JOC Article

Novel Photoreactions of 2-Aza-1,4-dienes in the Triplet Excited State and via Radical-Cation Intermediates. 2-Aza-di-π-methane Rearrangements Yielding Cyclopropylimines and *N*-Vinylaziridines

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Triplet-sensitized irradiation of 2-aza-1,4-dienes affords *N*-cyclopropylimines via 2-aza-di-π-methane (2-ADPM) rearrangement pathways. In the case of the pentaphenyl-substituted azadiene **1**, irradiation leads to formation of cyclopropylimine **2** as well as *N*-vinylaziridine **3**. The transformations represent the first examples of di-π-methane rearrangement reactions that yield three-membered heterocyclic products. SET-sensitized irradiation of 2-aza-1,4-dienes, by using 9,10-dicyanoanthracene (DCA) as an electron-acceptor sensitizer and biphenyl as cosensitizer, brings about regioselective formation of *N*-vinylaziridines. Under these conditions, azadiene **1** also affords cyclopropylimine **37**, resulting from an aryl-di-π-methane rearrangement. This result demonstrates that di-π-methane reactions can also take place via radical−cation intermediates. In some instances, imine and olefin centered cation−radical intermediates, generated by SET-sensitized irradiation, undergo alternative reactions to produce isoquinoline and benzoazepine products.

Introduction

Studies of excited state reactions of 1,4-unsaturated systems comprise one of the most fruitful areas of organic photochemistry. Substances in this family typically undergo unique and synthetically useful photoreactions. Examples of this are found in di-π-methane (DPM) rearrangements of 1,4-dienes,[1,2] oxa-di-π-methane (ODPM) photoreactions of β,γ-unsaturated ketones[1,3] and aldehydes,[1] 1,3-acyl migration processes of β,γ-unsaturated ketones,[3a−c] and 1-aza-di-π-methane (1-ADPM) rearrangements of 1-aza-1,4-dienes containing imine, oxime, and oxime ester groups.[1,4] Surprisingly, the photoreactivity of closely related 2-aza-1,4-diene derivatives has yet to be described although Mariano and co-workers[5] have previously documented the interesting SET-promoted photocyclization reactions of iminium salts derived from 2-aza-1,4-dienes.

Our earlier efforts exploring the excited-state chemistry of 1-aza-1,4-dienes[1,4] have been extended recently to include investigations with the potentially more interesting 2-aza-1,4-dienes. Our interest in these substrates was stimulated by the fact that di-π-methane-type rearrangements of 2-aza-1,4-dienes would lead to the production of vinylaziridines and/or cyclopropylimines, substances which have the capability of undergoing thermal transformation to five-membered *N*-heterocyclic products.[6] Results arising from this investigation have demonstrated that 2-aza-1,4-diene systems participate in unprecedented photorearrangement reactions to produce

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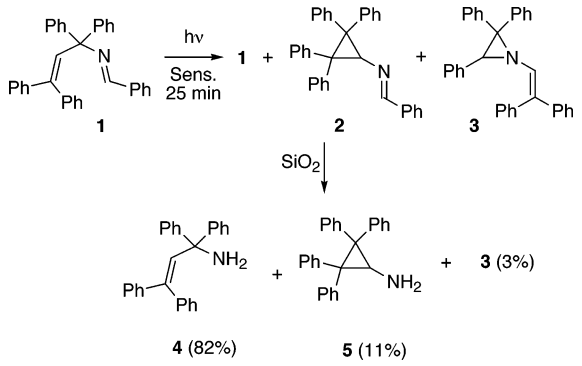
SCHEME 1



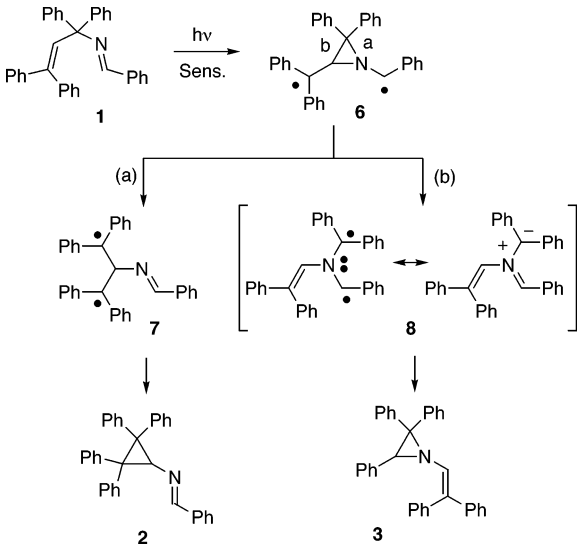
N-vinylaziridine and *N*-cyclopropylimine products, respectively, under SET- and triplet-sensitized irradiation conditions. These processes are the first examples of 2-aza-di-π-methane (2-ADPM) rearrangements. Perhaps of greater interest are observations which show that 2-ADPM rearrangements take place via radical−cation intermediates.[7,8] A portion of the results described here has been the subject of a preliminary communication.[9]

Results and Discussion

Triplet-Sensitized Irradiation of 2-Aza-1,4-dienes. Previous studies have shown that diphenyl substitution at the central methane carbon promotes highly efficient DPM, ODPM, and 1-ADPM reactions in acyclic 1,4-dienes,[10] β,γ-unsaturated aldehydes,[11] and 1-aza-1,4-dienes,[12] respectively. On the basis of these observations, pentaphenyl-2-aza-1,4-diene **1**[9] was selected for our initial studies. Acetophenone, triplet-sensitized irradiation of (*E*)-**1** in CH_2Cl_2 for 25 min, followed by column chromatography on silica gel, affords propenylamine **4** (82%), resulting from hydrolysis of the starting material. In addition, two new products, identified as cyclopropylamine **5** (11%) and vinylaziridine **3** (3%), are formed in this process (Scheme 1). The former substance arises by hydrolysis of cyclopropylimine **2** during chromatography. The identity of **5** was established by use of spectroscopic methods while unambiguous structure assignment of **3** was made by using X-ray diffraction analysis.[9]

The production of **2** and **3** in this photoreaction is in accord with the operation of a mechanistic pathway, involving generation and competitive cleavage of aziridinyl-dicarbinyl biradical **6** (Scheme 2). Thus, the major photoproduct **2** is formed by C−N bond cleavage in **6**,

SCHEME 2



which affords 1,3-biradical **7** that cyclizes to generate cyclopropylimine **2** (path a). Competitive C−C bond fragmentation in **6** provides the intermediate **8**, the precursor of vinylaziridine **3** (path b). This photoreaction represents the first example of a 2-aza-di-π-methane rearrangement that occurs via a three-membered-ring heterocyclic biradical and brings about the formation of a heterocyclic product.[13] It is worth noting that intermediate **8** could be either a triplet 1,3-biradical or a singlet azomethine ylide, depending on whether ISC occurs prior to C−C bond cleavage in **6**. Only the singlet azomethine ylide is capable of undergoing cyclization to form **3**.

Direct irradiation of (*E*)-**1** in CH_2Cl_2 for 10 h by use of Pyrex filtered light (λ >290 nm), followed by column chromatography on silica gel, affords propenylamine **4** (82%) and **5** (4%). The direct irradiation reaction is qualitatively less efficient than the triplet-sensitized process. In addition, the direct irradiation photoreaction of **1** is quenched by 1,3-cyclooctadiene, suggesting that it also occurs via the triplet excited-state manifold.

To determine the scope of this novel rearrangement reaction, studies were extended to the 2-azadienes **9a** and **9b**. Compound **9a** was prepared by condensation of amine **10a** with benzaldehyde. Compound **10a** was synthesized starting with methyl 4,4-diphenyl-3-butenoate[14] by using standard procedures. The synthesis of **9b** has been described previously.[9] *m*-Methoxyacetophenone-sensitized irradiation of (*E*)-**9a** in *t*-BuOH for 6 h, followed by column chromatography on silica gel, affords amine **10a** (81%), resulting from hydrolysis of the starting material, and cyclopropylimine (*E*)-**11a** (5%) (Scheme 3). Irradiation of (*1E*,4*Z*)-**9b** for 9.5 h, using *m*-methoxyacetophenone as sensitizer, followed by column chromatography on silica gel, affords amine **10b** (78%), as a 3:2 mixture of *Z*:*E* diastereoisomers, and cyclopropylimine **11b** (4%),

(7) (a) Recent studies carried out by us show that 1-aza-1,4-dienes also undergo SET-sensitized 1-ADPM rearrangements (refs 7b and 7c). (b) Ortiz, M. J.; Agarrabeitia, A. R.; Aparicio-Lara, S.; Armesto, D. *Tetrahedron Lett.* **1999**, *40*, 1759−1762. (c) Armesto, D.; Ortiz, M. J.; Agarrabeitia, A. R.; Aparicio-Lara, S.; Martin-Fontecha, M.; Liras, M.; Martinez-Alcazar, M. P. *J. Org. Chem.* **2002**, *67*, 9397−9405.

(8) (a) Within this area of SET-promoted di-π-methane rearrangements, we have described recently the first examples of 1-ADPM and DPM rearrangements that take place via radical−anion intermediates (ref 8b). (b) Armesto, D.; Ortiz, M. J.; Agarrabeitia, A. R.; Martin-Fontecha, M. *J. Am. Chem. Soc.* **2001**, *123*, 9920−9921.

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(10) Zimmerman, H. E.; Boetcher, R. J.; Braig, W. *J. Am. Chem. Soc.* **1973**, *95*, 5, 2155−2163.

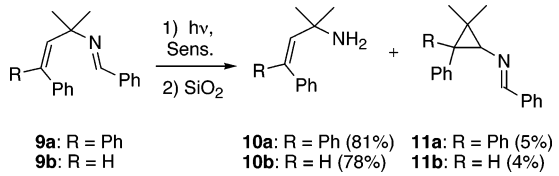
(11) Armesto, D.; Ortiz, M. J.; Romano, S.; Agarrabeitia, A. R.; Gallego, M. G.; Ramos, A. *J. Org. Chem.* **1996**, *61*, 1459−1466.

(12) Armesto, D.; Horspool, W. M.; Langa, F.; Ramos, A. *J. Chem. Soc., Perkin Trans. 1* **1991**, 223−228.

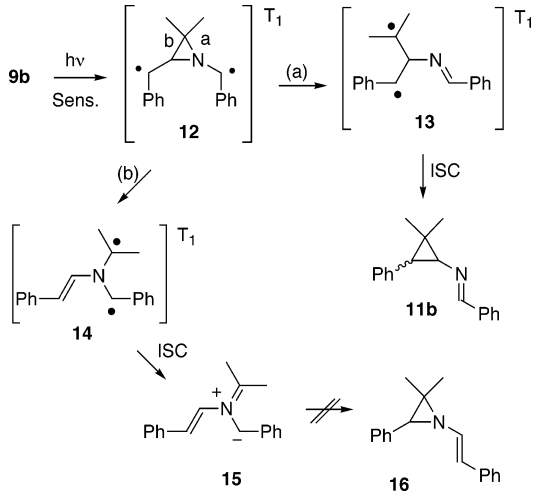
(13) (a) Previous attempts by Adam et al. (ref 13b) to promote the formation of oxiranes by the DPM rearrangement were unsuccessful. (b) Adam, W.; Berkessel, A.; Krimm, S. *J. Am. Chem. Soc.* **1986**, *108*, 4556−4561.

(14) Johnson, W. S.; Petersen, J. W.; Scheneider, W. P. *J. Am. Chem. Soc.* **1947**, *69*, 74−79.

SCHEME 3



SCHEME 4

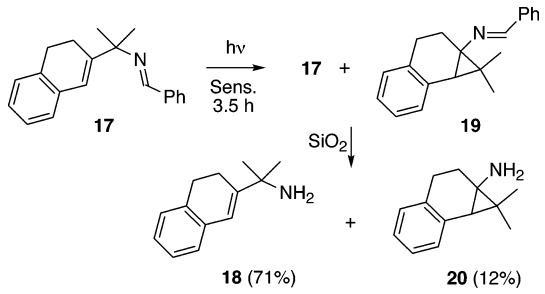


as a 3:2 mixture of (Z_{cyclo},E_{C-N}):(E_{cyclo},E_{C-N}) diastereoisomers (Scheme 3).[15]

The corresponding *N*-vinylaziridines are not produced in the two photoreactions. These results, particularly in the case of **9b**, are surprising because it is anticipated that competitive ring opening of a triplet aziridinyldicarbinyl biradical intermediate **12** would afford comparably stable triplet 1,3-birradicals **13** and **14**, the respective precursors of **11b** and aziridine **16** (Scheme 4). Intersystem crossing in **13** would afford a singlet biradical that cyclizes to form cyclopropylimine **11b** (path a) while intersystem crossing within biradical **14** would yield the zwitterionic intermediate **15** (path b). The latter intermediate is not stabilized by phenyl substitution, as in the case of **8** (Scheme 2). Literature precedents[16] show that nonstabilized 1,3-dipolar intermediates similar to **15** do not cyclize to three-membered heterocycles but rather undergo different reactions including 1,4-hydrogen migration to yield enamines, which could undergo hydrolysis during isolation to produce a complex mixture of products. This interpretation is speculative and additional studies are required to establish its accuracy.

The study was extended to the azadiene **17**, which has a substitution pattern that is observed to promote efficient 1-ADPM rearrangement of an 1-aza-1,4-diene analog[17] and ODPM of a β,γ-unsaturated aldehyde analogue.[11] The synthesis of **17** was achieved by condensation of amine **18**, obtained from β-tetralone, with benzaldehyde. *m*-Methoxyacetophenone sensitized irradiation of (*E*)-**17** in *t*-BuOH, for 3.5 h, after column chromatography on silica gel, affords amine **18** (71%), cyclopropylamine **20** (12%), and a new, as of yet unidentified, compound (10%).[18] Amines **18** and **20** result from hydrolysis of the starting material **17** and the 2-ADPM product **19**, respectively, during chromatography (Scheme 5). The identity of **20** was established by comparison of its spectral data with those reported for related compounds.[11,17] Again, the corresponding *N*-vinylaziridine was not formed in this photoreaction.

SCHEME 5



The results obtained from our studies of triplet-sensitized irradiations of **1**, **9a**, **9b**, and **17** indicate that the 2-ADPM rearrangement process occurs in low yields on a number of differently substituted 2-azadienes. Attempts to increase the chemical efficiencies of these reactions have not been successful. Prolonged irradiation results in destruction of the starting materials and photoproducts. The corresponding regioisomeric product, *N*-vinylaziridine **3**, is formed only in the photoreaction of **1**. The reasons for the high regioselectivities of these processes are still unclear, but it is obvious that dimethyl substitution at the methane carbon in the 2-aza-1,4-diene system suppresses the formation of the corresponding *N*-vinylaziridines. This observation supports the idea that nonstabilized zwitterions that could be formed in these instances probably decompose to a complex mixture of products, instead of undergoing cyclization to the corresponding aziridines.

In our preliminary communication we reported the lack of 2-ADPM reactivity in the triplet-sensitized irradiation of compound **21a**.[9] Thus, *m*-methoxyacetophenone-sensitized irradiation of (*E*)-**21a**, after column chromatography on silica gel, affords amine **22** (66%), resulting from hydrolysis of the starting imine, along with a complex mixture of products. However, a more careful examination of the fractions obtained from the chromatography allowed us to isolate a new product in 6% yield, whose spectral and analytical properties are consistent with structure **23a** (Scheme 6). To confirm this structural assignment, compound (*E*)-**21b** was irradiated under the same conditions used for **21a**, for one third of the time, affording, after column chromatography on silica gel, amine **22** (43%), compound **23b** (16%), and recovered starting material (*E*)-**21b** in 16% yield (Scheme 6).

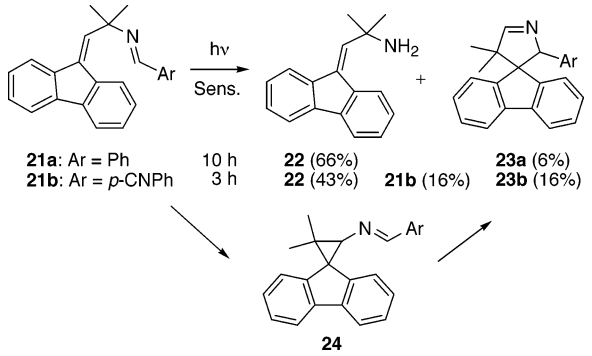
(15) This compound was reported as unreactive in the 2-ADPM mode in a preliminary communication (ref 9). In this experiment CH_2Cl_2 was used as solvent. However, when the reaction was repeated in *t*-BuOH the cyclopropylimine **11b** was isolated in low yield.

(16) (a) Grigg, R.; Thornton-Pett, M.; Yoganathan, G. *Tetrahedron* **1999**, *55*, 1763−1780. (b) Pearson, W. H.; Clark, R. B. *Tetrahedron Lett.* **1999**, *40*, 4467−4471.

(17) Armesto, D.; Ortiz, M. J.; Ramos, A.; Horspool, W. M.; Mayoral, E. P. *J. Org. Chem.* **1994**, *59*, 8115−8124.

(18) At this point it is not possible to establish the structure of the minor product based on spectroscopic evidence. Our aim is to obtain a crystalline sample that would permit us to determine its structure by X-ray diffraction analysis.

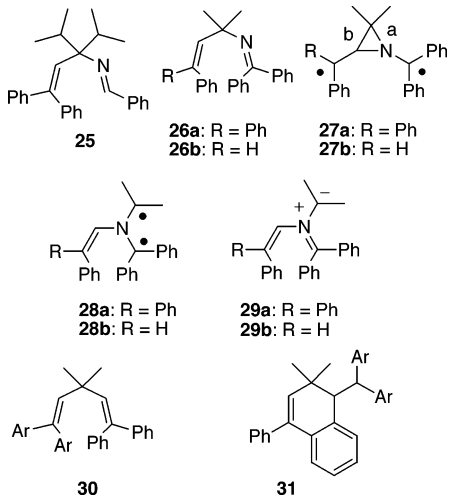
SCHEME 6



Compound **23b** was crystallized from hexane and its structure was determined by X-ray diffraction analysis.[19]

It is difficult to envisage how **23** are formed as primary products from photoreaction of azadienes **21**. An alternative possibility is that **23** is produced by secondary ring expansion reactions (e.g., vinylcyclopropane rearrangement)[20] of the initially formed cyclopropylimines **24**, the initial 2-ADPM rearrangement products, in the photolysis medium or upon chromatographic separation (Scheme 6).

Several features of the 2-ADPM rearrangement make it different from the DPM, ODPM, and 1-ADPM versions studied previously. This is clearly demonstrated by the results obtained in studies with the 2-azadiene **25**, bearing diisopropyl substitution at the central carbon, and the ketoimines **26a** and **26b**. Azadiene **25** was prepared by condensation of the corresponding amine with benzaldehyde while **26a** and **26b** were derived by using two-step sequences starting with the respective azadienes **9a** and **9b**. Triplet-sensitized irradiation of **25** and **26a**−**b**, followed by column chromatography on silica gel, gave the amines resulting from hydrolysis of the starting materials and a complex mixture of products, in which the cyclopropylimines or *N*-vinylaziridines were not present. The lack of 2-ADPM reactivity of **25** is surprising since previous studies on the DPM[21] and ODPM[22] rearrangement processes have shown that replacement of two methyl groups at the methane carbon by two isopropyl groups significantly increases the reaction efficiencies. However, the situation is opposite for the 2-ADPM process. Thus, while the dimethyl-substituted 2-azadienes **9a** and **9b** undergo the 2-ADPM rearrangement to afford the corresponding cyclopropylimines **11a** and **11b** (Scheme 3), the diisopropyl-substituted azadiene **25** does not react by this mode.



The lack of reactivity of ketoimines **26a**−**b** is also surprising, considering the fact that the aziridinyl dicarbinyl biradical intermediates **27** should either have comparable or greater stability than the corresponding intermediates derived from aldimines **9**. The absence of 2-ADPM products in the photoreaction of ketoimines **26** could be due to the presence of two phenyl rings at C-1 of the azadiene system that favor preferential ring opening of the aziridinyl intermediates **27** by breaking bond b to afford 1,3-biradicals **28**. Intersystem crossing in **28** would give azomethine ylide intermediates **29** that could decompose to a mixture of products, instead of undergoing cyclization to the corresponding vinylaziridines.

In summary, the results obtained from investigations of the triplet-sensitized photochemistry of a series of 2-aza-1,4-dienes have uncovered the first examples of 2-ADPM rearrangements yielding cyclopropylimines. In the case of azadiene **1**, *N*-vinylaziridine **3** was also obtained in the first example of a di-π-methane rearrangement that yields a heterocyclic product. Azadienes **21** afford spirodihydropyrrols **23** that probably result from a spontaneous vinylcyclopropane rearrangement of the initially formed cyclopropylimines **24**. The studies have demonstrated that features of the 2-ADPM rearrangement make it different from the other versions of the rearrangement previously described. Further studies are needed to understand the mechanistic aspects of the 2-ADPM rearrangement and the factors that control how substituents affect the nature of the reaction. Finally, although the isolated yields of products in these reactions are low, better estimates of the chemical efficiencies of these reactions are obtained when product yields are calculated based on converted starting materials (Table 1).

SET-Sensitized Irradiation of 2-Aza-1,4-dienes. To gain a more complete understanding of the photoreactivity of 2-aza-1,4-dienes, we have subjected substances in this family to 9,10-dicyanoanthracene (DCA) electron-

(19) X-ray data of **23b**: crystallized from hexane; $C_{25}H_{20}N_2$ (M_r = 348.43); monoclinic; space group *P*2(1)/*c*; a = 11.692(2) Å, b = 20.932(3) Å, c = 8.007(1) Å, β = 102.600(3)°; V = 1912.4(4) Å^3; Z = 4; dc = 1.210 mg·m^{-3}; μ = 0.071 mm^{-1}; F(000) = 736. A transparent crystal of 0.3 × 0.3 × 0.3 mm^3 was used; 9902 reflections were measured on a Bruker Smart CCD diffractometer, 3357 independent reflections [R(int)= 0.06]. The structure was solved by direct methods and Fourier synthesis. The refinement was done by full-matrix least-squares procedures on F^2 (SHELXTL version 5.1). The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions, R1 = 0.047 for 1429 observed reflections and *w*R2 = 0.134 (all data). Further crystallographic details for the structure reported in this paper may be obtained from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, U.K.; depository no. CCDC-198688.

(20) For reviews see: (a) Hudlicky, T.; Reed, J. W. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, UK, 1991; Vol. 5, pp 899−970. (b) Wong, H. N. C.; Hon, M.-Y.; Tse, C.-W.; Yip, Y.-C.; Tanko, J.; Hudlicky, T. *Chem. Rev.* **1989**, *89*, 165−198. (c) Goldschmidt, Z.; Crammer, B. *Chem. Soc. Rev.* **1988**, *17*, 229−267. (d) Hudlicky, T.; Kutchan, T. M.; Naqvi, S. M. *Org. React.* **1985**, *33*, 247−335.

(21) Zimmerman, H. E.; Schissel, D. N. *J. Org. Chem.* **1986**, *51*, 196−207.

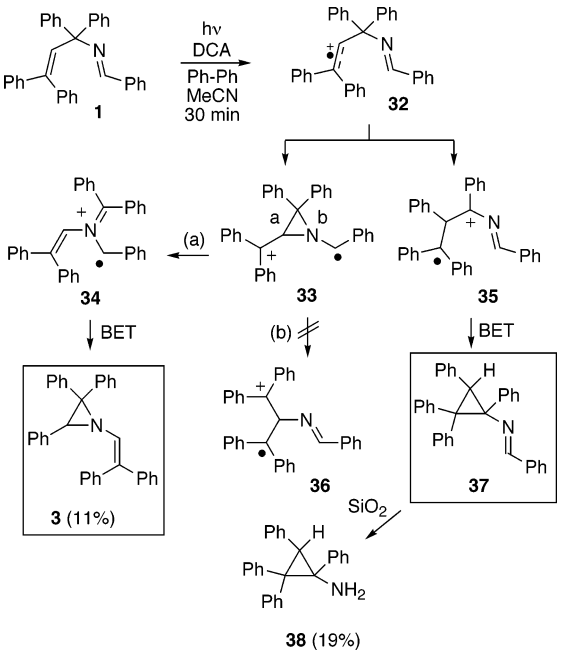
(22) Zimmerman, H. E.; Cassel, J. M. *J. Org. Chem.* **1989**, *54*, 3800−3816.

TABLE 1. Reaction Conditions and Yields of Products Based on Converted Starting Material (SM) in the Triplet- and DCA-Sensitized Irradiation of 2-Aza-1,4-dienes

compd	irra. time	sens.	2-ADPM cyclopropanes (yield, %)	2-ADPM aziridines (yield, %)	other products (yield, %)	converted SM (%)
1	25 min	triplet	**2** (61)[a]	**3** (16)		(18)[a]
9a	6 h	triplet	**11a** (26)			(19)[a]
9b	9.5 h	triplet	**11b** (18)			(22)[a]
17	3.5 h	triplet	**19**[a](41)			(29)[a]
21a	10 h	triplet			**23a** (18)	(34)[a]
21b	3 h	triplet			**23b** (39)	(41)[b]
1	30 min	DCA		**3** (19)	**37**[a] (32)	(59)[a]
9b	2 h	DCA		**39a** (11)		(44)[a]
21a	1 h	DCA		**41** (42)	**42** (28)	(57)[a]
25	15 min	DCA		**39b** (31)		(45)[a]
26a	10 min	DCA			**45a** (82)	(67)[b]
26b	40 min	DCA			**45b** (80)	(89)[a]
40	12 min	DCA		**39c** (40)		(33)[a]

[a] Isolated as the corresponding amine. [b] Isolated as a mixture of starting azadiene and the corresponding amine resulting from hydrolysis.

SCHEME 7



acceptor sensitized photoreactions. Previous studies by Zimmerman and Hoffacker[23] have shown that aryl-substituted 1,4-pentadienes **30** do not undergo DCA-sensitized DPM rearrangement reactions but, rather they are transformed to the corresponding dihydronaphthalenes **31** under these conditions.

Irradiation of azadiene (*E*)-**1** in acetonitrile for 30 min, using DCA as a sensitizer and biphenyl as a cosensitizer, followed by column chromatography on silica gel, yields propenylamine **4** (41%), vinylaziridine **3** (11%), and a new cyclopropylamine **38** (19%) resulting from the hydrolysis of imine **37** (Scheme 7). The identity of **38** was established by using spectroscopic methods.

The products generated in this photoreaction appear to arise by a pathway in which an initially formed olefin-localized cation−radical intermediate **32** bridges by C−N bond formation to give aziridinyl cation−radical **33**. Ring opening in **33**, by path a, generates **34**, which by back electron transfer and biradical cyclization yields **3**. The alternative ring opening of **33**, by path b, which would have produced the corresponding cyclopropylimine, does not occur, perhaps because the intermediate radical−cation **36** is less stable than **34**. A competitive route involving phenyl migration in **32** generates cation−radical **35**, the precursor of **37** (Scheme 7). The 1,2-phenyl shift in **32** is probably promoted by the greater degree of stabilization of the radical−cation intermediate **35**.

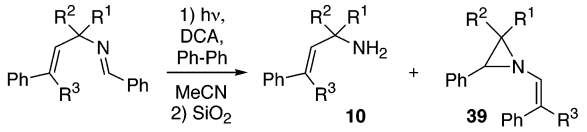
To our knowledge, these reactions represent the first examples of SET-promoted rearrangements in 1,4-unsaturated systems (a 2-ADPM reaction generating **3** and an aryl-di-π-methane rearrangement yielding **37**) that afford three-membered-ring products.[7−9] Of equal interest is the fact that the same vinylaziridine **3** is obtained in both the triplet- and SET-sensitized photoreactions of **1**. The formation of **37** in this reaction suggests that DPM rearrangements of other allylbenzene derivatives and 1,4-dienes could also occur via radical−cation intermediates.

This study was extended to azadienes **9a**, **9b**, **17**, and **25**. DCA-sensitized irradiation of azadiene (*E*)-**9a** under the conditions used for compound **1** for 15 min, followed by chromatography, gave amine **10a** (79%), resulting from hydrolysis of the starting material, and a complex mixture of products in which the corresponding vinylaziridine was not present (by ^{1}H NMR analysis). The use of longer irradiation times results in the complete consumption of the starting material. Irradiation of (1*E*,4*Z*)-**9b** for 2 h, following column chromatography on silica gel, affords *N*-vinylaziridine **39a** (5%), as a 2:1 mixture of *Z*:*E* isomers, and amine **10b** (56%), as a 7:3 mixture of *Z*:*E* diastereoisomers. Irradiation of (*E*)-**25** for 15 min under the above conditions yields the corresponding *N*-vinylaziridine **39b** (14%) and amine **10c** (55%) (Scheme 8). However, DCA-sensitized irradiation of (*E*)-**17** for 90 min gave, after column chromatography on silica gel, 1-methyl-1-naphthalen-2-yl-ethylamine (78%), resulting from aromatization of the dihydronaphthalene unit. This observation shows that oxidation of the dihydronaphthalene moiety takes preference over the 2-ADPM reaction.

The results summarized above demonstrate that the novel 2-ADPM rearrangement of 2-aza-1,4-dienes to form *N*-vinylaziridines, occurring via radical−cation interme-

(23) Zimmerman, H. E.; Hoffacker, K. D. *J. Org. Chem.* **1996**, *61*, 6526−6534.

SCHEME 8



9b: $R^1 = R^2$ = Me; R^3 = H
25: $R^1 = R^2$ = *i*-Pr; R^3 = Ph
40: R^1 = Me; $R^2 = R^3$ = Ph

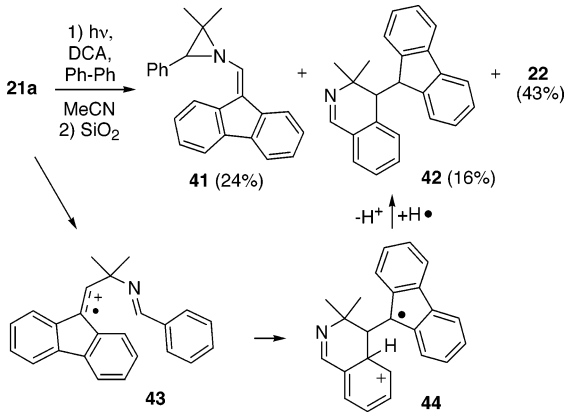
10b, **39a**: $R^1 = R^2$ = Me; R^3 = H
10c, **39b**: $R^1 = R^2$ = *i*-Pr; R^3 = Ph
10d, **39c**: R^1 = Me; $R^2 = R^3$ = Ph

diates, is not restricted to **1** but can be extended to azadienes **9b** and **25**. However, there are clear differences between the 2-ADPM rearrangement in the triplet excited state and the corresponding reaction via radical−cation intermediates. Probably the most significant of these is the regiochemistry. Thus, while the triplet reaction yields cyclopropylimines, SET-promoted rearrangement affords the corresponding *N*-vinylaziridines. Although the reasons for the triplet regioselectivity are still unclear, formation of the vinylaziridines can be easily explained based on the differences in stability between the two possible radical−cation intermediates resulting from ring opening of the intermediate aziridinyl radical−cation (Scheme 7). Another important difference has been observed in the reactions of **9a** and **25**. Thus, while **9a** undergoes triplet 2-ADPM rearrangement in low yield, the corresponding aziridine is not formed in its SET-sensitized reaction. On the other hand, azadiene **25** reacts to produce aziridine **39b** via radical−cation intermediates but does not rearrange under triplet-sensitization conditions. These results are difficult to interpret at this point, but they clearly show that the structural factors that control these two reactions are very different.

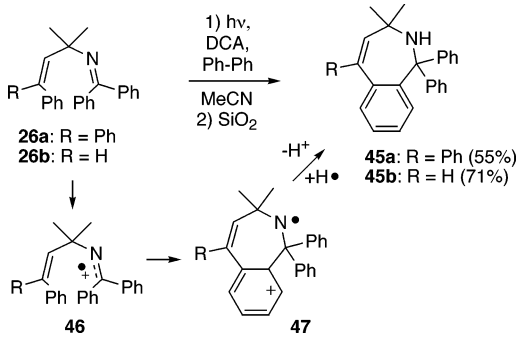
Attempts to uncover additional examples of the SET-promoted 2-ADPM rearrangement led to studies with azadienes **40**, **21a**, **21b**, **26a**, and **26b**. Compound **40** was obtained by condensation of amine **10d** with benzaldehyde by standard procedures. DCA-sensitized irradiation of (*E*)-**40** for 12 min, followed by column chromatography on silica gel, yields *N*-vinylaziridine **39c** (13%), propenylamine **10d** (67%), arising by hydrolysis of the starting material, and an unidentified[24] minor product (ca. 4%) that is isomeric with the starting material (Scheme 8).

Irradiation of (*E*)-**21a** for 1 h, under the above conditions, followed by column chromatography on silica gel, leads to *N*-vinylaziridine **41** (24%), amine **22** (43%), and a new compound (16%), identified as dihydroisoquinoline **42** (Scheme 9). The latter product is formed by electrophilic addition of the olefin-localized radical−cation **43** on the phenyl ring at C-1 yielding intermediate **44**, the precursor of **42** (Scheme 9). This cyclization process is similar to the one observed by Zimmerman and Hoffacker in their study of the DCA-sensitized irradiation of aryl-substituted 1,4-pentadienes **30**.[23] However, irradiation of (*E*)-**21b** for 35 min, under the same conditions used for **21a**, after column chromatography, affords amine **22**

SCHEME 9



SCHEME 10



(70%) and recovered starting material (*E*)-**21b** in 10% yield, along with a complex mixture of products in which the corresponding *N*-vinylaziridine and the dihydroisoquinoline are not present. Although not completely understood, the lack of 2-ADPM reactivity of **21b** could be due to the fact that the *p*-cyano substituent reduces the nucleophilicity of the imine moiety. As a result, an initially formed cation−radical related to **43** (Scheme 9) would not be able to participate in C−N or C−C bonding by nucleophilic addition of either the nitrogen or aryl centers.

Finally, irradiation of compounds **26a** and **26b** under the SET-sensitized conditions for short time periods affords the respective amines **10a** and **10b** and the corresponding dihydrobenzoazepines **45a** and **45b**, respectively, in good isolated yields (Scheme 10). The fact that the corresponding *N*-vinylaziridines are not generated in these processes shows that diphenyl substitution at C-1 in ketoimines **26** allows an alternative dihydrobenzoazepine forming cyclization to occur in preference to 2-ADPM rearrangement.

The formation of **45** is consistent with a mechanism involving the generation of an imine-localized radical−cation **46** that reacts to yield **47**, the precursor of **45**, by electrophilic attack on the phenyl ring at C-5 (Scheme 10). The high product yields obtained in the DCA-sensitized irradiation of **26** suggest that this process might be applicable to the synthesis of dihydrobenzoazepines from β,γ-unsaturated ketoimines.

The yields of vinylaziridine photoproducts obtained in the SET-sensitized irradiation of 2-azadienes are usually low. Attempts to increase the yield of products by prolonged irradiation resulted in destruction of the

(24) This minor photoproduct proved to be isomeric with the starting material. However, at this point it is not possible to establish its structure based on spectroscopic evidence. Our aim is to obtain a crystalline sample that would permit us to determine its structure by X-ray diffraction analysis. The triplet-sensitized photoreactivity of **40** was also explored. ^{1}H NMR analysis of the photomixture indicates the presence of two cyclopropane derivatives. However, all the attempts to isolate them resulted in decomposition of the photoproducts. No *N*-vinylaziridine was detected in this instance.

starting materials and photoproducts. However, a better estimation of the chemical efficiency of these reactions is obtained when the yield of products is calculated based on converted starting material (Table 1). Attempts have been made to increase them by using longer irradiation times but without success.

The results obtained from studies of the SET-sensitized irradiation of azadienes **21a** and **26** demonstrate that in addition to the 2-ADPM rearrangement to *N*-vinylaziridines, alternative cyclization paths are open to the radical−cation intermediates, yielding dihydroisoquinolines and dihydrobenzoazepines, respectively. Further studies are needed to determine if it is possible to control the outcome of the photoreactions by modifying the substituents present on the 2-azadiene's skeleton. Something worth noting in regard to the formation of compounds **42** and **45** is that, while dihydroisoquinoline **42** results from a radical−cation centered in the alkene unit, compounds **45** are formed from radical−cations centered in the imine moiety. This is somewhat surprising and demonstrates that two different radical−cation intermediates can be generated from the alkene and imine functional groups, which have different ionization potentials. A similar situation has been observed in our studies of the SET-sensitized photochemistry of 1-aza-1,4-dienes.[7c]

Conclusions

In summary, the results outlined above clearly demonstrate that 2-aza-1,4-dienes undergo novel photochemical reactions. Our studies of the triplet-sensitized photoreactions of these compounds have led us to uncover the first examples of 2-ADPM rearrangements that yield cyclopropylimines. In the case of azadiene **1**, the reaction also affords *N*-vinylaziridine **3**, representing the first example of a di-π-methane rearrangement that yields a three-membered heterocyclic photoproduct. However, azadienes containing a substitution pattern that has been demonstrated to promote efficient DPM, ODPM, and 1-ADPM reactions do not undergo the 2-ADPM rearrangement. This result shows that the structural factors that control the former reactions do not govern the latter process. A possible reason for this difference might reside in the unique involvement of azomethine ylides in the 2-ADPM rearrangement.

A more significant conclusion of this study is that 2-ADPM rearrangements can also take place under SET-sensitized irradiation conditions to generate *N*-vinylaziridines regioselectively. In the case of azadiene **1**, cyclopropylimine **37**, resulting from an aryl-di-π-methane reaction via a radical−cation intermediate, is observed. An alternative cyclization mode has been detected with azadiene **21a** yielding the corresponding dihydroisoquinoline **42**. Ketoimines **26** do not undergo the 2-ADPM rearrangement. Rather, these substances react to produce the corresponding dihydrobenzoazepines **45** in good yield. It is our belief that the results coming from these studies have led to new views of an old but still important photochemical rearrangement process. Further work is in progress to determine the scope, synthetic applications, and mechanistic aspects of these reactions.

Experimental Section

Azadienes **1**,[9] **9b**,[9] and **21a**[9] were synthesized by the methods previously described.

General Procedure for the Synthesis of Azadienes 9a, 17, 21b, 25, and 40. These azadienes were synthesized from the corresponding β,γ-unsaturated esters by a procedure consisting of hydrolysis, transformation into the acid chloride, Curtius reaction, and condensation of the corresponding amines with benzaldehyde or *p*-cyanobenzaldehyde, according to the following general procedures. When describing the experimental procedure below for individual products, a further reference to the general procedure is not always given.

Hydrolysis of β,γ-unsaturated esters: A solution of KOH and the ester in dry EtOH was refluxed for different times (for specific cases, see below). The ester/KOH ratio was 1:3 for all experiments. The solvent was evaporated to dryness, and the residue was dissolved in water. The aq solution was extracted with Et_2O to remove unreacted starting material and the aq layer was acidified with a 20% aq HCl solution and extracted with Et_2O. The organic phases were dried ($MgSO_4$), filtered, and evaporated to dryness. The β,γ-unsaturated acids were purified by flash chromatography on silica gel, using hexane/Et_2O (7:3) as eluent.

Transformation of β,γ-unsaturated acids into the acid chlorides: The corresponding β,γ-unsaturated acid and $SOCl_2$ were heated at reflux for different times (for specific cases, see below). The acid/$SOCl_2$ ratio was 1:1.5 for all experiments. The residual $SOCl_2$ was removed under reduced pressure yielding the corresponding acid chloride, which was used without further purification.

Curtius reaction: A solution of the corresponding acid chloride in CH_2Cl_2 containing tetrabutylammonium bromide was cooled in an ice bath. Sodium azide dissolved in water was added and the reaction mixture was stirred vigorously at 0 °C for 2 h. The acid chloride/sodium azide ratio was 1:1.2 for all experiments. The organic layer was separated, washed with H_2O, dried ($MgSO_4$), filtered, and evaporated to dryness. A solution of acylazide in toluene under argon was refluxed for different times (for specific cases, see below). The solvent was evaporated to dryness yielding the corresponding isocyanate, which was used without further purification. A solution of 8 M HCl and the isocyanate was refluxed for different times (for specific cases, see below). The mixture was extracted with Et_2O and the aq layer was neutralized with a 10% aq NaOH solution and extracted with Et_2O. The organics layers were separated, washed with H_2O, dried ($MgSO_4$), filtered, and evaporated to dryness. The amine was purified by distillation.

Condensation of amines with benzaldehyde or *p*-cyanobenzaldehyde: A solution of the corresponding amine and aldehyde in anhyd Et_2O was refluxed for different times (for specific cases, see below). The amine/aldehyde ratio was 1:1 for all experiments. The solvent was evaporated and the imine was purified by recrystallization or by distillation.

3,3-Dimethyl-1,5,5-triphenyl-2-aza-1,4-pentadiene (9a). Compound **9a** was synthesized from methyl 2,2-dimethyl-4,4-diphenyl-3-butenoate. This ester was converted into the corresponding acid chloride by the method previously described.[7c] 2,2-Dimethyl-4,4-diphenyl-3-butenoyl chloride (4.81 g, 17 mmol), tetrabutylammonium bromide (0.02 g, 0.05 mmol) in CH_2Cl_2 (100 mL), and sodium azide (1.34 g, 20.6 mmol) in water (19 mL) yielded **2,2-dimethyl-4,4-diphenyl-3-butenoylazide** (4.9 g) as a yellow oil; IR (neat) ν 2135, 1714 cm^{-1}.

2,2-Dimethyl-4,4-diphenyl-3-butenoylazide (4.9 g, 17 mmol) in toluene (30 mL) was refluxed for 4 h yielding **1,1-dimethyl-3,3-diphenyl-2-propenyl isocyanate** (4.9 g) as a yellow oil; IR (neat) ν 2260 cm^{-1}.

1,1-Dimethyl-3,3-diphenyl-2-propenyl isocyanate (4.9 g, 17 mmol) and 8 M HCl (60 mL) were refluxed for 4 h yielding **1,1-dimethyl-3,3-diphenyl-2-propenylamine** (**10a**) (2.77 g, 69%) as an oil: bp 110 °C (0.2 mbar); ^{1}H NMR (300 MHz) δ 7.40−7.18 (m, 10H), 6.24 (s, 1H), 2.44 (br s, 2H), 1.23 (s, 6H); ^{13}C NMR (63 MHz) δ 143.5−127.0, 51.8, 32.6; IR (neat) ν 3440

cm^{-1}; MS *m/e* (%) 237 (M$^+$, 6), 222 (100), 205 (15), 178 (8), 165 (8), 77 (11), 58 (32).

Compound **10a** (1.13 g, 4.8 mmol) and benzaldehyde (0.5 g, 4.8 mmol) in anhyd Et_2O (35 mL) were refluxed for 10 h yielding **(*E*)-3,3-dimethyl-1,5,5-triphenyl-2-aza-1,4-pentadiene** (**9a**) (1.24 g, 80%) as a white solid: mp 78−79 °C (hexane); ^{1}H NMR (300 MHz) δ 8.21 (s, 1H), 7.62−7.13 (m, 15H), 6.26 (s, 1H), 1.31 (s, 6H); ^{13}C NMR (63 MHz) δ 156.9, 143.7−126.9, 62.0, 30.0; IR (neat) ν 1635 cm^{-1}; UV (CH_2Cl_2) λ_{max} 247 (ϵ 25 185); MS *m/e* (%) 325 (M$^+$, 9), 310 (7), 269 (100), 221 (41), 191 (44), 143 (56), 91 (70), 77 (30), 51 (24). Anal. Calcd for $C_{24}H_{23}N$: C, 88.57; H, 7.13; N, 4.31. Found: C, 88.82; H, 7.23; N, 4.14.

3-(3,4-Dihydro-2-naphthalenyl)-3-methyl-1-phenyl-2-aza-1-butene (17). Compound **17** was synthesized from ethyl 2-(3,4-dihydro-2-naphthalenyl)-2-methylpropanoate.[25] This ester was converted into the corresponding acid chloride by the method previously described.[17] 2-(3,4-Dihydro-2-naphthalenyl)-2-methylpropanoyl chloride (2.1 g, 8.9 mmol), tetrabutylammonium bromide (9 mg, 0.03 mmol) in CH_2Cl_2 (30 mL), and sodium azide (0.7 g, 10.8 mmol) in water (6 mL) yielded **2-(3,4-dihydro-2-naphthalenyl)-2-methylpropanoylazide** (2.12 g) as a yellow oil; IR (neat) ν 2133, 1709 cm^{-1}.

2-(3,4-Dihydro-2-naphthalenyl)-2-methylpropanoylazide (2.12 g, 8.8 mmol) in toluene (15 mL) was refluxed for 4 h yielding **2-(3,4-dihydro-2-naphthalenyl)-2-methylethyl isocyanate** (1.87 g) as a yellow oil; IR (neat) ν 2257 cm^{-1}.

2-(3,4-Dihydro-2-naphthalenyl)-2-methylethyl isocyanate (1.87 g, 8.8 mmol) and 8 M HCl (30 mL) were refluxed for 1.5 h yielding **1-(3,4-dihydro-2-naphthalenyl)-1-methylethylamine** (**18**) (1.28 g, 78%) as an oil; ^{1}H NMR (300 MHz) δ 7.25−7.03 (m, 4H), 6.45 (s, 1H), 2.79 (t, J = 8.0 Hz, 2H), 2.33 (t, J = 8.0 Hz, 2H), 1.54 (br s, 2H), 1.31 (s, 6H); ^{13}C NMR (75 MHz) δ 149.3−119.0, 53.0, 29.5, 28.7; IR (neat) ν 3360, 3290 cm^{-1}.

Compound **18** (0.3 g, 1.6 mmol) and benzaldehyde (0.17 g, 1.6 mmol) in anhyd Et_2O (25 mL) were refluxed for 9 h yielding **(*E*)-3-(3,4-dihydro-2-naphthalenyl)-3-methyl-1-phenyl-2-aza-1-butene** (**17**) (0.39 g, 89%) as an oil: bp 175 °C (0.4 mbar); ^{1}H NMR (300 MHz) δ 8.33 (s, 1H), 7.78−7.75 (m, 2H), 7.42−7.40 (m, 3H), 7.20−7.08 (m, 4H), 6.52 (s, 1H), 2.77 (t, J = 8.0 Hz, 2H), 2.26 (t, J = 8.0 Hz, 2H), 1.50 (s, 6H); ^{13}C NMR (75 MHz) δ 158.1, 146.2−122.5, 63.8, 28.4, 27.3, 24.2; IR (neat) ν 1640 cm^{-1}; UV (CH_2Cl_2) λ_{max} 247 (ϵ 20 886); MS *m/e* (%) 275 (M$^+$, 15), 260 (48), 219 (12), 171 (100), 155 (47), 141 (25), 129 (50), 115 (28), 106 (60), 91 (31), 77 (14).

1-(4-Cyanophenyl)-4-(fluoren-9-yliden)-3,3-dimethyl-2-aza-1-butene (21b). 2-(Fluoren-9-yliden)-1,1-dimethylethylamine[9] (**22**) (0.33 g, 1.4 mmol) and *p*-cyanobenzaldehyde (0.18 g, 1.4 mmol) in anhyd Et_2O (25 mL) were refluxed for 7 h yielding **(*E*)-1-(4-cyanophenyl)-4-(fluoren-9-yliden)-3,3-dimethyl-2-aza-1-butene** (**21b**) (0.29 g, 59%) as a white solid: mp 134.5−135.5 °C (hexane); ^{1}H NMR (300 MHz) δ 8.38 (s, 1H), 7.86−7.61 (m, 8H), 7.35−7.11 (m, 4H), 6.95 (s, 1H), 1.75 (s, 6H); ^{13}C NMR (75 MHz) δ 157.8, 141.7−113.7, 61.8, 30.9; IR (KBr) ν 2240, 1640 cm^{-1}; UV (CH_2Cl_2) λ_{max} 258 (ϵ 64 963); MS *m/e* (%) 348 (M$^+$, 28), 292 (100), 219 (27), 165 (16), 129 (4), 115 (8). Anal. Calcd for $C_{25}H_{20}N_2$: C, 86.17; H, 5.79; N, 8.04. Found: C, 86.10; H, 5.73; N, 7.86.

3,3-Diisopropyl-1,5,5-triphenyl-2-aza-1,4-pentadiene (25). Compound **25** was synthesized from methyl 2,2-diisopropyl-4,4-diphenyl-3-butenoate, obtained by the method previously described for the corresponding ethyl ester.[22] Methyl 2,2-diisopropyl-4,4-diphenyl-3-butenoate (1 g, 3 mmol) and 1 M *t*-BuOK in anhyd DMSO (45 mL) were heated for 30 min at 100 °C yielding **2,2-diisopropyl-4,4-diphenyl-3-butenoic acid** (0.72 g, 75%) as a white solid: mp 143−143.5 °C (hexane); ^{1}H NMR (200 MHz) δ 7.34−7.16 (m, 10H), 6.15 (s, 1H), 2.21 (sept, J = 6.8 Hz, 2H), 0.97 (d, J = 6.8 Hz, 6H), 0.92 (d, J = 6.8 Hz, 6H); ^{13}C NMR (50 MHz) δ 180.7, 145.4−126.8, 60.4, 31.0, 19.4, 18.7; IR (KBr) ν 3058, 1687 cm^{-1}; MS *m/e* (%) 322 (M$^+$, 4), 279 (100), 251 (23), 233 (88), 219 (28), 191 (35), 178 (10), 165 (10), 91 (24). Anal. Calcd for $C_{22}H_{26}O_2$: C, 81.99; H, 8.07. Found: C, 82.19; H, 8.33.

2,2-Diisopropyl-4,4-diphenyl-3-butenoic acid (0.88 g, 2.7 mmol) and $SOCl_2$ (0.49 g, 4.1 mmol) were refluxed for 1 h yielding 0.93 g of a 1:1 mixture of **2,2-diisopropyl-4,4-diphenyl-3-butenoyl chloride** and 2,2-diisopropyl-4-phenyl-2*H*-naphthalen-1-one, as a yellow oil; ^{1}H NMR (300 MHz) δ 8.12−7.13 (m, 10H), 6.23 (s, 0.5H), 6.00 (s, 0.5H), 2.40−2.15 (m, 2H), 0.96−0.87 (m, 12H).

The mixture of 2,2-diisopropyl-4,4-diphenyl-3-butenoyl chloride and 2,2-diisopropyl-4-phenyl-2*H*-naphthalen-1-one (0.93 g), tetrabutylammonium bromide (3 mg, 0.01 mmol) in CH_2Cl_2 (13 mL), and sodium azide (0.22 g, 3.3 mmol) in water (2 mL) yielded 0.93 g of a 1:1 mixture of **2,2-diisopropyl-4,4-diphenyl-3-butenoylazide** and 2,2-diisopropyl-4-phenyl-2*H*-naphthalen-1-one, as a yellow oil; IR (neat) ν 2131, 1695, 1662 cm^{-1}.

2,2-Diisopropyl-4,4-diphenyl-3-butenoylazide and 2,2-diisopropyl-4-phenyl-2*H*-naphthalen-1-one (0.93 g) in toluene (20 mL) were refluxed for 4 h yielding 0.85 g of a 1:1 mixture of **1,1-diisopropyl-3,3-diphenyl-2-propenyl isocyanate** and 2,2-diisopropyl-4-phenyl-2*H*-naphthalen-1-one, as a yellow oil; IR (neat) ν 2275, 1662 cm^{-1}.

1,1-Diisopropyl-3,3-diphenyl-2-propenyl isocyanate and 2,2-diisopropyl-4-phenyl-2*H*-naphthalen-1-one (0.85 g) in 8 M HCl (25 mL) were refluxed for 30 min. The mixture was extracted with Et_2O and the organic layer was washed with H_2O, dried ($MgSO_4$), filtered, and evaporated to dryness yielding 2,2-diisopropyl-4-phenyl-2*H*-naphthalen-1-one (0.4 g, 49%) as an oil. The aq layer was neutralized with a 10% aq NaOH solution and extracted with Et_2O. The organics layers were separated, washed with H_2O, dried ($MgSO_4$), filtered, and evaporated to dryness yielding **1,1-diisopropyl-3,3-diphenyl-2-propenylamine** (**10c**) (0.35 g, 44%) as an oil. **2,2-Diisopropyl-4-phenyl-2*H*-naphthalen-1-one**: ^{1}H NMR (200 MHz) δ 8.12−7.90 (m, 1H), 7.52−7.13 (m, 8H), 6.00 (s, 1H), 2.34 (sept, J = 7.0 Hz, 2H), 0.94 (d, J = 7.0 Hz, 6H), 0.89 (d, J = 7.0 Hz, 6H); ^{13}C NMR (50 MHz) δ 203.3, 140.0−126.4, 58.5, 34.1, 17.3, 17.2; IR (neat) ν 1662 cm^{-1}; MS *m/e* (%) 304 (M$^+$, 3), 276 (3), 262 (100), 247 (61), 215 (13), 202 (23), 178 (6), 165 (7), 91 (7). **10c**: ^{1}H NMR (200 MHz) δ 7.40−7.15 (m, 10H), 5.95 (s, 1H), 1.87 (sept, J = 6.8 Hz, 2H), 0.99 (d, J = 6.9 Hz, 6H), 0.91 (d, J = 6.7 Hz, 6H); ^{13}C NMR (50 MHz) δ 144.1−126.7, 63.1, 34.8, 18.0, 16.8; IR (neat) ν 3400, 3350 cm^{-1}; MS *m/e* (ESI) 294 (M + 1), 207, 178, 129.

Compound **10c** (0.35 g, 1.2 mmol) and benzaldehyde (0.13 g, 1.19 mmol) in anhyd Et_2O (25 mL) were refluxed for 10 h yielding **(*E*)-3,3-diisopropyl-1,5,5-triphenyl-2-aza-1,4-pentadiene** (**25**) (0.41 g, 90%) as an oil: bp 163 °C (0.05 mbar); ^{1}H NMR (200 MHz) δ 8.01 (s, 1H), 7.27−7.11 (m, 15H), 6.10 (s, 1H), 2.32 (sept, J = 6.7 Hz, 2H), 1.03 (d, J = 6.6 Hz, 6H), 0.81 (d, J = 6.6 Hz, 6H); ^{13}C NMR (50 MHz) δ 154.7, 145.5−125.5, 72.5, 31.9, 18.7, 17.1; IR (neat) ν 1645 cm^{-1}; UV (CH_2Cl_2) λ_{max} 248 (ϵ 23 938); MS *m/e* (%) 381 (M$^+$, <1), 338 (100), 294 (5), 233 (7), 218 (9), 203 (5), 191 (10), 165 (6), 115 (5), 91 (19).

3-Methyl-1,3,5,5-tetraphenyl-2-aza-1,4-pentadiene (40). Compound **40** was synthesized from ethyl 2-methyl-2,4,4-triphenyl-3-butenoate. This ester was obtained in three steps from diethyl phenylmalonate according to the following procedure: to a solution of sodium ethoxide (3.6 g, 52.9 mmol) in dry EtOH (30 mL) under argon was added diethyl phenylmalonate (6 g, 25.4 mmol) and MeI (4.33 g, 30.5 mmol). After refluxing for 3 h, the solvent was evaporated to dryness and the mixture was extracted with Et_2O. The organic layer was washed with H_2O, dried ($MgSO_4$), filtered, and evaporated to dryness. The crude product was distilled under reduced pressure yielding **diethyl 2-methyl-2-phenylmalonate** (5.14 g, 81%) as a yellow oil: bp 76 °C (0.05 mbar); ^{1}H NMR (200 MHz) δ 7.41−7.23 (m, 5H), 4.22 (q, J = 7.1 Hz, 4H), 1.86 (s,

(25) Armesto, D.; Ramos, A. *Tetrahedron* **1993**, *49*, 7159−7168.

3H), 1.24 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (50 MHz) δ 171.5, 138.4, 128.1−127.4, 61.6, 58.8, 22.3, 13.9; IR (neat) ν 1732 cm^{-1}; MS *m/e* (%) 250 (M$^+$, 29), 235 (3), 206 (4), 177 (100), 160 (8), 149 (43), 131 (45), 105 (25), 103 (39), 91 (24), 77 (23).

To a solution of diethyl 2-methyl-2-phenylmalonate (12.11 g, 48.4 mmol) in anhyd CH_2Cl_2 (100 mL) under argon and at −78 °C was added DIBALH (97 mL, 1 M in toluene). The mixture was stirred for 3 h at −78 °C before quenching with a saturated aq NH_4Cl solution (16.7 mL) and 4% aq HCl (16.7 mL). The white solid obtained was filtered and the organic layer was washed with H_2O, dried ($MgSO_4$), filtered, and evaporated to dryness. Chromatography with hexane/Et_2O (95:5) yielded **ethyl 2-formyl-2-phenylpropionate** (5.09 g, 51%) as an oil; ^{1}H NMR (300 MHz) δ 9.88 (s, 1H), 7.43−7.21 (m, 5H), 4.28 (q, $J = 7.1$ Hz, 2H), 1.69 (s, 3H), 1.28 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (75 MHz) δ 196.9, 171.6, 136,6−126.9, 62.0, 61.8, 17.8, 14.0; IR (neat) ν 2845, 2725, 1750, 1720 cm^{-1}; MS *m/e* (%) 207 (M + 1, 1), 178 (100), 149 (33), 132 (91), 105 (80), 77 (44).

To a solution of diethyl benzhydrylphosphonate[26] (3.65 g, 12 mmol) in anhyd DME (20 mL) under argon and at 0 °C was added dropwise BuLi (7.5 mL, 1.6 M in hexane). After the mixture was stirred for 1 h at 0 °C, a solution of ethyl 2-formyl-2-phenylpropionate (2.05 g, 10 mmol) in anhyd DME (20 mL) was added dropwise. The resulting solution was stirred for 2.5 h at 0 °C before quenching with H_2O and extracted with Et_2O. The organic layer was washed with H_2O and saturated aq NaCl, dried ($MgSO_4$), filtered, and evaporated to dryness. Chromatography with hexane/Et_2O (98:2) yielded **ethyl 2-methyl-2,4,4-triphenyl-3-butenoate** (2.61 g, 74%) as a yellow oil; ^{1}H NMR (300 MHz) δ 7.36−7.20 (m, 13H), 7.00−6.97 (m, 2H), 6.73 (s, 1H), 3.85 (q, $J = 7.1$ Hz, 1H), 3.76 (q, $J = 7.1$ Hz, 1H), 1.56 (s, 3H), 1.07 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (75 MHz) δ 174.8, 144.9−126.6, 61.0, 52.5, 25.1, 13.8; IR (neat) ν 1728 cm^{-1}; MS *m/e* (%) 356 (M$^+$, 6), 341 (1), 310 (2), 283 (100), 268 (12), 205 (96), 191 (15), 178 (9), 165 (15), 105 (25), 91 (27), 77 (10).

Ethyl 2-methyl-2,4,4-triphenyl-3-butenoate (3.41 g, 9.6 mmol) and KOH (1.60 g, 28.6 mmol) in dry EtOH (30 mL) were refluxed for 20 h yielding **2-methyl-2,4,4-triphenyl-3-butenoic acid** (2.9 g, 92%) as a white solid: mp 155−156 °C (hexane); ^{1}H NMR (200 MHz) δ 7.40−7.18 (m, 10H), 7.13−7.03 (m, 3H), 7.00−6.87 (m, 2H), 6.76 (s, 1H), 1.58 (s, 3H); ^{13}C NMR (50 MHz) δ 181.0, 143.9−127.0, 52.2, 24.5; IR (KBr) ν 3500, 1697 cm^{-1}; MS *m/e* (%) 328 (M$^+$, 4), 312 (6), 283 (71), 205 (100), 191 (80), 178 (18), 167 (27), 105 (23), 91 (44), 77 (15); Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.15; H, 6.10. Found: C, 83.87; H, 6.18.

2-Methyl-2,4,4-triphenyl-3-butenoic acid (1.40 g, 4.3 mmol) and $SOCl_2$ (0.5 mL, 6.9 mmol) were refluxed for 1 h yielding **2-methyl-2,4,4-triphenyl-3-butenoyl chloride** (1.49 g) as a yellow oil; ^{1}H NMR (200 MHz) δ 7.49−7.12 (m, 13H), 6.97−6.92 (m, 2H), 6.82 (s, 1H), 1.57 (s, 3H).

2-Methyl-2,4,4-triphenyl-3-butenoyl chloride (1.49 g, 4.3 mmol), tetrabutylammonium bromide (4 mg, 0.013 mmol) in CH_2Cl_2 (20 mL), and sodium azide (0.34 g, 5.2 mmol) in water (3 mL) yielded **2-methyl-2,4,4-triphenyl-3-butenoylazide** (1.51 g) as a yellow oil; IR (neat) ν 2135, 1711 cm^{-1}.

2-Methyl-2,4,4-triphenyl-3-butenoylazide (1.51 g, 4.3 mmol) in toluene (30 mL) was refluxed for 2 h yielding **1-methyl-1,3,3-triphenyl-2-propenyl isocyanate** (1.39 g) as a yellow oil; IR (neat) ν 2257 cm^{-1}.

1-Methyl-1,3,3-triphenyl-2-propenyl isocyanate (1.39 g, 4.3 mmol) and 8 M HCl (40 mL) were refluxed for 3 h yielding **1-methyl-1,3,3-triphenyl-2-propenylamine** (**10d**) (0.46 g, 36%) as an oil: bp 140 °C (0.05 mbar); ^{1}H NMR (200 MHz) δ 7.42−7.36 (m, 2H), 7.31−7.14 (m, 11H), 6.96−6.90 (m, 2H), 6.60 (s, 1H), 1.53 (s, 2H), 1.52 (s, 3H); ^{13}C NMR (50 MHz) δ 150.2−125.4, 56.7, 33.6; IR (neat) ν 3383, 3306 cm^{-1}; MS *m/e* (%) 300 (M + 1, 17), 299 (M$^+$, 67), 284 (100), 267 (19), 256 (22), 222 (74), 205 (14), 165 (16), 120 (40), 77 (18).

Compound **10d** (0.12 g, 0.4 mmol) and benzaldehyde (0.04 g, 0.4 mmol) in anhyd Et_2O (25 mL) were refluxed for 20 h yielding ***(E)*-3-methyl-1,3,5,5-tetraphenyl-2-aza-1,4-pentadiene** (**40**) (0.14 g, 90%) as an oil; ^{1}H NMR (300 MHz) δ 8.29 (s, 1H), 7.70−7.68 (m, 2H), 7.45−7.09 (m, 16H), 6.95−6.92 (m, 2H), 6.56 (s, 1H), 1.51 (s, 3H); ^{13}C NMR (75 MHz) δ 158.4, 148.1−126.3, 67.7, 30.3; IR (neat) ν 1643 cm^{-1}; UV (CH_2Cl_2) λ_{max} 248 (ϵ 28 639); MS *m/e* (%) 387 (M$^+$, 15), 372 (3), 310 (5), 299 (3), 283 (19), 269 (100), 205 (57), 191 (49), 178 (11), 165 (20), 152 (9), 131 (64), 105 (18), 91 (30), 77 (17).

General Procedure for the Synthesis of Azadienes 26a and 26b. Azadienes **26a** and **26b** were synthesized in two steps from azadienes **9a** and **9b**, respectively, by a procedure consisting of reaction of these imines with PhLi[27] and oxidation with the radical di-*tert*-butyliminoxyl,[28] according to the following general procedures.

To a solution of 2-aza-1,4-diene in anhyd Et_2O under argon was added dropwise PhLi. The 2-aza-1,4-diene/PhLi ratio was 1:1.1 for all experiments. The resulting mixture was refluxed for 6 h before quenching with H_2O. The organic layer was separated, washed with H_2O, dried ($MgSO_4$), filtered, and evaporated under reduced pressure to give, after purification by flash chromatography on silica gel with hexane/Et_2O (99:1), the corresponding amines.

To a solution of radical di-*tert*-butyliminoxyl in pentane under argon was added the corresponding amine. The radical di-*tert*-butyliminoxyl/amine ratio was 3:1 for all experiments. The solution was stirred for 4 days at room temperature. The solvent was evaporated to dryness and the crude product was purified by recrystallization or by distillation.

3,3-Dimethyl-1,1,5,5-tetraphenyl-2-aza-1,4-pentadiene (26a). (*E*)-3,3-Dimethyl-1,5,5-triphenyl-2-aza-1,4-pentadiene (**9a**) (0.92 g, 2.8 mmol) in anhyd Et_2O (40 mL) and PhLi (1.73 mL, 1.8 M in hexane) yielded ***N*-benzhydryl-1,1-dimethyl-3,3-diphenyl-2-propenylamine** (0.58 g, 51%) as an oil; ^{1}H NMR (200 MHz) δ 7.41−6.93 (m, 20H), 6.10 (s, 1H), 5.04 (s, 1H), 1.58 (s, 1H), 1.00 (s, 6H); ^{13}C NMR (50 MHz) δ 146.6−126.5, 62.5, 56.7, 30.0; IR (neat) ν 3350, 1596 cm^{-1}; MS *m/e* (%) 403 (M$^+$, 1), 388 (42), 236 (30), 220 (55), 205 (100), 183 (21), 167 (70), 106 (87), 77 (28).

N-Benzhydryl-1,1-dimethyl-3,3-diphenyl-2-propenylamine (0.55 g, 1.4 mmol) and radical di-*tert*-butyliminoxyl in pentane (18 mL, 0.18 M) yielded **3,3-dimethyl-1,1,5,5-tetraphenyl-2-aza-1,4-pentadiene** (**26a**) (0.4 g, 73%) as a white solid: mp 146−147 °C (Et_2O); ^{1}H NMR (200 MHz) δ 7.52−6.93 (m, 20H), 5.97 (s, 1H), 1.19 (s, 6H); ^{13}C NMR (50 MHz) δ 165.0, 143.4−126.5, 60.5, 31.5; IR (KBr) ν 1710 cm^{-1}; UV (CH_2Cl_2) λ_{max} 250 (ϵ 32 232); MS *m/e* (%) 401 (M$^+$, 6), 386 (2), 220 (49), 205 (97), 180 (100), 104 (37), 77 (39). Anal. Calcd for $C_{30}H_{27}N$: C, 89.73; H, 6.78; N, 3.49. Found: C, 89.91; H, 6.99; N, 3.61.

3,3-Dimethyl-1,1,5-triphenyl-2-aza-1,4-pentadiene (26b). (*1E*,4*Z*)-3,3-dimethyl-1,5-diphenyl-2-aza-1,4-pentadiene (**9b**) (0.65 g, 2.61 mmol) in anhyd Et_2O (30 mL) and PhLi (1.6 mL, 1.8 M in hexane) yielded ***(E)*-*N*-benzhydryl-1,1-dimethyl-3-phenyl-2-propenylamine** (0.48 g, 56%) as an oil; ^{1}H NMR (200 MHz) δ 7.40−7.12 (m, 15H), 6.38 (d, $J = 16.0$ Hz, 1H), 6.11 (d, $J = 16.0$ Hz, 1H), 4.92 (s, 1H), 1.58 (s, 1H), 1.21 (s, 6H); ^{13}C NMR (50 MHz) δ 146.4−126.2, 61.9, 55.7, 28.2; IR (neat) ν 3336, 1660 cm^{-1}; MS *m/e* (%) 327 (M$^+$, 1), 321 (60), 167 (100), 145 (26), 91 (13), 77 (8).

(*E*)-*N*-Benzhydryl-1,1-dimethyl-3-phenyl-2-propenylamine (0.66 g, 2 mmol) and radical di-*tert*-butyliminoxyl in pentane (35 mL, 0.17 M) yielded **3,3-dimethyl-1,5,5-triphenyl-2-aza-1,4-pentadiene** (**26b**) (0.6 g, 92%) as an oil and as a 1:4 mixture of *Z*:*E* isomers: bp 150 °C (0.1 mbar); ^{1}H NMR (300 MHz) δ 7.59−7.10 (m, 15H), 6.09 (s, 1.6H, *E*-isomer), 6.08 (d,

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J = 12.0 Hz, 0.2H, *Z*-isomer), 5.42 (d, J = 12.0 Hz, 0.2H, *Z*-isomer), 1.43 (s, 4.8H, *E*-isomer), 1.36 (s, 1.2H, *Z*-isomer); ^{13}C NMR (75 MHz) δ 165.6, 165.1, 141.6−125.4, 60.3, 59.7, 31.6, 30.3; IR (neat) ν 1660 cm^{-1}; UV (CH_2Cl_2) λ_{max} 256 (ϵ 34 095); MS *m*/*e* (%) 325 (M$^+$, 21), 310 (9), 165 (17), 145 (100), 130 (11), 91 (24), 77 (14).

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

Triplet- and **DCA-sensitized irradiations** of **1** were described in a preliminary communication.[9]

Triplet-Sensitized Irradiation of 9a. Azadiene (*E*)-**9a** (250 mg, 0.80 mmol) and *m*-methoxyacetophenone (550 mg, 3.7 mmol) were irradiated for 6 h. Chromatography with hexane/Et_2O (99:1) as eluent gave cyclopropylimine (*E*)-**11a** (13 mg, 5%), as a colorless oil, and benzaldehyde (65 mg). Further elution with Et_2O afforded 25 mg of highly polar material. Final elution with EtOH yielded amine **10a** (148 mg, 81%), resulting from hydrolysis of the starting azadiene. Compound (*E*)-**11a**: ^{1}H NMR (200 MHz) δ 8.58 (s, 1 H), 7.68−7.08 (m, 15H), 3.46 (s, 1H), 1.30 (s, 3H), 1.12 (s, 3H); ^{13}C NMR (50 MHz) δ 157.7, 145.1−125.6, 62.5, 48.0, 30.6, 24.8, 20.1; IR (neat) ν 1664 cm^{-1}; MS *m*/*e* (%) 325 (M$^+$, 9), 310 (9), 220 (66), 205 (20), 165 (10), 117 (100), 105 (9), 90 (34).

DCA-Sensitized Irradiation of 9a. Azadiene (*E*)-**9a** (200 mg, 0.60 mmol), DCA (30 mg, 0.13 mmol), and biphenyl (95 mg, 0.60 mmol) were irradiated for 15 min. Chromatography with hexane/Et_2O (99:1) as eluent gave biphenyl (92 mg) and benzaldehyde (50 mg). Further elution with Et_2O afforded 15 mg of highly polar material. Final elution with EtOH yielded amine **10a** (115 mg, 79%), resulting from hydrolysis of the starting azadiene.

Triplet-Sensitized Irradiation of 9b. Azadiene (*1E*,*4Z*)-**9b** (256 mg, 1 mmol) and *m*-methoxyacetophenone (550 mg, 3.7 mmol) were irradiated for 9.5 h. Chromatography with hexane/Et_2O (98:2) as eluent gave cyclopropylimine **11b** (10 mg, 4%) as a colorless oil and as a 3:2 mixture of (Z_{cyclo},E_{C-N}):(E_{cyclo},E_{C-N}) diastereoisomers and benzaldehyde (82 mg). Further elution with Et_2O afforded 17 mg of highly polar material. Final elution with EtOH yielded amine **10b**[9] (126 mg, 78%) as a 3:2 mixture of *Z*:*E* diastereoisomers, resulting from hydrolysis of the starting azadiene. Compound **11b**: ^{1}H NMR (200 MHz) δ 8.43 (s, 0.4H, *E*-isomer), 8.37 (s, 0.6H, *Z*-isomer), 7.68−7.57 (m, 2H), 7.37−7.09 (m, 8H), 3.18 (d, J = 4.0 Hz, 0.4H, *E*-isomer), 3.10 (d, J = 7.5 Hz, 0.6H, *Z*-isomer), 2.43 (d, J = 4.0 Hz, 0.4H, *E*-isomer), 2.19 (d, J = 7.5 Hz, 0.6H, *Z*-isomer), 1.39 (s, 1.2H, *E*-isomer), 1.26 (s, 1.8H, *Z*-isomer), 1.10 (s, 1.8H, *Z*-isomer), 0.88 (s, 1.2H, *E*-isomer); ^{13}C NMR (50 MHz) δ 158.7, 157.9, 38.8−125.5, 59.1, 57.9, 39.4, 37.4, 28.6, 27.8, 26.4, 22.0, 20.9, 16.3; IR (neat) ν 1631 cm^{-1}; MS *m*/*e* (%) 249 (M$^+$, 13), 234 (26), 219 (3), 206 (5), 144 (10), 129 (16), 117 (100), 91 (22).

DCA-Sensitized Irradiation of 9b. Azadiene (*1E*,*4Z*)-**9b** (200 mg, 0.80 mmol), DCA (30 mg, 0.13 mmol), and biphenyl (124 mg, 0.80 mmol) were irradiated for 2 h. Chromatography with hexane/Et_2O (99:1) as eluent gave biphenyl (120 mg), *N*-vinylaziridine **39a** (10 mg, 5%), as a yellow oil and as a 2:1 mixture of *Z*:*E* isomers, and benzaldehyde (50 mg). Further elution with Et_2O afforded 64 mg of highly polar material. Final elution with EtOH yielded amine **10b** (72 mg, 56%), as a 7:3 mixture of *Z*:*E* isomers, resulting from hydrolysis of the starting azadiene. **39a**: ^{1}H NMR (300 MHz) δ 7.58−7.09 (m, 10H), 6.96 (d, J = 14.0 Hz, 0.33H, *E*-isomer), 6.07 (d, J = 9.0 Hz, 0.67H, *Z*-isomer), 6.05 (d, J = 14.0 Hz, 0.33H, *E*-isomer), 5.80 (d, J = 9.0 Hz, 0.67H, *Z*-isomer), 2.94 (s, 0.33H, *E*-isomer), 2.77 (s, 0.67H, *Z*-isomer), 1.38 (s, 0.99H, *E*-isomer), 1.23 (s, 2.01H, *Z*-isomer), 1.11 (s, 2.01H, *Z*-isomer), 1.03 (s, 0.99H, *E*-isomer); ^{13}C NMR (50 MHz) δ 138.5, 138.2, 129.0−123.7, 116.0, 115.8, 54.2, 52.8, 48.6, 45.3, 21.2, 20.6, 20.3, 19.6; IR (neat) ν 1630 cm^{-1}; MS *m*/*e* (%) 249 (M$^+$, 22), 248 (58), 219 (3), 193 (27), 158 (9), 144 (100), 115 (37), 91 (65), 77 (50), 51 (25).

Triplet-Sensitized Irradiation of 17. Azadiene (*E*)-**17** (236 mg, 0.90 mmol) and *m*-methoxyacetophenone (550 mg, 3.7 mmol) were irradiated for 3.5 h. Chromatography with hexane/Et_2O (99:1) as eluent gave benzaldehyde (73 mg). Further elution with Et_2O afforded 64 mg of highly polar material. Final elution with EtOH yielded a mixture of two products that was further separated by column with chloroform/MeOH (95:5) to give cyclopropylamine **20** (19 mg, 12%) as an oil, resulting from hydrolysis of cyclopropylimine **19**, and amine **18** (114 mg, 71%), resulting from hydrolysis of starting azadiene **17**. **20**: ^{1}H NMR (200 MHz) δ 7.40−7.09 (m, 4H), 4.03 (s, 1H), 2.84 (td, J = 13.5, 5.8 Hz, 1H), 2.64−2.30 (m, 4H), 1.86 (td, J = 13.8, 5.3 Hz, 1H), 1.32 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (50 MHz) δ 137.3−126.1, 68.9, 56.7, 51.2, 27.7, 26.7, 25.8, 21.9; IR (neat) ν 3392 cm^{-1}; MS *m*/*e* (%) 187 (M$^+$, 1), 172 (4), 171 (6), 143 (10), 129 (9), 105 (9), 91 (14), 84 (36), 58 (100).

DCA-Sensitized Irradiation of 17. Azadiene (*E*)-**17** (250 mg, 0.91 mmol), DCA (30 mg, 0.13 mmol), and biphenyl (140 mg, 0.91 mmol) were irradiated for 90 min. Chromatography with hexane/Et_2O (99:1) as eluent gave biphenyl (130 mg) and benzaldehyde (20 mg). Further elution with Et_2O afforded 35 mg of highly polar material. Final elution with EtOH yielded amine **18** (16 mg, 7%), resulting from hydrolysis of the starting azadiene, and amine **1-methyl-1-naphthalen-2-yl-ethylamine** (128 mg, 78%), resulting from aromatization of the dihydronaphthalene unit. **1-Methyl-1-naphthalen-2-yl-ethylamine**: ^{1}H NMR (200 MHz) δ 7.91−7.40 (m, 7H), 2.75 (br s, 2H), 1.60 (s, 6H); ^{13}C NMR (50 MHz) δ 133.4−122.7, 53.0, 32.4; IR (neat) ν 3285, 1599 cm^{-1}; MS *m*/*e* (%) 186 (M + 1, 53), 185 (M$^+$, 32), 170 (98), 169 (66), 155 (100), 141 (27), 129 (48), 128 (33), 115 (23), 105 (23), 58 (51).

Triplet-Sensitized Irradiation of 21a. Azadiene (*E*)-**21a** (250 mg, 0.80 mmol) and *m*-methoxyacetophenone (5.7 g, 38 mmol) were irradiated for 10 h. Chromatography with hexane/Et_2O (99:1) as eluent gave benzaldehyde (47 mg). Further elution with hexane/Et_2O (85:15) afforded dihydropyrrol **23a** (15 mg, 6%), as a colorless oil. Final elution with Et_2O yielded amine **22**[9] (105 mg, 66%), resulting from hydrolysis of the starting azadiene. Compound **23a**: ^{1}H NMR (300 MHz) δ 7.95 (d, J = 3.0 Hz, 1H), 7.71−6.81 (m, 13H), 5.83 (d, J = 3.0 Hz, 1H), 1.36 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (75 MHz) δ 176.4, 145.0−119.4, 58.3, 79.9, 68.5, 55.8, 23.7, 21.3; IR (neat) ν 1626 cm^{-1}; MS *m*/*e* (%) 324 (M + 1, 38), 323 (M$^+$, 100), 308 (52), 291 (6), 280 (7), 267 (20), 254 (12), 252 (11), 219 (23), 203 (12), 191 (17), 165 (17), 145 (5), 131 (7), 117 (50), 90 (23), 77 (3).

DCA-sensitized irradiation of **21a** was described in a preliminary communication.[9]

Triplet-Sensitized Irradiation of 21b. Azadiene (*E*)-**21b** (200 mg, 0.6 mmol) and *m*-methoxyacetophenone (6.22 g, 41.5 mmol) were irradiated for 3 h. Chromatography with hexane/Et_2O (9:1) as eluent gave starting azadiene (*E*)-**21b** (32 mg, 16%) and *p*-cyanobenzaldehyde (33 mg). Further elution with Et_2O afforded a mixture of two products. Chromatography of this mixture with hexane/ethyl acetate (9:1) yielded dihydropyrrol **23b** (31 mg, 16%), as a white solid (mp 239−240 °C (hexane)) and amine **22** (59 mg, 43%), resulting from hydrolysis of the starting azadiene. **23b**: ^{1}H NMR (200 MHz) δ 7.97 (d, J = 2.9 Hz, 1H), 7.75−6.88 (m, 12H), 5.82 (d, J = 2.9 Hz, 1H), 1.43 (s, 3H), 0.73 (s, 3H); ^{13}C NMR (50 MHz) δ 177.2,

144.4−110.2, 79.2, 68.6, 56.1, 23.8, 20.8; IR (KBr) ν 2230, 1610 cm^{-1}; MS *m/e* (%) 349 (M + 1, 30), 348 (M^+, 100), 333 (41), 316 (4), 305 (7), 292 (20), 279 (25), 219 (36), 206 (39), 191 (48), 178 (11), 165 (31), 156 (18), 142 (47), 115 (25). Anal. Calcd for $C_{25}H_{20}N_2$: C, 86.17; H, 5.79; N, 8.04. Found: C, 85.97; H, 5.83, N, 8.16. The structure assignment was established by X-ray crystallography.[19]

DCA-Sensitized Irradiation of 21b. Azadiene (*E*)-**21b** (250 mg, 0.70 mmol), DCA (30 mg, 0.1 mmol), and biphenyl (111 mg, 0.70 mmol) were irradiated for 35 min. Chromatography with hexane/Et_2O (99:1) as eluent gave biphenyl (105 mg), azadiene (*E*)-**21b** (26 mg, 10%), and *p*-cyanobenzaldehyde (65 mg). Further elution with Et_2O afforded 20 mg of highly polar material. Final elution with EtOH yielded amine **22** (118 mg, 70%), resulting from hydrolysis of the starting azadiene.

Triplet-Sensitized Irradiation of 25. Azadiene (*E*)-**25** (53 mg, 0.10 mmol) and *m*-methoxyacetophenone (550 mg, 3.7 mmol) were irradiated for 6 h. Chromatography with hexane/Et_2O (98:2) as eluent gave benzaldehyde (10 mg) and amine **10c** (31 mg, 76%), resulting from hydrolysis of the starting material. Further elution with Et_2O afforded 8 mg of highly polar material.

DCA-Sensitized Irradiation of 25. Azadiene (*E*)-**25** (197 mg, 0.50 mmol), DCA (30 mg, 0.13 mmol), and biphenyl (80 mg, 0.50 mmol) were irradiated for 15 min. Chromatography with hexane/Et_2O (99:1) as eluent gave biphenyl (78 mg), *N*-vinylaziridine **39b** (27 mg, 14%), and benzaldehyde (30 mg). Further elution with Et_2O afforded amine **10c** (84 mg, 55%), resulting from hydrolysis of the starting azadiene. Final elution with EtOH yielded 35 mg of highly polar material. **39b**: ^{1}H NMR (200 MHz) δ 7.29−6.91 (m, 15H), 6.85 (s, 1H), 2.58 (s, 1H), 1.83 (sept, J = 7.1 Hz, 1H), 1.52 (sept, J = 7.3 Hz, 1H), 1.32 (d, J = 7.1 Hz, 3H), 1.26 (d, J = 7.1 Hz, 3H), 1.03 (d, J = 7.3 Hz, 3H), 0.71 (d, J = 7.3 Hz, 3H); ^{13}C NMR (50 MHz) δ 142.5−125.9, 58.9, 56.3, 35.5, 30.7, 23.1, 20.8, 20.6, 19.4; IR (neat) ν 1595 cm^{-1}; MS *m/e* (%) 382 (M + 1, 4), 381 (M^+, 32), 338 (24), 282 (14), 269 (100), 206 (20), 191 (56), 178 (27), 165 (15), 91 (42).

Triplet-Sensitized Irradiation of 26a. Azadiene **26a** (165 mg, 0.40 mmol) and *m*-methoxyacetophenone (660 mg, 4.40 mmol) were irradiated for 1 h. Chromatography with hexane/Et_2O (98:2) as eluent gave azadiene **26a** (98 mg, 59%) and benzophenone (13 mg). Further elution with Et_2O afforded 24 mg of highly polar material. Final elution with EtOH yielded amine **10a** (18 mg, 18%), resulting from hydrolysis of the starting azadiene.

DCA-Sensitized Irradiation of 26a. Azadiene **26a** (150 mg, 0.40 mmol), DCA (20 mg, 0.09 mmol), and biphenyl (57 mg, 0.40 mmol) were irradiated for 10 min. Chromatography with hexane/Et_2O (99:1) as eluent gave biphenyl (40 mg), dihydrobenzoazepine **45a** (83 mg, 55%), as a white solid (mp 142−143 °C (hexane)), azadiene **26a** (13 mg, 9%), and benzophenone (16 mg). Further elution with Et_2O afforded 10 mg of highly polar material. Final elution with EtOH yielded amine **10a** (21 mg, 24%), resulting from hydrolysis of the starting azadiene. **45a**: ^{1}H NMR (200 MHz) δ 7.58−6.95 (m, 19H), 6.59 (s, 1H), 0.92 (s, 6H); ^{13}C NMR (50 MHz) δ 142.7−126.1, 56.7, 50.7, 22.0; IR (neat) ν 3369 cm^{-1}; MS *m/e* (%) 401 (M^+, 53), 386 (11), 345 (9), 221 (100), 207 (11), 178 (27), 165 (29), 91 (39). Anal. Calcd for $C_{30}H_{27}N$: C, 89.73; H, 6.78; N, 3.49. Found: C, 90.03; H, 7.08, N, 3.69.

Triplet-Sensitized Irradiation of 26b. A 1:4 mixture of *Z*:*E* isomers of azadiene **26b** (179 mg, 0.60 mmol) and *m*-methoxyacetophenone (750 mg, 4.40 mmol) were irradiated for 45 min. Chromatography with hexane/Et_2O (98:2) as eluent gave azadiene **26b** (125 mg, 70%), as a 15:85 mixture of *Z*:*E* diastereoisomers, and benzophenone (18 mg). Further elution with Et_2O afforded 15 mg of highly polar material. Final elution with EtOH yielded amine (*E*)-**10b** (16 mg, 18%), resulting from hydrolysis of the starting azadiene.

DCA-Sensitized Irradiation of 26b. A 1:4 mixture of *Z*:*E* isomers of azadiene **26b** (170 mg, 0.50 mmol), DCA (20 mg, 0.09 mmol), and biphenyl (80 mg, 0.50 mmol) were irradiated for 40 min. Chromatography with hexane/Et_2O (99:1) as eluent gave biphenyl (78 mg), dihydrobenzoazepine **45b** (121 mg, 71%), as a colorless oil, and benzophenone (10 mg). Further elution with Et_2O afforded 30 mg of highly polar material. Final elution with EtOH yielded amine (*E*)-**10b** (9 mg, 11%), resulting from hydrolysis of the starting azadiene. **45b**: ^{1}H NMR (200 MHz) δ 7.43−7.04 (m, 14H), 6.80 (d, J = 14.2 Hz, 1H), 6.13 (d, J = 14.2 Hz, 1H), 1.24 (s, 6H); ^{13}C NMR (50 MHz) δ 140.5−118.1, 58.3, 49.5, 22.5; IR (neat) ν 3360 cm^{-1}; MS *m/e* (%) 325 (M^+, 29), 310 (9), 269 (29), 191 (32), 165 (24), 145 (100), 129 (10), 103 (16), 91 (27), 77 (14).

DCA-Sensitized Irradiation of 40. Azadiene (*E*)-**40** (140 mg, 0.40 mmol), DCA (12 mg, 0.05 mmol), and biphenyl (56 mg, 0.40 mmol) were irradiated for 12 min. Chromatography with hexane/Et_2O (99:1) as eluent gave biphenyl (54 mg), *N*-vinylaziridine **39c** (18 mg, 13%), as a colorless oil, and benzaldehyde (25 mg). Further elution with Et_2O afforded amine **10d** (72 mg, 67%), resulting from hydrolysis of the starting azadiene. Final elution with EtOH yielded 11 mg of highly polar material. **39c**: ^{1}H NMR (200 MHz) δ 7.29−6.98 (m, 12H), 6.90−6.82 (m, 6H), 6.76 (s, 1H), 6.64−6.60 (m, 2H), 2.72 (s, 1H), 1.66 (s, 3H); ^{13}C NMR (50 MHz) δ 142.2−126.2, 55.9, 54.2, 22.5; IR (neat) ν 1612 cm^{-1}; MS *m/e* (%) 388 (M + 1, 19), 387(M^+, 54), 370 (16), 282 (34), 269 (100), 220 (12), 206 (35), 191 (61), 178 (42), 165 (24), 152 (12), 115 (22), 91 (36), 77 (14).

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Supporting Information Available: General procedures and ^{1}H NMR spectra for all compounds lacking analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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