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Determination of the Relative Rates of Formation, Fates, and Structures of Triplet 1,4-Biradicals Generated in the Photochemical Cycloaddition Reactions of 2-Cyclopentenones with 2-Methylpropene[1]

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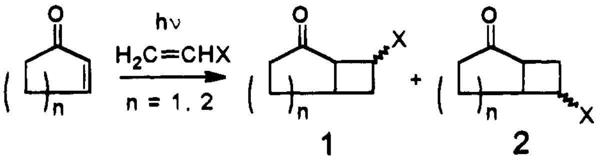
Abstract: The structures and relative rates of formation of the isomeric triplet 1,4-biradical intermediates generated in the photocycloaddition reactions between 2-methylpropene and each of 2-cyclopentenone, 2-methyl-2-cyclopentenone, and 3-methyl-2-cyclopentenone were determined. This was accomplished by using hydrogen selenide as a hydrogen atom donor to trap quantitatively the 1,4-biradicals formed in each reaction. The quantum yields of cycloadduct formation in the photocycloaddition reactions were measured as a function of alkene concentration. For each reaction the relative rates of formation of the biradicals and the quantum yield data were combined to determine quantitatively how each biradical partitions between closure (or disproportionation) to product and fragmentation to ground state enone and alkene. It is concluded that the regiochemistry of the enone−alkene photocycloaddition reactions studied is dominated by the manner in which the biradical intermediates partition between products and ground state precursors and not by the relative rates at which they are formed. It is also concluded that methyl substitution at the 3-position of cyclopentenone has little effect on either the relative rates of formation of the various isomeric biradical intermediates or the manner in which they partition between products and starting materials. However, methyl substitution at the 2-position of cyclopentenone slows formation of biradicals in which the alkene is bonded to the enone 2-position and also inhibits closure to cyclobutane products of biradicals formed by bonding of the alkene to the 3-position of the enone. These results can be rationalized if it is assumed that the enone triplet excited state possesses a planar carbon at the 2-position and a pyramidalized carbon at the 3-position, and if it is also assumed that in the biradicals, radical centers at the cyclopentanone 2-position are planar and at the 3-position are pyramidalized.

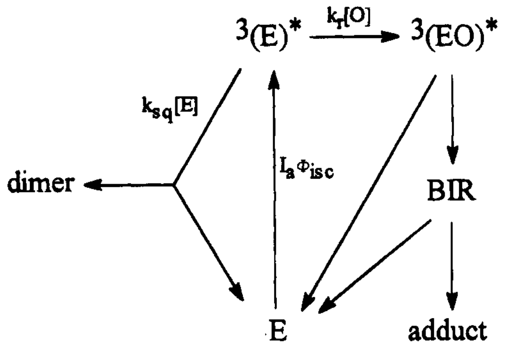
Introduction

The photochemical cycloaddition reaction of alkenes with cyclic enones has been studied from both mechanistic and synthetic standpoints for over 30 years.[2] Depending on the structure of the alkene, up to four new chiral centers are formed in the reaction and two regioisomeric modes of addition are possible (Scheme 1). Corey[3] showed that little stereochemical control of the reaction could be achieved; this has been interpreted in terms of a nonconcerted pathway in which one of the new C−C bonds is formed from interaction of the triplet excited state of the enone with one terminus of the alkene to produce a triplet 1,4-biradical intermediate.[2] Kinetic evidence for the intermediacy of such a biradical species was found by Loutfy and de Mayo.[4] Early work on the reaction also revealed evidence for regioselectivity when polar alkenes were used; for example, ultraviolet light irradiation of 2-cyclohexenone with ethoxyethene gave mainly the head-to-tail regioisomer **2**, while acrylonitrile was found to produce the head-to-head isomer **1**.[3] These observations led to the development of a mechanistic model for the reaction, generally referred to as the Corey−de Mayo mechanism, which is summarized in Scheme 2.[2] In this mechanism the triplet excited state of the enone ("E") can decay

Scheme 1



Scheme 2



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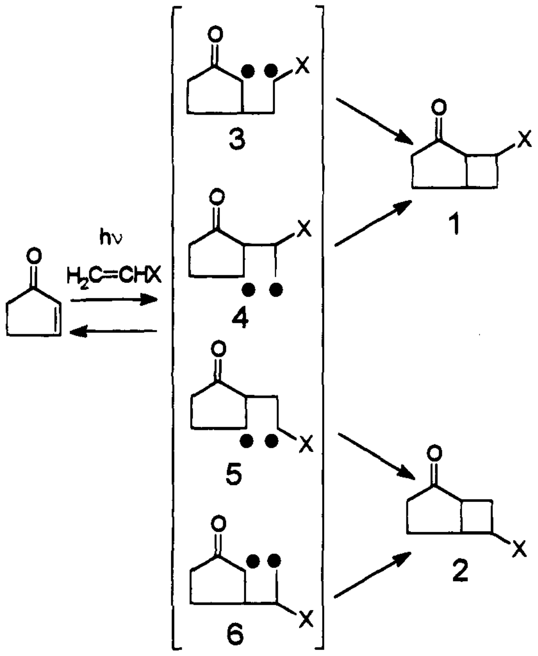
to the ground state by unimolecular photophysical processes, by self quenching, or by interaction with alkene ("O") to give an exciplex. It was proposed that the orientation of the dipoles of the excited enone and the ground state alkene in this exciplex were responsible for the regiochemical outcome of the reaction. This exciplex intermediate has never been detected unambiguously, and no indirect evidence of its existence in this reaction has ever been reported.

In recent years an increasing number of examples have appeared in which the reaction is not regioselective, or in which the regiochemical outcome is the reverse of that predicted by the Corey–de Mayo model, especially when alkenes substituted by electron withdrawing groups are used.[5] In addition, evidence has been presented which suggests that the rate constant for interaction of the enone triplet excited state with alkenes does not vary with the electron demand of the alkene substituents in the manner that would be expected if an electron donor–acceptor complex were to be formed.[6] These observations imply that exciplex intermediates are not responsible for directing the regiochemistry of the reaction and suggest that exciplexes are not, in fact, necessary intermediates in the reaction mechanism.

Some years ago Bauslaugh proposed an alternative explanation of the reaction regiochemistry.[7a] This explanation recognized that for a given enone–alkene pair several isomeric biradical intermediates can, in principle, be formed. Bauslaugh suggested that depending upon their relative stabilities some of these biradicals would be formed faster than others and that some would show a greater propensity to close to products, while others would show a preference for fragmentation to the ground state enone and alkene precursors. Wagner has discussed the kinetic consequences of this and has pointed out that the product ratios are defined by the mathematical product of the ratio for rates of biradical formation times the ratio for biradical partitioning.[7b] We have recently demonstrated that elements of Bauslaugh's hypothesis are correct by using hydrogen selenide as a hydrogen atom donor to trap the triplet 1,4-biradical intermediates quantitatively.[5f,8,9] In this way we have shown that in the reaction of 2-cyclopentenone with ethoxyethene or with methyl acrylate the cycloadduct product distribution is controlled by the way in which the biradicals partition between closure and fragmentation as well as by the amount of each biradical formed. For example, with ethoxyethene the possible biradical intermediates are **3**–**6** (X = OEt in Scheme 3). Of these only **3** and **5** are formed, and they are produced in similar amounts; however, **5** closes to product more efficiently than does **3** so that the ratio of regioisomeric cycloadducts **1**:**2** (X = OEt) is approximately 1:3. Similarly, with methyl acrylate as the alkene partner the biradicals **3**–**6** (X = CO_2Me) are formed in the ratio $<$1:5:50:45, whereas the regioisomeric cycloadducts **1** and **2** (X = CO_2Me) are formed in the ratio 46.5:53.5.[5f]

Scheme 3



In this paper we report experiments designed to test this conclusion and to understand the structural factors governing the amount of each of the biradical intermediates formed and the factors determining the extent to which each biradical fragments to starting materials or closes to cycloadduct product. In this work we have used hydrogen selenide to trap quantitatively the biradical intermediates formed in the photochemical cycloaddition reaction between the alkene 2-methylpropene and the enones 2-cyclopentenone, 2-methyl-2-cyclopentenone, and 3-methyl-2-cyclopentenone. In addition, the quantum yields of cycloaddition for each of these enone–alkene combinations have been measured as a function of alkene concentration. From these data it has been possible to extract quantitative information about the rates of formation and the fates of each of the biradical intermediates.

Results

Products of the Photochemical Cycloaddition Reactions between 2-Methylpropene and 2-Cyclopentenone, 2-Methyl-2-cyclopentenone, and 3-Methyl-2-cyclopentenone.

Photocycloaddition Reaction of 2-Cyclopentenone with 2-Methylpropene. The photochemical cycloaddition reaction of 2-methylpropene with 2-cyclopentenone to give a pair of cyclobutane adducts has been described in the literature.[10] The regiochemistry of the 2 + 2 cycloadducts obtained was assigned based on the chemical shift differences of the two methyl groups in each adduct.[10a] In the study reported here the reaction was repeated in order to confirm the published result and the assignment. Irradiation of a benzene solution of 2-cyclopentenone and 2-methylpropene with Pyrex filtered light from a medium pressure mercury lamp resulted in the formation of products **7**–**10** (Scheme 4) in the ratio 69.5:18.6:2.9:9.1. These ratios were determined at 5% conversion of cyclopentenone so as to avoid secondary photolysis of the products. Compounds **7** and **8** were isolated by conversion to their dinitrophenylhydrazones, chromatography, and hydrolysis to regenerate the parent ketones. Their structures were confirmed by analysis of their ^{1}H-NMR and ^{13}C-NMR spectra recorded in the presence of a lanthanide shift reagent to disperse the signals. Using a combination of ^{1}H–^{1}H COSY and ^{1}H–^{13}C HETCOR experiments in conjunction with selective ^{1}H–^{1}H decoupling experiments it was possible to identify unambiguously the cyclobutane

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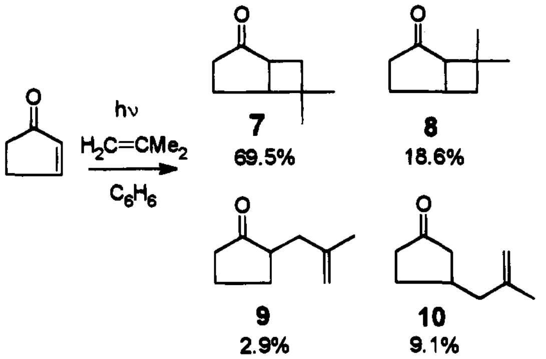
Scheme 4



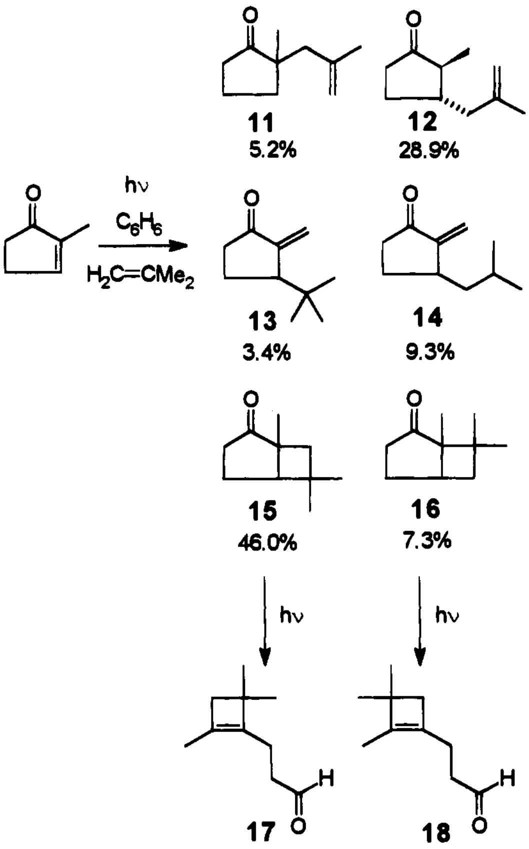
methines and methylene signals and establish their coupling relationships and hence the regiochemistry of the cycloadducts. The ring fusion stereochemistry in these and all other cyclobutane adducts prepared in this study was assumed to be *cis*; no examples of *trans*-fused bicyclo[3.2.0]heptanes have ever been reported as products of enone photocycloaddition reactions. The assignment of structures to these and other compounds described in this paper is discussed more fully in the supplementary material.

Compounds **9** and **10** could not be separated completely from **7** and **8**; their structures were deduced from their NMR spectra following subtraction of the signals corresponding to **7** and **8**. The regiochemistry of **9** and **10** was established from their ^{13}C-NMR spectra by inspection of the positions and multiplicities of the signals of the carbons adjacent to the carbonyl group. The structures of **9** and **10** reveal them to be so-called "ene" products arising from intramolecular disproportionation of the intermediate triplet 1,4-biradicals.[2]

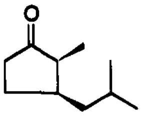
Photocycloaddition Reaction of 2-Methyl-2-cyclopentenone with 2-Methylpropene. Irradiation of a benzene solution of 2-methylcyclopentenone and 2-methylpropene with Pyrex filtered light from a medium pressure mercury lamp resulted in the formation of products **11**–**18** (Scheme 5). Products **17** and **18** only appeared at high conversion of the enone and their growth paralleled a decrease in yield of products **15** and **16** relative to **11**–**14**. In separate experiments it was determined that photolysis of a benzene solution of **15** yields **17** and that photolysis of a benzene solution of **16** yields **18**. These arise from Norrish type I cleavage followed by intramolecular disproportionation; when the photolysis of **15** and **16** was carried out in benzene containing methanol small amounts of ester were also produced, corresponding to the trapping of ketenes formed by the expected alternative modes of disproportionation. At 3% conversion of 2-methyl-2-cyclopentenone secondary photolysis of **15** and **16** to give **17** and **18** had not commenced, and the ratio of **11**:**12**:**13**:**14**:**15**:**16** was 5.2:28.9:3.4:9.3:46.0: 7.3.

The regiochemistry of **15** and **16** was readily determined following the identification of the cyclobutane methylene signals in the ^{1}H-NMR spectrum; in the case of **15** these appeared as an AB system with no coupling to an adjacent methine. The structural assignments of **11** and **12** were straightforward and followed from the appearance of their ^{1}H-NMR and ^{13}C-NMR spectra. The stereochemical assignment of **12** was based upon two observations. Firstly the structure is that of an ene product arising from intramolecular disproportionation of a triplet 1,4-biradical intermediate; it would be geometrically impossible for the *cis* isomer of **12** to be formed by such a process. Secondly, catalytic hydrogenation of **14** gave a 1:1 mixture of the diastereomers **19** and **20**. Base catalyzed epimerization of these resulted in equilibration to the more stable *trans* isomer **20**. This product was identical with that obtained by hydrogenation of **12**.

Scheme 5



The structures of **13** and **14** were also readily determined from the appearance of their ^{1}H-NMR and ^{13}C-NMR spectra and were confirmed by the results of hydrogenation experiments. Those for **14** are described above; in the case of **13** hydrogenation yielded a mixture of **21** and **22**; as with **19** and **20**, base catalyzed epimerization resulted in equilibration to give the more stable *trans* product **22**.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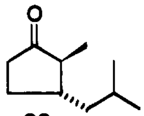
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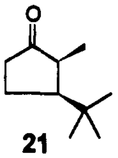
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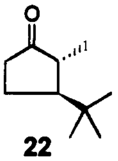
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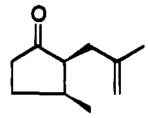
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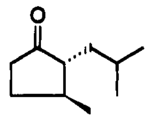
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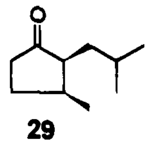
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Photocycloaddition Reaction of 3-Methyl-2-cyclopentenone with 2-Methylpropene. Irradiation of a benzene solution

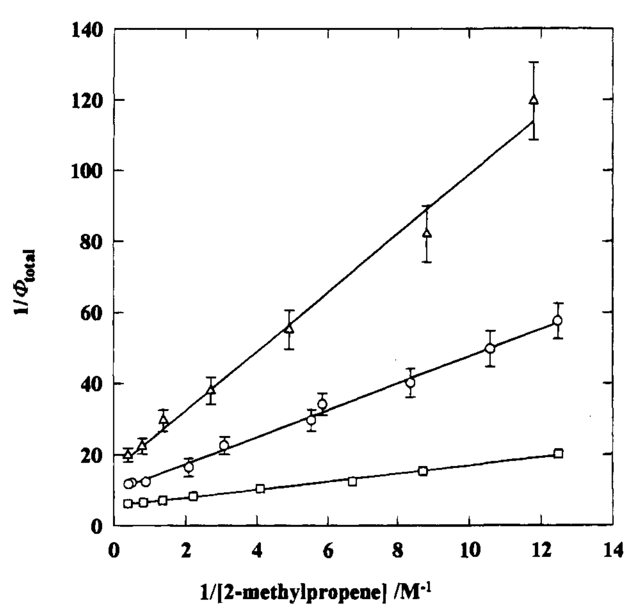


Figure 1. Plot of reciprocal of total product quantum yield against reciprocal of alkene concentration for the photochemical cycloaddition reaction between 2-methylpropene and 2-cyclopentenone (○), 2-methyl-2-cyclopentenone (△), and 3-methyl-2-cyclopentenone (□). Solvent: benzene. [enone]: 0.04 M.

Scheme 6

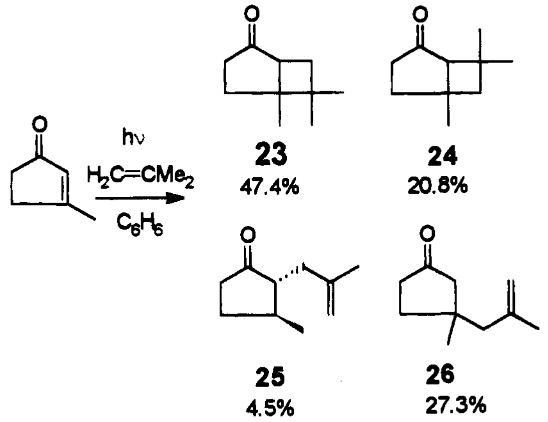


Table 1. Weighted Least Squares Regression Analysis Results for the Quantum Yield Determinations in Photocycloaddition Reaction of 2-Methylpropene with Various 2-Cyclopentenones

product	rel product yield (%)[a]	1/Φ versus 1/[alkene] regression parameters: slope (M^{-1})	intercept	1/intercept	r^b
Photocycloaddition Reaction of 2-Methylpropene with 2-Cyclopentenone[c]					
all		3.8 ± 0.1	9.7 ± 0.6	0.10 ± 0.01	0.998
9	2.9	131 ± 4	136 ± 21	0.0030 ± 0.0002	
7	69.5	5.4 ± 0.1	14.0 ± 0.9	0.071 ± 0.004	
8	18.5	20.4 ± 0.5	52 ± 3	0.019 ± 0.001	
10	9.1	41.6 ± 1.0	107 ± 7	0.0093 ± 0.0006	
Photocycloaddition Reaction of 2-Methylpropene with 2-Methyl-2-cyclopentenone[c]					
all		8.3 ± 0.4	15.6 ± 2.3	0.063 ± 0.009	0.993
16	7.3	114 ± 5	216 ± 31	0.0046 ± 0.0006	
15	46.0	18.1 ± 0.8	34 ± 5	0.029 ± 0.004	
11	5.2	160 ± 8	306 ± 44	0.0033 ± 0.0004	
12	28.9	29 ± 2	55 ± 8	0.018 ± 0.002	
13	3.4	244 ± 12	465 ± 67	0.0022 ± 0.0003	
14	9.3	89 ± 4	170 ± 25	0.0059 ± 0.0007	
Photocycloaddition Reaction of 2-Methylpropene with 3-Methyl-2-cyclopentenone[c]					
all		1.13 ± 0.05	5.6 ± 0.3	0.18 ± 0.01	0.998
24	20.8	5.4 ± 0.2	27 ± 1	0.037 ± 0.002	
25	4.5	25 ± 1	125 ± 5	0.0080 ± 0.0005	
23	47.4	2.4 ± 0.1	11.8 ± 0.5	0.084 ± 0.004	
26	27.3	4.1 ± 0.2	20.6 ± 0.8	0.049 ± 0.003	

[a] Normalized to 100%; relative error of 2%. [b] Correlation coefficient. [c] Solvent: benzene; [enone]: 0.04 M.

of 3-methyl-2-cyclopentenone and 2-methylpropene with Pyrex filtered light from a medium pressure mercury lamp resulted in the formation of products **23**, **24**, **25**, and **26** in the ratio 47.4: 20.8:4.5:27.3 (Scheme 6). These product ratios were determined at 5% conversion of 3-methyl-2-cyclopentenone.

The regiochemistry of the two cycloadducts **23** and **24** was determined by examining their ^1H NMR spectra. In **23** the cyclobutane methylene hydrogens were each observed as a double doublet with a geminal coupling constant of 11.9 Hz; these were coupled to the cyclobutane methine hydrogen with vicinal coupling constants of 10 and 7.3 Hz, indicative of head-to-tail regiochemistry. In **24** the cyclobutane methylene hydrogens gave rise to an ABX pattern with $J_{AB} = 12.5$ Hz, $J_{AX} = 0$ Hz, and $J_{BX} = 2$ Hz. The absence of strong vicinal coupling is indicative of head-to-head regiochemistry; the 2 Hz coupling is assigned to diagonal coupling with the cyclobutane methine across the cyclobutane ring.

The structures of the adducts **25** and **26** are those expected from intramolecular disproportionation of the triplet 1,4-biradical intermediates. The presence of the isobutenyl group was readily ascertained from the ^1H-NMR and ^{13}C-NMR spectra. The position of attachment was indicated by the number of methine and quaternary signals in the ^{13}C-NMR spectra and the multiplicities of the higher field methyl signals in the ^1H-NMR spectra. The stereochemistry of **25** was inferred from the fact that base catalyzed epimerization resulted in equilibration with a minor component presumed to be the less stable *cis* isomer **27**. Hydrogenation of **25** gave **28** which also equilibrated upon treatment with base to yield a minor component presumed to be the less stable *cis* isomer **29**; hydrogenation of the base equilibrated mixture obtained from **25** (i.e., **25** + **27**) also gave a mixture of **28** and **29** and in a similar ratio to that obtained by base treatment of **28**. This result is consistent with the notion that **25** is formed by intramolecular disproportionation of a biradical precursor; formation of the *cis* isomer **27** by this process is geometrically impossible.

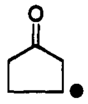
Quantum Yields of Product Formation for the Photochemical Reactions of 2-Cyclopentenone, 2-Methyl-2-Cyclopentenone, and 3-Methyl-2-cyclopentenone with 2-Methylpropene. The quantum yields of formation of the products obtained in the photochemical reaction of 2-methylpropene with each of 2-cyclopentenone, 2-methyl-2-cyclopentenone, and 3-methyl-2-cyclopentenone were measured at various alkene concentrations in benzene. The concentration of the enone was kept constant (0.04 M) and the 2-methylpropene concentration was varied from 0.08 to 2.5 M. The relative yield of each product obtained in the three photocycloaddition reactions did not vary as the alkene concentration was increased.

A linear correlation was obtained when the reciprocal of the total quantum yield of formation of the products from each enone was plotted against the reciprocal of the 2-methylpropene concentration. Figure 1 shows the plots obtained for each enone. The slope and intercept parameters obtained from the weighted least squares regression analyses of the data shown in Figure 1 are listed in Table 1. The corresponding slope and intercept parameters for individual products obtained in each of the photocycloaddition reactions were calculated by dividing the regression parameters obtained from the plots shown in Figure 1 by the relative yield of each product (normalized to unity).

The errors quoted for each slope and intercept parameter represent one standard deviation unit for the parameter as determined in the weighted least squares analysis of the data. The significance of the intercept and slope parameters obtained will be addressed in the Dicussion section.

Products of Trapping with Hydrogen Selenide in the Photochemical Cycloaddition Reaction between 2-Methylpropene and 2-Cyclopentenone, 2-Methyl-2-cyclopentenone, and 3-methyl-2-Cyclopentenone. General Description of Biradical Trapping Experiments. Each enone (cyclopentenone, 2-methyl-2-cyclopentenone, and 3-methyl-2-cyclopentenone) was irradiated with Pyrex filtered ultraviolet light in benzene solutions containing hydrogen selenide and 2-methylpropene. The appearance of products in these reaction mixtures was monitored by GC/MS; the progress of each of the reactions was compared with that of identical reaction mixtures which were kept in the dark. No cycloadducts were observed in the irradiated solutions; however, products presumed to result from (or consistent with) reduction of 1,4-biradicals intermediates by hydrogen selenide were seen. No products resulting from hydrogen selenide trapping of 1,4-biradicals were observed in the dark control reactions. The absence of cycloadducts in the solutions irradiated in the presence of hydrogen selenide is consistent with the presumption that the triplet 1,4-biradicals responsible for their formation had been trapped quantitatively and that none were undergoing their normal competitive fates of closure or disporportionation to adducts or fragmentation to ground state starting materials.

In addition to the products resulting from the reduction of 1,4-biradicals, cyclopentanone, 2-methyl-2-cyclopentanone, or 3-methyl-2-cyclopentanone were also observed in the reaction mixtures exposed to UV light. These result from photoreduction of the enone triplet excited state by hydrogen selenide and presumably involve the intermediacy of one or more of the radicals **30**−**32**. We have pointed out elsewhere[5f,8] that these radicals are reduced by hydrogen selenide to give the cyclopentanones at a rate which is several orders of magnitude faster than their rate of addition to an alkene. This excludes the possibility that the radicals **30**−**32** could be the source of the products identified as trapped triplet 1,4-biradical intermediates produced by interaction of the triplet excited enone with the alkene.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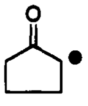
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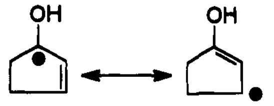
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Slow product formation was observed in the dark control reactions (i.e., those reaction mixtures which were not exposed to ultraviolet light). These products were also observed in the solutions that were exposed to ultraviolet light, although the amount formed was small in comparison with the products resulting from reduction of the 1,4-biradicals. The structures of these dark products were not determined; however the results of GC-MS analysis suggested that they are cyclopentanones joined by a diselenide linkage. Since selenols are readily oxidized in air to diselenides, these products probably arise from Michael addition of hydrogen selenide to the enone.

As will be outlined below, the structures of the products of biradical trapping indicate that they result from hydrogen selenide reduction of one radical center followed either by reduction of the second radical center or by disproportionation of the hydrogen selenyl radical and the second radical center. No products were seen corresponding to coupling of the second radical center with the hydrogen selenyl radical. This was confirmed by Raney nickel deselenization of the entire reaction mixture and by the use of inert internal standards to ensure that all converted enone was accounted for.

Products of Trapping with Hydrogen Selenide in the Photochemical Cycloaddition Reaction between 2-Methylpropene and 2-Cyclopentenone. Irradiation of a benzene solution of hydrogen selenide (0.3 M), 2-methylpropene (1.35 M), and 2-cyclopentenone (0.1 M) with Pyrex filtered light from a medium pressure mercury lamp resulted in the formation of six photochemical products identified as **9** and **33**−**37** (Scheme 7). Based upon their structures, these correspond to trapping of the biradicals **38**−**41**, either by complete reduction by hydrogen selenide or by partial reduction of one radical site followed by disproportionation between the second radical site and the hydrogen selenyl radical produced in the first reduction step. The ratio of products **9** and **33**−**37** at 5% conversion of 2-cyclopentenone was determined to be 10.0:2.3:15.3:7.5:0.4:64.5, respectively; this indicates that their biradical precursors **38**, **40**, and **41** are formed in the ratio 35.1:0.4:64.5, respectively, and that biradical **39** is not an important intermediate.

Compounds **33** and **36** were recovered together as a 1:1.5 mixture. The low relative yields of these two compounds along with their chromatographic similarity precluded further separation. Their structures were, however, readily assigned from the NMR and GC-MS spectra of the mixture and, in the case of **33**, by hydrogenation to give **34**. The ^{13}C-NMR spectrum of **33** indicated the presence of two vinylic methines which places the double bond at either the 3- or 4-position of the cyclopentanone ring. In the ^{1}H-NMR spectrum these vinylic methines appeared as a two proton multiplet at 6.07 ppm; this indicates that the double bond is not conjugated with the carbonyl group and so places it at the 3-position of the cyclopentanone ring. The presence of the *tert*-butyl group in **36** was confirmed by the observation of an intense methyl signal and a quaternary carbon signal in the ^{13}C-NMR spectrum. The point of attachment of the *tert*-butyl group to the cyclopentanone ring was deduced from the multiplicities of the carbons adjacent to the carbonyl group in the ^{13}C-NMR spectrum.

The structures of **34** and **37** followed from the appearance of their ^{1}H-NMR spectra which exhibited the signals expected for the isobutyl side chain; the point of attachment of the isobutyl groups to the cyclopentanone rings was determined from the multiplicities of the carbons adjacent to the carbonyl groups.

The structure of compound **35** was deduced from the ^{1}H-NMR spectrum which showed signals for the isobutyl group and a one proton multiplet at 7.24 ppm assigned to the vinylic proton at the 3-position of the enone. The chemical shifts of the vinylic proton of 2-alkyl-2-cyclopentenones and 3-alkyl-2-cyclopentenones are characteristic; the 3-position proton appears downfield of 7 ppm, while the 2-position proton appears upfield of 6 ppm.[11]

The structure of **9** was determined by comparison of its ^{1}H-NMR, ^{13}C-NMR, and mass spectra with those of **9** formed in the photocycloaddition reaction performed in the absence of hydrogen selenide. It can be concluded that **9** produced in the presence of hydrogen selenide does not originate from disproportionation of biradical **38** (as it does in the absence of hydrogen selenide) but rather is formed by reduction of one radical center of **38** by hydrogen selenide followed by disproportionation between the second radical center and the hydrogen selenyl radical produced. This is because in the absence of hydrogen selenide **9** and **7** are both produced competitively from the common biradical precursor **38**; if **9** were being formed from

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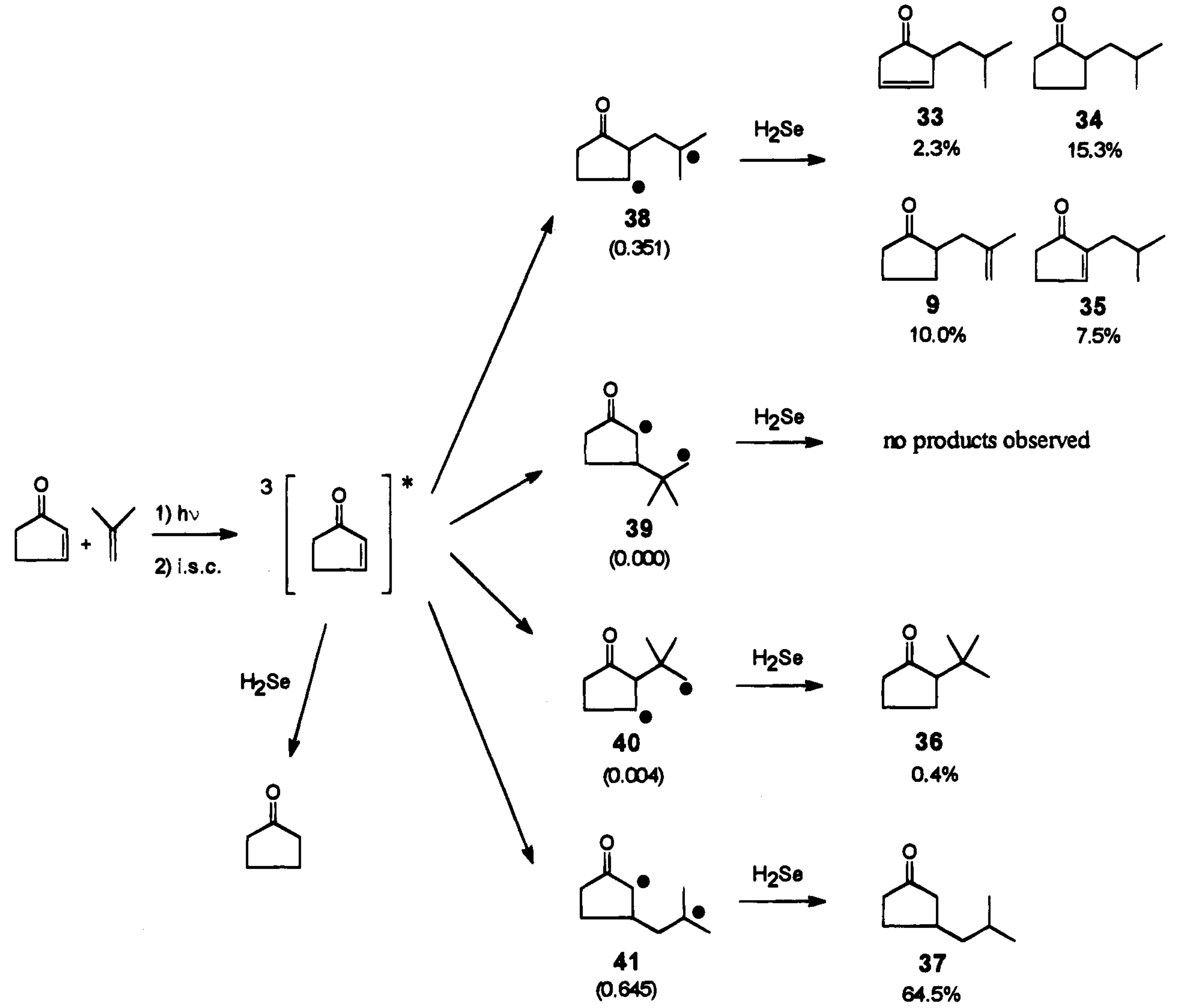
(11) Al-Jallo, H. N. A.; Waight, E. S. *J. Chem. Soc. B* **1966**, 73.

Scheme 7

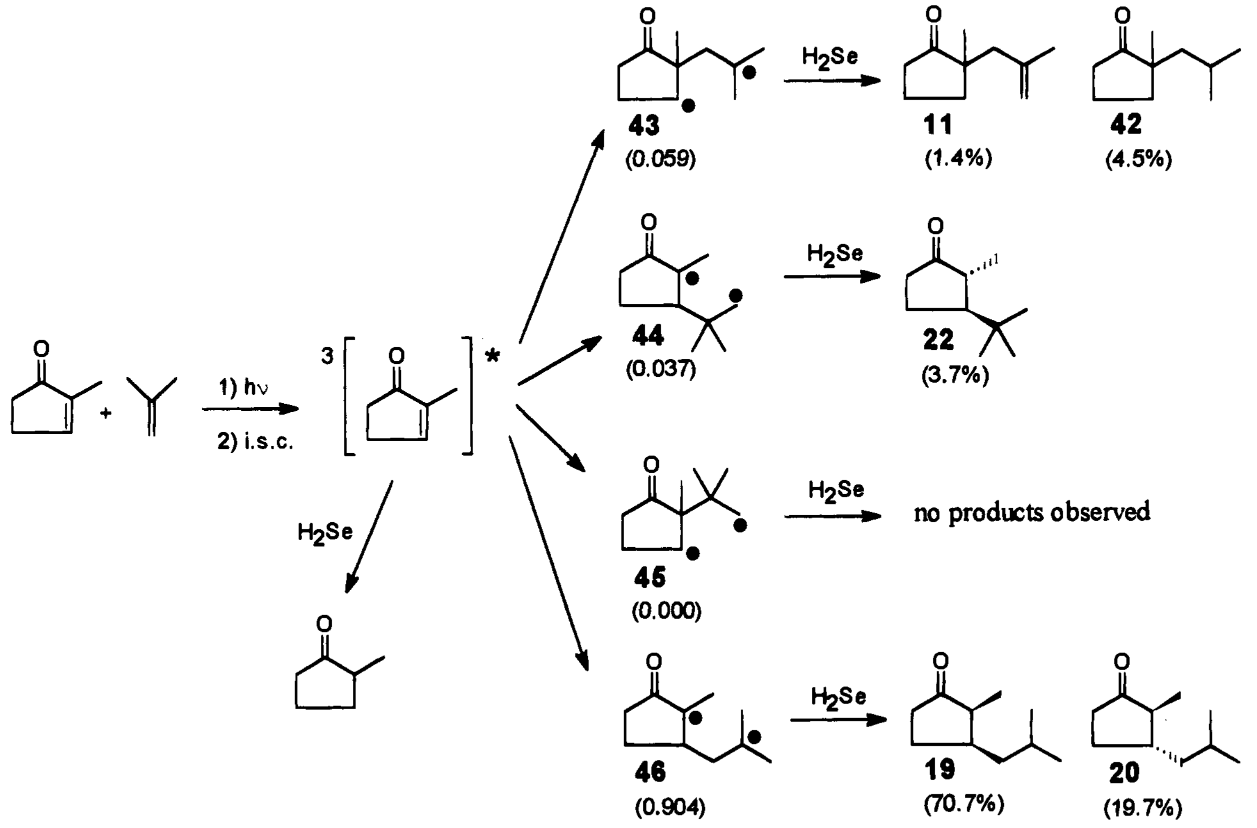


disproportionation of **38** in the presence of hydrogen selenide, then **7** should also be formed. Since it is not, **9** must originate from hydrogen selenide reduction of **38**.

Products of Trapping with Hydrogen Selenide in the Photochemical Cycloaddition Reaction between 2-Methylpropene and 2-Methyl-2-cyclopentenone. Irradiation of a benzene solution containing hydrogen selenide (0.30 M), 2-methylpropene (2.0 M), and 2-methyl-2-cyclopentenone (0.1 M) with Pyrex filtered light from a medium pressure mercury lamp resulted in the formation of the products **11**, **19**, **20**, **22**, and **42** in the ratio 1.4:70.7:19.7:3.7:4.5 (Scheme 8). This ratio was determined at 59% conversion of the 2-methyl-2-cyclopentenone, although only 4% of the enone had been converted to the trapped products; the remainder of the enone (i.e., 55%) had been converted to 2-methylcyclopentanone. The product ratio was not dependent upon the extent of enone conversion. No 2-methylcyclopentanone nor any of the trapped products were formed in reaction mixtures which were not exposed to ultraviolet light. The products **11, 19, 20, 22,** and **42** correspond to trapping of the biradicals **43, 44,** and **46**, and their ratio and structures indicate that biradicals **43, 44,** and **46** are formed in the ratio 5.9:3.7:90.4 as summarized in Scheme 8. The results indicate that biradical **45** is not an important intermediate in the reaction. Because of the apparent ease of interception of the triplet excited enone by the hydrogen selenide, it was not possible to perform preparative irradiations on a scale sufficient to allow isolation of the trapped products; however, an authentic sample of **11** was available from the photocycloaddition reaction of 2-methyl-2-cyclopentenone with 2-methylpropene in the absence of hydrogen selenide, while **19, 20, 22,** and **42** were available from the products of the same reaction. Thus **19** and **20** were obtained by hydrogenation and epimerization of **14**, and **22** was obtained by hydrogenation of **13** and **42** by hydrogenation of **11**. Using these independently synthesized samples the products of the reaction in the presence of hydrogen selenide were identified by GC coinjection and by comparison of their mass spectra obtained by coupled GC-MS. Even though **11** is also a product formed in the absence of hydrogen selenide, its presence in the trapping mixture does not represent a failure to trap all of the biradical intermediates. This is because **11** and **15** are both derived from the same biradical intermediate **43**; consequently, if not all of **43** were being trapped, then both **11** and **15** would be observed in the product mixture obtained in the presence of hydrogen selenide. However, none of **15** was formed when hydrogen selenide was present.

Products of Trapping with Hydrogen Selenide in the Photochemical Cycloaddition Reaction between 2-Methylpropene and 3-Methyl-2-cyclopentenone. The irradiation of a benzene solution containing hydrogen selenide (0.32 M), 2-methylpropene (1.9 M), and 3-methyl-2-cyclopentenone (0.11 M) with Pyrex filtered light from a medium pressure mercury lamp resulted in the formation of the products **25, 27, 28, 29,** and **47** in the ratio 5.6:4.9:13.5:5.5:70.5 (Scheme 9). As with the 2-methyl isomer considerable photoreduction of the enone

Scheme 8



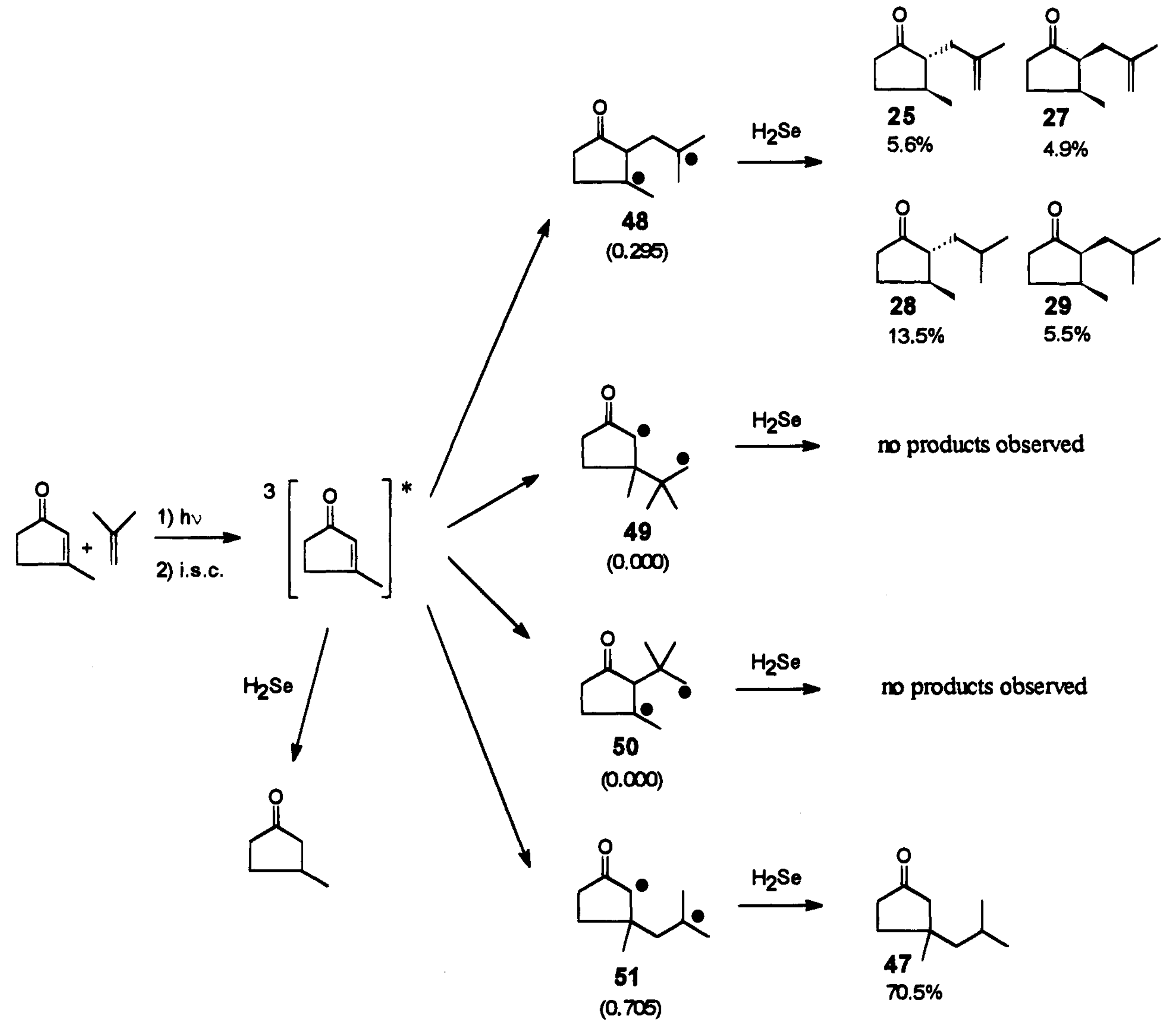
triplet occurred to give 3-methylcyclopentanone; at 32% conversion of 3-methyl-2-cyclopentenone 28% had been converted to the cyclopentanone and 5% had been converted to the trapped products. The products were identified by comparison (GC coinjection and identity of mass spectra) with **25**, **27**, **28**, **29**, and **47** obtained from the reaction of 3-methyl-2-cyclopentenone with 2-methylpropene performed in the absence of hydrogen selenide; these authentic samples were prepared by epimerization of **25** (to give **27**) followed by hydrogenation (to give **28** and **29**) and by hydrogenation of **26** (to give **47**). The relative yields of the trapped products indicate that their biradical precursors **48** and **51** are formed in the ratio 29.5:70.5 and that biradicals **49** and **50** are not important intermediates in the reaction.

Discussion

The structures and relative yields of the products of the photochemical reaction of 2-methylpropene with either 2-cyclopentenone, 2-methyl-2-cyclopentenone or 3-methyl-2-cyclopentenone in the absence of hydrogen selenide are summarized in Schemes 4–6; the product distributions indicate that intramolecular disproportionation of the intermediate triplet 1,4-biradicals is an important process in all three systems and that it increases in importance following methyl substitution on the cyclopentenone ring. The structures of the disproportionation products indicate that their biradical precursors are produced by bonding of both the 2- and the 3-position of the cyclopentenone ring to the alkene. The structures of the disproportionation products also indicate that, in the main, their biradical precursors are formed by attachment of the triplet excited enone to the less substituted end of the alkene; only one minor product (compound **13** from the reaction of 2-methyl-2-cyclopentenone) is observed which has its origins in a biradical resulting from attack at the more substituted end of the alkene. This does not, however, necessarily indicate that attack of the enone on the more substituted end of the alkene is an unimportant process since the resulting biradicals could indeed be formed but then either close to cycloadduct or revert to ground state precursors more rapidly than they undergo the disproportionation process. However, the hydrogen selenide trapping study shows that this is not in fact the case (*vide infra*). It would also appear from the product distribution in the absence of hydrogen selenide that methyl substitution on the enone ring increases the chemical yield of disproportionation products by sterically inhibiting closure to cyclobutane adducts (or possibly inhibiting fragmentation to ground state enone and alkene) rather than by offering an extra source of abstractable hydrogen for the disproportionation reaction. Thus biradical disproportionation products account for only 12% of the products in the 2-cyclopentenone reaction (i.e., **9** + **10** in Scheme 4); this increases to 31.8% in the 3-methyl-2-cyclopentenone reaction (i.e., **25** + **26** in Scheme 6), and none of the disproportionation involves the methyl substituent. With 2-methyl-2-cyclopentenone 46.8% of the products derive from disproportionation with slightly less than one quarter of these arising from disproportionation involving the methyl substituent (i.e., **11** and **12** *versus* **13** and **14** in Scheme 5).

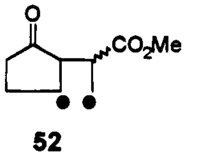
The relative yield and hence relative rates of formation of the triplet 1,4-biradical intermediates deduced from the hydrogen selenide trapping studies support some of these conclusions. The relative yields of the biradical intermediates, normalized to unity, are shown in Schemes 7–9. The structures and yields of the trapped products confirm that the biradicals are formed by bonding of the alkene to both the 2- and the 3-position of the enones and that bonding to the more substituted end of the alkene is a minor process. The data do not reveal whether this selectivity arises from steric causes (i.e., the bulk of the methyl groups directing the enone to the less substituted end of the alkene) or electronic factors (i.e., methyl group stabilization of the radical site forming on the alkene end of the biradical). A

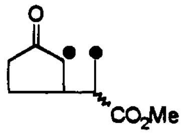
Scheme 9



surprising feature is the comparative lack of influence of the enone methyl substituent on the proportion of biradicals produced by bonding to each of the 2- and the 3-position of the enones. It might be expected that a methyl substituent on the enone would sterically inhibit alkene attack at its point of attachment and at the same time stabilize a developing radical center at the attached enone carbon resulting from alkene attack at the alternative enone carbon. This is not the case; with 2-cyclopentenone (Scheme 7) 64.5% of the biradicals result from bonding of the alkene to the 3-position, while with 3-methyl-2-cyclopentenone (Scheme 9) the figure is 70.5%. Only with 2-methyl-2-cyclopentenone is an effect seen; the proportion of biradicals arising from alkene attack at the 3-position rises to 94%. It has frequently been argued that the triplet excited state of an enone is a diradicaloid species which is twisted about the 2−3 positions;[2c,d] if it is assumed that in the twisted state the 2-position retains an sp^2 configuration because of conjugation with the carbonyl group and that the 3-position adopts an sp^3 configuration, then it is possible to rationalize the observation that the 3-methyl substituent does not perturb the relative rates of biradical production. A methyl group attached to a planar carbon at the 2-position would block the approach of an alkene terminus to the 2-position, while a methyl group attached to a tetrahedral carbon at the 3-position would offer less of a steric barrier to overlap of the partially occupied sp^3-like orbital with the incoming alkene π-orbital.

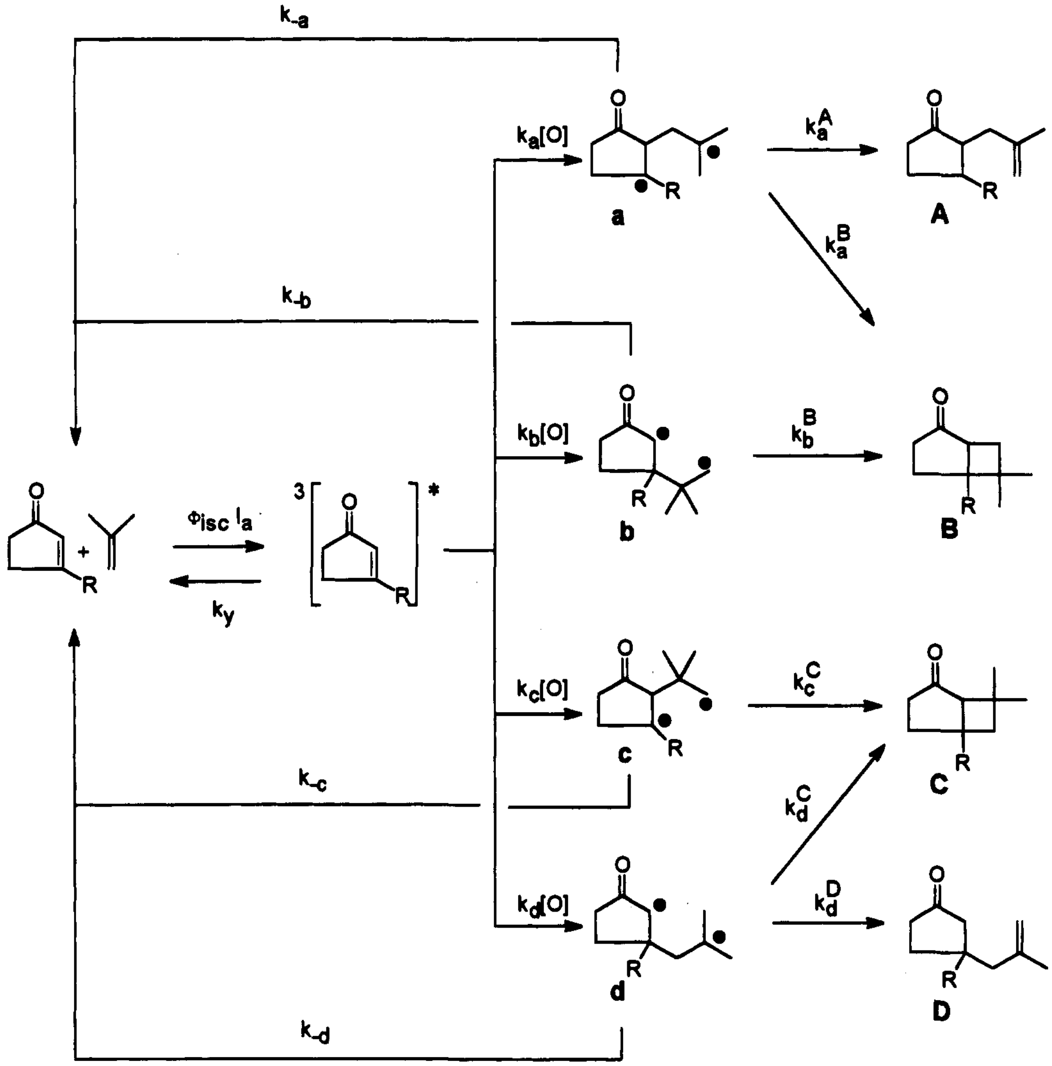
As noted above, with one minor exception the biradicals from the three enones studied do not result from attack on the more substituted end of 2-methylpropene. A similar result was obtained by us in the photocycloaddition reaction of cyclopentenone with ethoxyethene;[5f,8] however, with methyl acrylate we found that primary radical containing biradicals resulting from attack of the enone 2- and 3-position on the more substituted end of the alkene double bond (i.e., biradicals **52** and **53**) were important, product-forming intermediates.[5f] The reason for this is not obvious but may reflect the similarity of the triplet energies of the enone and the alkene.[12]


52


53

The regiochemical outcome of the photocycloaddition reactions of the three enones studied with 2-methylpropene in the absence of hydrogen selenide does not correlate with the distribution of their biradical precursors as determined by quantitative trapping with hydrogen selenide. For example, the cyclopentenone derived biradical **38** (Scheme 7), which leads to the head-to-tail cycloadduct **7**, is formed in 35.1% relative

Scheme 10



yield, but the products formed from this biradical which are isolated in the absence of hydrogen selenide (i.e., **7** and **9**) are formed in a combined relative yield of 72.4%; on the other hand, biradicals **40** and **41**, which lead to the head-to-head cycloadduct **8**, are formed in a combined relative yield of 64.9%, while the products produced from these biradicals in the absence of hydrogen selenide (i.e., **8** and **10**) are generated in a combined relative yield of 27.7%.

The discrepancy between relative product yields and relative biradical yields arises from the different extents to which each of the biradical intermediates partition between closure and disproportionation to give products and fragmentation to regenerate the ground state enone and alkene. It is possible to estimate the partitioning coefficients for each biradical by combining the relative yields of the intermediate biradicals obtained from the hydrogen selenide trapping experiments with the quantum yield data summarized in Figure 1 and Table 1. The methodology for achieving this is described below.

A kinetic mechanism which describes the addition of 2-methylpropene to a triplet cyclopentenone is shown in Scheme 10. In this scheme the various rate constants for the production and decay of the biradical intermediates and of the triplet excited state of the enone are defined. In addition, [O] is the concentration of 2-methylpropene, I_a is the light intensity, and Φ_{isc} is the quantum yield of intersystem crossing for conversion of the enone S_1 state to its T_1 state. This is assumed to be unity for all three enones studied.[4,13] In Scheme 10 the products and their biradical precursors have been relabeled **A**–**D** and **a**–**d**, respectively, in order to emphasize their relationships to the rate constants defined in Scheme 10 for their formation and decay. Application of the steady state approximation to the appropriate intermediates in Scheme 10 allows the derivation of a relationship between the quantum yield for formation of each product and the alkene concentration. For example, eq 1

$$\Phi_B = \Phi_{isc}\left[\left(\frac{k_a^B}{k_{-a} + k_a^A + k_a^B}\right)\left(\frac{k_a[O]}{(k_a + k_b + k_c + k_d)[O] + k_y}\right) + \left(\frac{k_b^B}{k_{-b} + k_b^B}\right)\left(\frac{k_b[O]}{(k_a + k_b + k_c + k_d)[O] + k_y}\right)\right] \quad (1)$$

shows the relationship between the quantum yield of formation of product **B**, Φ_B, and the rate constants for formation and decay of its possible biradical precursors **a** and **b**. Taking the reciprocal of eq 1, putting Φ_{isc} equal to unity and substituting $\varrho_a^\beta = k_a^B/(k_a^B + k_a^A + k_{-a})$, $\varrho_b^B = k_b^B/(k_b^B + k_{-b})$, $\alpha_a = k_a/(k_a + k_b + k_c + k_d)$, and $\alpha_b = k_b/(k_a + k_b + k_c + k_d)$, yields eq 2.

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(12) Weedon, A. C.; Wong, D. F. *J. Photochemistry* **1987**, *38*, 289.

(13) Wagner, P. J.; Bucheck, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 5090.

$$\frac{1}{\Phi_B} = \frac{1}{\varrho_a^B\alpha_a + \varrho_b^B\alpha_b} + \frac{k_y}{\varrho_a^B k_a + \varrho_b^B k_b}\cdot\frac{1}{[O]} \tag{2}$$

The terms $\varrho_i{}^I$ represent the fraction of biradical "i" which results in the formation of product "I", and the terms α_i represent the rate of formation of biradical "i" relative to the other three biradicals. A similar equation can be derived for Φ_C, the quantum yield of formation of the second cyclobutane adduct **C**. The analogous quantum yield expressions derived for the disproportionation products **A** and **D** are similar but simpler; this is because each result from the disproportionation of a single biradical. The relationship for **A** is shown in eq 3

$$\Phi_A = \Phi_{isc}\left(\frac{k_a^A}{k_{-a} + k_a^A + k_a^B}\right)\left(\frac{k_a[O]}{(k_a + k_b + k_c + k_d)[O] + k_y}\right) \tag{3}$$

and the reciprocal form obtained by substituting appropriate values of α_i and $\varrho_i{}^I$ and putting Φ_{isc} to unity is shown in eq 4.

$$\frac{1}{\Phi_A} = \frac{1}{\varrho_a^A\alpha_a} + \frac{k_y}{\varrho_a^A k_a}\cdot\frac{1}{[O]} \tag{4}$$

Relationships analogous to eqs 1–4 can also be derived for the products from the reaction of 2-methylpropene with 2-methyl-2-cyclopentenone and 3-methyl-2-cyclopentenone. The form of eqs 2 and 4 indicate that a plot of reciprocal quantum yield for each product against reciprocal alkene concentration should be linear; Figure 1 reveals this to be the case when the total product quantum yield (i.e., $1/(\Phi_A + \Phi_B + \Phi_C + \Phi_D)$) is plotted against reciprocal alkene concentration. The product distribution for each system was found to be independent of reactant concentration; consequently, linear correlations are also obtained when the inverse of individual product quantum yields are plotted against the inverse of alkene concentration. The gradients and intercepts of these plots are listed in Table 1.

For the reactions of 2-methylpropene with 2-cyclopentenone and with 3-methyl-2-cyclopentenone the quantum yield expression for Φ_B (eq 2), and the analogous expression for Φ_C, can be simplified since the primary radical containing biradicals **b** and **c** (Scheme 10) are not product forming intermediates. Consequently, in eq 2 the rate constant k_b is zero and the fraction of triplets forming biradical **b**, i.e., α_b, is also zero. In the analogous expression for Φ_C, k_c and α_c would be zero. This means that the intercept of the plot of Φ_B against $1/[O]$ becomes $1/\varrho_a{}^{\beta}\alpha_a$. The value of α_a is known since it is equal to the relative yield of biradical **a**, normalized to unity, as determined by the hydrogen selenide trapping experiment. Since α_a is known (the values of all α_i are summarized in Schemes 7–9), then $\varrho_a{}^B$ can be estimated. The fraction of biradical **a** disproportionating to product **A** (i.e., $\varrho_a{}^A$) and the fraction reverting to ground state enone and alkene (defined as ϱ_{-a}) can be calculated using the normalization relationship $1 = \varrho_a{}^A + \varrho_a{}^B + \varrho_{-a}$ and using the fact that the ratio $\varrho_a{}^A/\varrho_a{}^B$ is equal to the ratio of products **A/B** formed in the reaction. A value of $\varrho_a{}^A$ can also be calculated from the intercept of the plot of $1/\Phi_A$ against $1/[O]$ according to eq 4. In an analogous fashion values for $\varrho_d{}^C$, $\varrho_d{}^D$, and ϱ_{-d} can be obtained from the plots of $1/\Phi_C$ and $1/\Phi_D$. The calculated values of ϱ_{-i} and $\varrho_i{}^I$, expressed as percent, are summarized for the reactions of 2-cyclopentenone and 3-methyl-2-cyclopentenone in Scheme 11; figures in parentheses are for the methyl substituted enone. The quantum yields shown in Scheme 11 correspond to the inverse of the values of the intercept in eq 2 and the analogous equations for formation of **A**, **C**, and **D** and represent the quantum yields of product formation at infinite alkene concentration. Under these conditions all of the enone triplets are captured and converted to biradicals.[14]

The contribution of the biradicals containing primary radical sites to product formation was ignored in the kinetic analysis of the photocycloaddition reactions of 2-methylpropene with 2-cyclopentenone and 3-methyl-2-cyclopentenone. This assumption is valid because the trapping experiments demonstrated that the rates of formation of the primary radical containing biradicals **39, 40, 49,** and **50** were very slow compared to the rates of formation of the other biradicals. This is not the case in the photocycloaddition reaction of 2-methyl-2-cyclopentenone with 2-methylpropene. The primary radical containing biradical **44** (Scheme 8) is formed at a rate similar to that of biradical **43**. Therefore, the kinetic analysis of this photocycloaddition reaction must include the contribution of biradical **44** to product formation. Unfortunately, the inclusion of biradical **44** makes it impossible to obtain unique values of $\varrho_i{}^I$ for **43** and **44**; this is because it is not possible to determine how much of cycloadduct **15** (Scheme 5) results from closure of biradical **44** and how much results from of closure of biradical **43**. In terms of eq 2 this corresponds to the fact that the intercept contains two unknowns, $\varrho_b{}^B$ and $\varrho_a{}^B$. However, since the relative yields of biradicals **43** and **44** and of the products **11, 13,** and **15** are known it is possible to calculate the maximum and minimum proportions of biradicals **43** and **44** that can close to product, disproportionate, or fragment using the normalization relationship $1 = \varrho_{-i} + \varrho_i{}^I + \varrho_i{}^Y$. By this means it is possible to show that the product distribution obtained is only consistent with a limited range of biradical fates; these are shown in Scheme 12 for biradicals **43** and **44**, where the fraction x governing the partitioning of the biradicals could have a value anywhere from zero to 0.49. Thus, for example, between 0 and 49% of biradical **43** can close to **15** concurrent with closure of between 79 and 0% of biradical **44**. Determination of the actual value of x would require that either the biradical **43** or **44** be generated by an independant route and the ratio of products and of 2-methyl-2-cyclopentenone formed by its collapse determined. Scheme 12 also summarizes the fates of the biradical **46** that is formed in the addition of 2-methylpropene to 2-methyl-2-cyclopentenone. Since products **12, 14,** and **16** are formed from biradical **46** only and biradical **45** is not an important intermediate, the fates of **46** can be determined uniquely.

Equations 2 and 4 reveal that the rate constant for formation of each biradical relative to the rate constant for decay of the enone triplet, k_y, can be calculated from the slope/intercept ratio of the $1/\Phi$ versus $1/[O]$ plots. For example, the slope/intercept ratio for the linear relationship defined by eq 4 is $(k_y\alpha_a)/k_a$. By substituting the value for α_a determined from hydrogen selenide trapping it is possible to determine the ratio of k_y/k_a. The rates of biradical formation relative to the rates of decay of each triplet enone are shown in Schemes 11 and 12. The lifetime of the triplet excited state of 2-cyclopentenone in cyclohexane has been determined as a function of enone concentration using laser flash photolysis.[15] The lifetime is dependent on the unimolecular triplet decay rate constant and self quenching rate constant as defined by eq 5, where [E] is the enone concentration.

$$k_y = (5.4 \times 10^6\ \mathrm{s^{-1}}) + (5.9 \times 10^8\ \mathrm{M^{-1}\ s^{-1}})[E] \tag{5}$$

According to this equation, a 2-cyclopentenone concentration of 0.0401 M (the concentration used in the quantum yield

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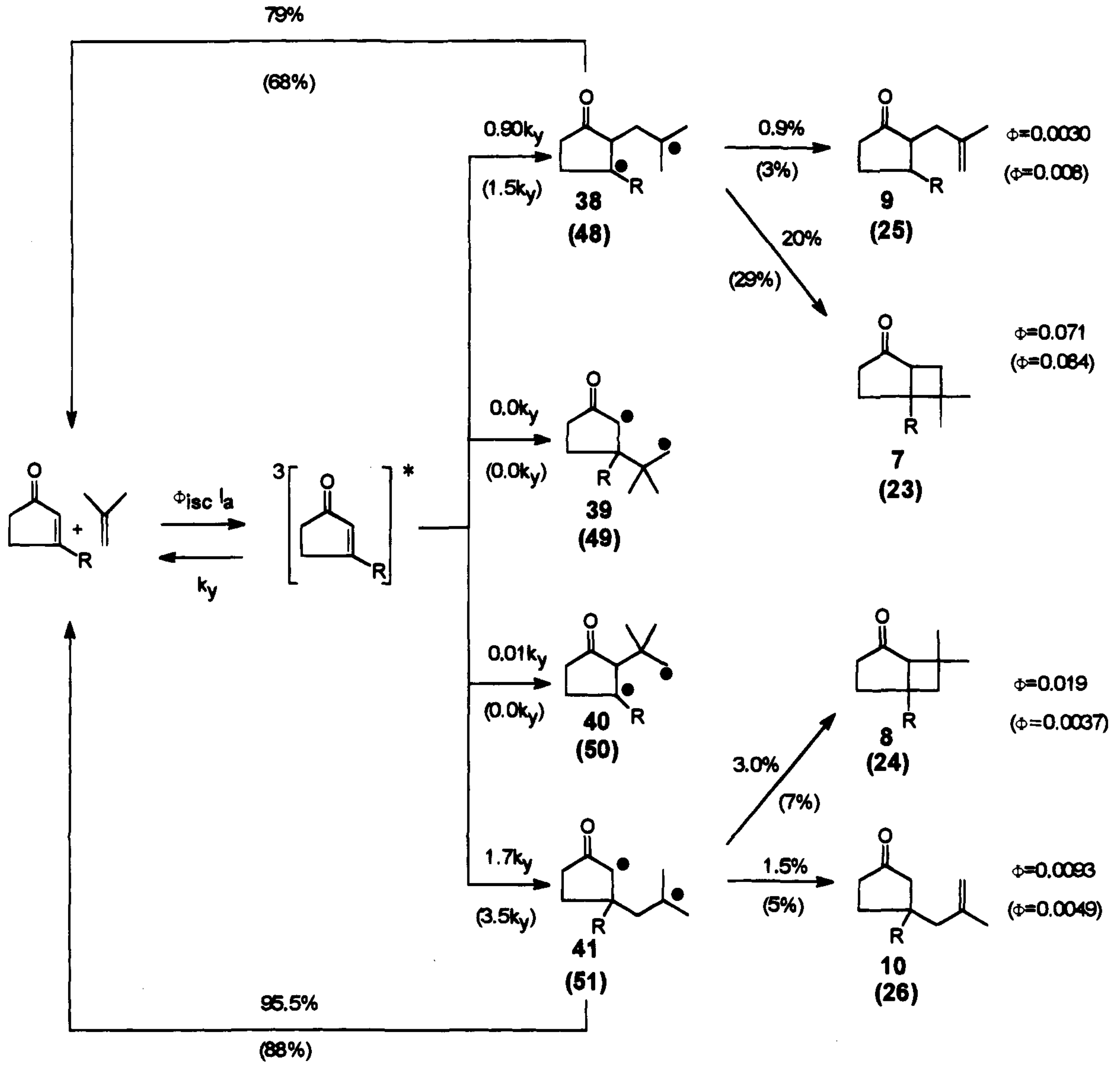
[14] The method of derivation of values of α_i and $\varrho_i{}^I$ assumes that in the presence of sufficient hydrogen selenide the sole routes for triplet decay are collapse to ground state enone, photoreduction to cyclopentanone, or formation of the trapped biradicals; it assumes that the triplets do not decay by formation of biradicals that are not only too short-lived to be trapped but also decay exclusively to ground state enone and alkene.

[15] Caldwell, R. A.; Tang, W.; Schuster, D. I.; Heibel, G. E. *Photochem. Photobiol.* **1991**, *53*, 159.

Scheme 11

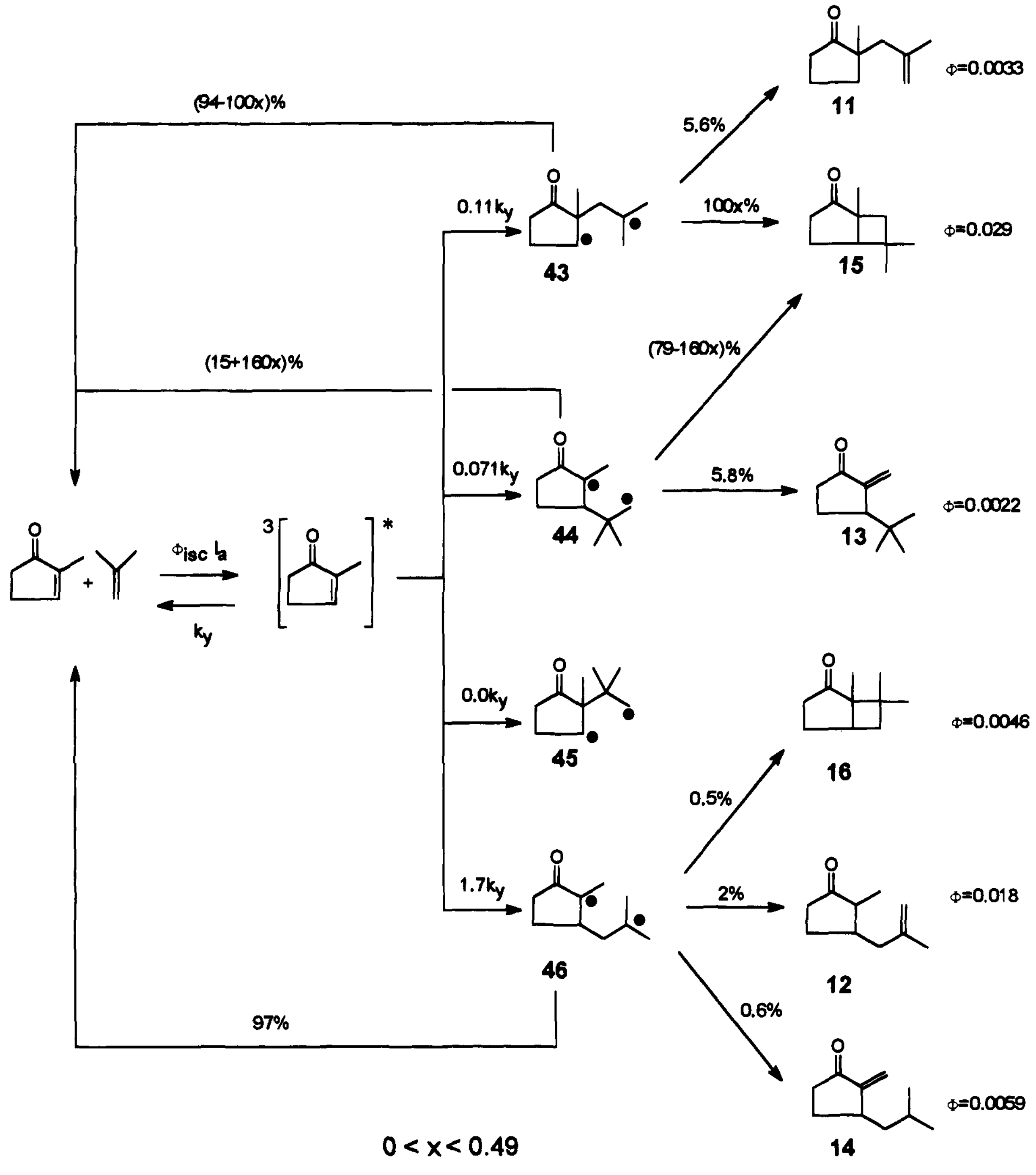


R = H (numbers in parentheses are for R = Me)

determinations in this work) results in an apparent first order rate constant of decay of 2.9 × 10^7 s^{-1} for the triplet enone. If this rate constant also holds true for benzene solutions of 2cyclopentenone, it can be used to determine the absolute values of the rates of formation of biradicals **38** and **41** since it is equal to k_y in Scheme 11. The values so calculated for the rate constants for formation of biradicals **38** and **41**, respectively, are 2.6 × 10^7 and 4.9 × 10^7 M^{-1} s^{-1}; it should be stressed, however, that these estimates of the rate constants are based on the assumption that the cyclopentenone triplet excited state lifetime is the same in both benzene and cyclohexane. The concentration dependencies of the triplet lifetimes of 2-methylcyclopentenone and 3-methylcyclopentenone have not been determined; therefore, absolute rate constants for the formation of the 1,4-biradicals generated in these systems could not be calculated.

Schemes 11 and 12 summarize the manner in which the biradicals produced in the photocycloaddition reaction of 2-methylpropene and the three enones studied partition between formation of products by closure and disproportionation and fragmentation to ground state enone and alkene. The partitioning properties of each biradical allow an assessment of the effect of the methyl substituents on the fates of the biradicals and reveal how the methyl groups influence the reaction regiochemistry and product distribution. The most obvious general conclusion that may be extracted from all the kinetic data presented in Schemes 11 and 12 is that the major products formed in each of the photocycloaddition reactions do not originate from the biradicals formed at the fastest rates. In each of the three photocycloaddition reactions studied, the biradical formed by initial bonding at the 3-position of the enone has the fastest rate of formation; however, these biradicals are responsible for the formation of the minor cycloaddition products. In the most extreme example, that of 2-methylcyclopentenone, 90.4% of the biradicals possess structure **46** which is responsible for the formation of the head-to-head cycloadducts; however, 97% of **46** reverts to the ground state enone and alkene so that only 3% of the isolated products are derived from **46**. With 2-cyclopentenone and 3-methyl-2-cyclopentenone the biradicals **41** and **51** which are responsible for head-to-head products, and which arise from bonding of the alkene to the enone 3-position, are formed in 64.5% and 70.5% relative yields; these fragment to enone and alkene in 95.5% and 88% yields, respectively. In contrast, at least for 2-cyclopentenone and 3-methyl-2-cyclo-

Scheme 12



pentenone, the biradicals formed by bonding of the alkene to the enone 2-position, **38** and **48**, which give rise to head-to-tail products, fragment to a lesser extent (79% and 68%), respectively, and so dictate the product regiochemistry, despite their being the minor biradicals in the reaction. Therefore, as we have concluded for other alkenes,[5e,f,8,9,16] the product distributions resulting from the reaction of 2-methylpropene with the three enones studied here are dominated by the way each biradical partitions between reversion to starting materials and disproportionation or closure to products.

Scheme 11 demonstrates that biradicals resulting from bonding of the alkene to the 3-position of the enone (i.e., **41** and **51**) revert to starting materials more efficiently than do those resulting from bonding to the 2-position (i.e., **38** and **48**). This may be because reversion is faster or because closure of **41** and **51** to a cyclobutane adduct is slower than for **38** and **48**. A possible explanation for this difference in rates is the configuration of the radical centers; in **38** and **48** the cyclopentyl radical center can possess sp^3 character, while in **41** and **51** it may be sp^2 hybridized and delocalized into the carbonyl group. Overlap of the isobutyl radical orbital with the cyclopentyl radical orbital to give cyclobutane adducts would be more readily achieved with the more localized sp^3 orbital of **38** and **48** than with the delocalized radical orbital of **41** and **51**.

The fates of the biradicals generated in the photocycloaddition reactions of 2-methylpropene with 2-cyclopentenone and with 3-methyl-2-cyclopentenone are surprisingly similar. The kinetic data presented in Scheme 11 indicate that the presence of the methyl group in biradicals **48** and **51** does not sterically hinder closure of these biradicals relative to closure of biradicals **38**

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Table 2. Quantum Yields of Product Formation at Various Alkene Concentrations for the Photocycloaddition Reactions of 2-Methylpropene with Each of 2-Cyclopentenone, 2-Methyl-2-cyclopentenone, and 3-Methyl-2-cyclopentenone in Benzene

cyclopentenone (0.0401 M)		2-methylcyclopentenone (0.0407 M)		3-methylcyclopentenone (0.0407 M)	
[alkene] (M)	Φ (±8%)	[alkene] (M)	Φ (±12%)	[alkene] (M)	Φ (±10%)
0.0803	0.0174	0.0848	0.00834	0.0800	0.0498
0.0944	0.0201	0.113	0.0122	0.115	0.0654
0.120	0.0249	0.204	0.0181	0.149	0.0800
0.171	0.0292	0.369	0.0263	0.244	0.0954
0.181	0.0337	0.725	0.0338	0.452	0.122
0.324	0.0443	1.266	0.0446	0.735	0.141
0.478	0.0609	2.525	0.0503	1.219	0.154
1.117	0.0814			2.557	0.160
1.973	0.0829				
2.401	0.0849				

and **41**; in fact, a slightly greater fraction of biradicals **48** and **51** close to form cycloadducts compared to biradicals **38** and **41**. The absence of a steric effect of the methyl group on the closure of the cyclobutane ring in **41** is not unexpected; however, steric inhibition of the closure reaction would be anticipated for **48** but is not seen. Arguably, this supports the idea that the radical center in the 3-position of the cyclopentyl ring adopts an sp^3 configuration since this could direct the methyl group away from the approaching isobutyl radical in the closure reaction of **48**. This interpretation is supported by comparison of the closure efficiency of **38, 48, 41,** and **51** with the pattern followed in the photocycloaddition reaction of 2-methylpropene with 2-methyl-2-cyclopentenone. In this reaction the methyl group clearly interferes with cyclobutane formation in biradical **46** since disproportionation products **12** and **14** are formed in preference to the cycloadduct **16** (the ratio of (**12** + **14**):**16** is ca. 5:1); in contrast, closure of biradical **48** to cyclobutane **23** is ten times more efficient than disproportionation to give **25**. In **46** the methyl group is attached to the sp^2 hybridized radical center and so inhibits approach of the isobutyl radical to a greater extent.

The triplet 1,4-biradical intermediates trapped in this work must undergo spin inversion to give the singlet 1,4-biradical before they can partition between closure to cyclobutane products, disproportionation to enone products, and fragmentation to ground state enone and alkene. The triplet 1,4-biradicals have been estimated to have a lifetime of the order of 50 ns[17,18] and so should be conformationally equilibrated. However, the singlet biradicals should be very short-lived and so would be expected to partition between closure, disproportionation, and fragmentation in a manner dependent on the conformation in which spin inversion occurred. If this is the case then it should be possible to interpret the propensity of the biradicals examined in this work to close or fragment in terms of the populations of the more stable conformations of the biradicals. A complicating factor is that spin inversion of the biradicals is itself conformation dependent so that the singlet 1,4-biradicals may in fact be formed from higher energy conformations of the biradicals. Examination of the likely stable conformations of the biradicals **43**–**46**, **38**–**41**, and **48**–**51** (estimated from both molecular models and molecular mechanics calculations) does not show any obvious correlation with the partitioning properties of the biradicals determined in this work. In order to probe this further we have examined the partitioning properties of the biradicals involved in the photocycloaddition reaction between 2-cyclopentenone and both *cis*- and *trans*-2-butene. Details of this work will be the subject of a future paper.

Conclusions

In the photochemical cycloaddition reaction of 2-methylpropene with 2-cyclopentenone and its 2-methyl and 3-methyl derivatives the major biradical intermediates are formed by bonding of the less substituted terminus of the alkene to both the 2- and the 3-position of the enone; the regiochemical outcome of the reaction is determined by the manner in which the isomeric biradical intermediates partition between products and starting materials and not by the relative rates of formation of the various biradicals. Therefore, it is not necessary to include an exciplex in the reaction mechanism to explain the reaction regiochemistry. With the exception of methyl acrylate (where attack of the enone at the more substituted end of the alkene is also observed), these results confirm our earlier findings concerning the structures and properties of the triplet 1,4-biradical intermediates involved in the photochemical cycloaddition reaction of cyclopentenones with other alkenes.[5e,f,8,9,16]

It is also concluded that a methyl substituent at the 3-position of the enone has little effect on the relative rates of formation of the various biradical intermediates, nor does it affect their partitioning properties. However, a methyl-substituent in the 2-position of the enone slows the relative rate of formation of biradicals in which the alkene is bonded to the enone 2-position and also inhibits closure to cyclobutane products of biradicals formed by bonding of the alkene to the 3-position of the enone. These results can be rationalized if it is assumed that in both the enone triplet excited state and in the biradicals odd electron spin density at the 2-position of the five-membered ring is located in a p-type orbital while odd electron density at the 3-position is located in an sp^3-type orbital.

Experimental Section

General Experimental Details. Cyclopentenone was prepared by singlet oxygen oxidation of cyclopentene using the method of Mihelich and Eickhoff and was purified by distillation (56 °C at 23 mm Hg).[19]

The grey selenium powder and aluminum powder used in the preparation of aluminum selenide were obtained from the Aldrich Chemical Company. The Al_2Se_3 was prepared by ignition of a mixture of Al and Se powder using a magnesium flare according to the literature method.[20] The Al_2Se_3 was ground to a powder and stored in a desiccator until required. ***ALUMINUM SELENIDE REACTS VIGOROUSLY WITH WATER TO PRODUCE HYDROGEN SELENIDE. HYDROGEN SELENIDE IS AN EXTREMELY TOXIC GAS. IT SHOULD BE GENERATED IN A WELL VENTILATED HOOD AND EXCESS GAS DESTROYED USING BLEACH SOLUTION.***

The 2-methylpropene, 2-methylcyclopentenone, and 3-methylcyclopentenone were obtained from the Aldrich Chemical Company. The two methylated enones were both distilled under reduced pressure prior to use. The 2-methylpropene was also distilled using a dry ice condenser.

Preparative irradiations were performed using water and Pyrex filtered light from a medium pressure mercury lamp. Solutions were purged with nitrogen prior to irradiation or addition of hydrogen selenide; irradiations were performed in closed vessels with nitrogen gas in the head space.

Irradiation of 2-Cyclopentenone with 2-Methylpropene. A solution of 2-cyclopentenone (2.42 g, 0.118 M) and 2-methylpropene (25 g, 1.78 M) in benzene (250 mL) was prepared. Addition of the 2-methylpropene was accomplished by condensing the alkene onto a

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dry-ice/acetone cold finger and allowing the condensate to drip into the preweighed, stirred benzene solution. The solution was transferred to an immersion well photochemical reactor and irradiated for 3.75 h with a 450 W Hanovia medium pressure mercury lamp fitted with a Pyrex filter and water cooling jacket. The relative product yields for **7**, **8**, **9**, and **10** were determined by GC at 5% conversion of cyclopentenone to be 69.5%, 18.6%, 2.9%, and 9.1%, respectively. After the 3.75 h irradiation period, GC analyses revealed that 47% of the cyclopentenone was converted to cycloadducts. The solvent was removed under reduced pressure, and the remaining concentrate (3.21 g) was separated into its components by silica gel column chromatography (190 g, 60–200 mesh silica gel, 95:5 (v/v) hexanes/diethyl ether solvent). The following fractions were obtained and analyzed by GC: I, 0.0503 g of **7** and **9** (2:1); II, 0.303 g of **7, 8** and **9** (1:1:7); III, 1.23 g of **8** and **9** (7:1); IV, 0.352 g of **8** and **10** (1:1). After collecting the four fractions described above, the column was flushed with methanol to yield 1.28 g of cyclopentenone.

Compounds **8** and **9** were purified further by performing thin layer chromatography on fractions II and III. After TLC, compounds **8** and **9** were obtained about in 90% and 85% purity. These were further purified by conversion to their DNP derivatives, chromatography and hydrolysis to regenerate the ketones. Further purification of fractions **7** and **10** was unsuccessful. Spectral data for compounds **7** and **10** were deduced by subtracting the spectra of **8** and **9** from the spectra obtained for fractions I and IV.

Preparation of 2,4-Dinitrophenylhydrazone Derivatives. A reagent solution was prepared by dissolution of 2,4-dinitrophenylhydrazine (2.0 g) in hot 85% phosphoric acid (50 mL). The solution was cooled, and 95% ethanol (50 mL) was added. This solution was filtered prior to use. Preparation of each DNP derivative was accomplished by treatment of the ketone with the DNP solution in the ratio 1 mmol of ketone to 10 mL of the reagent solution, heating the mixture, and recovering the crystalline product by filtration.

Regeneration of the ketone from the hydrazone derivative was accomplished by hydrolysis in the presence of excess levulinic acid (1:9 v/v water/levulinic acid). The aqueous reaction mixture was extracted with diethyl ether. The diethyl ether extracts were washed with 10% Na_2CO_3, dried over $MgSO_4$, and concentrated under reduced pressure to yield the original ketone.

For 7: ^{1}H NMR (300 MHz, in $CDCl_3$) δ 1.65 (dt, $J = 1.5$ Hz, $J = 0.75$ Hz, 3H), 1.7–2.5 (complex), 4.65 (mult, 1H), 4.72 (mult, 1H); ^{13}C NMR (75 MHz, in $CDCl_3$) δ 220.9 (C=O), 143.4 (C), 111.6 (CH_2), 47.3 (CH), 38.0 (CH_2, two signals), 29.3 (CH_2), 20.5 (CH_2), 21.9 (CH_3); mass spectrum (EI, 70 eV) *m*/*e* (%) 138(40), 123(10), 110(15), 95(30), 82(100); calculated M^+ for $C_9H_{14}O$ 138.1045 (found 138.1049).

For 8: ^{1}H NMR (300 MHz, in $CDCl_3$) δ 0.99 (s, 3H), 1.15 (s, 3H), 1.68 (dd, $J = 12.5$ Hz, $J = 5.9$ Hz, 1H, assigned Hc), 1.9–2.1 (mult partially overlapping Hb, 2H, assigned He), 2.09 (ddd, $J = 1.8$ Hz, $J = 12.5$ Hz, $J = 10.7$ Hz, 1H, assigned Hb), 2.18–2.32 (mult, 1H, assigned to one proton at Hf), 2.44–2.75 (complex, 3H, assigned to Hd, Ha and one Hf). In a lanthanide induced chemical shift ^{1}H NMR study, Hd was shifted away from the Hf and Ha protons and was observed as a doublet, $J = 1.8$ Hz, of quartets $J = 6 \pm 1$ Hz: ^{13}C NMR (75 MHz, in $CDCl_3$) δ 222.6 (C=O), 44.2 (CH), 39.3 (CH), 37.5 (CH_2), 37.4 (CH_2), 35.0 (C), 31.4 (CH_3), 24.3 (CH_3), 21.9 (CH_2); mass spectrum (EI, 70 eV) *m*/*e* (%) 138(4), 123(8), 109(2), 95(12), 83(100); calculated M^+ for $C_9H_{14}O$ 138.1045 (found 138.1048).

For 9: ^{1}H NMR (300 MHz, in $CDCl_3$) δ 0.89 (s, 3H), 1.21 (s, 3H), 1.69 (dd, $J = 7.3$ Hz, $J = 12.3$ Hz, 1H, assigned Hb or Hc), 1.8–2.4 (complex, 5H), 2.50 (ddd, $J = 19$ Hz, $J = 9.2$ Hz, $J = 12.2$ Hz, 1H, assigned to one H at Hf), 2.94 (quintet, $J = 7.5$ Hz, 1H, assigned Hd). In a lanthanide induced chemical shift ^{1}H NMR study the following additional resonance was resolved: a doublet with $J = 7 \pm 1$ Hz, assigned Ha: ^{13}C NMR (75 MHz, in $CDCl_3$) δ 221.6 (C=O), 55.4 (CH), 38.7 (CH_2), 37.9 (CH_2), 34.7 (C), 31.2 (CH_3), 29.9 (CH), 27.4 (CH_2), 25.1 (CH_3); mass spectrum (EI, 70 eV) *m*/*e* (%) 138(2), 109(4), 95(2), 83(100); calculated M^+ for $C_9H_{14}O$ 138.1045 (found 138.1041).

For 10: ^{1}H NMR (300 MHz, in $CDCl_3$) δ 1.64 (br s, 3H), 1.7–2.4 (complex), 4.61 (mult, 1H), 4.67 (mult, 1H); ^{13}C NMR (75 MHz, in $CDCl_3$) δ 219.3 (C=O), 143.5 (C), 111.5 (CH_2), 44.8 (CH_2), 43.7 (CH_2), 38.0 (CH_2), 34.7 (CH), 29.0 (CH_23), 22.2 (CH_3); mass spectrum (EI, 70 eV) *m*/*e* (%) 138(2), 123(3), 109(3), 95(8), 83(75), 82(35), 55(100); calculated M^+ for $C_9H_{14}O$ 138.1045 (found 138.1042).

Irradiation of 2-Methyl-2-Cyclopentenone with 2-Methylpropene. A solution of 2-methyl-2-cyclopentenone (2.017 g, 0.100 M) and 2-methylpropene (19.1 g, 1.62 M) in benzene (210 mL) was prepared. The solution was transferred to an immersion well photochemical reactor and irradiated with a 450 W Hanovia medium pressure mercury lamp which was fitted with a Pyrex filter and water cooling jacket. The reaction mixture was analyzed frequently by GC. The relative product yields determined at 3% conversion of the enone were 5.2%, 28.9%, 3.4%, 9.3%, 46.0%, and 7.3% for products **11, 12, 13, 14, 15,** and **16**, respectively. Compounds **17** and **18** began to appear at later irradiation times. The growth of **18** and **18** mirrored depletion of products **15** and **16** relative to the other products. Analysis of the irradiation solution by GC indicated that 65% of the enone was converted to products after 20 h. The relative product yields determined by GC at 65% conversion were 5.2%, 27.2%, 3.2%, 7.5%, 29.1%, 4.6%, 20.1%, and 3.1% for **11, 12, 13, 14, 15, 16, 17,** and **17,** respectively. After 20 h of irradiation the solvent was removed under reduced pressure to yield a yellow oil (2.78 g). The yellow oil was separated into its components by silica gel column chromatography (160 g, 60–200 mesh silical gel, 97:3 (v/v) hexanes/diethyl ether solvent). The following fractions were recovered and analyzed by GC: I, 0.418 g of **17** and **18** (1:7); II, 0.463 g of **18, 17, 16, 15, 11, 13, 14** (1:5:6:26:4:1:4); III, 1.073 g of **16, 15, 11, 12, 13,** and **14** (2:12:2:13:1:2); IV, 0.156 g of **15, 12, 13, 14** (3:18:1:1). The column was flushed with methanol in order to elute the unreacted enone (0.700 g of 2-methylcyclopentenone was recovered).

Preparative GC was performed on fractions I, II, III, and IV. Separation of compounds **17** and **18** in fraction I was unsuccessful. Fraction II was separated into four fractions (all of which were oils): IIa contained **17** and **18** (1:7); IIb contained **16, 15,** and **11** (1:7:1); IIc contained **13** and **14** (2:5); and IId also contained **13** and **14** (2:1). Fraction III was separated into two fractions (both of which were oils): IIIa contained **16, 15,** and **11** (3:29:1); IIIb contained **12, 13,** and **14** (15:1:2). Fraction IV was separated into two fractions (both of which were oils): IVa contained **15, 12, 13,** and **14** (1:5:1:2); IVb contained **12** with traces of **15**. Fraction IVb was used to obtain spectral data for **12**. Fraction IIIa was used to obtain NMR spectral data for **15**. The NMR spectral data for **13** and **14** were deduced from IIc and IId. Similarly, NMR spectral data were deduced for **16** and **11** from fractions IIb and IIIa by subtracting the signals due to **15**.

For 18: ^{1}H NMR (300 MHz, in $CDCl_3$) δ 1.03 (s, 6H), 1.47 (tt, $J = 1.2$ Hz, $J = 2.2$ Hz, 3H), 9.74 (t, $J = 1.8$ Hz, 1H), remaining protons obscured by **17** signals; ^{13}C NMR (75 MHz, in $CDCl_3$) δ 202.6 (HC=O), 146.0 (C), 132.9 (C), 43.2 (CH_2), 42.7 (CH_2), 40.7 (C), 24.5 (CH_3), 20.8 (CH_2), 18.9 (CH_3); mass spectrum (EI, 70 eV) *m*/*e* (%) 152(16), 137(4), 123(10), 119(8), 110(100), 109(40), 95(80), 81(52), 67(48).

For 17: ^{1}H NMR (300 MHz, in $CDCl_3$) δ 1.08 (s, 6H), 1.59 (quin, $J = 1.2$ Hz, 3H), 2.00 (mult 2H), 2.20–2.28 (t, $J = 7.5$ Hz, of mult $J < 1$ Hz, 2H), 2.4–2.6 (t, $J = 7.5$ Hz, of mult $J < 1$ Hz, 2H), 9.75 (t, $J = 1.8$ Hz, 1H); ^{13}C NMR (75 MHz, in $CDCl_3$) δ 202.5 (HC=O), 145.7 (C), 133.5 (C), 45.5 (CH_2), 41.8 (CH_2), 41.3 (C), 25.4 (CH_3), 18.4 (CH_2), 14.0 (CH_3). Mass spectrum (EI, 70 eV) *m*/*e* (%) 152(42), 137(64), 119(34), 110(32), 109(66), 95(88), 93(100), 81(90), 67(94).

For 16: ^{1}H NMR (200 MHz, in $CDCl_3$) δ 0.96 (s, 3H), 0.84 (s, 3H), 1.08 (s, 3H), remaining methine and methylene signals not identified due to overlapping signals of the other components of the mixture; ^{13}C NMR (75 MHz, in $CDCl_3$) δ 223.1 (C=O), 54.3 (C), 38.3 (CH), 38.1 (CH_2), 37.3 (CH_2), 35.6 (C), 26.5 (CH_3), 25.2 (CH_3), 25.0 (CH_2), 15.1 (CH_3); mass spectrum (EI, 70 eV) *m*/*e* (%) 152(1), 137(0.8), 125(2), 123(3), 97(100), 69(15), 68(20), 67(20).

For 15: ^{1}H NMR (200 MHz, in $CDCl_3$) δ 0.96 (s, 3H), 1.17 (s, 3H), 1.18 (s, 3H), 1.71 (AB with $J_{AB} = 12.5$ Hz, $\Delta\nu_{AB} = 14.2$ Hz or $\Delta\delta_{AB} = 0.071$ ppm), 1.8–2.4 (complex, 4H), 2.59 (ddd, $J = 10$ Hz, $J = 11$ Hz, $J = 19$ Hz, 1H); ^{13}C NMR (75 MHz, in $CDCl_3$) δ 223.8 (C=O), 49.9 (CH), 44.5 (CH_2), 42.6 (C), 37.1 (CH_2), 32.4 (CH_3), 31.6 (C), 24.6 (CH_3), 20.8 (CH_2), 20.5 (CH_3); mass spectrum (EI, 70 eV) *m*/*e* (%) 152(5), 137(5), 109(5), 97(100), 69(12), 68(12), 67(12).

For 11: ^{1}H NMR (300 MHz, in $CDCl_3$) δ 0.97 (s, 3H), 1.64 (br s, 3H), methylene region complex due overlapping signals from other components of the mixture, 4.66 (br s, 1H), 4.80 (mult $J \sim 1.5$ Hz, 1H); ^{13}C NMR (75 MHz, in CDCl$_3$) δ 224.6 (C=O), 142.4 (C), 114.8 (CH$_2$), 48.4 (C), 44.6 (CH$_2$), 37.4 (CH$_2$), 35.3 (CH$_2$), 24.2 (CH$_3$), 22.7 (CH$_3$), 18.6 (CH$_2$); mass spectrum (EI, 70 eV) *m/e* (%) 152(48), 137(12), 123(10), 110(5), 109(28), 96(52), 97(50), 81(100), 67(18).

For 12: ^{1}H NMR (300 MHz, in CDCl$_3$) δ 0.94 (d, $J = 6.7$ Hz, 3H), 1.61 (br s, 3H), 1.7−2.3 complex, 4.61 (mult $J < 1.0$ Hz, 1H), 4.64 (mult $J < 1.0$ Hz, 1H); ^{13}C NMR (75 MHz, in CDCl$_3$) δ 220.3 (C=O), 143.2 (C), 111.6 (CH$_2$), 50.0 (CH), 43.1 (CH$_2$), 42.3 (CH), 36.9 (CH$_2$), 27.0 (CH$_2$), 22.1 (CH$_3$), 12.5 (CH$_3$); mass spectrum (EI, 70 eV) *m/e* (%) 152(1), 137(1), 123(2), 97(100), 81(25), 69(65).

For 13: ^{1}H NMR (300 MHz, in CDCl$_3$) δ 0.91 (s, 9H), 5.34 (t, $J =$ 1.8 Hz, 1H), 6.12 (t, $J = 1.8$ Hz, 1H), 1.2−2.6 complex; ^{13}C NMR (75 MHz, in CDCl$_3$) δ 208.3 (C=O), 146.8 (C), 120.2 (CH$_2$), 60.6 (CH), 36.8 (CH$_2$), 33.9 (C), 27.5 (CH$_3$), 21.7 (CH$_2$); mass spectrum (EI, 70 eV) no parent ion peak, *m/e* (%), 137(10), 96(100), 57(90); mass spectrum (CI, isobutane) *m/e* (%) 153 (M$^+$, 90), 137(30), 109(10), 97(75), 96(100), 95(35), 68(40), 67(60).

For **14**: ^{1}H NMR (300 MHz, in CDCl$_3$) δ 0.92 (d, $J = 6.6$ Hz, 3H), 0.94 (d, $J = 6.6$ Hz, 3H), 5.20 (dd, $J = 0.9$ Hz, $J = 2.9$ Hz, 1H), 5.98 (dd, $J = 0.9$ Hz, $J = 2.6$ Hz, 1H), 1.2−2.7 complex; ^{13}C NMR (75 MHz, in CDCl$_3$) δ 207.6 (C=O), 149.7 (C), 116.2 (CH$_2$), 43.6 (CH$_2$), 39.0 (CH), 37.2 (CH$_2$), 26.6 (CH$_2$), 25.4 (CH), 23.6 (CH$_3$), 21.8 (CH$_3$); mass spectrum (EI, 70 eV) *m/e* (%) 152(2), 137(4), 110(20), 97(100), 96(30), 95(85), 81(40), 68(60), 67(40).

Irradiation of 3-Methyl-2-cyclopentenone with 2-Methylpropene. A solution of 3-methyl-2-cyclopentenone (2.601 g) and 2-methylpropene (20 g) in benzene (270 mL) was prepared. The solution was transferred to an immersion well photochemical reactor and irradiated with a 450W Hanovia medium pressure mercury lamp which was fitted with a Pyrex filter and water cooling jacket. The reaction mixture was analyzed frequently by GC. The relative product yields determined at 5% conversion of the enone were 20.8%, 4.5%, 47.4%, and 27.3% for products **24, 25, 23,** and **26,** respectively. Analysis of the irradiated solution by GC indicated that 69% of the enone was converted to products after 9 h. After irradiation the solvent was removed under reduced pressure to yield a yellow oil (3.65 g). The yellow oil was separated into its components by silica gel column chromatography (160 g, 60−200 mesh silica gel; 97:3 (v/v) hexanes/diethyl ether). The following fractions were recovered and analyzed by GC: I, 0.019 g of **24** and **25** (1:4.6); II, 0.23 g of **24** and **25** (1.4:1); III, 0.39 g of **24, 25, 23,** and **26** (10:1.4:1.4:1); IV, 1.58 g of **24, 23,** and **26** (1:3.5:2.2); V, 0.47 g of **23** and **26** (1.7:1); VI, 0.16 g of **23** and **26** (3:1). The column was flushed with methanol in order to elute the unreacted enone (0.78 g of 3-methylcyclopentenone was recovered).

Preparative GC was performed on fractions II, VI, and V in order to obtain enriched samples of **24, 25, 26,** and **23.** It was not possible to completely separate **26** from **23.** Using preparative GC fraction II was separated into two fractions: IIa contained **24** (with traces of **25**), and IIb contained **25** (92% pure with **24** impurity). Fraction VI was separated into two fractions: VIa contained **23** (contaminated with a trace of **26**), and VIb contained **23** and **26** (1:1.5). Fraction V was separated into two fractions: Va contained **23** and **26** (3:1), and Vb contained **23** and **26** (1.2:1). All fractions were isolated as oils.

For 24: ^{1}H NMR (200 MHz, in CDCl$_3$) δ 0.90 (s, 3H), 1.25 (s, 3H), 1.32 (s, 3H), 1.5−1.8 (mult, 2H, assigned to the two Hd protons), 1.84 (ABX pattern with $J_{AB} = 12.5$ Hz, $\Delta\nu_{AB} = 20.7$ Hz, $J_{AX} = 0$ Hz, $J_{BX} = 2.0$ Hz, $\delta_A = 1.89$ ppm, $\delta_B = 1.79$ ppm, B = Hb, A = Hc, X = Ha), 2.02 (brd s, 1H, assigned Ha), 2.32 (ddt, $J = 18$ Hz, $J = 8.9$ Hz, $J = 1.9$ Hz, 1H, assigned He or Hf), 2.52 (dddd, $J = 18$ Hz, $J =$ 12 Hz, $J = 8.9$ Hz, $J = 0.7$ Hz, 1H, assigned He or Hf); ^{13}C NMR (50 MHz in CDCl$_3$) δ 221.2 (C=O), 60.4 (CH), 45.1 (CH$_2$), 39.6 (CH$_2$), 36.6 (CH$_2$), 36.4 (C), 31.7 (CH$_3$), 31.6 (C), 27.9 (CH$_3$), 25.5 (CH$_3$); mass spectrum (EI, 70 eV) *m/e* (%) 152(3), 137(1), 109(5), 97(100), 83(50), 67(8).

For 25: ^{1}H NMR (300 MHz, in CDCl$_3$) δ 1.10 (d, $J = 6.1$ Hz, 3H), 1.66 (brd s, 3H), 1.6−2.5 (complex, 8H), 4.66−4.78 (mult, 2H); ^{13}C NMR δ (75 MHz, in CDCl$_3$) 220.9 (C=O), 143.5 (C), 112.4 (CH$_2$), 54.4 (CH), 37.7 (CH$_2$), 37.4 (CH), 37.1 (CH$_2$), 29.5 (CH$_2$), 22.3 (CH$_3$), 19.9 (CH$_3$); mass spectrum (EI, 70 eV) *m/e* (%) 152(15), 137(20), 110(100), 109(30), 97(60), 96(62), 95(50), 81(50), 67(30).

For 23 (NMR spectral data obtained from fractions Va, Vb, and VI): ^{1}H NMR (300 MHz, in CDCl$_3$) δ 0.98 (s, 3H), 1.05 (s, 3H), 1.10 (s, 3H), 1.58 (ddd, $J = 5.6$ Hz, $J = 10$ Hz, $J = 14$ Hz, 1H, assigned to one proton at Hd), 1.74 (dd, $J = 7.3$ Hz, $J = 11.9$ Hz, 1H, assigned to Hc), 2.00 (dd, $J = 10$ Hz, $J = 11.9$ Hz, 1H, assigned to Hb), 2.2−2.6 (Ha, Hc, Hf and one of Hd all overlapping; however, in the presence of Eu(fod)$_3$ the Hd proton was observed as a triplet of doublets, $J =$ 9.0 Hz, $J = 14$ Hz); ^{13}C NMR (75 MHz, in CDCl$_3$) δ 221.6 (C=O), 48.0 (CH), 46.6 (C), 39.1 (CH$_2$), 37.3 (C), 35.9 (CH$_2$), 30.1 (CH$_2$), 26.5 (CH$_3$), 23.0 (CH$_3$), 21.0 (CH$_3$); mass spectrum (EI, 70 eV) *m/e* (%) 152 (very weak), 137(2), 119(1.5), 109(4), 97(100), 81(20), 67(20); mass spectrum (CI, isobutane) *m/e* (%) 153(16), 137(2), 109(2), 97(100), 81(10), 67(10).

For 26 (NMR spectral data obtained from fractions Va, Vb, and VI): ^{1}H NMR (300 MHz, in CDCl$_3$) δ 1.03 (s, 3H), 1.75 (br s, 3H), 1.7−2.5 complex, 4.66 (d, J =2 .3 Hz, of quart, $J = 0.87$ Hz, 1H), 4.85 (d, $J = 2.3$ Hz, or quart, $J = 1.5$ Hz, 1H); ^{13}C NMR (75 MHz, in CDCl$_3$) δ 219.5 (C=O), 142.5 (C), 114.5 (CH$_2$), 52.5 (CH$_2$), 49.4 (CH$_2$), 39.6 (C), 36.5 (CH$_2$), 35.6 (CH$_2$), 25.2 (CH$_3$), 24.6 (CH)$_3$; mass spectrum (EI, 70 eV) *m/e* (%) 152 (very weak), 137(2), 123(2), 109(3), 97(90), 96(30), 81(10), 69(100); mass spectrum (CI, isobutane): m/e(%) 153(7), 137(4), 123(2), 109(4), 97(100), 81(12), 69(84).

Small Scale Irradiation of 15 and 16. Approximately 0.01 g of a mixture of **16, 15,** and **11** in a ratio of 3:29:1 was dissolved in 2 mL of benzene. To this solution was added 0.008 mg of decane (internal standard). The solution was then irradiated with the light from a 400 W Hanovia medium pressure mercury lamp fitted with a Pyrex filter and water cooling jacket. After 10 min of irradiation, the mixture was analyzed by GC. These analyses indicated that **18** and **17** were formed during the reaction. The ratio of **18:17:16:15:11** was 1.4:15:1.4:16:1.0 at 10 min. After 15 min of irradiation the ratio of the same compounds was 2.1:20:1:9:1. The ratio of the combined GC peak area of compounds **18, 17, 16, 15,** and 11 to the GC peak area of the internal standard did not change during the 15 min irradiation. Therefore, it was concluded that no other products were formed. It was also concluded that compound **16** forms **18** upon photolysis and **15** forms **17**.

Method of Hydrogenation of Unsaturated Compounds. An absolute ethanol solution (10 mL) containing approximately 0.01 g of 10% Pd on carbon catalyst was saturated with hydrogen gas. To this mixture, the compound containing the alkene functionality (approximately 0.010 g) was added. Hydrogen gas was bubbled through the mixture for an additional 15 min during which time periodic GC analyses were performed in order to monitor the growth of the saturated compound(s). The catalyst was removed by filtration and product analysis was accomplished by GC and coupled GC-MS. This general method was applied to compounds **9−14, 25,** and **26.** All mass balances were greater than 94%.

Method of Epimerization of Ketones. The starting ketone (approximately 0.075 g) was dissolved in methanol (10 mL) containing NaOH (0.5 mol/L). The reaction mixture was gently heated under reflux for 20 min after which time 20 mL of water was added. The mixture was extracted with diethyl ether (3 × 20 mL), washed with water (2 × 10 mL) and saturated NaCl/water (2 × 10 mL), and dried over MgSO$_4$. The resulting ether solution was subjected to GC and GC-MS analysis and then concentrated under reduced pressure. This general method was applied to compounds **28, 12, 20, 19, 22,** and **21.** All mass balances were greater than 96%.

Epimerization and Hydrogenation Results for 25. Epimerization of **25** resulted in formation of a 6.9:1 mixture of **25** and **27.** Hydrogenation of this mixture resulted in a 6.8:1 mixture of **28** and **29.** Hydrogenation of **25** resulted in formation of **28.** Epimerization of **28** resulted in formation of a 6.3:1 mixture of **28** and **29.** Compound **27** mass spectrum (EI 70 eV) was identical to that obtained for **25.** Compound **28** mass spectrum (EI, 70 eV) *m/e* (%) 154(8), 139(2), 125(5), 111(4), 97(100), 96(20), 83(10), 81(10), 69(20). Compound **29** mass spectrum (EI, 70 eV) *m/e* (%) 154(0.5), 123(1), 109(1), 97(100), 96(30), 81(14), 69(90).

Hydrogenation Results for 26. Hydrogenation of a 1.2:1 mixture of **23** and **26** resulted in the formation of a 1.2:1 mixture of **23** and the saturated analogue of **26,** which had mass spectrum (EI, 70 eV) *m/e* (%) 154(42), 139(10), 125(22), 111(18), 97(100), 96(70), 83(60), 69(80).

Hydrogenation Results for 11. Hydrogenation of a 1:7:1 mixture of **16**, **15**, and **11** resulted in formation of a 1:7:1 mixture of **16**, **15**, and the saturated analogue of **62**, which had mass spectrum (EI, 70 eV): parent ion not observed, *m/e* (%) 98(100), 83(20), 69(10); (CI, isobutane) *m/e* (%) 155(3), 111(2), 98(100), 83(15), 69(20).

Epimerization and Hydrogenation Results for 12. Epimerization of **12** resulted in formation of a 12:1 mixture of **12** and its *cis* diastereomer, which possessed a mass spectrum identical to that of **12**. Hydrogenation of this mixture resulted in a 12:1 mixture of **19** and **20**. Hydrogenation of **12** resulted in formation of **20**. Epimerization of **20** resulted in formation of a 13:1 mixture of **20** and **19**. Compound **19** mass spectrum (EI 70 eV) *m/e* (%) 154(50), 124(20), 111(18), 110(100), 97(55), 83(40), 69(60). Compound **19** mass spectrum (EI 70 eV) was identical to that obtained for **20**.

Epimerization and Hydrogenation Results of a Mixture of 13 and 14. Hydrogenation of a 1:2.5 mixture of **13** and **14** resulted in the formation of a 2.8:1.0:1.4:3.0 mixture (GC ratio) of **20**, **22**, **21**, and **19**, respectively. The ratio of **22** plus **21** to **20** plus **19** was determined to be 1:2.4 by GC. Epimerization of this mixture of four compounds resulted in a mixture containing **20**, **22**, and **19** in a 12:5.5:1 ratio. The ratio of **22**:**20** plus **19** in the epimerized mixture was therefore determined to be 1:2.4. The identity of **20** and **19** was confirmed by GC co-injection with authentic samples obtained from the hydrogenation followed by epimerization of **12**. Compound **22** mass spectrum (EI, 70 eV): m/e (%) 154(20), 139(4), 111(4), 110(4), 98(40), 97(55), 83(28), 69(20), 57(100). Compound **21** mass spectrum (EI, 70 eV) was identical to that obtained for **22**.

Hydrogenation of a 2:1 mixture of **13** and **14** resulted in the formation of a 1:1.9:2.3:1.2 mixture of **20**, **22**, **21**, and **19**, respectively. Epimerization of this mixture of four compounds resulted in a mixture containing **20**, **22**, and **19** in a 9:17:1 ratio.

Quantum Yield Measurements. All quantum yields were determined at ≤6% conversion of the enone using a PTI QUANTACOUNT instrument equipped with a high pressure 100 W mercury lamp. The light flux was calibrated using an azoxybenzene actinometer.[21] The absolute amount of cycloadducts formed in each irradiation was determined by GC analysis using decane as an internal standard. Calibration curves were constructed for the GC FID detector using pure samples of cycloadducts. It was assumed that regio- and stereoisomers of the photocycloaddition products had the same GC FID response factor. The samples were degassed by three freeze–pump–thaw cycles after which the residual pressure in each cell was below 2×10^{-4} mbar. In each irradiation, benzene was the solvent, and the excitation wavelength was fixed at 340 nm. The concentration of enone used in the cyclopentenone plus 2-methylpropene quantum yield determinations was 0.0401 mol/L. The concentration of enone used in the quantum yield determinations involving 2-methylcyclopentenone and 2-methylpropene was 0.0407 mol/L. The same concentration of enone was used in the quantum yield determinations involving 3-methylcyclopentenone and 2-methylpropene. The quantum yield measurements are summarized in Table 2.

Irradiation of 2-Cyclopentenone and 2-Methylpropene in the Presence of H_2Se. ***ALUMINUM SELENIDE REACTS VIGOROUSLY WITH WATER TO PRODUCE HYDROGEN SELENIDE. HYDROGEN SELENIDE IS AN EXTREMELY TOXIC GAS. IT SHOULD BE GENERATED IN A WELL VENTILATED HOOD AND EXCESS GAS DESTROYED USING BLEACH SOLUTION.*** A solution of 2-cyclopentenone (2.05 g, 0.100 M) and 2-methylpropene (19.5 g, 1.39 M) in benzene (250 mL) was prepared. Addition of the alkene was accomplished by condensation of the alkene on a dry-ice/acetone cold finger and dissolution of the condensate in the benzene solution containing the enone. Aluminum selenide (5 g) was placed in a separate flask fitted with a gas outlet and dropping funnel. A pipet was connected to the gas outlet of the flask containing Al_2Se_3, and its tip was submerged into the benzene solution. The benzene solution was chilled in ice water, and the entire system was flushed with nitrogen. Distilled water was added to the flask containing Al_2Se_3 at an initial rate of 1 drop per 20 s via the dropping funnel. The hydrogen selenide gas liberated was allowed to pass through the gas outlet and bubble through the benzene solution. After the first few drops of water had been added to the Al_2Se_3 powder, the rate of addition was increased until all of the Al_2Se_3 was consumed. An aliquot of the benzene solution was analyzed by ^{1}H NMR spectroscopy to check the concentrations of the volatile components: $[H_2Se] = 0.30$ M and [2-methylpropene] = 1.35 M. The benzene solution was placed in a quartz immersion-well reactor fitted with a water cooled lamp jacket. The solution was irradiation with a 450 W Hanovia medium pressure mercury lamp fitted with a Pyrex filter for 2 h. Aliquots were withdrawn every 15 min and analyzed by GC. The relative ratios of the recovered products were determined by GC at 5% conversion of cyclopentenone: **36**(0.40%), **33**(2.3%), **34**(15.3%), **9**(10.0%), **35**(7.5%), **37**(64.5%). Prolonged irradiation was not possible due to a build-up of elemental selenium on the lamp jacket. Subsequent GC analyses of similar irradiations carried out in the presence of a hydrocarbon standard (2-methylnonane) revealed that only 25% of the cyclopentenone was converted to trapped products under these conditions. An additional 30% of the cyclopentenone was converted to cyclopentanone, while approximately 45% was left unreacted. No cyclopentanone nor products identified as trapped biradicals were observed in reactions mixtures containing cyclopentenone, 2-methylpropene, and H_2Se that were not exposed to UV light. Separation of the reaction mixture after removal of the benzene solvent was accomplished by silica gel column chromatography in which a stationary phase consisting of 60–200 mesh silica gel and a mobile phase consisting of 97% hexanes and 3% diethyl ether (v/v) were employed. Chromatographic separation of the concentrate (2.53 g) resulted in the following fractions which were analyzed by GC: I, 0.012 g of **36** and **33** (1:1.5); II, 0.013 g of **36**, **33**, **34** (1:4:3.5); III, 0.041 g of **34**; IV, 0.145 g of **34**, **9** and **37** (1.5:1:1.7); V, 0.554 g of **37**; VI, 0.100 g of **37** and **35** (3.5:1); VII, 0.083 g of **37** and **35** (1:2). The NMR spectral data for **9** and **35** were deduced by subtracting the spectra of the mixtures IV and VII from the spectra obtained for **34** and **37**. The NMR spectra of compound **9** obtained in the trapping reactions were identical to the spectra of the same compound isolated from the reaction mixture resulting from the photocycloaddition of 2-methylpropene and 2-cyclopentenone in the absence of H_2Se.

For 36 and 33 (1:1.5 mixture): ^{1}H NMR (200 MHz, in $CDCl_3$) δ 0.88 (d, $J = 6.5$ Hz, 3H), 0.90 (d, $J = 6.5$ Hz, 3H), 0.96 (singlet, 9H), 1.1–2.9 (complex), 6.07 (m, 2H); ^{13}C NMR (50 MHz, in $CDCl_3$) δ 220.5 (C=O), 219.7 (C=O), 133.6 (CH), 127.1 (CH), 57.9 (CH), 50.5 (CH), 42.4 (CH_2), 40.3 (CH_2), 39.9 (CH_2), 32.5 (C), 27.7 (CH_3, very intense), 26.4 (CH_2), 26.1 (CH), 23.2 (CH_3), 22.0 (CH_3), 20.2 (CH_2); mass spectrum of **36** (EI, 70 eV) *m/e* (%) 140(15), 125(10), 97(10), 84(85), 78(100); mass spectrum of **33** (EI, 70 eV) *m/e* (%) 138(4), 123(55), 110(12), 95(42), 82(100), 81(5). Hydrogenation of the 1:1.5 mixture of **36** and **33** resulted in a 1:1.5 mixture of **36** and **34** (see method of hydrogenation below).

For 34: ^{1}H NMR (200 MHz, in $CDCl_3$) δ 0.87 (d, $J = 6.3$ Hz, 3H), 0.91 (d, $J = 6.3$ Hz, 3H), 1.4 to 2.4 (complex, 10H); ^{13}C NMR (50 MHz, in $CDCl_3$) δ 222.0 (C=O), 47.5 (CH), 38.9 (CH_2), 38.0 (CH_2), 30.1 (CH_2), 26.2 (CH), 23.3 (CH_3), 21.5 (CH_3), 20.8 (CH_2); mass spectrum (EI, 70 eV) *m/e* (%) 140(6), 125(5), 83(5), 84(100).

For 9 (data obtained from mixture described above): ^{1}H NMR (200 MHz, in $CDCl_3$) δ 1.65 (br s, 3H), 4.64 (multiplet, 1H), 4.70 (multiplet, 1H), remaining signals not identified due to overlap of **9**, **34**, and **37** resonances; ^{13}C NMR (50 MHz, in $CDCl_3$) δ 220.8 (C=O), 143.3 (C), 111.5 (CH_2), 47.2 (CH), 37.9 (CH_2, 2 signals), 29.3 (CH_2), 20.5 (CH_2), (CH_3) 22.0; mass spectrum (EI 70 eV) *m/e* (%) 138(4), 123(10), 110(20), 95(30), 83(5), 82(100). It was also determined that **9** hydrogenates to **34**.

For 37: ^{1}H NMR (200 MHz, in $CDCl_3$) δ 0.80 (d, $J = 6.6$ Hz, 6H), 1.22 (t, $J = 6.8$ Hz, 2H), 1.3 to 2.3 (complex, 8H); ^{13}C NMR (50 MHz, in $CDCl_3$) δ 219.5 (C=O), 45.2 (CH_2), 45.0 (CH_2), 38.3 (CH_2), 34.8 (CH), 29.6 (CH_2), 26.2 (CH), 22.7 (CH_3), 22.5 (CH_3); mass spectrum (EI, 70 eV) *m/e* (%) 140(50), 125(16), 111(40), 96(62), 83(100).

For 35 (data obtained from the mixture described above): ^{1}H NMR (200 MHz, in $CDCl_3$); δ 0.81 (d, $J = 6.6$ Hz, 6H), 1.75 (sept, $J = 6.7$ Hz, 2H), 1.99 (dd, $J = 6.8$ Hz, $J = 1.4$ Hz, 2H), 2.30–2.36 (mult, 2H), 2.48–2.56 (mult, 2H), 7.24 (tt, $J = 1.35$ Hz, $J = 2.5$ Hz, 1H); ^{13}C NMR (50 MHz, in $CDCl_3$) δ 209.9 (C=O), 158.3 (CH), 145.1 (C), 34.4 (CH_2), 33.8 (CH_2), 26.9 (CH), 26.3, 22.4 (CH_3); mass spectrum (EI, 70 eV) *m/e* (%) 138(80), 123(60), 96(100), 95(40), 81(8), 82(8), 83(5). It was also determined that **35** hydrogenates to **34**.

Small Scale Irradiation of 2-Methyl-2-cyclopentenone and 2-Methylpropene in the Presence of H_2Se. A solution of 2-methyl-2-cyclopentenone (0.10 mol/L) and 2-methylpropene (2.08 mol/L) in benzene (10 mL) was prepared. Addition of the alkene was accomplished by condensation of the alkene on a dry-ice/acetone cold finger and dissolution of the condensate in the benzene solution containing the enone. Hydrogen selenide gas was bubbled through this solution in exactly the same way as described above for the 2-cyclopentenone plus 2-methylpropene solution. An aliquot of the benzene solution was analyzed by ^1H NMR spectroscopy to check the concentrations of the volatile components: $[H_2Se] = 0.30$ mol/L and [2-methylpropene] = 2.0 mol/L. The benzene solution was placed in a Pyrex irradiation tube and irradiated with a 450 W Hanovia medium pressure mercury lamp fitted with a Pyrex filter for 3 h. After 3 h of irradiation only 4% of the 2-methylcyclopentenone was converted to trapped products; however, 55% of the 2-methylcyclopentenone was converted to 2-methylcyclopentanone. Prolonged irradiation was not possible due to a build-up of elemental selenium on the inside of the irradiation vessel. No 2-methylcyclopentanone nor products identified as trapped biradicals were observed in reaction mixtures containing 2-methylcyclopentenone, 2-methylpropene, and H_2Se that were not exposed to UV light. The following relative product yields were determined by GC after 3 h of irradiation: 4.5%, 1.4%, 70.7%, 3.7%, and 19.7% for compounds **42, 11, 19, 22,** and **20,** respectively. The identity of these trapped products was determined by GC co-injections with authentic samples obtained from the reactions described above.

Small Scale Irradiation of 3-Methyl-2-cyclopentenone and 2-Methylpropene in the Presence of H_2Se. A solution of 3-methyl-2-cyclopentenone (0.11 mol/L) and 2-methylpropene (2.21 mol/L) in benzene (10 mL) was prepared. Hydrogen selenide gas was bubbled through this solution in exactly the same way as described above for the 2-cyclopentenone plus 2-methylpropene solution. An aliquot of the benzene solution was analyzed by ^1H NMR spectroscopy to check the concentrations of the volatile components: $[H_2Se] = 0.32$ mol/L and [2-methylpropene] = 1.9 mol/L. The benzene solution was placed in a Pyrex irradiation tube and irradiated with a 450 W Hanovia medium pressure mercury lamp fitted with a Pyrex filter for 1 h. After 1 h of irradiation only 5% of the 3-methylcyclopentenone was converted to trapped products; however, 28% of the 3-methylcyclopentenone was converted to 3-methylcyclopentanone. Prolonged irradiation was not possible due to a build-up of elemental selenium on the inside of the irradiation vessel. No 3-methylcyclopentanone nor products identified as trapped biradicals was observed in reaction mixtures containing 3-methylcyclopentenone, 2-methylpropene, and H_2Se that were not exposed to UV light. The following relative product yields were determined by GC after 1 h of irradiation: 13.5%, 5.6%, 5.5%, 70.5%, and 4.9% for compounds **28, 25, 29, 47,** and **27,** respectively. The identity of these trapped products was determined by GC co-injections with authentic samples obtained from the reactions described above and comparison of the mass spectra using GC-MS.

Supplementary Material Available: Details of arguments used to make structural assignments from spectroscopic data (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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