Unexpected Oxadi-π-methane Rearrangement of β,γ-Unsaturated Aldehydes

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The oxadi-π-methane rearrangement (ODPM) is considered to represent the normal photochemical behavior of β,γ-unsaturated ketones in the triplet excited π,π^* state. However, the usual photoreactivity reported for the majority of β,γ-unsaturated aldehydes is decarbonylation. There are only two published reports of β,γ-unsaturated aldehydes that undergo the ODPM rearrangement. We now report efficient ODPM rearrangement in the triplet-sensitized irradiation of twelve cyclic and acyclic β,γ-unsaturated aldehydes, namely, 2,2-dimethyl-4,4-diphenyl-3-butenal (**6**), 1-methyl-3-phenyl-2-cyclohexene-1-carbaldehyde (**7**), 1-methyl-3-phenyl-2-cyclopentene-1-carbaldehyde (**14a**), 1-methyl-3-phenyl-2-cycloheptene-1-carbaldehyde (**14b**), 2,2-dimethyl-4-phenyl-3-butenal (**18**), 2-(3,4-dihydro-2-naphthyl)-2-methylpropanal (**23**), 3-(9-fluorenylidene)-2,2-dimethylpropanal (**24**), 5-cyclopentylidene-2,2-dimethyl-3-pentenal (**27**), 2,2,6-trimethyl-3,5-heptadienal (**28**), 2,2,4,4-tetraphenyl-3-butenal (**35**), 2-methyl-4,4-diphenyl-2-vinyl-3-butenal (**36**), and 4-methyl-2,2-diphenyl-3-pentenal (**47**). All of them afford the corresponding cyclopropyl aldehydes in 8−96% yield. Our results show that the ODPM rearrangement of aldehydes should be considered a normal photoreactivity of this type of compound. In one case (**7**), the formation of the corresponding 1,3-formyl migrated product was also observed. Aldehydes **35** and **47** undergo, in addition to the ODPM rearrangement, decarbonylation to the alkenes **37** and **51**, respectively. The ODPM reaction takes place when the triplet energy from the sensitizer is efficiently transferred to the alkene moiety generating a T_1 ($^3\pi,\pi^*$) excited state and, furthermore, when the biradical intermediates are stabilized by phenyl or vinyl substitution. Thus, 2,2,4-trimethyl-3-pentenal (**46**), in which these two requirements are not met, undergoes decarbonylation exclusively. Some structural factors that influence the efficiency of other di-π-methane processes, such as the di-π-methane (DPM) and azadi-π-methane (ADPM) rearrangements, are also operative in the ODPM rearrangement of aldehydes. Thus, diphenyl substitution on the central carbon of the β,γ-unsaturated aldehyde, as in **47**, also promotes the ODPM rearrangement. In cases in which the competition between the ODPM and the DPM processes can occur, the selectivity observed depends on the relative stabilities of the 1,4-bridged biradical intermediates. Thus, aldehyde **36** yields the ODPM product exclusively, while 2-(2,2-diphenylvinyl)-2-methyl-4,4-diphenyl-3-butenal (**43**) affords the DPM product **44** only.

Introduction

The photochemistry of carbonyl compounds has held the interest of organic photochemists for many years.[1] The number of studies of this class of compounds exceeds that of any of the other functional groups. Among all the different types of carbonyl compounds, β,γ-unsaturated ketones have been the subject of extensive studies.[2] The results obtained show that, in simple terms, direct irradiation of β,γ-unsaturated ketones usually yields the corresponding 1,3-acyl migration product,[2a,b] while the triplet photochemical reactivity of these compounds brings about the formation of the corresponding cyclopropyl ketones by an oxadi-π-methane (ODPM) rearrangement.[2b,c] However, there are exceptions to this general rule, and many β,γ-unsaturated carbonyl compounds do not undergo the ODPM rearrangement.[2] β,γ-Unsaturated aldehydes are the most typical example of carbonyl compounds that do not undergo either 1,3-formyl migration or the ODPM reaction. According to the literature, the normal photochemical reactivity of such compounds, both on direct or sensitized irradiations, is decarbonylation to the corresponding alkene.[2] There are only two examples of aldehydes that do not follow this general rule. The first example of an ODPM rearrangement in a β,γ-unsaturated aldehyde was reported by Schaffner *et al.*[3] in the direct irradiation of the steroidal aldehyde **1** that gives the ODPM product **2** in 30% yield in addition to two other compounds derived from 1,3-formyl migration and decarbonylation. Many years later, Zimmerman and Cassel[4] reported the ODPM reactivity of the sterically hindered aldehyde **3** that yields the cyclopropyl aldehyde **4** on acetophenone-sensitized irradiation. However, apart from these two cases, all the studies carried out on the photochemical reactivity of β,γ-unsaturated aldehydes failed to detect the ODPM rearrangement, and decarbonylation to the corresponding alkenes was the only reaction observed.[2] Thus, Schaffner,

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(1) For example, see: (a) Calvert, G. J.; Pitts, J. N. *Photochemistry*; John Wiley: New York, 1966. (b) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin Cummings Publishing Co.: Menlo Park, CA, 1978. (c) Horspool, W. M.; Armesto, D. *Organic Photochemistry*; Ellis Horwood and PTR Prentice Hall: Chichester, England, 1992. (d) *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Song, P., Ed.; CRC Press: Boca Raton, FL, 1995.

(2) (a) Houk, K. N. *Chem. Rev.* **1976**, *76*, 1. (b) Schuster, D. I. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 167−279. (c) Demuth, M. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1991; Vol. 11, pp 37−109.

(3) Pfenninger, E.; Poel, D. E.; Berse, C.; Wehrli, H.; Schaffner, K.; Jeger, O. *Helv. Chim. Acta* **1968**, *51*, 772.

(4) Zimmerman, H. E.; Cassel, J. M. *J. Org. Chem.* **1989**, *54*, 3800.

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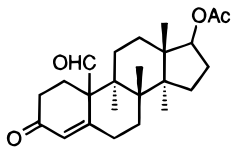
Jeger, and co-workers published, about 20 years ago, a series of papers on the photoreactivity of differently substituted steroidal and cyclic β,γ-unsaturated aldehydes.[3,5] The main photochemical reaction observed for the aldehydes studied was decarbonylation to the corresponding alkenes. Apart from compound **1**, none of them underwent the ODPM rearrangement. Dürr *et al.*[6] have studied the photochemistry of some aryl-substituted 2-cyclopentene-1-carbaldehydes **5**. In this instance, *cis*-stilbene-type electrocyclic cyclization and decarbonylation were the only reactions observed. Surprisingly, the triplet photoreactivity of acyclic β,γ-unsaturated aldehydes has merited very little attention. The only two cases reported on the reactivity of this type of compound in the triplet excited state were aldehydes **3** and **6**. As mentioned before, aldehyde **3** undergoes the ODPM rearrangement on sensitized excitation.[4] However, the reactivity reported for **6** on direct irradiation was decarbonylation and what the author described as "ambiguous results" on acetophenone sensitization.[7]



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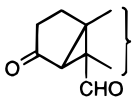

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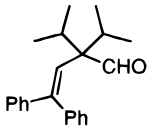

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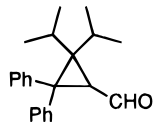

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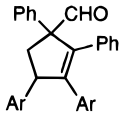

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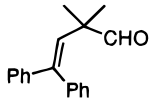

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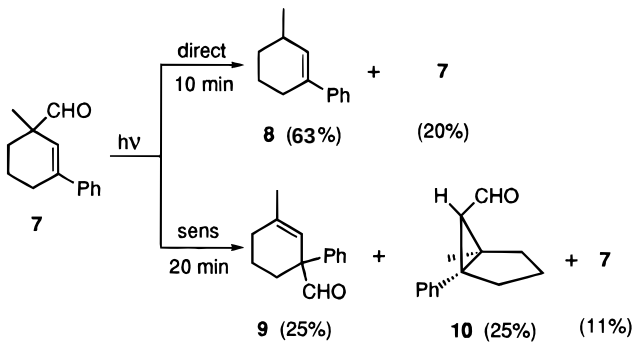
From all these precedents a general conclusion that is reflected in all the reviews and monographs is that decarbonylation is the normal photochemical fate of β,γ-unsaturated aldehydes. The ODPM reaction is considered to be an exception with only two precedents. We wish to report here a serendipitous discovery that changes the accepted ideas about the photoreactivity of β,γ-unsaturated aldehydes. Some of the results described here have been the subject of a preliminary communication.[8]

Results and Discussion

The ODPM Rearrangement of 1-Methyl-3-phenyl-2-cycloalkene-1-carbaldehydes. Our interest in the azadi-π-methane rearrangement (ADPM) has led us to a study of its application to the synthesis of bicyclo[n.1.0]-alkanes.[9] An extension of such a study was aimed at identifying ring contraction processes. To this end the known aldehyde **7**,[10] which could be transformed into different imine derivatives, was selected as the target molecule. Since the photochemistry of the aldehyde **7** was not described, it was of importance to establish the photochemical behavior of this compound to compare its reactivity with that of the corresponding nitrogen derivatives. Brief (10 min) direct irradiation of **7** afforded, after workup, a mixture of starting material (20%) and the known alkene **8**[11] (63%) resulting from decarbonylation of aldehyde **7** (Scheme 1). This result was not a surprise since, as mentioned above, it has been established that decarbonylation is the main photochemical reactivity of β,γ-unsaturated aldehydes. However, acetophenone-sensitized irradiation of **7** for 20 min brought about different reactions and afforded the 1,3-migration product (**9**, 25%), the ODPM product (**10**, 25%), and starting material (11%) (Scheme 1).[8] The identity of aldehyde **9** was established by IR and MS evidence, showing that this compound was isomeric with starting material. The ^{1}H and ^{13}C NMR resonances also agree with the structure proposed for **9**. The structure of the bicyclic aldehyde **10** was unequivocally established by reduction, using $LiAlH_4$, to the known alcohol **11**.[10] By this method it was also possible to assign the stereochemistry of the photoproduct **10** as the *endo*-isomer exclusively. The stereoselectivity observed in this reaction is similar to that reported by Mariano and Ko[10] in the sensitized irradiation of the 1,4-diene **12** that yields the *endo*-isomer of the corresponding di-π-methane product **13** exclusively. The formation of the 1,3-migration product **9** under sensitized conditions involving the T_2 excited state has been reported for several β,γ-unsaturated ketones.[12] However, it is extremely rare to observe such a reaction with analogous aldehydes, and even more surprising is the formation of the ODPM product **10**. At this point it was difficult to explain the photoreactivity observed in the irradiation of **7**, although it was thought to be due to the influence of some unknown structural factors present in **7**.

Scheme 1



Compounds **14a** and **14b** were synthesized to determine whether this unexpected reactivity could be extended to other related aldehydes. The synthesis of **14a** was achieved by the one-pot conversion of 3-phenyl-2-cyclopentenone,[13] according to the method described by Martin *et al.*[14] for similar compounds. Aldehyde **14b** was

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(6) (a) Dürr, H.; Heitkämper, P.; Herbst, P. *Tetrahedron Lett.* **1970**, 1599. (b) Dürr, H.; Herbst, P.; Heitkämper, P.; Leismann, H. *Chem. Ber.* **1974**, *107*, 1835.

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(8) Armesto, D.; Ortiz, M. J.; Romano, S. *Tetrahedron Lett.* **1995**, *36*, 965.

(9) Armesto, D.; Ramos, A. *Tetrahedron* **1993**, *49*, 7159.

(10) Mariano P. S.; Ko, J. *J. Am. Chem. Soc.* **1973**, *95*, 8670.

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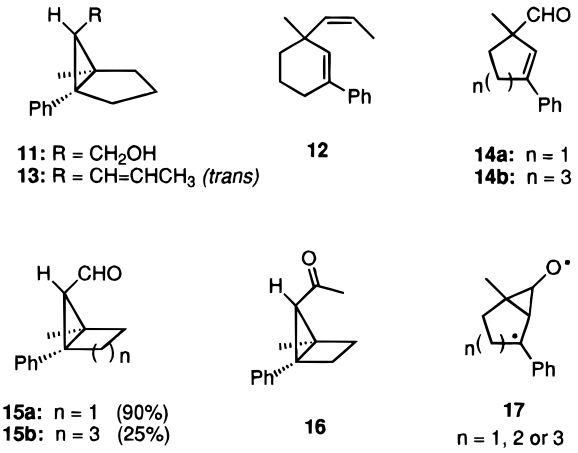
(12) (a) Dalton, J. C.; Shen, M.; Snyder, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 5023. (b) Schaffner, K. *Tetrahedron* **1976**, *32*, 641. (c) Schuster, D. I.; Calcaterra, L. T. *J. Am. Chem. Soc.* **1982**, *104*, 6397.

(13) Farnum, D. G.; Mostashari, A.; Hagedorn, A. A. *J. Org. Chem.* **1971**, *36*, 698.

(14) Martin, S. F.; Phillips, G. W.; Puckette, T. A.; Colapret, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 5866.

obtained from 2-phenylcycloheptanone[15] according to the method described by Mariano and Ko for the synthesis of aldehyde **7**.[10] Acetophenone-sensitized irradiation (5 min) of **14a** afforded, after conventional workup, the ODPM product **15a** in 90% isolated yield. In this instance, a careful study of the ^{1}H and ^{13}C NMR spectra of the crude photolysate demonstrated that the 1,3-formyl migration product is not formed. The identity of **15a** was established by comparison of the ^{1}H NMR resonances from **15a** with those reported by Schaffner *et al.*[16] for the analogous ketone **16**. Thus, the ^{1}H NMR spectrum of **16** shows a singlet at δ 1.3 and a multiplet at δ 1.7−2.5 corresponding to the angular methyl group and the cycloalkane hydrogens, respectively. The ^{1}H NMR spectrum of aldehyde **15a** is very similar, showing a singlet at δ 1.3 and a multiplet at δ 1.4−2.6. The assignment of structure was also confirmed by the analogy between the ^{1}H and ^{13}C NMR spectra recorded for this compound with those obtained for the bicyclic aldehyde **10.** The *endo*-configuration was also established on the basis of this comparison. Thus, the aldehyde proton in **15a** appears as a doublet at δ 9.9, with a coupling constant of 6.0 Hz and, similarly, compound **10** shows a doublet at δ 9.7, with a coupling constant of 6.3 Hz for the aldehyde proton. The result obtained in the irradiation of **14a** demonstrates that the ODPM reactivity observed for **7** can be extended to other cyclic β,γ-unsaturated aldehydes. However, it is still unclear why **14a** does not undergo the 1,3-formyl migration and only yields the ODPM product. This might be due to an inefficient energy transfer from the triplet sensitizer to the formyl group. Similarly, acetophenone-sensitized irradiation (10 min) of **14b** afforded, after workup, the ODPM product **15b** in 25% isolated yield and recovered starting material (60%). No product resulting from a 1,3-formyl migration was observed. The identity of **15b** was established by comparison of its ^{1}H and ^{13}C NMR resonances with those recorded for **10** and **15a**. In qualitative terms, the efficiency of the rearrangement of **14a** is greater than that observed for **7** and **14b**. This could be due to the suppression in **14a** of other alternative routes of deactivation of the excited state, such as *E,Z*-isomerization around the C−C double bond, that can be operative in the six- and seven-membered rings present in **7** and **14b**.[17]

The ODPM Rearrangement of Acyclic β,γ-Unsaturated Aldehydes. The ODPM reactivity of the cyclic derivatives **7**, **14a**, and **14b** was very surprising considering the precedents on the photochemistry of β,γ-unsaturated aldehydes. At this point, it was clear that there must be structural features in compounds **7**, **14a**, and **14b** that are critical for the success of the ODPM process. This is evident, not only from the fact that compounds **7** and **14** undergo rearrangements that have seldom been seen in related compounds, but also because of the very high efficiency of the rearrangement. The most likely controlling features are (a) the excitation of the molecule to the T_1 ($^3\pi,\pi^*$) excited state, (b) the stabilizing influence of the phenyl group on the bridging 1,4-biradical reaction intermediates **17**, and (c) the difficulty of deactivation of the excited state by the free rotor effect of the vinyl component in cyclic alkenes. In order to determine



whether the partial suppression of the free rotor effect was essential for the success of the rearrangement the study was extended to the aldehyde **18**.[18] When **18** was irradiated (15 min) under similar conditions to those used for **7** and **14**, the cyclopropyl aldehyde **19**, resulting from an ODPM rearrangement, was obtained in 90% isolated yield. The identity of **19** was easily determined by comparison of its ^{1}H and ^{13}C NMR resonances with those previously reported by us for the corresponding oxime acetate **20**.[19] In this case, the reaction is stereoselective, yielding the *trans*-isomer exclusively. Further proof of the structure proposed for **19** was obtained by its conversion, using standard procedures, into the oxime acetate **20.** This result demonstrated clearly that the ODPM reactivity of β,γ-unsaturated aldehydes is not restricted to cyclic compounds, such as **7** and **14**, but can also be extended to acyclic analogs. Therefore, the suppression of the free rotor effect is not essential for the success of the ODPM rearrangement.

The efficient ODPM reactivity of **18** was extremely surprising considering that Pratt[7] had reported in an early study the absence of such a rearrangement in the direct and sensitized irradiations of the closely related diphenyl-substituted aldehyde **6**. The reactivity observed for **6** was decarbonylation on direct irradiation, and what the author described as "ambiguous results", on acetophenone sensitization. No evidence for the formation of the corresponding ODPM product was obtained. Therefore, a logical extension of our study was to reinvestigate the photoreactivity of the aldehyde **6**. Surprisingly, *m*-methoxyacetophenone-sensitized irradiation of **6** (2 h) brought about the formation of the previously described cyclopropyl aldehyde **21**,[20] resulting from an ODPM rearrangement, in 57% isolated yield and recovered starting material (30%). It is worth noting that the corresponding methyl ketone **22** was also investigated by Pratt.[7] In that early study the acetophenone-sensitized irradiation of **22** for 97 h did not lead to formation of the corresponding ODPM product.[7] We have reinvestigated the photoreactivity of ketone **22** using *m*-methoxyacetophenone as sensitizer. Under these conditions, only starting material (80%) and a mixture of highly polar compounds were obtained after 11 h of irradiation, confirming Pratt's observation. Thus, this

(15) Gutsche, C. D.; Jason, E. F. *J. Am. Chem. Soc.* **1956**, *78*, 1184.
(16) Gonzenbach, H. V.; Tegmo-Larsson, I. M.; Grosclaude, J. P.; Schaffner, K. *Helv. Chim. Acta* **1977**, *60*, 1091.
(17) Kropp, P. J. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1979; Vol. 4, p 1.
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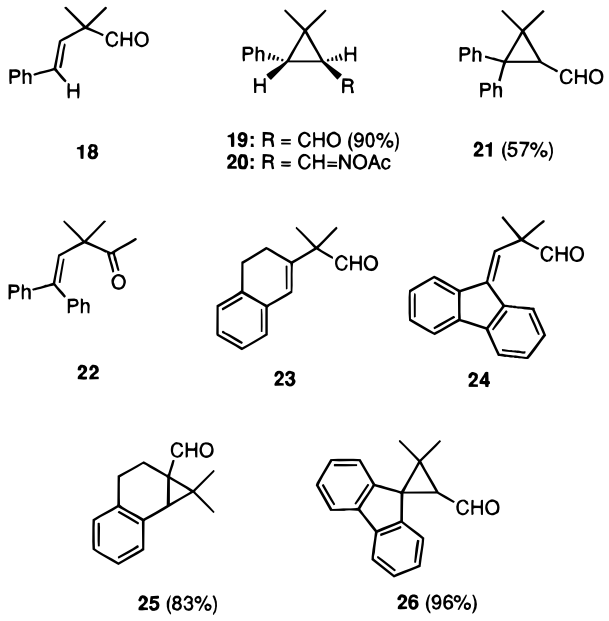
(19) Armesto, D.; Horspool, W. M.; Gallego, M. G.; Agarrabeitia, A. R. *J. Chem. Soc., Perkin Trans. 1* **1992**, 163.
(20) Zimmerman, H. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1969**, *91*, 1718.

is the first example of a situation in which a β,γ-unsaturated aldehyde undergoes efficient ODPM reactivity while the corresponding methyl ketone is inert toward the rearrangement.[21]

The ODPM Rearrangement of β,γ-Unsaturated Aldehydes Promoted by Aryl and Vinyl Substitution at C-4. The results obtained in the sensitized irradiation of compounds **6**, **7**, **14a**, **14b**, and **18** show that, contrary to general opinion, β,γ-unsaturated aldehydes can undergo the ODPM rearrangement very efficiently. Particularly, the reactivity observed in simple compounds such as **6** and **18** demonstrates that the ODPM reactivity of aldehydes is not restricted to molecules with special structural features as in the two cases previously reported. The question that remains to be answered is: which factors control the ODPM reactivity of aldehydes? On the basis of precedent it seems logical to assume that the stabilization of the corresponding 1,4-cyclopropyl biradical intermediate by conjugation with a phenyl ring might be essential for the success of the rearrangement. In order to test this hypothesis, the study was extended to aldehydes **23**[9] and **24.**[22] Thus, *m*-methoxyacetophenone-sensitized irradiation of **23** for 10 min brought about the formation of cyclopropane **25** in 83% yield. The identity of **25** was demonstrated by its conversion into the corresponding oxime, previously described by us.[23] A similar result was obtained in the *m*-methoxyacetophenone-sensitized irradiation of **24**. In this instance, the spirocyclopropyl aldehyde **26**, previously described by us,[22] was obtained in 96% yield, after 2 h of irradiation. It is clear from these results that aryl substitution at the γ-position of the β,γ-unsaturated aldehyde skeleton promotes highly efficient ODPM reactivity in the triplet excited state.



The next question to be answered was whether or not substituents other than phenyl at that position could also promote the reaction. In order to answer this question, the known aldehydes **27** and **28**, with differently substituted vinyl units at the γ position, were synthesized.[22] Previously, we have observed efficient ADPM rearrangement of the corresponding oxime acetates **29** and **30** showing that the substitution pattern present in **27** and **28** was suitable for promoting DPM reactivity.[22] Brief (20 min) *m*-methoxyacetophenone-sensitized irradiation of **27** afforded, after workup, starting material (30%), as a 3:2 mixture of *E:Z* isomers, and the cyclopropyl derivative **31** (47%) as a 1:8 mixture of *cis:trans* isomers. Similarly, irradiation of **28**, for 15 min, under the same conditions used for **27**, yielded **32** (52%) as the *trans* isomer exclusively and starting material (42%). The identity of compounds **31** and **32** was established by comparison with authentic samples, previously obtained by us.[22] The rearrangements of aldehydes **27** and **28** demonstrated that the ODPM reactivity of β,γ-unsaturated aldehydes is not restricted to phenyl-substituted compounds but can also be extended to systems in which the intermediate biradicals are stabilized by conjugation with a vinyl group. Furthermore, the efficient synthesis of compounds **31** and **32** is of importance since it opens a novel photochemical route to chrysanthemic acid and other cyclopropyl components present in pyrethrins and pyrethroids.[24]

Influence of Phenyl and Vinyl Substitution at C-2 on the ODPM Reactivity of β,γ-Unsaturated Aldehydes. Competition between the ODPM and the DPM Processes. The next step in this study was to determine whether other substitution patterns that have been demonstrated to increase the efficiency of DPM processes could also promote ODPM reactivity in β,γ-unsaturated aldehydes, namely phenyl or vinyl substitution at position 2 of the β,γ-unsaturated system. Zimmerman *et al.*[25] have demonstrated that diphenyl substitution at that position increases the quantum yield of the rearrangement and also allows DPM reactivity of acyclic 1,4-dienes in the triplet excited state. Our studies have shown that oximes **33a**[23] and **34a**[23] and oxime acetates **33b**[26] and **34b**[23b] undergo efficient ADPM rearrangement. Therefore, the known aldehydes **35**[25a] and **36**[23] were selected for this study. The photoreactivity of aldehyde **35** on direct irradiation has been reported by Adam *et al.*[27] Under these conditions the only observed product was the alkene **37**, resulting from decarbonylation of the starting aldehyde. However, in our study, acetophenone-sensitized irradiation of **35** for 10 min afforded, after workup, the ODPM product **38**[25a] (82%) and the alkene **37** (8%).

In the case of aldehyde **36** two alternative rearrangements, the DPM and the ODPM, are open to the excited state. Irradiation of **36** using *m*-methoxyacetophenone as sensitizer, for 10 min, afforded recovered starting material (55%) and the cyclopropyl aldehyde **39** (19%), as a 3:2 mixture of *RS,SR:RR,SS* isomers, resulting from

(21) It is difficult at this point to explain why aldehyde **6** undergoes the ODPM rearrangement while the analogous methyl ketone **22** does not. It will be necessary to carry out additional studies in order to establish the possible analogies and differences between the reactivity of β,γ-unsaturated aldehydes and ketones before giving a reasonable explanation for this observation.

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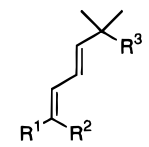
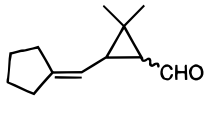
(25) (a) Zimmerman, H. E.; Boettcher, R. J.; Braig, M. *J. Am. Chem. Soc.* **1973**, *95*, 2155. (b) Zimmerman, H. E.; Armesto, D.; Amezua, M. G.; Gannett, T. P.; Johnson, R. *J. Am. Chem. Soc.* **1979**, *101*, 6367. (c) Zimmerman, H. E.; Factor, R. E. *Tetrahedron*, **1971**, *37*, Suppl. 1, 125.

(26) Armesto, D.; Horspool, W. M.; Langa, F.; Ramos, A. *J. Chem. Soc., Perkin Trans. 1* **1991**, 223.

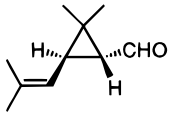
(27) Adam, W.; Berkessel, A.; Hildenbrand, K.; Peters, E. M.; Peters, K.; Schnering, H. G. *J. Org. Chem.* **1985**, *50*, 4899.

an ODPM rearrangement exclusively.[28] The assignment of the structure and the stereochemistry of **39** was achieved by NMR spectroscopy. The ^{1}H NMR spectrum of **39** shows resonances at δ 1.2 and δ 1.6 for two methyl groups of the *RS,SR* and *RR,SS* isomers, respectively, and two doublets at the correct resonance position for hydrogens in a three-membered ring (δ 2.53 and δ 2.57). The ^{13}C NMR spectrum of **39** shows two methyl groups at δ 15.4 and δ 20.2 and six cyclopropyl carbon atoms (δ 37.5, 38.0, 44.9, 47.0, 52.1 and 52.7), as well as two aldehyde carbons (δ 200.8 and 201.0), corresponding to the *RS,SR* and *RR,SS* isomers. These resonances are only compatible with the proposed structure **39**. Furthermore, final proof of structure and the assignment of the stereochemistry were obtained by comparison of the ^{1}H and ^{13}C NMR spectra of **39** with those reported for both stereoisomers of the corresponding nitrile.[23b] The other possible isomer **40**, resulting from the alternative DPM reaction path, was not observed, showing that in this instance the ODPM rearrangement dominates over the DPM process. A similar regioselectivity has been observed by us in the irradiation of the oxime **34a**[23] and the oxime acetate **34b**.[23b] In these two cases the ADPM rearrangement took precedence over the alternative DPM process. The regioselectivity observed was interpreted as being dependent on the relative stabilities of the 1,4-bridged biradicals for the two possible rearrangement paths.[23b]



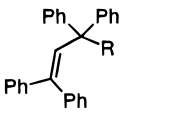


31 (47%)

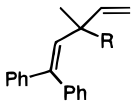


32 (52%)

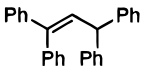
27: $R^1 = R^2 = -(CH_2)_4-$; R^3 = CHO
28: $R^1 = R^2$ = Me; R^3 = CHO
29: $R^1 = R^2 = -(CH_2)_4-$; R^3 = CH=NOAc
30: $R^1 = R^2$ = Me; R^3 = CH=NOAc



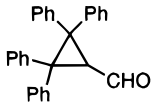
33a: R = CH=NOH
33b: R = CH=NOAc
35: R = CHO



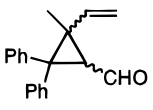
34a: R = CH=NOH
34b: R = CH=NOAc
36: R = CHO



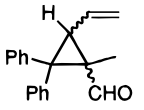
37 (8%)



38 (82%)



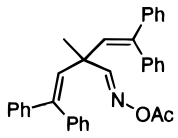
39 (19%)



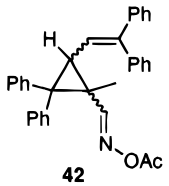
40

In our previous study on the competition between the ADPM and DPM rearrangements, we observed that sensitized irradiation of the oxime acetate **41** affords the DPM product **42** exclusively as a 3:2 mixture of stereoisomers (*RR,SS:RS,SR*).[23b] It was of interest, therefore, to study the reactivity of aldehyde **43** in order to determine whether the DPM or the ODPM rearrangements will be predominant. The known aldehyde **43**[23b] was irradiated using *m*-methoxyacetophenone as sensitizer, for 15 min, yielding starting material (46%) and the cyclopropane **44** (48%), resulting from a DPM rearrangement, as a 1:1 mixture of *RR,SS:RS,SR* isomers. The identity of **44** was demonstrated by its conversion into the corresponding oxime.[23b] This result indicates that the same factors that control the competition between the ADPM and the DPM rearrangements are also operative in controlling the competition between the DPM and ODPM rearrangement of aldehydes.

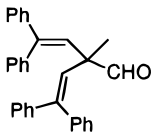
From all of the foregoing it is evident that β,γ-unsaturated aldehydes in the T_1 ($^3\pi,\pi^*$) excited state, which can give rise to sufficiently stable 1,4-cyclopropyl biradical intermediates (schematically represented by structure **45**) by conjugation with phenyl or vinyl substituents, undergo efficient ODPM rearrangement. This is in clear contrast with the general opinion that decarbonylation is the normal photochemical reaction of this type of compound.



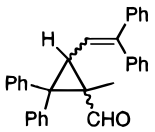
41



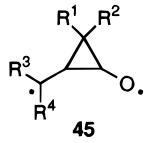
42



43



44 (48%)



45

R^1 = Me or Ph
R^2 = Me, Ph or vinyl
R^3 = Ar or vinyl
R^4 = H, Ph or alkyl

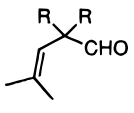
Influence of Dimethyl Substitution at C-4 on the ODPM Reactivity of β,γ-Unsaturated Aldehydes. The next question to be answered is: would it be possible to observe ODPM rearrangement in β,γ-unsaturated aldehydes with a smaller degree of stabilization of the intermediate 1,4-cyclopropyl biradicals? Compounds **46**[29] and **47**[30] were synthesized in an attempt to answer this question. Both aldehydes would give 1,4-cyclopropyl biradicals **48a** and **48b** that will be stabilized by dimethyl substitution. The photoreactivity of aldehyde **46** has been studied previously by us.[26] However, because of the unexpected results obtained in this study, the irradiation of **46** was repeated in an attempt to detect ODPM reactivity. In agreement with our previous report, sensitized irradiation of **46** using acetone as sensitizer yielded the diene **49** resulting from the dimerization of the radical **50**, formed by decarbonylation of **46**. However, irradiation of **47** for 30 min, under the same conditions used for **46**, afforded the corresponding cyclopropyl aldehyde **21** (8%), the decarbonylation product

(28) The stereochemical results observed by us for the ODPM rearrangements of aldehydes **7**, **14**, **18**, **27**, **28**, and **36** are similar to those reported in the photochemistry of related 1,4-dienes,[10] β,γ-unsaturated ketones,[16] and β,γ-unsaturated oxime acetates.[19,22,23] Apparently, the same factors that control the stereochemistry of these compounds in the triplet excited state also operate for β,γ-unsaturated aldehydes.

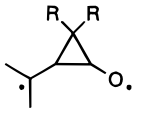
(29) Rasek, R. H.; Clark, R. D.; Chaudet, J. H. *J. Org. Chem.* **1961**, *26*, 3130.

(30) Zimmerman, H. E.; Oaks, F. L.; Campos, P. *J. Am. Chem. Soc.* **1989**, *111*, 1007.

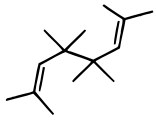
51[18] (14%), and starting material (70%). This result demonstrated that the ODPM rearrangement of aldehydes can occur even when there is a relatively low degree of stabilization of the 1,4-cyclopropyl biradical intermediates. The reactivity observed for **47** could be due to the facile ring opening of the 1,4-cyclopropyl biradical **48b**, formed by vinyl−vinyl bridging, yielding the intermediate **52**. This interpretation is in agreement with similar increases in efficiency and triplet reactivity promoted by phenyl substitution at the methane carbon, observed by Zimmerman *et al.* in the DPM process.[4,25]



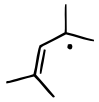
46: R = Me
47: R = Ph



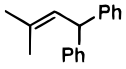
48a: R = Me
48b: R = Ph



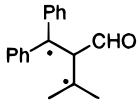
49



50



51 (14%)



52

Conclusions

It is our belief that the results described herein will change the ideas that most photochemists have on the photoreactivity of β,γ-unsaturated aldehydes. From the work carried out mainly by Schaffner, Dürr, and Pratt on the study of a series of compounds of this type a general consensus surrounding their lack of ODPM reactivity was originated. Most of the compounds studied previously underwent decarbonylation, with only two exceptions. The decarbonylation takes place *via* either the S_1 (^{1}n,π^*) or T_2 (^{3}n,π^*) excited states.[12] However, on the basis of studies with analogous ketones the ODPM rearrangement of β,γ-unsaturated aldehydes almost surely occurs *via* the T_1 ($^3\pi,\pi^*$) excited state.[2] The lack of ODPM reactivity of the aldehydes previously studied is probably due to the absence of the adequate substitution pattern that would allow both efficient transfer of the triplet energy from the sensitizer to the alkene moiety and stabilization of the biradical intermediates. However, our study shows that suitably substituted β,γ-unsaturated aldehydes undergo the ODPM rearrangement with high chemical efficiency. The results obtained herein indicate that the ODPM rearrangement of β,γ-unsaturated aldehydes occurs when the triplet energy from the sensitizer is efficiently transferred to the alkene moiety generating a T_1 ($^3\pi,\pi^*$) excited state and, furthermore, when the biradical intermediates are stabilized by phenyl or vinyl substitution. Further studies are planned to determine the scope of this novel rearrangement.

Experimental Section

Melting points were determined in open capillaries and are uncorrected. UV/vis spectra were recorded in CH_2Cl_2 solution. Column chromatography was performed using silica gel 60 (40−63 μm) from Merck. Commercially available starting materials and reagents were purchased from Aldrich.

Aldehydes 6,[7] **7**,[10] **18**,[18] **23**,[9] **24**,[22] **27**,[22] **28**,[22] **35**,[25a] **36**,[23] **43**,[23b] **46**,[29] and **47**[30] were synthesized by the methods previously described.

1-Methyl-3-phenyl-2-cyclopentene-1-carbaldehyde (14a). To a solution of diethyl [(*N*-benzylideneamino)methyl]phosphonate[31] (1.5 g, 6 mmol) in dry THF (5 mL) under argon and at −78 °C was added *n*-BuLi (4 mL, 1.6 M in hexane) in dry THF (10 mL) slowly dropwise. The resulting red solution was stirred at −78 °C for 1 h, and then 3-phenyl-2-cyclopentenone[13] (0.7 g, 4.4 mmol) in THF (4 mL) was added. The reaction mixture was stirred at −40 °C for 20 min, and then *n*-BuLi (4 mL, 1.6 M in hexane) was added at −78 °C. After the mixture was stirred at −78 °C for 1 h, MeI (1 mL, 17.6 mmol) was added dropwise. The reaction was quenched with 1 M aqueous HCl (22.7 mL), and the resulting heterogeneous mixture was stirred vigorously at 0 °C for 20 min. A saturated aqueous solution of NaCl (11.4 mL) was added, and the aqueous layer was extracted with Et_2O. The organic layer was washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), filtered, and concentrated to dryness. Flash chromatography of the residue using hexane/Et_2O (95:5) yielded aldehyde **14a** (141 mg, 18%) as an oil: ^{1}H NMR (300 MHz) δ 1.2 (s, 3 H), 1.7 (m, 1 H), 2.4 (m, 1 H), 2.8 (m, 2 H), 5.8 (s, 1 H), 7.2−7.4 (m, 5 H), 9.5 (s, 1 H); ^{13}C NMR (75 MHz) δ 20.0, 31.7, 32.6, 60.9, 125.7, 126.0, 127.8, 128.2, 135.1, 146.3, 201.9; IR (neat) 1725 cm^{-1}; UV λ_{max} 259 (ϵ 13 900).

1-Methyl-3-phenyl-2-cycloheptene-1-carbaldehyde (14b). This compound was synthesized in four steps from 2-phenylcycloheptanone[15] according to the method previously described for the synthesis of the corresponding cyclohexyl derivative,[10] under the following reaction conditions:

Sodium (2,75 g, 0.12 mol), 2-phenylcycloheptanone[15] (5 g, 0.026 mol) and ethyl formate (7.96 g, 0.1 mol) yielded 2-oxo-3-phenylcycloheptane-1-carbaldehyde (3.5 g, 63%) as a slightly yellow oil: ^{1}H NMR (300 MHz) δ 1.3−2.5 (m, 8 H), 3.9 (m, 1 H), 7.0−7.4 (m, 6 H); IR (neat) 1730, 1690 cm^{-1}.

2-Oxo-3-phenylcycloheptane-1-carbaldehyde (3.5 g, 0.016 mol), *i*-PrOH (40 mL), benzene (30 mL), and *p*-toluensulfonic acid (1 mg) yielded 2-(isopropoxymethylidene)-7-phenylcycloheptanone (3.35 g, 81%) as an oil: ^{1}H NMR (300 MHz) δ 1.2 (d, J = 6.5 Hz, 6 H), 1.5−2.5 (m, 8 H), 3.9 (m, 1 H), 4.0 (m, 1 H), 7.1−7.5 (m, 6 H).

2-(Isopropoxymethylene)-7-phenylcycloheptanone (3.3 g, 13 mmol) and $LiAlH_4$ (0.5 g, 13 mmol) yielded 3-phenyl-1-cycloheptene-1-carbaldehyde (1.97 g, 77%) as a brown oil: ^{1}H NMR (300 MHz) δ 1.3−2.3 (m, 6 H), 2.6 (m, 1 H), 2.9 (m, 1 H), 3.8 (m, 1 H), 6.8 (m, 1 H), 7.2−7.4 (m, 5 H), 9.3 (s, 1 H); IR (neat) 1730 cm^{-1}.

3-Phenyl-1-cycloheptene-1-carbaldehyde (1.9 g, 9.5 mmol), MeI (1.2 mL, 0.019 mmol), and *t*-BuOK (106 g, 0.014 mol) in *t*-BuOH (10 mL) at 50 °C yielded 1-methyl-3-phenyl-2-cycloheptene-1-carbaldehyde (**14b**) (0.6 g, 30%) as a colorless oil: ^{1}H NMR (300 MHz) δ 1.2 (s, 3 H), 1.6−2.0 (m, 6 H), 2.3 (m, 1 H), 2.6 (m, 1 H), 5.7 (s, 1 H), 7.2−7.3 (m, 5 H), 9.5 (s, 1 H); ^{13}C NMR (75 MHz) δ 21.9, 23.3, 25.0, 26.4, 31.8, 51.4, 125.6−129.7, 145.0, 146.0, 203.3; IR (neat) 1690 cm^{-1}; UV (CH_2Cl_2) λ_{max} 248 (ϵ 5500).

General Procedure for Preparative Photolyses. The photolyses were carried out in a quartz immersion well apparatus with a Pyrex filter and a 400-W medium-pressure Hg arc lamp. Solutions of the compounds and the sensitizer (in the sensitized irradiations) in dry CH_2Cl_2 (420 mL) were purged for 1 h with argon and irradiated under a positive pressure of argon. After completion of the irradiation, the solvent (and the acetophenone or *m*-methoxyacetophenone in sensitized irradiations) was removed under reduced pressure, and the products were separated by flash chromatography on silica gel.

Direct Irradiation of 7. Compound **7** (300 mg, 1.5 mmol) was irradiated for 10 min. Flash chromatography using hexane/Et_2O (9:1) gave 162 mg (63%) of 3-methyl-1-phenylcyclohexene[11] (**8**): ^{1}H NMR (300 MHz) δ 1.1 (d, J = 6.8 Hz, 3 H), 1.2−2.4 (m, 7 H), 5.9 (br s, 1 H), 7.2−7.4 (m, 5 H); IR (KBr) 1620 cm^{-1}. Further elution gave recovered starting material (60 mg, 20%).

(31) Ratcliffe, R. W.; Christensen, B. G. *Tetrahedron Lett.* **1973**, *46*, 4645.

Acetophenone-Sensitized Irradiation of 7. Compound **7** (308 mg, 1.54 mmol) and acetophenone (21.7 g, 0.18 mol) were irradiated for 20 min. Flash chromatography using hexane/Et_2O (9:1) as eluent gave 34 mg (11%) of **7**, 77 mg (25%) of **9**, and 78 mg of **10** (25%) as oils.

Compound 9: ^{1}H NMR (300 MHz) δ 1.8 (s, 3 H), 1.4−2.4 (m, 6 H), 5.5 (s, 1 H), 7.1−7.4 (m, 5 H), 9.4 (s, 1 H); ^{13}C NMR (75 MHz) δ 18.9, 24.3, 29.8, 30.5, 37.3, 117.9, 124.8−130.1, 135.7, 141.3, 199.3; IR (KBr) 1695 cm^{-1}.

Compound 10: ^{1}H NMR (300 MHz) δ 0.9 (s, 3 H), 1.8 (d, J = 6.3 Hz, 1 H), 1.5−2.4 (m, 6 H), 7.1−7.5 (m, 5 H), 9.7 (d, J = 6.3 Hz, 1 H); ^{13}C NMR (75 MHz) δ 20.3, 22.8, 34.7, 37.3, 43.3, 45.3, 50.5, 126.6−128.9, 132.9, 140.9, 201.5; IR (KBr) 1690 cm^{-1}. This compound was further characterized by reduction to the corresponding alcohol **11**.[10] A solution of **10** (107 mg, 0.53 mmol) in dry Et_2O (20 mL) was added dropwise at 0 °C to a suspension of $LiAlH_4$ (43 mg, 1.1 mmol) in dry Et_2O (20 mL). The resulting mixture was stirred overnight at rt. The residual $LiAlH_4$ was decomposed by addition of a saturated aqueous solution of sodium sulfate, followed by water. The ethereal layer was separated, and the aqueous layer was extracted with $CHCl_3$. The combined organic extracts were dried ($MgSO_4$), filtered, and evaporated to dryness, giving 98 mg (91%) of an oil which was characterized as 6-*endo*-(hydroxymethyl)-5-methyl-1-phenylbicyclo[3.1.0] hexane (**11**). Spectral data were identical in all respects to those previously described.[10]

Acetophenone-Sensitized Irradiation of 14a. Compound **14a** (65 mg, 0.35 mmol) and acetophenone (15.8 g, 0.13 mol) were irradiated for 5 min. Flash chromatography using hexane as eluent gave 58.5 mg (90%) of the *endo* isomer of the bicyclic aldehyde **15a** as an oil: ^{1}H NMR (300 MHz) δ 1.3 (s, 3 H), 1.9 (d, J = 6.0 Hz, 1 H), 1.4−2.6 (m, 4 H), 7.1−7.3 (m, 5 H), 9.9 (d, J = 6.0 Hz, 1 H); ^{13}C NMR (63 MHz) δ 17.3, 23.4, 24.6, 29.6, 41.8, 44.4, 126.4−128.3, 201.9; IR (neat) 1700 cm^{-1}.

Acetophenone-Sensitized Irradiation of 14b. Compound **14b** (201 mg, 0.93 mmol) and acetophenone (4.5 g, 37.5 mol) were irradiated for 10 min. Flash chromatography using hexane/Et_2O (9:1) as eluent gave 121 mg (60%) of **14b** and 51 mg (25%) of the *endo* isomer of the bicyclic aldehyde **15b** as an oil: ^{1}H NMR (300 MHz) δ 1.3 (s, 3 H), 1.8 (d, J = 6.7 Hz, 1 H), 1.5−2.3 (m, 8 H), 6.8−7.5 (m, 5 H), 9.8 (d, J = 6.7 Hz, 1 H); ^{13}C NMR (75 MHz) δ 14.0, 22.6, 29.3, 29.5, 29.6, 32.0, 42.0, 46.0, 128.2, 128.5, 130.0, 133.1, 138.5, 202.0; IR (neat) 1705 cm^{-1}.

Acetophenone-Sensitized Irradiation of 18. Compound **18** (213 mg, 1.22 mmol) and acetophenone (20 g, 0.16 mol) were irradiated for 15 min. Flash chromatography using hexane/Et_2O (9:1) as eluent gave 192 mg (90%) of cyclopropyl aldehyde **19** as a colorless oil: ^{1}H NMR (300 MHz) δ 0.9 (s, 3 H), 1.4 (s, 3 H), 2.2 (dd, J = 5.5, 5.0 Hz, 1 H), 2.9 (d, J = 5.5 Hz, 1 H), 7.1−7.4 (m, 5 H), 9.6 (d, J = 5.0 Hz, 1 H); ^{13}C NMR (75 MHz) δ 21.6, 21.9, 32.1, 38.7, 41.1, 126.5−128.5, 132.9, 136.3, 200.7; IR 1705 cm^{-1}. This compound was further characterized by conversion into the corresponding oxime acetate **20**.[19] Thus, the aldehyde **19** (192 mg, 1.1 mmol), hydroxylamine hydrochloride (85 mg, 1.23 mmol), and pyridine (97 mg, 1.23 mmol) were refluxed in EtOH (20 mL) for 2 h. The solvent was evaporated, and the crude was dissolved in Et_2O and washed with aqueous HCl (10%), water, and brine. The extract was dried ($MgSO_4$), filtered, and evaporated to dryness. Flash chromatography using hexane/Et_2O (8:2) as eluent gave 166 mg (80%) of the corresponding oxime: ^{1}H NMR (300 MHz) δ 0.9 (s, 3 H), 1.3 (s, 3 H), 2.2 (d, J = 5.6 Hz, 1 H), 2.5 (dd, J = 5.6, 8.4 Hz, 1 H), 6.5 (d, J = 8.4 Hz, 1 H), 7.2−7.4 (m, 5 H); ^{13}C NMR (75 MHz) δ 21.6, 22.8, 24.8, 26.6, 38.2, 126.2−128.8, 152.4; IR (neat) 3100, 1610 cm^{-1}. To a solution of this oxime (100 mg, 0.5 mmol) in pyridine (1 mL) at 0 °C was added acetyl chloride (0.05 mL, 0.8 mmol). The mixture was stirred for 1 h at 0 °C. The crude was dissolved in Et_2O (100 mL) and washed successively with 10% aqueous $NaHCO_3$ and brine. The organic layer was dried ($MgSO_4$), filtered and evaporated to dryness. Flash chromatography using hexane/Et_2O (9:1) as eluent gave 75 mg (62%) of oxime acetate **20**[19] as a colorless oil. Spectral data were identical to those previously described.

***m*-Methoxyacetophenone-Sensitized Irradiation of 6.** Compound **6** (500 mg, 2 mmol) and *m*-methoxyacetophenone (5 g, 33.3 mmol) were irradiated for 2 h. Flash chromatography using hexane/Et_2O (9:1) as eluent gave 150 mg (30%) of recovered **6** and 285 mg (57%) of cyclopropyl aldehyde **21**.[20]

***m*-Methoxyacetophenone-Sensitized Irradiation of 22.** Compound **22** (60 mg, 0.2 mmol) and *m*-methoxyacetophenone (2 g, 13.3 mmol) were irradiated for 11 h. Flash chromatography using hexane/Et_2O (9:1) as eluent gave 48 mg (80%) of recovered starting material.

***m*-Methoxyacetophenone-Sensitized Irradiation of 23.** Compound **23** (291 mg, 1.5 mmol) and *m*-methoxyacetophenone (2.2 g, 14.7 mmol) were irradiated for 10 min. Flash chromatography using hexane/Et_2O (99:1) as eluent gave 242 mg (83%) of cyclopropyl aldehyde **25** as a colorless oil: ^{1}H NMR (300 MHz) δ 0.8 (s, 3 H), 1.5 (s, 3 H), 1.6 (m, 1 H), 2.5 (m, 2 H), 2.6 (s, 1 H), 2.9 (m, 1 H), 7.0−7.1 (m, 4 H), 9.4 (s, 1 H); ^{13}C NMR (75 MHz) δ 18.7, 19.2, 22.3, 28.4, 34.5, 34.9, 41.0, 126.1−137.8, 202.1; IR (neat) 1700, 1610 cm^{-1}. This compound was further characterized by its conversion into the corresponding oxime using standard procedures.[23b]

***m*-Methoxyacetophenone-Sensitized Irradiation of 24.** Compound **24** (400 mg, 1.6 mmol) and *m*-methoxyacetophenone (10 g, 66 mmol) were irradiated for 2 h. Flash chromatography using hexane/Et_2O (9:1) as eluent gave 385 mg (96%) of cyclopropyl aldehyde **26** as a colorless oil: ^{1}H NMR (300 MHz) δ 1.4 (s, 3 H), 1.7 (s, 3 H), 2.7 (d J = 5.4 Hz, 1 H), 7.1−7.8 (m, 8 H), 9.9 (d, J = 5.4 Hz, 1 H); IR (neat) 1690 cm^{-1}. The spectral data of this compound were identical in all respects with those described previously.[22]

***m*-Methoxyacetophenone-Sensitized Irradiation of 27.** Compound **27** (300 mg, 1.7 mmol) and *m*-methoxyacetophenone (1.7 g, 11 mmol) were irradiated for 20 min. Flash chromatography using hexane/Et_2O (9:1) as eluent gave 90 mg (30%) of aldehyde **27** as a 3:2 mixture of *E:Z* isomers and 140 mg (47%) of cyclopropyl aldehyde **31** as an oil and as a 1:8 mixture of *cis:trans* isomers.

***E:Z* isomers 27:** ^{1}H NMR (250 MHz) δ 1.13 (s, 3.6 H, *E*-isomer), 1.16 (s, 2.4 H, *Z*-isomer), 1.6 (m, 4 H), 2.3 (m, 4 H), 5.1 (d, J = 11.2 Hz, 0.4 H, *Z*-isomer), 5.3 (d, J = 15.4 Hz, 0.6 H, *E*-isomer), 5.9 (m, 1 H), 6.1 (m, 1 H), 9.3 (s, 0.6 H, *E*-isomer), 9.4 (s, 0.4 H, *Z*-isomer); ^{13}C NMR (63 MHz) δ 21.6, 23.5, 26.1, 26.2, 26.3, 26.4, 29.2, 29.5, 34.1, 34.5, 48.0 (*Z*-isomer), 48.8 (*E*-isomer), 115.5, 120.0, 128.7, 129.3, 129.6, 130.9, 148.8 (*E*-isomer), 151.8 (*Z*-isomer), 202.3 (*E*-isomer), 203.7 (*Z*-isomer); IR (neat) 2810, 2710, 1730, 1640 cm^{-1}.

Compound 31: ^{1}H NMR (250 MHz) δ 1.12 (s, 2.64 H, *trans*-isomer), 1.14 (s, 0.36 H, *cis*-isomer), 1.26 (s, 2.64 H, *trans*-isomer), 1.32 (m, 0.36 H, *cis*-isomer), 1.6 (m, 5.88 H), 2.0 (m, 0.12 H, *cis*-isomer), 2.2 (m, 4 H), 5.0 (dt, J = 8.5, 2.3 Hz, 0.88 H, *trans*-isomer), 5.4 (dt, J = 8.5, 2.3 Hz, 0.12 H, *cis*-isomer), 9.37 (d, J = 6.5 Hz, 0.88 H, *trans*-isomer), 9.38 (s, J = 5.6, 0.12 H, *cis*-isomer); IR (neat) 1700 cm^{-1}. The spectral data of this compound were identical in all respects with those described previously.[22]

***m*-Methoxyacetophenone-Sensitized Irradiation of 28.** Compound **28** (300 mg, 2 mmol) and *m*-methoxyacetophenone (1.3 g, 8.6 mmol) were irradiated for 15 min. Flash chromatography using hexane/Et_2O (98:2) as eluent gave 127 mg (42%) of aldehyde **28** as a 1:1 mixture of *E:Z* isomers and 155 mg (52%) of *trans*-cyclopropyl aldehyde **32** as a colorless oil: ^{1}H NMR (300 MHz) δ 1.2 (s, 3 H), 1.3 (s, 3 H), 1.61 (m, 1 H), 1.70 (s, 3 H), 1.72 (s, 3 H), 2.1 (m, 1 H), 4.91 (d, J = 7.8 Hz, 1 H), 9.4 (d, J = 5.4 Hz, 1 H); ^{13}C NMR (63 MHz) δ 18.6, 21.8, 22.3, 25.7, 29.8, 31.6, 34.7, 45.2, 120.1, 135.9, 200.6; IR (neat) 2720, 1700 cm^{-1}. The spectral data of this compound were identical in all respects with those described previously.[22]

Acetophenone-Sensitized Irradiation of 35. Compound **35** (350 mg, 94 mmol) and acetophenone (5.7 mL, 46.6 mmol) were irradiated for 10 min. Flash chromatography of the crude using hexane/Et_2O (98:2) as eluent gave 28 mg (8%) of 1,1,3,3-tetraphenylpropene (**37**)[27] and 287 mg (82%) of cyclopropyl aldehyde **38** as a white solid: mp 200−202 °C (lit.[25a] mp 205−207 °C); ^{13}C NMR (75 MHz) δ 42.4, 51.6, 126.4−142.3, 202.5.

***m*-Methoxyacetophenone-Sensitized Irradiation of 36.** Compound **36** (300 mg, 1.15 mmol) and *m*-methoxyacetophenone (1.25 mg, 8.3 mmol) were irradiated for 10 min. Flash

chromatography using hexane/Et_2O (98:2) as eluent gave 164 mg (55%) of **36** and 56 mg (19%) of cyclopropyl aldehyde **39** as an oil and as a 3:2 mixture of *RS,SR:RR,SS* isomers: ^{1}H NMR (300 MHz) δ 1.2 (s, 1.8 H, *RS,SR* isomer), 1.6 (s, 1.2 H, *RR,SS* isomer), 2.53 (d, $J = 7.3$ Hz, 0.6 H, *RS,SR* isomer), 2.57 (d, $J = 7.3$ Hz, 0.4 H, *RR,SS* isomer), 5.0−5.25 (m, 1.8 H), 5.34 (dd, $J = 1.2$, 17.1 Hz, 0.6 H, *RS,SR* isomer), 6.1 (dd, $J = 10.4$, 17.1 Hz, 0.6 H, *RS,SR* isomer), 7.1−7.4 (m, 10 H), 9.25 (d, $J = 7.3$ Hz, 0.6 H, *RS,SR* isomer), 9.26 (d, $J = 7.3$ Hz, 0.4 H, *RR,SS* isomer); ^{13}C NMR (75 MHz) δ 15.4, 20.2, 37.5, 38.0, 44.9, 47.0, 52.1, 52.7, 113.1, 114.6, 126.2−130.5, 137.3, 138.6, 139.0, 141.8, 142.6, 200.8, 201.0.

***m*-Methoxyacetophenone-Sensitized Irradiation of 43.** Compound **43** (280 mg, 0.67 mmol) and *m*-methoxyacetophenone (4.3 g, 28.6 mmol) were irradiated for 15 min. Flash chromatography using hexane/Et_2O (9:1) as eluent gave 130 mg (46%) of **43** and 134 mg (48%) of cyclopropyl aldehyde **44** as a 1:1 mixture of *RR,SS:RS,SR* isomers and as a white solid: ^{1}H NMR (300 MHz) δ 0.9 (s, 1.5 H, *RR,SS* isomer), 1.3 (s, 1.5 H, *RS,SR* isomer), 2.6 (d, $J = 9$ Hz, 0.5 H, *RR,SS* isomer), 3.1 (d, $J = 9$ Hz, 0.5 H, *RS,SR* isomer), 5.6 (d, $J = 9$ Hz, 0.5 H, *RS,SR* isomer), 6.2 (d, $J = 9$ Hz, 0.5 H, *RR,SS* isomer), 6.8−7.8 (m, 20 H), 8.4 (s, 0.5 H, *RS,SR* isomer), 9.3 (s, 0.5 H, *RR,SS* isomer); ^{13}C NMR (75 MHz) δ 11.4, 15.3, 34.7, 39.4, 43.5, 43.8, 49.2, 52.4, 122.5, 123.1, 126−130.8, 138.0, 138.9, 139.2, 139.5, 141.8, 142.4, 142.8, 144.6, 145.3, 201.8, 201.9; IR (neat) 1695 cm^{-1}. This compound was further characterized by conversion into the corresponding oxime using standard procedures.[23b]

Acetone-Sensitized Irradiation of 46. Compound **46** (660 mg, 5.2 mmol) and acetone (450 mL) were irradiated for 3.5 h. Flash chromatography of the crude using hexane/Et_2O (95:5) as eluent gave 100 mg (19%) of 2,4,4,5,5,7-hexamethyl-2,6-octadiene (**49**)[32] and 520 mg (79%) of **46**.

Acetone-Sensitized Irradiation of 47. Compound **47** (130 mg, 0.52 mmol) and acetone (450 mL) were irradiated for 30 min. Flash chromatography of the crude using hexane/Et_2O (95:5) as eluent gave 16 mg (14%) of 3-methyl-1,1-diphenyl-2-butene (**51**),[18] 10 mg (8%) of cyclopropane **21**,[20] and 97 mg (75%) of **47**.

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Supporting Information Available: ^{1}H NMR spectra of **9**, **14b**, **15b**, and **44** as well as ^{13}C NMR spectra of **10**, **14a**, **15a**, **19**, **25**, and **39** (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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