A Study of the Competition between the Di-π-methane and the Azadi-π-methane Processes in 2-Vinyl-β,γ-unsaturated Oxime Derivatives. The Novel Azadi-π-methane Reactivity of β,γ-Unsaturated Oximes

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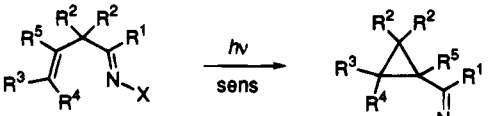
A study aimed at detecting intramolecular competition between the di-π-methane (DPM) rearrangement and the azadi-π-methane (ADPM) process has been carried out. The results show that direct or acetophenone-sensitized irradiation of 2-(2,2-diphenylvinyl)-2-methyl-4,4-diphenyl-3-butenal oxime acetate **3** and the corresponding oxime trifluoroacetate **11** undergo only the DPM process to yield cyclopropanes. Similar DPM rearrangement was observed for 2-methyl-4,4-diphenyl-2-vinyl-3-butenonitrile **22**. These are examples of triplet DPM reactivity in acyclic substrates where the central carbon has only one electron-withdrawing group. There is only one case of such reactivity in the aryl di-π-methane process. However, 2-methyl-4,4-diphenyl-2-vinyl-3-butenal oxime acetate **26** and the corresponding trifluoroacetate **15** undergo the ADPM rearrangement exclusively on direct or acetophenone-sensitized irradiation. The selectivity observed is interpreted as being dependent on the relative stabilities of the 1,4-bridged biradical intermediates. Based on previous failures to observe the ADPM reactions of β,γ-unsaturated oximes, an attempt to suppress the ADPM reactivity in compounds with a substitution pattern such as that present in **15** and **26** was made using the parent oxime **21**. Surprisingly this compound reacts efficiently by the ADPM process and affords cyclopropane **30**. This is the first example of ADPM reactivity of an acyclic β,γ-unsaturated oxime. All the rearrangements described are stereoselective. This reaction was extended to other oximes **45**, **47a** and **47b** and also to the oxime ether **36**. The photoreaction of **47b** shows that the ADPM rearrangement of oximes can be extended to ketone derivatives. Previous studies have shown that such reactivity is uncommon. β,γ-Unsaturated oximes are usually considered to be photochemically inert but these results have shown that changes in substitution can promote efficient ADPM reactivity.

Introduction

Over the past decade we have demonstrated that the ADPM rearrangement of 1-aza-1,4-dienes is very general in acyclic systems.[1a–n] Recently the reaction has been extended to cyclic derivatives in a novel synthesis of oxime acetates derivatives of 1-carbaldehydobicyclo[n.1.0]-alkanes (Scheme 1).[1o] Indeed its synthetic usefulness probably surpasses that of the oxadi-π-methane (ODPM) analog.[2]

The reaction described by us arises from the triplet state and in this respect there are similarities with the oxygen counterpart. Furthermore the ADPM reaction has been shown by us to be extremely efficient and in some cases to be more efficient than the DPM rearrangement. In contrast to the triplet state reactivity of the ADPM reaction, however, the acyclic DPM process occurs usually from the singlet state although there are some examples where this generality is not followed.[3] Our interest at this stage was to study the possibility of having control on which process would occur: direct excitation effecting the DPM process and triplet sensitization the ADPM reaction, for example. Others[4] have

Scheme 1



X = R, OCOR or NHCOR
R^1 = H or Me
R^2 = Me or Ph
R^3 = Ph, Me, -CH=CR_2, COOEt, or CN, etc.
R^4 = Ph, Me or H
R^3 = R^5 = -$(CH_2)_3$-, -$(CH_2)_4$-, $(CH_2)_2$-

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(1) (a) Armesto, D.; Martín, J. F.; Perez-Ossorio, R.; Horspool, W. M. *Tetrahedron Lett.* **1982**, *23*, 2149. (b) Armesto, D.; Horspool, W. M.; Martín, J. F.; Pérez-Ossorio, R. *J. Chem. Research (S)* **1986**, 46. (c) Armesto, D.; Langa, F.; Fernandez-Martin, J. A.; Perez-Ossorio, R.; Horspool, W. M. *J. Chem. Soc., Perkin Trans. 1* **1987**, 743. (d) Armesto, D.; Horspool, W. M.; Langa, F.; Perez-Ossorio, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1039. (e) Armesto, D.; Horspool, W. M.; Langa, F. *J. Chem. Soc., Chem. Commun.* **1987**, 1874. (f) Armesto, D.; Horspool, W. M.; Langa, F. *J. Chem. Soc., Perkin Trans. 2* **1989**, 903. (g) Armesto, D.; Gallego, M. G.; Horspool, W. M. *Tetrahedron Lett.* **1990**, *31*, 2475. (h) Armesto, D.; Agarrabeitia, A. R.; Horspool, W. M.; Gallego, M. G. *J. Chem. Soc., Chem. Commun.* **1990**, 934. (i) Armesto, D.; Gallego, M. G.; Horspool, W. M. *Tetrahedron* **1990**, *46*, 6185. (j) Armesto, D.; Horspool, W. M.; Mancheño, M. J.; Ortiz, M. J. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2348. (k) Armesto, D.; Horspool, W. M.; Langa, F.; Ramos, A. *J. Chem. Soc., Perkin Trans. 1* **1991**, 223. (l) Armesto, D.; Horspool, W. M.; Gallego, M. G.; Agarrabeitia, A. R. *J. Chem. Soc., Perkin Trans. 1* **1992**, 163. (m) Armesto, D.; Horspool, W. M.; Mancheño, M. J.; Ortiz, M. J. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2325. (n) Armesto, D.; Horspool, W. M.; Gallego, M. G.; Bermejo, F. ES. P. 9100648 (13th March 1991); Patent PCT/ ES 92/ 00017 (13th February 1992). (o) Armesto, D.; Ramos, A. *Tetrahedron* **1993**, *49*, 7159.

(2) (a) Houk, K. N. *Chem. Rev.* **1976**, *76*, 1. (b) Demuth, M. *Org. Photochem.* **1991**, *11*, 37.

(3) Zimmerman, H. E. *Org. Photochem.* **1991**, *11*, 1.

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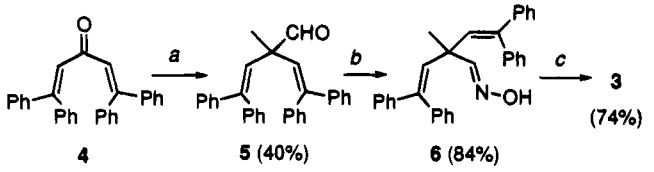
Scheme 2[a]

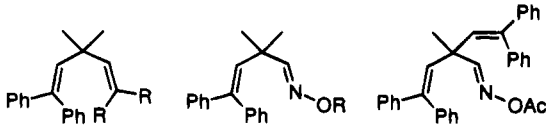


[a] Reagents: (a) (i) PhCH=NCHPO(OEt)$_2$Li, (ii) *n*-BuLi, MeI, (iii) H_3O^+; (b) NH_2OH·HCl, pyridine; (c) MeCOCl, pyridine.

described a similar but largely unsuccessful search for competition between the DPM and the ODPM processes. Thus because of the efficiency of the ADPM reaction and its synthetic utility it is of considerable interest to compare the relative reactivities (ADPM *vs.* DPM) in a situation where both reactions could take place in the same molecule. Some of the results described here have been the subject of a preliminary communication.[5]

Results and Discussion

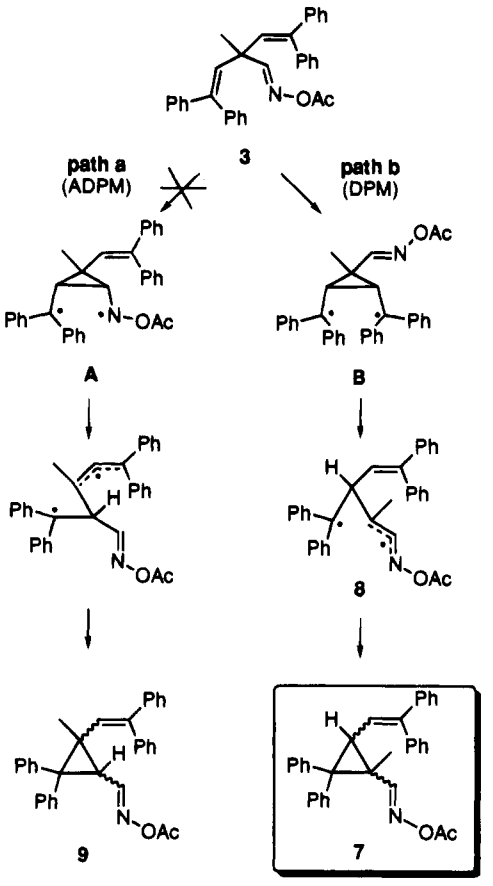
To study competition between the DPM and the ADPM processes it was necessary to design molecules with the essential components suitably placed with respect to each other. The criterion used to choose the components for the appropriate molecule for the study was that the quantum efficiency of the two types of reactivity should be comparable. Our decision of the components to be included within the target molecule is based on the observations of Zimmerman and Mariano[6] who demonstrated that the tetraphenyl-1,4-diene **1a** underwent the DPM rearrangement with a quantum yield of 0.08 while from our own studies[1k] the diphenylvinyl oxime acetate **2a** undergoes the ADPM reaction with a similar efficiency of 0.12. Putting these components together meant that the target molecule should be the azatriene **3**.



This molecule was synthesized using dienone **4** as the starting material. This is transformed into the aldehyde **5**, the oxime **6** and the oxime acetate **3** (Scheme 2).

Compound **3** was irradiated for 1h under the direct conditions in methylene dichloride. The conversion, in chemical terms, was efficient and afforded a cyclopropane in 75% yield and recovered starting material making up the balance. The identity of the cyclopropane was established by the conventional methods and ^{1}H NMR spectroscopy showed it to be a 3:2 mixture of stereoisomers of **7**. An examination of the possible routes to this product, illustrated in Scheme 3, shows that **7** arises exclusively from the DPM rearrangement (path b). Proof of this structural assignment relies on an analysis of the ^{1}H NMR spectrum showing that the imine hydrogen absorption in the *RR,SS* isomer appears as a singlet at

Scheme 3

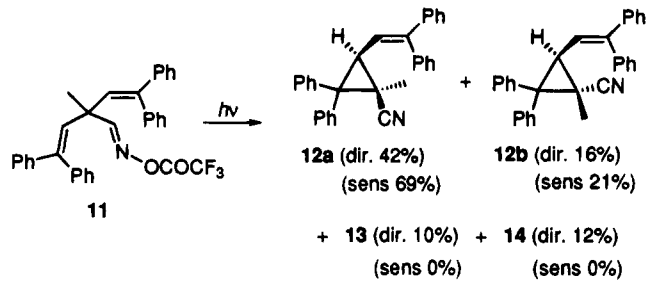


δ 7.6 and at δ 6.8 in the *RS,SR* while the vinyl hydrogen absorption is a doublet at δ 5.8 in the former and a doublet at δ 5.7 in the latter. This identifies the regioisomer obtained as that shown in **7**. The other regioisomer **9**, if it had been formed, would have the imine hydrogen as a doublet and the vinyl hydrogen as a singlet. No evidence was obtained for the intervention of the alternative reaction mode, the ADPM rearrangement (path a) yielding cyclopropane **9**, or formation of other products such as pyrrolines that could have arisen by alternative cyclization modes of the intermediate biradical **8**.

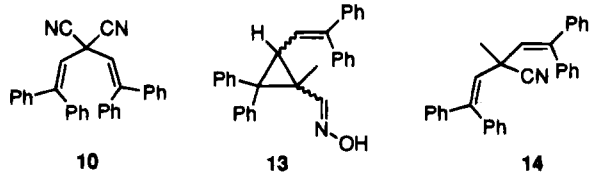
At this stage this was not surprising since we have already established that the ADPM reaction is much more efficient on sensitized irradiation, while the DPM process is generally a reaction arising from the singlet state in acyclic systems. However, sensitized irradiation of **3** (acetophenone in benzene for 15 min) also failed to provide evidence for the ADPM reaction path and again **7** (as a mixture of stereoisomers) was obtained in an even better yield of 84% (Scheme 3). However, it is surprising that the DPM reaction mode is operative from the triplet state in this system. Zimmerman *et al.*[7] have shown in some cases, *e.g.* **10**, that the DPM rearrangement can arise from the triplet state. The key to this reactivity is the presence of two electron-withdrawing groups on the central carbon. Others have observed, in the aryl di-π-methane process, that rearrangement from the triplet state can occur with only one electron-withdrawing substituent, a keto group, on the central carbon.[8] However, here we have demonstrated that the acyclic divinyl

(4) Van der Veen, R. H.; Kruk, C.; Cerfontain, H. *J. Am. Chem. Soc.* **1983**, *105*, 4367.
(5) Armesto, D.; Ramos, A.; Mayoral, E. P. *Tetrahedron Lett.* **1994**, *35*, 3785.
(6) Zimmerman, H. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1969**, *91*, 1718.
(7) Zimmerman, H. E.; Armesto, D.; Amezua, M. G.; Gannett, T. P.; Johnson, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 6367.

Scheme 4



DPM reaction will also occur very efficiently from the triplet state with only one electron-withdrawing substituent, an acetoxyimino group, at that position. Thus it was clear that our original premise, that the di-π- and the azadi-π-reactions should take place with comparable quantum efficiency, was incorrect.



Previously, we have shown that the ADPM reaction is even more efficient in trifluoroacetate oxime derivatives.[1m] Compound **11**, prepared from **6** by esterification with trifluoroacetic anhydride, incorporates this substitution but irradiation under direct and sensitized conditions failed again to provide any evidence for the operation of the ADPM reaction and only the products from the DPM path are obtained (Scheme 4). The thermal sensitivity of the trifluoroacetyl derivatives that we have observed[1m] previously is also seen here with elimination of trifluoroacetic acid to afford the cyclopropylnitriles **12a** and **12b** or hydrolysis to yield the oxime **13**. The diene **14** is essentially recovered starting material from which elimination of trifluoroacetic acid has occurred. These eliminations and hydrolyses occur during work-up.

Previous work by us[1c] and others[9] has demonstrated that acyclic β,γ-unsaturated oximes and oxime ethers do not undergo the ADPM process. The lack of ADPM reactivity in the preceding experiments indicated to us that there was no need to use oxime esters and the irradiation of **6** follows the path established already for **3** and **11**. On both direct and sensitized irradiation **6** is converted into a mixture of stereoisomers of the cyclopropane **13** (direct 66% yield after 1 h; sensitized 82% yield after 15 min).

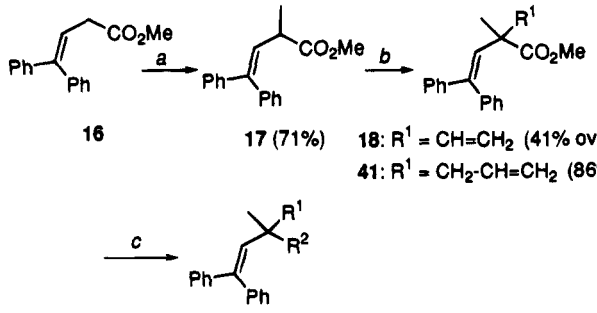
The assignment of structure of the mixtures of isomers of cyclopropanes **7**, **13**, and **12**, obtained in the irradiations of **3**, **6**, and **11** respectively, was carried out by the ^{1}H NMR analysis of the cyclopropane isomers **12a** and **12b** obtained from the irradiation of **11**. These derivatives, **12a** and **12b**, were separated by column chromatography. ^{1}H NMR analyses, specifically NOE experiments on the individual compounds, permitted the structural assignment of **12a** and **12b** as the *RR,SS* and *RS,SR* diastereoisomers respectively. Thus, irradiation at 1.2 ppm enhanced the signal at 2.4 ppm (9%) in isomer **12a**, while irradiation at 1.5 ppm produced no enhancement of the signal at 2.9 ppm in isomer **12b**. Using these assignments it was possible to analyze the inseparable mixtures of stereoisomers obtained from the irradiations of **3** and **6**. The percentage of stereoisomers was established in all the cases by ^{1}H NMR analyses of the crude photolysates. Thus the mixture of isomers from **3** was composed of 60% *RR,SS* and 40% *RS,SR* while those from **6** and **11** contained 75% *RR,SS* and 25% *RS,SR*. Similar stereoselectivity was observed for the sensitized irradiations of **3**, **6**, and **11**. The ring closure within the intermediate 1,3-biradicals, such as **8**, (Scheme 3, path b) to afford the cyclopropane occurs stereoselectively and always yields a predominance of the isomer in which the diphenylvinyl group is *cis* to the cyano or imino group.

From the foregoing experiments it appears that the DPM rearrangement always takes precedence over the ADPM process even in situations where the quantum yield for the latter, in the isolated system, is marginally better than the corresponding quantum yield for the DPM rearrangement. A possible reason for this could be due to the difference in the stability of the 1,4-bridged biradical, or subsequent 1,3-biradical obtained after bond rupture, for the two possible rearrangement paths (paths a and b, Scheme 3). Scheme 3 shows that in simple terms the DPM process, involving biradical **B**, will be preferred to the ADPM rearrangement, involving biradical **A**, since the biradical **B** is more stable. The same argument applies to the outcome of the irradiation of **6** and **11**. If this proposal is correct the implication is that a decrease in the stability of the biradical **B**, while maintaining the stability of biradical **A**, might lead to a situation where the rearrangement would follow the ADPM path, i.e., the stability of biradical **A** will dominate. As a consequence, the criterion for a target molecule within which there could be competition between the DPM and the ADPM rearrangements has to be changed so that the ADPM reaction would be more competitive. These conditions are satisfied by compound **15**. Studies have shown that the quantum yield for the DPM reactivity of 3,3-dimethyl-1,1-diphenyl-1,4-pentadiene (**1b**)[9] is 0.02 while that for the ADPM rearrangement of **2a** is 0.12.[1k] In this case the ADPM process is more efficient and, therefore, it should stand a better chance of competing.

Compound **15** was prepared from oxime **21** by reaction with trifluoroacetic anhydride. The synthetic approach to **21** is outlined in Scheme 5 starting from methyl 4,4-diphenyl-3-butenoate (**16**). Irradiation of compound **15** under sensitized conditions afforded a mixture of the three products shown in Scheme 6. The oxime **21** and the diene **22** are artifacts of the work-up procedure and result from hydrolysis and elimination of trifluoroacetic acid, respectively, from the starting material. The third product **23** is a cyanocyclopropane formed by elimination of trifluoroacetic acid from the corresponding oxime trifluoroacetate. The substitution pattern on this cyclopropane shows that it can arise only by the ADPM path. Justification for this assignment comes from the fact that the cyclopropyl hydrogen appears as a singlet at δ 2.38 in the *RS,SR* isomer and at δ 2.41 in the *RR,SS*. Compound **23** was obtained as a 2:3 mixture of isomers. The relative stereochemical assignment was made on the basis of NOE experiments of the mixture of isomers. Irradiation at 1.2 ppm, which corresponds to the methyl group of the major isomer, enhanced the signal at 2.38 (5%) which corresponds to the cyclopropyl-H of the same isomer. However, irradiation at 1.5 ppm (methyl group of the minor isomer) produced no enhancement of the

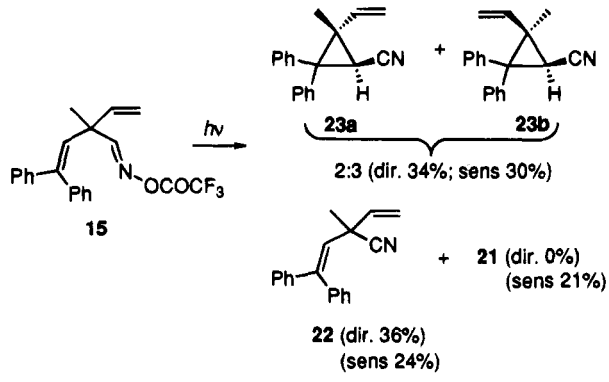
(8) Koppes, M.; Beentjes, P.; Cerfontain, H. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 313.
(9) Pratt, A. C.; Abdul-Majid, Q. *J. Chem. Soc., Perkin Trans. 1* **1987**, 359.

Scheme 5[a]



[a] Key: (a) LDA, MeI; (b) for **18**: (i) NaH, $PhSOCH{=}CH_2$, (ii) heating at 200 °C for 30 min; for **41**: KBu^{t}O, $CH_2{=}CHCH_2Br$; (c) reduction of **18** and **41** using $LiAlH_4$ afforded alcohols **19** and **42**, respectively. Oxidation of **19** and **42** with PCC gave aldehydes **20** and **43**. Condensation of these with NH_2OH yielded oximes **21** and **44**, respectively. Treatment of **21** with $(CF_3CO)_2O$ gave trifluoroacetate **15**.

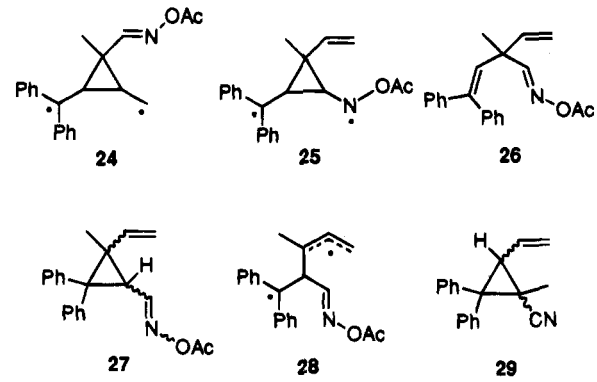
Scheme 6



signal at 2.41 ppm (cyclopropyl-H of the same isomer). Thus the mixture of isomers from **15** was composed of 40% *RR,SS* (**23a**) and 60% *RS,SR* (**23b**).

This result supports our earlier postulate and in this example the bridged 1,4-biradical **24**, leading to the DPM product, is considerably less stable than the biradical **B** in Scheme 3. At the same time biradical **25**, leading to the ADPM product, is comparable in stability to biradical **A** (Scheme 3). Therefore, the reaction follows the ADPM rearrangement. This ADPM path is followed also by oxime acetate **26** which on irradiation for 10 min under sensitized conditions affords a cyclopropane **27**. Thermal elimination of acetic acid gives cyclopropane **23** (30% yield) as a mixture of two stereoisomers. No evidence was obtained for the formation of other products such as cyclopentenes that could have arisen by alternative cyclization modes of the biradical intermediate **28** resulting from the ring opening of biradical **25**.

In the two examples studied it was not possible to observe competition between the ADPM and the DPM paths. However, by changing the relative stability of the bridging 1,4-cyclopropyl biradical it is possible to bring about exclusively either the DPM or the ADPM rearrangement. Nevertheless the reactions can be used to synthesize different cyclopropane regioisomers. Whereas

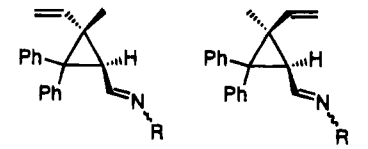


irradiation of **15** and **26** yields **23** by the ADPM path, irradiation of **22** follows the DPM reaction mode and yields the isomeric cyclopropane **29** (52%, 4:1 ratio of *RR,SS*:*RS,SR*). The ^{1}H NMR spectrum of **29** shows the cyclopropyl hydrogen as a doublet at δ 2.5 coupled with the vinylic hydrogen confirming its identity. Comparison of this datum with that of the regioisomer **23**, where the cyclopropyl hydrogen is singlet, is a clear demonstration of the regioselectivity in the two reactions. We have demonstrated already that the ADPM process does not take place with nitriles[1c] thus it is no surprise to find that the DPM process is operational. This demonstration of triplet state DPM reactivity of **22** is another example of a system where the central carbon is substituted with one electron-withdrawing group.

In view of our previous results[1c] where it was demonstrated that the oxime **2c** did not undergo the ADPM process, a logical extension of our studies was to examine the photobehavior of the oxime **21**. Zimmerman *et al.*[10] have shown that the 1,4-diene moiety in **21** (cf. **1b**) is capable of undergoing the DPM rearrangement, albeit with a comparatively low quantum yield. Therefore, it was expected that in this case the DPM rearrangement would be operative. This compound **21** is a further example where the central carbon is substituted with a single electron-withdrawing group thus it was anticipated that the reaction should take place on sensitization. Indeed irradiation under these conditions was shown to be efficient and conversion to a cyclopropane (in a yield of 30%) took place within 20 min. The same cyclopropane was obtained on direct irradiation of **21** although the process was much less efficient and required irradiation times of 4.75 h to produce 21% of the photoproduct. The great surprise was the identification of the cyclopropane as **30** that can only arise by the ADPM reaction path as illustrated in Scheme 7. The product was obtained as a mixture of four stereoisomers. Column chromatography permits the separation of the *RS,SR*/*RR,SS* pair of *E*-oxime isomers from the pair of *Z*-isomers. However, the *E,Z*-conversion occurs very readily at room temperature. ^{1}H NMR analysis was used to establish that the ratio of *RS,SR*:*RR,SS* was 3:2. Confirmation that this ratio is as recorded is achieved by conversion of cyclopropanes **30** into the cyanocyclopropanes **23** obtained previously by the irradiation of **15**. This confirms the reaction as an ADPM process.

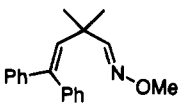
The photorearrangement by the ADPM path of the oxime was extremely surprising and unexpected in view of the failure of **2c**[1c] and related derivatives[9] **31** and **32** to undergo the ADPM process. As far as we are aware this is the first example of the ADPM reaction of an

(10) Zimmerman, H. E.; Klun, R. T. *Tetrahedron* **1978**, *34*, 1775.



30a: R = OH
37a: R = OMe

30b: R = OH
37b: R = OMe



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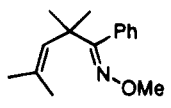
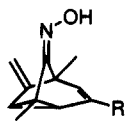
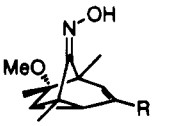


32





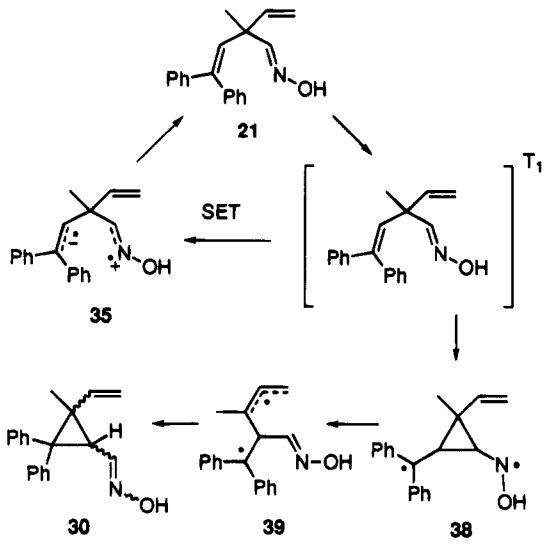
33: R = H or Me **34**: R = H or Me

acyclic β,γ-unsaturated oxime. An experiment, using 1,3-cyclooctadiene as quencher, demonstrated that this ADPM process is occurring from the triplet state since the formation of **30** was completely suppressed under these conditions. This triplet reactivity is in accord with all of the other ADPM processes we have described. The literature contains two other examples of the ADPM reaction of oximes in the highly constrained environment of the tricyclic compounds **33** and **34**.[11]

In earlier studies we proposed that the failure of oximes to undergo the ADPM reaction was due to the ease with which electron transfer could occur from the oxime lone pair to the diphenylvinyl moiety. This electron transfer was proposed as an energy-wasting step and once the zwitterionic biradical is formed this decays to starting material.[1d,f] We were able to overcome the failure of oximes to rearrange by the ADPM path by their conversion to oxime acetates and other derivatives where an electron-withdrawing group was attached to the oxime nitrogen.[1e,k] With these derivatives it was argued that the increase in the ionization potential of the nitrogen lone pair minimized the electron transfer and thus the ADPM reaction became operative and efficient with quantum yields of up to 0.82 and almost quantitative chemical yields in some cases. If this argument is to be used in explanation of the photoreactivity of the oxime **21**, then a method by which the ionization potential of the oxime nitrogen lone pair can be increased must be available to the molecule. One possibility is that the hydroxy group of the oxime could form a hydrogen bond with the 2-vinyl-substituent. That this is inoperative is shown by the experiment using the ether **36**. Sensitized irradiation of this also brings about its conversion into a mixture of isomers of the cyclopropane **37** (45%, 2.6:3.6 ratio of *RR,SS*:*RS,SR*) that can only arise from the ADPM process. Again this is surprising in view of earlier studies that demonstrated[9] the failure of the oxime ethers **31** and **32** to rearrange. A possible explanation for the successful ADPM rearrangement of the oxime **21**, while other oximes fail to undergo such a reaction, might be related to differences between the energy barriers for the various processes that are open to the excited state of

(11) (a) Nitta, M.; Inoue, O.; Tada, M. *Chem. Lett.* **1977**, 1065. (b) Nitta, M.; Kasahara, I.; Kobayashi, T. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1275.

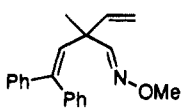
Scheme 7



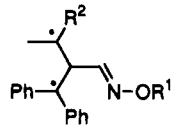
the molecule in question. The principal processes of concern are: (i) the conversion of the excited state via the bridging 1,4-biradical **38** to the biradical **39** and (ii) SET to the zwitterionic biradical **35**, the presumed energy wasting step. This line of argument is outlined in Scheme 7.

Thus, if the energy barrier for conversion of the excited state to the 1,3-biradical and thence to the ADPM product is lower than that for the SET process, ultimately leading back to starting material, then the ADPM process dominates. In the opposite situation SET will dominate and no rearrangement reaction will be observed. It is likely that subtle changes in substitution would be sufficient to alter the balance in reactivity. Thus, for the examples discussed above, the additional stability given to the biradical **39** (Scheme 7) by the vinyl substituent is sufficiently important to bring about the ADPM rearrangement and the SET process does not compete effectively. The converse must hold for the 1,3-biradicals **40a** and **40b** that would be formed by rearrangement of the oxime **2c** or its ether **31** respectively. In this situation the SET process is less energetic and is preferred to the ring opening of the 1,4-bridged biradical. Thus the oxime **2c** and the ether **31** fail to undergo the ADPM process. If the rearrangement of oximes is to be general then the 1,3-biradical has to be sufficiently stable so that the rearrangement can compete with the SET, the energy wasting step. As a test of this the sensitized irradiation of the oxime **44** was carried out. The synthesis of this oxime is outlined in Scheme 5. However, the irradiation of **44** failed to yield a product from the ADPM process and a complex inseparable mixture was obtained. This result supports the suggestion that the stability of the 1,3-biradical is crucial for the success of the ADPM process with oximes. Indeed the 1,3-biradical **40c** from oxime **44** is of the same stability as biradical **40a** generated from oxime **2c** or biradical **40b** from its ether **36**, both of which fail to react. The failure of the oxime **44** to rearrange also removes the possibility that a complex between the 2-vinyl group and the oxime group in **21** or between the oxime group and the 2-propenyl substituent in **44** would be a controlling feature in the ADPM rearrangement of such systems. The concept of the need to have a stable 1,3-biradical was tested further using the oxime **45**. Here again the sensitized reaction is rapid in qualitative terms and chemically efficient and

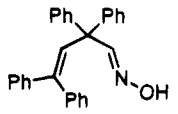
yields the ADPM product **46** in 74% after 30 min irradiation.



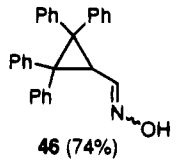
36 (73%)



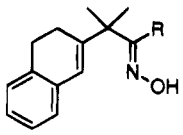
40a: R^1 = H, R^2 = Me
40b: R^1 = Me, R^2 = Me
40c: R^1 = H, R^2 = CH_2-CH=CH_2



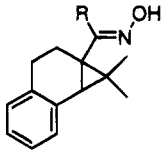
45



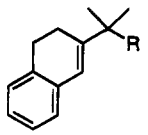
46 (74%)



47a: R = H
47b: R = Me (65%)



48a: R = H (63%)
48b: R = Me (66%)



49a: R = COOEt
49b: R = COOH (76%)
49c: R = COMe (78%)

In the systems described above the question of energy wasting by the free rotor effect, i.e. rotation of the alkene double bond in the excited state, was not addressed. Such a process is well known to be an efficient deactivator of triplet excited states in the DPM process.[3] The problem was examined using compound **47a**. Sensitized irradiation shows that in qualitative terms conversion to the corresponding cyclopropane **48a** is efficient (63% yield in 20 min). More surprisingly we have observed that the ketoxime derivative **47b** is also reactive. This compound is synthesized by the sequence **49a–c**. This is readily transformed into the oxime **47b** by standard procedures. Sensitized irradiation of **47b** affords the cyclopropane **48b** efficiently in 66% yield after 15 min of irradiation. Our previous studies with β,γ-unsaturated imines and oxime acetates from ketones had demonstrated that these compounds underwent the ADPM rearrangement very inefficiently.[1c,k] Thus, this is the first example of a chemically efficient ADPM rearrangement in a keto derivative with the added novelty that the reaction is taking place in a β,γ-unsaturated oxime. The results obtained in the irradiation of oximes **47a** and **47b** show that the stability of the intermediate biradicals is not the only factor controlling the ADPM reactivity of β,γ-unsaturated oximes. The suppression of some of the deactivation routes open to the excited state, such as the free rotor effect, can also enhance ADPM reactivity. This observation opens the possibility of extending the ADPM reaction to many other β,γ-unsaturated oximes considered previously to be inert toward the rearrangement. Currently we are studying the scope of the ADPM rearrangement in β,γ-unsaturated oximes and the different factors that control the photochemical reactivity of these compounds.

Conclusions

Our results provide the first examples of triplet DPM reactivity in acyclic divinyl substrates where the central carbon has only one electron-withdrawing group. The rearrangements to cyclopropanes occur stereoselectively and efficiently. By changing the substitution on the β,γ-unsaturated oxime it is possible to obtain compounds that undergo the ADPM rearrangement efficiently and stereoselectively. The question of whether the DPM or the ADPM reaction is operative in a given system is interpreted as being dependent on the relative stabilities of the 1,4-bridged biradical intermediates. β,γ-Unsaturated oximes are usually considered to be photochemically inert but examples of efficient ADPM reactivity of such molecules are reported herein. The ADPM rearrangement of oximes has been observed by us in cases in which the intermediate biradicals are stabilized by conjugation with a vinyl or a phenyl substituent. In the absence of this stabilizing effect the suppression of the deactivation of the excited state by rotation of the alkene double bond, also permits the observation of efficient ADPM reactivity in an aldoxime and, more surprisingly, in a ketoxime. This study has increased the knowledge of the factors that control the DPM and the ADPM reactions and has permitted the extension of the ADPM rearrangement to novel stable derivatives of the CN double bond.

Experimental Section

Melting points were determined in open capillaries and are uncorrected. UV/visible 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.

2-(2,2-Diphenylvinyl)-2-methyl-4,4-diphenyl-3-butenal (5). A solution of *n*-BuLi (3.4 mL, 1.6 M in hexane) in dry THF (23 mL) under dry argon at −78 °C was added slowly to a solution of diethyl *N*-benzylidenaminomethyl phosphonate[12] (1.39 g, 5.5 mmol) in dry THF (2.3 mL), and the resulting red solution was stirred at −78 °C for 1 h. Then a solution of ketone **4**[13] (1.76 g, 4.6 mmol) in THF (2.3 mL) was added and the mixture was allowed to warm to room temperature. After refluxing for 2 h, the solution was cooled to −78 °C and *n*-BuLi (5.7 mL, 1.6 M in hexane) was added. The reaction mixture was stirred at −78 °C for 1 h and then MeI (0.85 mL, 13.6 mmol) was added. The cooling bath was removed and the reaction mixture was stirred at room temperature for 12 h. The solution was then added to 1 M aqueous HCl (22.7 mL), and the resulting heterogeneous mixture was stirred vigorously at room temperature for 2 h. A saturated aqueous solution of NaCl (11.4 mL) was added, and the aqueous layer was extracted with Et_2O. The organic solution was washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), filtered and concentrated to dryness. Flash chromatography of the residue using hexane/Et_2O (92:8) yielded **5** (0.75 g, 40%) as an oil: ^{1}H NMR (300 MHz) δ 1.3 (s, 3H), 6.0 (s, 2 H), 7.0–7.4 (m, 20 H), 9.0 (s, 1 H); IR (neat) 1725 cm^{-1}.

Methyl 2-Methyl-4,4-diphenyl-3-butenoate (17). To a solution of *i*-Pr_2NH (6.7 mL, 48 mmol) in 100 mL of dry THF were added successively, at −78 °C under argon, *n*-BuLi (48 mmol, 1.6 M in hexane) and HMPA (8.5 mL, 48 mmol). The resulting mixture was stirred for 1 h and then a solution of the ester **16**[14] (10 g, 40 mmol) in 50 mL of dry THF was added slowly over 10 min. After 1 h at −78 °C the solution was allowed to warm to −40 °C, and MeI (2.5 mL, 40 mmol) was added in one portion. The reaction mixture was stirred at −40 °C for 1 h, then the temperature was raised to −10 °C and the solution was quenched with 10% aqueous NH_4Cl. The mixture was extracted with Et_2O and the organic layer was washed with 5% aqueous HCl, water and brine. The extract was dried ($MgSO_4$), filtered and evaporated to dryness. Flash

(12) Ratcliffe, R. W.; Christensen, B. G. *Tetrahedron Lett.* **1973**, *46*, 4645.
(13) Marin, G. *Bull. Soc. Chim. Fr.* **1958**, 1594.
(14) Johnson, W. S.; Petersen, J. W.; Scheneider, W. P. *J. Am. Chem. Soc.* **1947**, *69*, 74.

chromatography of the residue using hexane/Et_2O (9:1) as eluent yielded the desired ester **17** (7.5 g, 71%) as a colorless oil: ^1H NMR (300 MHz) δ 1.3 (d, J = 7.5 Hz, 3 H), 3.3 (dq, J = 10.2, 7.5 Hz, 1 H), 3.7 (s, 3 H), 6.1 (d, J = 10.2, 1 H), 7.2–7.4 (m, 10 H); ^{13}C NMR (75 MHz) δ 18.3, 40.1, 51.7, 127.2–129.5, 139.1, 141.6, 142.9, 175.1; IR (neat) 1740 cm^{-1}; MS: 266 (M^+, 65), 208 (44), 207 (100); HRMS calcd for $C_{18}H_{18}O_2$ (M^+) 266.1307, found 266.1308.

Methyl 2-Methyl-4,4-diphenyl-2-vinyl-3-butenoate (18). Ester **17** (4.9 g, 18 mmol) in 100 mL of dry benzene was added dropwise to a suspension of 0.8 g of 60% NaH (20 mmol) in 100 mL of dry benzene, and the solution was stirred for 3 h at room temperature. Then, the reaction mixture was refluxed gently and a solution of phenylvinylsulfoxide (2.4 mL, 18 mmol) in 50 mL of benzene was added during 1 h. After refluxing for 12 h the reaction mixture was cooled and extracted with 5% aqueous NH_4Cl. The aqueous layer was washed with Et_2O, and the combined organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated to dryness. Flash chromatography of the residue afforded 4.7 g (61%) of a 1:1 mixture of stereoisomers of **methyl 2-methyl-4,4-diphenyl-2-(2-phenylsulfinylethyl)-3-butenoate** as a colorless oil: ^1HNMR (300 MHz) δ 1.229, 1.233 (2 s, 3 H), 2.0, 2.8 (2 m, 4 H), 3.27, 3.28 (2 s, 3H), 5.96, 5.98 (2 s, 1 H), 6.9–7.3 (m, 10 H), 7.5–7.6 (m, 5 H); ^{13}C NMR (75 MHz) δ 24.3, 31.9, 46.5, 51.4, 52.1, 123.8–143.1, 175.5; IR (neat) 1730 cm^{-1}.

Methyl 2-methyl-4,4-diphenyl-2-(2-phenylsulfinylethyl)-3-butenoate (4.7 g, 11 mmol) was heated at 200 °C for 30 min. Flash chromatography of the reaction mixture using hexane/CH_2Cl_2 (8:2) as eluent yielded 0.47 g of diphenyldisulfide. Further elution using hexane/CH_2Cl_2 (1:1) yielded the ester **18** (2.2 g, 67%) as a colorless oil: ^1H NMR (250 MHz) δ 1.4 (s, 3 H), 3.2 (s, 3 H), 5.10 (dd, J = 10.5, 0.6 Hz, 1 H), 5.15 (dd, J = 17.7, 0.6 Hz, 1 H), 6.0 (s, 1 H), 6.1 (dd, J = 17.7, 10.5 Hz, 1 H), 7.1–7.4 (m, 10 H); ^{13}C NMR (63 MHz) δ 25.3, 50.5, 51.6, 113.7, 127.0–130.1, 140.0, 141.8, 142.5, 142.9, 174.5; IR (neat) 1735, 1630 cm^{-1}; MS: 292 (M^+, 46), 233 (100); HRMS calcd for $C_{20}H_{20}O_2$ (M^+) 292.1463, found 292.1464.

2-Methyl-4,4-diphenyl-2-vinyl-3-buten-1-ol (19). A solution of the ester **18** (2.2 g, 7.5 mmol) in dry Et_2O (70 mL) was added slowly at 0 °C to a suspension of $LiAlH_4$ (0.29 g, 7.5 mmol) in Et_2O (50 mL). The resulting mixture was stirred at room temperature for 1 h. The residual $LiAlH_4$ was decomposed by addition of acetone, followed by aqueous NH_4Cl, and the ethereal layer was washed with brine. The extract was dried ($MgSO_4$), filtered and evaporated to dryness. Flash chromatography of the residue using hexane/Et_2O (8:2) as eluent yielded **19** (1.5 g, 75%) as a colorless oil: ^1H NMR (300 MHz) δ 1.0 (s, 3 H), 1.6 (s, 1 H), 3.4 (s, 2 H), 4.93 (dd, J = 10.2, 1.2 Hz, 1 H), 4.95 (dd, J = 17.9, 1.2 Hz, 1 H), 5.7 (dd, J = 17.9, 10.2 Hz, 1 H), 6.1 (s, 1 H), 7.2–7.4 (m, 10 H); ^{13}C NMR (63 MHz) δ 21.0, 45.8, 70.3, 113.9, 126.7–133.1, 140.3, 142.9, 143.3, 143.6; IR (neat) 3400, 1640 cm^{-1}; MS: 264 (M^+, 5), 233 (99), 155 (25), 105 (26), 91 (100); HRMS calcd for $C_{19}H_{20}O$ (M^+) 264.1514, found 264.1516.

2-Methyl-4,4-diphenyl-2-vinyl-3-butenal (20). Alcohol **19** (2.8 g, 11 mmol) and PCC (3.5 g, 16 mmol) were allowed to react in CH_2Cl_2 (50 mL) at room temperature for 24 h. The reaction mixture was filtered through silica gel and the solvent evaporated to give the desired aldehyde **20** (2.37 g, 85%) as a colorless oil which was used in the next step without further purification: ^1H NMR (250 MHz) δ 1.3 (s, 3 H), 5.20 (dd, J = 17.5, 0.6 Hz, 1 H), 5.23 (dd, J = 10.5, 0.6 Hz, 1 H), 5.9 (dd, J = 17.5, 10.5 Hz, 1 H), 6.1 (s, 1 H), 7.1–7.4 (m, 10 H), 9.0 (s, 1 H); ^{13}C NMR (63 MHz) δ 22.1, 53.6, 117.0, 126.7–132.6, 139.1, 139.5, 142.4, 144.2, 198.0; IR (neat) 2820, 2720, 1730, 1660 cm^{-1}; MS: 262 (M^+, 0.7), 182 (91), 105 (100); HRMS calcd for $C_{19}H_{18}O$ (M^+) 262.1358, found 262.1336.

Methyl 2-(2,2-Diphenylvinyl)-2-methyl-4-pentenoate (41). A solution of the ester **17** (2.0 g, 7.5 mmol) in dry DMSO (100 mL) was added slowly to a solution of t-BuOK (1 g, 8.9 mmol) in DMSO (30 mL). After the addition was complete, the mixture was stirred for 15 min and the solution of the anion was then added dropwise to a solution of allyl bromide (1.1 g, 9.1 mmol) in DMSO (20 mL) at such a rate that the mixture was decolorized before another drop was added. The reaction mixture was stirred for 2 h and then poured into ice water. The solution was extracted with Et_2O and the organic layer was washed with 10% aqueous HCl, saturated aqueous $NaHCO_3$ and brine. The extract was dried ($MgSO_4$), filtered and evaporated to dryness. The crude product was purified by distillation under reduced pressure to yield 2 g (86%) of the ester **41** as a colorless oil: bp 150 °C/0.1 mm Hg; ^1H NMR (300 MHz) δ 1.2 (s, 3H), 2.4 (Y of AXY, dd, J_{AY} = 7.6, J_{XY} = 13.5 Hz, 1 H), 2.5 (X of AXY, dd, J_{AX} = 7.3, J_{XY} = 13.5 Hz, 1 H), 3.3 (s, 3 H), 5.1 (m, 2 H), 5.8 (m, 1 H), 6.1 (s, 1 H), 7.1–7.4 (m, 10 H); ^{13}C NMR (63 MHZ) δ 23.9, 45.5, 47.4, 51.5, 118.6, 127.2–129.9, 132.7, 133.6, 139.1, 142.0, 143.2, 174.6; IR (neat) 1735, 1635 cm^{-1}. Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.31; H, 7.20. Found: C, 81.88; H, 7.26.

2-(2,2-Diphenylvinyl)-2-methyl-4-penten-1-ol (42). The same procedure used for the synthesis of **19** was followed in this case. Thus, from ester **41** (2.0 g, 6.5 mmol) and $LiAlH_4$ (0.25 g, 6.5 mmol), **42** (0.9 g, 50%) was obtained as a colorless oil: ^1H NMR (250 MHz) δ 0.8 (s, 3 H), 1.5 (br s, 1 H), 2.1 (m, 2 H), 3.3 (s, 2 H), 5.1 (m, 2 H), 5.9 (m, 1 H), 6.0 (s, 1 H), 7.2–7.4 (m, 10 H); ^{13}C NMR (63 MHz) δ 22.9, 42.4, 43.8, 70.4, 117.5, 126.8–129.8, 134.4, 135.0, 140.3, 142.4, 143.6; IR (neat) 3350, 1645 cm^{-1}; MS: 278 (M^+, 12), 237 (100). Anal. Calcd for $C_{20}H_{22}O$: C, 86.28; H, 7.95. Found: C, 85.67; H, 8.09.

2-(2,2-Diphenylvinyl)-2-methyl-4-pentenal (43). The same procedure used for the synthesis of **20** was followed in this case. Thus, from **42** (338 mg, 1.2 mmol) and PCC (0.33 g, 1.5 mmol), aldehyde **43** (313 g, 93%) was obtained as a colorless oil which was used in the next step without further purification: ^1H NMR (300 MHz) δ 1.1 (s, 3 H), 2.3 (m, 2 H), 5.1 (m, 2 H), 5.8 (m, 1 H), 6.1 (s, 1 H), 7.1–7.4 (m, 10 H), 9.2 (s, 1 H); ^{13}C NMR (75 MHz) δ 21.2, 42.2, 51.4, 118.7, 126.8–143.7, 201.0; IR (neat) 2700, 2600, 1715, 1660 cm^{-1}.

2-[2-(3,4-Dihydronaphthalenyl)]-2-methylpropanoic Acid (49b). A solution of **49a**[10] (7 g, 29 mmol) in dry EtOH (25 mL) was added to a solution of NaOH (1.28 g, 32 mmol) in EtOH (100 mL). After refluxing for 24 h, the solvent was removed and the residue dissolved in water. The aqueous solution was extracted with Et_2O to remove any unreacted ester and then acidified. The acid was extracted with Et_2O, and the organic layer was dried ($MgSO_4$), filtered and concentrated to dryness, yielding **49b** (4.7 g, 76%) as a white solid: mp 126–128 °C (hexane); ^1H NMR (300 MHz) δ 1.4 (s, 6 H), 2.2 (m, 2 H), 2.7 (m, 2 H), 6.4 (s, 1 H), 7.1 (m, 4 H), 11.0 (s, 1 H); ^{13}C NMR (75 MHz) δ 23.8, 24.9, 28.2, 47.3, 121.8, 126.1–126.8, 134.0, 134.7, 142.6, 182.5; IR (KBr) 3000, 1700, 1640 cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.89; H, 7.52.

3-[2-(3,4-Dihydronaphthalenyl)]-3-methyl-2-butanone (49c). The acid **49b** (1.5 g, 6.9 mmol) was converted into the corresponding acid chloride by refluxing in $SOCl_2$ (2 mL) for 2 h. Removal of excess $SOCl_2$ by rotary evaporation yielded a yellowish oil which was used immediately in the next step.

To a solution of CuI (1.6 g, 8.4 mmol) in dry Et_2O (20 mL) at −40 °C (acetone/CO_2 bath), and under an atmosphere of argon, MeLi (17 mmol, 1.6 M) was added via syringe. The cooled solution was stirred for 30 min and then a solution of the acid chloride in Et_2O (20 mL) was added dropwise. The solution was stirred at −40 °C for 30 min and then at 0 °C for a further 30 min. The reaction mixture was quenched with 5% aqueous NH_4Cl. The ketone was extracted with Et_2O and the organic layer was dried ($MgSO_4$), filtered and evaporated to dryness. Flash chromatography of the residue using hexane/Et_2O (9:1) as eluent gave the desired ketone **49c** (1.16 g, 78%) as an oil: ^1H NMR (300 MHz) δ 1.3 (s, 6 H), 2.14 (s, 3 H), 2.16 (m, 2 H), 2.8 (m, 2 H), 6.5 (s, 1 H), 7.1 (m, 4 H); ^{13}C NMR (75 MHz) δ 22.5, 24.7, 28.2, 53.7, 122.4, 125.8–134.5, 143.4, 211.9; IR (neat) 1710, 1640 cm^{-1}; MS: 214 (M^+, 4), 171 (100). Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.75; H, 8.29.

General Procedure for the Synthesis of Oximes 6, 21, 44, and 47b. The corresponding aldehyde, hydroxylamine hydrochloride and pyridine were refluxed in EtOH (50 mL) for 1 h. The aldehyde/hydroxylamine/pyridine ratio was 1:1.2:1.2 for all the experiments. The solvent was evaporated and

the crude product was dissolved in Et_2O, washed with 10% aqueous HCl, water and brine. The extract was dried ($MgSO_4$), filtered and evaporated to dryness. The oximes were isolated and purified by flash chromatography on silica gel using hexane/Et_2O (9:1) as eluent.

2-(2,2-Diphenylvinyl)-2-methyl-4,4-diphenyl-3-butenal Oxime (6). From **5** (457 mg, 1.1 mmol) yielded the oxime **6** (398 mg, 84%) as a colorless oil: ^1H NMR (300 MHz) δ 1.3 (s, 3 H), 6.0 (s, 2 H), 6.9–7.3 (m, 20 H), 8.2 (s, 1 H); ^{13}C NMR (75 MHz) δ 27.5, 44.5, 126.8–133.8, 139.1, 141.0, 142.7, 155.4; IR (neat) 3300, 1620 cm^{-1}; UV (CH_2Cl_2) λ_{max} 254 (ϵ 19 500); MS: 429 (M^+, 5), 414 (11), 412 (100); HRMS calcd for $C_{31}H_{27}NO$ (M^+) 429.5623, found 429.5620.

2-Methyl-4,4-diphenyl-2-vinyl-3-butenal Oxime (21). From **20** (720 mg, 2.75 mmol), yielded the oxime **21** (583 mg, 77%) as a white solid: mp 102–104 °C (hexane); ^1H NMR (300 MHz) δ 1.3 (s, 3 H), 4.95 (dd, J = 10.5, 0.9 Hz, 1 H), 4.98 (dd, J = 17.3, 0.9 Hz, 1 H), 5.8 (dd, J = 17.3, 10.5 Hz, 1 H), 5.9 (s, 1 H), 6.9 (s, 1 H), 7.0–7.2 (m, 10 H), 7.3 (s, 1 H); ^{13}C NMR (75 MHz) δ 25.0, 45.5, 113.4, 127.0–131.9, 138.9, 142.1, 142.6, 142.7, 155.3; IR (KBr) 3250, 1630 cm^{-1}; UV (CH_2Cl_2) λ_{max} 250 (ϵ 14 900); MS: 277 (M^+, 7), 260 (100). Anal. Calcd for $C_{19}H_{19}NO$: C, 82.27; H, 6.90; N, 5.04. Found: C, 81.96; H, 6.91; N, 4.93.

2-(2,2-Diphenylvinyl)-2-methyl-4-pentenal Oxime (44). From **43** (313 mg, 1.1 mmol), yielded the oxime **44** (249 mg, 75%) as a colorless oil: ^1H NMR (250 MHz) δ 1.2 (s, 3 H), 2.3 (m, 2 H), 5.1 (m, 2 H), 5.8 (m, 1 H), 6.0 (s, 1 H), 7.0 (s, 1 H), 7.1–7.4 (m, 10 H), 7.5 (s, 1 H); ^{13}C NMR (63 MHz) δ 24.4, 42.3, 45.9, 118.6, 127.1–130.2, 133.7, 133.9, 139.4, 157.1; IR (neat) 3300, 1650 cm^{-1}; UV (CH_2Cl_2) λ_{max} 249 (ϵ 14 000); HRMS calcd for $C_{20}H_{21}NO$ (M^+) 291.1618, found 291.1616.

3-[2-(3,4-Dihydronaphthalenyl)]-3-methyl-2-butanone Oxime (47b). From **49c** (0.96 g, 45 mmol), yielded the oxime **47b** (0.67 g, 65%) as a white solid: mp 144–146 °C (hexane); ^1H NMR (300 MHz) δ 1.3 (s, 6 H), 1.7 (s, 3 H), 2.1 (m, 2 H), 2.6 (m, 2 H), 6.3 (s, 1 H), 7.0 (m, 4 H), 9.5 (br s, 1 H); ^{13}C NMR (63 MHz) δ 11.3, 24.2, 24.5, 28.6, 46.5, 119.6, 122.2–127.3, 134.6, 135.0, 145.4, 162.5; IR (KBr) 3240, 1640 cm^{-1}; MS: 230 (M^+ + 1, 100); UV (CH_2Cl_2) λ_{max} 272 (ϵ 12 770), 264 (12850). Anal. Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11. Found: C, 78.85; H, 8.26; N, 6.16.

General Procedure for the Synthesis of Oxime Acetates 3 and 26. Acetyl chloride was added to a solution of the oxime in pyridine (3 mL) at 0 °C. The oxime/acetyl chloride ratio was 1:1.2 for all the experiments. The mixture was stirred for 2 h at room temperature and then Et_2O was added. The solution was washed successively with 10% aqueous HCl, saturated aqueous solution of $NaHCO_3$ and brine. The extract was dried ($MgSO_4$), filtered and evaporated to dryness. The product was purified by flash chromatography on silica gel using hexane/Et_2O (9:1) as eluent.

2-(2,2-Diphenylvinyl)-2-methyl-4,4-diphenyl-3-butenal Oxime Acetate (3). From oxime **6** (236 mg, 0.55 mmol) yielded oxime acetate **3** (192 mg, 74%) as a colorless oil: ^1H NMR (300 MHz) δ 1.5 (s, 3 H), 1.9 (s, 3 H), 6.0 (s, 2 H), 7.0–7.3 (m, 21 H); ^{13}C NMR (75 MHz) δ 19.4, 27.2, 45.0, 126.8–132.9, 138.9, 141.4, 142.1, 161.1, 168.0; IR (neat) 1770, 1620 cm^{-1}; UV (CH_2Cl_2) λ_{max} 256 (ϵ 20 000); MS: 412 (M^+ – 59, 75), 384 (44), 293 (12), 178 (32), 167 (100); HRMS calcd for $C_{33}H_{29}NO_2$ (M^+) 471.5997, found 471.5990.

2-Methyl-4,4-diphenyl-2-vinyl-3-butenal Oxime Acetate (26). From oxime **21** (434 mg, 1.57 mmol) yielded oxime acetate **26** (360 mg, 72%) as a colorless oil: ^1H NMR (250 MHz) δ 1.4 (s, 3 H), 1.9 (s, 3 H), 5.07 (d, J = 10.4 Hz, 1 H), 5.08 (d, J = 17.5 Hz, 1 H), 5.90 (dd, J = 17.5, 10.4 Hz, 1 H), 5.97 (s, 1 H), 7.1–7.3 (m, 11 H); ^{13}C NMR (63 MHz) δ 19.4, 24.8, 46.1, 114.7, 126.7–142.9, 161.6, 168.4; IR (neat) 1760, 1620 cm^{-1}; UV (CH_2Cl_2) λ_{max} 251 (ϵ 9 900); MS: 319 (M^+, 9), 260 (100); HRMS calcd for $C_{21}H_{21}NO_2$ (M^+) 319.1572, found 319.1577.

Procedure for the Synthesis of Oxime Trifluoroacetate Derivatives 11 and 15. The corresponding oxime and pyridine were dissolved in dry Et_2O (60 mL) and cooled to –60 °C under an atmosphere of argon. An equimolecular amount of trifluoroacetic anhydride was added dropwise. The mixture was kept at 0 °C for 2 h and then was poured into 10% aqueous HCl and extracted with Et_2O. The organic layer was washed with saturated aqueous $NaHCO_3$ and water. The extract was dried ($MgSO_4$), filtered and evaporated to dryness.

2-(2,2-Diphenylvinyl)-2-methyl-4,4-diphenyl-3-butenal Oxime Trifluoroacetate (11). From oxime **6** (350 mg, 0.82 mmol) yielded **11** (419 mg, 99%) as an unstable colorless oil which was used without further purification: ^1H NMR (300 MHz) δ 1.6 (s, 3 H), 6.0 (s, 2 H), 7.0–7.3 (m, 21 H); ^{13}C NMR (75 MHz) δ 14.0, 44.1, 114.7 (q, $J_{C,F}$ = 285 Hz), 127.8–131.0, 137.1, 140.8, 154.0 (q, $J_{C,F}$ = 40 Hz), 163.9; IR (neat) 1820, 1625 cm^{-1}; UV (CH_2Cl_2) λ_{max} 257 (ϵ 20 500).

2-Methyl-4,4-diphenyl-2-vinyl-3-butenal Oxime Trifluoroacetate (15). From oxime **21** (253 mg, 0.91 mmol) yielded **15** (300 mg, 88%) as an unstable colorless oil which was used without further purification: ^1H NMR (300 MHz) δ 1.4 (s, 3 H), 5.118 (d, J = 10.3 Hz, 1 H), 5.121 (d, J = 17.6 Hz, 1 H), 5.86 (dd, J = 17.3, 10.3 Hz, 1 H), 5.90 (s, 1 H), 7.0–7.3 (m, 11 H); ^{13}C NMR (75 MHz) δ 24.4, 46.3, 114.2 (q, $J_{C,F}$ = 286 Hz), 115.9, 126.8–130.3, 138.0, 140.3, 141.6, 143.0, 157.3 (q, $J_{C,F}$ = 42 Hz), 165.6; IR (neat) 1815, 1625 cm^{-1}; UV (CH_2Cl_2) λ_{max} 260 (ϵ 18 300).

***O*-Methyl Ether of 2-Methyl-4,4-diphenyl-2-vinyl-3-butenal Oxime (36).** From **20** (386 mg, 1.5 mmol), *O*-methyl hydroxylamine hydrochloride (150 mg, 1.8 mmol) and pyridine (0.15 mL 1.8 mmol). The residue was distilled at 130 °C (0.1 mm Hg) to yield 314 mg (73%) of **36** as a colorless oil: ^1H NMR (250 MHz) δ 1.3 (s, 3 H), 3.5 (s, 3 H), 4.95 (d, J = 10.4 Hz, 1 H), 4.98 (d, J = 17.4 Hz, 1 H), 5.8 (dd, J = 17.5, 10.5 Hz, 1 H), 5.9 (s, 1 H), 6.8 (s, 1 H), 7.0–7.4 (m, 10 H); ^{13}C NMR (63 MHz) δ 25.2, 45.4, 60.9, 113.2, 127.0–132.5, 142.5, 154.2; IR (neat) 1635 cm^{-1}; UV (CH_2Cl_2) λ_{max} 254 (ϵ 31 500); MS: 291 (M^+, 5), 260 (100); HRMS calcd for $C_{20}H_{21}NO$ (M^+) 291.1618, found 291.1615.

2-Methyl-4,4-diphenyl-2-vinyl-3-butenonitrile (22). The oxime **21** (250 mg, 0.9 mmol) was refluxed in dry acetic anhydride (2 mL) for 20 min. The reaction mixture was dissolved in water and extracted with Et_2O. The organic layer was washed with 10% aqueous $NaHCO_3$, water and brine. The extract was dried ($MgSO_4$), filtered and evaporated to dryness. Flash chromatography of the crude using hexane/Et_2O (9:1) as eluent yielded the desired nitrile **22** (182 mg, 78%) as a colorless oil: ^1H NMR (300 MHz) δ 1.5 (s, 3 H), 5.0 (d, J = 10.0 Hz, 1 H), 5.2 (d, J = 16.8 Hz, 1 H), 5.6 (dd, J = 16.8, 10.0 Hz, 1 H), 5.7 (s, 1 H), 7.1–7.3 (m, 10 H); ^{13}C NMR (75 MHz) δ 28.9, 40.2, 114.5, 120.5, 126.4–130.0, 137.7, 138.0, 141.8, 145.6; IR (neat) 2225 cm^{-1}; UV (CH_2Cl_2) λ_{max} 254 (ϵ 31 600); MS: 259 (M^+, 100); HRMS calcd for $C_{19}H_{17}N$ (M^+) 259.1361, found 259.1345.

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 in dry CH_2Cl_2 or benzene (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 in sensitized irradiations) was removed under reduced pressure, and the products were separated by flash chromatography on silica gel.

Direct Irradiation of 3. Compound **3** (191 mg, 0.40 mmol) was irradiated in CH_2Cl_2 for 1 h. Flash chromatography using hexane/ethyl acetate (9:1) as eluent gave 41 mg (22%) of **3** and 142 mg (75%) of a 3:2 mixture of diastereoisomeric (*RR,SS*:*RS,SR*) cyclopropanes **7** as a white solid: mp 62–63 °C (EtOH); ^{13}C NMR (75 MHz) δ 18.0, 19.4, 33.9, 34.2, 38.0, 48.0, 50.2, 123.9–130.8, 139.1, 139.3, 142.0, 143.0, 143.9, 162.3, 164.0, 168.0; IR (KBr) 1780 cm^{-1}; MS: 411 (M^+ – 60, 40), 334 (17), 264 (15), 191 (23), 167 (44), 78 (79), 60 (55), 43 (100). Anal. Calcd for $C_{33}H_{29}NO_2$: C, 84.07; H, 6.15; N, 2.97. Found: C, 84.30; H, 6.18; N, 3.01. ***RR,SS* isomer:** ^1H NMR (300 MHz) 1.2 (s, 3 H), 2.1 (s, 3 H), 2.5 (d, J = 9.9 Hz, 1 H), 5.8 (d, J = 9.9 Hz, 1 H), 7.1–7.5 (m, 20 H), 7.6 (s, 1 H). ***RS,SR* isomer:** ^1H NMR (300 MHz) 1.5 (s, 3 H), 2.0 (s, 3 H), 2.6 (d, J = 9.9 Hz, 1 H), 5.7 (d, J = 9.9 Hz, 1 H), 6.8 (s, 1 H), 7.1–7.5 (m, 20 H).

Acetophenone-Sensitized Irradiation of 3. Compound **3** (163 mg, 0.34 mmol) and acetophenone (2.14 g, 17.8 mmol)

were irradiated in benzene for 15 min. Flash chromatography using hexane/ethyl acetate (8:2) as eluent gave 137 mg (84%) of a 3:2 mixture of diastereoisomeric cyclopropanes **7**.

Direct Irradiation of 11. Compound **11** (150 mg, 0.29 mmol) was irradiated in CH_2Cl_2 for 1 h. Flash chromatography using hexane/Et_2O (92:8) gave: 12.4 mg (10%) of cyclopropane **13**; 14 mg (12%) of diene **14** as a colorless oil: ^1H NMR (300 MHz) δ 1.6 (s, 3 H), 6.0 (s, 2 H), 7.0−7.4 (m, 20 H); IR (neat) 2220, 1620 cm^{-1}; 50 mg (42%) of cyclopropane **12a** as a white solid: mp 175 °C (EtOH); ^1H NMR (250 MHz) δ 1.2 (s, 3 H), 2.4 (d, J = 10 Hz, 1 H), 5.6 (d, J = 10 Hz, 1 H), 7.2−7.9 (m, 20 H); ^{13}C NMR (63 MHz) δ 19.8, 23.6, 36.3, 47.5, 121.2, 124.0, 127.2−130.3, 138.4, 139.8, 140.4, 141.3, 145.1; IR (KBr) 2230, 1610 cm^{-1}; MS: 411 (M^+, 48), 191 (51), 165 (100). Anal. Calcd for $C_{31}H_{25}N$: C, 90.51; H, 6.08; N, 3.41. Found: C, 90.81; H, 6.18; N, 3.46; and 20 mg (16%) of cyclopropane **12b** as a white solid: mp 172 °C (EtOH); ^1H NMR (250 MHz) δ 1.5 (s, 3 H), 2.9 (d, J = 10 Hz, 1 H), 5.5 (d, J = 10 Hz, 1 H), 7.2−7.5 (m, 20 H); ^{13}C NMR (63 MHz) δ 16.2, 22.7, 35.3, 46.6, 121.2, 122.3, 127.4−130.4, 136.9, 139.1, 141.8, 142.8, 146.7; IR (KBr) 2220, 1620 cm^{-1}; MS: 411 (M^+, 28), 269 (21), 191 (46), 165 (100). Anal. Calcd for $C_{31}H_{25}N$: C, 90.51; H, 6.08; N, 3.41. Found: C, 90.45; H, 6.30; N, 3.63.

Acetophenone-Sensitized Irradiation of 11. Compound **11** (300 mg, 0.57 mmol) and acetophenone (17 g, 0.14 mol) were irradiated in benzene for 10 min. Flash chromatography using hexane/Et_2O (92:8) as eluent gave 161 mg (69%) of cyclopropane **12a** and 50 mg (21%) of cyclopropane **12b**.

Direct Irradiation of 6. Compound **6** (150 mg, 0.35 mmol) was irradiated in CH_2Cl_2 for 1 h. Flash chromatography using hexane/Et_2O (92:8) gave 39 mg (26%) of oxime **6** and 100 mg (66%) of a 3:1 mixture of diastereoisomeric cyclopropanes **13** (*RR,SS:RS,SR*) as a white solid: mp 68−69 °C (EtOH); ^{13}C NMR (75 MHz) δ 18.6, 30.0, 33.4, 37.1, 37.3, 48.0, 49.0, 124.7−130.9, 139.4, 139.6, 141.9, 143.3, 143.8, 154.8, 154.9; IR (KBr) 3300, 1630 cm^{-1}. Anal. Calcd for $C_{31}H_{27}NO$: C, 86.71; H, 6.29; N, 3.26. Found: C, 86.91, H, 6.31; N, 3.36. ***RR,SS* isomer:** ^1H NMR (300 MHz) δ 1.1 (s, 3 H), 2.5 (d, J = 11 Hz, 1 H), 5.8 (d, J = 11 Hz, 1 H), 7.1−7.5 (m, 21 H), 7.8 (s, 1 H). ***RS,SR* isomer:** ^1H NMR (300 MHz) δ 1.5 (s, 3 H), 2.6 (d, J = 11 Hz, 1 H), 5.7 (d, J = 11 Hz, 1 H), 6.6 (s, 1 H), 7.1−7.5 (m, 20 H).

Acetophenone-Sensitized Irradiation of 6. Compound **6** (119 mg, 0.28 mmol) and acetophenone (14.9 g, 0.12 mol) were irradiated in benzene for 15 min. Flash chromatography using hexane/Et_2O (8:2) gave 12 mg (10%) of oxime **6** and 98 mg (82%) of cyclopropane **13** as a 3:1 mixture of (*RR,SS*:*RS,SR*) diastereoisomers.

Direct Irradiation of 15. Compound **15** (300 mg, 0.8 mmol) was irradiated in CH_2Cl_2 for 2.5 h. Flash chromatography using hexane/Et_2O (97:3) as eluent gave 76 mg (36%) of diene **22** and 71 mg (34%) of cyclopropane **23** as a 2:3 mixture of diastereoisomers (*RR,SS:RS,SR*): ^{13}C NMR (75 MHz) δ 17.0, 18.7, 23.0, 23.5, 34.1, 34.4, 48.0, 114.9, 115.3, 118.13, 126.9−141.1; IR (neat) 2245 cm^{-1}; MS: 259 (M^+, 88), 258 (85), 244 (100); HRMS calcd for $C_{19}H_{17}N$ (M^+) 259.1358, found 259.1361. ***RS,SR* isomer:** ^1H NMR (300 MHz) δ 1.2 (s, 3 H), 2.38 (s, 1 H), 5.0−5.7 (m, 3 H), 7.0−7.5 (m, 10 H). ***RR,SS* isomer:** ^1H NMR (300 MHz) δ 1.5 (s, 3 H), 2.41 (s, 1 H), 5.0−5.7 (m, 3 H), 7.0−7.5 (m, 10 H).

Acetophenone-Sensitized Irradiation of 15. Compound **15** (276 mg, 0.74 mmol) and acetophenone (2 g, 17 mmol) were irradiated in CH_2Cl_2 for 7 min. Flash chromatography using hexane/Et_2O (97:3) as eluent gave 46 mg (24%) of diene **22**, 58 mg (30%) of cyclopropane **23** as a 2:3 mixture of isomers (*RR,SS:RS,SR*) and 43 mg (21%) of oxime **21**.

Acetophenone-Sensitized Irradiation of 26. Compound **26** (173 mg, 0.54 mmol) and acetophenone (1 g, 8.3 mmol) were irradiated in CH_2Cl_2 for 10 min. The solvent was evaporated and the crude was refluxed in toluene (10 mL) for 17 h. After evaporation of the toluene, flash chromatography of the residue using hexane/Et_2O (97:3) as eluent yielded 42 mg (30%) of diene **22** and 42 mg (30%) of cyclopropane **23** as a 2:3 mixture of isomers (*RR,SS:RS,SR*).

Acetophenone-Sensitized Irradiation of 22. Compound **22** (230 mg, 0.9 mmol) and acetophenone (6 g, 50 mmol) were irradiated in CH_2Cl_2 for 1 h. Flash chromatography using hexane/Et_2O (98:2) as eluent gave 100 mg (43%) of diene **22**, and 70 mg (30%) of cyclopropane **29** as a 4:1 mixture of diastereoisomers (*RR,SS:RS,SR*). The major isomer precipitates from this mixture by treatment with hexane giving a white solid: mp 114−116 °C (hexane); ^1H NMR (300 MHz) δ 1.3 (s, 3 H), 2.5 (d, J = 9.0 Hz, 1 H), 5.3−5.6 (m, 3 H), 7.2−7.5 (m, 10 H); ^{13}C NMR (63 MHz) δ 19.9, 22.5, 39.3, 46.7, 118.0, 120.9, 127.2−140.4; IR (neat) 2250 cm^{-1}; MS: 259 (M^+, 30), 244 (33), 217 (28), 205 (25), 165 (100). Anal. Calcd for $C_{19}H_{17}N$: C, 87.99; H, 6.60; N, 5.40. Found: C, 88.10; H, 6.80; N, 5.44.

Acetophenone-Sensitized Irradiation of 21. Compound **21** (370 mg, 1.33 mmol) and acetophenone (2 g, 17 mmol) were irradiated in CH_2Cl_2 for 20 min. Flash chromatography using hexane/Et_2O (9:1) as eluent gave 145 mg (39%) of starting material and 113 mg (30%) of cyclopropane **30** as a colorless oil. The product was determined to be a 1.5:2.2:1:1.5 mixture of the four possible stereoisomers **(*Z*)-30a:(*Z*)-30b:(*E*)-30a:(*E*)-30b** by ^1H NMR integration. Further chromatography of this fraction using hexane/ethyl acetate (98:2) as eluent allowed the separation of the isomers **(*E*)-30a**, **(*E*)-30b** from **(*Z*)-30a** and **(*Z*)-30b**. However, after separation, the *Z-E* isomerization occurs very readily at room temperature: ^{13}C NMR (75 MHz) δ 15.7, 19.82, 19.88, 30.3, 31.9, 33.60, 33.62, 33.64, 33.8, 34.4, 35.8, 47.6, 35.8, 47.7, 48.2, 48.6, 49.2, 112.0, 112.07, 113.5, 113.6, 126.3−143.8, 149.3, 149.8, 150.9, 151.3; IR (neat) 3220, 1635 cm^{-1}; HRMS calcd for $C_{19}H_{19}NO$ (M^+) 277.1462, found 277.1463. **(*Z*)-30a:** ^1H NMR (300 MHz) δ 1.30 (s, 3 H), 3.20 (d, J = 8.3 Hz, 1 H), 4.8−5.8 (m, 3 H), 6.45 (d, J = 8.3 Hz, 1 H), 7.0−7.4 (m, 10 H), 9.8 (br s, 1 H). **(*Z*)-30b**: ^1H NMR (300 MHz) δ 1.10 (s, 3 H), 3.13 (d, J = 8.3 Hz, 1 H), 4.8−5.8 (m, 3 H), 6.52 (d, J = 8.3 Hz, 1 H), 7.0−7.4 (m, 10 H), 9.8 (br s, 1 H). **(*E*)-30a:** ^1H NMR (300 MHz) δ 1.27 (s, 3 H), 2.62 (d, J = 9.8 Hz, 1 H), 4.8−5.8 (m, 3 H), 7.0−7.4 (m, 11 H), 9.4 (br s, 1 H). **(*E*)-30b:** ^1H NMR (300 MHz) δ 1.08 (s, 3 H), 2.56 (d, J = 9.8 Hz, 1 H), 7.0−7.4 (m, 11 H), 9.4 (br s, 1 H).

Another sample of oxime **21** (279 mg, 1 mmol) and acetophenone (2 g, 17 mmol) in CH_2Cl_2 (420 mL) was irradiated for 15 min. After elimination of the solvent and the sensitizer, the crude was refluxed in Ac_2O (1 mL) for 20 min. Water was added to the reaction mixture and the aqueous solution was extracted with Et_2O. The organic layer was washed with saturated aqueous solution of $NaHCO_3$ and water, and then dried ($MgSO_4$), filtered and evaporated to dryness. Flash chromatography using hexane/Et_2O (95:5) as eluent gave 102 mg (39%) of diene **22** and 77 mg (29%) of cyclopropane **23** as a 3:2 mixture of (*RS,SR:RR,SS*) isomers.

Direct Irradiation of 21. Oxime **21** (403 mg, 1.45 mmol) was irradiated for 5 h. Flash chromatography of the crude using hexane/Et_2O (9:1) gave 187 mg (46%) of starting material, and 85 mg (21%) of cyclopropane **30**. The product was determined to be a 2:2.4:1:1.8 mixture of the four possible stereoisomers **(*Z*)-30a:(*Z*)-30b:(*E*)-30a:(*E*)-30b** by integration of the ^1H NMR signals.

Irradiation of 21 with 1,3-Cyclooctadiene as Triplet Quencher. Compound **21** (403 mg, 1.4 mmol) in a 0.4 M CH_2Cl_2 solution of 1,3-cyclooctadiene was irradiated for 5 h. Flash chromatography using hexane/Et_2O (9:1) as eluent gave 271 mg (67%) of starting material and 163 mg of a complex mixture of products in which compound **30** was not present as shown by ^1H NMR.

Acetophenone-Sensitized Irradiation of 36. Compound **36** (256 mg, 0.9 mmol) and acetophenone (25 g, 0.2 mol) were irradiated in CH_2Cl_2 for 20 min. Flash chromatography using hexane/Et_2O (99:1) as eluent gave 55 mg (21%) of starting material and 114 mg (45%) of cyclopropane **37** as a colorless oil. The product was determined to be a 1:1.6:1.6:2 mixture of the four possible stereoisomers **(*Z*)-37a:(*Z*)-37b:(*E*)-37a:(*E*)-37b** respectively by ^1H NMR integration: ^{13}C NMR (75 MHz) δ 15.8, 15.9, 20.1, 31.2, 32.5, 33.79, 33.87, 33.90, 34.00, 34.7, 36.1, 47.9, 48.4, 48.8, 49.3, 61.6, 61.7, 61.8, 62.1, 112.1, 112.2, 113.7, 113.8, 126.5−144.0, 148.5, 149.0, 149.8, 150.2; IR (neat) 1615 cm^{-1}; HRMS calcd for $C_{20}H_{21}NO$ (M^+) 291.1618, found 291.1618. **(*Z*)-37a:** ^1H NMR (300 MHz) δ 1.28 (s, 3 H), 3.06 (d, J = 9.0 Hz, 1 H), 4.0 (s, 3 H), 4.8−5.7 (m, 3 H), 6.30 (d, J = 9.0 Hz, 1 H), 7.0−7.4 (m, 10 H). **(*Z*)-37b:** ^1H NMR (300

MHz) δ 1.08 (s, 3 H), 3.00 (d, J = 9.0 Hz, 1 H), 4.0 (s, 3 H), 4.8–5.7 (m, 3 H), 6.37 (d, J = 9.0 Hz, 1 H), 7.0–7.4 (m, 11 H). **(*E*)-37a:** ^{1}H NMR (300 MHz) δ 1.25 (s, 3 H), 2.57 (d, J = 11.2 Hz, 1 H), 3.82 (s, 3 H), 4.8–5.7 (m, 3 H), 7.0–7.4 (m, 10 H). **(*E*)-37b:** ^{1}H NMR (300 MHz) δ 1.08 (s, 3 H), 2.48 (d, J = 11.2 Hz, 1 H), 3.79 (s, 3 H), 4.8–5.7 (m, 3 H), 7.0–7.4 (m, 11 H).

Acetophenone-Sensitized Irradiation of 44. Compound **44** (252 mg, 0.87 mmol) and acetophenone (5.2 g, 43 mmol) were irradiated in CH_2Cl_2 for 1 h. The ^{1}H NMR of the crude product was complex. None of the resonances could be assigned to the corresponding cyclopropane oxime. Flash chromatography using hexane/Et_2O (95:5) as eluent gave 80 mg (32%) of oxime **44**.

Acetophenone-Sensitized Irradiation of 45. Compound **45**[1k] (257 mg, 0.66 mmol) and acetophenone (2 g, 17 mmol) were irradiated in CH_2Cl_2 for 30 min. Flash chromatography of the crude using hexane/Et_2O (8:2) as eluent gave 30 mg (12%) of starting material and 189 mg (74%) of a 47:53 mixture of isomers (*Z*:*E*) of cyclopropane **46** as a white solid: mp 234–237 °C (browns on heating at ca. 200 °C); ^{1}H NMR ($CDCl_3$) δ 3.6 (d, J = 9.6 Hz, 0.53 H), 4.3 (d, J = 8.2 Hz, 0.47 H), 6.7 (d, J = 8.2 Hz, 0.47 H), 6.9–7.5 (m, 20.53 H), 8.0 (br s, 1H); ^{13}C NMR (75 MHz) δ 32.4, 47.6, 48.6, 125.8–131.6, 139.4, 139.6, 143.0, 153.3; IR (KBr) 3250 cm^{-1}. This compound was further characterized by transformation into the corresponding acetate.[1k]

Acetophenone-Sensitized Irradiation of 47a. Compound **47a**[1o] (190 mg, 0.88 mmol) and acetophenone (6 g, 50 mmol) were irradiated for 20 min. Flash chromatography of the crude using hexane/Et_2O (95:5) as eluent gave 120 mg (63%) of cyclopropane **48a** as a white solid mp 97–99 °C (hexane): ^{1}H NMR (300 MHz) δ 0.7 (s, 3 H), 1.2 (s, 3 H), 1.6 (m, 1 H), 2.0 (s, 1 H), 2.4 (m, 2 H), 2.6 (m, 1 H), 7.0–7.1 (m, 4 H), 7.4 (s, 1 H), 8.1 (s, 1 H); ^{13}C NMR (75 MHz) δ 18.3, 22.7, 23.5, 28.3, 29.3, 31.0, 31.9, 125.8–138.4, 160.0; IR (KBr) 3250, 1645 cm^{-1}; MS: 215 (M^+, 1), 198 (100). Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 77.81; H, 7.85; N, 6.62.

Acetophenone-Sensitized Irradiation of 47b. Compound **47b** (333 mg, 1.5 mmol) and acetophenone (2 g, 17 mmol) were irradiated in CH_2Cl_2 for 15 min. Flash chromatography using hexane/Et_2O (9:1) as eluent gave 78 mg (23%) of oxime **47b** and 221 mg (66%) of cyclopropane **48b** as a white solid mp 147–149 °C (hexane): ^{1}H NMR (300 MHz) δ 0.7 (s, 3 H), 1.1 (s, 3 H), 1.7 (m, 1 H), 1.9 (s, 3 H), 2.0 (m, 1 H), 2.1 (s, 1 H), 2.4 (m, 1 H), 2.7 (m, 1 H), 6.8–7.2 (m, 4 H), 8.6 (br s, 1 H); ^{13}C NMR (75 MHz) δ 15.0, 18.5, 24.2, 25.4, 29.0, 29.3, 29.7, 35.4, 126.4–139.3, 161.5; IR (KBr) 3220, 1610 cm^{-1}; MS: 229 (M^+, 11), 212 (100). Anal. Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11. Found: C, 78.65; H, 8.36; N, 6.12.

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Supplementary Material Available: ^{1}H NMR spectra of **5**, **11**, **14**, **15**, **17**, **18**, **19**, **20**, **22**, **23**, **26**, **30**, **37**, and **42** as well as ^{13}C NMR spectra of **3**, **6**, **36**, **41**, **43**, and **44** (20 pages). This material is contained in the 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.