaction mechanism was to rationalize the generalizations regarding the regiochemistry of the cycloadducts. The exciplex was thought to consist of a complex in which the enone and alkene were oriented in such a fashion that destabilizing dipolar interactions were minimized. It was hypothesized that the dipole moment of the excited triplet enone resulted in an electronic charge distribution in which a slightly positive charge resided on the α carbon of the enone and a slightly negative charge on the β carbon.[5] The predicted orientations of the exciplex for the cases of electron-rich and electron-poor alkenes reacting with 2-cyclopentenone are shown in Scheme 1.

Despite the fact that this mechanistic rationalization of the reaction regiochemistry has become widely accepted and cited in the literature, there are relatively few examples of the reaction in which alkenes bearing electron-withdrawing groups react with the triplet excited state of cyclic enones to yield major products with head-to-head regiochemistry. In fact, the number of examples in which alkenes substituted with electron-withdrawing groups react with cyclic enones to form cyclobutane adducts with head-to-tail regiochemistry now rivals the number of examples in which head-to-head products are favored. For example, Rao and co-workers established that the major adduct resulting from the photocycloaddition of acrylonitrile and 4,4-dimethylcyclohexenone has head-to-tail regiochemistry,[6] while

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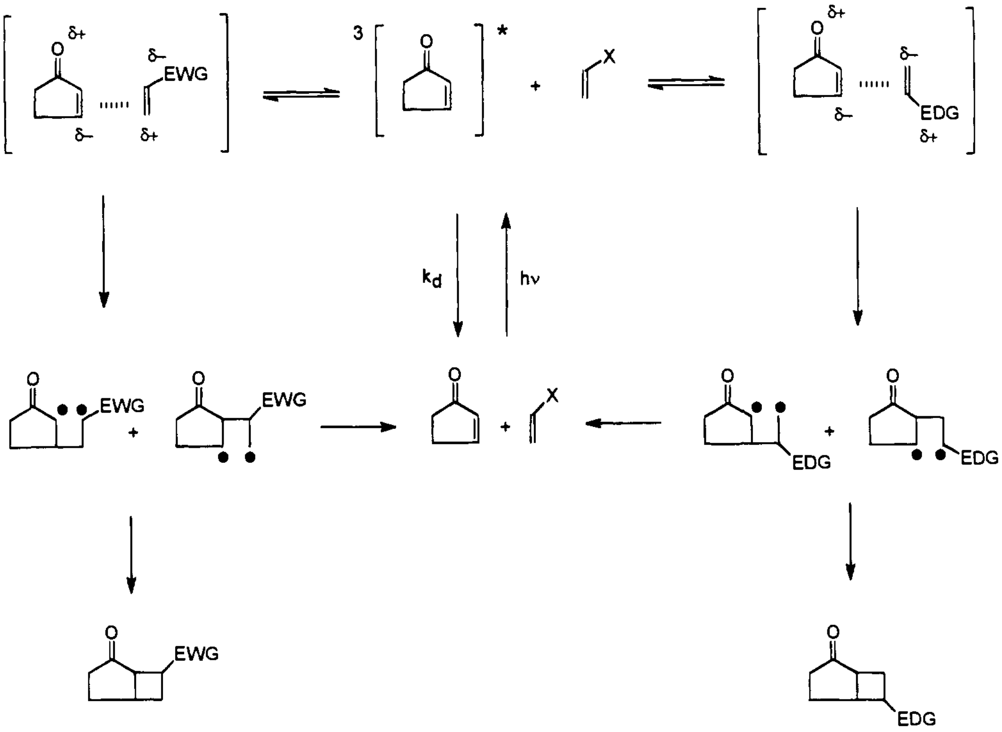
[2] (2) For reviews see: (a) de Mayo, P. *Acc. Chem. Res.* **1971,** *4,* 41. (b) Schuster, D. I. In *The Chemistry of Enones*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989; pp 623–756. (c) Weedon, A. C. In *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum Press: New York, 1984; pp 61–144. (d) Schuster, D. I.; Lem, G.; Kaprinidis, N. A. *Chem. Rev.* **1993,** *93,* 3.

[3] (3) Corey, E. J.; Bass, J. D.; LeMahieu, R.; Mitra, R. B. *J. Am. Chem. Soc.* **1964,** *86,* 5570.

[4] (4) Loutfy, R. O.; de Mayo, P. *J. Am. Chem. Soc.* **1977,** *99,* 3559.

[5] (5) Zimmerman, H. E.; Swenton, J. S. *J. Am. Chem. Soc.* **1964,** *86,* 1436.

Scheme 1



in this laboratory it has been found that the ratio of head-to-head to head-to-tail photocycloadducts obtained from reaction of 2-cyclopentenone with acrylonitrile is 40:60.[7] It has also been shown recently that methyl cycloalkene-1-carboxylates react with 2-cyclohexenones to give photocycloadducts in which the dominant regiochemistry depends upon the size of the cycloalkene ring.[8,9] Furthermore, some years ago it was reported that the photocycloaddition of methyl acrylate to ring-fused 2-cyclopentenone derivatives yields mainly the head-to-tail cycloadducts.[10] Finally, it has long been known that the photodimerization of 2-cyclopentenone yields a mixture of head-to-head and head-to-tail cyclobutane dimers in which the latter dominates;[11] the ground state enone partner in this reaction can be regarded as an alkene substituted by an electron-withdrawing group.

These exceptions to the regiochemical rule suggest that incorporation of an oriented exciplex into the reaction mechanism may be unnecessary if its sole purpose is to explain the reaction regiochemistry. Furthermore, Schuster has argued recently against the intermediacy of exciplexes in this reaction on the grounds that the rate constants for deactivation of the triplet excited state of enones by various alkenes measured by flash photolysis do not correlate with the expected ability of the alkenes to form a charge transfer complex with the triplet excited state of the enones.[12]

An alternative explanation for the regiochemistry of the photocycloaddition reaction of polarized alkenes with cyclic enones has been suggested by Bauslaugh.[13] This explanation focuses on the biradical intermediates and how they partition between closure and fragmentation after intersystem crossing to the singlet ground state surface has occurred. The explanation postulates that the regiochemistry is partly determined by the degree to which each of the isomeric biradicals shown in Scheme 1 closes to yield cyclobutane products in competition with fragmentation to yield ground state starting materials. In order to investigate this hypothesis, one must have a knowledge of the structures and relative rates of formation of the biradicals generated in a particular cycloaddition reaction in order to be able to determine their fates and, in particular, how they partition between starting materials and products.

Until recently little was known about the structures and relative yields of the various possible isomeric triplet 1,4-biradical intermediates, and essentially no information was available about what proportion of each biradical proceeds to product in competition with reversion to ground state precursors. Corey[3] found that in the photocycloaddition reaction of 2-cyclohexenone with 2-methylbutene byproducts are formed which appear to arise from intramolecular disproportionation of the biradical intermediates. These byproducts yield information about the structures of the biradical intermediates leading to their formation; specifically, their structures suggest that isomeric biradicals are formed by bonding of the alkene to both the 2-position and the 3-position of the enone. The generality of this conclusion has been the subject of some controversy[14,15] but is supported by the results of our recent study of the photocycloaddition reaction between 2-cyclopentenone and vinylcyclopropane.[16] In this reaction the biradical intermediates possess a cyclopropylcarbinyl radical which can rearrange in competition with closure or fragmentation; the products of the rearrangement reveal information about the structures of the biradical intermediates and indicate that they are indeed produced by bonding of the alkene to both the 2-position and

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(6) Swapna, G. V. T.; Lakshmi, A. B.; Rao, J. M.; Kumwar, A. C. *Tetrahedron* **1989**, *45*, 1777.

(7) Krug, P.; Rudolph, A.; Weedon, A. C. *Tetrahedron Lett.* **1993**, *34*, 7221.

(8) Tada, M.; Nieda, Y. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1416.

(9) Lange, G. L.; Organ, M. G.; Lee, M. *Tetrahedron Lett.* **1990**, *31*, 4689.

(10) Tobe, Y.; Nakayama, A.; Kakiuchi, K.; Odaira, Y.; Kai, Y.; Kasai, N. *J. Org. Chem.* **1987**, *52*, 2639.

(11) Eaton, P. E. *J. Am. Chem. Soc.* **1962**, *84*, 2454.

(12) Schuster, D. I.; Heibel, G. E.; Brown, P. B.; Turro, N. J.; Kumar, C. V. *J. Am. Chem. Soc.* **1988**, *110*, 8261.

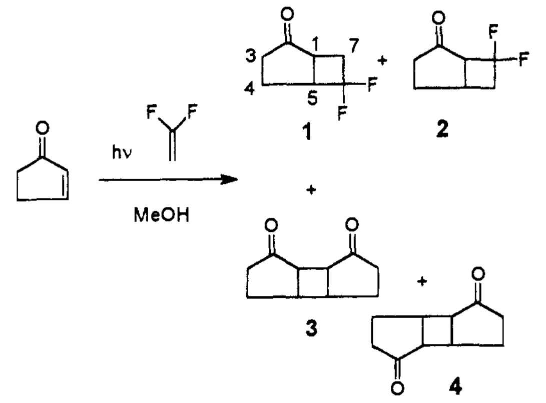
(13) Bauslaugh, P. G. *Synthesis* **1970**, 287.

(14) Dilling, W. L.; Tabor, D. E.; Boer, F. P.; North, P. P. *J. Am. Chem. Soc.* **1970**, *92*, 1399.

(15) Loutfy, R. O.; de Mayo, P. *Can. J. Chem.* **1972**, *50*, 3465.

(16) Rudolph, A.; Weedon, A. C. *Can. J. Chem.* **1990**, *68*, 1590.

Scheme 2



the 3-position of the enone. By using the rearrangement reaction as a clock, the biradical lifetimes were estimated to be ca. 50 ns, which is in agreement with their lifetimes subsequently estimated by photoacoustic spectroscopy.[17]

Knowledge concerning the structures and the relative yields of the biradical intermediates could be gained if the biradicals generated in a particular cycloaddition reaction could be quantitatively trapped to yield isolable products. In a communication to this journal we recently reported the use of hydrogen selenide for trapping the biradicals generated in the photocycloaddition reaction between ethyl vinyl ether and 2-cyclopentenone.[18] We have also been successful in using hydrogen selenide as a biradical trap in photocycloaddition reactions between 2-cyclopentenone derivatives and alkyl substituted alkenes such as various isomeric butenes,[19] as well as between 2-cyclopentenone and allene.[20] Hydrogen selenide was used as the biradical trap for two reasons. First, Kambe et al. had reported that H_2Se is effective as a hydrogen atom donor in the interception of 1,4-biradicals generated in the Norrish type II reaction of ketones.[21] Second, the 50 ns lifetime estimated for the 1,4-biradicals generated in the cycloaddition of vinylcyclopropane to cyclopentenone[16] is almost two orders of magnitude larger than the time required for hydrogen atom abstraction from 1 M H_2Se by alkyl centered radicals. The rate constant for this process has been estimated to be 2×10^9 $L{\cdot}mol^{-1}{\cdot}s^{-1}$.[21] We present here the details of the trapping experiments involving ethyl vinyl ether and 2-cyclopentenone as well as the results of new experiments in which we have attempted to use hydrogen selenide to trap the biradicals generated by the photocycloaddition reaction of methyl acrylate and of 1,1-difluoroethene with the 2-cyclopentenone.

Results

Photocycloaddition Reaction of 1,1-Difluoroethene with 2-Cyclopentenone. When a methanol solution of 2-cyclopentenone (0.040 mol/L) saturated at 25 °C with 1,1-difluoroethene (0.15 mol/L) was irradiated with Pyrex-filtered light from a medium-pressure mercury lamp, the formation of cycloadducts **1** and **2** as well as the two enone dimers **3** and **4** was observed (Scheme 2). The 2-cyclopentenone:**1**:**2**:**3**:**4** product ratio was 17:13:4.7:22:43. Identification of the enone dimers was accomplished by comparing the GC retention times and the mass spectra of the products with those resulting from the irradiation of a solution of 2-cyclopentenone (0.1 mol/L) in benzene. The regiochemical assignment of the dimers was made by comparing the relative yields of the dimers with the head-to-head:head-to-tail dimer ratio reported by Wagner and Bucheck.[22]

Table 2. Relative Product Yields, Determined by GC and Quoted in Percent, for the Photocycloaddition Reaction between 1,1-Difluoroethene and 2-Cyclopentenone Carried Out in Acetonitrile in the Presence of Various Concentrations of H_2Se

$[H_2Se]$, % saturation[a]	2-cyclopentenone	cyclopentanone	1	2	enone dimers
100 (dark rxn)	100.0	0.0	0.0	0.0	0.0
0	66.0	0.0	5.6	2.0	26.4
15	76.0	11.6	1.7	0.6	10.2
50	72.1	24.0	0.5	0.2	3.1
100	71.3	27.3	0.0	0.0	1.4

[a] Concentrations were calculated by diluting a solution containing a saturation concentration of H_2Se in acetonitrile at room temperature.

Following their separation by chromatography the regiochemistry of each of the cycloadducts **1** and **2** was determined using the results obtained from $^{13}C-^{1}H$ heteronuclear NMR correlation (HETCOR) experiments in conjunction with the magnitude of the chemical shift of each ^{13}C resonance. The regiochemical assignments were confirmed using the magnitudes of the $^{13}C-^{19}F$ coupling constants. The ^{13}C NMR data are summarized in Table 1 in the supplementary material along with the detailed arguments used to assign the structures.

Attempted Biradical Trapping: Photocyloaddition Reaction of 1,1-Difluoroethene with 2-Cyclopentenone. Attempts were made using hydrogen selenide to trap the biradicals assumed to be intermediates in the photocycloaddition reaction between 1,1-difluoroethene and 2-cyclopentenone. Acetonitrile solutions containing 2-cyclopentenone (0.040 mol/L) and 1,1-difluoroethene (saturation concentration at −10 °C in acetonitrile) were irradiated in the presence of various concentrations of H_2Se; however, no evidence of the formation of trapped biradicals was detected by GC/MS. The reaction was investigated for three concentrations of H_2Se: the saturation concentration in acetonitrile at room temperature, 0.5 times the saturation concentration, and 0.15 times the saturation concentration. The products obtained from the reactions in which each of these concentrations of H_2Se was used are summarized in Table 2. The only products observed when these solutions were irradiated with UV light were 2-cyclopentenone, cyclopentanone, cycloadducts **1** and **2**, and enone dimers **3** and **4**. As the concentration of H_2Se was increased, the relative yields of **1**, **2**, and the enone dimers were reduced and the relative yield of cyclopentanone was increased; however, no evidence of products resulting from the H_2Se trapping of biradical precursors of these products was observed. The origin of the cyclopentanone is explained in the Discussion section. No products resulting from dark reactions involving cyclopentenone and 1,1-difluoroethene in H_2Se-saturated acetonitrile were observed (first entry in Table 2).

Photocycloaddition of Methyl Acrylate with 2-Cyclopentenone. The irradiation of a solution of 2-cyclopentenone (0.0978 mol/L) and methyl acrylate (0.679 mol/L) in benzene with Pyrex-filtered light from a medium-pressure mercury lamp resulted in the formation of cycloadducts **5**−**8** (Scheme 3). The relative stereochemistry of the head-to-head adducts **5** and **6** was determined by treatment of each of the adducts **5**−**8** with $NaBH_4$. The reduction of adduct **6** with $NaBH_4$ in methanol resulted in the formation of one product which was assigned

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[17] (a) Caldwell, R. A.; Tang, W.; Schuster, D. I.; Heibel, G. E. *Photochem. Photobiol.* **1991**, *53*, 159. (b) Kaprinidis, N. A.; Lem, G.; Courtney, S. H.; Schuster, D. I. *J. Am. Chem. Soc.* **1993**, *115*, 3324.

[18] Hastings, D. J.; Weedon, A. C. *J. Am. Chem. Soc.* **1991**, *113*, 8525.

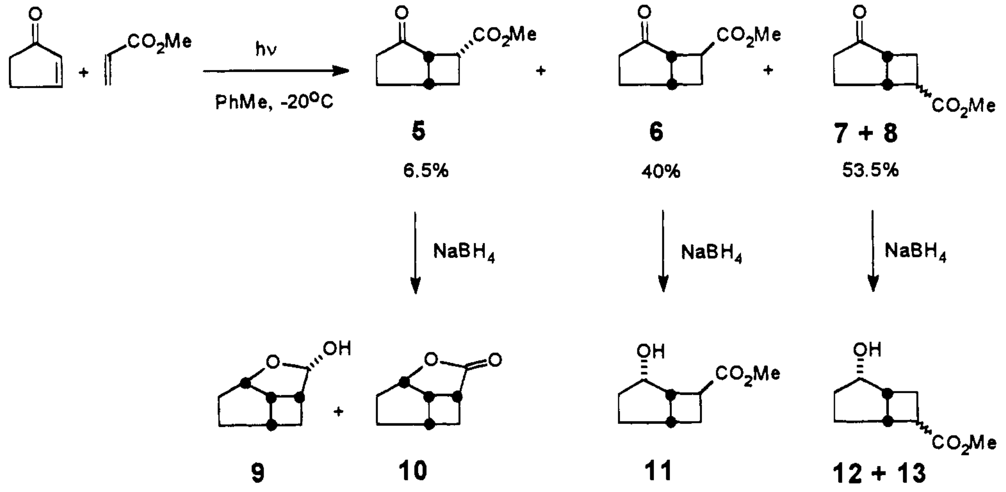
[19] Andrew, D.; Hastings, D. J.; Oldroyd, D. L.; Rudolph, A.; Weedon, A. C. *Pure Appl. Chem.* **1992**, *64*, 1327.

[20] Maradyn, D. J.; Sydnes, L. K.; Weedon, A. C. *Tetrahedron Lett.* **1993**, *34*, 2413.

[21] Kambe, N.; Masawaki, T.; Kondo, K.; Miyoshi, N.; Ogawa, A.; Sonoda, N. *Chem. Lett.* **1987**, 1907.

[22] Wagner, P. J.; Bucheck, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 5090.

Scheme 3



structure 11. No evidence of the epimeric alcohol (i.e. the alcohol possessing the exo stereochemistry) was detected. Similarly, only one epimer was observed in the reductions of each of compounds **7** and **8** to give **12** and **13**. This is the result expected for selective hydride attack on the less hindered face of the ketone carbonyl. The reduction of adduct **5** under the same conditions resulted in the formation of a lactone identified as compound **9** as well as another product, compound **10**, which was identified as a product resulting from over-reduction of the lactone. The only cycloadduct which possesses a stereochemistry from which lactonization could occur after reduction of the ketone group is cycloadduct **5**. It was not possible to ascertain the *endo* or *exo* stereochemistry of the ester functionality in cycloadducts **7** and **8** by inspection of the NMR spectra of these adducts or the corresponding alcohols **12** and **13**.

The **5**:**6**:**7**:**8** ratio of cycloadducts in the irradiation reaction mixture could not be determined by GC since compounds **6** and **7** co-eluted under all conditions examined. The product ratios were determined instead by quantitative ^{13}C NMR spectroscopy of reaction mixtures before separation of the cycloadducts.[23] The **5**:**6**:**7**:**8** product ratio so determined was 6.5:40:35:18.5. In order to show that this ratio represents the primary product ratio and is unperturbed by secondary photolysis, mixtures containing cyclopentenone and methyl acrylate were irradiated in toluene at −20 °C through a $SnCl_2$ in 10% HCl/H_2O light filter instead of a Pyrex filter. This yielded the same product ratio. The $SnCl_2$ filter removes all light of wavelength shorter than 327 nm so that secondary photolysis of the cycloadducts does not occur; this was confirmed by irradiating a solution of compounds **5**−**8** in $CDCl_3$ using $SnCl_2$-filtered light from a medium-pressure mercury lamp. No change was detected in the cycloadduct ratios after 4 h of irradiation.

(a) Identification of 5−8. The minor cycloadduct **5** could not be obtained as a pure compound; consequently it was identified in a mixture containing **5** and **7** in a 25:75 ratio. By using this mixture in conjunction with a sample of **7** it was possible to deduce that compound **5** reduces to compounds **9** and **10** upon treatment with sodium borohydride in methanol. This observation alone defines both the regiochemistry and stereochemistry of the cycloadduct.

The regiochemistry of each of the cycloadducts **6**−**8** was determined by using a combination of ^{13}C-NMR and ^{1}H-NMR spectroscopy to identify the methine at the 5-position of the adducts (see Scheme 2 for the structure numbering system used). The appearance of this methine in the ^{1}H-NMR spectrum revealed whether it was adjacent to one or two methines, and hence allowed assignment of the adduct regiochemistry. A detailed description of the structural assignments is provided in the Supplementary Material.

Biradical Trapping: Photocycloaddition Reaction of Methyl Acrylate with 2-Cyclopentenone. A solution of 2-cyclopentenone (0.200 mol/L) and methyl acrylate (1.00 mol/L) in toluene at −20 °C was saturated with hydrogen selenide gas and then irradiated with Pyrex-filtered light from a medium-pressure mercury lamp. When the reaction mixture was analyzed by GC and coupled GC/MS it was determined that the formation of cycloadducts was completely suppressed. Instead of the cycloadducts, five new products, **14**−**18**, were separated from the reaction mixture and identified (Scheme 4). These compounds were not formed in solutions containing 2-cyclopentenone, methyl acrylate, and hydrogen selenide that were not exposed to UV light. After determining the structures of these five compounds, we were able to conclude that they were the reduction products resulting from an interaction between hydrogen selenide and 1,4-biradicals generated in the cycloaddition reaction.

Scheme 4 shows the biradicals from which each of compounds **14**−**18** were formed. In this scheme there are two pairs of biradicals that are diastereomers. Similarly, two pairs of trapped products were determined to be diastereomers. The individual diastereomers in each pair could not be separated; consequently the diastereomers were isolated and characterized as a mixture. Thus, a mixture of **14** and **15** was characterized as a single fraction as was a mixture of **16** and **17**. Because the diastereomers were not individually characterized, the **14**:**15** and **16**:**17** ratios were not determined.

The combined yield of compounds **14** and **15** and the combined yield of compounds **16** and **17** were measured relative to the yield of trapped compound **18** at 6% conversion of cyclopentenone. From these yields the ratios of the relative rates of biradical formation, (**20** + **21**):(**22** + **23**):**24**, were determined to be 5.0:45:50. The product of trapping of biradical **25**, compound **19**, was not detected in the reaction mixture. Hence it was concluded that biradical **25** is not an intermediate leading to cyclobutane products in the photocycloaddition reaction.

Small-scale experiments were also carried out in which varying amounts of hydrogen selenide were added to toluene solutions of 2-cyclopentenone and methyl acrylate. These

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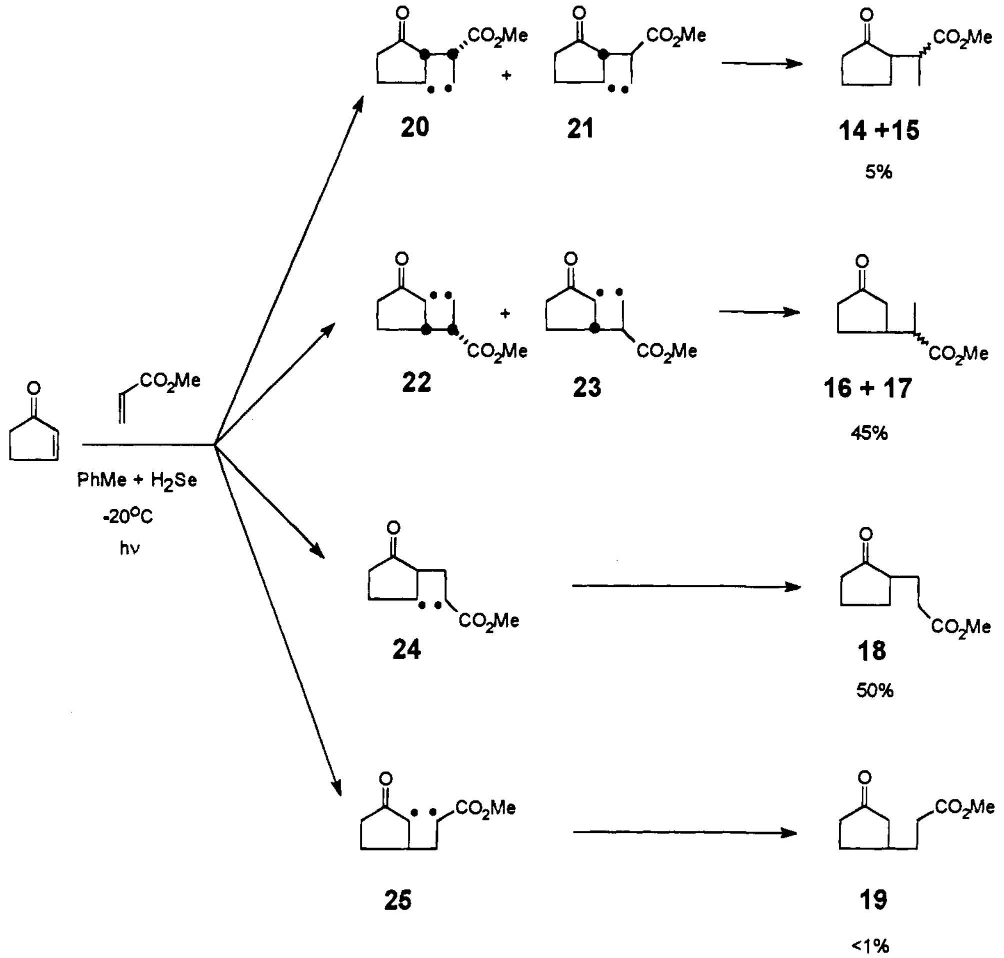
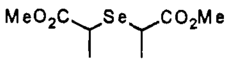
[23] A methodology for performing quantitative ^{13}C NMR on complex mixtures has been developed by Shoolery. See: Shoolery, J. N. *Prog. Nucl. Magn. Reson. Spectrosc.* **1977**, *11*, 79.

Scheme 4

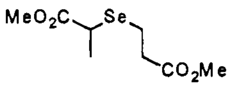


solutions were irradiated with Pyrex-filtered light from a medium pressure mercury lamp and the relative product yields of the trapped products and cycloadducts were determined in each solution by GC. Figure 1 shows a plot of the ratio of the trapped product yield to the trapped product plus cycloadduct combined product yield (which also can be expressed as a ratio of quantum yields) versus the hydrogen selenide concentration. The ratio of quantum yields does not extrapolate to unity because the saturated concentration of H_2Se in toluene at 25 °C is not high enough to effect complete trapping of the biradicals; however, in the preparative experiments described above, the concentration of H_2Se in toluene saturated with the gas at −20 °C is high enough to completely suppress cycloadduct formation. Due to practical problems in handling saturated solutions of H_2Se in toluene at low temperatures we were unable to accurately determine the concentration of H_2Se in those mixtures in which complete biradical trapping was observed. The tendency of the plot shown in Figure 1 to approach a plateau at a trapped product yield to total product yield ratio of 1.0 indicates that trapping of the 1,4-biradicals is almost complete using saturated concentrations of H_2Se in toluene at room temperature.

Four additional products, other than those resulting from the reduction of 1,4-biradicals by hydrogen selenide, were isolated from the reaction mixture containing 2-cyclopentenone, methyl acrylate, and hydrogen selenide that was irradiated with UV light. These products were characterized as cyclopentanone, **26**, **27**, and **28**. Cyclopentanone was not formed in reaction mixtures containing 2-cyclopentenone, methyl acrylate, and hydrogen selenide that were kept dark. Compounds **26**, **27**, and **28** were also formed in the dark reaction mixtures; however, the rate of formation of these compounds in the dark was considerably slower than their rate of formation in the reaction mixtures that were exposed to UV light. Cyclopentanone, as will be argued in the Discussion section, is the product of reaction of the triplet excited state of 2-cyclopentenone with hydrogen selenide. Compounds **26** and **27** are presumed to result from addition of a hydrogen selenyl radical to the 2-position of methyl acrylate followed by radical addition of this intermediate to the 2-position of another methyl acrylate molecule. Compound **28** is presumed to be formed in a similar fashion by the addition of the methyl 2-(hydroselenyl)propanoate intermediate to the 3-position of methyl acrylate, instead of the 2-position. In addition to compounds **26**, **27**, and **28**, the presence of another compound exhibiting a parent molecular ion with an isotopic pattern consistent with the incorporation of one selenium atom was also observed in coupled GC/MS analyses of the trapping experiment reaction mixture. The mass of the parent molecular ion of this compound containing the isotope ^{80}Se was 254, which is the same as the mass of the



26 + 27



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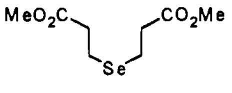

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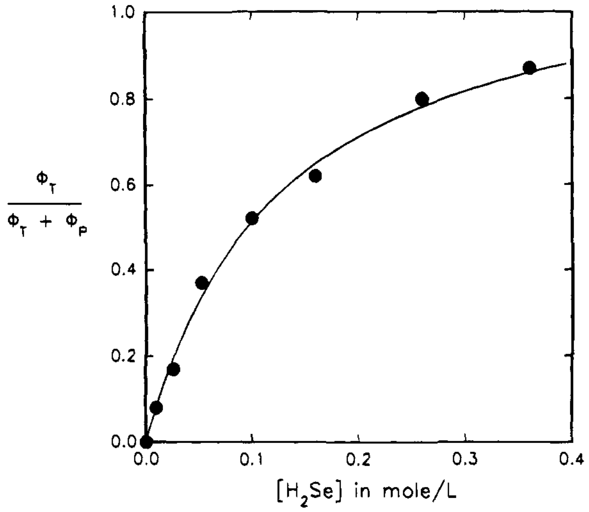


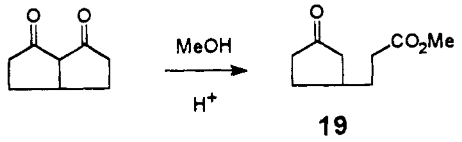
Figure 1. Photochemical reaction of 2-cyclopentenone with methyl acrylate in the presence of hydrogen selenide: dependence of the ratio of the quantum yield of trapped products to the combined quantum yield of trapped products plus cycloadducts on the hydrogen selenide concentration.

parent molecular ions observed for **26**, **27**, and **28**. The compound apparently decomposed on silica gel as it was not isolated by column chromatography; however, we postulate that its structure may be compound **29**. It should be noted that since hydrogen selenide and methyl acrylate were present in a large excess in the trapping reactions, their depletion by the formation of compounds **26**, **27**, **28**, and **29** did not lead to a change in the ratio of the products assigned as trapped biradicals.

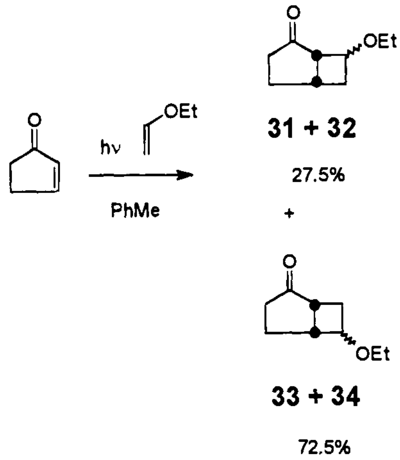
We were concerned that the trapping of the biradicals generated in the cycloaddition reaction between 2-cyclopentenone and methyl acrylate could follow a course other than simple reduction of each biradical by two successive hydrogen atom abstractions. It seemed to us that reduction of one of the radical sites in the biradical should yield a hydrogen selenyl radical along with a carbon centered radical as a radical pair; these could then couple to give an alkyl selenol in competition with reduction of the remaining radical center. Since alkyl selenols are quite reactive, trapped compounds such as these would be oxidized on workup to give diselenides or they would react under the reaction conditions with excess methyl acrylate in radical-initiated addition reactions. All of the selenium-containing products resulting from coupling of partially reduced biradicals with the hydrogen selenyl radical would be reduced by Raney Nickel to give **14**–**19**. When Raney Nickel reduction of the trapping reaction mixtures was carried out using a large excess of active Raney Nickel, no change in the ratio of the identified trapped products was observed; however, compounds **26**, **27**, **28**, and **29** were completely destroyed. Therefore, it was concluded that no selenium-containing products derived from the intermediate biradicals were formed in the reactions involving 2-cyclopentenone, methyl acrylate, and hydrogen selenide.

A mass balance based on 2-cyclopentenone was also determined for the trapping reaction. In a large-scale reaction in which 2.132 g of 2-cyclopentenone was used as starting material, 2.123 g of the 2-cyclopentenone was recovered in the form of trapped biradicals, cyclopentanone, and unreacted 2-cyclopentenone. This translates into a 99% recovery of the initial 2-cyclopentenone added to the reaction mixture. Based on this excellent recovery the conclusion can be drawn that all of the biradicals that were trapped by hydrogen selenide were recovered and isolated as the stable compounds **14**–**18**.

Scheme 5



Scheme 6

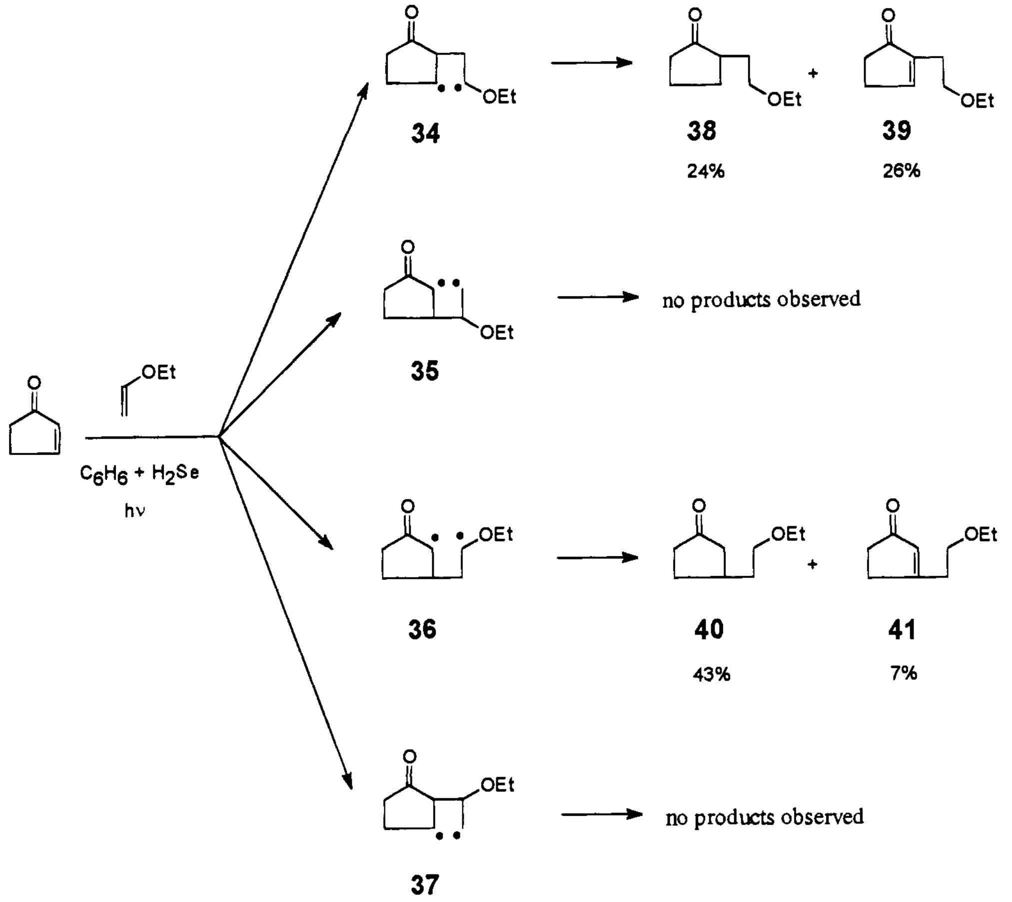


(a) **Identification of 14**–**18.** The presence of two CH_3 signals (in addition to the ester methoxyls) in the APT ^{13}C NMR spectra of each of **14**–**17** indicated that these compounds are products resulting from a reaction between H_2Se and biradicals which contain primary radical centers. The ^{13}C-NMR spectra of **14** and **15** were very similar. The spectra of **16** and **17** were also very smilar but were significantly different from those of **14** and **15**. This observation supports the hypothesis that compounds **14** and **15** are diastereomers as are **16** and **17**, and that **14** and **15** are structural isomers of **16** and **17**. Selective decoupling of the distinct resonances in the ^1H-NMR spectra of **14** and **15** (in C_6D_6) revealed that the 2-position of the methyl propanoate side chain was connected to the 2-position of the cyclopentanone ring, and therefore that the 2-position of the methyl propanoate side chain must be connected to the 3-position of the cyclopentanone ring in **16** and **17**. A more detailed discussion of these structural assignments is given in the Supplementary Material.

The ^{13}C APT NMR spectrum of compound **18** was found to contain only one methine resonance and no methyl resonances other than the ester methoxyl. This indicates that compound **18** is the result of a hydrogen selenide reduction of a biradical which contained two secondary radical centers (i.e. either biradical **24** or **25**). The position of substitution on the cyclopentanone ring was determined by preparing an authentic sample of **19** and comparing this compound with the product obtained from the trapping reaction. Compound **19** was prepared by acid-catalyzed methanolysis of bicyclo[3.3.0]octane-2,8-dione (Scheme 5). Since the physical properties of **19** and the compound isolated from the trapping reaction mixture, namely compound **18**, were different, it was concluded that **18** must have a structure in which the 3-position of methyl propanoate is connected to the 2-position of the cyclopentanone ring.

Photocycloaddition Reaction of Ethyl Vinyl Ether with 2-Cyclopentenone. The photocycloaddition reaction between 2-cyclopentenone and ethyl vinyl ether has been reported previously and the products **31**–**34** (Scheme 6) have been characterized.[24,25] We repeated the reaction in order to determine the product ratio in benzene at room temperature; the **31**:**32**:**33**:**34** ratio obtained was 9.9:17.6:29.9:42.6 which yields a

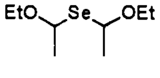
Scheme 7



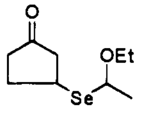
head-to-head:head-to-tail ratio of 27.5:72.5. This is comparable to the previously reported regioisomeric ratios.[24,25]

Biradical Trapping: Photocycloaddition of Ethyl Vinyl Ether with 2-Cyclopentenone. A solution of 2-cyclopentenone (0.06 mol/L) and ethyl vinyl ether (8 mol/L) in benzene which had been saturated with hydrogen selenide at room temperature was irradiated with Pyrex-filtered light from a medium-pressure mercury lamp. Seven new products were observed; three of these were also observed in a control reaction which had not been exposed to light and are designated "dark" products. Their structures were not fully characterized as they are not products of trapping of the biradical intermediates of interest; however, tentative assignments are made below. The four photochemical products possessed different GC retention times from the cycloadducts **31**–**34** produced in a parallel reaction performed in the absence of hydrogen selenide. These four photochemical products were identified as **38**–**41** (Scheme 7) and they were formed in the ratio 24:26:43:7.

(a) **Identification of the "Dark" Products.** The mass spectra of two of the three "dark" products indicated that they were adducts comprised of a single hydrogen selenide molecule attached to two molecules of ethyl vinyl ether. The fragmentation patterns observed were consistent with their being diastereomers of **42**; this is a reasonable structure since hydrogen selenide is sufficiently acidic (pK = 3.48) for polar addition to an electron rich alkene to occur.[26] The mass spectrum of the third "dark" product indicated it to be an adduct of a single hydrogen selenide molecule with one molecule of ethyl vinyl ether and one molecule of 2-cyclopentenone. The fragmentation pattern indicated that the enone and the alkene were connected through a selenium atom as in **43** since intense selenium-containing daughter ions were observed corresponding to loss of the cyclopentanone ring from the molecular ion and also loss of the alkene from the molecular ion. This "dark" product is not therefore a product of partial reduction of one of the biradicals **34**–**37** followed by combination of the carbon centered radical and the hydrogen selenyl radical produced.



42



43

(b) **Identification of 38–41.** The mass spectra of all four trapped products exhibited molecular ions with masses consistent with the assigned structures. In addition, the ^{1}H-NMR spectra of all four compounds possessed a two-proton triplet at ca. 3.5 ppm, assigned to the 2′-position, and the absence of a three-proton doublet at high field; consequently, all four products are derived from biradicals **34** and **36**, and do not come from trapping of biradicals **35** and **37**. The chemical shift of the vinylic hydrogens in the ^{1}H-NMR spectra of **39** and **41** allowed unambiguous determination of the position of substitution of the ethoxyethyl side chain on the 2-cyclopentenone ring; in **39** the vinylic hydrogen appeared at 7.45 ppm, which is typical for the 3-position of 2-substituted 2-cyclopentenones, while in **41** it appeared at 5.95 ppm, which is typical for the 2-position of 3-substituted 2-cyclopentenones.[27] The structures of **38** and **40** followed from the fact that they were produced by catalytic

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(24) Griesbeck, A. G.; Stadtmuller, S.; Busse, H.; Bringmann, G.; Buddrus, J. *Chem. Ber.* **1992**, *125*, 933.

(25) Termount, D.; De Keukeleire, D.; Vandewalle, M. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2349.

(26) Mehra, M. C.; Gubeli, A. O. *Can. J. Chem.* **1870**, *48*, 3491.

hydrogenation of **39** and **41**, respectively. The position of substitution of the ethoxyethyl side chain on the cyclopentanone ring was confirmed by the observation of an efficient McLafferty Type II rearrangement in the mass spectral fragmentation pattern of **38** and the absence of such a fragmentation in the mass spectrum of **40**.

Discussion

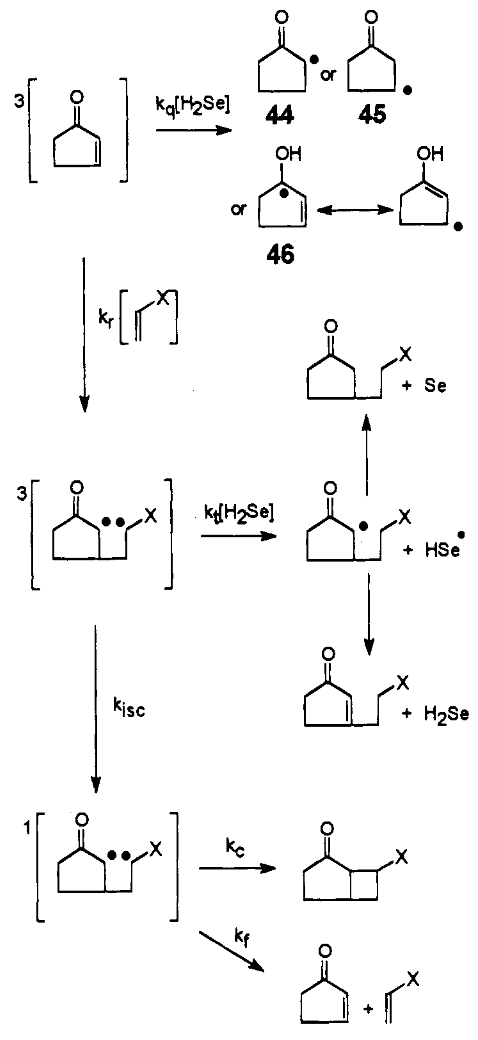
The initial aim of this work was to investigate the mechanism of the photocycloaddition reaction between cyclic enones and alkenes and in particular to probe the origin of the regiochemistry of the cycloadduct products that are formed in the reactions with polar alkenes. As described in the introduction, the generalization accepted in the literature states that alkenes bearing electron-donating groups react with cyclic enones to give cycloadducts that possess predominantly head-to-tail regiochemistry while alkenes bearing electron withdrawing groups react to give cycloadducts that possess predominantly head-to-head regiochemistry. The systems studied in the present investigation do not support this generalization. Both 1,1-difluoroethene and methyl acrylate underwent a photocycloaddition reaction with 2-cyclopentenone to produce substantial quantities of cycloadducts that had head-to-tail regiochemistry. In the case of the 1,1-difluoroethene, the head-to-head:head-to-tail ratio was 26:74. In the case of methyl acrylate the reaction proceeded non-regioselectively to give products with a head-to-head:head-to-tail ratio of 48:52. These findings add to the increasing number of examples in which electron-deficient alkenes produce cycloadducts with head-to-tail regiochemistry.

The head-to-head regioselectivity observed by Corey for the addition of acrylonitrile to cyclohexenone led, in part, to the development of the Corey–de Mayo mechanistic description of the reaction shown in Scheme 1. It would appear, however, that this regioselectivity is not general; the growing number of examples of electron-deficient alkenes that do not yield head-to-head regioisomers as the major product challenges the postulate that the intermediacy of an oriented exciplex governs the reaction regiochemistry.

This conclusion is supported by the results of the experiments in which biradical trapping with hydrogen selenide was performed. A key premise of the Corey–de Mayo mechanism is that the relative orientation of the triplet enone and the polarized alkene in the exciplex dictates the regiochemical outcome of the reaction. If this were the case then the structures of the major biradical intermediates that form after the exciplexes on the reaction pathway should reflect the regiochemistry of the major regioisomer to which they close. Consequently, the mechanism predicts that the biradicals which lead to production of the minor regioisomer have a slower rate of formation than the biradicals that lead to the production of the major regioisomer. In the present investigation, this hypothesis was tested by determining the relative rates of formation and the structures of all the biradicals that are formed during the photocycloaddition reaction between 2-cyclopentenone and ethyl vinyl ether or methyl acrylate. This was accomplished by intercepting the biradicals generated in these two photocycloadditions with hydrogen selenide as a hydrogen atom donor.

When 2-cyclopentenone was irradiated in the presence of ethyl vinyl ether and hydrogen selenide in benzene solution, the formation of all cycloadducts was completely suppressed while compounds **38**, **39**, **40**, and **41** (Scheme 7) were formed in a ratio of 24:26:43:7. The complete suppression of all cycloadduct formation indicates that each triplet biradical responsible for cycloadduct formation in the absence of $\mathrm{H_2Se}$ was quantitatively trapped as a stable product before intersystem crossing followed by closure could occur. In terms of the rate constants defined in Scheme 8 this indicates that $k_t[\mathrm{H_2Se}]$ is much larger than k_{isc}. Since closure and fragmentation are competing unimolecular processes for a common biradical intermediate, we can conclude that the absence of products resulting from one of the processes, namely the closure process, indicates that both processes are effectively quenched by the bimolecular reaction of $\mathrm{H_2Se}$ with the biradical intermediate.

Scheme 8



The formation of compounds **38** and **40** results from complete reduction of biradicals **34** and **36** by hydrogen selenide. Compounds **39** and **41** are apparently the result of abstraction of a hydrogen atom from hydrogen selenide by one radical site of the biradical followed by an in-cage disproportionation reaction between the second radical site and the resulting hydrogen selenyl radical (see Scheme 8). The structures of the trapped products suggest that biradicals **35** and **37** are not formed in detectable amounts during the cycloaddition reaction between 2-cyclopentenone and ethyl vinyl ether. If they are formed then they must be too short-lived to be trapped by hydrogen selenide; more importantly, if they are formed, then they must revert exclusively to the ground state enone and alkene and so play no part in the photocycloaddition reaction except to reduce the reaction efficiency. Slower formation of **35** and **37** relative to

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(27) (a) Emsley, J. W.; Phillips, L.; Wray, V. *Prog. Nucl. Magn. Reson. Spectrosc.* **1977**, *10*, 85. (b) Bovey, F. A. *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Academic Press Inc.: San Diego, 1988; pp 457–460. (c) Breitmaier, E.; Voelter, W. *^{13}C NMR Spectroscopy*, Verlag Chemie: Weinheim Bergstr., 1974; pp 133–137. (d) Grutzner, J. B.; Jautelat, M.; Dence, J. B.; Smith, R. A.; Roberts, J. D. *J. Am. Chem. Soc.* **1970**, *92*, 7107. (e) Maciel, G. E.; Dorn, H. C. *J. Am. Chem. Soc.* **1971**, *93*, 1268.

34 and **36** correlates with their higher energy (they each contain a primary radical center) and suggests that **34** and **36** may be formed faster because they are the more stable intermediates; alternatively, formation of **34** and **36** could be favored because approach of the triplet enone to the less substituted terminus of the alkene is less impeded sterically.

The relative yields of trapped products **38**, **39**, **40**, and **41** indicate that biradicals **34** and **36** are formed in a ratio of 1.0: 1.0 and so are produced at the same rate. The products formed by the closure of biradicals **34** and **36** in the absence of H_2Se, namely cycloadducts **30**, **31**, **32**, and **33**, are obtained with a head-to-head:head-to-tail ratio of 1.0:2.6. Comparison of these ratios indicates that the mechanistic processes and the intermediates that exist on the photocycloaddition reaction pathway prior to biradical formation are not the primary factors governing the regiochemical outcome of the reaction between 2-cyclopentenone and ethyl vinyl ether. If intermediates preceding biradical formation, such as exciplexes, were responsible for controlling the regioselectivity of the reaction, then the relative yields of **34** and **36** (as reflected in the yields of **38**–**41**) would be expected to resemble the head-to-tail:head-to-head ratio. Instead the regioselectivity of the reaction between ethyl vinyl ether and triplet 2-cyclopentenone is apparently a reflection of the extent to which each of the biradicals **34** and **36** partition between closure to give cycloadducts and reversion to give ground state enone and alkene. In this particular reaction the two biradicals are formed at the same rate; however, biradical **34** closes to cycloadducts 2.6 times more efficiently than biradical **36**. Consequently, based on these results, the inclusion of an exciplex intermediate in the reaction pathway is unnecessary.

The structures and relative rates of formation of the biradicals formed in the photocycloaddition reaction between 2-cyclopentenone and methyl acrylate, as determined by trapping the biradicals with hydrogen selenide, support this conclusion. When 2-cyclopentenone was irradiated in the presence of methyl acrylate and hydrogen selenide, cycloadduct formation was quenched while products **14**, **15**, **16**, **17**, and **18** (Scheme 4) were formed in significant amounts. The pair of compounds **14** and **15** were determined to be a set of diastereomers as were compounds **16** and **17**. The (**14** + **15**):(**16** + **17**):**18** ratio was determined to be 1.0:9.1:10.3. The absence of **19** in the cycloaddition reactions that were carried out in the presence of H_2Se was confirmed by independently synthesizing the compound and comparing its NMR spectra with those of all of the chromatographic fractions collected from the trapping reaction mixture. In addition, based on the detection limit of the GC/MS method that was used, it was concluded that the relative yield of compound **19** in the reaction mixture was less than 1% of the combined yield of all other trapped products.

The relative yields of the trapped products **14**–**18** indicate that 95% of all the biradicals formed could lead to head-to-tail cycloadduct formation while only 5% of the biradicals could lead to head-to-head cycloadducts. Comparison of these biradical relative yields with the head-to-head:head-to-tail ratio of 46.5:53.5 for the cycloadducts formed when H_2Se is absent from the reaction indicates that the cycloadduct regiochemistry is governed by the fact that most of the biradical intermediates responsible for head-to-tail product formation fail to close to products; instead, the biradicals fragment to ground state starting materials. In addition, the dominant biradicals are not those that would be predicted on the basis of an oriented exciplex with the charge distribution indicated in Scheme 1.

Comparison of the structures of the biradicals trapped in the ethyl vinyl ether reaction with those from the methyl acrylate reaction reveals two points of difference. First, the trapping of the biradicals in the ethyl vinyl ether reaction yields products arising from partial reduction and disproportionation as well as complete reduction. Second, in the ethyl vinyl ether reaction no primary radical containing biradicals are detected, whereas in the methyl acrylate reaction 50% of the biradical intermediates result from attack of the enone on the more substituted end of the alkene.

One of the products of the trapping reactions was cyclopentanone. This product was produced in large quantities in all of the cycloaddition reactions that were carried out in the presence of H_2Se. The cyclopentanone appears to be the result of photoreduction of the excited enone triplet by H_2Se (see Scheme 8) occurring in competition with interception of the enone triplet by alkene. Thus as the concentration of H_2Se was increased the yield of cyclopentanone also increased while the relative yield of both cycloadducts and products of biradical trapping decreased. In the case of 1,1-difluoroethene, where no biradicals were trapped, the yield of cycloadducts decreased and the yield of cyclopentanone increased at higher H_2Se concentrations. These observations are consistent with photoreduction of the enone by H_2Se; the failure to observe trapped biradicals in the case of 1,1-difluoroethene may indicate that in this system the biradicals are shorter lived than is the case when ethyl vinyl ether or methyl acrylate is the alkene partner.

The photoreduction of cyclopentenone could, in principle, lead to one or more of the radicals **44**–**46**. Addition of these radicals to an alkene could generate a new radical which, after reduction by H_2Se, would yield compounds identical with the products assigned as trapped biradicals, i.e. compounds **14**–**18** and **38**–**41**. The importance of this route as an alternative pathway for the formation of **14**–**18** and **38**–**41** can be discounted since the rate constant for addition of an alkyl radical to a double bond is known and is three orders of magnitude smaller than the rate constant for abstraction of hydrogen from H_2Se by an alkyl radical.[28] Consequently, the radicals **44**–**46** arising from cyclopentenone photoreduction would be reduced to cyclopentanone far faster than they could react with alkene.

Conclusion

The structures and relative rates of formation of the triplet 1,4-biradicals generated in the photocycloaddition reaction between 2-cyclopentenone and ethyl vinyl ether and between 2-cyclopentenone and methyl acrylate have been determined by trapping the biradicals with H_2Se. The results indicate that comparable proportions of the biradicals are formed by bonding of the 2-position and the 3-position of the enone to one of the alkene termini; in the case of ethyl vinyl ether the enone selectively bonds to the less substituted end of the alkene while no such selectivity is observed with methyl acrylate. In addition, the regiochemistry of the intermediate biradicals generated in each cycloaddition does not determine the regiochemistry of the cycloaddition products. The major cycloadducts do not come from the biradicals which are formed at the fastest rates; rather, the major products come from the biradicals which show a greater propensity to close to products instead of fragmenting to the ground state enone and alkene precursors. These results suggest that it is unnecessary to introduce an exciplex as an intermediate along the reaction pathway in enone-alkene photocycloaddition reactions in order to explain the product regiochemistry; the data obtained do not, however, allow one

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(28) (a) Denisov, E. T. *Liquid Phase Reaction Rate Constants*, Plenum Press: New York, 1974; pp 351–362. (b) Kochi, J. K. *Free Radicals*, Wiley: New York, 1973, pp 91–91.

(29) Waitkins, G. R.; Shutt, R. In *Inorganic Syntheses*; Fernelius, W. C., Ed.; New York, 1946; Vol. II, p. 184.

to predict or explain the relative rates of formation and the different fates of the isomeric biradical intermediates. A more detailed investigation of the structural effects in the alkene and the enone that determine which biradicals are formed fastest, and that govern how biradicals partition between closure to cyclobutane products and reversion to ground state enone and alkene will be the subject of future papers.

Experimental Section

Irradiation of 2-Cyclopentenone and 1,1-Difluoroethene. A solution of cyclopentenone (1.638 g; 0.0399 mol/L) in methanol (0.50 L) was saturated at 25 °C with 1,1-difluoroethene by bubbling the gas through a fine frit for 20 min. (In a separate experiment, the concentration of 1,1-difluoroethene in CD_3OD at saturation was determined by ^{1}H NMR to be 0.15 mol/L.) The solution was irradiated at room temperature with Pyrex-filtered light from a 450-W Hanovia medium-pressure mercury lamp for 7 h. The solvent was removed under reduced pressure at 50 °C to yield 1.785 g of crude product. The reaction mixture was analyzed by GC and coupled GC/MS and it was determined that the mixture contained 16% of unreacted 2-cyclopentenone, 65% of two 2-cyclopentenone dimers in a ratio of 1.9:1.0, and 18% of two enone plus alkene cycloadducts in a ratio of 2.8:1.0. The reaction mixture was separated by column chromatography in which a 3 cm x 80 cm column containing 130 g of 60–200 mesh silica gel packed in 1:1 diethyl ether–hexanes was used. The column was eluted with 0.5 L of 1:1 diethyl ether–hexanes followed by 1 L of 2:1 diethyl ether–hexanes. Three fractions were collected and analyzed by GC: I, 0.335 g of cycloadducts **1** and **2** in a 2.8:1.0 ratio; II, 0.280 g of cyclopentenone; III, 1.17 g of two enone dimers in a 1.9:1.0 ratio. Fraction I was separated further by preparative GC into two fractions: IV, 0.240 g of pure 1; and V, 0.086 g of 98% pure **2** with the 2% contaminant consisting of **1**. All fractions were recovered as colorless oils.

(a) **Characterization of 1.** ^{1}H NMR (300 MHz, in $CDCl_3$): δ 2.04 (dq, $J = 14.1, 9.6$ Hz, 1H), 2.2 to 2.7 (complex, 5H), 2.94 (dtt, $J = 3.3, 10.6, 14.4$ Hz, 1H), 3.36 (m, 1H). ^{13}C NMR (300 MHz, proton decoupled ^{19}F coupled, in $CDCl_3$): δ 218.2 (d, $J = 4.0$ Hz, C=O), 119.9 (dd, $J = 285, 282$ Hz, CF_2), 47.9 (dd, $J = 23.5, 25.1$ Hz, CH), 38.8 (t, $J = 25.3$ Hz, CH_2), 36.3 (s, CH_2), 34.5 (dd, $J = 7.5, 10.6$ Hz, CH), 19.6 (dd, $J = 2.9, 5.8$ Hz, CH_2). ^{19}F NMR (300 MHz, reference $CFCl_3$, in $CDCl_3$): δ −98.9 (dtt, $J_{FF} = 196$ Hz, $J_{HF} = 5.7, 11.0$ Hz), −88.4 (dddt, $J_{FF} = 196$ Hz, $J_{HF} = 3.5, 11.0, 14.7$ Hz). ^{13}C−^{1}H heteronuclear correlation results for clearly defined resonances (^{13}C δ; ^{1}H δ): (19.6; 2.04), (38.8; 2.94), (47.9; 3.36). Mass spectrum (EI, 70 eV): *m/e* (%) 146 (64), 91 (12), 90 (15), 82 (100), 55 (80), 54 (40), calculated M^+ for $C_7H_8OF_2$ 146.05431 (found 146.0539).

(b) **Characterization of 2.** ^{1}H NMR (300 MHz, in $CDCl_3$): δ 2.00 (dddd, $J = 3.5, 1.3, 9.0, 13.5$ Hz, 1H), 2.1 to 2.5 (complex, 3H), 2.61 (ddd, $J = 18.5, 11.3, 9.5$ Hz, 1H), 2.8 to 3.1 (complex 2H), 3.23 (m, 1H). ^{13}C NMR (300 MHz, proton decoupled ^{19}F coupled, in $CDCl_3$): δ 212.2 (dd, $J = 3.0, 1.5$, C=O), 115.8 (dd, $J = 282, 289$ Hz, CF_2), 57.8 (t, $J = 23.3$ Hz, CH), 40.3 (t, $J = 22.4$ Hz, CH_2), 36.7 (d, $J = 4.0$ Hz, CH_2), 27.0 (d, $J = 2.8$ Hz, CH_2), 25.6 (dd, $J = 6.1, 11$ Hz, CH). ^{19}F NMR (300 MHz, reference $CFCl_3$, in $CDCl_3$): δ −88.6 (dddt, $J_{FF} = 198$ Hz, $J_{HF} = 11, 2.6, 6.4$ Hz), −91.6 (d, $J_{FF} = 198$ Hz, J_{HF} coupling results in an undetermined muliplet). ^{13}C−^{1}H heteronuclear correlation results for clearly defined resonances (^{13}C δ; ^{1}H δ): (57.8; 3.23), (36.7; 2.61), (27.0; 2.00). Mass spectrum (EI, 70 eV): *m/e* (%) 146 (45), 91 (62), 90 (24), 82 (100), 55 (45), 54 (72), calculated M^+ for $C_7H_8OF_2$ 146.05431 (found 146.0548).

Preparation of Al_2Se_3. Aluminum selenide was prepared according to the method of Waitkins and Shutt[29] with the following modifications. Finely ground aluminum powder (6 g; 0.222 mol) and finely ground gray selenium powder (10 g; 0.127 mol) were thoroughly mixed. Approximately 2 g of this mixture was placed in a dry crucible and ignited with a burning magnesium strip. Once ignited, additional 2 g quantities of the aluminum/selenium mixture were added to the crucible at 5 s intervals. **Caution:** This is a very exothermic reaction. After the crucible was allowed to cool, the solid Al_2Se_3 pellet was removed and ground with a mortar and pestle into a course powder. The Al_2Se_3 was stored in a desiccator until needed.

Irradiation of 2-(cyclopentenone and 1,1-Difluoroethene in the Presence of H_2Se. **Caution:** Al_2Se_3 reacts violently with H_2O to produce H_2Se. Hydrogen selenide is an extremely toxic gas. Aluminum selenide (5 g) was placed in a 100 mL two-neck round bottom flask that was fitted with a gas outlet and dropping funnel. The gas outlet was attached to a constricted pipet which was inserted into another 100 mL two-neck round-bottom flask containing acetonitrile (50 mL). After the entire system had been flushed with nitrogen, 20 mL of water was added to the aluminum selenide dropwise over 20 min. The addition of water to the aluminum selenide was regulated so that the rate of evolution of H_2Se gas in the acetonitrile solution (solution A) was constant. Four irradiation tubes were filled with the following solutions: I, 5 mg of decane, 33 mg of 2-cyclopentenone, 10 mL of solution A; II, same as I; III, 5 mg of decane, 33 mg of 2-cyclopentenone, 5 mL of solution A, 5 mL of acetonitrile; IV, 5 mg of decane, 33 mg of 2-cyclopentenone, 1.5 mL of solution A, 8.5 mL of acetonitrile. (The decane was used as a GC standard.) All four solutions were then chilled in an ice/salt bath at −10 °C while 1,1-difluoroethene was bubbled into each solution through a frit. Solutions I, III, and IV were allowed to warm to room temperature and then irradiated with Pyrex filtered light from a 450-W Hanovia medium-pressure mercury lamp for 30 min. Solution II was allowed to warm to room temperature and kept dark for 30 min. All four solutions were analyzed by GC to determine the relative ratio of their components (excluding the 1,1-difluoroethene): I, 11.6% cyclopentanone, 76.0% 2-cyclopentenone, 1.7% **1**, 0.6% **2**, 10.2% of two enone dimers (1.2:1); II, only 2-cyclopentenone detected; III, 24.0% cyclopentanone, 72.1% 2-cyclopentenone, 0.5% **1**, 0.2% **2**, 3.1% of two enone dimers (1:1); IV, 27.3% cyclopentanone, 71.3% 2-cyclopentenone, 0.0% **1**, 0.0% **2**, 1.4% of two enone dimers (1:1). No evidence of trapped biradicals was detected by GC/MS.

Irradiation of 2-Cyclopentenone and Methyl Acrylate. A Pyrex irradiation tube was filled with a solution of 2-cyclopentenone (1.445 g; 0.0978 mol/L) and freshly distilled methyl acrylate (10.8 g; 0.679 mol/L) in 180 mL of benzene. The solution was irradiated with Pyrex-filtered light from a 450-W Hanovia medium-pressure mercury lamp for 12 h. The solution temperature during the irradiation was maintained at 10 °C by means of a recirculating water bath. Analysis of the reaction mixture by GC/MS revealed the 2-cyclopentenone: cycloadducts:enone dimers ratio was 24:70:6. The benzene solvent was removed under reduced pressure at 50 °C to yield a thick white syrup. Addition of 50 mL of diethyl ether to the product resulted in the precipitation of a white polymeric material. The polymeric material was removed by filtration and washed by five additional 50 mL portions of diethyl ether. The diethyl ether extracts were combined and concentrated under reduced pressure at 50 °C to yield 1.53 g of a faint yellow oil. The product was dissolved in 100 mL of benzene and flash chromatographed through 20 g of silica gel. The products were eluted with five additional 150 mL portions of benzene. The benzene portions where combined and concentrated under reduced pressure to yield 1.43 g of oil. This was found, by GC, to contain only 2-cyclopentenone and enone plus methyl acrylate cycloadducts in the same ratio as in the crude reaction mixture. The mixture resulting after flash chromatography was separated further by column chromatography in which a 3 cm × 80 cm column contain 155 g of 60–200 mesh silica gel packed in 1:4 diethyl ether–hexanes was used. The column was eluted with a 1:5 diethyl ether–hexanes solution and the following fractions were obtained: I, 0.215 g of **6**; II, 0.259 g of **5**:**6**:**7** (12:54:34); III, 0.496 g of **6**:**7** (36:64); IV, 0.110 g of 2-cyclopentenone; V, 0.350 g of **7**:**8** (38:62). All fractions were isolated as colorless oils.

Purification of Column Fractions. Fraction II (0.118 g) was further purified by column chromatograph by employing a 2.5 cm × 80 cm column containing 85 g of silica gel packed in 1:10 diethyl ether–hexanes. Two fractions were collected after eluting the column with 1:10 diethyl ether–hexanes: IIa, 0.065 g of **6**; IIb, 0.054 g of **5**:**7** (25:75). Preparative GC was not useful in separating IIb further; therefore, **5** was not obtained pure.

Fraction V (0.162 g) was further purified by column chromatograph by employing a 2.5 cm × 80 cm column containing 100 g of silica gel packed in 1:8 diethyl ether–hexanes. Two fractions were collected after the column was eluted with 1:8 diethyl ether–hexanes: Va, 0.049 g of **7**:**8** (85:15); Vb, 0.112 g of **7**:**8** (20:80). These two subfractions were enriched in their major components by peak trimming in preparative gas chromatograghy (resolved GC peaks were not obtained under a variety of conditions). Thus, compounds **7** and **8** were obtained in 92% and 90% purity, respectively.

(b) Characterization of 5 in Fraction IIb. ^{1}H NMR (300 MHz, in $CDCl_3$): δ 3.57 (s, CH_3O), remaining resonances unressolved due to the presence of **7**. ^{13}C NMR (300 MHz, in $CDCl_3$): δ 219.7 (C=O), 172.4 (C=O), 51.7 (OCH_3), 47.1 (CH), 37.3 (CH_2), 36.5 (CH), 32.2 (CH), 27.7 (CH_2), 26.6 (CH_2). Mass spectrum (EI, 70 eV): *m/e* (%) 168 (4), 137 (8), 136 (4), 113 (21), 109 (18), 108 (8), 87 (16), 83 (8), 82 (100), 81 (46), 67 (18), calculated M^+ for $C_9H_{12}O_3$ 168.0786 (found 168.0784).

(c) Characterization of 6. ^{1}H NMR (300 MHz, in C_6D_6): δ 1.21 (dddd, J = 2.3, −4.1, 9.4, 13.5 Hz, 1H), 1.44 (ddt, J = 7.7, 13.6, 9.8 Hz, 1H), 1.61 (ddd, J = 5.5, 8.9, 12.4 Hz, 1H), 1.89 (dddd, J = 1.50, 4.1, 9.7, 18.4 Hz, 1H), 2.15 (dt, J = 18.6, 9.3 Hz, 1H), 2.32 (dddd, J = 2.1, 5.5, 9.2, 12.5 Hz, 1H), 2.57 (br quintet, J = 7−9 Hz), 2.68 to 2.82 (complex, 2H), 3.34 (s, 3H). ^{13}C NMR (300 MHz, in C_6D_6): δ 217.7 (C=O), 174.2 (C=O), 51.6 (OCH_3), 47.3 (CH), 38.3 (CH), 36.6 (CH_2), 33.1 (CH), 28.6 (CH_2), 27.2 (CH_2). ^{13}C NMR (300 MHz, in $CDCl_3$): δ 219.3 (C=O), 174.2 (C=O), 51.9 (OCH_3), 47.2 (CH), 38.1 (CH), 36.7 (CH_2), 33.0 (CH), 28.6 (CH_2), 27.2 (CH_2). ^{13}C−^{1}H heteronuclear correlation results for clearly defined resonances, in C_6D_6 (^{13}C δ; ^{1}H δ): (51.6; 3.34), (47.3; 2.68−2.82), (38.3; 2.68−2.82), (33.1; 2.57), (28.6; 2.32 and 1.61), (36.6; 2.15 and 1.89), (27.2; 1.44 and 1.21). IR (neat film, cm^{-1}): 1734 (vs, C=O), 1208, 1167, 1239, 2953, 1437, 1275, 1354. Mass spectrum (EI, 70 eV): *m/e* (%) 168 (35), 137 (5), 113 (30), 109 (33), 108 (47), 82 (18), 81 (90), 80 (41), 79 (54), 67 (48), 55 (100), calculated M^+ for $C_9H_{12}O_3$ 168.0786 (found 168.0783).

(d) Characterization of 7. ^{1}H NMR (300 MHz, in C_6D_6): δ 1.25 to 1.37 (complex, 2H), 1.70 to 1.83 (m, 1H), 1.88 (dddd, J = 18.8, 9.0, 2.5, 1.4 Hz, 1H), 2.03 (dt, J = 18.8, 10.2 Hz, 1H), 2.16−2.26 (m, 1H), 2.36−2.54 (complex, 2H), 2.78 (br quartet, J = 7−9 Hz, 1H), 3.30 (s, 3H). ^{13}C NMR (300 MHz, in $CDCl_3$): δ 221.5 (C=O), 174.8 (C=O), 51.9 (OCH_3), 41.7 (CH), 40.7 (CH), 40.2 (CH), 36.3 (CH_2), 27.1 (CH_2), 24.9 (CH_2). Mass spectrum (EI, 70 eV): *m/e* (%) 168 (65), 140 (20), 137 (32), 136 (18), 109 (22), 108 (38), 84 (15), 82 (100), 81 (80), 67 (40), 55 (96), calculated M^+ for $C_9H_{12}O_3$ 168.0786 (found 168.0786).

(e) Characterization of 8. ^{1}H NMR (300 MHz, in $CDCl_3$): δ 1.88 (dddd, J = 14.2, 9.0, 5.1, 3.0 Hz, 1H), 2.0 to 2.7 (complex, 5H), 2.76 (dt, J = 9.3, 6.5 Hz, 1H), 3.21 (br quartet, J = 7−9 Hz, 1H), 3.46 (dt, J = 8.3, 9.5 Hz, 1H), 3.69 (s, 3H). ^{13}C NMR (300 MHz, in $CDCl_3$): δ 220.2 (C=O), 173.5 (C=O), 51.5 (OCH_3), 41.4 (CH), 38.4 (CH), 37.4 (CH_2), 37.0 (CH), 24.6 (CH_2), 23.6 (CH_2). ^{13}C−^{1}H heteronuclear correlation results for clearly defined resonances, in $CDCl_3$ (^{13}C δ; ^{1}H δ): (51.5; 3.69), (38.4; 3.46), (37.0; 3.21), (41.4; 2.76), (23.6; 1.88). Mass spectrum (EI, 70 eV): *m/e* (%) 168 (1), 137 (8), 136 (18), 109 (11), 108 (8), 87 (35), 82 (100), 81 (29), 79 (14), 67 (16), calculated M^+ for $C_9H_{12}O_3$ 168.0786 (found 168.0781).

Analytical Determination of Product Ratios in the 2-Cyclopentenone plus Methyl Acrylate Photocycloaddition. A solution of 2-cyclopentenone (1.493 g; 0.101 mol/L) and methyl acrylate (25.0 g; 1.61 mol/L) in 180 mL of toluene was placed in a Pyrex irradition tube. The tube was chilled to −20 °C in an $CaCl_2$/ice bath and irradiated for 8 h with filtered light (λ > 327 nm) from a 450-W Hanovia medium-pressure mercury lamp which was surrounded by 1.5 cm of a 0.4 mol/L $SnCl_2$ in 10% HCl/H_2O filter. The temperature of the irradiation vessel was maintained at −20 °C during the irradiation. The toluene was removed under reduced pressure at 65 °C to yield a thick syrup. The addition of 100 mL of diethyl ether to the product resulted in the precipitation of a white polymer. The polymer was extracted with additional portions of diethyl ether until no cycloaddition products were detected in the washings. The washings were combined and concentrated under reduced pressure to yield 1.726 g of a colorless oil. A solution of 0.30 g of this oil dissolved in 1.0 g of $CDCl_3$ was analyzed by quantitative ^{13}C NMR spectroscopy (i.e. small pulse width and a delay of approximately 2 times the longest T_1 between pulses). The **5**:**6**:**7**:**8** ratio was determined to be 6.5:40:35:19 (with a relative error of 5%) by integrating the corresponding OCH_3 ^{13}C signal in each molecule. The highest field CH ^{13}C signal in each molecule was also integrated and these results were consistent with the product ratios listed above. The cycloadducts in $CDCl_3$ solution were irradiated for 4 h with filtered light (λ > 327 nm) from a 450-W Hanovia medium-pressure mercury lamp which was surrounded by 1.5 cm of a 0.4 mol/L $SnCl_2$ in 10% HCl/H_2O filter. The cycloadduct ratios, as determined by ^{13}C NMR spectroscopy, were not changed after irradiation.

Reduction of 2-Cyclopentenone plus Methyl Acrylate Photocycloadducts. A methanol solution (65 mL) of a cycloadduct mixture (0.755 g; 4.50 mmol) was chilled to 0 °C in a ice bath. The **5**:**6**:**7**:**8** ratio was 6.5:40:35:19. Sodium borohydride (0.200 g; 5.29 mmol) was added over a period of 5 min, after which the reaction mixture was stirred for an additional 1.1 h at 0 °C. Approximately 1 g of potassium dihydrogen phosphate was added and then the reaction mixture was allowed to warm to room temperature. The mixture was diluted with water (100 mL) and extracted with 4 × 60 mL of CH_2Cl_2. The CH_2Cl_2 extracts were combined, washed with saturated $NaCl/H_2O$ (80 mL), dried over $MgSO_4$, and concentrated under reduced pressure to yield a colorless oil (0.717 g; 94% yield). The product mixture was analyzed by GC and the **9**:**10**:**11**:**12**:**13** ratio was found to be 2:3:42:34:18. The products were separeted by column chromatography in which a 3 cm × 80 cm column containing 150 g of 60−200 mesh silica gel packed in 3:7 diethyl ether−hexanes was used. The column was eluted with 1 L of a 3:7 diethyl ether−hexanes solution and 1.5 L of a 4:6 diethyl ether−hexanes solution to yield the following fractions: I, 0.020 g of **9** and **10** (4:6); II, 0.041 g of **11**; III, 0.220 g of **11** and **12** (6:4); IV, 0.278 g of **11**, **12**, and **13** (1:1.2:1); V, 0.063 g of **13**.

(a) Characterization of Fraction I (9 and 10). ^{1}H NMR (300 MHz, in $CDCl_3$): δ 5.15 (br s, exchanged in D_2O), 5.02 (dd, J = 6.4, 4.0 Hz), 4.56 (dd, J = 5.5, 3.3 Hz), 3.30 (br quartet, J = 6−7 Hz), 3.09 (br quartet, J = 5−7 Hz), remaining signals complex. ^{13}C NMR (300 MHz, in $CDCl_3$): δ 180.6 (C=O), 105.5 (CH), 86.0 (CH), 85.5 (CH), 47.7 (CH), 44.3 (CH), 40.8 (CH), 36.1 (CH), 36.0 (CH_2), 35.6 (CH), 34.5 (CH_2), 33.3 (CH), 32.7 (CH_2), 31.3 (CH_2), 31.2 (CH_2), 30.6 (CH_2). IR (neat film, cm^{-1}): 3510 (br), 1770 (vs, C=O), 1003 (s), 2934 (s), 1169 (s), 1046, 1088, 1204. Mass spectrum for **9** (EI, 70 eV): *m/e* (%) 138 (20), 110 (4), 109 (5), 95 (5), 93 (7), 91 (6), 84 (40), 83 (19), 82 (14), 81 (15), 79 (46), 77 (15), 67 (42), 66 (100), 55 (48), calculated M^+ for $C_8H_{10}O_2$ 138.06811 (found 138.0686). Mass spectrum for **9** (CI, isobutane): *m/e* (%) [M + 1] 139 (100), 138 (6), 113 (11), 93 (6), 84 (16), 79 (22), 67 (64), 66 (49). Mass spectrum for **10** (EI, 70 eV): *m/e* (%) 140 (2), 123 (1), 112 (1), 111 (1), 94 (10), 84 (4), 83 (14), 79 (38), 67 (20), 66 (100), calculated M^+ for $C_8H_{12}O_2$ 140.0837 (found 140.0840). Mass spectrum for 10 (CI, isobutane): *m/e* (%) [M + 1] 141 (10), 123 (91), 94 (15), 83 (14), 79 (38), 67 (35), 66 (100).

(b) Characterization of 11. ^{1}H NMR (300 MHz, in $CDCl_3$): δ 1.4 to 2.1 (complex, 5H), 2.27 (br s, 1H), 2.45−2.65 (complex, 2H), 2.84 (br quartet, J = 6−7 Hz, 1H), 3.09 (dt, J = 9.3, 6.0 Hz, 1H), 3.64 (s, 3H), 4.21 (dt, J = 10.2, 6.8 Hz, 1H). ^{13}C NMR (300 MHz, in $CDCl_3$): δ 176.6 (C=O), 74.0 (CH), 51.8 (OCH_3), 45.0 (CH), 33.6 (CH), 32.7 (CH), 31.4 (CH_2), 29.3 (CH_2), 27.7 (CH_2). IR (neat film, cm^{-1}): 3428 (br), 1732 (vs, C=O), 1173, 2952, 1076, 1267, 1437, 1236, 1362. Mass spectrum (EI, 70 eV): *m/e* (%) 170 (7), 152 (5), 139 (18), 138 (28), 127 (18), 115 (11), 111 (15), 96 (20), 87 (63), 84 (33), 83 (71), 82 (16), 81 (24), 67 (34), 55 (100), calculated M^+ for $C_9H_{14}O_3$ 170.09430 (found 170.0939).

(c) Characterization of 12 in Fraction III. ^{13}C NMR (300 MHz, in $CDCl_3$): δ 176.4 (C=O), 73.9 (CH), 51.5 (OCH_3), 40.9 (CH), 40.5 (CH), 37.5 (CH), 31.3 (CH_2), 28.9 (CH_2), 18.8 (CH_2). Mass spectrum of 12 (EI, 70 eV): *m/e* (%) 170 (2), 152 (4), 139 (16), 138 (12), 114 (13), 113 (11), 109 (13), 110 (15), 93 (23), 87 (80), 84 (66), 83 (76), 82 (27), 81 (26), 67 (38), 66 (56), 55 (100).

(d) Characterization of 13. ^{1}H NMR (300 MHz, in $CDCl_3$): δ 1.3 to 2.0 (complex, 5H), 2.36 (ddd, J = 6.5, 8.8, 15.4 Hz, 1H), 2.39 (br s, 1H), 2.71 (d of quartets, J = 9.0, 6.7 Hz, 1H), 2.90 (br quartet, J = 7−9 Hz, 1H), 3.32 (dt, J = 8.9, 10.0 Hz, 1H), 3.64 (s, 3H), 4.12 (dt, J = 9.6, 6.9 Hz, 1H). ^{13}C NMR (300 MHz, in $CDCl_3$): δ 173.7 (C=O), 74.7 (CH), 51.2 (CH), 39.2 (CH), 38.1 (CH), 37.6 (CH), 32.2 (CH_2), 25.4 (CH_2), 18.6 (CH_2). IR (neat film, cm^{-1}): 1733 (vs, C=O), 3420 (br), 1170, 2950, 1075. Mass spectrum (CI, isobutane): *m/e* (%) [M + 1] 171 (23), 154 (8), 153 (80), 139 (63), 110 (18), 94 (12), 93 (20), 87 (100), 84 (20), 83 (30), 82 (26), 81 (18), 67 (68), 66 (70).

Small-Scale Reduction of 5, 6, 7, and 8. A solution of the pure cycloadduct or a mixture of cycloadducts (0.050 g) dissolved in methanol (7 mL) was chilled to 0 °C in an ice bath. Sodium borohydride (0.013 g) was added to the solution and the mixture was stirred for 1.3 h. Potassium dihydrogen phosphate (0.1 g) was added to the reaction mixture followed by 20 mL of water. The aqueous layer was extracted with 3 × 30 mL of CH_2Cl_2. The combined extacts were dried over $MgSO_4$ and concentrated to 10 mL under reduced pressure. The resulting concentrate was analyzed by GC and the products of the concentrate were identified by GC co-injection with the products isolated from the large scale reduction of the cycloadduct mixture. The following was determined: (1) A 25:75 mixture of **5**:**7** reduced to a 10:15:75 mixture of **9**:**10**:**12**; (2) pure **6** reduced to compound **11**; (3) compound **7** reduced to compound **12**; (4) compound **8** reduced to compound **13**.

Irradiation of 2-Cyclopentenone and Methyl Acrylate in the Presence of H_2Se. A solution of cyclopentenone (2.132 g; 0.200 mol/L) and methyl acrylate (11.19; 1.00 mol/L) dissolved in toluene (130 mL) was chilled to −20 °C in a $CaCl_2$/ice bath. The solution was saturated with H_2Se at −20 °C by bubbling the gas through a constricted pipet. Hydrogen selenide was produced from the reaction of Al_2Se_3 and water (see the method descibed above). The solution was irradiated with Pyrex filtered light eminating from a 450-W Hanovia medium-pressure mercury lamp for 7 h. The (**14** + **15**):(**16** + **17**):**18** product ratio was determined by GC after 1 h of irradiation (approximately 6% of enone converted to products) to be 5:45:50. After 7 h of irradiation GC analysis of the solution revealed that 21% of the 2-cyclopentenone was converted to trapped products, 26% was converted to cyclopentanone, and 53% remained unreacted. The reaction mixture was concentrated under reduced pressure with heating to a volume of 5 mL. The concentrate was subjected to column chromatograph in which a 3 cm × 80 cm column containing 160 g of 60−200 mesh silica gel packed in 1:4 diethyl ether−hexanes was used. The column was eluted with 1:4 diethyl ether−hexanes to yield the following fractions: I, 0.538 g of cyclopentanone; II, 0.241 g of **26** and **27**; III, 0.181 g of **28**; IV, 0.045 g of (**14** + **15**) approximately 80% pure with other unidentified dark reaction products; V, 0.419 g of 2-cyclopentenone:(**16** + **17**):**18** in the ratio 1:2:7; VI, 0.807 g of 2-cyclopentenone:(**16** + **17**):**18** in the ratio 44:38:18; VII, 0.776 g of 2-cyclopentenone.

(a) **Mass Balance.** Amount of cyclopentenone reclaimed in fractions: 1.174 g. Amount of cyclopentanone isolated: 0.538 g. Total amount of trapped products (MM = 170) isolated: 0.874 g. Mass of 2-cyclopentenone converted into trapped products: 0.421 g. Mass of 2-cyclopentenone converted to cyclopentanone: 0.525 g. Total amount of 2-cyclopentenone reclaimed in the form of cyclopentanone, trapped products (MM = 170), and 2-cyclopentenone: 2.123 g (99% recovery).

(b) **Purification of Column Fractions.** Fraction IV was purified using preparative GC to yield fraction IVa which contained only **14** and **15** in a 1:1 ratio. Fraction V was purified by preparative GC to yield three fractions: Va, 2-cyclopentenone; Vb, **16** and **17** in a 1:1 ratio; Vc, **18** 95% pure with traces of **16** and **17**.

(c) **Characterization of a 1:1 Mixture of 14 and 15 (Fraction IVa).** ^1H NMR (300 MHz, in $CDCl_3$): δ 1.085 (d, J = 7.2 Hz, 3H), 1.237 (d, J = 7.3 Hz, 3H), 1.6−2.4 (complex, 13H), 2.54 (dddd, J = 1.2, 5.6, 8.1, 12.0 Hz, 1H), 2.80 (d of quartets, J = 5.8, 7.1 Hz, 1H), 3.03 (d of quartets, J = 4.4, 7.3 Hz, 1H), 3.63 (s, 3H), 3.68 (s, 3H). ^1H NMR (300, in C_6D_6): δ 1.00 (d, J = 7.2 Hz, 3H), 1.07 (d, J = 7.3 Hz, 3H), 1.1−1.7 complex, 1.75 (ddd, J = 4.5, 8.2, 11.2 Hz, 1H), 1.8−2.0 complex, 2.28 (dddd, J = 1.2, 5.8, 8.1, 12.0 Hz, 1H), 2.76 (d of quartets, J = 5.8, 7.1 Hz, 1H), 2.95 (d of quartets, J = 4.4, 7.3 Hz, 1H), 3.24 (s, 3H), 3.38 (s, 3H). ^{13}C NMR (300 MHz, in $CDCl_3$): δ 51.7 (OCH_3, two isochronous signals), 51.54 (CH), 51.47 (CH), 39.1 (CH), 38.8 (CH), 38.1 (CH_2, two isochronous signals), 26.1 (CH_2), 25.9 (CH_2), 20.6 (CH_2), 20.5 (CH_2), 15.2 (CH_3), 13.7 (CH_3), due to the very low concentration of the sample the carbonyl peaks were not identified. IR (neat film, cm^{-1}): 1732 (vs, C=O). Mass spectrum for **14** (EI, 70 eV): *m/e* (%) 170 (22), 139 (22), 138 (18), 127 (14), 111 (50), 110 (28), 88 (21), 84 (33), 83 (50), 74 (71), 59 (100), calculated M^+ for $C_9H_{14}O_3$ 170.0943 (found 170.0944). Mass spectrum for **15** (EI, 70 eV): exactly the same fragmentation as **14**, M^+ found 170.0943.

(d) **Characterization of a 1:1 Mixture of 16 and 17 (Fraction Vb).** ^1H NMR (300 MHz, in $CDCl_3$): δ 1.17 (d, J = 6.6 Hz, 3H), 1.20 (d, J = 6.6 Hz, 3H), 1.4−2.5 complex, 3.65 (s, 3H), 3.68 (s, 3H). ^{13}C NMR (300 MHz, in $CDCl_3$): δ 218.1 (C=O), 218.0 (C=O), 175.9 (C=O), 175.8 (C=O), 51.7 (OCH_3, two isochronous signals), 44.5 (CH), 44.4 (CH), 43.4 (CH_2), 42.7 (CH_2), 40.3 (CH), 40.0 (CH), 38.6 (CH_2), 38.5 (CH_2), 27.7 (CH_2), 27.2 (CH_2), 15.9 (CH_3), 15.1 (CH_3). Mass spectrum of **16** (EI, 70 eV): *m/e* (%) 170 (2), 139 (6), 113 (11), 111 (15), 97 (16), 88 (63), 83 (100), 82 (17), 69 (12), 55 (64), calculated M^+ for $C_9H_{14}O_3$ 170.0943 (found 170.0944). Mass spectrum for **17** (EI, 70 eV): exactly the same fragmentation as **16**, M^+ found 170.0943.

(e) **Characterization of 18.** ^1H NMR (300 MHz, in $CDCl_3$): δ 1.40−2.34 complex, 2.38 (t, J = 7.3 Hz, 2H), 3.62 (s, 3H). ^1H NMR (300 MHz, in C_6D_6): δ 0.83−0.98 (m, 1H), 1.02−1.20 (m, 1H), 1.3−1.44 (m, 1H), 1.47 (ddd, J = 6.7, 7.7, 13.5 Hz, 1H), 1.54−1.68 (complex, 3H), 1.84 (dddd J = 18.8, 8.7, 2.8, 1.4 Hz, 1H), 1.99 (ddt, J = 5.4, 13.5, 7.6 Hz, 1H), 2.20 (t, J = 7.7 Hz with second-order effects, 2H), 3.34 (s, 3H). ^{13}C NMR (300 MHz, in $CDCl_3$): δ 219.9 (C=O), 173.5 (C=O), 51.4 (OCH_3), 48.2 (CH), 37.9 (CH_2), 31.9 (CH_2), 29.5 (CH_2), 25.0 (CH_2), 20.6 (CH_2). Mass spectrum (EI, 70 eV): *m/e* (%) 170 (14), 139 (42), 138 (100), 111 (11), 110 (40), 97 (19), 84 (16), 83 (24), 82 (24), 74 (20), 59 (28), 55 (78), calculated M^+ for $C_9H_{14}O_3$ 170.0943 (found 170.0942).

(f) **Characterization of a 1:1 Mixture of 26 and 27 (Fraction II).** ^1H NMR (200 MHz, in $CDCl_3$): δ 1.42 (d, J = 7.2 Hz, 3H), 1.49 (d, J = 7.2 Hz, 3H), 3.60−3.75 (two overlapping quartets, J = 7.2 Hz), 3.61 (s, 3H), 3.63 (s, 3H). ^{13}C NMR (200 MHz, in $CDCl_3$): δ 173.8 (C=O), 173.6 (C=O), 51.9 (OCH_3), 33.7 (CH), 33.4 (CH), 17.9 (CH_3), 17.2 (CH_3). Mass spectrum for **26** (EI, 70 eV): *m/e* (%) for ions containing ^{80}Se, 254 (10), 222 (15), 195 (10), 135 (30); *m/e* (%) for ions containing no Se, 88 (90), 59 (100). Mass spectrum for **27** (EI, 70 eV): exactly the same fragmentation as **26**.

(g) **Characterization of 28 (Fraction III).** ^1H NMR (200 MHz, in $CDCl_3$): δ 1.47 (d, J = 7.1 Hz, 3H), 2.65−3.05 complex, 3.64 (s, 3H), 3.67 (s, 3H), methine proton under methoxy signals. ^{13}C NMR (300 MHz, in $CDCl_3$): δ 174 (C=O), 172.4 (C=O), 52.1 (OCH_3), 51.7 (OCH_3), 35.0 (CH_2), 31.9 (CH), 18.2 (CH_2), 17.3 (CH_3). Mass spectrum for (EI, 70 eV): *m/e* (%) for ions containing ^{80}Se, 254 (36), 222 (36), 195 (14), 135 (26); *m/e* (%) for ions containing no Se, 88 (100), 59 (100).

Synthesis of Compound 19. Bicyclo[3.3.0]octa-2,8-dione[30] (0.132 g; 0.953 mmol) was added to 50 mL of 0.50 mol/L H_2SO_4 in methanol and the reaction mixture was heated under gentle reflux for 4 h. The mixture was allowed to cool to room temperature, diluted with 200 mL of diethyl ether, neutralized by slowly adding solid Na_2CO_3 (6 g), and then washed with water (2 × 100 mL). The ether extracts were washed with saturated NaCl/water (1 × 100 mL), dried over $MgSO_4$, and concentrated under reduced pressure to yield a yellow oil. The oil was disolved in 1 mL of diethyl ether and this solution was added to a column (0.5 × 9.0 cm) containing 2 g of silica gel in diethyl ether. The column was eluted with 12 mL of diethyl ether. The elutant was concentrated under reduced pressure to yield pure **19** (0.130 g; 0.765 mmol; 80%).

(a) **Characterization of 19.** ^1H NMR (300 MHz, in $CDCL_3$): δ 1.36 to 1.50 (m, 1H), 1.64−1.76 complex, 1.98−2.34 complex, 2.28 (t, J = 7.3 Hz, 2H), 3.58 (s, 3H). ^{13}C NMR (300 MHz, in $CDCl_3$): δ 218.0 (C=O), 173.3 (C=O), 51.3 (OCH_3), 44.6 (CH_2), 38.1 (CH_2), 36.4 (CH), 32.2 (CH_2), 30.4 (CH_2), 29.0 (CH_2). Mass spectrum (EI, 70 eV): *m/e* (%) 170 (5), 152 (5), 139 (21), 110 (6), 97 (21), 96 (67), 84 (10), 83 (100), 82 (25), 74 (39), 67 (13), calculated M^+ for $C_9H_{14}O_3$ 170.0943 (found 170.0941).

Irradiation of 2-Cyclopentenone and Ethyl Vinyl Ether in the Presence of Hydrogen Selenide. Benzene (30 mL) was purged with nitrogen gas for 10 min to remove oxygen. Hydrogen selenide gas generated by the addition of water to aluminun selenide (1.3 g) was bubbled through the benzene for 20 min. A solution of 2-cyclopentenone (155 mg) in ethyl vinyl ether (18.8 g) was prepared and an aliquot (0.5 mL) was removed and diluted with an equal volume of benzene ("solution A"); the remainder was mixed with the benzene solution of hydrogen selenide ("solution B"). A sample (1 mL) of the

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(30) Bicyclo[3.3.0]octa-2,8-dione was generously donated by Andreas Rudolph. The compound was prepared according to the method of Duthaler and Maienfisch; see: Duthaler, R. O.; Maienfisch, P. *Helv. Chim. Acta* **1984**, *67*, 856.

latter solution was removed and placed in a tube wrapped with aluminum foil ("solution C"). All solutions containing hydrogen selenide were manipulated in such a manner as to prevent contact with atmospheric oxygen. Immediately after their preparation solutions A, B, and C were placed in front of a medium-pressure mercury lamp housed in a Pyrex water jacket for 10 min; they were then immediately analyzed by GC and GC/MS.

Solution A showed 27% conversion of 2-cyclopentenone to four products identified as **31**−**34** by comparison of their mass spectral fragmentation patterns with those reported in the literature.[24,25]

Solution C (the "dark reaction") showed 50% conversion of cyclopentenone after 40 min and the formation of three major products (ratio 1:1:1) by GC. Continued monitoring by GC revealed that the amount of these products grew with time and after 2 h all of the cyclopentenone had been converted. Analysis by GC/MS revealed that all three products contained one selenium atom. Two of the dark products possessed similar retention times and identical mass spectra (*m*/*e* 226 (M^+), 181, 153, 74) and were tentatively identified as diastereomers of **42**. The third dark product posessed a longer retention time and *m*/*e* 236 (M^+), 191, 163, 83, and 74 and was tentatively identified as selenide **43**.

Analysis of solution B by GC immediately after the irradiation revealed 32% conversion of cyclopentenone and the formation of two sets of product peaks. One set was identical to the products observed in solution C; the second set of products (which were not observed in solution C) was assigned as the trapped biradicals **38**−**41**. They were formed in the ratio 3.23:3.45:5.73:1.00. The non-callibrated GC ratio of the dark products to light-induced products was 5:1. None of the cycloadducts **31**−**34** formed in solution A were observed in irradiated solution B.

Immediately after the irradiation the volatiles in solution B were removed under reduced pressure and at room temperature to yield a yellow oil (220 mg); the GC of this oil revealed the two sets of products in unchanged ratio.

The irradiation was performed twice more with fresh solutions of reactants (183 and 220 mg of cyclopentenone) and the irradiation times were extended to 30 min. This did not affect the ratios of the products **38**−**41**. Immediately after each irradiation the yellow solution obtained was filtered and the solvent removed under reduced pressure and at room temperature to prevent further dark reaction.

The products from all three irradiations were combined to yield a yellow oil (627 mg). Chromatography (preparative TLC, silica gel, 30% ether/70% hexanes) of the oil (365 mg) separated the dark products (band 1, 23.9 mg) from the photochemical products (band 2, 53.2 mg, and band 3, 32.5 mg). GC analysis revealed that band 2 contained a mixture of **38**−**40** and band 3 contained a mixture of **39** and **41**. Further preparative TLC of each band allowed isolation of pure samples of **38** (14 mg), **39** (5 mg), and **41** (4 mg) and a sample of **40** contaminated with **38**. The amount of cyclopentanone formed in the reaction was not quantified.

For **38**: ^{1}H NMR δ ($CDCl_3$) 3.49 (t, $J = 6$ Hz, 2H), 3.45 (q, $J = 7$ Hz, 2H), 2.35−2.00 (m, 7H), 1.65 (m, 2H), 1.20 (t, $J = 7$ Hz, 3H); ^{13}C NMR δ ($CDCl_3$) 200.1 (C=0), 68.5, 66.0, 38.0, 29.7, 29.6, 20.8 (CH_2), 46.5 (CH), 15.2 (CH_3); *m*/*s* (%) M^+ 156 (25), 84 (100), 73 (96), 59 (24); M^+ calc 156.11503, found 156.11492.

For **39**: ^{1}H NMR δ ($CDCl_3$) 7.45 (m, 1H), 3.55 (t, $J = 8$ Hz, 2H), 3.49 (q, $J = 7$ Hz, 2H), 2.58 (m, 2H), 2.45 (td, $J = 8$ and 2 Hz, 2H), 2.35 (m, 2H), 1.19 (t, $J = 7$ Hz, 3H); ^{13}C NMR δ ($CDCl_3$) 68.2, 66.0, 34.2, 29.6, 26.5 (CH_2), 15.0 (CH_3); *m*/*s* (%) M^+ 154 (12), 125 (100), 110 (25), 98 (44), 84 (34), 59 (75); M^+ calc 154.09938, found 154.1002.

For **41**: ^{1}H NMR δ ($CDCl_3$) 5.95 (m, 1H), 3.62 (t, $J = 8$ Hz, 2H), 3.45 (q, $J = 7$ Hz, 2H), 2.61 (m, 2H), 2.45 (br m, 4H), 2.35 (m, 2H), 1.15 (t, $J = 7$ Hz, 3H); ^{13}C NMR δ ($CDCl_3$) 68.2, 66.0, 34.1, 29.6, 26.5 (CH_2), 15 (CH_3); *m*/*s* (%) M^+ 154 (2.5), 126 (9), 125 (100), 110 (25), 59 (76); M^+ calc 154.09938, found 154.1003.

For **40**: isolated as a 2:1 mixture with **38** as the minor component; ^{13}C NMR δ ($CDCl_3$) 217.1 (C=O), 69.2, 68.7, 34.6, 29.9, 29.8, 21.0 (CH_2), 53.7 (CH), 15.4 (CH_3); *m*/*e* (%) M^+ 156 (1.3), 110 (100), 83 (60), 59 (80); M^+ calc 156.11503, found 156.11503.

Samples of **39** and **41** (1.5 mg of each) in methanol (0.5 mL) were hydrogenated over 10% palladium on carbon at atmospheric pressure to give **38** and **40**, respectively, confirmed by GC co-injection and comparison of mass spectral fragmentation patterns.

Supplementary Material Available: Details of arguments used for structure identification and Tables 1 and 3 containing a listing of NMR data (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.