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Regiochemistry and Stereochemistry of Intramolecular [2 + 2] Photocycloaddition of Carbon–Carbon Double Bonds to Cyclohexenones

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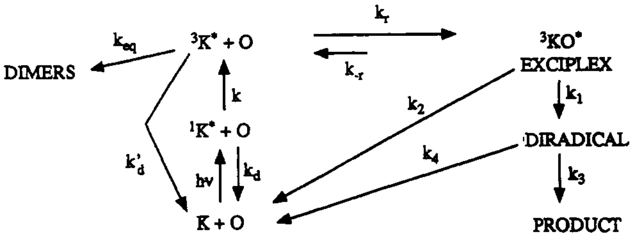
The intramolecular [2 + 2] photocycloaddition mechanism of alkenes tethered by a three-methylene chain to cyclohexenones has been studied. It was found that the reversion from a 1,4-diradical intermediate to starting material is slow relative to the rate of photoadduct formation. Only "straight" closure was observed in the systems studied. For compounds 1–3 and 5, the assumption that the first bond is formed between the β-carbon of the enone and C-4′ leading to a 1,4-diradical is supported. For the formation of compounds 6–11, possible mechanisms are discussed.

The mechanism and the synthetic potential of the [2 + 2] photocycloaddition have been studied for more than 30 years and have been reviewed lately.[1] The first mechanism, proposed by Corey[2] in 1964, was based on a careful study of the intermolecular photocycloadditions of carbon–carbon double bonds to cyclohexenone and was proposed primarily on the basis of product analysis and of preliminary studies of relative rates derived from competition experiments. This mechanism has been extended by De Mayo[3] as depicted in Scheme I, and the latter has been used frequently for analyzing experimental data. De Mayo's extension was supported by comprehensive kinetic studies of intermolecular photocycloadditions of olefins to cycloalkenones. The assumption that an exciplex is an intermediate in the reaction has been questioned lately by Schuster and Turro.[4]

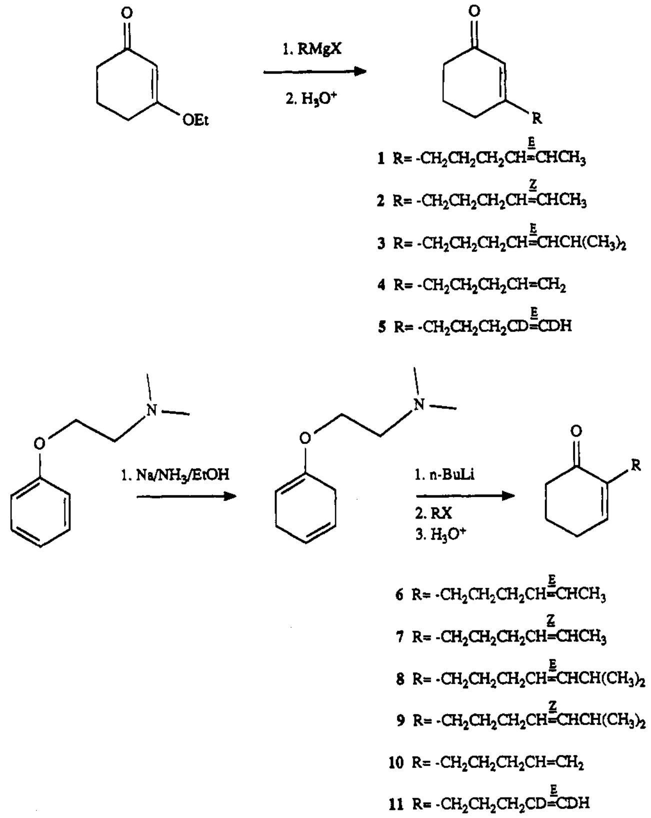
Another approach to obtaining information on the structure of the intermediates involved in the photocycloaddition was based on product analysis[5] of addition of *Z* or *E* olefins. In the case of intermolecular [2 + 2] photocycloaddition, de Mayo[3] found that the rate of cyclization from the diradical to product (k_3) is at least 10 times slower than the rate of its reversion (k_4) to starting materials. This reversion is not stereoselective, and hence isomerization of *Z* to *E* and vice versa must be very facile relative to the rate of adduct formation. For that reason any attempt to obtain information about the structure of the intermediates from product analysis using geometrical isomers cannot be conclusive.

Since it is known that intramolecular processes are more efficient than intermolecular reactions, we have undertaken a careful study of the intramolecular photocycloaddition of olefins to cyclohexenones. It was hoped that in such systems the ratio of product formation and reversion to starting materials would be large enough ($k_3/k_4 > 5$) to enable product analysis. The main goal was to obtain information about the order of bond formation by studying the stereochemistry of the photoadducts. It is important to note at this point that, parallel to our work, Agosta has carried out a thorough and fundamental study on the photochemistry of intramolecular photocycloadditions of 1,5-hexadienes[6a] and 1,6-heptadienes.[6b] However, the majority of his cycloalkenones were five-membered-ring compounds, whereas we have studied cyclohexenones.

Scheme I



Scheme II



Results

The first system studied had a propylenic chain attached at the β-carbon of the enone. Its synthesis by reaction of

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[1] (a) Schuster, D. I. *The Chemistry of Enones*; Rappoport, Z., Ed.; Wiley: New York, 1989; Part 2, pp 623–756. (b) Becker, D.; Haddad, N. *Organic Photochemistry*; Padwa, A., Ed.; Dekker Inc.: New York, 1989; Vol. 10, pp 1–162. (c) Crimmins, M. T. *Chem. Rev.* **1988**, *88*, 1453–1473.

[2] Corey, E. J.; Bass, J. D.; LeMahieu, R.; Mitra, R. B. *J. Am. Chem. Soc.* **1964**, *86*, 5570–5583.

[3] de Mayo, P.; Loutfy, R. O. *J. Am. Chem. Soc.* **1977**, *99*, 3559–3565.

[4] Schuster, D. I.; Heibel, G. E.; Brown, P. B.; Turro, N. J.; Kumar, C. V. *J. Am. Chem. Soc.* **1988**, *110*, 8261–8263.

[5] (a) Loutfy, R. O.; de Mayo, P. *Can. J. Chem.* **1972**, *50*, 3465–3471. (b) Pete, N. P.; Cargill, R. L.; Bushey, D. E. *J. Org. Chem.* **1973**, *38*, 1218–1221.

[6] (a) Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 1292–1299. (b) Matlin, A. R.; George, C. F.; Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 3385–3394.

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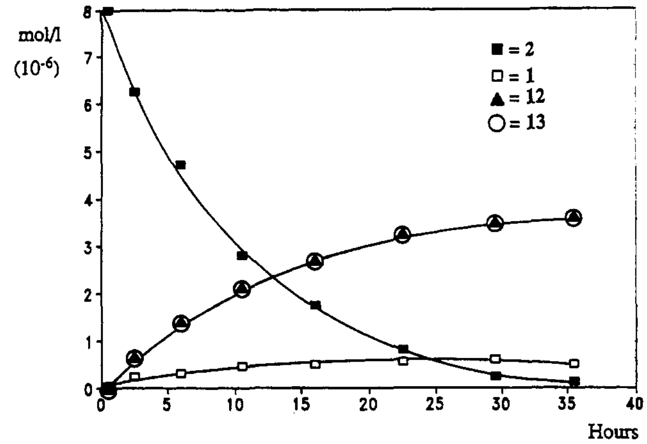


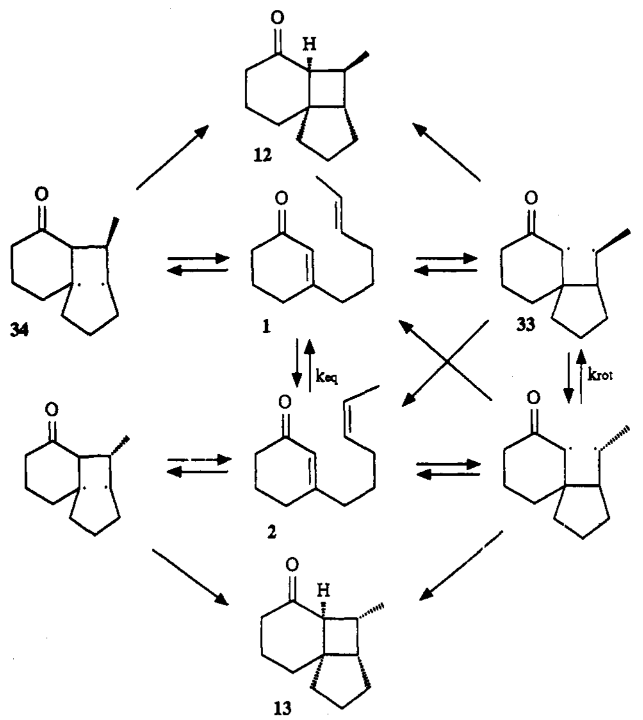
Figure 1. Irradiation of 2 in cyclohexane followed by UV spectroscopy and gas chromatography.

the corresponding Grignard reagent with the enol ether of 1,3-cyclohexanedione[7] followed by acid hydrolysis is shown in Scheme II.

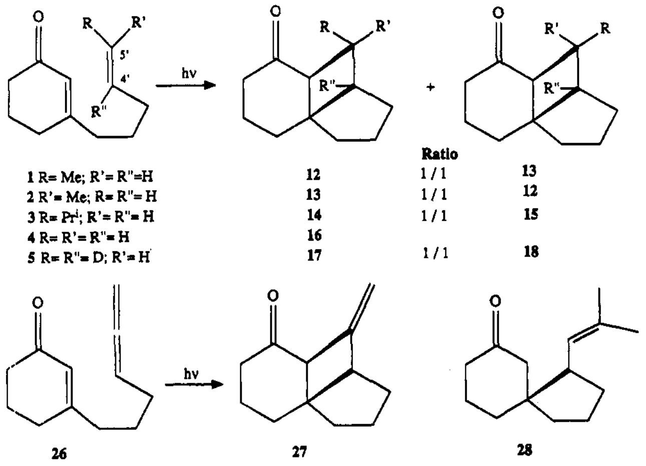
It was found that terminal olefin bonds add with very high regioselectivity and in excellent yield to give the "straight" photoadduct. While this work was in its preliminary stage, there was a brief report by Cargill[8] that 4 and 10 cyclize with high regioselectivity to give the "straight" photoadducts 16 and 23, respectively, in high yield. Encouraged by these results, we prepared the substituted compounds 1 and 2. Irradiation of either at $\lambda >$ 330 nm (uranium glass filter) in cyclohexane led in nearly quantitative yield to the same mixture of two stereoisomers 12 and 13 in a 1:1 ratio. The structures of these were established by comparison to material that had been prepared by an alternative route: intramolecular photocycloaddition of 26 to give 27, which was reduced to give both 12 and 13 in a 1:1.9 ratio.[9] In order to draw mechanistic conclusions from the fact that both geometrical isomers 1 (E) and 2 (Z) give the same photoadduct mixture, the possibility of fast equilibration between the Z and E isomers had first to be excluded. Both enones 1 and 2 were irradiated at $\lambda = 366$ nm in a UV cell, and the reaction was followed by UV and GC analysis. The results are represented in Figure 1 for 2; similar results were obtained for 1, which was found to react somewhat less efficiently.

It was also found that on irradiation (via a uranium filter) in a regular immersion reactor the isomerization from E to Z and vice versa is inefficient relative to the [2 + 2] photocycloaddition. The photoadducts were separated and irradiated for periods three times longer than required for cyclization (10 h) and found to be inactive photochemically. It can therefore be concluded that 12 and 13 are primary photoproducts and are produced in equal amounts. As can be seen in Figure 1, the isomerization of 2 to 1 is highly inefficient relative to the formation of the photoproducts 12 and 13. Thus, it can be concluded that the rate of cyclization is much higher than the rate of reversion of the diradical to 1 and 2, on the one hand, and on the other, that direct isomerization from 2 to 1 is negligible under these conditions ($k_{eq} \ll k_c$). In other words, the scrambling process from E to Z and vice versa, which had been found to be very facile in intermolecular photocycloadditions, hardly occurs in this system.

Scheme III



Scheme IV



The quantum yields for product formation were measured[10] and found to be 0.43, 0.55, 0.42, and 0.5 for 1, 2, 3, and 4,[7] respectively. The Stern–Volmer curve for 1 was studied by using di-*tert*-butyl nitroxide (DBN) in a concentration range 0–0.04 mol/L; a straight line was obtained. These data are in complete agreement with the assumption that a triplet intermediate is involved in the process. It is important to note that in this experiment also both products 12 and 13 were formed in a 1:1 ratio. (The results for the photoreactions of 1 and 2 are summarized in Scheme III.)

In order to study whether steric effects affect the 1:1 ratio in the photoadducts, compound 3 has been prepared and irradiated. Here both isomers 14 and 15 are formed in equal amounts, and isomerization from Z to E is also marginal in this compound. We have found that using the right kind of filter in these irradiations is crucial. Thus, if compound 3 is irradiated via a Pyrex and not a uranium filter, the main photoproduct is 28. Irradiation of the photoproduct mixture 14 + 15 via a Pyrex filter also gives

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[7] Conia, J. M.; Rouessac, F. *Bull. Soc. Chim. Fr.* **1963**, 1925–1928.

[8] Cargill, R. L.; Dalton, J. R.; O'Connor, S.; Michels, D. G. *Tetrahedron Lett.* **1978**, 4465–4466.

[9] Becker, D.; Harel, Z.; Nagler, M.; Gillon, A. *J. Org. Chem.* **1982**, *47*, 3297–3306.

[10] Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London* **1956**, *A235*, 518–536.

28 in good yield, and it can therefore be concluded that the latter is a secondary photoproduct. This type of rearrangement is well documented in the literature[11] for similar systems. (See Scheme IV.)

The next step was to minimize steric interference at the diradical stage and determine the effect of this on the ratio between the two stereoisomers. This has been achieved by studying compound **5**. In order to determine the ratio of photoadducts **17** and **18** which were formed on irradiation of **5**, the ^{2}H NMR spectrum was measured. The analysis was based on assignment of the chemical shifts of the relevant protons on the four-membered-ring in the unlabeled photoadduct **16** by applying modern NMR techniques (heteronuclear ^{13}C–^{1}H correlation, high-resolution COSY-45 and NOE). The ratio of **17** to **18** was determined to be 1:1 by integrating the corresponding absorptions in the ^{2}H NMR[12] spectrum. Compound **5** was irradiated as usual to 50% conversion, and a sample was analyzed by ^{1}H and ^{2}H NMR. No geometrical isomer of **5** could be detected. Hence, in this compound too, the rate of cyclization must be much faster than the rate of reversion of the diradical intermediate to the starting materials. It can be summarized at this point that in all four compounds **1**, **2**, **3**, and **5** the ratio of the stereoisomers in the photoadducts is 1:1. On this basis, it can be concluded that the first bond is formed to the β-carbon of the enone. Such preferential bonding is in full agreement with the "rule of five",[13] which predicts that a five-membered-ring diradical intermediate will be formed.

At this stage it was of interest to determine whether the "rule of five" would also control the bonding order in a model where the chain is tethered to the enone α-carbon. If so, then the first bond formed would be to the same α-carbon and proceed via a five-membered-ring diradical intermediate. Such a diradical would have to lead also to a mixture of two photoadducts. Alternatively, if the first bond were to be formed to the β-carbon of the enone, only one isomer could be expected, and the intermediate would not be the one predicted by the "rule of five". Obviously, the validity of the test would depend on whether the efficiency of cyclization from the diradical intermediate is much higher than the efficiency of its reversion to starting material.

Systems **6**–**11** were prepared by alkylation of a protected Birch reduction product with the corresponding alkenyl halide as shown in Scheme II.[14] On irradiation of **6** (*E*), the major photoadduct was **19** (95% yield) accompanied by less than 3% of its stereoisomer **20** as shown by GC analysis. The structure of **19** was established by careful NMR analysis (high-resolution COSY-45 and NOE). Following the course of this photocycloaddition process by both UV and GC established unequivocally that, in this system too, the efficiency of cyclization is at least 10 times that of reversion to the starting material; the results are represented in Figure 2. The fact that the ratio of **19** to **20** is 35:1 can be explained by assuming that in this system, too, the first bond is formed between C-5′ and the β-carbon of the enone (initial bonding 1,7). The possibility that initial bonding could be 1,7 in some heptadienes has been considered already by Agosta[6b] in order to explain his experimental results.

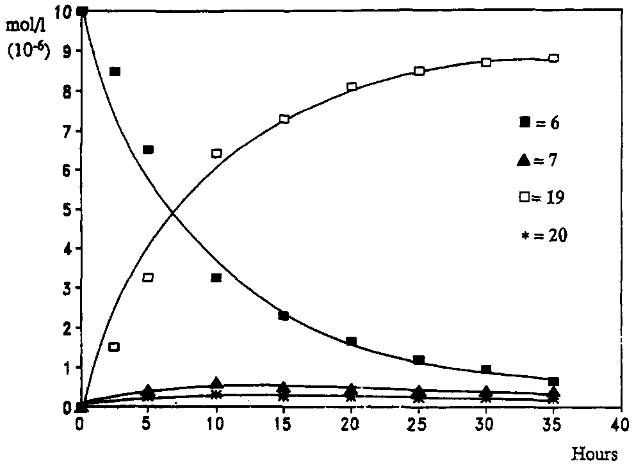
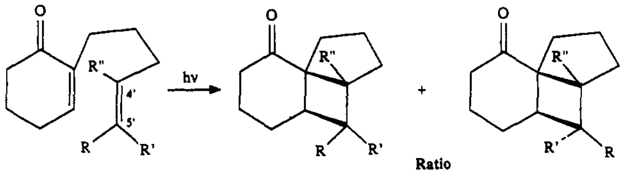


Figure 2. Irradiation of **6** in cyclohexane followed by UV spectroscopy and gas chromatography.

Scheme V



		Ratio	
6 R= Me; R'= R''= H	**19**	35 / 1	**20**
7 R'= Me; R= R''= H	**20**	1 / 5.8	**19**
8 R= Pr^{i}; R'= R''= H	**21**	3.8/ 1	**22**
9 R'= Pr^{i}; R= R''= H	**22**	1 / 1.4	**21**
10 R= R'= R''= H	**23**		
11 R= R''= D; R'= H	**24**	2 / 1	**25**

The next step was to irradiate the *Z* stereoisomer **7** and see whether **20** would be formed as the main photoadduct. In fact, two photoadducts **19** and **20** were formed in 95% yield, but surprisingly the ratio of **19** to **20** was found to be 5.8:1, respectively. Following the reaction by GC showed that the *E* isomer was formed slowly, to constitute up to 14% of the reaction mixture; but its formation cannot account for the formation of isomer **20**. Competition experiments demonstrated that the ratios of the quantum yields for product formation were close to 1 (the *Z* isomer reacted slightly more efficiently than the *E* isomer).

In order to determine the influence of steric effects on the ratio of the two stereoisomers, compounds **8**, **9**, and **11** were studied. The results are summarized in Scheme V, and they indicate that increasing steric hindrance by replacing a methyl substituent with isopropyl diminished the stereoselectivity. On irradiation of deuterium-labeled olefin **11**, a mixture of two stereoisomers was formed in a 2:1 ratio as was determined by ^{2}H NMR, applying the same procedure as was described for system **5**.[12] Compound **11** was irradiated as usual to 50% conversion; and the sample was then analyzed by ^{1}H and ^{2}H NMR. No geometrical isomer could be detected in the reaction mixture.

Discussion

The first step in the [2 + 2] photocycloaddition is excitation of the enone to the singlet state followed by fast intersystem crossing (ISC) to the triplet state. In the last decade, new techniques like laser flash[15] and time-resolved photoacoustic calorimetry[16] have been used extensively in

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[11] Hoye, T. R.; Martin, S. J.; Peck, D. R. *J. Org. Chem.* **1982**, *47*, 331–337.

[12] Becker, D.; Haddad, N. *Isr. J. Chem.* **1989**, *29*, 303–305.

[13] (a) Srinivasan, R.; Carlough, K. H. *J. Am. Chem. Soc.* **1967**, *89*, 4932–4936. (b) Liu, R. S. H.; Hammond, G. S. *J. Am. Chem. Soc.* **1967**, *89*, 4936–4944.

[14] Amupitan, J.; Sutherland, J. K. *J. Chem. Soc., Chem. Commun.* **1978**, 852–853.

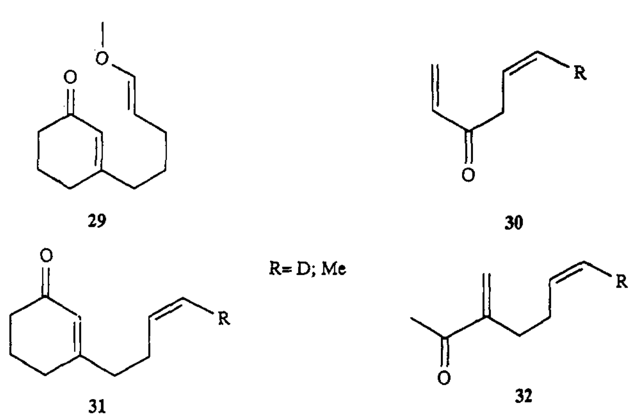
[15] Bonneau, R. *J. Am. Chem. Soc.* **1980**, *102*, 3816–3822.

[16] Ni, T.; Caldwell, R. A.; Melton, L. A. *J. Am. Chem. Soc.* **1989**, *111*, 457–464.

order to determine the physical and chemical properties of reactive intermediates in photochemistry. These studies indicate that simple cyclohexenones are twisted in their triplet state.[1a] However, whether this is the conformation of the reactive triplet state is not yet known. Lack of this kind of information is one of the main reasons for low predictability. Since it is accepted that [2 + 2] photoaddition is a stepwise process, one of the crucial questions is the sequence in which the two new σ-bonds are formed; in other words, what is the structure of the diradical intermediate? In some systems a structure for such an intermediate was proposed on the assumption that byproducts formed during the irradiation have a common intermediate with the [2 + 2] photocycloadducts. It is questionable whether this is justified. For intramolecular photocycloaddition the "rule of five" has been used frequently as a guideline for predicting the structure of the favored 1,4-diradical.[6a,b] The "rule of five" is a generalization made by Srinivasan[13a] and Hammond[13b] on the mode of addition, straight versus cross, for intramolecular photocycloaddition of 1,4-pentadienes, 1,5-hexadienes, and 1,6-heptadienes. The rule predicts that a five-membered diradical intermediate is the most favored one, because it is the most stable. The rule has lately received an alternative explanation by Gleiter[17] taking into consideration electronic and steric factors in the products and transition states.

Our first goal was to determine whether intramolecular [2 + 2] photocycloadditions carried out on *E* or *Z* olefins can provide information about the structure of the 1,4-diradical intermediates. It was found that, in the intramolecular [2 + 2] photocycloaddition, reaction of $C=C$ bonds attached by a trimethylene chain to cyclohexenone takes place with high regioselectivity and in very high yield. It was also found that the reaction is a very efficient one and that the quantum yields are of the order of 0.5. In order to draw any mechanistic conclusion from the structure of the photoadducts, the possibility of fast scrambling between two geometrical isomers had to be studied. In a preliminary publication,[18] we have described that in compounds **1**, **2**, and **3** the isomerization from *E* to *Z* and vice versa is inefficient relative to the rate of product formation. This was based on careful monitoring of the photochemical reaction by UV and GC. Since then, similar behavior has been found by Gleiter,[19] who studied the photocycloaddition of enol ether **29**, by Agosta[20] in 3-ketohexadienes **30**, and by us in compounds **5**–**9** and **11**. On the other hand Agosta has found that in both compounds **31** and **32** the *Z* to *E* conversion, probably via diradical reversion is very efficient relative to the rate of cyclization, and also that both stereoisomeric photoadducts were formed in a 1:1 ratio as soon as they were detectable by GC (<0.5%). At that stage of the reaction the concentration of the *E* isomer was determined to be less than 2%. Therefore predicting the efficiency for cyclization relative to the reversion process for a new system is not possible at this stage. (See Scheme VI.)

Scheme VI



Since the UV absorption spectra of **1** and **2** are identical in the wavelength range in which irradiations were carried out, and since the quantum yields of photoadduct formation are similar, it can be concluded that **12** and **13** are formed from the starting material and not from its geometrical isomer. As can be seen in Figure 1, the geometric isomer **1** is formed slowly in relation to product formation. This means that any process that could cause its formation, such as energy transfer from the enone or reversion of the diradical intermediate, is inefficient. Since the quantum yields for **1**, **2**, **3**, and **4** have been found to be in the range of 0.5, and the chemical yields for [2 + 2] photocycloaddition are higher than 90%, it can be concluded that the reaction path from the diradical intermediate to the adducts is a very efficient one. The fact that cyclization is very efficient in intramolecular photocycloadditions probably arises from the fact that the 1,4-diradical intermediate in the intra process has only 1 degree of freedom to rotate around a σ-bond and is kept by the five-membered spiro ring in the right position for cyclization once spin inversion from triplet to singlet has occurred. The observation that both stereoisomers were formed in a 1:1 ratio in all of the compounds studied so far can be accounted for the assuming a common 1,4-diradical intermediate that enables fast rotation. Lifetimes of triplet 1,4-diradicals in nonpolar solvents were determined by spectroscopic methods to be in the range of 10–100 ns.[21a,b] Experimental results obtained lately in our laboratory[21c] show that the lifetimes of a triplet 1,4-diradicals in systems studied by us are also of the order of nanoseconds. The factors that control the formation of diradical **33** rather than **34** (see Scheme III) can be similar to those that control the photocyclization of 1,5-dienes, the "rule of five", or alternatively a stereoelectronic effect that makes the β-carbon of the enone in the triplet excited state the most reactive center. The fact that the β-carbon in π–π^* triplet cycloalkenones is the reactive site in reactions like hydrogen abstraction is well documented in the literature.[22]

The possible importance of the second explanation was tested by studying systems in which the propyl chain was attached to the α-carbon of the enone. Our working hypothesis was based on the following assumptions: (1) if the formation of the first bond is determined by the "rule of five", two stereoisomers should be formed, because the 1,4-diradical intermediate enables fast rotation; (2) on the other hand, if the first bond is formed at the β-carbon, only one stereoisomer should be produced. In the event, it was found that on irradiation of **6** one main stereoisomer was

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(17) Gleiter, R.; Sander, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 566–568.

(18) Becker, D.; Nagler, M.; Hirsh, S.; Ramun, J. *J. Chem. Soc., Chem. Commun.* **1983**, 371–373.

(19) (a) Fischer, E.; Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 925–927. (b) Fischer, E. Ph.D. Thesis, 1988, Heidelberg.

(20) Schroder, C.; Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1987**, *109*, 5491–5497.

(21) (a) Caldwell, R. A.; Gupta, S. C. *J. Am. Chem. Soc.* **1989**, *111*, 740–742. (b) Johnston, L. J.; Scaiano, J. C.; Sheppard, J. W. *Chem. Phys. Lett.* **1986**, 493–498. (c) Becker, D.; Haddad, N.; Sahali, Y. *Tetrahedron Lett.* **1989**, *30*, 2661–2664.

(22) (a) Wolff, S.; Schreiber, W. L.; Smith, A. B., III; Agosta, W. C. *J. Am. Chem. Soc.* **1972**, *94*, 7797–7806. (b) Tobe, Y.; Iseki, T.; Kakiuchi, K.; Odaria, Y. *Tetrahedron Lett.* **1984**, *25*, 3895–3896. (c) Schuster, D. I.; Nunez, M. I.; Chan, C. B. *Tetrahedron Lett.* **1981**, *22*, 1187–1190.

formed in a ratio of 35:1; its stereochemistry can be explained by assuming parallel approach and formation of the first bond between C-5′ and the β-carbon of the enone. In this compound too we observed that conversion of the 1,4-diradical to the photoadduct is much more efficient than reversion to starting material (see Figure 2). Seemingly, the "rule of five" does not operate in this compound. Our results support Agosta's proposal[6b] that initial 1,7-bonding should be considered as an alternative to the "rule of five" in certain cases.

When **7** was irradiated, a mixture of two stereoisomers was formed in a 5.8:1 ratio. The main stereoisomer was found to be **19**, whereas initial bonding of the *Z* olefin to the β-carbon should have led mainly to the stereoisomer **20**. Although it was found that *Z* to *E* isomerization in compound **7** was more effective than in **6**, it never exceeded 14% of the starting material. It was ruled out, by low-conversion studies, that **19** could be formed from **6**, since the concentration of **6** at that stage of the process was very low. It should be emphasized that efficiencies of product formation from **6** and **7** are similar. The results on **8** and **9** showed a similar trend, in that the *E* olefin showed higher selectivity than the *Z*, but both have much lower stereoselectivity than the methyl-substituted olefin. Here, too, the major photoadduct of **9** had the same stereochemistry as the major photoadduct of **8**. In order to verify to what extent steric factors control the stereochemistry of the photoadducts, the deuterium-labeled olefin **11** was prepared and irradiated. It was determined by ^2H NMR that in this case, too, the isomerization is negligible relative to the cyclization process and the ratio of the two stereoisomers **24** to **25** is 2:1. This result emphasized the fact that, from one geometrical isomer **11**, two stereoisomers are formed.

In view of the results obtained for compounds **6**–**11**, careful analysis is needed in order to understand the factors that control the [2 + 2] photocycloaddition process. Assuming that preliminary bonding takes place between the α-carbon of the enone and the 4′-carbon, this would lead to a 1,4-diradical intermediate in which free rotation would be expected. Were this to be the case with **11** (H, D), then two stereoisomers could be expected in a 1:1 ratio, since steric effects are negligible. On the other hand, a steric effect might influence the ratio of **19** to **20**, but that effect should be identical for **6** and **7**, hence a common intermediate is expected. Our experimental results rule out this assumption, since **11** forms two stereoisomers in a 2:1 ratio and it was found that **6** led to different compositions of stereoisomers than **7**.

The fact that the deuterium-labeled compound **11** produced a mixture of two products in a 2:1 ratio suggests competition between preliminary bonding to the α-carbon and fast rotation before ring closure resulting in a 1:1 mixture, and formation of the first bond to the β-carbon which should produce **24** only. From the product ratio it can be calculated that the diradical which is formed by α-carbon bonding leads to products twice as fast as the diradical formed by bonding to the β-carbon. Applying this kind of analysis to compound **6** (*E*) will mean that first bonding to β-carbon is a dominant process. However, there is no way to explain the results obtained for **7** (*Z*) assuming a competition between the two possible bonding sites, without postulating that the 1,4-diradical intermediate cyclizes preferentially to **19**.

As things stand at present we cannot suggest one general mechanism for the intramolecular [2 + 2] photocycloaddition of C=C double bonds to cyclohexenones. It appears that for compounds **1**–**5** our results support strongly the assumption that the first bonding is between C-4′ and the β-carbon of the excited enone, which leads to a 1,4-diradical intermediate, as **33**. For compounds **6**–**11** the mechanism is far from clear, and the results are not consistent with one simple mechanism.

Experimental Section

General Data. Nuclear magnetic resonance spectra were obtained on a Bruker AM-400 400-MHz NMR instrument equipped with an Aspect 3000 computer, and on a Varian T-60 instrument. High-resolution MS were measured on a Varian MAT-711 instrument, and GC–MS on an HP 5890 instrument using a Carbowax capillary column (25 m, 0.25 mm). A Perkin-Elmer 298 instrument was used for IR. GC analyses were carried out on an HP 5890 instrument using the following columns: (a) Carbowax capillary column, 69 m, 0.25 mm; (b) OV1 capillary column, 50 m, 0.25 mm; (c) preparative column, 15% CW-20M, Gas-Chromosorb Q, 72–100 mesh, 4 m, 5/32 in.

Irradiations. Irradiations were carried out in cyclohexane as solvent under a nitrogen atmosphere. The commercial cyclohexane was purified by shaking with concentrated sulfuric acid and then with 10% sodium carbonate, irradiation through quartz using a 450-W Hanovia lamp for 4 h, and distillation. The photocyclizations were carried out in concentrations <0.05 mol by using a 450-W Hanovia lamp or an 80-W Hanau mercury vapor lamp (Q-81) with uranium ($\lambda > 330$ nm) or Pyrex ($\lambda > 295$ nm) glass filters. The photoreactions were followed by UV absorption of the starting material and/or GC analysis (columns a or b). Preparative GC was carried out by collecting the product in glass tubes, i.d. = 2 mm, using a gradient oven (200 °C to −170 °C); for our compounds it had an efficiency of >95%.

4-Hexyn-1-ol. Ohloff's[23] procedure was used for preparation of 4-hexyn-1-ol from tetrahydrofurfuryl chloride (12.05 g, 0.1 mmol), lithium amide (prepared from lithium, 2.14 g, 0.31 mmol) in 150 mL of liquid ammonia, and methyl iodide (17.1 g, 0.12 mmol). Aqueous 20% NH_4Cl (100 mL) was added, and the product was extracted with hexane (3 × 25 mL), washed with brine (15 mL) and aqueous 10% $AgNO_3$ (10 mL), and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the product was distilled (70–80 °C, 20 mmHg) to give 6.1 g of 4-hexyn-1-ol in 62% yield: IR ($CHCl_3$) 3600 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 3.53 (2 H, t), 1.8 (3 H, t).

(*Z*)-4-Hexen-1-ol. Reduction of 4-hexyn-1-ol (4.7 g, 48 mmol) was carried out in hexane (50 mL) by using Lindlar catalyst (100 mg) and H_2 (1 atm.). After 1 h, reaction was complete; the catalyst was filtered and the solvent removed to give 4.4 g of (*Z*)-4-hexen-1-ol in 92% yield: IR ($CHCl_3$) 3630 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 5.25 (2 H, m), 3.3 (1 H, s), 3.53 (2 H, t), 1.6 (3 H, d).

(*E*)-4-Hexen-1-ol. Campbell's[24] procedure was used for reduction of 4-hexyn-1-ol (4.0 g, 40 mmol) with Na (1.2 g, 52 mmol) in liquid ammonia (400 mL) to give 3.45 g of (*E*)-4-hexen-1-ol in 86% yield: IR ($CHCl_3$) 3640 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 5.35 (2 H, m), 4.0 (1 H, s) 3.5 (2 H, t), 1.7 (3 H, d).

7-Chloro-2-methyl-3-heptyne. To a suspension of $LiNH_2$ (Li, 2.4 g, 350 mmol) in liquid ammonia (250 mL) was added slowly 1,1-dichloro-3-methylbutane (14.1 g, 100 mmol) during 80 min. The reaction mixture was stirred for 1 h at −33 °C, and 1-bromo-3-chloropropane (18.9 g, 120 mmol) dissolved in THF (20 mL) was added. The cooling bath was removed, and the reaction mixture was kept at room temperature overnight. Water (100 mL) was added, the solvent was removed under reduced pressure, and the product was extracted with CH_2Cl_2 (3 × 25 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure to give 10.8 g of 7-chloro-2-methyl-3-heptyne in 75% yield; the product was used in the next step without further purification: ^1H NMR (60 MHz, CCl_4) δ 3.67 (2 H, t), 1.17 (6 H, d).

(*Z*)-7-Chloro-2-methyl-3-heptene. Reduction of 7-chloro-2-methyl-3-heptyne (0.9 g, 62 mmol) was carried out in methanol (10 mL) by using 5% $Pd/BaSO_4$ (0.35 g) and three drops of freshly distilled quinoline under H_2 (1 atm). The reaction was stopped after uptake of 1 equiv of hydrogen, the catalyst was filtered, and

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[23] Ohloff, G.; Vial, C.; Naf, F.; Pawlak, M. *Helv. Chim. Acta* **1977**, *60*, 1161–1174.

[24] Campbell, K. N.; Eby, L. T. *J. Am. Chem. Soc.* **1941**, *63*, 216–219.

the solvent was removed under reduced pressure to give 0.82 g of (*E*)-7-chloro-2-methyl-3-heptene in 90% yield: ^{1}H NMR (60 MHz, CCl_4) δ 5.12 (2 H, m), 3.6 (2 H, t), 0.97 (6 H, d).

(*E*)-6-Methyl-4-hepten-1-ol. 3-Chloro-2-(1-methylethyl)-tetrahydropyran (9.5 g, 58.6 mmol), prepared from 2,3-dichlorotetrahydropyran and isopropylmagnesium bromide, was converted into (*E*)-6-methyl-4-hepten-1-ol in 68% yield as described by Paul:[25] IR ($CHCl_3$) 3600 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) δ 5.38 (2 H, m), 3.5 (2 H, t), 0.97 (6 H, d).

(*E*)-4,5-Dideuterio-4-penten-1-ol. 4-Pentyn-1-ol (2.95 g, 35.1 mmol) was dissolved in dry benzene (70 mL) and reduced over Lindlar catalyst (150 mg) by using D_2 (1 atm). The reaction was followed by GC and was complete after 7 h. The catalyst was filtered, and the solvent was removed under reduced pressure to give 2.77 g of product in 90% yield: IR ($CHCl_3$) 3600 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.95 (1 H, m), 3.5 (2 H, t); ^{2}H NMR (400 MHz, C_6H_6) δ 5.67 (1 D, s), 4.91 (1 D, s).

(*E*)-1,2-Dideuterio-5-iodo-1-pentene. Iodination of (*E*)-4,5-dideuterio-4-penten-1-ol (0.5 g, 5.68 mmol) was carried out according to Garegg's[26] method. The product was chromatographed on a short silica gel column and eluted with hexane to give 0.52 g (43% yield) of (*E*)-1,2-dideuterio-5-iodo-1-pentene: ^{1}H NMR (60 MHz, CCl_4) δ 4.95 (1 H, m), 3.2 (2 H, t).

(*Z*)-6-Bromo-2-hexene. To a solution of (*Z*)-4-hexen-1-ol (0.7 g, 7.0 mmol) and triethylamine (1.2 mL, 8.4 mmol) in THF (14 mL) at 0 °C was added dropwise methanesulfonyl chloride (0.96 g, 8.4 mmol). The reaction mixture was stirred for 30 min at 0 °C and 30 min at room temperature and then quenched with H_2O (20 mL), and the solvent was removed under reduced pressure. The reaction mixture was extracted with CH_2Cl_2 (3 × 20 mL), washed with H_2O (20 mL), and dried over $MgSO_4$. The solvent was removed to give 0.87 g of crude mesylate, which was used in the next step without further purification.

To a solution of this mesylate (0.87 g) in THF (20 mL) was added LiBr (anhyhdrous, 1.2 g, 14 mmol), and the reaction mixture was refluxed for 4 h under N_2. After cooling to room temperature, H_2O (10 mL) was added and the solvent removed under reduced pressure. The organic materials were extracted with CH_2Cl_2 (3 × 15 mL), washed with H_2O (20 mL), and dried with $MgSO_4$, and the solvent was removed. The crude bromide was chromatographed over silica gel (eluent hexane) to give 0.68 g of (*Z*)-6-bromo-2-hexene in 60% yield: ^{1}H NMR (60 MHz, CCl_4) δ 5.25 (2 H, m), 3.28 (2 H, t), 1.58 (3 H, d).

(*E*)-6-Bromo-2-hexene. (*E*)-4-Hexen-1-ol (5.5 g, 55 mmol) was converted into the corresponding bromide as described for (*Z*)-6-bromo-2-hexene, in 55% yield: ^{1}H NMR (60 MHz, CCl_4) δ 5.35 (2 H, m), 3.3 (2 H, t), 1.5 (3, H, d).

(*E*)-7-Bromo-2-methyl-3-heptene. (*E*)-6-Methyl-4-hepten-1-ol (5.6 g, 44 mmol) was converted to the corresponding bromide as described for (*Z*)-6-bromo-2-hexene, in 58% yield: ^{1}H NMR (60 MHz, CCl_4) δ 5.3 (2 H, m), 3.3 (2 H, t), 0.95 (6 H, d).

3-[(*E*)-4-Hexenyl]-2-cyclohexen-1-one (1). Enone 1 was prepared by following Conia's procedure. A solution of 6-bromo-(*E*)-2-hexene (1.1 g, 6.7 mmol) in dry ether (20 mL) was added dropwise to magnesium (0.2 g, 8.2 mmol) at room temperature. The reaction mixture was stirred for 15 min, and 3-ethoxy-2-cyclohexen-1-one (0.94 g, 6.7 mmol) was added slowly to the Grignard reagent. After a 3-h reflux, the reaction mixture was cooled to room temperature and quenched with 1 N hydrochloric acid. The organic phase was separated, the water layer was extracted with ether (3 × 20 mL), the organic layers were combined, washed with water, and dried over magnesium sulfate, and the solvent was removed under reduced pressure to give 2 g of crude oil. This oil was chromatographed over silica gel (hexane:ether = 4.1) to give 0.95 g of pure 1 (80% yield): IR ($CHCl_3$) 1670 cm^{-1}; UV (hexane)λ_{max} = 227 (ϵ = 15000) nm; ^{1}H NMR (60 MHz, CCl_4) δ 5.8 (1 H, s), 5.41 (2 H, m), 1.6 (3 H, d). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 81.12; H, 10.16.

3-[(*Z*)-4-Hexenyl]-2-cyclohexen-1-one (2). A Grignard reagent was prepared from 6-bromo-(*Z*)-2-hexene and used as described for the preparation of 1, to give 2 in 83% yield: IR ($CHCl_3$) 1670 cm^{-1}; UV (hexane)λ_{max} = 227 (ϵ = 15000) nm; ^{1}H NMR (60 MHz, CCl_4) δ 5.8 (1 H, s), 5.4 (2 H, m), 1.6 (3 H, d). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.66; H, 10.18.

3-[6-Methyl-(*E*)-4-heptenyl]-2-cyclohexen-1-one (3). A Grignard reagent was prepared from 7-bromo-2-methyl-(*E*)-3-heptene, and the reaction mixture was refluxed for 4 h. The preparation followed the procedure for 1, to give 3 in 78% yield: IR ($CHCl_3$) 1670 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) δ 5.8 (1 H, br s), 5.4 (2 H, m) 0.97 (6 H, d, *J* = Hz); HRMS calcd for $C_{14}H_{22}O$ 206.1770, found 206.1745.

3-[4,5-Dideuterio-(*E*)-4-pentenyl]-2-cyclohexen-1-one (5). A Grignard reagent was prepared from (*E*)-1,2-dideuterio-5-bromo-1-pentene and was used as described for the preparation of 1. The yield of 5 was 75% after chromatography: IR ($CHCl_3$) 1675 cm^{-1}; UV (hexane)λ_{max} = 227 (ϵ = 15000) nm; ^{1}H NMR (60 MHz, CCl_4) δ 5.8 (1 H, s), 5.0 (1 H, m); HRMS calcd for $C_{11}H_{14}D_2O$ 166.1326, found 166.1322.

2-[(*E*)-4-Hexenyl]-2-cyclohexen-1-one (6). To a solution of 1-[2′-(*N*,*N*-dimethylamino)ethoxy]-1,4-cyclohexadiene (1.05 g, 6.1 mmol) in tetrahydrofuran (15 mL) and hexamethylphosphoramide (1.5 mL), at −78 °C, was added *n*-butyllithium (4.07 mL, 1.5 mol in hexane, 6.1 mmol) under N_2. After stirring for 0.5 h, 6-bromo-(*E*)-2-hexene (1 g, 6.1 mmol) was added and the reaction mixture was stirred for 20 min at −78 °C and 3 h at room temperature. Brine (10 mL) was added, and the solvents were removed under reduced pressure. The mixture was extracted with hexane (3 × 30 mL), washed with brine, and dried, and the solvent was removed to give 1.32 g (87% yield) of 2-[2′-(*N*,*N*-dimethylamino)ethoxy]-3-[(*E*)-4-hexynyl]-1,4-cyclohexadiene as a crude yellow oil: ^{1}H NMR (60 MHz, CCl_4) δ 5.58 (2 H, m), 5.31 (2 H, m), 4.7 (1 H, br s), 3.7 (2 H, t), 2.7 (2 H, t), 2.2 (6 H, s), 1.6 (3 H, br d). This oil was dissolved in acetone (40 mL), 2 N hydrochloric acid (20 mL) was added, and the solution was stirred vigorously at 50 °C for 2 h. Brine (40 mL) was added, the solvent was removed under reduced pressure, the product was extracted with methylene chloride (3 × 30 mL), the extract was washed with a 5% solution of sodium hydroxide, 5% HCl, and brine and dried, and the solvent was removed under reduced pressure. The crude oil was chromatographed over silica gel (eluent hexane:methylene chloride = 1:1) to give 0.685 g of 6 in 63% yield: IR ($CHCl_3$) 1680 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.6 (1 H, m), 5.31 (2 H, m), 1.61 (3 H, d); HRMS calcd for $C_{12}H_{18}O$ 178.1357, found 178.1373. Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 81.06; H, 10.24.

2-[(*Z*)-4-Hexenyl]-2-cyclohexen-1-one (7). Enone 7 was prepared from 6-bromo-(*Z*)-2-hexene in 68% yield as described for 6: IR ($CHCl_3$) 1680 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.6 (1 H, br t), 5.4 (2 H, m), 1.59 (3 H, d); HRMS calcd for $C_{12}H_{18}O$ 178.1357, found 178.1369. Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 81.06; H, 10.24.

2-[6-Methyl-(*E*)-4-heptenyl]-2-cyclohexen-1-one (8). Enone 8 was prepared from 6-bromo-2-methyl-(*E*)-3-heptene in 61% yield as described for 6: IR ($CHCl_3$) 1670 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) δ 6.6 (1 H, br t), 5.35 (2 H, m), 0.97 (6 H, d, *J* = 6 Hz); HRMS calcd for $C_{14}H_{22}O$ 206.1670, found 206.1626. Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.48; H, 11.00.

2-[6-Methyl-(*Z*)-4-heptenyl]-2-cyclohexen-1-one (9). Enone 9 was prepared from 6-bromo-2-methyl-(*Z*)-3-heptene in 60% yield as described for 6: IR ($CHCl_3$) 1665 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) δ 6.6 (1 H, br t), 5.24 (2 H, m), 0.97 (6 H, d, *J* = 6 Hz); HRMS calcd for $C_{14}H_{22}O$ 206.1670, found 206.1677.

2-(4-Pentenyl)-2-cyclohexen-1-one (10). Enone 10 was prepared from 5-bromo-1-pentene in 65% yield as described for 6: IR ($CHCl_3$) 1670 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) δ 6.59 (1 H, br t), 5.35 (1 H, m), 4.92 (1 H, d), 4.87 (1 H, d).

2-[(*E*)-4,5-Dideuterio-4-pentenyl]-2-cyclohexen-1-one (11). Enone 11 was prepared from 5-iodo-(*E*)-1,2-dideuterio-1-pentene in 70% yield as described for 6: IR ($CHCl_3$) 1670 cm^{-1}; UV (hexane)λ_{max} = 277 (ϵ = 15000) nm; ^{1}H NMR (400 MHz, C_6D_6) δ 6.15 (1 H, m), 5.0 (1 H, m); ^{2}H NMR (400 MHz, C_6D_6) δ 5.76 (1 D, s), 4.96 (1 D, s); HRMS calcd for $C_{11}H_{14}D_2O$ 166.1327, found 166.1355.

Irradiation of Enone Olefin 1. Enone 1 (0.10 g, 0.56 mmol) was dissolved in 150 mL of purified cyclohexane and irradiated

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[25] Paul, R.; Riobe, O.; Maumy, M. *Organic Syntheses*; Wiley: New York, 1988; Collect. Vol. VI, pp 675–678.

[26] Garegg, P. J.; Samuelsson, B. *J. Chem. Soc., Perkin Trans. 1* 1980, 2866–2868.

by a 450-W Hanovia lamp using a uranium glass filter under nitrogen. The reaction was followed by TLC and GC using column a; no starting material was detected after 2 h of irradiation. The solvent was removed at reduced pressure to give the photoadducts in 94% yield. The two isomers were separated by preparative GC, oven temperature 210 °C, to give 46 mg of **12** and 46 mg of **13**. **12**: IR ($CHCl_3$) 1690 cm^{-1}; ^1H NMR (60 MHz, C_6D_6) δ 0.916 (3 H, d, J = 6 Hz); HRMS calcd for $C_{12}H_{18}O$ 178.1358, found 178.1369. Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.59; H, 10.24. **13**: IR ($CHCl_3$) 1690 cm^{-1}; ^1H NMR (60 MHz, C_6D_6) δ 0.87 (3 H, d, J = 6 Hz); HRMS calcd for $C_{12}H_{18}O$ 178.1358, found 178.1364. Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.78; H, 9.96.

Irradiation of Enone Olefin 3. A solution of **3** (0.185 g, 0.9 mmol) in 150 mL of cyclohexane was irradiated as described for **1** to give a mixture of two photoadducts in a 1:1 ratio according to GC analysis on column a, in 90% yield: IR ($CHCl_3$) 1680 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.81 (6 H, d, J = 6 Hz); HRMS calcd for $C_{14}H_{22}O$ 206.1670, found 206.1676.

Irradiation of Enone Olefin 5. A solution of **5** (0.05 g, 0.3 mmol) in 28 mL of cyclohexane was irradiated by an 80-W Philips lamp via a uranium glass filter for 3 h under nitrogen. The solvent was removed under reduced pressure, and the oil was purified by preparative GC to give, in 92% yield, the photoadducts **17** and **18**: IR ($CHCl_3$) 1690 cm^{-1}; HRMS calcd for $C_{11}H_{14}D_2O$ 166.1326, found 166.1324.

Irradiation of Enone Olefin 6. Enone **6** (0.032 g, 1.8 mmol) was irradiated for 3 h as described for **5**. The reaction was followed by GC using column a; the photoadducts were isolated in 95% yield. Two products were identified, **19** and **20**, in a 35:1 ratio, respectively, by GC analysis on column a. **19**: IR ($CHCl_3$) 1680 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 1.07 (3 H, d, J = 6 Hz); HRMS calcd for $C_{12}H_{18}O$ 178.1357, found 178.1347. Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.77; H, 10.11.

Irradiation of Enone Olefin 7. Enone **7** (0.045 g, 0.25 mmol) was irradiated for 3 h as described for **5**. The reaction was followed by GC using column a; photoadducts **19** and **20** were formed in a 5.8:1 ratio and were isolated in 95% yield. Spectral data of the mixture: IR ($CHCl_3$) 1680 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ_{19} 1.07 (3 H, d, J = 6 Hz), δ_{20} 0.93 (3 H, d, J = 6 Hz). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.80; H, 10.13.

Irradiation of Enone Olefin 8. Enone **8** (0.029 g, 0.14 mmol) was irradiated for 4 h as described for **5**. The reaction was followed by GC using column b; photoadducts **21** and **22** were formed in a 3.8:1 ratio and were isolated in 90% yield. Spectral data of the mixture: IR ($CHCl_3$) 1680 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.90 (6 H, d, J = 6 Hz), 0.80 (6 H, d, J = 6 Hz). Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.51; H, 10.99.

Irradiation of Enone Olefin 9. Enone **9** (0.021 g, 0.1 mmol) was irradiated for 4 h as described for **5**. Photoadducts **21** and **22** were formed in 1.4:1 ratio, according to GC using column b, and isolated in 90% yield.

Irradiation of Enone Olefin 10. Enone **10** (0.142 g, 0.86 mmol) was irradiated as described for **1**, and a single photoadduct, **23**, was isolated in 95% yield: IR ($CHCl_3$) 1680 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 2.43 (1 H, m), 2.34 (1 H, m), 2.31 (1 H, m), 1.93 (2 H, m), 1.8–1.7 (2 H, m), 1.64 (1 H, m), 1.59–1.5 (2 H, m), 1.4–1.3 (5 H, m) 1.14 (1 H, m); HRMS calcd for $C_{11}H_{16}O$ 164.1201, found 164.1205.

Irradiation of Enone Olefin 11. Enone **11** (0.023 g, 0.14 mmol) was irradiated as described for **5**. The photoadduct was isolated in 92% yield: IR ($CHCl_3$) 1680 cm^{-1}; ^2H NMR (400 MHz, C_6D_6) δ 2.43 (1 D, s), 1.57 ($^2/_3$ D, s), 1.32 ($^1/_3$ D, s); HRMS calcd for $C_{11}H_{14}D_2O$ 166.1327, found 166.1310.

Supplementary Material Available: ^1H NMR spectra for relevant compounds (18 pages). Ordering information is given on any current masthead page.

Notes

Preparation of Fullerenes with a Simple Benchtop Reactor

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Though the de novo synthesis of buckminsterfullerene, C_{60}, remains an interesting challenge to the organic chemist,[1] the fullerenes are currently prepared by electric-arc graphite decomposition[2,3] in machines that are the domain of chemical physicists, physicists, materials scientists, and electrical engineers. Basically, an arc between two graphite rods is sparked at 60–150 A in a He (100 Torr) atmosphere in a commercial metal evaporator and the soot resulting from the decomposition is collected, extracted with toluene, and separated by chromatography.[4] A rather complicated machine, for more efficient preparations, in which two $^1/_4$-in. rods are held horizontally and kept in arcing contact manually by a screw mechanism, has recently been described.[5] More recently, mixtures of fullerenes ("soot extract") were made commercially available,[6] albeit at relatively high price.

In this publication, we describe a fullerene benchtop reactor that is easily assembled from commercial preparative chemistry glassware and a minimum of machine shop work (total cost, parts and labor $700). The apparatus is shown schematically below and in full detail in

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(1) Chapman, O. Private communication, 1987. Pascal, R. Private communication, 1990.

(2) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.

(3) Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, *94*, 8634.

(4) Ajie, H.; Alvarez, M. M.; Anz, S. J.; Beck, R. D.; Diederich, F.; Fostiropoulos, K.; Huffman, D. R.; Krätschmer, W.; Rubin, Y.; Schriver, K. E.; Sensharma, D.; Whetten, R. L. *J. Phys. Chem.* **1990**, *94*, 8630. Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. *J. Chem. Soc., Chem. Commun.* **1990**, 1423. Tycko, R.; Haddon, R. C.; Dabbagh, G.; Glarum, S. H.; Douglass, D. C.; Mujsce, A. M. *J. Phys. Chem.* **1991**, *95*, 518. Johnson, R. D.; Meijer, G.; Bethune, D. S. *J. Am. Chem. Soc.* **1990**, *112*, 8983. Cox, D. M.; Behal, S.; Disko, M.; Gorun, S.; Greaney, M.; Hsu, C. S.; Kollin, E.; Miliar, J.; Robbins, J.; Robbins, W.; Sherwood, R.; Tindall, P. *Mat. Res. Soc. Proc.* **1991**, *206*, in press; *J. Am. Chem. Soc.* **1991**, *113*, in press. The structure of a derivative has appeared: Hawkins, J. M.; Lewis, T. A.; Loren, S. D.; Meyer, A.; Heath, J. R.; Saykally, R. J.; Hollander, F. J. *Science* **1991**, *252*, 312.

(5) Haufler, R. E.; Chai, Y.; Chibante, L. P. F.; Conceicao, J.; Jin, C.; Wang, L. S.; Maruyama, S.; Smalley, R. E. *Mat. Res. Soc. Symp. Proc.* **1991**, in press.

(6) Materials & Electrochemical Research Corp. (MER Corp.), 7960 So. Kolb Rd., Tucson Az 85706; $250/100 mg, $1200.00/1000 mg. Texas Fullerene Corp.; $100/10 g of crude soot. We thank Prof. R. Smalley for this information.

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