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Photochemical Reactivity of 1-Substituted-1-aza-1,4-dienes Promoted by Electron-Acceptor Sensitizers. Di-π-methane Rearrangements and Alternative Reactions via Radical-Cation Intermediates

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Irradiation of a series of β,γ-unsaturated imines, oxime acetates, and oxime methyl ethers, using 9,10-dicyanoanthrathene (DCA) or dicyanodurene (DCD) as electron acceptor sensitizers, affords the corresponding cyclopropanes resulting from 1-aza-di-π-methane rearrangements via radical cations. In some cases, alternative reactions of these intermediates occur to yield nitriles, dihydroquinolines, dihydronaphthalene derivatives, and cycloaddition products. Some of these products result from reactions via alkene radical-cation intermediates while others arise by pathways involving imine radical-cation intermediates. The yields of products formed in these processes were significantly higher when DCD was used as electron-acceptor sensitizer instead of DCA.

Introduction

Since their discovery in 1967 by Zimmerman and coworkers,[1] the photoinduced di-π-methane rearrangement has been a major topic of research in the area of organic photochemistry. Efforts by numerous research groups have focused on different versions of this rearrangement. The work has led to the discovery of the di-π-methane (DPM) rearrangement of 1,4-dienes, the oxa-di-π-methane (ODPM) rearrangement of β,γ-unsaturated ketones and aldehydes, and the 1-aza-di-π-methane (1-ADPM) rearrangement of 1-aza-1,4-dienes.[2] These reactions are general and typically take place with high chemical and quantum efficiencies to afford cyclopropanes that, in many instances, are difficult or impossible to obtain by alternative preparative routes. In addition, the high degree of stereoselectivity, reported for some cases, makes these processes useful tools in synthetic organic chemistry.[2d,h]

For many years, the di-π-methane and closely related rearrangements have been the paradigm of processes that take place in the excited state only.[2] Biradical or concerted mechanisms have been proposed to account for the reactions.[2] The ODPM and the 1-ADPM rearrangements are regioselective, yielding the corresponding cyclopropane derivatives exclusively. The alternative regioisomeric products, oxiranes and aziridines, that would be formed in the respective ODPM and 1-ADPM reactions have not been observed.

Recent results obtained in our laboratory have led to a drastic modification of these ideas. Thus, in a report on the photoreactivity of 2-aza-1,4-dienes, we described the first example of a 2-aza-di-π-methane (2-ADPM) rearrangement, promoted by triplet-sensitized irradiation of compound **1**, that yields the vinylaziridine **2** and the cyclopropylimine **3**.[3] The importance of this result lies in the fact that it is the first example of a di-π-methane reaction, which occurs via a three-membered ring heterocyclic biradical, yielding a heterocyclic product. However, the most interesting observation made in this study was that irradiation of compound **1**, using 9,10-dicyanoanthrathene (DCA) as an electron-acceptor sensitizer, leads to formation of the vinylaziridine **2**, resulting from a 2-ADPM reaction, and the cyclopropylimine **4**, arising

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(1) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967**, *89*, 3932−3933.

(2) For specific and general reviews on the different versions of di-π-methane rearrangements see: (a) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531−551. (b) Zimmerman, H. E. In *Rearrangements in Ground and Excited States*; DeMayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 131−166. (c) Zimmerman, H. E. In *Organic Photochemistry*; Padwa, A. Ed.; Marcel Dekker: New York, 1991; Vol. 11, pp 1−36. (d) Zimmerman, H. E.; Armesto, D. *Chem. Rev.* **1996**, *96*, 3065−3112. (e) Dauben, G. W.; Lodder, G.; Ipaktschi, J. *Top. Curr. Chem.* **1975**, *54*, 73−114. (f) Houk, K. N. *Chem. Rev.* **1976**, *76*, 1−74. (g) Schuster D. I. In *Rearrangements in Ground and Excited States*; DeMayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 167−279. (h) Demuth, M. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1991; Vol. 11, pp 37−109. (i) Armesto, D. In *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Soon, P.-S., Eds.; CRC Press: New York, 1995; pp 915−930. (j) Armesto, D. *EPA Newsl.* **1995**, *53*, 6−21.

(3) Armesto, D.; Caballero, O.; Amador, U. *J. Am. Chem. Soc.* **1997**, *119*, 12659−12660.

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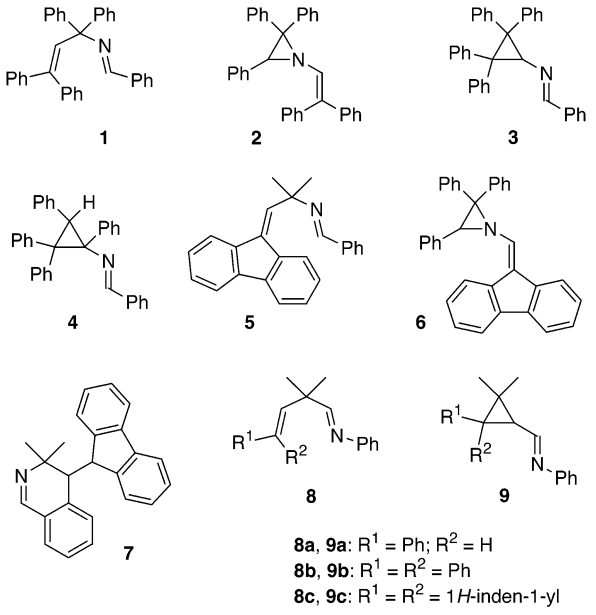
by an aryl-di-π-methane process. DCA-sensitized irradiation of azadiene **5** also results in production of a vinylaziridine **6** and the dihydroisoquinoline **7**. The formation of **2**, **4,** and **6** represents the first examples of di-π-methane rearrangements that take place via radical-cation intermediates.[3,4]

The results, summarized above, suggest that other β,γ-unsaturated compounds might also be capable of participating in di-π-methane type rearrangements via radical-cation intermediates. To test this proposal, we have conducted photochemical studies with a series of 1-substituted-1-aza-1,4-dienes. The results demonstrate that these substances undergo novel 1-ADPM rearrangements via radical cations promoted by single electron transfer (SET) sensitization. In some instances alternative cyclizations have been observed. Some of the results described here have been the subject of a preliminary communication.[5]



Results and Discussion

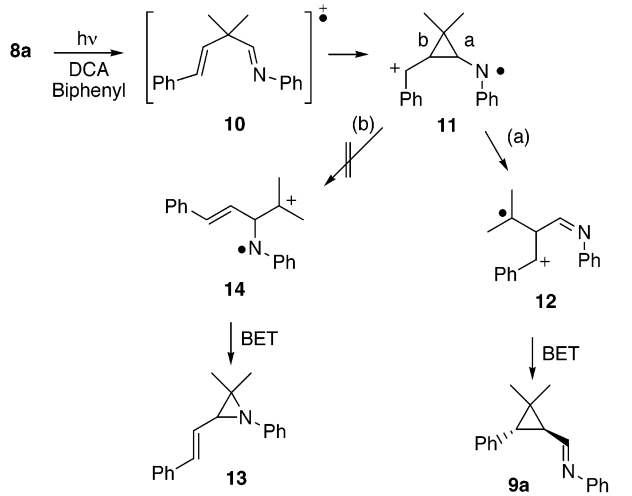
DCA-Sensitized Irradiation of Imines. The compounds selected for our initial studies are the imines **8a**−**c**, the syntheses of which have been described previously.[4b,6] Irradiation of a 1:1 mixture of (1*E*,4*E*)/(1*E*,4*Z*) diastereoisomers of **8a**,[4b] in acetonitrile for 7 h, using DCA as an electron-acceptor sensitizer and biphenyl as a cosensitizer, leads to formation of the cyclopropylimine **9a** and recovered starting material as a 2:1 mixture of (1*E*,4*E*)/(1*E*,4*Z*) diastereoisomers (^{1}H NMR analysis of the crude photolyzate). Silica gel chromatography yields 2,2-dimethyl-4-phenyl-3-butenal[7] (65%, 2:1 mixture of *E*- and *Z*-diastereoisomers), *trans*-2,2-dimethyl-3-phenylcyclopropanecarbaldehyde[8] (13%), and unidentified high polar materials (Table 1). The aldehydes are formed by hydrolysis of the corresponding imines **8a** and **9a** during chromatography.

TABLE 1. Reaction Conditions and Yields of Products in the Irradiation of 1-Aza-1,4-dienes Using DCA and DCD as Electron-acceptor Sensitizers

substr.	irrad time (h)	SET-sens.	1-ADPM (yield, %)	other products (yield, %)	S. M. yield (%)
8a	7	DCA	**9a** (13)[a]		65[a]
8a	2	DCD	**9a** (46)[a]		30[a]
8b	3	DCA	**9b** (2)[a]	**16** (10)	81[a]
8b	0.5	DCD	**9b** (11)[a]	**16** (13)	63[a]
8c	0.5	DCA	**9c** (4)[a]	**21** (13)	63[a]
24a	2.5	DCA	**25a** (15)	**26** (2)	66
24a	1	DCD	**25a** (60)		33
24b	3	DCA	**25b** (28)	**27** (8)	30
24b	1.5	DCD	**25b** (55)		15
24c	1	DCA	**25c** (16)	**28** (9), **31** (18)	26
24d	0.75	DCA	**25d** (4)		71
24d	0.25	DCD	**25d** (33)		34
24e	2	DCA	**25e** (2)	**29** (14)	68
24e	0.4	DCD	**25e** (44)		41
34a	13.5	DCA	**35a** (10)		40
34a	3	DCD	**35a** (7)	**39** (23)	37
34b	4	DCA			19
34b	1	DCD			61
34c	2	DCA	**35c** (3)	**36** (7)	30

[a] Isolated as the corresponding aldehyde.

SCHEME 1



This result demonstrates that, like the 2-aza-1,4-dienes analogues, **1** and **5**, 1-aza-1,4-diene **8a** also undergoes a di-π-methane type radical-cation rearrangement reaction. The mechanism shown in Scheme 1 accounts for the formation of **9a**. It involves initial generation of the radical-cation intermediate **10** that undergoes bonding to give the cyclopropane ring containing radical-cation **11**. Ring opening by bond a cleavage in **11** generates **12**, which, by back electron transfer and biradical cyclization, yields **9a**. The alternative route, involving cleavage of bond b and forming the vinylaziridine **13**, does not par-

(4) Within this area of SET-promoted di-π-methane rearrangements, we have recently described the first examples of 1-ADPM and DPM rearrangements that take place via radical-anion intermediates (ref 4b). (b) Armesto, D.; Ortiz, M. J.; Agarrabeitia, A. R.; Martin-Fontecha, M. *J. Am. Chem. Soc.* **2001**, *123*, 9920−9921.

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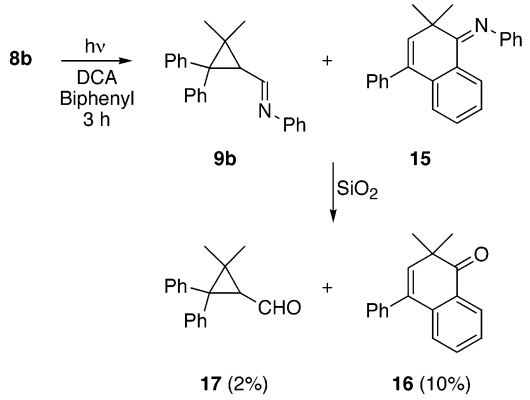
(7) van der Weerdt, A. J. A.; Cerfontain, H. *Tetrahedron*, **1981**, *37*, 2121−2130.

(8) Armesto, D.; Ortiz, M. J.; Romano, S. *Tetrahedron Lett.* **1995**, *36*, 965−968. (b) Armesto, D.; Ortiz, M. J.; Romano, S.; Agarrabeitia, A. R.; Gallego, M. G.; Ramos, A. *J. Org. Chem.* **1996**, *61*, 1459−1466.

SCHEME 2



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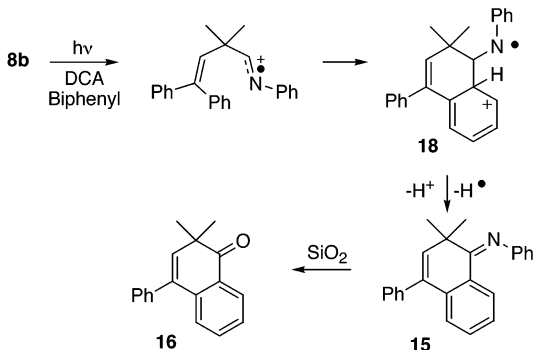
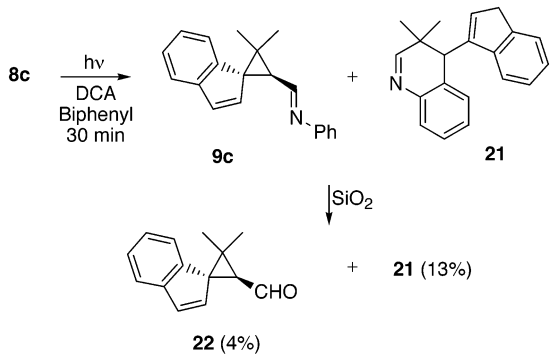


ticipate, because the resulting radical-cation **14** would be considerably less stable than intermediate **11** (Scheme 1).

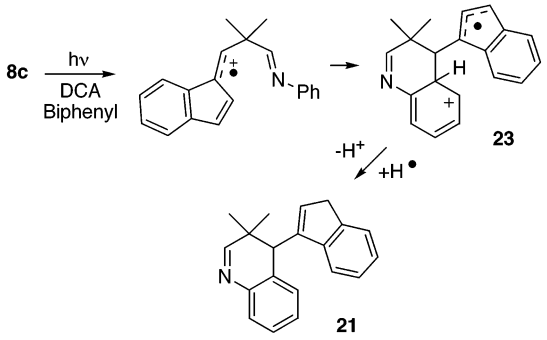
Irradiation of imine (*E*)-**8b**[6] for 3 h, under the above conditions, affords the cyclopropylimine **9b** and a new substance **15** (^{1}H NMR analysis of the crude photolyzate). Separation by silica gel column chromatography gives 2,2-dimethyl-4,4-diphenyl-3-butenal[9] (81%), 2,2-dimethyl-4-phenyl-2*H*-naphthalen-1-one **16** (10%), and the cyclopropanecarbaldehyde **17**[10] (2%). The isolated carbonyl compounds are formed by hydrolysis of the corresponding imines **8b**, **9b**, and **15** during chromatography (Scheme 2).

The identity of **16** was assigned based on its spectroscopic properties and by independent synthesis from methyl 2-methyl-4,4-diphenyl-3-butenoate[11] (Experimental Section). This result shows that two different reaction paths are open to the radical-cation intermediate derived from **8b**. The first involves 1-ADPM rearrangement leading to **9b,** and the other is promoted by cyclization affording **15**, which is the more efficient reaction in this instance. A possible mechanism to justify the formation of **15** could involve intramolecular electrophilic attack of a radical cation centered in the C−N double bond to one of the phenyl rings at C5 to afford the intermediate **18**, which losses a proton and a hydrogen radical yielding **15** (Scheme 3). A similar cyclization process has been observed by Zimmerman and co-workers in their study

SCHEME 4



SCHEME 5



of the electron-acceptor sensitized photoreactions of 1,4-dienes **19** which yield benzhydryldihydronaphthalenes **20**.[12] However, it is interesting to note that dienes **19** do not undergo radical-cation rearrangements of the di-π-methane type.

When imine (1*E*,4*E*)-**8c**[4b] is irradiated for 30 min under the same conditions used for **8a** and **8b**, it reacts to form the (*E*)-cyclopropylimine **9c** and a new compound (^{1}H NMR analysis of the crude photolyzate). Separation of the photoproduct mixture by column chromatography on silica gel yields 3-(1-indenylidene)-2,2-dimethylpropanal[13] (63%, 2:1 mixture of *E*/*Z* diastereoisomers), dihydroquinoline **21** (13%), and the spirocarbaldehyde **22**[13] (4%). The isolated carbonyl compounds are formed by hydrolysis of the corresponding imines **8c** and **9c** during isolation (Scheme 4).

The identity of **21** was established based on the comparison of its spectroscopic properties with those of closely related compounds.[3,12] The mechanism shown in Scheme 5 accounts for the formation of dihydroquinoline **21**. In the route, an olefin centered radical cation undergoes intramolecular electrophilic addition to the phenyl ring attached to nitrogen, generating the intermediate **23**, which, by aromatization and hydrogen abstraction, yields **21**.

The results obtained from studies of the DCA-sensitized photoreactions of imines **8a**−**c** demonstrate that these compounds react to afford the corresponding cyclopropylimines **9a**−**c** in low yields. These processes represent second examples of di-π-methane type rearrangements that take place via radical-cation intermedi-

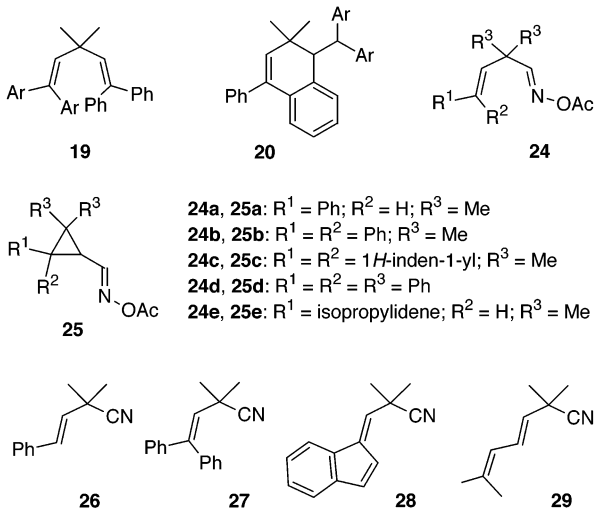
(9) Zimmerman, H. E.; Pratt, A. C. *J. Am. Chem. Soc.* **1970**, *92*, 6259−6267.
(10) Zimmerman, H. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1969**, *91*, 1718−1727.
(11) Armesto, D.; Ortiz, M. J.; Ramos, A.; Horspool, W. M.; Mayoral, E. P. *J. Org. Chem.* **1994**, *59*, 8115−8124.
(12) Zimmerman, H. E.; Hoffacker, K. D. *J. Org. Chem.* **1996**, *61*, 6526−6534.
(13) Armesto, D.; Gallego, M. G.; Horspool, W. M.; Agarrabeitia, A. R. *Tetrahedron* **1995**, *51*, 9223−9240.

ates. However, the main photoproducts obtained in the photoreactions of **8b** and **8c** are the dihydronaphthalenone derivative **16** and the dihydroquinoline **21**, respectively. With regard to the formation of these two products, it is worth noting that while compound **15** results from a radical cation centered in the imine moiety, the quinoline **21** is formed from a radical cation centered in the alkene unit. This surprising result suggests that, under these reaction conditions, two different and competitively reactive radical-cation intermediates are generated from two donor centers with different ionization potentials (the alkene and the imine).

DCA-Sensitized Irradiation of Oxime Acetates. Previous studies have shown that β,γ-unsaturated oxime acetates undergo the 1-ADPM rearrangement more efficiently that do the corresponding imines in the triplet excited state.[14] In addition, the former compounds have the advantage over the imines that they do not hydrolyze readily and, therefore, are easier to handle. Consequently, our studies of SET-sensitized photoreactions were extended to the oxime acetates (1*E*,4*E*)-**24a**,[15] (*E*)-**24b,**[14] and (1*E*,4*E*)-**24c**,[13] which are structurally related to the imines **8a**−**c**. DCA-sensitized irradiation of compounds **24a**−**c**, using biphenyl as cosensitizer, for variable times, afford the corresponding cyclopropanes (*E*,*E*)-**25a**[15] (15%), (*E*)-**25b**[14] (28%), and (*E*,*E*)-**25c**[13] (16%), respectively, resulting from 1-ADPM rearrangements (Table 1).

The results show that the 1-ADPM rearrangement via radical-cation intermediates can be extended to β,γ-unsaturated oxime acetates. The qualitative efficiencies of the reactions of oxime acetates **24a**−**c** and the yields of products are clearly higher than those for the imines **8a**−**c** (Table 1). Additional investigations showed that irradiation of oxime acetates **24d**−**e**,[13,14b] under the above conditions, also leads to formation of the corresponding 1-ADPM photoproducts (*E*)-**25d**[14b] (4%) and (1*E*,4*E*)-**25e**[13] (2%), respectively (Table 1). For unknown reasons, the yield of isolated products in these two processes is considerably lower than those for reaction of **24a**−**c**, even though azadienes **24d** and **24e** give the corresponding cyclopropanes in high yield in the triplet-sensitized photoreactions. In addition to the cyclopropane (*E*,*E*)-**25a**, SET-sensitized photoreaction of (1*E*,4*E*)-**24a** also generates recovered starting material (66%), as a mixture 3:1 of (1*E*,4*E*)/(1*E*,4*Z*) diastereoisomers, and the nitrile (*E*)-**26** (2%), resulting from elimination of acetic acid.

The same type of elimination reaction is observed in the irradiations of **24b**, **24c,** and **24e** that give the corresponding nitriles **27** (8%), **28** (9%), and **29** (14%), respectively (Table 1). The identity of these nitriles was easily established by use of conventional spectroscopic techniques. The possibility that this elimination process is thermally activated seems unlikely, since nitrile products were not observed to form in the triplet-sensitized irradiations of oxime acetates **24**. The formation of these nitriles could by explained by a pathway



(Scheme 6) involving generation of a C−N bond centered radical-cation **30** that eliminates acetic acid to yield the nitrile radical cation. Back electron transfer then yields the nitrile.

Irradiation of oxime acetate **24c** gives, in addition to the cyclopropane **25c** and the nitrile **28**, unchanged recovered started material (26%) and a new product that was identified as the dihydroisoxazole **31** (18%), by comparing its spectroscopic properties to those of related substances.[16,17] A possible mechanism to justify formation of **31** involves cyclization within the radical-cation **32** to generate the intermediate **33**, which by elimination of acetic acid yields **31** (Scheme 7). In this instance, it is difficult to know whether the reaction is promoted by a radical cation centered in either the alkene or the oxime acetate moieties.

The results obtained in the study of the DCA electron-acceptor sensitized photoreactivity of β,γ-unsaturated oxime acetates **24** show that these compounds undergo 1-ADPM rearrangement via radical-cation intermediates qualitatively more efficiently than the corresponding imines **8**. In some cases, radical-cation intermediates, generated from these substances, also undergo elimination of acetic acid to form the corresponding nitriles. Obviously, the alternative cyclization to dihydroquinoline **21** observed in the irradiation of imine **8c**, which involves the phenyl ring attached to nitrogen, cannot take place in oxime acetates. Finally, in one instance (**24c**), an alternative cyclization to dihydroisoxazole **31** was observed.

DCA-Sensitized Irradiation of Oxime Ethers. β,γ-Unsaturated oxime ethers are hydrolytically stable C−N double bond derivatives that are easier to handle than the corresponding imines. However, previous photochemical studies showed that oxime ethers do not undergo 1-ADPM rearrangement.[18] Therefore, it was interesting to probe the DCA-SET-sensitized photochemical behavior of oxime ethers **34** in order to determine if the lack of 1-ADPM reactivity of these compounds in the triplet

(14) Armesto, D.; Horspool, W. M.; Langa, F. *J. Chem. Soc., Chem. Commun.* **1987**, 1874−1875. (b) Armesto, D.; Horspool, W. M.; Langa, F.; Ramos, A. *J. Chem. Soc., Perkin Trans. 1* **1991**, 223−228.

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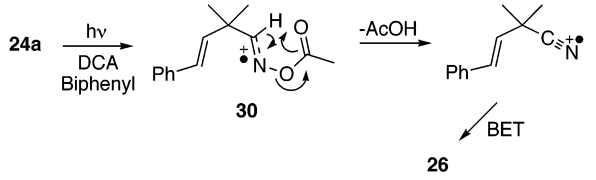
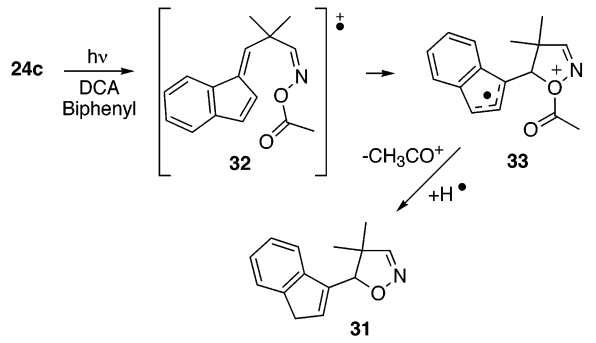
(17) Armesto, D.; Ramos, A.; Ortiz, M. J.; Horspool, W. M.; Mancheño, M. J.; Caballero, O.; Mayoral, E. P. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1535−1541.

(18) Pratt, A. C.; Abdul-Majid, Q. *J. Chem. Soc., Perkin Trans. 1* **1987**, 359−364.

SCHEME 6

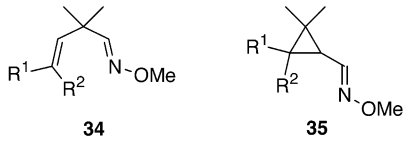


SCHEME 7

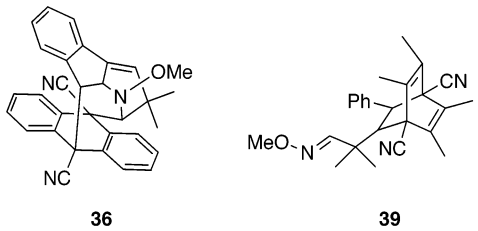


excited state could be circumvented by generating the corresponding radical cations.

Oxime ether **34b** has been described previously,[18] and the related substances, **34a** and **34c**, were synthesized from the corresponding aldehydes by use of conventional procedures. DCA-sensitized irradiation of **34a** for 13.5 h promotes formation of the 1-ADPM rearrangement derived cyclopropane **35a** (10%), recovered starting material (40%), and a complex mixture of products. Irradiation of **34b**, under the same conditions used for **34a**, for 4 h gives recovered starting material (19%) and a complex mixture of products. ^{1}H NMR analysis of the crude photolyzate showed that it does not contain the corresponding 1-ADPM product.

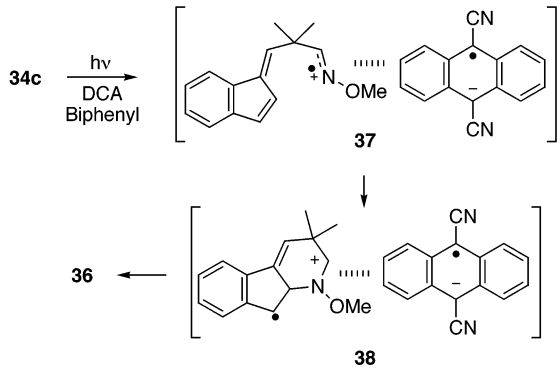


34a, **35a**: R^1 = Ph; R^2 = H
34b: $R^1 = R^2$ = Ph
34c, **35c**: $R^1 = R^2$ = 1*H*-inden-1-yl



Oxime ether (1*E*,4*E*)-**34c**, when irradiated under the above conditions for 2 h, yields the spirocyclopropane **35c** (3%), recovered starting material (30%) as a 3:4 mixture of (1*E*,4*Z*)/(1*E*,4*E*) diastereoisomers, and a new compound (7%) that was identified as the [4 + 4]-cycloadduct **36** by using X-ray diffraction analysis. The identities of **35a** and **35c** were established based on their spectroscopic properties and by independent synthesis from the corresponding cyclopropyl aldehydes (Experimental Section).

SCHEME 8

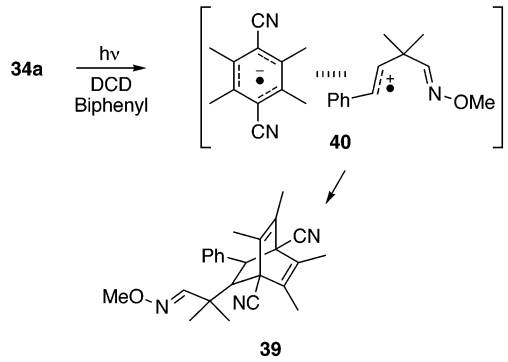


A possible mechanism for formation of **36** involves the generation of radical-cation/radical-anion pair **37**. Intramolecular cyclization of the radical cation within the solvent cage generates the radical-cation/radical-anion pair **38**, which by intermolecular cycloaddition yields **36**. The results obtained in studies with β,γ-unsaturated oxime ethers show that these compounds are unreactive in the 1-ADPM mode.[18] However, oxime ethers **34a** and **34c** undergo the 1-ADPM rearrangement via radical-cation intermediates in low yields. The formation of cycloadduct **36** from **34c** is surprising, and it demonstrates that unexpected alternative reaction routes are opened to the intermediate radical cations in some instances.

Influence of the Electron-Acceptor Sensitizers on the Photoproduct Yields. The results summarized thus far indicate that 1-substituted-1-aza-1,4-dienes undergo 1-ADPM rearrangements upon irradiation using DCA as an electron-acceptor sensitizer. In addition, β,γ-unsaturated oxime acetates **24** were found to react qualitatively more efficiently than the corresponding β,γ-unsaturated imines **8** while the β,γ-unsaturated oxime ethers **34** are less reactive. In some instances, alternative reaction modes have been observed, yielding naphthalene derivatives, dihydroquinolines, dihydroisoxazoles, [4 + 4] cycloadducts, and products resulting from elimination reactions. However, from a synthetic point of view, these reactions have little interest, since the product yields are usually low (Table 1). Previous studies have shown that SET-photoreaction sensitized by dicyanodurene (DCD) often occurs with higher yields.[19] However, this sensitizer has the disadvantage that it absorbs light at shorter wavelengths than does DCA and, therefore, it cannot be used when the electron-donor molecules absorb strongly above 300 nm. In an attempt to increase the yield of products, we have explored the photoreactivity of 1-aza-1,4-dienes **8a**, **8b**, **24a**, **24b**, **24d**, **24e**, **34a,** and **34b**, all of which do not absorb strongly above 300 nm, using DCD as the electron-acceptor sensitizer and biphenyl as the cosensitizer. The results obtained, summarized in Table 1, show that reactions under these conditions require shorter irradiation times, in most cases, and result in increased yields of the 1-ADPM photoproducts. For instance, DCA-sensitized irradiation of imine **8a**, for 7 h, affords cyclopropane **9a** in 13% yield, while DCD-sensitized reaction of this substance for 2 h gives **9a** in

(19) Gassman, P. G.; De Silva, S. A. *J. Am. Chem. Soc.* **1991**, *113*, 9870−9872.

SCHEME 9



46% yield. Similar enhancements in the yields of 1-ADPM products occur with the other substances. One exception to this trend is seen with oxime ether **34a**, which gives **35a** in a 10% yield upon 13.5 h irradiation using DCA. In contrast, 3 h irradiation of **34a** with DCD affords **35a** in lower yield of 7% along with a new product (23%), identified based on spectroscopic evidence as the [4 + 2] cycloadduct **39**. This result is intriguing, because this is the only case in which we have observed preferential formation of a [4 + 2] cycloaddition product. A possible mechanism for the formation of **39** involves initial SET from the alkene group in **34a** to excited DCD, yielding the radical-cation/radical-anion pair **40**. Intermolecular [4 + 2] cycloaddition of this intermediate affords **39** (Scheme 9).

Finally, irradiation of oxime ether **34b**, under both DCA- and DCD-sensitization conditions, results in consumption of the starting material and formation of a complex mixture of products. This result shows that this substance does not undergo either DCA- or DCD-SET-sensitized 1-ADPM rearrangement. An interesting difference in reactivity upon DCA versus DCD sensitized irradiation is observed in the cases of the oxime acetates. Thus, while DCA-sensitized irradiation of compounds **24a**, **24b**, and **24e** affords the corresponding nitriles **26**, **27**, and **29**, respectively, DCD-sensitized irradiation yields the corresponding cyclopropanes **25a**, **25b**, and **25e**, exclusively. These observations suggest the possibility that the radical-cation centered in the C−N double bond, postulated as being responsible for elimination of acetic acid (Scheme 6), might not be formed under DCD-sensitization conditions. Therefore, the 1-ADPM product yield enhancements seen with the DCD-sensitized reactions might be due to the selective formation of a radical cation centered in the C−C double bond. In summary, the yields of 1-ADPM products and the efficiencies of the reaction can be increased considerably by using DCD as an electron-acceptor sensitizer instead of DCA. Furthermore, the use of DCD suppresses alternative reaction modes, such as the elimination of acetic acid.

Conclusions

The results of this investigation show that β,γ-unsaturated imines, oxime acetates, and oxime ethers undergo 1-ADPM rearrangements, using DCA or DCD as electron-acceptor sensitizers. These processes represent the second example of di-π-methane rearrangements occurring via radical cations. Oxime acetates react more efficiently than the corresponding imines, while the oxime ethers are the least reactive. Alternative reaction modes are followed, in some cases yielding nitriles, dihydronaphthalenes, dihydroquinolines, and cycloaddition products. Some of these products arise from radical cations centered in the alkene unit, while others are formed from radical cations located in the C−N double bond moiety. The results show that, under SET-sensitization conditions, the substrates can yield two different radical cations by initial SET from two functional groups with different ionization potentials. Changing the SET-sensitizer from DCA to DCD results in considerably increased reaction efficiencies in all cases studied. The yields of isolated products are also enhanced, making these reactions useful from a synthetic perspective. In addition, nitriles obtained in the DCA-sensitized irradiation of oxime acetates are not obtained when DCD is used as the SET sensitizer, suggesting that radical cations centered in the C−N double bond are not formed under the latter conditions. These results open new lines of research in the area of di-π-methane photochemistry. Further studies are needed to determine the factors that control the different reaction paths open to the radical-cation intermediates and the role of the electron-acceptor sensitizer on the outcomes of these photoreactions.

Experimental Section

General Procedures. Starting materials and reagents are commercially available unless synthesis is decribed. Spectral data of the known compounds were in accordance with the literature data. Flash chromatography was performed using silica gel 60 (40−63 μm). NMR spectra were recorded in $CDCl_3$ solution. Chemical shifts, δ, are expressed in parts per million (ppm), and coupling constants J are given in hertz (Hz). UV−vis spectra were recorded in CH_2Cl_2 solution. Melting points were determined in open capillaries and are uncorrected.

Imines **8a**,[4b] **8b**,[6] **8c**,[4b] oxime acetates **24a**,[15] **24b**,[14b] **24c**,[13] **24d**,[14b] **24e**,[13] and oxime ether **34b**[18] were synthesized by the methods previously described.

General Procedure for the Synthesis of β,γ-Unsaturated Oxime Ethers. The corresponding aldehyde, *O*-methylhydroxylamine hydrochloride, and pyridine were refluxed in EtOH (50 mL) for 1 h. The aldehyde/*O*-methylhydroxylamine/pyridine ratio was 1:1.2:1.2 for all the experiments. The solvent was evaporated, the crude product was dissolved in Et_2O, and the solution was washed with 10% aqueous HCl, water, and brine. The extract was dried ($MgSO_4$), filtered, and evaporated to dryness. The oxime ethers were isolated and purified by flash chromatography using hexane/Et_2O (9:1) as eluent.

***O*-Methyl Ether of 2,2-Dimethyl-4-phenyl-3-butenal Oxime (34a).** From 2,2-dimethyl-4-phenyl-3-butenal[7] (230 mg, 1.3 mmol) as a 1:1 mixture of *Z*/*E* isomers, *O*-methylhydroxylamine hydrochloride (201 mg, 1.4 mmol) and pyridine (0.2 mL, 1.4 mmol) yielded the oxime ether **34a** (208 mg, 77%) as an oil and as a 1:1 mixture of (1*E*,4*Z*)/(1*E*,4*E*) isomers: ^{1}H NMR (300 MHz) δ 7.40−7.12 (m, 5.5H), 7.05 (s, 0.5H, *Z*-isomer), 6.53 (d, J = 12.3 Hz, 0.5H, *Z*-isomer), 6.29 (AB system, J = 16.3 Hz, 1H, *E*-isomer), 5.59 (d, J = 12.3 Hz, 0.5H, *Z*-isomer), 3.84 (s, 1.5H, *E*-isomer), 3.65 (s, 1.5H, *Z*-isomer), 1.30 (s, 3H, *E*-isomer), 1.22 (s, 3H, *Z*-isomer); ^{13}C NMR (75 MHz) δ 156.5, 155.8, 137.9−126.2, 61.3, 60.9, 39.1, 39.0, 27.4, 25.4; IR (neat) ν 1623, 1616 cm^{-1}; UV (CH_2Cl_2) λ_{max} 249 (ϵ 13 116); MS *m*/*e* (%) 145 (M^+ − 58, 100), 134 (22), 129 (15), 115 (23), 91 (44), 77 (19).

***O*-Methyl Ether of (1*E*,4*E*)-3-(1-Indenylidene)-2,2-dimethylpropanal Oxime (34c).** From (*E*)-3-(1-indenylidene)-2,2-dimethylpropanal[13] (1.10 g, 5.1 mmol), *O*-methylhydroxylamine hydrochloride (0.50 g, 6.1 mmol), and pyridine (0.5

mL, 6.1 mmol) yielded the oxime ether (1*E*,4*E*)-**34c** (881 mg, 76%) as a yellow oil: ^{1}H NMR (200 MHz) δ 7.53 (s, 1H), 7.32−7.11 (m, 4H), 6.82 (dd, J = 5.7, 1.0 Hz, 1H), 6.76 (d, J = 5.7 Hz, 1H), 6.57 (br s, 1H), 3.88 (s, 3H), 1.45 (s, 6H); ^{13}C NMR (50 MHz) δ 156.0, 136.5−118.8, 61.5, 39.9, 27.5; IR (neat) ν 1606 cm^{-1}; UV (CH_2Cl_2) λ_{max} 256 (ϵ 42 102); MS *m*/*e* (%) 227 (M^+, 33), 196 (100), 181 (96), 167 (18), 115 (60), 57 (38).

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. In the irradiations with DCA, a filter solution of sodium *m*-vanadate 0.07M in 5% sodium hydroxide was used. Solutions of the compounds, the sensitizer (DCA or DCD), and the cosensitizer (biphenyl) in dry CH_3CN (450 mL), were purged for 1 h with argon and irradiated under a positive pressure of argon. After completion of the irradiation, the solvent was removed under reduced pressure. In the DCA runs, the sensitizer was removed by precipitation with Et_2O and filtered, and the biphenyl and the products were separated by flash chromatography on silica gel. When DCD was used, the photomixture was separated by flash chromatography on silica gel.

DCA-Sensitized Irradiation of 8a. A 1:1 mixture of (1*E*,4*E*)/(1*E*,4*Z*)-imine **8a** (497 mg, 2.0 mmol), biphenyl (306 mg, 2.0 mmol), and DCA (30 mg, 0.13 mmol) was irradiated for 7 h. Chromatography using hexane/Et_2O (97:3) as eluent gave 2,2-dimethyl-4-phenyl-3-butenal[7] (220 mg, 65%) as a 2:1 mixture of *E*/*Z* isomers and *trans*-2,2-dimethyl-3-phenylcyclopropanecarbaldehyde[8] (45 mg, 13%), resulting from hydrolysis of the corresponding imines. Further elution with Et_2O afforded 209 mg of highly polar material.

DCD-Sensitized Irradiation of 8a. Imine (1*E*,4*E*)−**8a** (254 mg, 1.0 mmol), biphenyl (1.52 g, 9.9 mmol), and DCD (1.4 g, 7.6 mmol) were irradiated for 2 h yielding 2,2-dimethyl-4-phenyl-3-butenal[7] (54 mg, 30%) as a 1:1 mixture of *Z*/*E* isomers and *trans*-2,2-dimethyl-3-phenylcyclopropanecarbaldehyde[8] (83 mg, 46%), resulting from hydrolysis of the corresponding imines. Further elution with Et_2O afforded 56 mg of highly polar material.

DCA-Sensitized Irradiation of 8b. Imine (*E*)-**8b** (391 mg, 1.2 mmol), biphenyl (185 mg, 1.2 mmol), and DCA (30 mg, 0.13 mmol) were irradiated for 3 h. Chromatography using hexane/Et_2O (95:5) as eluent gave ketone **16** (30 mg, 10%) as a white solid (mp 116−117 °C (EtOH)), 2,2-dimethyl-4,4-diphenyl-3-butenal[9] (243 mg, 81%), and cyclopropanecarbaldealdehyde **17**[10] (6 mg, 2%), resulting from hydrolysis of the corresponding imines. Further elution with Et_2O afforded 23 mg of highly polar material. Ketone **16**: ^{1}H NMR (200 MHz) δ 8.06 (d, J = 7.5 Hz, 1H), 7.47−7.06 (m, 7H), 6.72 (d, J = 7.5 Hz, 1H), 5.96 (s, 1H), 1.27 (s, 6H); ^{13}C NMR (50 MHz) δ 203.7, 140.2−126.5, 45.3, 26.1; IR (neat) ν 1678 cm^{-1}; MS *m*/*e* (%) 248 (M^+, 100), 233 (59), 218 (9), 205 (29), 189 (8), 203 (19), 127 (4), 101 (20), 77 (7). This compound was further characterized by independent synthesis.

Independent Synthesis of 2,2-Diphenyl-4-phenyl-1-(2*H*)naphthalenone (16). To a solution of *i*-Pr_2NH (0.7 mL, 5.2 mmol) in 50 mL of dry THF were added successively, at −78 °C under argon, BuLi (2.1 mmol, 1.6 M in hexane) and HMPA (0.9 mL, 5.2 mmol). The resulting mixture was stirred for 1 h, and then a solution of methyl 2-methyl-4,4-diphenyl-3-butenoate[11] (1.2 g, 4.7 mmol) in 25 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 (0.3 mL, 5.6 mmol) was added in one portion. The reaction mixture was stirred at −40 °C for 1 h, the temperature was then 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. Chromatography of the residue using hexane/Et_2O (9:1) as eluent yielded **methyl 2,2-dimethyl-4,4-diphenyl-3-butenoate** (1 g, 79%) as a yellow solid: mp 66−67 °C (EtOH); ^{1}H NMR (300 MHz) δ 7.37−7.11 (m, 10H), 6.07 (s, 1H), 3.29 (s, 3H), 1.32 (s, 6H); ^{13}C NMR (75 MHz) δ 176.7, 143.2−127.1, 51.5, 44.0, 27.9; IR (neat) ν 1740 cm^{-1}; MS *m*/*e* (%) 280 (M^+, 19), 221 (100), 203 (10), 143 (64), 91 (42), 77 (13). Anal. Calcd for $C_{19}H_{21}O_2$: C, 81.39; H, 7.19. Found: C, 81.69; H, 7.17.

A solution of methyl 2,2-dimethyl-4,4-diphenyl-3-butenoate (1.0 g, 3.7 mmol) in dry EtOH (20 mL) was added to a solution of KOH (621 mg, 11 mmol) in EtOH (20 mL). After the mixture was allowed to reflux for 24 h, the solvent was removed and the residue was 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 **2,2-dimethyl-4,4-diphenyl-3-butenoic acid** (840 mg, 89%) as a white solid: mp 94−95 °C (hexane); ^{1}H NMR (300 MHz) δ 7.33−7.16 (m, 10H), 6.14 (s, 1H), 1.29 (s, 6H); ^{13}C NMR (75 MHz) δ 182.9, 142.9−127.1, 43.9, 27.2; IR (neat) ν 3100−2650, 1740 cm^{-1}; MS *m*/*e* (%) 266 (M^+, 38), 221 (100), 178 (17), 143 (77), 128 (31), 91 (70), 51 (22). Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.16; H, 6.82. Found: C, 81.25; H, 7.06.

2,2-Dimethyl-4,4-diphenyl-3-butenoic acid (840 mg, 3.3 mmol) was converted into the corresponding acid chloride by refluxing in $SOCl_2$ (0.44 mL, 4.9 mmol) for 1 h. Removal of excess $SOCl_2$ by rotary evaporation yielded an oil which was used immediately in the next step.

To a solution of anhyd $AlCl_3$ (0.44 g, 3.3 mmol) in dry CH_2Cl_2 (10 mL) at 0 °C and under an atmosphere of argon, a solution of the acid chloride in CH_2Cl_2 (15 mL) was added dropwise. The solution was stirred for 15 min and then poured into ice water/HCl (50%) and stirred for a further 15 min. The mixture was extracted with Et_2O, and the organic layer was washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), filtered, and concentrated to dryness. Chromatography of the residue using hexane/Et_2O (95:5) yielded **16** (350 mg, 45%) as a white solid (mp 116−117 °C (EtOH)). This compound proved to be identical to the photoproduct obtained in the irradiation of **8b**.

DCD-Sensitized Irradiation of 8b. Imine (*E*)-**8b** (238 mg, 0.7 mmol), biphenyl (1.28 g, 8.3 mmol), and DCD (1.18 g, 6.4 mmol) were irradiated for 30 min. Chromatography using hexane/Et_2O (95:5) as eluent gave the ketone **16** (24 mg, 13%), 2,2-dimethyl-4,4-diphenyl-3-butenal[9] (115 mg, 63%), and cyclopropanecarbaldealdehyde **17**[10] (20 mg, 11%), resulting from hydrolysis of the corresponding imines. Further elution with Et_2O afforded 28 mg of highly polar material.

DCA-Sensitized Irradiation of 8c. Imine (1*E*,4*E*)-**8c** (270 mg, 0.98 mmol), biphenyl (152 mg, 0.98 mmol), and DCA (30 mg, 0.13 mmol) were irradiated for 30 min. Chromatography using hexane/Et_2O (95:5) as eluent gave 3-(1-indenylidene)-2,2-dimethylpropanal[13] (123 mg, 63%) as a 2:1 mixture of *E*/*Z* isomers, cyclopropanecarbaldealdehyde (*E*)-**22**[13] (8 mg, 4%), resulting from hydrolysis of the corresponding imines, and 4-(3*H*-inden-1-yl)-3,3-dimethyl-3,4-dihydroquinoline **21** (35 mg, 13%) as a brown oil. Further elution with Et_2O afforded 43 mg of highly polar material. Dihydroquinoline **21**: ^{1}H NMR (200 MHz) δ 8.01−6.54 (m, 9H), 5.25 (br s, 1H), 4.80 (br s, 1H), 4.49 (br s, 2H), 1.57 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (50 MHz) δ 146.5, 139.0−111.9, 58.3, 51.8, 31.7, 29.7, 25.8; IR (neat) ν 1660 cm^{-1}; MS *m*/*e* (%) 327 (M^+, 11), 286 (4), 273 (100), 258 (93), 228 (38), 191 (12), 170 (29), 155 (29), 115 (13), 104 (74), 77 (65), 57 (39). Anal. Calcd for $C_{20}H_{19}N$: C, 87.91; H, 6.96; N, 5.13. Found: C, 87.81; H, 6.76; N, 5.25.

DCA-Sensitized Irradiation of 24a. Oxime acetate (1*E*,4*E*)-**24a** (400 mg, 1.7 mmol), biphenyl (297 mg, 1.7 mmol), and DCA (30 mg, 0.13 mmol) were irradiated for 2.5 h. Chromatography using hexane/Et_2O (95:5) as eluent gave nitrile (*E*)-**26** (6 mg, 2%) as an oil, starting oxime acetate (262 mg, 66%) as a 3:1 mixture of (1*E*,4*E*):(1*E*,4*Z*) isomers, and cyclopropane (E_{cyclo},E_{C-N})-**25a**[15] (45 mg, 15%). Further elution with Et_2O afforded 65 mg of highly polar material. Nitrile **26**: ^{1}H NMR (300 MHz) δ 7.40−7.26 (m, 5H), 6.76 (d, J = 15.9 Hz, 1H), 6.03 (d, J = 15.9 Hz, 1H), 1.55 (s, 6H); ^{13}C NMR (75

MHz) δ 136.9, 130.4−126.5, 120.8, 35.0, 27.7; IR (neat) ν 2250 cm^{-1}; MS *m/e* (%) 171 (M$^+$, 1), 145 (11), 85 (23), 57 (100). Anal. Calcd for $C_{12}H_{13}N$: C, 84.21; H, 7.60; N, 8.19. Found: C, 84.20; H, 7.75; N, 8.01.

DCD-Sensitized Irradiation of 24a. Oxime acetate (1*E*,4*E*)-**24a** (263 mg, 1.14 mmol), biphenyl (20 mg, 0.13 mmol), and DCD (25 mg, 0.11 mmol) were irradiated for 1 h yielding recovered starting material **24a** (87 mg, 33%) as a 3:1 mixture of (1*E*,4*E*):(1*E*,4*Z*) isomers and cyclopropane (E_{cyclo},E_{C-N})-**25a**[15] (131 mg 60%). Further elution with Et_2O afforded 10 mg of highly polar material.

DCA-Sensitized Irradiation of 24b. Oxime acetate (*E*)-**24b** (325 mg, 1.05 mmol), biphenyl (163 mg, 1.05 mmol), and DCA (30 mg, 0.13 mmol) were irradiated for 3 h. Chromatography using hexane/Et_2O (95:5) as eluent gave nitrile **27**[6b] (20 mg, 8%), starting oxime acetate **24b** (97 mg, 30%), and cyclopropane (*E*)-**25b**[14b] (81 mg, 28%). Further elution with Et_2O afforded 97 mg of highly polar material.

DCD-Sensitized Irradiation of 24b. Oxime acetate (*E*)-**24b** (206 mg, 0.67 mmol), biphenyl (216 mg, 1.4 mmol), and DCD (200 mg, 1.08 mmol) were irradiated for 90 min, yielding recovered starting material **24b** (30 mg, 15%) and cyclopropane **25b**[14b] (112 mg, 55%) as a 3:1 mixture of *Z*/*E* isomers. Further elution with Et_2O afforded 60 mg of highly polar material.

DCA-Sensitized Irradiation of 24c. Oxime acetate (1*E*,4*E*)-**24c** (290 mg, 1.1 mmol), biphenyl (175 mg, 1.1 mmol), and DCA (30 mg, 0.13 mmol) were irradiated for 1 h. Chromatography using hexane/Et_2O (95:5) as eluent gave nitrile **28** (23 mg, 9%) as an oil and as a 1:3 mixture of *Z*:*E* isomers, 5-(3-indenyl)-4,4-dimethyl-4,5-dihydroisoxazole (**31**) (44 mg, 18%) as a yellow oil, starting oxime acetate **24c** (76 mg, 26%), and cyclopropane (E_{cyclo},E_{C-N})-**25c**[13] (46 mg, 16%). Further elution with Et_2O afforded 72 mg of highly polar material. Nitrile **28**: ^{1}H NMR (200 MHz) δ 7.49 (d, J = 5.7 Hz, 0.75H, *E*-isomer), 7.35−7.20 (m, 4H), 6.99 (d, J = 5.7 Hz, 0.75H, *E*-isomer), 6.79 (d, J = 5.4 Hz, 0.25H, *Z*-isomer), 6.31 (d, J = 5.4 Hz, 0.25H, *Z*-isomer), 6.28 (s, 0.75H, *E*-isomer), 6.02 (s, 0.25H, *Z*-isomer), 1.76 (s, 1.5H, *Z*-isomer), 1.69 (s, 4.5H, *E*-isomer); ^{13}C NMR (50 MHz) δ 141.9−118.9, 35.8, 32.8, 29.5, 28.4; IR (neat) ν 2237 cm^{-1}; MS *m/e* (%) 195 (M$^+$, 96), 180 (70), 167 (47), 149 (100), 131 (27), 103 (37), 69 (46), 57 (52). Compound **31**: ^{1}H NMR (300 MHz) δ 7.53−7.19 (m, 4H), 7.03 (s, 1H), 6.58 (br s, 1H), 5.22 (br s, 1H), 3.43 (br s, 2H), 1.48 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (75 MHz) δ 155.7, 146.0−119.8, 86.2, 52.0, 37.8, 25.4, 20.7; IR (neat) ν 1635 cm^{-1}; MS *m/e* (%) 171 (M$^+$ − 42, 100), 155 (37), 149 (29), 141 (25), 129 (40), 115 (20), 106 (40), 91 (20).

DCA-Sensitized Irradiation of 24d. Oxime acetate (*E*)-**24d** (300 mg, 0.69 mmol), biphenyl (107 mg, 0.69 mmol), and DCA (30 mg, 0.13 mmol) were irradiated for 45 min. Chromatography using hexane/Et_2O (95:5) as eluent gave recovered starting material **24d** (214 mg, 71%) and cyclopropane (*E*)-**25d**[14b] (7 mg, 4%). Further elution with Et_2O afforded 52 mg of highly polar material.

DCD-Sensitized Irradiation of 24d. Oxime acetate (*E*)-**24d** (300 mg, 0.69 mmol), biphenyl (255 mg, 1.66 mmol), and DCD (235 mg, 1.27 mmol) were irradiated for 15 min, yielding recovered starting material **24d** (101 mg, 34%) and cyclopropane **25d**[14b] (99 mg, 33%) as a 1:2 mixture of *Z*/*E* isomers. Further elution with Et_2O afforded 70 mg of highly polar material.

DCA-Sensitized Irradiation of 24e. Oxime acetate (1*E*,4*E*)-**24e**[13] (290 mg, 1.38 mmol), biphenyl (213 mg, 1.38 mmol), and DCA (30 mg, 0.13 mmol) were irradiated for 2 h. Chromatography using hexane/Et_2O (95:5) as eluent gave nitrile (*E*)-**29** (30 mg, 14%) as an oil, starting oxime acetate **24e** (196 mg, 68%), and cyclopropane (E_{cyclo},E_{C-N})-**25e**[13] (5 mg, 2%). Further elution with Et_2O afforded 30 mg of highly polar material. Nitrile **29**: ^{1}H NMR (200 MHz) δ 6.51 (dd, J = 15.1, 10.8 Hz, 1H), 5.72 (d, J = 10.8 Hz, 1H), 5.30 (d, J = 15.1 Hz, 1H), 1.72 (s, 6H), 1.38 (s, 6H); ^{13}C NMR (50 MHz) δ 137.3, 130.7, 126.2, 123.5, 123.2, 34.4, 27.6, 25.8, 18.2; IR (neat) ν 2237, 1658 cm^{-1}; MS *m/e* (%) 149 (M$^+$, 94), 123 (17), 113 (18), 97 (26), 83 (34), 71 (65), 57 (100).

DCD-Sensitized Irradiation of 24e. Oxime acetate (1*E*,4*E*)-**24e** (300 mg, 1.43 mmol), biphenyl (430 mg, 2.79 mmol), and DCD (396 mg, 2.15 mmol) were irradiated for 25 min, yielding recovered starting material **24e** (122 mg, 41%) and cyclopropane (E_{cyclo},E_{C-N})-**25e**[13] (132 mg, 44%). Further elution with Et_2O afforded 38 mg of highly polar material.

DCA-Sensitized Irradiation of 34a. A 1:1 mixture of (1*E*,4*Z*)/(1*E*,4*E*) oxime ether **34a**, biphenyl (233 mg, 1.5 mmol), and DCA (30 mg, 0.13 mmol) was irradiated for 13.5 h. Chromatography using hexane/Et_2O (95:5) as eluent gave recovered starting material **34a** (122 mg, 40%) as a 1.3:1 mixture of (1*E*,4*Z*)/(1*E*,4*E*) isomers, cyclopropane (E_{cyclo},E_{C-N})-**35a** (25 mg, 8%) as an oil, and cyclopropane (E_{cyclo},Z_{C-N})-**35a** (6 mg, 2%) as an oil. Further elution with Et_2O afforded 123 mg of highly polar material. (E_{cyclo},E_{C-N})-**35a**: ^{1}H NMR (200 MHz) δ 7.37−7.09 (m, 6H), 3.79 (s, 3H), 2.18 (d, J = 5.7 Hz, 1H), 1.87 (dd, J = 8.5, 5.7 Hz, 1H), 1.23 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (50 MHz) δ 151.5, 129.8−126.2, 61.5, 38.2, 36.4, 28.8, 25.7, 22.6; IR (neat) ν 1624 cm^{-1}; MS *m/e* (%) 203 (M$^+$, 6), 175 (19), 171 (19), 157 (21), 145 (100), 129 (32), 105 (27), 91 (57), 71 (43), 57 (97), 55 (69). (E_{cyclo},Z_{C-N})-**35a**: ^{1}H NMR (200 MHz) δ 7.31−7.12 (m, 5H), 6.41 (d, J = 8.3 Hz, 1H), 3.86 (s, 3H), 2.47 (dd, J = 8.3, 5.7 Hz, 1H), 2.15 (d, J = 5.7 Hz, 1H), 1.30 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (50 MHz) δ 151.3, 129.0−126.4, 61.9, 38.5, 36.4, 25.7, 23.0, 21.8.

The oxime ether **35a** was further characterized by independent synthesis. From *trans*-2,2-dimethyl-3-phenylcyclopropanecarbaldehyde[8] (25 mg, 0.14 mmol), *O*-methylhydroxylamine hydrochloride (18 mg, 0.22 mmol), and pyridine (0.02 mL, 0.22 mmol) yielded (E_{cyclo},E_{C-N})-**35a** (11 mg, 38%) and (E_{cyclo},Z_{C-N})-**35a** (8 mg, 28%). The spectral characteristics of **35a** were identical to those observed for the photoproduct obtained in the DCA irradiation of **34a**.

DCD-Sensitized Irradiation of 34a. A 1:1 mixture of (1*E*,4*Z*)/(1*E*,4*E*) oxime ether **34a**, biphenyl (362 mg, 2.3 mmol), and DCD (333 mg, 1.8 mmol) were irradiated for 3 h, yielding recovered starting material **34a** (131 mg, 37%) as a 1.3:1 mixture of (1*E*,4*Z*)/(1*E*,4*E*) isomers, cyclopropane (E_{cyclo},E_{C-N})-**35a** (23 mg, 7%) as an oil, and **39** (137 mg, 23%) as an oil. Further elution with Et_2O afforded 100 mg of highly polar material. Compound **39**: ^{1}H NMR (200 MHz) δ 7.49 (s, 1H), 7.30−6.98 (m, 5H), 4.54 (d, J = 1.4 Hz, 1H), 4.13 (d, J = 1.4 Hz, 1H), 3.83 (s, 3H), 2.43 (s, 6H), 2.24 (s, 6H), 1.42 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (50 MHz) δ 191.5, 153.8, 138.2, 137.4, 135.7, 133.3, 128.9, 127.2, 118.0, 115.4, 77.3, 61.5, 56.6, 39.3, 22.9, 21.9, 18.7, 17.3; IR (neat) ν 2221, 1676, 1597 cm^{-1}; MS *m/e* (%) 387 (M$^+$, 26), 356 (11), 287 (25), 260 (21), 105 (26), 101 (100), 91 (27), 77 (22).

DCA-Sensitized Irradiation of 34b. Oxime ether **34b** (240 mg, 0.9 mmol), biphenyl (132 mg, 0.9 mmol), and DCA (30 mg, 0.13 mmol) were irradiated for 4 h. Chromatography using hexane/Et_2O (95:5) as eluent gave recovered starting material **34b** (45 mg, 19%). Further elution with Et_2O afforded 150 mg of highly polar material.

DCD-Sensitized Irradiation of 34b. Oxime ether **34b** (223 mg, 0.8 mmol), biphenyl (85 mg, 0.55 mmol), and DCD (119 mg, 0.43 mmol) were irradiated for 1 h, yielding recovered starting material **34b** (136 mg, 61%). Further elution with Et_2O afforded 80 mg of highly polar material.

DCA-Sensitized Irradiation of 34c. Oxime ether (1*E*,4*E*)-**34c** (404 mg, 1.8 mmol), biphenyl (274 mg, 1.8 mmol), and DCA (30 mg, 0.13 mmol) were irradiated for 2 h. Chromatography using hexane/Et_2O (95:5) as eluent gave recovered starting material **34c** (120 mg, 30%) as a 4:3 mixture of (1*E*,4*E*)/(1*E*,4*Z*) isomers, cyclopropane (E_{cyclo},E_{C-N})-**35c** (10 mg, 3%) as an oil, and **36** (52 mg, 7%) as a white solid (mp 200−202 °C (EtOH)). Further elution with Et_2O afforded 194 mg of highly polar material. Cyclopropane **35c**: ^{1}H NMR (200 MHz) δ 7.48 (d, J = 9.0 Hz, 1H), 7.33 (d, J = 7.2 Hz, 1H), 7.22−7.04 (m, 3H), 6.88 (d, J = 5.7 Hz, 1H), 6.40 (d, J = 5.7 Hz, 1H), 3.74 (s, 3H),

2.65 (d, J = 9.0 Hz, 1H), 1.46 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (50 MHz) δ 148.8, 144.4−121.4, 61.6, 48.7, 40.0, 33.5, 23.3, 21.5; IR (neat) ν 1625 cm^{-1}; MS *m*/*e* (%) 227 (M^+, 8), 212 (8), 197 (16), 182 (14), 166 (13), 152 (27), 139 (12), 115 (35), 87 (7), 91 (7). Compound **36**: ^{1}H NMR (200 MHz) δ 8.05−7.20 (m, 9H), 7.01 (d, J = 7.5 Hz, 1H), 6.85 (t, J = 6.7 Hz, 1H), 6.48 (dd, J = 7.8, 1.2 Hz, 1H), 5.20 (d, J = 3.1 Hz, 1H), 4.50 (dd, J = 7.2, 3.1 Hz, 1H), 3.80 (d, J = 7.2 Hz, 1H), 3.76 (s, 1H), 2.70 (s, 3H), 1.60 (s, 3H), 1.17 (s, 3H); ^{13}C NMR (50 MHz) δ 139.7−120.0, 81.3, 68.8, 59.9, 56.4, 52.8, 36.5, 32.0, 26.5; IR (neat) ν 2399 cm^{-1}; MS *m*/*e* (%) 429 (M^+− 2, 2), 398 (3), 383 (1), 355 (4), 228 (100), 207 (14), 196 (76), 181 (30), 152 (11), 127 (5), 101 (13), 87 (18). The structure assignment was established by X-ray crystallography.

Cyclopropane **35c** was further characterized by independent synthesis. From cyclopropane **22**[13] (49 mg, 0.24 mmol), *O*-methylhydroxylamine hydrochloride (25 mg, 0.29 mmol), and pyridine (0.02 mL, 0.29 mmol) yielded (E_{cyclo},E_{C-N})-**35c** (32 mg, 31%) and (E_{cyclo},Z_{C-N})-**35c** (32 mg, 31%). The spectral characteristics of (E_{cyclo},E_{C-N})-**35c** were identical to those observed for the photoproduct obtained in the DCA irradiation of **34c**. Cyclopropane (E_{cyclo},Z_{C-N})-**35c**: ^{1}H NMR (200 MHz) δ 7.42−7.13 (m, 4H), 6.95 (d, J = 5.7 Hz, 1H), 6.78 (d, J = 8.2 Hz, 1H), 6.50 (d, J = 5.7 Hz, 1H), 3.84 (s, 3H), 3.18 (d, J = 8.2 Hz, 1H), 1.54 (s, 3H), 1.48 (s, 3H); ^{13}C NMR (50 MHz) δ 148.0, 143.9−121.5, 61.8, 49.1, 41.3, 36.1, 23.3, 21.4.

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Supporting Information Available: ^{1}H NMR spectra for all compounds lacking analyses and X-ray crystallographic data for **36**. This material is available free of charge via the Internet at http://pubs.acs.org.

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