Radical Cyclization Reactions of α-Silyl Amine α,β-Unsaturated Ketone and Ester Systems Promoted by Single Electron Transfer Photosensitization

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Abstract: The results of a broad investigation of the preparative and mechanistic aspects of single electron transfer (SET) promoted photocyclization reactions of α-silyl amino and amido α,β-unsaturated esters and ketones are presented. A number of unique and synthetically useful features of these processes, driven by α-silyl amine and amide cation radical desilylation and by intramolecular conjugate addition of intermediate α-amino and α-amido carbon-centered radicals to unsaturated esters and ketones, are described. Comparisons of the SET-sensitized and direct irradiation promoted reactions of these systems have shown how the former method is superior in inducing photocyclization reactions in cases where the α,β-unsaturated ketone or ester excited states are too reactive to be quenched by SET from the tethered amine donors and where diradicals produced as intermediates in the direct-irradiation reactions undergo fragmentation rather than cyclization. The current efforts have also demonstrated that problems associated with the ready oxidation of intermediate α-amino radicals can be avoided by the proper selection of photosensitizer or amine N substituents. Lastly, the synthetic versatility of this chemistry, exemplified by its application to the preparation of a number of N-heterocyclic substances by pathways involving either exo or endo radical cyclization, is presented.

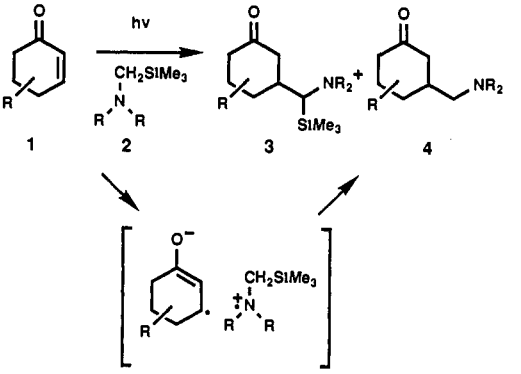
Introduction

In earlier studies[1] we have probed the mechanistic details of α-trimethylsilyl amine photoadditions to conjugated cyclohexenones. Results from that effort demonstrated that these processes (e.g., **1** + **2** → **3** and/or **4** in Scheme I) are promoted by single electron transfer (SET) from the silyl amines to the enone triplet excited states and that the resulting ion radical intermediates **5** are transformed to either silicon-containing (**3**) or non-silicon-containing (**4**) adducts by respective proton-transfer or desilylation pathways. In these investigations, we showed that the chemoselectivity of the photoreactions is subject to control by the medium. Acordingly, proton transfer in the intermediate ion radical pair is favored in aprotic solvents of low silophilicity (e.g. MeCN), resulting in preferential formation of the silicon-containing adducts **3**. On the other hand, adducts not possessing the trimethylsilyl group are formed predominantly in protic solvents of high silophilicity (e.g. MeOH, H_2O, etc.) or when oxophilic metal cations (e.g. Li^+) are present in high concentrations. Under these conditions, the enone anion radicals are highly solvated (H-bonding) or coordinated and, as a result, have low basicities. Consequently, amine cation radical desilylation becomes the favored reaction pathway.

In addition, we postulated that a portion of the photoaddition reactions leading to the non-silicon-containing adducts **4** proceeds via formation of "free" α-amino radicals and conjugate addition of these "nucleophilic" radicals to ground-state cyclohexenones. Evidence for the operation of this mechanistic pathway came from the observations that (1) photoadditions of silyl amines to cyclohexenones can be promoted by use of the SET photosensitizer, 9,10-dicyanoanthracene,[1,2] and (2) photoadditions of *N*,*N*-dimethylaniline and its TMS analogue to 4,4-dimethylcyclohexenone follow sequential radical addition–radical cyclization routes to produce tricyclic products.[3]

Our interests in developing synthetically useful photoinduced SET processes have stimulated a broad investigation of the preparative and mechanistic aspects of intramolecular versions of these reactions. The results of our studies of photocyclization reactions of α-trimethylsilyl amine α,β-unsaturated ketone and ester systems (**5** → **6**) are described below and in the following paper in this journal.[4] In the current publication, we point out a number of unique and intriguing features of the SET photochemistry of these systems, which is driven by α-silyl amine cation radical desilylation and by intramolecular conjugate addition of α-amino radicals **7** to unsaturated ester and ketone groupings. Comparisons of the SET-sensitized and direct irradiation promoted reactions of these systems have shown how the former method is superior in inducing photocyclization reactions in cases where the α,β-unsaturated ketone or ester excited states are too reactive to be quenched by SET from the tethered amine donors and where diradicals produced as intermediates in the direct-irradiation reactions undergo fragmentation rather than cyclization. The current efforts have also demonstrated that problems associated with the ready oxidation of intermediate α-amino radicals **7** can be avoided by the proper selection of photosensitizer or amine N substituents. Lastly, the synthetic versatility of this chemistry has been exemplified by its application to the preparation of a number of N-heterocyclic substances by pathways involving either exo or endo radical cyclization.

Scheme I



Results

Photocyclization Reactions of α,β-Unsaturated Silyl Amino Ester and Ketone Systems. The initial phases of our investigations were designed to probe the scope, limitations, and mechanistic

(1) Hasegawa, E.; Xu, W.; Mariano, P. S.; Yoon, U. C.; Kim, J. U. *J. Am. Chem. Soc.* **1988**, *110*, 8099.
(2) Hasegawa, E.; Brumfield, M. A.; Mariano, P. S.; Yoon, U. C. *J. Org. Chem.* **1988**, *53*, 5435.
(3) Zhang, X. M.; Mariano, P. S. *J. Org. Chem.* **1991**, *56*, 1655.
(4) Xu, W.; Zhang, X. M.; Mariano, P. S. *J. Am. Chem. Soc.*, following paper in this issue.

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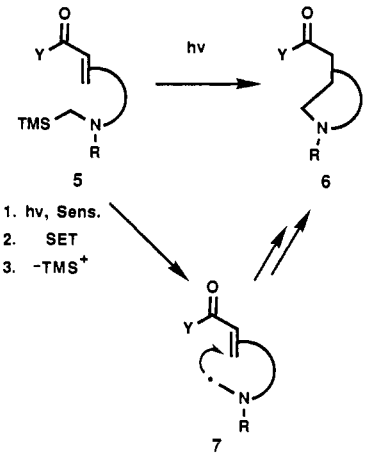
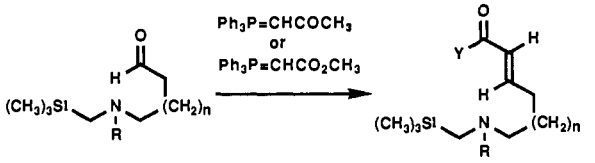


features of SET-induced photocyclization reactions of α,β-unsaturated silyl amino esters and ketones. The aminoheptenones **16** and **17** and related esters **18** and **19**, selected for this purpose, were prepared in modest yields (56–88%) by Wittig olefinations of the *N*-methyl and *N*-benzyl silyl aminobutyraldehydes **8** and **9** (supplementary material) with the known acetylmethylidene[5] and (methoxycarbonyl)methylidene[6] phosphoranes (Scheme II). The enone and enoate substrates possess substituents and structures that have enabled us to obtain extensive information about the SET photochemistry of these systems. The observations made are detailed below and discussed at a later point in this publication.

In order to determine the impact of incorporating the unsaturated ketone and ester moieties in acyclic environments, the direct-irradiation reactions of the silyl amino enones **16** and **17** were probed. The issue here is whether or not intramolecular SET from the tertiary amine groupings to the enone excited states would be competitive with the very rapid photoinduced cis–trans isomerization and deconjugation reactions of acyclic enone systems.[7] Direct-irradiation reactions of **16** and **17** in MeCN or MeOH were performed by using flint glass filtered light ($\lambda > 290$ nm). Under these conditions, the only reaction observed to occur is cis–trans isomerization about the enone C=C bond. Extended irradiations do lead to complete destruction of these enones but not to formation of any products characteristic of the operation of SET reaction pathways.

In contrast, sensitized irradiation of the enones **16** and **17** and related methyl esters **18** and **19** does indeed promote efficient SET-induced photocyclization reactions. For example, irradiation of deoxygenated N_2 or Ar-purged 15% MeOH–MeCN solutions containing the SET sensitizer 9,10-dicyanoanthracene[8] (DCA, 4×10^{-4} M) and silyl amino enones **16** or **17** (2 mM), employing uranium glass filtered light ($\lambda > 320$ nm), leads to formation of the acetonylpiperidines **28** (90%, molecular distillation) or **29** (78%, silica gel chromatography) (Scheme III). Interestingly, the acetonylpyrrolidine **30** is also produced (5%) in the DCA-sensitized reaction of the *N*-benzyl enone **17**. This substance, whose origin by a desilylmethylation pathway will be discussed more fully below, is not observed in the photolysate arising by 1,4-dicyanonaphthalene[9] (DCN, 1×10^{-2} M) or redox[10] (triphenylene and 1,4-dicyanobenzene)[11] SET-sensitized reactions

Scheme II



8 (n=1, R=CH_3)
9 (n=1, R=CH_2Ph)
10 (n=0 , R=CO_2CH_2Ph)
11 (n=1 , R=CO_2CH_2Ph)
12 (n=3, R=CH_2Ph)
13 (n=9, R=CH_2Ph)
14 (n=3 , R=CO_2CH_2Ph)
15 (n=9 , R=CO_2CH_2Ph)

16 (n=1, R=CH_3, Y=CH_3)
17 (n=1, R=CH_2Ph, Y=CH_3)
18 (n=1, R=CH_3, Y=OCH_3)
19 (n=1, R=CH_2Ph, Y=OCH_3)
20 (n=0 , R=CO_2CH_2Ph, Y=CH_3)
21 (n=1 , R=CO_2CH_2Ph, Y=CH_3)
22 (n=0 , R=CO_2CH_2Ph, Y=OCH_3)
23 (n=1 , R=CO_2CH_2Ph, Y=OCH_3)
24 (n=3, R=CH_2Ph, Y=CH_3)
25 (n=9, R=CH_2Ph, Y=CH_3)
26 (n=3 , R=CO_2CH_2Ph, Y=CH_3)
27 (n=9 , R=CO_2CH_2Ph, Y=CH_3)

Scheme III

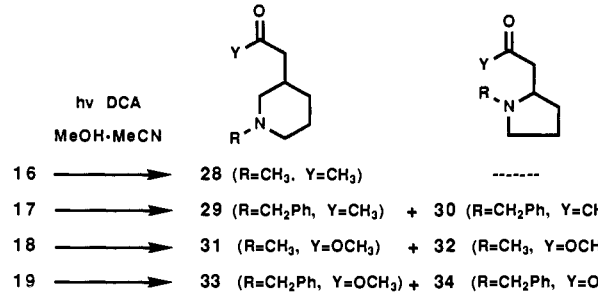


Table I. DCA Concentration Effects on the Pyrrolidine **34**:Piperidine **33** Ratio from Photocyclization of the Silyl Amino Ester **19** in 15% MeOH–CH_2Cl_2 and 5% MeOH–$CHCl_3$

5% MeOH–CH_2Cl_2		5% MeOH–$CHCl_3$	
[DCA] (mM)	**34**:**33**	[DCA] (mM)	**34**:**33**
0.2	2	0.7	7
0.9	3	1.8	13
2.6	7	2.4	14
4.4	11	2.8	15
		4.4	23

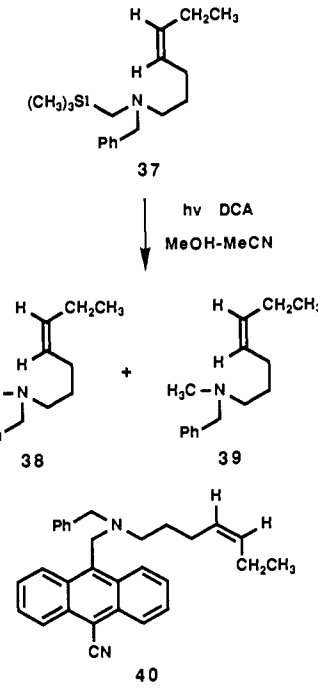
of **17**. In both of these cases, piperidine **29** is the only identifiable product formed, albeit in low isolated yields of 26% and 29%.

Studies with the silyl amino esters **18** and **19** have provided additional information about the scope and mechanistic details of these processes. Accordingly, DCA-sensitized (7×10^{-4} M) reaction of the *N*-methyl substrate **18** in 15% MeOH–MeCN gives the piperidine **31** and pyrrolidine **32** in respective yields of 67% and 20%. Likewise, piperidine **33** (39% isolated, 48% by GLC analysis) and pyrrolidine **34** (29% isolated, 41% by GLC analysis) are generated in the DCA-sensitized reaction of the silyl amino ester **9** (Scheme III).

Insight into the mechanistic sequence operating in the piperidine-forming reactions has come from deuterium labeling studies. In one pathway for these photocyclization processes, intermediate α-amino radicals related to **7** undergo intramolecular Michael addition to form α-carbonyl radicals, which then convert to products by either H-atom abstraction from solvent or back SET from the DCA anion radical (formed in the initial SET step between DCA^{S1} and the amine donor). Termination of the latter route would be by protonation of the formed enolate anion. Clearly, distinction between these two alternatives can be made by determining the source of the hydrogen introduced at the

(5) Ramirez, F.; Dershowitz, S. *J. Org. Chem.* **1957**, *22*, 41.
(6) Isler, V. O.; Montavon, M.; Ruegg, R.; Ryser, G.; Zeller, P. *Helv. Chem. Acta* **1957**, *139*, 1242.
(7) Schuster, D. I. The Photochemistry of Enones. In *The Chemistry of Enones*; Patai, S., Rappoport, Z., Eds.; J. Wiley and Sons: New York, 1989.
(8) (a) The reduction potential ($E_{1/2}$ (−)) and singlet excited-state energy ($E_{0,0}$) of DCA taken from ref 8b are $E_{1/2}$ (−) = −0.89 V and $E_{0,0}$ = 2.86 eV. (b) Chanon, M.; Eberson, L. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: New York, 1988; Part A, Chapter 1.11.
(9) For DCN, $E_{1/2}$ (−) = −1.28 V and $E_{0,0}$ = 3.45 eV, taken from ref 8b.
(10) Redox photosensitization has been described: Majima, T.; Pac, C.; Nakasone, A.; Sakurai, H. *J. Am. Chem. Soc.* **1981**, *103*, 4499. Pac, C.; Nakasone, A.; Sakurai, H. *Ibid.* **1977**, *99*, 5806.
(11) For DCB, $E_{1/2}$ (−) = −1.6 V and for TP, $E_{1/2}$ (+) = 2.12 V and $E_{0,0}$ = 3.62 eV, taken from ref 8b.

Scheme IV

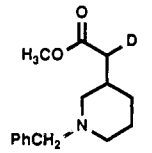


α-carbonyl center when reactions are conducted in the CH_3OH–CD_3CN and CH_3OD–CH_3CN solvent systems. Experiments of this type are meaningless when performed on the silyl amino enones, owing to the rapid rates of α-proton exchange of the acetonylpiperidines **28** and **29** with CH_3OD. The less acidic α-ester hydrogens in piperidines **31** and **33** are not readily exchanged with CH_3OD under the photolysis conditions. Therefore, DCA-sensitized reactions of silyl amino ester **19** were carried out in 15% CH_3OH–CD_3CN and 15% CH_3OD–CH_3CN and, in each case, the piperidine **33** was isolated and subjected to ^1H NMR analysis (integration of the ABM multiplets for the α-ester protons centered at 2.17 ppm). The results show that the monodeuterated (>90%) product **33-*d*** is formed only from reaction of **19** in 15% CH_3OD–CH_3CN.

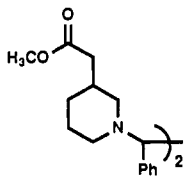
Another mechanistic issue addressed concerns the origin of the pyrrolidine products (e.g. **30**, **32**, and **34**) generated in the DCA-sensitized reactions of the silyl amino enone and ester systems. A likely sequence for formation of these substances involves competitive oxidation of the α-amino radicals of general structure **7**, which serve as intermediates in the pathways to the piperidine products. Thus, hydrolysis of the formaldiminium cations generated in this fashion would give secondary amine precursors of the pyrrolidines. Support for this proposal, identification of possible agents responsible for the α-amino radical oxidation, and methods for minimizing these side reactions have come from our further studies with the silyl amino ester **19**. For example, that oxygen could be responsible for at least part of the desilylmethylation process is demonstrated by the observation that pyrrolidine **34** is the major product (3:1 **34**:**33** ratio) obtained from DCA-sensitized reaction of **19** in an air-purged MeOH–MeCN solution. In addition, the sensitizer, DCA, serves as an α-amino radical oxidizing agent. We have observed that the pyrrolidine:piperidine (**34**:**33**) ratio increases significantly when the DCA concentration is increased (see Table I).

Owing to the low solubility of DCA in MeCN, the photoreactions used to accumulate the data in Table I were carried out in 15% MeOH–CH_2Cl_2 and 15% MeOH–$CHCl_3$ solutions in order to extend observations to the high [DCA] range. It is curious that plots of the **34**:**33** ratios vs [DCA] give nearly equal slopes (reflective of the near-equivalent effects of DCA) but nonzero and nonidentical **34**:**33** intercepts. For example, the **34**:**33** ratio is ca. 1 for [DCA] = 0 in the MeOH–CH_2Cl_2 reaction and ca. 5 for [DCA] = 0 in the MeOH–$CHCl_3$ process. The results suggest that halocarbon solvents also can serve as oxidants for the α-amino radical to formaldiminium cation conversion. Relevant to this conclusion is the observation that the DCA-sensitized (2 mM) reaction of **19** in 20% CCl_4–CH_2Cl_2 gives the pyrrolidine **34** exclusively (>25:1).

Efficient oxidation of α-amino radicals by DCA is not unexpected on the basis of the high ground-state reduction potential of this cyanoarene (−0.89 V)[8] and the low oxidation potentials of α-amino radicals (ca. −1.0 V).[12] This consideration led to the prediction that the use of cyanoarene SET sensitizers that have ground-state reduction potentials lower than ca. −1 V would minimize production of desilylmethylation side products. This proposal has gained experimental verification. Accordingly, irradiation of solutions containing DCN ($E_{1/2}^{SO}$ (−) = −1.3 V) and the amino ester **19** in 15% MeOH–MeCN leads to production of mainly piperidine **33** and dimeric piperidine **35** (one diastereomer of unknown stereochemistry) along with only minor amounts of pyrrolidone **34** (e.g., [DCN] = 1 mM yields **33** (27%), **35** (33%), and **34** (4%)). The piperidine (**33** + **35**) to pyrrolidine (**34**) product ratios are very high (ca. 23) in the DCN-sensitized reactions and invariant with changes in [DCN] from 1 to 6 mM. Finally, the pyrrolidine **34** is not generated from a photoreaction of **19** in 30% MeOH–MeCN sensitized by use of the triphenylene-1,4-dicyanobenzene ($E_{1/2}$ (−) = −1.6 V)[11] redox couple.[10] Under these conditions, the piperidine **33** and cyanophenyl analogue **36** are formed solely in respective isolated yields of 39% and 44%.



33-D



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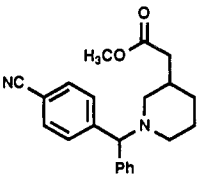

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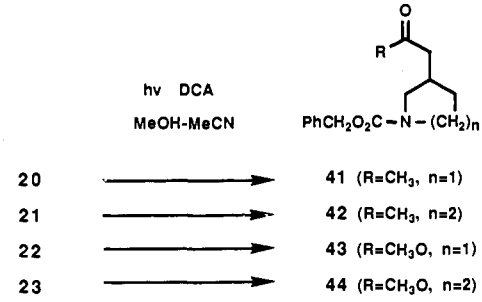
Photochemistry of a Silyl Aminoheptene. The results presented thus far suggest that the nature of the substituent on the olefin moiety involved in the SET-sensitized α-amino radical cyclization reactions is important in governing the chemical selectivity of the processes. As compared to the silyl amino ester reactions where pyrrolidine products are formed in significant quantities, the silyl amino enone photosensitized transformations yield piperidine products either exclusively or overwhelmingly. This difference appears to be due to the differential effects of the acetyl and methoxycarbonyl electron-withdrawing groups on the rates of intramolecular additions of electron-rich (high energy SOMO) α-amino radicals to the olefin functions (see the Discussion section). In light of this, we felt that it was important to probe the SET-sensitized photochemistry of a system that lacks EWG substitution on the π-moiety. The silyl aminoheptene **37** was prepared for this purpose by Wittig olefination (73%) of the amino aldehyde **9**. DCA-sensitized (4×10^{-4} M) irradiation of **37** in 15% MeOH–MeCN does not result in generation of the piperidine product expected from radical cyclization. Rather, silica gel chromatography of the crude photolysate led to isolation of the secondary amine **38** as the major (49%) product along with a trace quantity of the known[13] *N*-methyl compound **39** and the cyanoanthracene–amine adduct **40** (20%) (Scheme IV).

Photocyclization Reactions of Unsaturated Silyl Carbamido Enones and Esters. Above, we presented one possible solution to

(12) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132.
(13) Hasiak, B. *Bull. Soc. Chim. Fr.* **1974**, 2023.

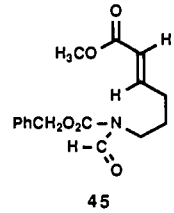
Scheme V



the problem, encountered in applications of the SET-sensitized radical cyclization methodology, associated with competitive oxidation of intermediate α-amino radicals by the cyanoarene sensitizer, DCA. The solution involves the use of sensitizers, such as DCN, that have low ground-state reduction potentials and, consequently, that do not efficiently participate in this redox chemistry. However, as we have shown, both the selectivities and yields of reactions sensitized by these alternative materials are low owing to other undesirable characteristics of these alternative sensitizers (Discussion section).

Another and, as it turns out, superior solution of this problem is based on the use of nitrogen substituents that increase the oxidation potential of the radical intermediates. We reasoned (see below) that incorporation of the silyl amino group into a carbamate function would result in a significant increase (from ca. −1.0 to ca. −0.5 V) in the N-substituted carbinyl radical oxidation potential and that this would markedly attenuate oxidation by DCA. Importantly, SET photosensitization of α-silyl carbamate photoreactions by DCA should still be possible owing to an anticipated strong thermodynamic driving force for the initial SET step ($E_{1/2}^{Si}$ (−) for DCA = ca. 2.0 V[8] and $E_{1/2}$ (+) for carbamates = ca. 1.4 V[17b]).

In order to test the viability of this methodology, the unsaturated α-silyl carbamido ketones, **20** and **21**, and esters, **22** and **23**, were prepared from the corresponding aldehydes **10** and **11** (supplementary material) in reasonably high yields (71–94%) by the Wittig processes shown in Scheme II. Photocyclization reactions of these substrates does indeed occur quite selectively when they are subjected to DCA-sensitized irradiation. In this way, the acetonyl-substituted pyrrolidine **41** (83% isolated, 95% by GLC) and piperidine **42** (75% isolated, 87% by GLC) and ester analogues **43** (88% isolated, 95% NMR) and **44** (78% isolated, 90% by GLC) are produced from the respective carbamates **20–23** (Scheme V). In none of these cases are products resulting from oxidative desilylmethylation detected, even when high DCA concentrations (0.6–1.5 mM) are used. Moreover, irradiation of an air-purged MeCN solution of DCA (9×10^{-4} M) and silyl carbamate **23** does not induce a reaction of this type but rather leads to generation (85%) of the formimide **45**.

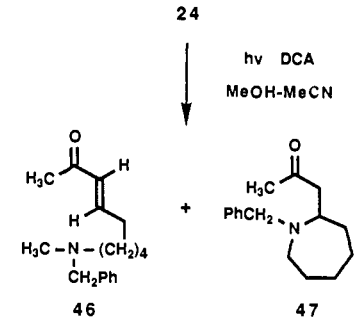


45

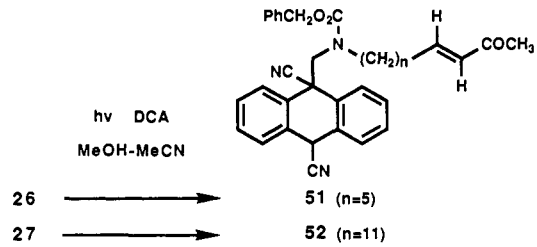
Photochemistry of Conjugated Silyl Aminononenones and -pentadecenones and Related Carbamates. For the purposes of exploring applications of this SET-photosensitization methodology to large-ring N-heterocycle synthesis, we have prepared the α,β-unsaturated silyl aminononenone **24**, -pentadecenone **25**, and corresponding carbamates **26** and **27** (see Scheme II).

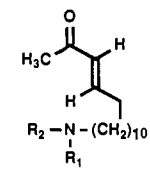
Unlike the behavior of their silyl aminoheptenone analogues **16** and **17**, DCA-sensitized irradiations of the chain-extended substrates **24** and **25** fail to promote the formation of products resulting from α-amino radical cyclizations. Instead, photoreaction of silyl aminononenone **24** under these conditions in 15% MeCN–MeOH gives rise to production of the *N*-methylamine **46** and hydroazepine **47** in respective isolated (silica gel) yields of 15% and 17% (Scheme VI). When the solvent used for this photoprocess is changed to pure MeOH, the seven-membered cyclic amine **47** resulting from a desilylmethylation route forms exclusively (35%). In a similar manner, DCA-sensitized reaction of the pentadecenone **25** in 15% MeOH–MeCN yields the secondary amine **48** (24%) and *N*-methyl analogue **49** (40%), whereas for reaction in MeOH the desilylmethylation product **48** forms solely (40%).

Scheme VI



Scheme VII





48 (R_1=CH_2Ph, R_2=H)

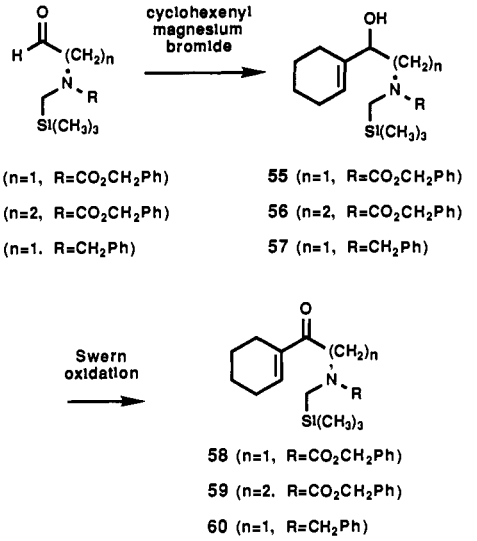
49 (R_1=CH_2Ph, R_2=CH_3)

50 (R_1=CO_2CH_2Ph, R_2=CH_3)

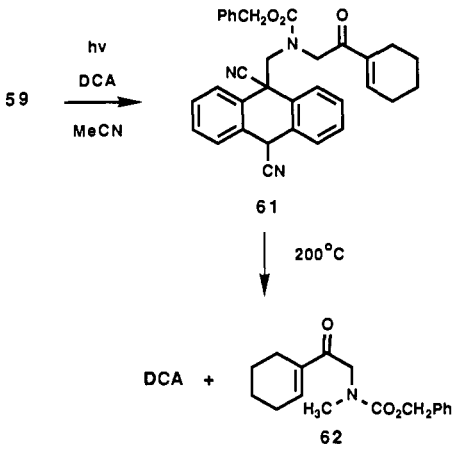
The SET photochemistry of the silyl carbamates **26** and **27** differs from that just described, but even in these cases products of radical cyclization are not formed. Thus, irradiation of MeCN solutions containing DCA and **26** or **27** results in the high-yielding (88–90% isolated by silica gel chromatography) production of diastereomeric mixtures of the carbamidodihydroanthracenes **51** and **52**, respectively (Scheme VII). Related adducts have been observed previously as products of ether and thioether photoadditions with DCA.[2] The structures of **51** and **52** were assigned on the basis of their spectroscopic properties and by comparisons with those of related[2] substances. Additional structural information is gained from the observation that adduct **52** is cleanly (90%) transformed to the *N*-methylamine **50** and DCA upon thermolysis in the neat state at 200 °C.

α-Amino Radical Endo Cyclization Processes. In order to further probe the scope and limitations of the SET-photosensitized methodology for N-heterocycle synthesis, the photochemistry of several silyl amino- and silyl amidocyclohexenyl ketones of general structure II was investigated. The main intent of these efforts was to explore the chemistry of systems in which α-amino radical cyclizations could occur either through endo-type (II → III) or exo-type (II → I) modes. In the reactions described thus far, regiochemistry (i.e., direction of addition to π-bonds) was governed in an additive way by stereoelectronic effects associated with preference for exo over endo radical cyclizations[14] and by sub-

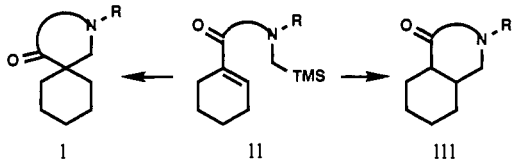
Scheme VIII



Scheme IX

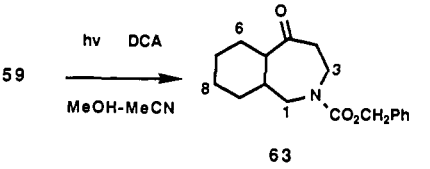


stituent effects arising from frontier orbital control in additions of electron-rich radicals to electron-poor olefins.[15] However, the regiochemical course of the SET-sensitized α-amino radical cyclizations when these factors are in opposition is not easily predicted.[16] In addition, the rates of endo radical cyclizations occurring as a result of overwhelming substituent controls should be slower than those for exo cyclizations that are driven by additive stereoelectronic and substituent effects. Consequently, the efficiencies of endo cyclizations of silicon-substituted aminocyclohexenyl ketones II could be low owing to competitive reactions of the key radical intermediates.

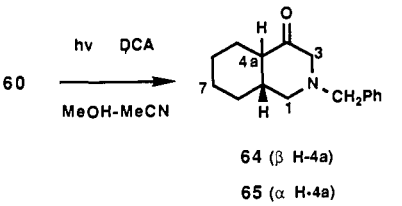


With these considerations in mind, we have synthesized (Scheme VIII) and subjected to photochemical studies the silyl carbamidomethyl and -ethyl cyclohexenyl ketones, **58** and **59**.

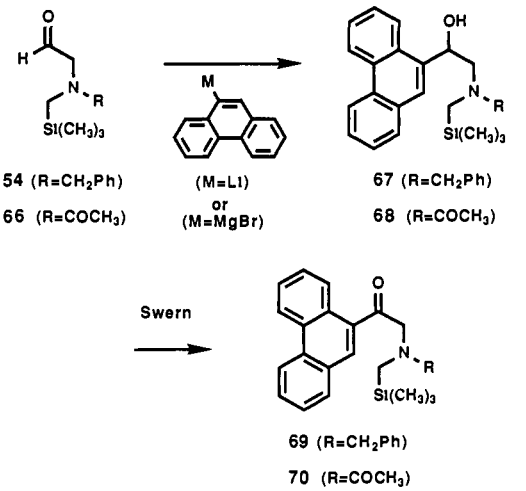
Scheme X



Scheme XI



Scheme XII



DCA-sensitized irradiation of the silyl carbamidomethyl enone **58** leads to exclusive and high-yielding (90%) production of the hydroanthracene adduct **61** (ca. 1:1 mixture of stereoisomers) (Scheme IX). As with the related adduct **52** (see above), thermolysis (200 °C, neat) of **61** gives DCA and the *N*-methyl carbamate **62** (90%). Products resulting from SET-promoted radical cyclization of **58** were not detected in the crude photolysate.

In contrast, the silyl amidoethyl ketone **59** is transformed to the fused bicyclic hydroazepinone **63** when subjected to DCA-sensitized irradiation in 15% MeOH–MeCN (Scheme X). Although **63** is formed as one isomer, its ring-fusion stereochemistry could not be elucidated on the basis of its spectroscopic properties. The yield of the DCA-sensitized endo cyclization of **59** to **63** is low (27%). Attempts to improve reaction efficiency by use of DCN or triphenylenedicyanobenzene redox photosensitization were not successful; a yield of 12% for the former and 30% for the latter method was obtained.

Photoinduced endo radical cyclization of the related silyl aminomethyl ketone **60** is a more viable process. This substance was prepared by Grignard reaction of the ethanal **54** (supplementary material) and Swern oxidation of the resulting allylic alcohol **57** (Scheme VIII). Irradiation of a 15% MeOH–MeCN solution containing DCA (1×10^{-4} M) and enone **60** gives, after alumina chromatography, the hydroisoquinoline stereoisomers **64** and **65** in 8% and 37% respective isolated yields (Scheme XI).

Analysis of the crude photolysate by GLC immediately following irradiation and prior to concentration and chromatography showed that it contains mainly the cis-fused isomer **64** (67% and 13% of **65**). Thus, it appears that the *cis*-hydroisoquinoline is the kinetically preferred product of this photocyclization and that decomposition and epimerization occur during chromatography.

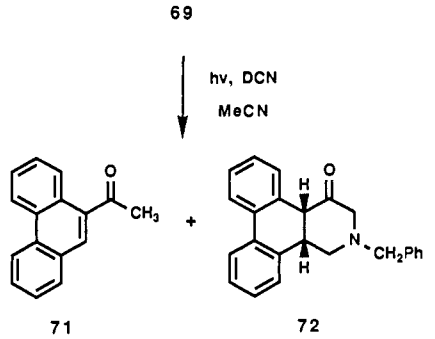
The final substrates investigated in our exploration of systems capable of undergoing endo-type cyclizations were the 9-phenanthrenyl silyl amino and silyl amido ketones **69** and **70**. The

(14) Beckwith, A. L. J.; Eaton, C. J.; Serelis, A. K. *J. Chem. Soc., Chem. Commun.* **1980**, 482. Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925 and references therein.

(15) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 753 and references therein.

(16) (a) Chuang, C. P.; Galluci, J. C.; Hart, D. J.; Hoffmann *J. Org. Chem.* **1988**, *53*, 3218. (b) Porter, N. A.; Magnin, D. R.; Wright, B. T. *J. Am. Chem. Soc.* **1986**, *108*, 2787. Porter, N. A.; Chang, V. H. T. *Ibid.* **1987**, *109*, 4976. Porter, N. A.; Chang, V. H. T.; Magnin, D. R.; Wright, B. T. *Ibid.* **1988**, *110*, 3554.

Scheme XIII

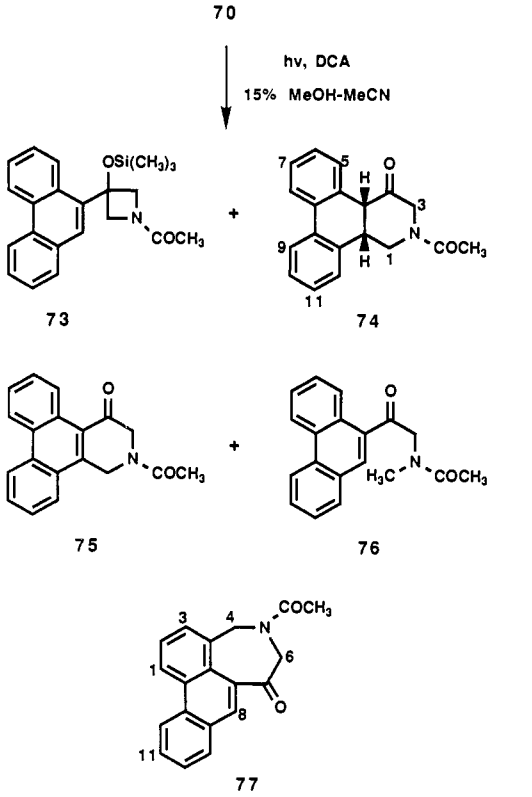


routes employed to prepare these compounds are shown in Scheme XII. In contrast to the high instability of amino ketone **69** (0 °C, 50% decomposition in 1 day), the amido analogue **70** is a more stable substance.

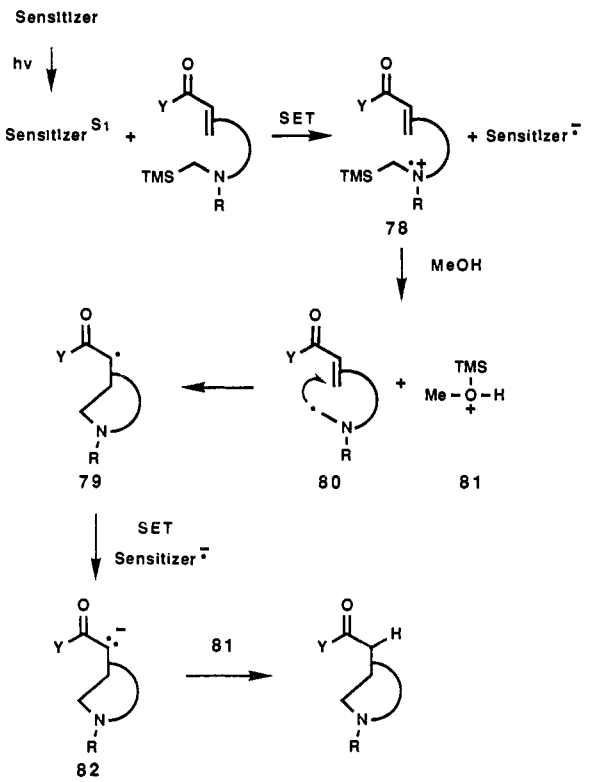
The best conditions found by experimentation for the photocyclization of **69** involve the use of DCN rather than DCA as sensitizer. Under these conditions ([DCN] = 3 mM, MeCN), **69** reacts to produce a mixture of 9-acetylphenanthrene (**71**) and the tetracyclic amino ketone **72** (Scheme XIII). While the isolated (silica gel) yields of these products are low (**71**, 9%; **72**, 12%), this is due to the high instability of **72**. Thus ^{13}C NMR analysis of the crude photolysate before chromatography showed that **71** and **72** are formed in 9% and 54% respective yields. The tetracyclic amino ketone **72** is produced as a single diastereomer, to which we have assigned the cis ring-fusion stereochemistry on the basis of its ^{1}H and ^{13}C NMR spectroscopic properties. Characteristic in this regard is the observed ^{1}H NMR coupling constant for the α-carbonyl methine proton of 6.0 Hz, indicative of an equatorial-axial vicinal ring-fusion proton alignment.

Two factors contribute to making DCN the best sensitizer for the conversion of **69** to **72**. First, it is necessary to use high sensitizer concentrations since (1) the phenanthrenyl ketone absorbs light at wavelengths (λ max = 310 nm) longer than the uranium glass filter cut-off (>320 nm), and (2) this substance undergoes an efficient direct-irradiation reaction to form a mixture of acetylphenanthrene **71** and tetracyclic piperidone **72** in an ca. 1:1 ratio. Second, DCA is not the sensitizer of choice when high concentrations are required, since, unlike DCN, it is capable of oxidizing the intermediate α-amino radical. This problem does not exist for the SET-sensitized reaction of the related silyl amido ketone **70** where the intermediate α-amido radical is more difficultly oxidized. However, in this case even with use of high DCA concentrations it is difficult to avoid the direct-irradiation reaction. Accordingly, DCA-sensitized irradiation of **70** in 15% MeOH–MeCN results in the production of the phenanthrenyl siloxyazetidine **73** (44%), tetracyclic amino ketones **74** (33%), **75** (17%), and **77** (4%), and a trace quantity (1%) of the *N*-methyl amide **76** (Scheme XIV). That the azetidine **73** is the direct-irradiation product was established by irradiation of an CD_3CN solution of **70**. The ring-fusion stereochemistry in **74** was determined to be cis on the basis of the 4.0-Hz and 5.7-Hz coupling constants observed between the methine protons α and β to the ketone carbonyl group in the ^{1}H NMR spectrum of the amide rotamer mixture. In addition, the structural assignment of phenanthreno azepinone **77** is consistent with the presence of the H-8 vinyl proton singlets at 8.24 and 8.26 ppm for both rotamers in its proton NMR spectrum.

Scheme XIV



Scheme XV



Discussion

The results presented above demonstrate a number of interesting features related to the mechanism and synthetic potential of SET-photosensitized radical cyclization reactions of conjugated α-silyl amino ketones and esters and their carbamate and amide analogues. Our goal to establish a mechanistic basis for understanding the scope and limitations of this process and, consequently, to define reaction conditions and substrate structure and substituent patterns that result in optimal reaction efficiencies has been met. In the sections that follow, observations that are pertinent to important mechanistic and synthetic features of these processes will be discussed in more detail.

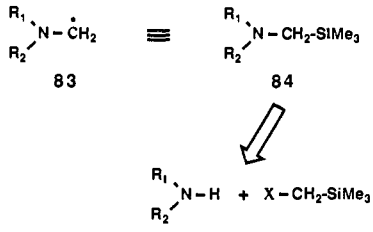
The stepwise mechanism for the SET-photosensitized radical cyclization reactions described above is outlined in Scheme XV. In this sequence, SET occurs from the nitrogen center of the α-silyl amino or amido ketones or esters to the singlet excited state of the cyanoarene sensitizer. In order to assure the operation of this pathway, the sensitizer must absorb light at wavelengths different from those of the α,β-unsaturated ketone and ester chromophores.

In addition, the excited-state reduction potential of the sensitizer needs to be higher than the oxidation potential of the silyl amine or silyl amide donor so that the SET step will be thermodynamically ($\Delta G_{SET} < 0$) and, thus, kinetically favorable. The cyanoarenes DCA ($E_{1/2}^{S1}$ (−) = 2.0 V)[8] and DCN ($E_{1/2}^{S1}$ (−) = 2.2 V)[9] have spectroscopic and excited-state electrochemical properties that fit these criteria. Thus, SET from α-silyl amines ($E_{1/2}$ (+) = ca. 1 V)[17a] and α-silyl carbamides ($E_{1/2}$ (+) = ca. 1.4 V)[17b] to the singlet excited states of these sensitizers should occur at diffusion-controlled rates. Activation of the redox SET-sensitized[10] reactions occurs by a different sequence. In this methodology, the arene triphenylene (TP) absorbs light and its singlet excited state transfers an electron to 1,4-dicyanobenzene (DCB) to produce the TP cation radical and DCB anion radical.[11] Oxidation of the silyl amine then occurs by SET to the TP cation radical.

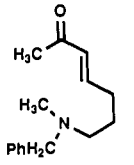
The α-silyl amine or amide cation radicals **78** generated in these ways undergo desilylation by transfer of the TMS group to solvent (e.g. MeOH). While the rates of these desilylation reactions are not known, measurements of related reactions of allyl- and benzylsilane cation radicals suggest that they should be large.[18-20] The low basicities (see below) of cyanoarene anion radicals dictate that deprotonation of the silyl amine or amide cation radicals will not be competitive with desilylation.[1,2] The desilylation step results in production of highly "nucleophilic" α-amino or α-amido radicals **80**, which then cyclize by conjugate addition to the ketone or ester substituted olefin moieties. In order to achieve high efficiencies, the radical cyclization step must be fast relative to other reactions (e.g., oxidation, H-atom abstraction, addition to the cyanoarene) open to the radical **80** (see below).

The process is terminated by back electron transfer from the sensitizer anion radical to the α-carbonyl radical **79**, giving an enolate anion **82** that is then protonated by reaction with the solvent-derived acid **81**. When the back electron transfer step is slow, alternative pathways (e.g., intramolecular H-atom abstraction) can be competitive in the deactivation of the radical intermediate **79**.

Synthetic Aspects. The radical cyclization methodology outlined above takes advantage of the by now well-established[1,2,18] sequential SET–desilylation processes to promote regioselective generation of α-amino or α-amido radical intermediates. In these sequences, α-silyl amines or amides of general structure **84** serve as the chemical equivalents of the corresponding radicals **83**. The silicon-containing precursors can be easily formed by N-alkylation reactions of secondary and primary amines with the readily available (trimethylsilyl)methyl halides. Consequently, the regioselectivity for radical generation in the SET-photosensitization methodology is easily controlled by simple synthetic manipulations and is preserved even when benzylic groups are attached to the nitrogen in **84** (e.g. $R_1 = CH_2Ph$). The latter feature is important since, in the absence of silicon substitution, the amine cation radicals that serve as the radical precursors are expected to undergo unselective deprotonation governed by the kinetic acidities of amine cation radical α-hydrogens.[4,21,22]



The incorporation of trimethylsilyl groups in the starting materials for these radical cyclization reactions has another important impact on cyclization reaction efficiencies. Since both the reactants and the products of these reactions are tertiary amines or amides, the oxidation conditions used to promote radical formation could also bring about secondary reactions of the products. The required selectivity for reaction of the substrates and not the products results from the effects of the Me_3Si group in lowering the amine oxidation potential by ca. 0.5 V[17,23] and increasing the rates of amine cation radical reaction (i.e., desilylation vs deprotonation) in competition with deactivation by back electron transfer from the sensitizer anion radical. The unique consequences of this feature are demonstrated by results obtained from studies with the non-silicon-containing amino enone **85**. DCA-photosensitized reaction of this substance under reaction conditions identical with those employed to transform its TMS analogue **17** to the piperidine **29** (>95%, Scheme III) results in decomposition of **85** but not production of **29** or any other products that would be expected from radical cyclizations.



85

Another unique and advantageous characteristic of the SET-sensitized radical cyclization methodology resides in the oxidative conditions used to promote formation of the α-amino and related radical intermediates. As with other photochemical and radical cyclization processes, the reaction conditions are mild and compatible with a range of functionalities. Of greater importance, however, is that the actual oxidant in these processes is the sensitizer singlet excited state. Owing to the extremely low steady-state concentrations of these agents during reaction, two electron oxidations caused by the facile oxidation of α-amino radicals can be avoided. In addition, alternative oxidative methods including electrochemistry and metal ion oxidants are not successful in inducing radical cyclization of the silyl amino enone **17**.[24]

As shown in the publication that follows,[4] related cyclization reactions of cyclic silyl amino enones can be promoted by direct irradiation. The SET-photoinduced method, however, represents a superior and more general procedure for carrying out these cyclization reactions in cases where the enone excited states, populated by direct irradiation, are deactivated by alternative reaction modes. This is the situation with acyclic enones where cis–trans isomerizations and Norrish Type II induced deconjugations of their triplet excited states are known to be quite rapid.[7] Also, the ultimate reactive intermediates in the direct-irradiation reactions are diradicals that can undergo fragmentation in competition with cyclization. This feature is responsible for the low yield of the tetracyclic amino ketone **72** from the direct-irradiation reaction of the phenanthrenyl silyl aminomethyl ketone **69**. Thus, cleavage of the 1,4-diradical intermediate **86**, formed from **69**, to produce 9-acetylphenanthrene (**71**) and an undetected formaldimine is competitive with its cyclization to generate **72**. Clearly, the SET-sensitized radical cyclization reaction is not complicated by this chemistry.

The final synthetic aspect of the SET-photosynthesized reactions of the silyl amino ketones and esters and related amides deserving of comment concerns the high exo vs endo radical cyclization regioselectivities. The accumulated results demonstrate that electron-withdrawing substituents play a dominant role over stereoelectronics in governing this selectivity. For example, radical

(17) (a) Cooper, B. E.; Owen, W. J. *J. Organomet. Chem.* **1971**, *29*, 33. (b) Yoshida, J.; Isoe, S. *Tetrahedron Lett.* **1987**, *28*, 6621.

(18) (a) Ohga, K.; Yoon, U. C.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 213. (b) Lan. A. J. Y.; Quillen, S. L.; Heuckeroth, R. O.; Mariano, P. S. *J. Am. Chem. Soc.* **1984**, *106*, 6439. Borg, R. M.; Heuckeroth, R. O.; Lan, A. J. Y.; Quillen, S. L.; Mariano, P. S. *Ibid.* **1987**, *109*, 2728.

(19) Unpublished observations by G. B. Schuster and P. S. Mariano.

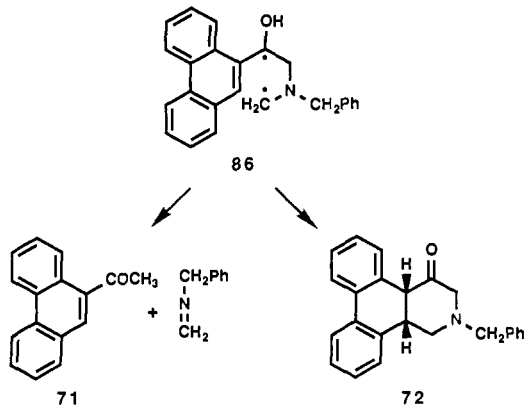
(20) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P.; Mattes, S. L. *J. Am. Chem. Soc.* **1989**, *111*, 8973.

(21) Lewis, F. D. *Acc. Chem. Res.* **1986**, *19*, 401 and references therein.

(22) Xu, W.; Mariano, P. S. *J. Am. Chem. Soc.* **1991**, *113*, 1431.

(23) Bock, H.; Kaim, W. *Acc. Chem. Res.* **1982**, *15*, 9. Bock, H.; Kaim, W. *J. Am. Chem. Soc.* **1980**, *102*, 4429. Bock, H.; Kaim, W.; Rohwer, H. E. *J. Organomet. Chem.* **1977**, *135*, C-14.

(24) In a collaborative effort with M. A. Fox and P. Martin, we have observed that electrochemical oxidation of **17** leads to exclusive formation of pyrrolidine **30**. Also, in unpublished studies by P. S. Mariano and X. M. Zhang we have found that iron(III) oxidation of **17** gives only **30**.



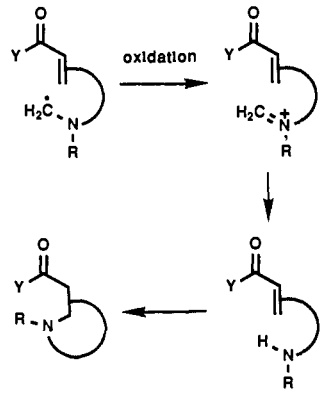
cyclization in reactions of the phenanthrenyl ketones **69** and **70** occur by endo cyclization modes exclusively. In contrast, endo cyclizations of related 1-hexenyl radicals are often only minor pathways.[14] Clearly, this difference is due to the high "nucleophilicity" of α-amino and α-amido radicals owing to their high SOMO energies. As a result, olefin LUMO coefficients and their control by electron-withdrawing substituents will play a major role in governing the direction of additions of these radicals.[14] The electronic nature of these radicals, however, leads to a limitation of this methodology. This is seen in the photochemistry of the silyl amino alkene **37** (Scheme IV) where no radical cyclization products are formed, presumably due to the low rate of α-amino radical intramolecular addition to the electron-rich alkene moiety.

Mechanistic Aspects. The efficiencies of these SET-sensitized reactions are influenced by the rates of cyclization of the intermediate α-amino and α-amido radicals since competitive reactions of these species are possible. Several factors appear to govern the rates of these cyclizations. For example, differences in yields for photoreactions of the silyl amine substrates having $COCH_3$ vs CO_2CH_3 or CH_2CH_3 substituted vinyl moieties are the result of substituent effects on the rates of addition of these electron-rich radicals to olefins.[15] In addition, slow α-amido and α-amino radical cyclizations in cases where medium (8-membered) or large (14-membered) rings are forming must be responsible for the failure of photosensitized reactions of the silyl amino and silyl amido enones **24**,**25** and **26**,**27**. Finally, familiar[14] stereoelectronic effects operate to make endo-type radical cyclizations less efficient than their exo analogues. Examples of this are found in the low (for **59**) and zero (for **58**) yields for SET-sensitized reactions of cyclohexenyl silyl amido and silyl amino ketones. In the endo cyclization processes we have noted a tendency for formation of 7-membered rings when nitrogen is part of a carbamate or an amide grouping. This is reflected in the successful 7-membered ring forming transformation of silyl carbamide **59** to **63** as compared to the failed cyclization of its homologue **58**. Moreover, a hydroazepine product is produced in the sensitized reaction of the phenanthrenyl ketone **70**, while reaction of its *N*-benzyl analogue **69** does not yield a related product. These differences are associated with strain introduced into the transition state for 6-membered ring formation by the sp^2-hybridized nitrogen in the silyl amido radical cyclizations.

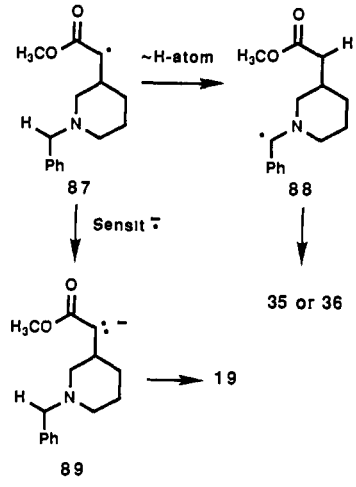
Processes that compete with cyclization of the α-amino and α-amido radicals include H-atom abstraction, coupling to cyanoarenes, and oxidation. The facilities of these competing reactions appear to be governed in part by the natures of the radicals and solvent. Thus, DCA-sensitized reactions of the long-chain silyl amino enones **24** and **25** give a predominance of H-atom abstraction over radical oxidation derived products when 15% MeOH–MeCN is used as the solvent, whereas oxidation products are generated nearly exclusively when photoreactions of these substrates are run in MeOH. These observations suggest that electron-rich α-amino and related radicals more rapidly abstract H-atoms from the EWG-substituted alkane MeCN than from the EDG-substituted alkane, MeOH.

Oxidation of the radicals serving as intermediates in these cyclization reactions is clearly one of the major problems associated

Scheme XVI



Scheme XVII



with this methodology when silyl amine substrates are used[25] and when radical cyclization rates are attenuated. This is best exemplified by the photochemistry of the silyl amino esters **18** and **19** where mixtures of piperidine and pyrrolidine products (Scheme III) arise as a result of competitive radical cyclization and oxidation (Scheme XVI). A search to uncover ways to minimize the deleterious effects of this competitive process has given rise to a number of mechanistically interesting observations and synthetically relevant conclusions.

In the DCA-sensitized reactions, ground-state DCA can serve as an α-amino radical oxidizing agent. The observed DCA concentration dependence of the pyrrolidine:piperidine ratio in the reaction of the silyl amino ester **19** evidences this conclusion. This makes sense from a thermodynamic viewpoint (DCA, $E_{1/2}$ (−) = −0.89 V and R_2NCH_2, $E_{1/2}$ (+) = ca. −1 V). The cyanoarenes, DCN and DCB, have lower ground-state reduction potentials (−1.28 and −1.6 V, respectively) and, as a result, do not oxidize intermediate α-amino radicals at rates that are competitive with their 6-exo radical cyclization. Indeed, photoreactions of the silyl amino ester **19** sensitized by DCN or redox sensitized with the TP–DCB system are not complicated by competitive formation of pyrrolidine products arising by oxidative desilylmethylation.

However, another problem is encountered when DCN and DCB are used to sensitize these photocyclizations. This is seen in the reactions of **19** where products (i.e., dimer **35** and cyanobenzene **36**) arising by intramolecular H-atom transfer from the *N*-benzylic position in the α-carbonyl radical intermediate **87** (Scheme XVII) are formed in significant quantities. The source of the differences observed for these cyanoarene-sensitized reactions must lie in the

(25) The oxidation of α-amino radicals to form iminium cations by SET pathways has been reported on several occasions. Cf. Bartholomew, R. F.; Davidson, R. S.; Howell, M. J. *J. Chem. Soc., Chem. Commun.* **1971**, 2804. Hall, L. R.; Iwamoto, R. T.; Hanzlik, R. P. *J. Org. Chem.* **1989**, *54*, 2446.

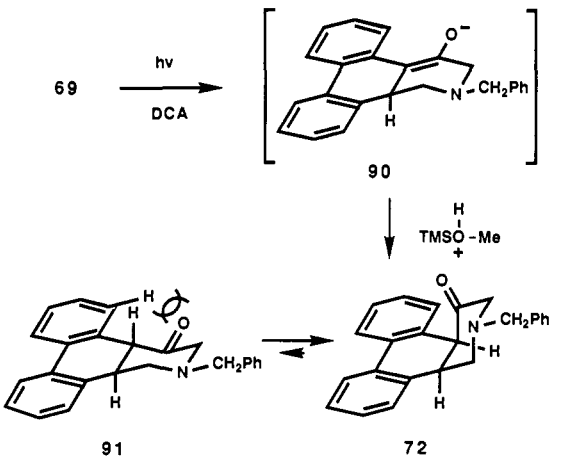
rates of α-carbonyl radical reduction by back SET from the cyanoarene anion radicals. Owing to the fact that the reduction potentials of the cyanoarenes decrease in the series DCA > DCN > DCB, the back SET process giving ester enolate anion **89** is thermodynamically more favorable with the DCN and DCB anion radicals. Thus, if kinetics parallel thermodynamics in these systems,[26] variations in the bimolecular rate constants for the conversions of **87** to **89** cannot be the source of the problem.

A plausible explanation for the differences noted in the cyanoarene-sensitized reactions can be found by considering the lifetimes and, thus, steady-state concentrations of the cyanoarene anion radicals. It is known that the anion radical of DCA has an exceptionally long lifetime[27] and a low basicity.[28] In comparison, less delocalized anion radicals like those derived from DCN and DCB should be more basic. Consequently, the DCN and DCB anion radicals would be more rapidly (and to a greater extent) protonated by the acid (MeOHTMS$^+$) produced in the solvent-induced amine cation radical desilylation step. Thus, the concentrations of these reductants could be low enough to cause α-carbonyl radical reduction to be slow. The fate of the *N*-benzyl radical **88** formed by the competitive intramolecular H-atom transfer process is also governed by the nature of the cyanoarene. Cyanobenzene adduct **36** likely forms by addition of the *N*-benzyl radical **88** to DCB or the related DCB-H radical. The absence of this type of process in the DCN-sensitized reaction suggests that this pathway is slow compared to radical dimerization with the more condensed cyanoarene.[30]

Other substances can promote oxidation of the α-amino radicals that serve as intermediates in the SET-sensitized processes. The effect of oxygen on the reaction of silyl amino ester **19** indicates that formaldiminium ion formation (Scheme XVI) can occur by SET to triplet oxygen ($E_{1/2}$ (−) = ca. −0.6 V)[31] or via α-amino-hydroperoxide formation by α-amino radical coupling to O_2 or superoxide ion (from DCA anion radical + O_2). Finally, the halomethanes, CCl_4 > $CHCl_3$ > CH_2Cl_2, can promote oxidative conversion of α-amino radicals to iminium cations by either SET[32] or halogen atom transfer.[33]

As the results presented above show, the best way to avoid the formation of undesired side products in the photocyclization reactions of unsaturated α-silyl amino ester and ketone systems is through the use of low concentrations of DCA as the SET sensitizer. While serving as an acceptable solution, this technique suffers from disadvantages, especially in cases where the photoreaction substrates can competitively absorb light and are capable of undergoing undesirable direct-irradiation reactions. An alternative and more generally applicable methodology utilizes α-silyl carbamate or amide derivatives instead of the tertiary amine analogues. Although the oxidation potentials of α-carbamido and α-amido radicals have not yet been measured, we anticipated that the presence of electron-withdrawing groups on nitrogen in these species would make their oxidation thermodynamically less favorable than for their α-amino radical counterparts. Thus, if the influence of the nitrogen substituents in the carbamate- and amide-derived radicals ($ROCONRCH_2^{\bullet}$ and $RCONRCH_2^{\bullet}$) is such

Scheme XVIII



to cause their oxidation potentials to be more than ca. 0.2 V higher than those of α-amino radicals ($E_{1/2}$ (+) = ca. −1 V),[12] the free energy for SET to ground-state DCA ($E_{1/2}$ (−) = 0.89 V) would become positive and, accordingly, the rate of SET would be slowed. Moreover, the α-silylcarbamates and amides are known[17b] to have oxidation potentials of ca. 1.4 V, so that initiation of the radical cyclizations by SET to the DCA singlet excited state ($E_{1/2}^{S1}$ (−) = ca. 2.0 V) should be energetically feasible.

The observation we have made in studies with the α-silyl carbamates **20–23** (Scheme V) and amide **70** (Scheme XIV) clearly demonstrate the validity of our reasoning. Accordingly, DCA-sensitized radical cyclizations of these substrates, which include both unsaturated ketones and esters, are quite efficient (ca. 90%) and are not complicated by competing desilylmethylation processes caused by intermediate carbamido radical oxidation. In addition, this methodology has flexibility in that the influential carbamate groupings also serve as versatile N-blocking groups, thus allowing further synthetic manipulation of the cyclization products. We would be remiss in not mentioning again that the carbamate and amide functions can have deleterious effects on the radical cyclization processes, as mentioned above in the context of the discussion of the photochemistry of cyclohexenyl ketones **59** and **58**.

One final issue requiring brief comment concerns the observed stereoselectivities of the SET-sensitized photocyclizations of the silyl amino cyclohexenyl and phenanthrenyl ketones **60** and **69**. These reactions lead to predominant (for **60**) or exclusive (for **69**) formation of cis-fused hydroisoquinoline products (Schemes XI and XIII). In the case of **60**, epimerization of the cis-fused product **64** occurs during chromatographic separation to yield the more stable trans stereoisomer **65** as the major isolated substance. In contrast, the cis stereoisomer **72**, obtained from cyclization of **69**, does not transform to the trans epimer **91** under these conditions, owing to the fact that the cis isomer is overwhelmingly (ΔSE = 4.2 kcal/mol, Macromodel, MM2) favored thermodynamically. The kinetic stereochemistry in these reactions is determined by factors controlling the direction of protonation of the final enolate anion intermediate (e.g., **90** in Scheme XVIII). Kinetic protonation of these species should occur preferentially from the sterically least encumbered convex face of the enolate, providing the cis-fused amino ketones (e.g. **72**). The source of the thermodynamic preference for **72** over its trans isomer **91** lies in $A_{1,2}$ strain existing in the lowest energy conformer (Macromodel) of **91** and missing in the lowest energy conformer of **72** (Scheme XVIII).

Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded on 500-, 400-, and 200-MHz instruments with $CDCl_3$ solutions. Column chromatography was performed with either Merck-EM Type 60 (230–400 mesh) silica gel (flash), Florisil (100–200 mesh), or Merck-Alcoa Type F-20 (80–200 mesh) alumina or flash alumina (Woelm N32-63). Preparative TLC was performed on 20 × 20 cm plates coated with Merck-EM Type 60 GF-254

(26) Of course, these processes could very well lie in the "inverted region", in which case the rate constant for SET from the cyanoarene radical anions to the α-ester radical would follow the series DCA > DCN > DCB.

(27) Kellet, M. A.; Whitten, D. G.; Gould, I. R.; Bergmark, W. R. *J. Am. Chem. Soc.* **1991**, *113*, 358.

(28) See: Lewis, F. D.; Petisce, J. R. *Tetrahedron* **1986**, *42*, 6207 (see also ref 29).

(29) Levanon, H.; Neta, P.; Trozzolo, A. M. *ACS Symp. Ser.* **1978**, 69.

(30) (a) This could be the reason why tertiary amine photoadditions to DCB (ref 30b) are more efficient that those to DCA (ref 2). (b) Ohashi, M.; Myake, K.; Tsujimoto, K. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1683.

(31) Rao, P. S.; Hayon, E. J. *J. Phys. Chem.* **1975**, *79*, 397.

(32) (a) Estimates of halomethane reduction potentials taken from ref 32b are −1.23 V (CH_3Cl) and −0.48 V ($CHCl_3$). (b) Eberson, L. *Acta Chem. Scand.* **1982**, *B36*, 533.

(33) (a) Halogen atom transfer to radicals is often an efficient reaction (ref 33b); the rates of these processes should depend on the energy of the resulting radicals, which are known (ref 33c) to vary in the following series: $ClH_2C^{\bullet}$ > $Cl_2HC^{\bullet}$ > $Cl_3C^{\bullet}$. (b) For example, see: Curran, D. P.; Chen, M.-H.; Kim, D. *J. Am. Chem. Soc.* **1989**, *111*, 6265 and references therein. (c) Holmes, J. L.; Lossing, F. P. *Ibid.* **1988**, *110*, 7343.

silica gel. Gas chromatographic analyses were conducted on chromatographs with flame ionization detection. High-performance liquid chromatography (HPLC) analyses and separations were carried out on a reverse-phase C-18 or normal-phase silica gel columns. All reactions were performed under a N_2 atmosphere. Drying of the organic layers obtained following workup of reaction mixtures was performed with anhydrous Na_2SO_4. All new compounds were isolated as oils and judged to be >90% pure by ^{13}C and ^1H NMR analysis unless otherwise specified.

Preparative photochemical reactions were conducted by using an apparatus consisting of a 450-W medium-pressure mercury lamp surrounded by a glass filter (for wavelength band selection) and within a quartz, water-cooled well that was immersed in the photolysis solution. The photolysis solutions were purged with O_2-free N_2 or Ar, both before and during irradiation. Analytical photochemical reactions were conducted in sealed quartz tubes (10 mL) containing solutions purged with Ar or N_2 prior to irradiation and with use of a merry-go-round photoreactor. The reactor was equipped with a quartz well, glass filter, and a 450-W medium-pressure mercury lamp. Photochemical reaction progress was monitored by gas chromatography, TLC, and/or analytical HPLC, and irradiations were stopped at 95–100% completion unless otherwise specified.

The solvents used in the photoreactions were spectrograde: CH_3CN (Baker) or CH_3OH (Baker) unless otherwise specified. 9,10-Dicyanoanthracene was purchased from Eastman Kodak and recrystallized ($CHCl_3$) prior to use. 1,4-Dicyanobenzene and 9-bromophenanthrene were purchased from Aldrich and recrystallized (benzene and ethanol, respectively) prior to use. Triphenylene, oxalyl chloride, PCC, and ethyltriphenylphosphonium bromide were purchased from Aldrich and used without further purification.

Synthetic squences used to prepare aldehydes **8–15**, **53**, **54**, and **56** are described in the supplementary material.

7-[*N*-Methyl-*N*-[(trimethylsilyl)methyl]amino]-3-hepten-2-one (16). A solution containing 1.7 g (5.3 mmol) of (acetylmethylidene)triphenylphosphorane[5] and 1.2 g (4.4 mmol) of 4-[*N*-methyl-*N*-[(trimethylsilyl)-methyl]amino]butanal hydrochloride (prepared by passing HCl gas into a solution of 1.0 g of aldehyde **8** in 10 mL of ether for 10 min at −78 °C, with subsequent concentration of the solution in vacuo) in 10 mL of CH_2Cl_2 was stirred at reflux for 12 h. The mixture was cooled to 25 °C, basified with 30 mL of aqueous NaOH, and extracted with Et_2O. The ethereal extracts were washed with brine, dried, and concentrated in vacuo to give a residue that was subjected to molecular distillation (40–65 °C, 0.05 mm) to yield 0.56 g (56%) of the desired amino enone **16**: ^1H NMR δ 0.02 (s, 9 H, $SiCH_3$), 1.59 (quintet, 2 H, H-6), 1.83 (s, 2 H, $SiCH_2$), 2.16 (s, 3 H, NCH_3), 2.20 (s, 3 H, H-1), 2.21 (m, 2 H, H-4), 2.30 (t, 2 H, H-7), 6.05 (dt, J = 15.9, ca. 1 Hz, 1 H, H-3), 6.79 (dt, J = 15.9, 6.8 Hz, 1 H, H-4); ^{13}C NMR δ −1.33 ($SiCH_3$), 26.2 (C-6), 26.8 (C-1, 30.2 (C-5), 40.0 (NCH_3), 49.7 ($SiCH_2$), 61.7 (C-7), 131.4 (C-3), 148.1 (C-4), 198.4 (C-2); IR 2940, 2775, 1710, 1665, 1575, 1257, 860; EIMS m/e (rel intensity) 227 (M^+, 6), 205 (10), 189 (6), 154 (78), 131 (79), 109 (100), 73 (32); HRMS m/e 227.1705 ($C_{12}H_{25}NOSi$ requires 227.1696).

7-[*N*-Benzyl-*N*-[(trimethylsilyl)methyl]amino]-3-hepten-2-one (17). A solution of 2.1 g (6.6 mmol) of (acetylmethylidene)triphenylphosphorane[5] and 1.3 g (4.5 mmol) of the HCl salt of aldehyde **9** (prepared by purging dry HCl gas into 10 mL of a solution of **9** in CH_2Cl_2 for 10 min at −78 °C, followed by subsequent concentration of the solution in vacuo) in 10 mL of CH_2Cl_2 was stirred at reflux for 12 h, cooled to 25 °C, diluted with ether, and washed with cold aqueous NaOH. The ethereal solution was dried and concentrated in vacuo to give a residue that was subjected to silica gel column chromatography (5% Et_2O–cyclohexane) to yield 0.82 g (61%) of the desired amino enone **17**: ^1H NMR δ 0.02 (s, 9 H, $SiCH_3$), 1.57 (quintet, 2 H, H-6), 1.92 (s, 2 H, $SiCH_2$), 2.16 (s, 3 H, H-1), 2.18 (t, 2 H, H-5), 2.29 (t, 2 H, H-7), 3.45 s, 2 H, benzylic), 5.97 (dt, J = 15.9, 1.4 Hz, 1 H, H-3), 6.68 (dt, J = 15.9, 6.8 Hz, 1 H, H-4), 7.29 (m, 5 H, aromatic); ^{13}C NMR δ −1.3 ($SiCH_3$), 25.8 (C-6), 26.7 (C-1), 29.5 (C-5), 46.1 ($SiCH_2$), 56.3 (benzylic), 62.2 (C-7), 126.8, 128.1, 128.7, and 138.3 (aromatic), 131.3 (C-3), 148.2 (C-4), 198.4 (C-2); IR 3017, 2988, 2956, 2898, 1707, 1671, 1250, 858; EIMS m/e (rel intensity) 303 (M^+, 4), 230 (58), 206, (40), 91 (100), 73 (26); HRMS m/e 303.2018 ($C_{18}H_{29}NOSi$ requires 303.2018).

Methyl 6-[*N*-Methyl-*N*-[(trimethylsilyl)methyl]amino]hex-2-enoate (18). A solution containing 1.5 g (6.8 mmol) of the HCl salt of the aldehyde **8** and 3.4 g (10 mmol) of [(methoxycarbonyl)methylidene]-triphenylphosphorane[6] in 15 mL of CH_2Cl_2 was stirred at reflux for 24 h, cooled to 25 °C, diluted with aqueous NaOH, and extracted with ether. The ethereal extracts were washed with brine, dried, and concentrated by fractional distillation, giving a residue that was subjected to molecular distillation (40–65 °C, 0.05 mm) to yield 1.3 g (61%) of the amino ester **18**: ^1H NMR δ 0.03 (s, 9 H, $SiCH_3$), 1.56 (quintet, 2 H, H-5), 1.82 (s, 2 H, $SiCH_2$), 2.16 (s, 3 H, CH_3N), 2.17 (dt, J = 7.9, 1.5 Hz, 2 H, H-4), 2.26 (t, 2 H, H-6), 3.70 (s, 3 H, CH_3O), 5.82 (dt, J = 15.9, ca. 1 Hz, 1 H, H-2), 6.95 (dt, J = 15.9, 6.8 Hz, 1 H, H-3); ^{13}C NMR δ −1.34 ($SiCH_3$), 26.1 (C-5), 30.0 (C-1), 46.0 (NCH_3), 49.7 ($SiCH_2$), 51.3 (OCH_3), 61.6 (C-6), 121.0 (C-2), 149.4 (C-3), 167.0 (CO); IR 2935, 2840, 2780, 1715, 1457, 1432, 1243, 845; EIMS m/e (rel intensity) 243 (M^+, 8), 228 (8), 170 (100), 130 (73), 119 (35), 84 (60); HRMS m/e 243.1652 ($C_{12}H_{25}NO_2Si$ requires 243.1650).

Methyl 6-[*N*-Benzyl-*N*-[(trimethylsilyl)methyl]amino]hex-2-enoate (19). A solution of 0.41 g (1.4 mmol) of the HCl salt of the aldehyde **9** and 0.70 g (2.1 mmol) of [(methoxycarbonyl)methylidene]triphenylphosphorane[6] was stirred at reflux for 12 h and subjected to the same workup and purification procedures as used for the synthesis of **17**. This provided 0.30 g (68%) of the amino ester **19**: ^1H NMR δ 0.06 (s, 9 H, $SiCH_3$), 1.58 (quintet, 2 H, H-5), 1.94 (s, 2 H, $SiCH_2$), 2.19 (dt, J = 6.9, ca. 1 Hz, 2 H, H-4), 2.33 (t, 2 H, H-6), 3.47 (s, 2 H, benzylic), 3.71 (s, 3 H, OCH_3), 5.77 (dt, J = 15.8, 1.3 Hz, 1 H, H-2), 6.93 (dt, J = 15.8, 6.9 Hz, 1 H, H-3), 7.29 (m, 5 H, aromatic); ^{13}C NMR δ −1.30 ($SiCH_3$), 24.6 (C-5), 25.7 (C-4), 46.0 ($SiCH_2$), 51.2 (OCH_3), 56.4 (benzylic), 62.1 (C-6), 120.9 (C-2), 126.9, 128.0, 128.7, and 139.9 (aromatic), 149.4 (C-3), 167.0 (C-1); IR 3064, 3016, 2953, 2792, 1716, 1670, 1225; EIMS m/e (rel intensity) 319 (M^+, 7), 246 (80), 228 (7), 206 (24), 91 (100), 73 (9); HRMS m/e 319.1972 ($C_{18}H_{29}NO_2Si$ requires 319.1976).

6-[*N*-(Benzyloxycarbonyl)-*N*-[(trimethylsilyl)methyl]amino]-3-hexen-2-one (20). A solution of 0.32 g (1.1 mmol) of the amido aldehyde **10** and 0.54 g (1.7 mmol) of (acetylmethylidene)triphenylphosphorane[5] in 15 mL of CH_2Cl_2 was stirred at reflux for 48 h, diluted with 15 mL of CH_2Cl_2 and 150 mL of cyclohexane, concentrated, and filtered. The filtrate was concentrated in vacuo, giving a residue that was subjected to silica gel chromatography (cyclohexane to 15% Et_2O–cyclohexane) to yield 0.34 g (94%) of the amido enone **20**: ^1H NMR δ −0.03 and 0.07 (s, 9 H, $SiCH_3$), 2.15 and 2.17 (s, 3 H, H-1), 2.43 (broad, 2 H, H-5), 2.73 (s, 2 H, $SiCH_2$), 3.37 (t, 2 H, H-6), 5.10 (s, 2 H, benzylic), 6.02 (d, J = 15.7 Hz, 1 H, H-3), 6.71 (broad, 1 H, H-4), 7.33 (broad, 5 H, benzylic); ^{13}C NMR δ −1.59 ($SiCH_3$), 26.8 (C-1), 31.0 (C-5), 39.1 ($SiCH_2$), 48.2 (C-6), 67.2 (benzylic), 128.0, 128.5, and 137.0 (aromatic), 132.9 (C-3), 143.9 (C-4), 156.0 (benzylic), 197.8 (C-2); IR 2975, 2930, 2880, 1690, 1683, 1675, 1620, 1455, 1240, 1110, 850; CIMS m/e (rel intensity) 334 (M^+ + 1, 13), 227 (3), 211 (3), 135 (11), 119 (6), 91 (22), 85 (39), 69 (100); HRMS m/e 334.1844 (M^+ + 1, $C_{18}H_{28}NO_3Si$ requires 334.1838).

7-[*N*-(Benzyloxycarbonyl)-*N*-[(trimethylsilyl)methyl]amino]-3-hepten-2-one (21). A solution of 0.36 g (1.2 mmol) of the amido aldehyde **11** in 12 mL of CH_2Cl_2 containing 0.56 g (1.8 mmol) of (acetylmethylidene)triphenylphosphorane[5] was stirred at reflux for 5 h, cooled to 25 °C, and concentrated in vacuo, giving a residue that was subjected to silica gel column chromatography (20% Et_2O–CH_2Cl_2) to provide 0.36 mg (86%) of the amido enone **21**: ^1H NMR δ −0.03 and 0.04 (s, 9 H, $SiCH_3$), 1.70 (broad, 2 H, H-6), 2.17 (broad, 5 H, H-1 and -5), 2.73 (s, 2 H, $SiCH_2$), 3.24 (t, 2 H, H-7), 5.07 (s, 2 H, benzylic), 6.03 (dd, J = 15.6, 8.6 Hz, 1 H, H-3), 6.70 (broad, 1 H, H-4), 7.31 (broad, 5 H, aromatic); ^{13}C NMR δ −1.60 ($SiCH_3$), 25.9 and 26.3 (C-6), 26.8 (C-1), 29.5 (C-5), 38.2 and 39.0 ($SiCH_2$), 48.5 and 48.9 (C-7), 67.0 (benzylic), 127.9, 128.4 and 136.9 (aromatic), 131.6 (C-3), 146.9 (C-4), 156.0 (benzylic), 198.1 (C-2); IR 2960, 2920, 2880, 1680, 1665, 1350, 1240, 845; CIMS m/e (rel intensity) 348 (M^+ + 1, 29), 304 (17), 214 (17), 212 (25), 156 (11), 122 (97); HRMS m/e 348.1985 (M^+ + 1, $C_{19}H_{30}NO_3Si$ requires 348.1995).

Methyl 5-[*N*-(Benzyloxycarbonyl)-*N*-[(trimethylsilyl)methyl]amino]-pent-2-enoate (22). A solution containing 0.64 g (2.2 mmol) of the amido aldehyde **10** and 1.1 g (3.3 mmol) of [(methoxycarbonyl)methylidene]-triphenylphosphorane[6] was stirred at reflux for 24 h. The mixture was diluted with cyclohexane, concentrated in vacuo, and filtered. The filtrate was concentrated in vacuo, giving a residue that was subjected to silica gel chromatography (cyclohexane to 15% Et_2O–cyclohexane) to yield 0.69 g (91%) of the amido ester **22**: ^1H NMR δ −0.03 and 0.05 (s, 9 H, $SiCH_3$), 2.42 (broad, 2 H, H-4), 2.74 (s, 2 H, $SiCH_2$), 3.33 (t, 2 H, H-5), 3.70 (s, 3 H, CH_3O), 5.08 (s, 2 H, benzylic), 5.82 (dd, J = 15.7, 10.3 Hz, 1 H, H-2), 6.86 (dt, J = 15.7, 8.3 Hz, 1 H, H-3), 7.32 (broad, 5 H, aromatic); ^{13}C NMR δ −1.62 ($SiCH_3$), 30.7 (C-4), 39.2 ($SiCH_2$), 48.3 (C-5), 51.3 (OCH_3), 67.1 (benzylic), 122.9 (C-2), 127.9, 128.4, and 136.9 (aromatic), 145.3 (C-3), 155.9 (NCO), 166.5 (C-1); IR 2970, 2925, 2875, 1715, 1675, 1450, 1425, 1255, 845; CIMS m/e (rel intensity) 350 (M^+ + 1, 10), 222 (7), 207 (2), 178 (6), 145 (8), 135 (8), 127 (4), 99 (19), 91 (32), 75 (100); HRMS m/e 350.1774 (M^+ + 1, $C_{18}H_{28}NO_4Si$ requires 350.1787).

Methyl 6-[*N*-(Benzyloxycarbonyl)-*N*-[(trimethylsilyl)methyl]amino]-hex-2-enoate (23). A solution of 0.70 g (2.2 mmol) of the amido aldehyde **11** and 1.1 g (3.3 mmol) of [(methoxycarbonyl)methylidene]-triphenylphosphorane[6] in 20 mL of CH_2Cl_2 was stirred at reflux for 78 h, cooled to 25 °C, and concentrated in vacuo, giving a residue that was

subjected to silica gel column chromatography (15% Et_2O–cyclohexane) to yield 0.57 g (71%) of the amino ester **23**: ^1H NMR δ –0.03 and 0.04 (s, 9 H, $SiCH_3$), 1.69 (broad, 2 H, H-5), 2.16 (broad, 2 H, H-4), 2.74 (s, 2 H, $SiCH_2$), 3.23 (t, 2 H, H-6), 3.70 (s, CH_3O), 5.08 (s, 2 H, benzylic), 5.80 (dd, J = 16.2, 6.1 Hz, 1 H, H-2), 6.91 (broad, 1 H, H-3), 7.32 (broad, 5 H, aromatic); ^{13}C NMR δ –1.60 ($SiCH_3$), 26.0 (C-5), 27.4 (C-4), 39.2 ($SiCH_2$), 48.2 (C-6), 51.5 (OCH_3), 67.3 (benzylic), 120.9 (C-3), 127.8, 128.6, and 136.8 (aromatic), 148.4 (C-3), 156.1 (NCO), 167.4 (C-1); IR 2960, 2925, 2885, 1720, 1695, 1678, 1425, 1195, 840, 710; EIMS m/e (rel intensity) 363 (M^+, 0.3), 348 (6), 272 (9), 246 (4), 206 (7), 182 (5), 124 (9), 91 (100), 73 (36); HRMS m/e 363.1888 ($C_{19}H_{29}NO_4Si$ requires 363.1866).

9-[*N*-Benzyl-*N*-[(trimethylsilyl)methyl]amino]-3-nonen-2-one (24). To a solution of 1.5 g (5.0 mmol) of (acetylmethylidene)triphenylphosphorane[5] in 10 mL of CH_2Cl_2 was added 0.9 g (3.1 mmol) of the amino aldehyde **12**, and the resulting mixture was stirred at reflux for 12 h. Concentration in vacuo gave a residue that was subjected to silica gel chromatography (15% Et_2O–hexane) to yield 0.6 g (1.9 mmol, 61%) of the amino enone **24**: ^1H NMR δ 0.03 (s, 9 H, $SiCH_3$), 1.25 (quintet, 2 H, H-7), 1.36 (quintet, 2 H, H-6), 1.43 (quintet, 2 H, H-8), 1.91 (s, 2 H, $SiCH_2$), 2.16 (dt, J = 7.45, 1.4 Hz, 2 H, H-5), 2.21 (s, 3 H, H-1), 2.28 (t, 2 H, H-9), 3.46 (t, 2 H, benzylic), 6.03 (dd, J = 16.0, 1.3 Hz, 1 H, H-3), 6.74 (dt, J = 16.0, 6.9 Hz, 1 H, H-4), 7.29 (m, 5 H, aromatic); ^{13}C NMR δ –1.29 ($SiCH_3$), 26.8 and 26.8 (C-6 and 7), 26.9 (C-1), 28.0 (C-8), 32.4 (C-5), 46.1 ($SiCH_2$), 57.0 (benzylic), 62.3 (C-9), 126.6, 128.1, 128.7, and 140.5 (aromatic), 131.3 (C-3), 148.2 (C-4), 198.4 (C-2); IR 2980, 2920, 2840, 1775, 1660, 1617, 1355, 1250, 1240, 900, 845; EIMS m/e (rel intensity) 331 (M^+, 1), 316 (2), 259 (10), 258 (54), 134 (4), 120 (1), 91 (100), 73 (12); HRMS m/e 331.2330 ($C_{20}H_{33}NOSi$ requires 331.2331).

15-[*N*-Benzyl-*N*-[(trimethylsilyl)methyl]amino]-3-pentadecen-2-one (25). A solution of 1.6 g (5.2 mmol) of (acetylmethylidene)triphenylphosphorane[5] and 1.2 (3.1 mmol) of the aminododecanal **13** in 10 mL of CH_2Cl_2 stirred at reflux for 33 h. The reaction mixture was concentrated in vacuo, giving a residue that was subjected to silica gel chromatography (10% Et_2O–hexane) to yield 0.87 g (68%) of the amino enone **25**: ^1H NMR δ 0.02 (s, 9 H, $SiCH_3$), 1.21 (broad, 14 H, H-7–H-13), 1.42 (m, 4 H, H-6, H-14), 1.89 (s, 2 H, $SiCH_2$), 2.19 (dt, J = 8.2, 1.5 Hz, 2 H, H-5), 2.22 (s, 3 H, H-1), 2.27 (t, 2 H, H-15), 3.44 (s, 2 H, benzylic), 6.03 (dt, J = 15.9, 1.4 Hz, 1 H, H-3), 6.78 (dt, J = 15.9, 6.9 Hz, 1 H, H-4), 7.27 (m, 5 H, aromatic); ^{13}C NMR δ –1.28 ($SiCH_3$), 27.0 (C-1), 26.8, 27.3, 28.1, 29.2 and 29.4 (C-6–C-14), 32.4 (C-5), 46.0 ($SiCH_2$), 57.0 (benzylic), 62.2 (C-15), 126.5, 128.0, 128.7 and 140.5 (aromatic), 131.3 (C-3), 148.4 (C-3), 198.4 (C-2); IR 2970, 2895, 2825, 1680, 1655, 1610, 1350, 1235, 895, 840; EIMS m/e (rel intensity) 415 (M^+, 1), 342 (6), 262 (1), 206 (9), 192 (1), 160 (3), 134 (17), 103 (10), 91 (100); HRMS m/e 415.3271 ($C_{26}H_{45}NOSi$ requires 415.3270).

9-[*N*-(Benzyloxycarbonyl)-*N*-[(trimethylsilyl)methyl]amino]-3-nonen-2-one (26). A solution of 0.52 g (1.6 mmol) of the amido aldehyde **14** in 20 mL of CH_2Cl_2 containing 0.75 g (2.3 mmol) of (acetylmethylidene)triphenylphosphorane[5] was stirred at reflux for 24 h. The reaction mixture was diluted with CH_2Cl_2–cyclohexane, concentrated in vacuo, and filtered. The filtrate was concentrated in vacuo to give a residue that was subjected to silica gel column chromatography (cyclohexane to 25% Et_2O–cyclohexane) to provide 0.57 g (98%) of the amido enone **26**: ^1H NMR δ –0.03 and 0.05 (s, 9 H, $SiCH_3$), 1.28 (broad, 2 H, H-7), 1.50 (broad, 4 H, H-6 and -8), 2.17 (broad, 2 H, H-5), 2.22 (s, 3 H, H-1), 2.73 (s, 2 H, $SiCH_2$), 3.20 (t, 2 H, H-9), 5.08 (s, 2 H, benzylic), 6.0 (d, J = 15.4 Hz, 1 H, H-3), 6.72 (broad, 1 H, H-4), 7.32 (broad, 5 H, aromatic); ^{13}C NMR δ –1.54 ($SiCH_3$), 26.3, 27.5, and 27.9 (C-6, -7, and -8), 26.8 (C-1), 32.2 (C-5), 38.7 ($SiCH_2$), 49.2 (C-9), 66.9 (benzylic), 127.8, 128.0, 128.4 and 137.2 (aromatic), 131.4 (C-3), 147.6 (C-4), 156.1 (NCO), 198.1 (C-2); IR 2970, 2900, 2830, 1680, 1600, 1450, 1240, 900, 840; CIMS m/e (rel intensity) 376 ($M^+ + 1$, 0.2), 107 (1), 99 (5), 91 (11), 75 (100); HRMS m/e 376.2313 ($M^+ + 1$, $C_{21}H_{34}NO_3Si$ requires 376.2308).

15-[*N*-(Benzyloxycarbonyl)-*N*-[(trimethylsilyl)methyl]amino]-3-pentadecen-2-one (27). A solution of 0.21 g (5.0×10^{-1} mmol) of the amido aldehyde **15** and 0.27 g (8.5×10^{-1} mmol) of (acetylmethylidene)triphenylphosphorane[5] in 10 mL of CH_2Cl_2 was stirred at reflux for 24 h. The reaction mixture was concentrated in vacuo, giving a residue that was subjected to silica gel column chromatography (cyclohexane to 15% Et_2O–cyclohexane) to yield 0.17 g (65%) of the amido enone **27**: ^1H NMR δ –0.04 and 0.04 (s, 9 H, $SiCH_3$), 1.23–1.47 (broad, 18 H, H-6–H-14), 2.17 (dt, 2 H, H-5), 2.21 (s, 3 H, H-1), 2.74 (s, 2 H, $SiCH_3$), 3.19 (t, 2 H, H-15), 5.07 (s, 2 H, benzylic), 6.03 (dt, J = 16.0, ca. 1 Hz, 1 H, H-3), 6.77 (dt, J = 16, 6.8 Hz, 1 H, H-4), 7.31 (broad, 5 H, aromatic); ^{13}C NMR δ –1.51 ($SiCH_3$), 26.8 (C-1), 27.8, 28.2, 29.2, 29.4, and 29.5 (C-6–C-14), 32.4 (C-5), 38.6 ($SiCH_2$), 49.5 (C-15), 66.9 (benzylic), 127.8, 128.4, and 137.4 (aromatic), 131.4 (C-3), 148.2 (C-4), 158.2 (NCO), 198.3 (C-2); IR 2970, 2925, 2860, 1712, 1680, 1450, 1427, 1255, 845; CIMS m/e (rel intensity) 460 ($M^+ + 1$, 24), 415 (21), 325 (8), 297 (17), 214 (23), 122 (98), 73 (21); HRMS m/e 460.3159 ($C_{27}H_{46}NO_3Si$ requires 460.3169).

DCA-Sensitized Irradiation of the Amino Enone 16. Preparation of Piperidine 28. A solution (100 mL) of 15% CH_3OH–CH_3CN containing 70 mg (3.1×10^{-1} mmol) of **16** and 15 mg (6.6×10^{-2} mmol) of 9,10-dicyanoanthracene was irradiated with uranium glass filtered light for 4 h. The photolysate was concentrated by fractional distillation to give a residue that was subjected to molecular distillation (40–65 °C, 0.05 mm) to yield 46 mg (96%) of 1-methyl-3-acetonylpiperidine (**28**): ^1H NMR δ 0.83 (ddd, J = 12.8, 11.0, 3.9 Hz, 1 H, H-4_{ax}), 1.56 (m, 4 H, H-2_{ax}, H-4_{eq}, H-5), 1.83 (dd, J = 9.8, 9.8 Hz, 1 H, H-2_{eq}), 2.07 (m, 1 H, H-3), 2.06 (s, 3 H, CH_3CO), 2.15 (s, 3 H, NCH_3), 2.26 (dd, J = 6.8, ca. 1 Hz, 2 H, H_2CCO), 2.63 (d, J = 10.0 Hz, 2 H, H-6); ^{13}C NMR δ 24.8 (C-5), 30.0 (C-3), 30.1 (C-4), 32.1 (CH_3CO), 46.4 (NCH_3), 48.3 (CH_2CO), 55.9 (C-6), 61.5 (C-2); IR 2971, 2940, 2854, 1712, 1466, 1449, 903; EIMS m/e (rel intensity) 155 (M^+, 4), 154 (12), 112 (10), 97 (100); HRMS m/e 155.1279 ($C_9H_{17}NO$ requires 155.1276).

DCA-Sensitized Irradiation of the Amino Enone 17. Preparation of Piperidine 29 and Pyrrolidine 30. A solution containing 61 mg (2.0×10^{-1} mmol) of the amino enone **17** and 7 mg (3.0×10^{-2} mmol) of DCA in 100 mL of 15% CH_3OH–CH_3CN was irradiated with uranium glass filtered light for 1 h. The photolysate was concentrated in vacuo, giving a residue that was subjected to silica gel column chromatography (2% CH_3OH–CH_2Cl_2) to yield 36 mg (78%) of 1-benzyl-3-acetonylpiperidine (**29**) and 2 mg (5%) of the pyrrolidine **30**.

29: ^1H NMR δ 0.92 (ddd, J = 10.5, 12.4, 3.5 Hz, 1 H, H-4 axial), 1.54–1.75 (m, 4 H, H-2 axial, H-4, equatorial, H-5), 1.96 (dd, J = 9.8, 9.8 Hz, 1 H, H-2 equatorial), 2.08 (s, 3 H, CH_3CO), 2.12 (m, 1 H, H-3), 2.27 and 2.34 (d of AB q, J = 7.0, 16.0 Hz, 2 H, CH_2CO), 2.69 (d, J = 9.8 Hz, 2 H, H-6), 3.42 and 3.48 (AB q, J = 13.2 Hz, 2 H, benzylic), 7.27 (m, 5 H, aromatic); ^{13}C NMR δ 24.7 (C-5), 30.2 (C-3), 30.6 (C-4), 32.1 (CH_3CO), 48.3 (CH_2CO), 53.9 (C-6), 59.5 (C-2), 61.5 (benzylic), 126.9, 128.1, 128.9, and 138.5 (aromatic), 207.9 (CO); IR ($CHCl_3$) 3065, 3018, 2936, 2856, 2764, 1710, 1454, 1439 cm^{-1}; EIMS m/z (rel intensity) 231 (M^+, 3), 230 (5), 173 (85), 160 (17), 91 (100), 65 (9); HRMS calcd for $C_{15}H_{21}NO$ 231.1619, found 231.1624.

30: ^1H NMR δ 1.44 (m, 1 H, H-3), 1.66 (m, 3 H, H-3 and 2 H-4), 2.10 (m, 1 H, H-5), 2.13 (s, 3 H, OCH_3), 2.46 (dd, J = 8.2, 16.2 Hz, 1 H, CH_2CO), 2.75 (dd, J = 3.9, 16.2 Hz, 1 H, CH_2CO), 2.86 (m, 2 H, H-2 and H-5), 3.25 and 3.89 (AB q, J = 13.0 Hz, 2 H, benzylic), 7.24 (m, 5 H, aromatic); ^{13}C NMR δ 22.3 (C-4), 30.9 (CH_3CO), 31.0 (C-3), 49.0 (CH_2CO), 53.9 (C-5), 58.8 (C-2), 60.1 (benzylic), 126.9, 128.2, 128.8 and 139.5 (aromatic), 208.3 (CO); IR ($CHCl_3$) 1710 cm^{-1}; EIMS m/z (rel intensity) 217 (M^+, 0.4), 160 (17), 159 (31), 158 (10), 92 (10), 91 (100), 82 (6), 68 (7), 65 (9); HRMS calcd for $C_{14}H_{19}NO$ 217.1467, found 217.1455.

DCN-Sensitized Irradiation of the Amino Enone 17. A solution (100 mL of 15% CH_3OH–CH_3CN in a quartz tube containing 38 mg (1.2×10^{-1} mmol) of the amino enone **17** and 85 mg (4.8×10^{-1} mmol) of DCN was irradiated with uranium glass filtered light for 1.5 h. The photolysate was concentrated in vacuo, giving a residue that was subjected to silica gel column chromatography (25% hexanes in ethyl acetate) to yield 7 mg of the recovered amino enone **17** and 6 mg (26% based on 80% conversion) of piperidine **30**.

Redox Photosensitized Reaction of the Amino Enone 17. A solution (100 mL) of 15% CH_3OH–CH_3CN in a quartz tube containing 31 mg (1.0×10^{-1} mmol) of the amino enone **17**, 128 mg (1.0 mmol) of 1,4-dicyanobenzene, and 230 mg (1.0 mmol) of triphenylene was irradiated with uranium glass filtered light for 1 h. The photolysate was concentrated in vacuo, giving a residue that was subjected to silica gel column chromatography (25% hexanes in ethyl acetate) to yield 3 mg of recovered amino enone **17** and 6 mg (29% based on 90% conversion) of piperidine **30**.

DCA-Sensitized Irradiation of Amino Ester 18. Preparation of Piperidine 31 and Pyrrolidine 32. A solution of (100 mL) of 15% CH_3OH–CH_3CN containing 50 mg (2.1×10^{-1} mmol) of the amino ester **18** and 15 mg (6.6×10^{-2} mmol) of DCA was irradiated with uranium glass filtered light for 4 h. The photolysate was concentrated by fractional distillation, and the residue was subjected to preparative GLC (120 °C, 5 × $^1/_8$ in. 15% SE-30), giving 1-methyl-3-(carbomethoxymethyl)-piperidine (**31**) and 1-methyl-2-(carbomethoxymethyl)pyrrolidine (**32**). The exact yields (**31** in 67% and **32** in 20%) were determined by using GLC and piperonal as an internal standard. The calculated relative ratios obtained were also confirmed by ^1H NMR analysis of the crude photolysates.

31: ^1H NMR δ 0.91 (ddd, J = 12.2, 10.4, 3.6 Hz, 1 H, H-4_{ax}), 1.64 (m, 4 H, H-2_{ax}, H-4_{eq}, H-5), 1.86 (dd, J = 10.6, 8.1 Hz, 1 H, H-2_{eq}), 2.05 (m, 1 H, H-3), 2.20 (q, J = 7.2 Hz, H_2CCO), 2.22 (s, 3 H, NCH_3),

2.74 (t, J = 12.6 Hz, 2 H, H-6); ^{13}C NMR δ 25.1 (C-5), 30.2 (C-4), 33.3 (C-3), 39.1 (CH_2CO), 46.6 (NCH_3), 51.4 (OCH_3), 56.0 (C-6), 61.7 (C-2), 172.6 (CO); IR 2950, 2935, 2806, 1734, 1261; EIMS m/e (rel intensity) 171 (M^+, 26), 170 (13), 140 (18), 98 (13), 71 (23), 58 (100); HRMS m/e 171.0380 ($C_9H_{17}NO_2$ requires 171.0378).

32: ^{1}H NMR δ 1.53 (m, 1 H, H-3), 1.60–1.80 (m, 2 H, H-3 and H-4), 2.04 (m, 1 H, H-4), 2.21 (dt, J = 9.0, ca. 1 Hz, 1 H, H-5), 2.26 (dd, J = 14.9, 8.0 Hz, 1 H, CH_2CO), 2.31 (s, 3 H, NCH_3), 2.49 (ddd, J = 15.8, 9.0, ca. 1 Hz, 1 H, H-5), 2.64 (dd, J = 14.9, 4.2 Hz, 1 H, CH_2CO), 3.03 (ddd, J = 16.0, 9.5, 2.8 Hz, 1 H, H-2), 3.68 (s, 3 H, OCH_3); ^{13}C NMR δ 22.2 (C-4), 31.3 (C-3), 39.3 (CH_2CO), 40.4 (NCH_3), 51.3 (OCH_3), 57.0 (C-5), 62.6 (C-2), 172.6 (CO); IR 2954, 2927, 2869, 1731, 1430, 1221; EIMS m/e (rel intensity) 156 (M^+, 15), 98 (13), 59 (100); HRMS m/e 157.0967 ($C_8H_{15}NO_2$ requires 157.0963).

DCA-Sensitized Irradiation of the Amino Ester 19. Preparation of Piperidine 33 and Pyrrolidine 34. A solution (100 mL) of 15% CH_3OH–CH_3CN containing 64 mg (2.0×10^{-1} mmol) of amino ester **19** and 15 mg (6.6×10^{-2} mmol) of DCA was irradiated with uranium glass filtered light for 1 h. The photolysate was concentrated in vacuo and subjected to silica gel column chromatography (25% Et_2O–hexane) to yield 19 mg (39%) of 1-benzyl-3-(carbomethoxymethyl)piperidine (**33**) and 13 mg (29%) of 1-benzyl-2-(carbomethoxymethyl)pyrrolidine (**34**). The yields (**33**, 67% and **33**, 22%) were determined on the crude photolysate by GLC employing chalcone as an internal standard.

33: ^{1}H NMR δ 0.95 (ddd, J = 19.7, 12.2, 3.9 Hz, 1 H, H-4_{ax}), 1.72 (m, 4 H, H-2_{ax}, H-4_{eq}, H-5), 1.92 (dd, J = 11.3, 8.1 Hz, H-2_{eq}), 2.00 (m, 1 H, H-3), 2.17 (q, J = 7.4 Hz, 2 H, H_2CCO), 2.69 (m, 2 H, H-6), 3.43 (q, J = 13.2 Hz, 2 H, benzylic), 3.59 (s, 3 H, OCH_3), 7.25 (m, 5 H, aromatic); ^{13}C NMR δ 24.7 (C-5), 30.5 (C-4), 33.1 (C-3), 38.9 (CH_2CO), 51.4 (OCH_3), 53.8 (C-6), 59.4 (C-2), 63.3 (benzylic), 127.0, 128.2, 129.7, and 138.5 (aromatic), 173.0 (CO); IR 3029, 3011, 2953, 2937, 2803, 1732, 1439, 1253 cm^{-1}; EIMS m/e (rel intensity) 247 (M^+, 40), 246 (37), 216 (51), 156 (39), 91 (100), 65 (11); HRMS m/e 247.1571 ($C_{15}H_{21}NO_2$ requires 247.1570).

34: ^{1}H NMR δ 1.24 (m, 1 H, H-3), 1.60 (m, 1 H, H-4), 1.67 (m, 2 H, H-3 and -5), 2.04 (m, 1 H, H-4), 2.15 (ddd, J = 16.7, 7.0, ca. 1 H, 1 H, H-5), 2.34 (dd, J = 14.9, 8.7 Hz, 1 H, CH_2CO), 2.65 (dd, J = 14.9, 4.4 Hz, 1 H, CH_2CO), 2.86 (ddd, J = 16.6, 9.4, 3.0 Hz, 1 H, H-2), 3.25 (d, J = 12.9 Hz, 1 H, benzylic), 3.65 (s, 3 H, OCH_3), 3.94 (d, J = 12.9 Hz, 1 H, benzylic), 7.28 (m, 5 H, aromatic); ^{13}C NMR 22.3 (C-4), 31.0 (C-3), 39.7 (CH_2CO), 51.4 (OCH_3), 54.0 (C-5), 58.7 (C-2), 60.8 (benzylic), 126.7, 128.2, 128.8, and 139.7 (aromatic), 173.5 (CO); IR 3021, 2956, 2932, 2874, 1731, 1428, 1215; EIMS m/e (rel intensity) 233 (M^+, 1), 232 (2), 160 (51), 130 (7), 91 (100), 65 (10); HRMS m/e 233.1409 ($C_{14}H_{19}NO_2$ requires 233.1405).

A solution (100 mL) of 15% CH_3OH–CH_3CN containing the same concentrations of the amino ester **19** and DCA as used above was air-saturated by purging with compressed air for 0.5 h before and during irradiation with uranium glass filtered light for 20 min. GLC analysis using chalcone as an internal standard suggested that the reaction produced pyrrolidine **34** in 25% yield and that the piperidine **33** had not formed.

DCA-Sensitized Irradiations of the Amino Ester 19 in Halocarbon Solvents and with Various Concentrations of DCA. Deoxygenated solutions (100 mL) of 5% CH_3OH–CH_2Cl_2 containing 48 mg (1.5×10^{-1} mmol) of the amino ester **19** with 100 mg (4.4 mM), 60 mg (2.6 mM), and 20 mg (8.8×10^{-1} mM) of DCA were irradiated with uranium glass filtered light for 3 h. The photolysates were concentrated in vacuo and the residues obtained were subjected to GLC analysis, giving the following yields of **33** and **34**: 8% of **33** and 88% of **34** (4.4 mM of DCA); and 12% of **33** and 83% of **34** (2.6 mM of DCA).

Deoxygenated solutions (100 mL) of 5% CH_3OH–$CHCl_3$ containing 42 mg (1.2×10^{-1} mmol) of the amino ester **19** with 100 mg (4.4 mM), 63 mg (2.8 mM), 56 (2.4 mM), 40 mg (1.8 mM), and 15 mg (6.6×10^{-1} mM) of DCA were irradiated with uranium glass filtered light for 1 h. GLC analysis of the concentrated photolysates gave the following **33** to **34** ratios: 23.3 (4.4 mM); 15.0 (2.8 mM); 14.8 (2.4 mM); 13.0 (1.8 mM); and 7.3 (6.6×10^{-1} mM).

Deoxygenated solutions (100 mL) of 5% CH_3OH–CH_2Cl_2–$CHCl_3$ (mole fraction of $CHCl_3$: 0.48 and 0.75) containing 35 mg (9.6×10^{-1} mM) of the amino ester **19** and 50 mg (2.2 mM) of DCA were irradiated with uranium glass filtered light for 1.5 h. The photolysates were concentrated and the ratios of **34** to **33** were determined by GLC. The ratios of **34** to **33** were 6.1 and 12.9 when the mole fractions of $CHCl_3$ were 0.48 and 0.75, respectively.

Deoxygenated solutions (100 mL) of 20% CCl_4–CH_2Cl_2 containing 42 mg (1.2×10^{-1} mmol) of the amino ester **19** and 50 mg (2.2 mM) of DCA were irradiated for 5 h with uranium glass filtered light under Ar atmosphere. GLC analysis revealed that the crude photolysate contained only pyrrolidine **34** and no piperidine **33**.

DCA-Sensitized Irradiation of the Amino Ester 19 in Deuterated Solvent Systems. Solutions (10 mL) of 17 mg (5.5×10^{-2} mmol) of amino ester **19** and 5 mg (2.2×10^{-2} mmol) of DCA in 15% CH_3OH–CD_3CN, CH_3OD–CH_3CN, and CD_3OD–CH_3CN were irradiated for 17 h with uranium glass filtered light. The photolysates were concentrated in vacuo and subjected to preparative GLC (170 °C, 5 ft × $^5/_8$ in., 15% SE-30) to separate the piperidine **33**. Deuterium incorporation in **33** was determined with ^{1}H NMR methods by comparing integrals for the α-ester protons at 2.17 ppm to those for other characteristic protons. These methods showed that for the CH_3OH–CD_3CN reaction, non-deuterium-labeled **33** (<10%) was formed and that the CH_3OD–CH_3CN and CD_3OD–CH_3CN reactions generated monodeuterated **33** (>90%). A control experiment in which a solution of 10 mg of **33** in 5 mL of CD_3OD was stirred for 36 h at 25 °C showed that deuterium incorporation does not occur (<10%).

DCN-Sensitized Irradiation of the Amino Ester 19. Preparation of Dimer 35. A deoxygenated solution (10 mL) of 15% CH_3OH–CH_3CN in a quartz tube containing 30.8 mg (9.6×10^{-2} mmol) of the amino ester **19** with 10 mg (5.6 mM) of DCN was irradiated with uranium glass filtered light. The photolysate was concentrated in vacuo and the residue obtained was subjected to Florisil column chromatography (25% hexanes in ethyl acetate), giving 3 mg (10%) of piperidine **33**, 0.5 mg (2%) of pyrrolidine **34**, and 8 mg (18%) of the dimer **35**.

35: ^{1}H NMR δ 0.81 (m, 2 H, H-4), 0.99 (m, 1 H, H-5′), 1.17 (m, 2 H, H-5), 1.20–1.38 (m, 3 H, H-5′, 2 H-4′), 1.56 (m, 1 H, H-3), 1.77 (m, 1 H, H-3′), 1.80–1.88 (m, 4 H, 1 H-2′, 3 CH_2CO_2), 1.88–1.98 (m, 2 H, 1 H-6′, 1 CH_2CO_2), 2.0–2.09 (m, 1 H, H-2), 2.09–2.25 (m, 2 H, H-6), 2.25–2.30 (m, 1 H, H-2), 2.30–2.37 (m, 1 H, H-6′), 2.52 (d, J = 9 Hz, 1 H, H-2′); ^{13}C NMR δ 24.1 (C-5, C-5′), 30.4 (C-4, C-4′), 32.6 (C-3′), 32.8 (C-3), 37.4 and 37.8 (CH_2CO), 49.6 (C-6′), 51.1 (C-6), 51.1 (OCH_3), 54.6 (C-2′), 55.9 (C-2), 69.6 (benzylic), 126.5, 127.3, 129.1, 129.2, 136.8 (aromatic), 173.6 (CO); IR ($CHCl_3$) 3010, 2910, 1720, 1430 cm^{-1}; CIMS m/e (rel intensity) 493 ($M^+ + 1$, 22), 336 (58), 247 (100), 246 (100); HRMS calcd for $C_{30}H_{41}N_2O_4$ 493.3066, found 493.3089.

Redox Photosensitized Reaction of the Amino Ester 19. Preparation of Adduct 36. A deoxygenated solution (100 mL) of 30% CH_3OH–CH_3CN in a quartz tube containing 33 mg (1.0×10^{-1} mmol) of the amino ester **19**, 128 mg (1.0 mmol) of 1,4-dicyanobenzene, and 228 mg (1.0 mmol) of triphenylene was irradiated with uranium glass filtered light for 15 h. The photolysate was extracted with aqueous HCl. The aqueous solution was washed with $CHCl_3$, basified with K_2CO_3, and extracted with ethyl acetate. The ethyl acetate extracts were dried and concentrated in vacuo, giving a residue that was subjected to silica gel column chromatography (25% hexanes in ethyl acetate) to yield 10 mg (39%) of piperidine **33** and 16 mg (44%) of the adduct **36**: ^{1}H NMR δ 1.03 (m, 1 H, H-4), 1.60 (m, 2 H, H-4, H-5), 1.71 (m, 2 H, H-5, H-3), 1.91–2.16 (m, 2 H, CH_2CO_2), 2.20 (m, 2 H, H-6), 2.61 (m, 2 H, H-2), 3.56, 3.58 (s, 3 H, OCH_3), 4.28 (s, 1 H, benzylic), 7.16–7.31 (m, 5 H, aromatic), 7.48–7.56 (m, 4 H, aromatic); ^{13}C NMR δ 24.7 (C-5), 30.5 (C-4), 33.2 (C-3), 38.5, 38.6 (CH_2CO_2), 51.4 (OCH_3), 52.1, 52.7 (C-6), 57.3, 57.9 (C-2), 75.7 (benzylic), 118.9 (CN), 110.6, 127.4, 128.0, 128.5, 128.7, 128.9, 132.3, 141.2, 148.8 (aromatic), 173.0 (CO_2); IR ($CHCl_3$) 2915, 2210, 1720, 1600, 1430, 1620, 1120 cm^{-1}; EIMS m/e (rel intensity) 348 (M^+, 2), 271 (14), 246 (10), 156 (6), 91 (100); HRMS calcd for $C_{22}H_{24}O_2N_2$ 348.1838, found 348.1830.

7-[*N*-Benzyl-*N*-[(trimethylsilyl)methyl]amino]-3-heptene (37). To a stirred suspension of 1.6 g (5.9 mmol) of *n*-propyltriphenylphosphonium bromide (Aldrich) in 20 mL of dry ether was added 2.82 mL of *n*-butyllithium (2 M in cyclohexane). The resulting deep red solution was cooled to 0 °C, and a solution of 0.74 g (2.9 mmol) of the aldehyde **9** in 10 mL of dry ether was added while maintaining the bath temperature at 0 °C. The reaction mixture was stirred for 12 h at 25 °C, diluted with 100 mL of ether, and washed with water. The ethereal layer was dried and concentrated in vacuo to give a residue that was subjected to silica gel column chromatography (hexane) to yield 0.58 g (73%) of amino olefin **37**: ^{1}H NMR δ 0.04 (s, 9 H, $SiCH_3$), 0.93 (t, J = 7.5 Hz, 3 H, H-1), 1.49 (q, J = 7.6 Hz, 2 H, H-6), 1.92 (s, 2 H, $SiCH_2$), 2.00 (m, 4 H, H-2 and -5), 2.32 (t, J = 7.7 Hz, 2 H, H-7), 3.47 (s, 2 H, benzylic), 5.31 (m, 2 H, H-3 and -4), 7.30 (m, 5 H, aromatic); ^{13}C NMR δ −1.29 ($SiCH_3$), 14.3 (C-1), 20.5 (C-2), 25.0 (C-6), 27.4 (C-5), 46.1 ($SiCH_2$), 57.1 (benzylic), 62.3 (C-7), 126.6 (C-3), 131.4 (C-4), 128.0, 128.7, 129.1, and 140.6 (aromatic); IR 3078, 3060, 2945, 2780, 1488, 1448, 1240; EIMS m/e (rel intensity) 289 (M^+, 2), 262 (1), 216 (23), 206 (10), 198 (4), 134 (4), 116 (4), 91 (100), 73 (27); HRMS m/e 289.2236 ($C_{18}H_{31}NSi$ requires 289.2245).

Irradiation of the Amino Olefin 37. Preparation of Aminoheptenes 39–39 and Adduct 40. A 100-mL solution of 15% CH_3OH–CH_3CN containing 89 mg (3.1×10^{-1} mmol) of the amino olefin **37** and 15 mg (6.6×10^{-2} mmol) of DCA was irradiated with uranium glass filtered

light for 2 h. The photolysate was concentrated in vacuo, giving a residue that was dissolved in 100 mL of CH_2Cl_2 and washed with aqueous NaOH. The organic layer was dried and concentrated in vacuo to give a residue that was subjected to silica gel column chromatography (1.5% CH_3OH–CH_2Cl_2) to yield 34 mg (49%) of 7-(*N*-benzylamino)-3-heptene (**38**), a trace amount of the known[13] 7-(*N*-benzyl-*N*-methylamino)-3-heptene (**39**), and 29 mg (6.9×10^{-2} mmol, 20%) of the adduct **40**.

38: ^{1}H NMR δ 0.93 (t, 3 H, H-1), 1.56 (quintet, 2 H, H-6), 1.96 (m, 4 H, H-2 and -5), 2.63 (t, 2 H, H-7), 3.77 (s, 2 H, benzylic), 5.35 (m, 2 H, H-3 and -4), 7.29 (m, 5 H, aromatic); ^{13}C NMR δ 14.0 (C-1), 22.4 (C-2), 24.9 (C-6), 30.3 (C-5), 54.0 (benzylic), 65.3 (C-7), 126.9 (C-3), 132.1 (C-4), 128.1, 128.4, 128.6, 140.6 (aromatic); IR 3560–3360, 3013, 2960, 2927, 2855, 1496, 1462, 1265; EIMS *m/e* (rel intensity) 203 (M^+, 1), 192 (1), 160 (6), 146 (5), 120 (24), 91 (99), 84 (100); HRMS *m/e* 203.1669 ($C_{14}H_{21}N$ requires 203.1673).

40: ^{1}H NMR δ 0.94 (dt, J = 7.5, 2.2 Hz, 2 H, H-1), 1.58 (quintet, 2 H, H-6), 2.03 (m, 4 H, H-2 and -5), 2.59 (dd, J = 13.8, 5.7 Hz, 2 H, H-7), 3.41 (d, J = 1.5 Hz, 2 H, benzylic), 3.63 (d, J = 1.6 Hz, 2 H, $DCACH_2$), 5.37 (m, 2 H, H-3 and -4), 7.31 (m, 5 H, aromatic), 7.84, 8.49 (m, 8 H, anthracenyl); ^{13}C NMR δ 14.0 (C-1), 20.5 (C-2), 24.7 (C-6), 27.0 (C-4), 53.3, 53.7 (benzylic and $AntCH_2$), 58.3 (C-7), 115.7 (CN), 127.8 (C-3), 132.3 (C-4), 111.8, 114.7, 126.4, 128.6, 129.1, 129.9, 130.8, 132.6, 133.1, 134.3, 137.4 (aromatic); IR 3075, 3025, 2975, 2920, 1525, 1430, 1220; EIMS *m/e* (rel intensity) 418 (M^+, 0.08), 293 (4), 265 (1), 228 (85), 203 (12), 149 (74), 91 (100); HRMS *m/e* 418.2416 ($C_{30}H_{30}N_2$ requires 418.2409).

DCA-Sensitized Irradiation of the Amido Enone 20. Preparation of Pyrrolidine 41. A solution of 53 mg (1.6×10^{-1} mmol) of the amido enone **20** and 20 mg (8.9×10^{-2} mmol) of DCA in CH_3CN was irradiated with uranium glass filtered light for 3 h. The photolysate was concentrated in vacuo and subjected to the same workup procedure used for the purification of **43** with CH_2Cl_2 and cyclohexane. The filtrate was concentrated in vacuo to yield 41 g (99%) of 1-(benzyloxycarbonyl)-3-acetonylpyrrolidine (**41**). The photolysate from a separate irradiation of 46 mg (1.4×10^{-1} mmol) of the amido enone **20** and 17 mg (7.3×10^{-2} mmol) of DCA in 100 mL of CH_3CN after workup was subjected to silica gel column chromatography ($CHCl_3$), giving 30 mg (83%) of **41**: ^{1}H NMR δ 1.47 (broad, 1 H, H-4_a), 2.06 (broad, 1 H, H-4_b), 2.12 (s, 3 H, CH_3CO), 2.51 (m, 2 H, CH_2CO), 2.57 (broad, 1 H, H-3_b), 2.92 (ddd, J = 19.1, 10.6, 8.5 Hz, 1 H, H-2_a), 3.34 (broad, 1 H, H-5_a), 3.49 (broad, 1 H, H-5_b), 3.66 (ddd, J = 10.6, 6.8, ca. 1 Hz, H-2_b), 5.10 (s, 2 H, benzylic), 7.34 (m, 5 H, aromatic); ^{13}C NMR δ 30.1 (CH_3CO), 30.8 and 31.5 (C-4), 33.3 and 34.2 (C-3), 45.3 and 45.6 (C-5), 46.8 (CH_2CO), 51.1 and 51.4 (C-2), 66.7 (benzylic), 127.9, 128.4, and 137.1 (aromatic), 154.8 (NCO). 206.8 (CH_3CO); IR 3010, 2925, 2855, 1715, 1710, 1680, 1665, 1440, 1420, 1350, 1115, 900; CIMS *m/e* (rel intensity) 262 (M^+ + 1, 100), 218 (31), 203 (13), 170 (10), 154 (7), 126 (8), 91 (42), 69 (69); HRMS *m/e* 262.1442 (M^+ + 1, $C_{15}H_{20}NO_3$ requires 262.1443).

DCA-Sensitized Irradiation of the Amido Enone 21. Preparation of Piperidine 42. A solution (100 mL) of 59 mg (1.7×10^{-1} mmol) of the amido enone **21** and 14 mg (6.0×10^{-2} mmol) of DCA in CH_3CN was irradiated with uranium glass filtered light for 3.5 h. Concentration of the photolysate in vacuo gave a residue that was subjected to the same procedure used for the purification of **43** with CH_2Cl_2 and cyclohexane. The filtrate was concentrated in vacuo, giving an oil (37 mg, 87%) that NMR analysis showed was pure (>90%) 1-(benzyloxycarbonyl)-3-acetonylpiperidine (**42**). This material was subjected to alumina column chromatography (CH_2Cl_2) to yield 32 mg (75%) of the pure **42**: ^{1}H NMR 1.14 and 1.50 (broad, 2 H, H-4), 1.63 and 1.79 (broad, 2 H, H-5), 2.09 (broad, 3 H, CH_3CO), 2.28 (dd, J = 11.3, 7.4 Hz, 2 H, CH_2CO), 2.37 (broad, 1 H, H-3), 2.70 and 2.96 (broad, 2 H, H-2), 3.87 (broad, 2 H, H-6), 5.11 (broad, 2 H, benzylic), 7.35 (m, 5 H, aromatic); ^{13}C NMR δ 24.2 (C-5), 30.3 (C-3), 30.4 (C-4), 44.5 (C-6), 46.9 (CH_2CO), 49.2 (C-2), 67.0 (benzylic), 127.8, 128.5, and 136.9 (aromatic), 155.3 (NCO), 207.0 (CH_3CO); IR 2975, 2900, 2830, 1715, 1695, 1665, 1420, 1350, 910, 680; EIMS *m/e* (rel intensity) 217 (M^+ – 58, 25), 173 (20), 140 (5), 91 (100), 73 (5); HRMS *m/e* 273.1523 ($C_{16}H_{21}NO_3$ requires 273.1521).

DCA-Sensitized Irradiation of the Amido Ester 22. Preparation of Pyrrolidine 43. A solution (100 mL) of CH_3CN containing 111 mg (3.2×10^{-1} mmol) of the enoate **22** and 34 mg (1.5×10^{-1} mmol) of DCA was irradiated with uranium glass filtered light for 9 h. The photolysate was concentrated in vacuo to give a residue that was dissolved in CH_2Cl_2–cyclohexane and again concentrated in vacuo and filtered. The filtrate was concentrated in vacuo to provide 90 mg (100%) of an oil that was shown by ^{1}H NMR analysis to be pure (>90%) 1-(benzyloxycarbonyl)-3-carbomethoxypyrrolidine (**43**). The photolysate from the separate irradiation of 60 mg (1.7×10^{-1} mmol) of the amido ester with 28 mg (1.2×10^{-1} mmol) of DCA was subjected to the silica gel column chromatography (CH_2Cl_2) to yield 42 mg (88%) of the pyrrolidine **43**: ^{1}H NMR δ 1.59 (m, 1 H, 4-H_a), 2.09 (m, 1 H, 4-H_b), 2.39 (m, 2 H, CH_2CO), 2.57 (m, 1 H, H-3_b), 3.00 (ddd, J = 17.5, 10.7, 7.0 Hz, H-2_a), 3.36 (dddd, J = 17.6, 10.7, 8.8, ca. 1 Hz, H-5_a), 3.52 (dddd, J = 17.6, 10.8, 8.6, 3.7 Hz, 1 H, H-5_b), 3.66 (s, 3 H, OCH_3), 3.67 (m, 1 H, H-2_b), 5.08 (s, 2 H, benzylic), 7.35 (m, 5 H, aromatic); ^{13}C NMR δ 30.8 and 31.5 (C-4), 34.5 and 35.3 (C-3), 37.3 (CH_2CO), 45.3 and 45.7 (C-5), 51.0 and 51.4 (C-2), 51.7 (OCH_3), 66.8 (benzylic), 127.9, 128.4, and 137.1 (aromatic), 154.8 (NCO), 172.3 (CH_2CO); IR 3110, 2925, 2860, 1720, 1660, 1410, 1350, 1110; CIMS *m/e* (rel intensity) 288 (M^+ + 1, 10), 176 (2), 158 (1), 135 (7), 119 (6), 91 (28), 75 (87), 69 (100); HRMS *m/e* 278.1398 (M^+ + 1, $C_{15}H_{20}NO_4$ requires 278.1392).

DCA-Sensitized Irradiation of the Amido Ester 23. Preparation of Piperidine 44 and Formamide 45. A solution (100 mL) of 89 mg (2.5×10^{-1} mmol) of the amido ester **23** and 19 mg (8.3×10^{-2} mmol) of DCA in CH_3CN was irradiated with uranium glass filtered light. The photolysate was concentrated in vacuo to give a residue that was shown by GLC analysis (piperonal as internal standard) to contain 1-(benzyloxycarbonyl)-3-(carbomethoxymethyl)piperidine (**44**), formed in 90% yield. The residue was subjected to silica gel column chromatography (10–30% Et_2O–cyclohexane) to yield 54 mg (78%) of the piperidine **44**: ^{1}H NMR δ 1.18 and 1.47 (broad, 2 H, H-4), 1.83 and 1.98 (broad, 2 H, H-5), 2.16 (dd, J = 15.3, 7.3 Hz, 2 H, CH_2CO), 2.24 (broad, 1 H, H-3), 2.64 and 2.88 (broad, 2 H, H-2), 3.62 (broad, 3 H, CH_3O), 3.91 and 3.94 (broad, 2 H, H-6), 5.10 (broad, 2 H, benzylic), 7.33 (m, 5 H, aromatic); ^{13}C NMR δ 24.5 (C-4), 30.5 (C-5), 32.8 (C-3), 38.0 (CH_2CO), 44.5 (C-6), 49.3 (C-2), 51.5 (CH_3O), 67.0 (benzylic), 127.8, 127.9, 128.5, and 137.0 (aromatic), 155.3 (NCO), 172.4 (CO); IR 2980, 2910, 2830, 1720, 1675, 1665, 1423, 1253, 1227, 1200, 1155, 760; EIMS *m/e* (rel intensity) 291 (M^+, 3) 246 (13), 216 (14), 200 (100), 184 (22), 137 (26), 156 (69); HRMS *m/e* 291.1468 ($C_{16}H_{21}NO_4$ requires 291.1470).

An air-saturated 100-mL CH_3CN solution containing 44 mg (1.2×10^{-1} mmol) of the amido ester **23** and 20 mg (8.8×10^{-2} mmol) of DCA was irradiated with uranium glass filtered light for 4 h and concentrated in vacuo, giving a residue that was subjected to silica gel column chromatography (cyclohexane to 10% Et_2O–cyclohexane) to yield 31 mg (85%) of methyl 6-[*N*-(benzyloxycarbonyl)-*N*-formylamino]hexen-2-oate (**45**): ^{1}H NMR δ 1.68 (quintet, 2 H, H-5), 2.17 (dt, J = 6.8, 1.4 Hz, 2 H, H-4), 3.64 (t, 2 H, H-6), 3.70 (s, 2 H, CH_3O), 5.28 (s, 2 H, benzylic), 5.81 (dt, J = 15.6, 1.5 Hz, 1 H, H-2), 6.89 (dt, J = 15.6, 6.8 Hz, 1 H, H-3), 7.36 (s, 5 H, aromatic), 9.21 (s, 1 H, COH); ^{13}C NMR δ 26.7 (C-5), 29.3 (C-4), 40.4 (C-6), 51.3 (OCH_3), 69.0 (benzylic), 121.8 (C-2), 128.4, 128.8, and 134.8 (aromatic), 147.5 (C-3), 153.8 (NCO), 162.6 (HCO), 166.8 (C-1); IR 3010, 2990, 2905, 1705, 1690, 1440, 1410, 1220, 1165, 1040, 770; EIMS *m/e* (rel intensity) 305 (M^+, 0.2), 228 (2), 206 (1), 167 (3), 138 (3), 124 (2), 111 (4), 107 (7), 91 (100); HRMS *m/e* 305.1277 ($C_{16}H_{19}NO_5$ requires 305.1263).

DCA-Sensitized Irradiation of the Amino Enone 24. Preparation of Aminononenone 46 and Hydroazepine 47. A solution (100 mL) of 15% CH_3OH–CH_3CN containing 80 mg (2.4×10^{-1} mmol) of the amino enone **24** and 15 mg (6.6×10^{-2} mmol) of DCA was irradiated with uranium glass filtered light for 5 h. The photolysate was concentrated in vacuo, giving a residue that was dissolved in 5 N HCl. The aqueous solution was extracted with $CHCl_3$, made basic with aqueous NaOH, and extracted with ether. The ethereal extracts were dried and concentrated in vacuo, giving a residue that was subjected to silica gel column chromatography (CH_2Cl_2 to 2.5% CH_3OH–CH_2Cl_2) to yield 9.0 mg (15%) of 9-(*N*-benzyl-*N*-methylamino)-3-nonen-2-one (**46**) and 4 mg (7%) of 2-acetonyl-1-benzylhexahydroazepine (**47**).

46: ^{1}H NMR δ 1.45 (m, 6 H, H-6, -7, and -8), 2.16 (dt, 2 H, H-5), 2.17 (s, 3 H, NCH_3), 2.24 (s, 3 H, H-1), 2.36 (t, 2 H, H-9), 3.49 (s, 2 H, benzylic), 6.05 (dd, J = 16.0, 1.3 Hz, 1 H, H-3), 6.77 (dt, J = 16.0, 7.0 Hz, 1 H, H-4), 7.29 (m, 5 H, aromatic); ^{13}C NMR δ 26.7, 26.7 (C-6 and -7), 27.2 (C-1), 30.7 (C-8), 32.2 (C-5), 41.9 (NCH_3), 56.9 (benzylic), 62.0 (C-9), 126.5, 128.0, 128.7, and 140.4 (aromatic), 131.3 (C-3), 148.2 (C-4), 198.5 (C-2); IR 3024, 3019, 2933, 1692, 1671, 1219; EIMS *m/e* (rel intensity) 259 (M^+, 1), 245 (0.2), 206 (1), 188 (11), 160 (2), 134 (39), 120 (3), 91 (100), 65 (7); HRMS *m/e* 259.1949 ($C_{17}H_{25}NO$ requires 259.1936).

47: ^{1}H NMR δ 1.40–1.67 (m, 8 H, H-3–H-6), 2.09 (s, 3 H, CH_3CO), 2.40 and 2.66 (dd, J = 15.1, 5.9 Hz, 2 H, CH_2CO), 2.60 and 2.76 (m, 2 H, H-7), 3.42 (m, 1 H, H-1), 3.66 and 3.80 (AB quartet, J = 13.9 Hz, benzylic), 7.33 (m, 5 H, aromatic); ^{13}C NMR δ 26.8, 28.6, 29.4, and 34.8 (C-3–C-6), 33.6 (CH_3CO), 50.1 (C-7), 50.7 (CH_2CO), 56.1 (benzylic), 60.3 (C-2), 128.0, 129.4, 129.8, and 132.8 (aromatic), 208.0 (CO); IR 3010, 2920, 2855, 1705, 1665, 1450, 1360, 1205; EIMS *m/e* (rel intensity) 245 (M^+, 1), 188 (44), 134 (3), 120 (4), 91 (100); HRMS *m/e* 245.1782 ($C_{16}H_{23}NO$ requires 245.1781).

Irradiation of 50 mg (1.5×10^{-1} mmol) of the amino enone **24** and 12 mg (5.2×10^{-2} mmol) of DCA in 100 mL of CH_3OH was conducted with use of the same procedure as above for 3 h and yielded 12 mg (35%)

of the azepine **47** as a single product after silica gel column chromatography (CH_2Cl_2 to 60% EtOAc–CH_2Cl_2).

DCA-Sensitized Irradiation of the Amino Enone 25. Preparation of Aminopentadecenones 48 and 49. A solution (100 mL) of 15% CH_3OH–CH_3CN containing 60 mg (1.5×10^{-1} mmol) of the amino enone **25** and 15 mg (6.6×10^{-2} mmol) of DCA was irradiated with uranium glass filtered light for 2 h. The photolysate was concentrated in vacuo, giving a residue that was subjected to silica gel column chromatography (0.3–1.0% CH_3OH–CH_2Cl_2) to provide 12 mg (24%) of 15-(*N*-benzylamino)-3-pentadecen-2-one (**48**) and 19 mg (40%) of 15-(*N*-benzyl-*N*-methylamino)-3-pentadecen-2-one (**49**). Irradiation of 60 mg of the amino enone **25** and 15 mg of DCA in 100 mL of CH_3OH was also performed with uranium glass filtered light for 7 h. Silica gel column chromatography with same solvent system as above provided 19 mg (40%) of the amine **48** and a trace amount of amine **49**.

48: ^{1}H NMR δ 1.23 (broad, 14 H, H-7–H-13), 1.43 and 1.50 (m, 4 H, H-6 and -14), 2.18 (dt, J = 8.7, 1.1 Hz, 2 H, H-5), 2.22 (s, 3 H, H-1), 2.60 (t, 2 H, H-15), 3.77 (s, 2 H, benzylic), 6.04 (dt, J = 15.9, 1.4 Hz, 1 H, H-3), 6.78 (dt, J = 15.9, 7.0 Hz, 1 H, H-4), 7.30 (m, 5 H, aromatic); ^{13}C NMR δ 27.3 (C-1), 28.1, 29.2, 29.3, 29.5, and 30.0 (C-6–C-14), 32.4 (C-5), 49.4 (C-15), 54.0 (benzylic), 126.9, 128.1, 128.4, and 138.0 (aromatic), 131.3 (C-3), 148.4 (C-4), 199.4 (C-2); IR 3550–3140, 2970, 2900, 2825, 1700, 1660, 1240; EIMS m/e (rel intensity) 329 (M^+, 0.05), 293 (2), 246 (2), 167 (2), 149 (19), 134 (7), 120 (68), 106 (44), 91 (100); HRMS m/e 329.2719 ($C_{22}H_{35}NO$ requires 329.2718).

49: ^{1}H NMR δ 1.24 (broad, 14 H, H-7–H-13), 1.51 (m, 4 H, H-6 and -14), 2.19 (s, 3 H, NCH_3), 2.20 (dt, J = 8.1, 1.7 Hz, 2 H, H-5), 2.22 (s, 3 H, H-1), 2.36 (t, 2 H, H-15), 3.49 (s, 2 H, benzylic), 6.04 (dt, J = 15.9, 1.3 Hz, 1 H, H-3), 6.78 (dt, J = 15.9, 6.9 Hz, 1 H, H-4), 7.29 (m, 5 H, aromatic); ^{13}C NMR δ 27.3 (C-1), 28.2, 29.3, 29.4, and 29.5 (C-6–C-14), 32.0 (C-5), 42.1 (NCH_3), 57.7 (benzylic), 62.3 (C-15), 126.6, 128.2, 128.7, and 139.0 (aromatic), 131.1 (C-3), 140.4 (C-3), 198.3 (C-2); IR 2910, 2900, 2825, 1720, 1678, 1250, 895; EIMS m/e (rel intensity) 343 (M^+, 1), 190 (1), 149 (5), 134 (100), 120 (8), 106 (3), 91 (79); HRMS m/e 343.2842 ($C_{23}H_{37}NO$ requires 343.2875).

DCA-Sensitized Irradiation of the Amido Enone 26. Preparation of Adduct 51. A CH_3CN solution (100 mL) of 63 mg (1.7×10^{-1} mmol) of the amido enone **26** and 40 mg (1.7×10^{-1} mmol) of DCA was irradiated for 5 h with uranium glass filtered light. The photolysate was subjected to the same workup procedure as used for the purification of **35**. The filtrate was concentrated in vacuo to give a residue that was subjected to silica gel column chromatography (cyclohexane to 20% Et_2O–cyclohexane) to give 81 mg (88%) of adduct **51**: ^{1}H NMR δ 1.20–1.78 (broad, 6 H, H-6, -7, and -8), 2.20 (m, 2 H, H-5), 2.22 (s, 3 H, H-1), 3.61 (m, 2 H, H-9), 4.40–5.54 (m, 6 H, benzylic and NCH_2), 6.00 (broad, 1 H, H-3), 6.72 (broad, 1 H, H-4), 7.03–7.84 (m, 13 H, aromatic); ^{13}C NMR δ 26.3, 27.5, and 27.9 (C-6, -7, and -8), 29.2 (C-5), 31.6 (C-1), 35.3 and 37.2 (10-DCA), 40.9 (DCACH_2N), 49.0 and 49.3 (9-DCA), 67.4 and 68.8 (benzylic), 117.5–139.0 (aromatics and CN), 131.4 (C-3), 147.5 (C-4), 156.1 (NCO), 198.5 (C-2); IR 2985, 2910, 2840, 1695, 1680, 1445, 1255, 1080; FABMS m/e (rel intensity) 532.409 (M^+ + 1, 0.2), 317 (0.1), 304 (15), 286 (100), 228 (27), 168 (5), 91 (23). Because of the adduct's instability at high temperature, HRMS measurements were not made.

DCA-Sensitized Irradiation of the Amido Enone 27. Preparation of Adduct 52. A solution (100 mL) of the amido enone **27** (90 mg, 2.0×10^{-1} mmol) and 45 mg (2.0×10^{-1} mmol) of DCA in CH_3CN was irradiated with uranium glass filtered light. The photolysate was subjected to the same workup procedure used for the purification of **43**, giving an oil (108 mg, 1.8×10^{-1} mmol, 90%) that NMR analysis showed was pure (>95%) adduct **52**: ^{1}H NMR δ 1.00–1.78 (m, 18 H, H-6–H-14), 2.18 (t, 2 H, H-5), 2.21 (s, 3 H, H-1), 3.60 (m, 2 H, H-15), 3.75–5.53 (m, 5 H, benzylic and NCH_2), 6.00 (dt, J = 16, ca. 1 Hz, H-3), 6.77 (dt, J = 16, 6.8 Hz, 1 H, H-4), 7.02–7.85 (m, 13 H, aromatics); ^{13}C NMR δ 26.5, 26.6, 26.9, 28.1, 29.1, and 29.4 (C-6–C-14), 26.7 (C-1), 32.3 (C-5), 36.4 (10-DCA), 40.9 (DCACH_2N), 48.9 and 49.1 (9-DCA), 67.4 (benzylic), 121.1–137.1 (aromatics and CN), 131.3 (C-3), 148.1 (C-4), 156.2 (NCO), 198.2 (C-2); IR 2985, 2910, 2835, 1682, 1660, 1455, 1407, 1250, 1085; FABMS m/e (rel intensity) 402 (45), 388.493 (M^+ – DCA, 100), 358 (100), 345 (19), 280 (15), 268 (24), 266 (42), 248 (92), 228 (DCA, 10). Because of the adduct's instability at high temperature, HRMS measurements were not made.

Pyrolysis of the DCA Adduct 52. Preparation of Aminopentadecenone 50. Neat **52** (25 mg, 4.1×10^{-2} mmol) was heated at 200 °C for 2 min, cooled, dissolved in cyclohexane, and filtered to remove DCA. The filtrate was concentrated in vacuo, giving an oil (15 mg, 92%) characterized as pure (>95%) **50**: ^{1}H NMR δ 1.00–1.78 (m, 18 H, H-6–H-14), 2.17 (t, 2 H, H-5), 2.23 (s, 6 H, H-1 and NCH_3), 3.60 (m, 2 H, H-15), 3.75–4.85 (m, 2 H, NCH_2), 5.02–5.27 (m, 2 H, benzylic), 6.05 (dt, J = 16, ca. 1 Hz, H-3), 6.77 (dt, J = 16, 6.6 Hz, 1 H, H-4), 7.35 (m, 5 H, aromatic); ^{13}C NMR 26.5, 26.7, 28.1, 29.0, and 29.4 (C-6–C-14), 26.7 (C-1), 30.8 (NCH_3), 32.5 (C-5), 67.5 (benzylic), 128.5–138.0 (aromatic), 156.6 (NCO), 202.5 (C-2); IR 2930, 2860, 1695, 1460, 1265, 1095; EIMS m/e (rel intensity) 387 (M^+, 7), 386 (26), 243 (18), 285 (6), 252 (7), 220 (100), 147 (6), 91 (18); HRMS m/e 388.2853 (M^+ + 1, 388.2851).

2-[*N*-(Benzyloxycarbonyl)-*N*-[(trimethylsilyl)methyl]amino]-1-(1′-cyclohexenyl)-1-ethanol (55). To a solution of the amido aldehyde **53** (0.41 g, 2.6 mmol) in 25 mL of dry THF was added a THF solution of 7.8 mL (ca. 3.9 mmol) of cyclohexenylmagnesium bromide at −78 °C. The resulting solution was stirred for 3 h at −15 °C, quenched with saturated aqueous NH_4Cl, and extracted with ether. The ethereal extracts were dried and concentrated in vacuo to give a residue that was subjected to Florisil column chromatography (15% Et_2O–cyclohexane) to yield 0.72 g (85%) of the allylic alcohol **55**: ^{1}H NMR δ −0.05 and 0.03 (s, 9 H, $SiCH_3$), 1.53 (broad, 4 H, H′-4 and -5), 1.97 (broad, 4 H, H′-3 and -6), 2.86 (m, 2 H, $SiCH_2$), 3.12–3.54 (m, 2 H, H-2), 4.21 (broad, 1 H, H-1), 5.09 (s, 2 H, benzylic), 5.64 and 5.73 (broad, 1 H, H′-2), 7.31 (m, 5 H, aromatic); ^{13}C NMR δ −1.55 ($SiCH_3$), 22.0, 22.3, 23.7, and 27.6 (C′-3–C′-6), 40.7 ($SiCH_2$), 55.9 (C-2), 67.5 (benzylic), 72.1 (C-1), 128.1 and 136.8 (aromatic), 138.5 (C′-1), 156.1 (NCO); IR 3600–3200, 2985, 2910, 2840, 1680, 1450, 1240, 1085, 845; CIMS m/e (rel intensity) 362 (M^+ + 1, 48), 354 (2), 344 (80), 334 (2), 318 (4), 310 (2), 280 (100), 266 (4), 254 (18), 238 (19), 163 (27), 91 (13); HRMS m/e 362.2152 (M^+ + 1, $C_{20}H_{32}NO_3Si$ requires 362.2151).

2-[*N*-Benzyl-*N*-[(trimethylsilyl)methyl]amino]-1-(1′-cyclohexenyl)-1-ethanol (57). To 1.5 g (6.1 mmol) of the amino aldehyde **54** in 30 mL of THF was added a solution of 15 mL (7.5 mmol) of cyclohexenylmagnesium bromide at −78 °C, and the resulting solution was stirred for 3 h at −15 °C. The reaction was quenched by addition of water, and the mixture was extracted with ether. The ethereal extracts were dried and concentrated in vacuo, giving a residue that was subjected to alumina column chromatography (10% Et_2O–cyclohexane) to yield 1.9 g (98%) of the amino alcohol **62**: ^{1}H NMR δ 0.06 (s, 9 H, $SiCH_3$), 1.56 (m, 6 H, H′-3, -4, and -5), 1.94 (m, 2 H, H′-6), 2.15 (AB quartet, 2 H, $SiCH_2$), 2.27 and 2.56 (t, 2 H, H-2), 3.58 (AB quartet, 2 H, benzylic), 4.00 (dd, 1 H, H-1), 5.68 (s, 1 H, H′-2), 7.32 (m, 5 H, aromatic); ^{13}C NMR δ −1.31 ($SiCH_3$), 21.8, 22.2, 24.0, and 25.0 (C′-3–C′-6), 46.5 ($SiCH_2$), 61.9 (C-2), 62.1 (benzylic), 71.4 (C-1), 123.4 (C′-2), 127.1, 128.4, 129.1, and 137.6 (aromatic), 138.9 (C′-1); IR 3600–3200, 2940, 2860, 2840, 1525, 1425, 1250, 1210, 1095, 855; CIMS m/e (rel intensity) 318 (M^+ + 1, 100), 300 (22), 240 (2), 228 (3), 206 (33), 192 (6), 171 (6), 111 (6), 91 (6); HRMS m/e 318.2274 (M^+ + 1, $C^{19}H_{32}NOSi$ requires 318.2253).

2-[*N*-(Benzyloxycarbonyl)-*N*-[(trimethylsilyl)methyl]amino]-1-(1′-cyclohexenyl)-1-ethanone (58). The allylic alcohol **55** (0.24 g, 6.6×10^{-1} mmol) was oxidized with 0.21 g (1.7 mmol) of oxalyl chloride and 0.26 g (3.2 mmol) of DMSO. The reaction was quenched by addition of 1.5 mL of triethylamine, diluted with pentane, and washed with water. The organic solution was dried and concentrated in vacuo to give an oil (0.23 g, 100%) that was shown to contain the amido enone **58**, (>90% pure) which was used without further purification: ^{1}H NMR δ 0.02 and 0.09 (s, 9 H, $SiCH_3$), 1.63 (broad, 4 H, H′-4 and -5), 2.26 (broad, 4 H, H′-3 and -6), 2.86 (s, 2 H, $SiCH_2$), 4.34 and 4.40 (s, 2 H, H-2), 5.07 and 5.13 (s, 2 H, benzylic), 6.79 and 6.92 (broad, 1 H, H′-2), 7.30 (m, 5 H, aromatic); ^{13}C NMR −1.82 and −1.65 ($SiCH_3$), 21.5, 21.8, 23.0, and 26.0 (C′-3–C′-6), 39.8 and 41.0 ($SiCH_2$), 54.5 and 54.6 (C-2), 67.1 and 67.3 (benzylic), 127.6, 127.7, 127.9, 128.1, 128.3, 128.4, 136.8, and 137.0 (aromatic), 138.0 (C′-1), 139.7 and 140.1 (C′-2), 156.2 and 156.8 (NCO), 194.9 (C-1); IR 3020, 2940, 2895, 1690, 1675, 1520, 1420, 1220, 1095; CIMS m/e 360 (M^+ + 1, 0.07), 344 (1), 268 (6), 224 (4), 206 (5), 196 (16), 181 (5), 154 (3), 109 (4), 91 (100), 73 (28); HRMS m/e 360.1996 (M^+ + 1, $C_{20}H_{30}NO_3Si$ requires 360.1995).

3-[*N*-(Benzyloxycarbonyl)-*N*-[(trimethylsilyl)methyl]amino]-1-(1′-cyanohexenyl)-1-propanone (59). To a solution of the amido aldehyde **10** (2.43 g, 8.3 mmol) in 25 mL of anhydrous THF was added 25 mL of a THF solution containing ca. 12.5 mmol of cyclohexenylmagnesium bromide at −78 °C. The resulting solution was stirred for 10 h at −15 °C, quenched by addition of saturated aqueous NH_4Cl, and extracted with ether. After being washed with saturated aqueous $NaHCO_3$, the extracts were dried and concentrated in vacuo to yield 2.84 g of the impure amido alcohol **56**. Due to the instability of this allylic alcohol, the crude mixture was subject to Swern oxidation with 0.96 g (7.6 mmol) of oxalyl chloride and 1.18 g (15.1 mmol) of DMSO. The reaction was completed by addition of 2.3 g (22.7 mmol) of triethylamine, and the resulting mixture was diluted with ethyl ether followed by washing with water. The organic layer was then washed with saturated $NaHCO_3$, dried, and concentrated in vacuo to give a residue that was subjected to Florisil column chromatography (10% ether in hexanes) to yield 0.78 g (25%) of the amido enone **59**: ^{1}H NMR (1:1 mixtures of two rotamers based on ^{1}H NMR integration) δ −0.03 and 0.04 (s, 9 H, $SiCH_3$), 1.56

(broad s, 4 H, H-3′ and H-6′), 2.77 (s, 2 H, $SiCH_2$), 2.81 and 2.93 (dd, J = 7.0, 7.0 Hz, 2 H, H-3), 3.48 (dd, J = 7.0, 7.0 Hz, 2 H, H-2), 5.07 and 5.09 (s, 2 H, benzylic), 6.72 and 6.95 (s, 1 H, H-2′), 7.26–7.34 (m, 5 H, aromatic); ^{13}C NMR δ −1.7 ($SiCH_3$), 21.5, 21.9, 23.0, 26.1 (C-3′–C-6′), 35.3 and 35.8 ($SiCH_2$), 39.2 and 39.6 (C-3), 45.6 and 46.3 (C-2), 67.0 (benzylic), 127.9, 128.1, 128.4, 139.2 (aromatic), 136.8, 137.0 (C-1′), 140.7 (C-2′), 155.8 and 156.0 (NCO), 199.5 and 199.8 (C-1); IR (neat) 3020, 2920, 1680, 1660, 1460, 1415, 1395, 1360, 1240, 1205, 1090, 840, 745 cm^{-1}; CIMS m/e (rel intensity) 374 (M^+ + 1, 51), 358 (12), 338 (5), 294 (5), 282 (17), 150 (8), 138 (30), 206 (9), 148 (12), 91 (100), 73 (56); HRMS calcd for $C_{21}H_{32}O_3NSi$ 374.2151, found 374.2152.

2-[*N*-Benzyl-*N*-[(trimethylsilyl)methyl]amino]-1-(1′-cyclohexenyl)-1-ethanone (60). The amino alcohol **57** (0.83 g, 2.6 mmol) was oxidized with 0.61 mL (6.9 mmol) of oxalyl chloride and 0.80 mL (12.5 mmol) of DMSO. The reaction was quenched by the addition of 3 mL of triethylamine, and the reaction mixture was diluted with ether and washed with water. The ethereal solution was dried and concentrated in vacuo, giving an oil (0.82 g, 100%) that was shown to contain the amino enone **60** (>90% pure), which was used without further purification: ^{1}H NMR δ 0.06 (s, 9 H, $SiCH_3$), 1.55 (m, 4 H, H′-4 and -5), 2.06 (s, 2 H, $SiCH_2$), 2.14 (m, 4 H, H′-3 and -6), 3.40 (s, 2 H, H-2), 3.58 (s, 2 H, benzylic), 6.88 (m, 1 H, H′-2), 7.36 (m, 5 H, aromatic); ^{13}C NMR δ −1.4 ($SiMe_3$), 21.4, 21.7, 23.1, and 26.1 (C′-3–C′-6), 46.4 ($SiCH_2$), 62.3 (benzylic), 62.7 (C-2), 127.6, 127.9, 128.3, and 136.8 (aromatic), 138.2 (C′-1, 141.2 (C′-2), 199.7 (CO); IR 3000, 2940, 2865, 1675, 1660, 1435, 1250, 855; EIMS m/e (rel intensity) 315 (M^+, 0.2), 220 (2), 206 (35), 183 (1), 149 (4), 109 (16), 91 (100), 73 (20); HRMS m/e 316.2088 (M^+ + 1, $C_{19}H_{30}NOSi$ requires 316.2096).

DCA-Sensitized Irradiation of the Amido Enone 58. Preparation of Adduct 61. A solution (100 mL) of 50 mg (1.4×10^{-1} mmol) of the amido enone **58** and 45 mg (2.0×10^{-1} mmol) of DCA in CH_3CN was irradiated with uranium glass filtered light. The photolysate was concentrated in vacuo, and the residue was subjected to Florisil column chromatography (CH_2Cl_2 to 0.2% CH_3OH–CH_2Cl_2) to yield 61 mg (91%) of adduct **61**: ^{1}H NMR δ 1.50–1.68 (m, 4 H, H′-4 and -5), 2.03–2.34 (m, 4 H, H′-3 and -6), 3.55–4.10 (m, 2 H, NCH_2), 4.37–4.91 (m, 4 H, H-2 and benzylic), 5.06–5.53 (m, 1 H, 9-DCAH), 6.42–6.79 (m, 1 H, H′-2), 6.96–7.83 (m, 13 H, aromatic); ^{13}C NMR δ 21.4, 21.6, 22.9, and 26.0 (C′-3–C′-6), 36.1 and 36.5 (10-DCA), 49.1 and 49.2 (9-DCA), 52.3 and 52.3 ($DCACH_2N$), 56.0 and 56.4 (C-2), 67.4 and 68.3 (benzylic), 117.2–140.5 (CN, aromatic), 141.1 and 141.4 (C′-2), 155.8 and 161.2 (NCO), 194.1 and 194.2 (C-1); IR 3070, 3020, 2980, 2840, 1700, 1675, 1455, 1420, 1210, 1090; FABMS m/e (rel intensity) 515.930 (M^+ + 1, 0.6), 316 (3), 242 (4), 152 (4), 109 (10), 91 (100), 73 (23). Because of the adduct's instability at high temperature, HRMS measurements were not made.

Pyrolysis of the DCA–Amido Enone Adduct 61. Preparation of Amido Enone 62. Neat **61** (20 mg, 3.9×10^{-2} mmol) was heated at 200 °C for 2 min, cooled, and subjected to silica gel column chromatography (10–30% Et_2O–cyclohexane) to yield 8.4 mg of DCA and 11 mg (90%) of the amido enone **62**: ^{1}H NMR δ 1.63 (broad, 4 H, H′-4 and -5), 2.25 (broad, 4 H, H′-3 and -6), 2.94 (s, 3 H, NCH_3), 4.34 and 4.42 (s, 2 H, H-2), 5.09 and 5.15 (s, 2 H, benzylic), 7.32 (m, 5 H, aromatic); ^{13}C NMR δ 21.5, 21.8, 23.0, and 26.0 (C′-3–C′-6), 30.8 (NCH_3), 53.6 and 54.4 (C-2), 67.4 and 68.1 (benzylic), 126.3, 127.8, 128.1, 128.5, 129.4, and 133.6 (aromatic), 138.0 (C′-1), 139.9 and 140.3 (C′-2), 156.2 and 156.8 (NCO), 194.4 (C-1); IR ($CHCl_3$) 3070, 3020, 2940, 2826, 1698, 1680, 1450, 1410, 1220, 1205, 1150, 1095; CIMS m/e (rel intensity) 288 (M^+ + 1, 6), 244 (5), 196 (9), 178 (10), 134 (28), 107 (37), 91 (100), 84 (19); HRMS m/e 288.1608 (M^+ + 1, $C_{17}H_{22}NO_3$ requires 288.1600).

DCA-Sensitized Irradiation of the Amido Enone 59. Preparation of Bicyclic Hydroazepinone 63. A deoxygenated solution (100 mL) of 15% CH_3OH–CH_3CN in a quartz tube containing 37 mg (1.0×10^{-1} mmol) of the amido enone **59** and 2 mg (1.0×10^{-2} mmol) of DCA was irradiated with uranium glass filtered light for 19 h. The photolysate was concentrated in vacuo, giving a residue that was subjected to preparative TLC separation (15% ethyl acetate in hexanes) to yield 8 mg (27%) of the bicyclic azepinone **63** (1:1 mixture of two rotamers based on ^{13}C NMR integration): ^{1}H NMR of rotamer A δ 1.2–1.9 (m, 8 H, H-6–H-9), 2.07 (m, 1 H, H-9a), 2.55 (m, 1 H, H-4), 2.67–2.79 (m, 2 H, H-4 and H-3), 3.36 (m, 1 H, H-5a), 3.41–3.50 (m, 1 H, H-1), 3.69–3.79 (m, 2 H, H-3 and H-1). 5.12 (bs, 2 H, benzylic), 7.30–7.50 (m, 5 H, aromatic), rotamer B δ 1.2–1.9 (m, 8 H, H-6–H-9), 2.19 (m, 1 H, H-9a), 2.55 (m, 1 H, H-4), 2.67–2.79 (m, 2 H, H-4 and H-1), 3.41–3.50 (m, 2 H, H-5a and H-3), 3.69–3.79 (m, 2 H, H-3 and H-1), 5.12 (bs, 2 H, benzylic), 7.30–7.50 (m, 5 H, aromatic); ^{13}C NMR of rotamer A δ 23.1, 23.3, 24.0, 24.2, 25.7, 26.1, 28.3 (C-6–C-9), 37.5 (C-9a), 43.0 (C-4), 43.6 (C-1), 50.9 (C-3), 51.0 (C-5a), 67.3 (benzylic), 127.9, 128.0, 128.5, 136.6 (aromatic), 155.7 (NCO), 212.2 (CO). rotamer B δ 23.1, 23.3, 24.0, 24.2, 25.7, 26.1, 28.3 (C-6–C-9), 37.0 (C-9a), 42.8 (C-4), 43.1 (C-3), 50.5 (C-1), 50.8 (C-5a), 67.3 (benzylic), 127.9, 128.0, 128.5, 136.6 (aromatic), 155.7 (NCO), 212.2 (CO); IR ($CHCl_3$) 3080, 2920, 2860, 1685, 1430, 1230, 910, 820 cm^{-1}; EIMS m/z (rel intensity) 301 (M^+, 41), 228 (29), 210 (18), 194 (12), 167 (36), 166 (27), 91 (100); HRMS calcd for $C_{18}H_{23}O_3N$ 301.1678, found 301.1672.

DCN-Sensitized Irradiation of the Amido Enone 59. A solution containing 38 mg (1.0×10^{-1} mmol) of the amido enone **59** and 41 mg (2.3×10^{-1} mmol) of DCN in 100 mL of 15% CH_3OH–CH_3CN was irradiated with flint glass filtered light. The photolysate was concentrated in vacuo, giving a residue that was subjected to silica gel column chromatography (10% ethyl acetate in hexanes) to yield 40 mg of DCN, 10 mg of enone **59**, and 3 mg (12% based on 74% conversion) of **63**.

Redox Photosensitized Reaction of the Amido Enone 59. A solution containing 41 mg (1.1×10^{-1} mmol) of the amido enone **59**, 47 mg (2.1×10^{-1} mmol) of triphenylene, and 0.132 g (1.0 mmol) of 1,4-dicyanobenzene in 100 mL of 15% CH_3OH–CH_3CN was irradiated with uranium glass filtered light. The photolysate was concentrated in vacuo, giving a residue that was subjected to silica gel column chromatography (10% ethyl acetate–hexane) to yield 0.159 g of a triphenylene and 1,4-dicyanobenzene mixture, 8 mg of enone **59**, and 8 mg (30% based on 79% conversion) of **63**.

DCA-Sensitized Irradiation of the Amino Enone 60. Preparation of Hydroisoquinolines 64 and 65. A solution containing 30 mg (1×10^{-1} mmol) of the amino enone **60** and 2 mg (1×10^{-2} mmol) of DCA in 100 mL of 15% CH_3OH–CH_3CN was irradiated with uranium glass filtered light for 1.5 h. The photolysate was concentrated in vacuo, giving a residue that was subjected to flash alumina chromatography (4% ethyl ether in cyclohexane) to yield 2 mg (8%) of *cis*-isoquinolinone **64** and **9** mg (3.5×10^{-2} mmol, 37%) of *trans*-isoquinolinone **65**. The exact yields and ratios of products formed from repetitive reactions were determined by GLC employing pyrene as an internal standard and were found to be 90% (4:1 **64**:**65**) at 64% conversion and 80% (5:1 **64**:**65**) at >95% conversion.

64: ^{1}H NMR δ 1.16–2.27 (m, 9 H, H-8a and H-5–H-8), 2.51 (m, 1 H, H-4a), 2.53 (dd, J = 11.4, 3.6 Hz, 1 H, H-1_{ax}), 2.71 (ddd, J = 11.4, 3.8, 1.6 Hz, 1 H, H-1_{eq}), 2.74 (d, J = 13.9 Hz, 1 H, H-3_{ax}), 3.14 (dd, J = 13.9, 1.6 Hz, 1 H, H-3_{eq}), 3.49 and 3.54 (AB q, J = 13.3 Hz, 2 H, benzylic), 7.20–7.53 (m, 5 H, aromatic); ^{13}C NMR δ 22.4, 24.5, 25.4, 28.9, (C-5–C-8), 37.4 (C-8a), 48.1 (C-4a), 57.4 (C-1), 62.5 (benzylic), 64.2 (C-3), 127.2, 128.3, 128.8, 137.8 (aromatic), 208.4 (CO); IR ($CHCl_3$) 3110, 3070, 2935, 1730, 1140, 860 cm^{-1}. EIMS m/e (rel intensity) 243 (M^+, 7), 215 (20), 214 (24), 124 (22), 91 (100); HRMS calcd for $C_{16}H_{21}NO$ 243.1623, found 243.1623.

65: ^{1}H NMR δ 1.06–1.72 (m, 8 H, H-5–H-8), 1.73–1.90 (m, 1 H, H-8a), 1.98–2.03 (m, 1 H, H-4a), 2.14 (dd, J = 11.1, 11.1 Hz, 1 H, H-1_{ax}), 2.75 (dd, J = 13.4, 0.7 Hz, 1 H, H-3_{ax}), 2.87 (ddd, J = 11.1, 3.6, 1.8 Hz, 1 H, H-1_{eq}), 3.23 (dd, J = 13.4, 1.8 Hz, 1 H, H-3_{eq}), 3.52 and 3.57 (AB q, J = 13.1 Hz, 2 H, benzylic), 7.22–7.32 (m, 5 H, aromatic); ^{13}C NMR δ 24.3, 25.3, 25.4, 30.8 (C-5–C-8), 41.4 (C-8a), 53.2 (C-4a), 58.7 (C-1), 62.6 (benzylic), 64.1 (C-3), 127.3, 128.3, 129.0, 137.3 (aromatic), 207.4 (CO); IR ($CHCl_3$) 3020, 2920, 2840, 1660, 1595, 1430, 830 cm^{-1}; EIMS m/e (rel intensity) 243 (M^+, 17), 215 (46), 214 (58), 166 (1), 152 (3), 124 (42), 91 (100); HRMS calcd for $C_{16}H_{21}NO$ 243.1623, found 243.1630.

2-[*N*-Benzyl-*N*-[(trimethylsilyl)methyl]amino]-1-(9′-phenanthrenyl)-1-ethanol (67). To a stirred solution of 9-bromophenanthrene (2.97 g, 11.5 mmol) in Et_2O (50 mL) was added 9.5 mL of a 1.2 N *n*-BuLi in hexane solution at 25 °C. After 10 min, 1.02 g of the amino aldehyde **61** (4.3 mmol) in 50 mL of Et_2O was added. After stirring for 1 h at 25 °C, the solution was quenched by the addition of water and extracted with Et_2O. The organic layer was washed with saturated aqueous $NaHCO_3$, dried, and concentrated in vacuo, giving a residue that was subjected to column chromatography (Florisil, 10% Et_2O–hexanes) to give 1.14 g (64%) of alcohol **67**: ^{1}H NMR δ 0.16 (s, 9 H, $Si(CH_3)_3$), 2.05 and 2.44 (AB q, J = 14.6 Hz, 2 H, CH_2Si), 2.73 (dd, J = 9.9, 12.8 Hz, 1 H, H-2), 2.86 (dd, J = 3.6, 12.8 Hz, 1 H, H-2), 3.45 and 4.08 (AB q, J = 13.0 Hz, 2 H, benzylic), 4.39 (bs, 1 H, OH), 5.48 (dd, J = 3.6, 9.9 Hz, 1 H, H-1), 7.30–7.38 (m, 5 H, aromatic), 7.53–7.64 (m, 4 H, H-2′, H-3′, H-6′, and H-7′), 7.86–7.92 (m, 2 H, H-1′ and H-8′), 7.97 (s, 1 H, H-10′), 8.63 (d, J = 8.1 Hz, 1 H, H-5′), 8.72 (d, J = 8.1 Hz, 1 H, H-6′); ^{13}C NMR δ −1.3 ($Si(CH_3)_3$), 46.9 (CH_2Si), 62.3 (C-2), 64.2 (benzylic), 67.0 (C-1), 122.3, 123.3, 123.5, 124.0, 126.0, 126.4, 126.6, 127.4, 128.5, 128.8, 129.2 (aromatic CH), 129.8, 129.9, 130.6, 131.7, 135.8, 138.7 (aromatic C); IR ($CHCl_3$) 3410, 3080, 3040, 2970, 2910, 2840, 1695, 1610, 1500, 1255, 855 cm^{-1}; CIMS m/e (rel intensity) 414 (M^+ + 1, 2), 207 (23), 206 (100), 178 (20); HRMS calcd for $C_{27}H_{32}NOSi$ 414.2253, found 414.2253.

2-[*N*-Acetyl-*N*-[(trimethylsilyl)methyl]amino]-1-(9′-phenanthrenyl)-1-ethanol (68). To a stirred solution of amido aldehyde **66** (54 mg, 0.29

mmol) in 1 mL of Et_2O was added 1.5 mL of a 0.55 N solution of 9-phenanthrenylmagnesium bromide in Et_2O at 0 °C. The reaction mixture was stirred at 20 °C for 10 h and then quenched with water and extracted with ethyl acetate. The organic layer was washed with saturated aqueous $NaHCO_3$, dried, and concentrated in vacuo, giving a residue that was subjected to column chromatography (F-20 Alumina, 25% ethyl acetate in hexanes) to give 46 mg (44%) of the amido alcohol **68** (1:4 mixture of two rotamers based on ^1H NMR integration): ^1H NMR of rotamer A δ 0.07 (s, 9 H, $Si(CH_3)_3$), 2.18 (s, 3 H, CH_3), 2.66 and 2.85 (AB q, J = 16.3 Hz, 2 H, CH_2Si), 3.67 (dd, J = 7.9, 14.3 Hz, 1 H, H-2), 3.87 (dd, J = 2.10, 14.3 Hz, 1 H, H-2), 4.84 (d, J = 3.7 Hz, 1 H, OH), 5.73 (m, 1 H, H-1), 7.57–7.71 (m, 4 H, H-2′, H-3′, H-6′, and H-7′), 7.90–7.93 (m, 1 H, H-1′), 8.09 (s, 1 H, H-10′), 8.18–8.21 (m, 1 H, H-8′), 8.64–8.67 and 8.73–8.78 (m, 2 H, H-4′ and H-5′), rotamer B δ −0.01 (s, 9 H, $Si(CH_3)_3$), 2.10 (s, 3 H, CH_3), 2.66 and 2.85 (AB q, J = 16.3 Hz, 2 H, CH_2Si), 3.67 (dd, J = 7.9, 14.3 Hz, 1 H, H-2), 3.87 (dd, J = 2.10, 14.3 Hz, 1 H, H-2), 4.84 (d, J = 3.7 Hz, 1 H, OH), 5.85 (m, 1 H, H-1), 7.57–7.71 (m, 4 H, H-2′, H-3′, H-6′, and H-7′), 7.90–7.93 (m, 1 H, H-1′), 8.09 (s, 1 H, H-10′), 8.18–8.21 (m, 1 H, H-8′), 8.64–8.67 and 8.73–8.78 (m, 2 H, H-4′ and H-5′); ^{13}C NMR of rotamer A δ −1.1 ($Si(CH_3)_3$), 21.5 (CH_3), 38.6 (CH_2Si), 57.4 (C-2), 69.1 (C-1), 122.4, 123.0, 123.3, 123.5, 124.7, 126.2, 126.5, 126.7, 128.8 (aromatic CH), 129.2, 131.3, 131.5, 135.7, 136.1 (aromatic C), 170.5 (NCO), rotamer B δ −1.7 ($Si(CH_3)_3$), 21.8 (CH_3), 42.6 (CH_2Si), 56.1 (C-2), 70.5 (C-1), 122.4, 123.0, 123.3, 123.5, 124.3, 126.2, 126.5, 126.7, 128.8 (aromatic CH), 129.5, 130.0, 130.5, 131.5, 136.1 (aromatic C), 172.4 (NCO); IR (CCl_4) 3354 (br), 3078, 2955, 1620, 1417, 855 cm^{-1}; CIMS m/e (rel intensity) 366 (M^+ + 1, 10), 350 (19), 220 (11), 107 (19), 206 (31), 178 (51), 116 (100); HRMS calcd for $C_{22}H_{28}NO_2Si$ 366.1889, found 366.1911.

2-[*N*-Benzyl-*N*-[(trimethylsilyl)methyl]amino]-1-(9′-phenanthrenyl)-1-ethanone (69). The amino alcohol **67** (1.03 g, 2.5 mmol) was subjected to the Swern oxidation procedure with 0.95 g (7.5 mmol) of oxalyl chloride and 1.16 g (14.8 mmol) of DMSO in 10 mL of CH_2Cl_2 at −78 °C for 3 h. The reaction was completed by the addition of 2.3 g (22.7 mmol) of triethylamine, and the reaction was diluted with Et_2O and washed with water. The organic layer was washed with saturated aqueous $NaHCO_3$, dried, and concentrated in vacuo to give 0.988 (97%) of amino ketone **69**: ^1H NMR δ −0.02 (s, 9 H, $Si(CH_3)_3$), 2.32 (s, 2 H, CH_2Si), 3.79 (s, 2 H, H-2), 3.88 (s, 2 H, benzylic), 7.26–7.44 (m, 5 H, phenyl), 7.62–7.72 (m, 4 H, H-2′, H-3′, H-6′, and H-7′), 7.82 (d, J = 1.6 Hz, 1 H, H-1′), 7.94 (s, 1 H, H-10′), 8.57 (d, J = 1.9 Hz, 1 H, H-8′), 8.66–8.72 (m, 2 H, H-5′ and H-4′); ^{13}C NMR δ −1.5 ($Si(CH_3)_3$), 47.1 (CH_2Si), 61.9 (benzylic), 65.7 (C-2), 122.6, 122.8, 126.2, 126.4, 126.86, 126.93, 127.4, 128.4, 128.5, 128.6, 128.8, 129.3, 129.6, 129.8, 130.2, 130.6, 131.7, 138.8 (aromatics), 203.4 (CO); IR ($CHCl_3$) 3070, 3040, 2960, 2900, 2800, 1680, 1530, 1500, 1450, 1250, 850 cm^{-1}; CIMS m/e (rel intensity) 412 (M^+ + 1, 2), 206 (100), 205 (22), 177 (18), 91 (100); HRMS calcd for $C_{27}H_{29}NOSi$ 411.2018, found 411.2013.

2-[*N*-Acetyl-*N*-[(trimethylsilyl)methyl]amino]-1-(9′-phenanthrenyl)-1-ethanone (70). The amido alcohol **68** (121 mg, 0.33 mmol) was subjected to the Swern oxidation procedure with 130 mg (1.02 mmol) of oxalyl chloride and 160 mg (2.05 mmol) of DMSO in 3 mL of CH_2Cl_2 at −78 °C for 3 h. The reaction was completed by the addition of 300 mg (2.96 mmol) of triethylamine, and the mixture was diluted with $CHCl_3$ followed by washing with water. The organic layer was washed with saturated aqueous $NaHCO_3$, dried, and concentrated in vacuo, giving a residue that was subjected to column chromatography (F-20 Alumina, 50% ethyl acetate in hexanes) to give 81 mg (67%) of amido ketone **70** (1:2.5 mixture of two rotamers based on ^1H NMR integration): ^1H NMR of rotamer A δ 0.12 (s, 9 H, $Si(CH_3)_3$), 2.19 (s, 3 H, CH_3), 3.07 (s, 2 H, CH_2Si), 4.76 (s, 2 H, H-2), 7.58–7.80 (m, 4 H, H-2′, H-3′, H-6′, and H-7′), 7.94 (d, J = 7.7 Hz, 1 H, H-1′), 8.07 (s, 1 H, H-10′), 8.54–8.73 (m, 3 H, H-4′, H-5′, and H-8′), rotamer B δ 0.16 (s, 9 H, $Si(CH_3)_3$), 2.08 (s, 3 H, CH_3), 3.00 (s, 2 H, CH_2Si), 4.81 (s, 2 H, H-2), 7.58–7.80 (m, 4 H, H-2′, H-3′, H-6′, and H-7′), 7.94 (d, J = 7.7 Hz, 1 H, H-1′), 8.17 (s, 1 H, H-10′), 8.54–8.73 (m, 3 H, H-4′, H-5′, and H-8′); ^{13}C NMR of rotamer A δ −1.3 ($Si(CH_3)_3$), 21.1 (CH_3), 40.6 (CH_2Si), 59.7 (C-2), 122.8, 122.9, 126.2, 127.2, 127.3, 127.6, 127.9, 129.4, 129.8 (aromatic CH), 130.7, 130.8, 131.8, 132.2, 133.4 (aromatic C), 170.8 (NCO), 197.4 (CO), rotamer B δ −1.7 ($Si(CH_3)_3$), 21.4 (CH_3), 41.9 (CH_2Si), 56.8 (C-2), 122.6, 122.8, 126.4, 127.1, 127.2, 127.6, 128.8, 129.2, 129.8 (aromatic CH), 130.7, 130.8, 131.8, 132.2, 133.4 (aromatic C), 170.8 (NCO), 198.9 (CO); IR (CCl_4) 3077, 2956, 1698, 1650, 1451, 804 cm^{-1}; EIMS m/e (rel intensity) 363 (M^+, 11), 348 (72), 205 (100); HRMS calcd for $C_{22}H_{25}NO_2Si$ 363.1655, found 363.1639.

DCN-Sensitized Irradiation of the Amino Enone 69. Preparation of Amino Ketone 72. A solution containing 40 mg (1×10^{-1} mmol) of the amino enone **69** and 51 mg (2.9×10^{-1} mmol) of DCN in 100 mL of CH_3CN was irradiated with uranium glass filtered light. The photolysate was concentrated in vacuo, giving a residue that was subjected to flash silica gel column chromatography (prewashed with 5% triethylamine in hexane, 20% ether in hexanes) to yield 50 mg of DCN, 2 mg (9%) of commercially available (Aldrich) 9-acetylphenanthrene (**71**), and 4 mg (12%) of the tetracyclic amino ketone **72**. The exact yield of products was determined by integrations of ^{13}C NMR resonances of aromatic carbons and were found to be 54% for amino ketone **72** and 9% for 9-acetylphenanthrene (**71**).

72: ^1H NMR δ 2.60 (dd, J = 11.2, 11.9 Hz, 1 H, H-1), 2.79 (dd, J = 4.7, 11.9 Hz, 1 H, H-1), 3.00 and 3.21 (AB q, J = 13.7 Hz, 2 H, H-3), 3.46 and 3.55 (AB q, J = 13.1 Hz, 2 H, benzylic), 3.52–3.58 (m, 1 H, H-12b), 3.93 (d, J = 6.0 Hz, 1 H, H-4a), 6.96 (d, J = 7.6 Hz, 1 H, H-5), 7.18–7.39 (m, 10 H, aromatic), 7.76 (d, J = 7.6 Hz, 1 H, H-9), 7.83 (d, J = 8.0 Hz, 1 H, H-8); ^{13}C NMR 40.5 (C-12b), 52.0 (C-4a), 53.6 (C-1), 61.5 (benzylic), 62.2 (C-3), 116.2, 122.6, 123.9, 124.0, 127.0, 127.4, 127.7, 127.9, 128.0, 128.1, 129.7 (aromatic CH), 130.0, 130.6, 131.8, 133.3, 137.0 (aromatic C), 206.8 (CO); IR ($CHCl_3$) 3153, 2928, 1715, 923, 894 cm^{-1}; EIMS m/e (rel intensity) 339 (M^+, 5), 205 (7), 191 (11), 178 (51), 133 (100); HRMS calcd for $C_{24}H_{21}NO$ 339.1623, found 339.1628.

DCA-Sensitized Irradiation of the Amido Enone 69. A solution containing 40 mg (1×10^{-1} mmol) of the amino enone **69** and 7 mg (3×10^{-2} mmol) of DCA in 100 mL of CH_3CN was irradiated with uranium glass filtered light for 20 min. The photolysate was concentrated in vacuo, giving a residue that was shown by ^1H NMR spectroscopic analysis to consist of a mixture of 9-acetylphenanthrene (**71**) and amino ketone **72** in a 1:0.9 ratio.

Direct Irradiation of the Amino Enone 69. A 100-mL solution containing 40 mg (1×10^{-1} mmol) of the amino enone **69** in CH_3CN was irradiated with uranium glass filtered light for 20 min. The photolysate was concentrated in vacuo, giving a residue that was shown by ^1H NMR spectroscopic analysis to consist of a mixture of 9-acetylphenanthrene (**71**) and amino ketone **72** in a 1:0.8 ratio.

DCA-Sensitized Irradiation of the Amido Enone 70. Preparation of Photoproducts 73–77. A solution containing 37 mg (0.1 mmol) of the amido enone **70** and 7 mg (0.03 mmol) of DCA in 100 mL of 15% CH_3OH–CH_3CN was irradiated with uranium glass filtered light for 4 h. The photolysate was concentrated in vacuo, giving a residue that was subjected to column chromatography (Florisil, 50% ethyl acetate–hexane) to yield 6 mg of DCA, 7 mg of enone **70**, 13 mg of **73**, and 16 mg of a mixture of four compounds. This mixture was then subjected to reverse-phase HPLC (40% H_2O in MeOH) to yield 5 mg (17%) of **74**, 4 mg (14%) of **75**, 1 mg of **76**, and 2 mg (7%) of **77**. The actual yields of these substances were determined by the HPLC method to be 44% of **73**, 33% of **74**, 17% of **75**, 1% of **76**, and 4% of **77**.

73: ^1H NMR δ −0.26 (s, 9 H, $OSi(CH_3)_3$), 1.88 (s, 3 H, CH_3), 4.42 and 4.92 (AB q, J = 10.4 Hz, 2 H, H-2 or H-4), 4.64 and 4.67 (AB q, J = 8.8 Hz, 2 H, H-4 or H-2), 7.58–7.70 (m, 4 H, H-2′, H-3′, H-6′, and H-7′), 7.74 (s, 1 H, H-10′), 7.88 (d, J = 7.9 Hz, 1 H, H-1′), 8.03 (d, J = 8.3 Hz, 1 H, H-8′), 8.65 (d, J = 8.3 Hz, 1 H, H-4′ or H-5′), 8.73 (d, J = 8.2 Hz, 1 H, H-5′ or H-4′); ^{13}C NMR δ 0.9 ($OSi(CH_3)_3$), 19.0 (CH_3), 61.0 (C-2 or C-4), 65.7 (C-4 or C-2), 73.5 (C-3), 122.5, 123.4, 125.3, 126.4, 126.6, 126.8, 127.1, 127.6, 129.1 (aromatic CH), 129.5, 130.5, 130.6, 131.4, 135.2 (aromatic C), 170.7 (NCO); IR (CCl_4) 3080, 2960, 1665, 1435, 995 cm^{-1}; EIMS m/e (rel intensity) 363 (M^+, 25), 348 (7), 292 (85), 291 (100); HRMS calcd for $C_{22}H_{25}NO_2Si$ 363.1655, found 363.1658.

74 (1:1.2 mixture of two rotamers based on ^1H NMR integration): ^1H NMR of rotamer A δ 2.00 (s, 3 H, CH_3), 3.42 (dd, J = 10.7, 12.3 Hz, 1 H, H-1), 3.47–3.54 (m, 1 H, H-12b), 3.70 (dd, J = 4.1, 12.3 Hz, 1 H, H-1), 3.97 and 4.56 (AB q, J = 18.0 Hz, 2 H, H-3), 4.01 (d, J = 4.04 Hz, 1 H, H-4a), 7.02–7.05 (m, 1 H, aromatic), 7.27–7.44 (m, 5 H, aromatic), 7.76–7.85 (m, 2 H, H-8 and H-9), rotamer B δ 3.51 (m, 1 H, H-12b), 3.77 (dd, 1 H, J = 8.6, 13.8 Hz, H-1), 3.96 (d, 1 H, J = 5.7 Hz, H-4a), 4.00 and 4.10 (AB q, 2 H, J = 16.3 Hz, H-3), 4.11 (dd, J = 3.8, 13.8 Hz, 1 H, H-1), 7.02–7.05 (m, 1 H, aromatic), 7.27–7.44 (m, 5 H, aromatic), 7.76–7.85 (m, 2 H, H-8 and H-9); ^{13}C NMR of rotamer A δ 21.6 (CH_3), 39.8 (C-12b), 46.4 (C-1), 51.8 (C-4a), 55.3 (C-3), 124.4, 124.5, 124.6, 127.3, 127.9, 128.4, 128.6, 128.9 (aromatic CH), 127.7, 128.4, 130.1, 133.4 (aromatic C), 169.5 (NCO), 204.6 (CO), rotamer B δ 21.6 (CH_3), 39.5 (C-12b), 41.7 (C-1), 50.1 (C-3), 52.6 (C-4a), 124.4, 124.5, 124.6, 127.3, 127.9, 128.4, 128.6, 128.9 (aromatic CH), 127.7, 128.4, 130.1, 133.4 (aromatic C), 169.5 (NCO), 203.8 (CO); IR (CCl_4) 2970, 2930, 2880, 1730, 1670, 1425, 1220 cm^{-1}; EIMS m/e (rel intensity) 291 (M^+, 18), 192 (17), 178 (88), 113 (100); HRMS calcd for $C_{19}H_{17}NO_2$ 291.1259, found 291.1260.

75 (1:2.9 mixture of two rotamers based on ^1H NMR integration): ^1H NMR of rotamer A δ 2.27 (s, 3 H, CH_3), 4.66 (s, 2 H, H-1), 5.28 (s, 2 H, H-3), 7.65–7.85 (m, 4 H, H-6, H-7, H-10, and H-11), 8.22 (d, J = 8.2 Hz, 1 H, H-12), 8.66–8.77 (m, 2 H, H-8 and H-9), 9.29 (dd, J

= 3.9, 5.9 Hz, 1 H, H-5), rotamer B δ 2.25 (s, 3 H, CH_3), 4.49 (s, 2 H, H-3), 5.46 (s, 2 H, H-1), 7.65–7.85 (m, 4 H, H-6, H-7, H-10, and H-11), 8.22 (d, J = 8.2 Hz, 1 H, H-12), 8.66–8.77 (m, 2 H, H-8 and H-9), 9.29 (dd, J = 3.9, 5.9 Hz, 1 H, H-5); ^{13}C NMR of rotamer A δ 21.4 (CH_3), 46.1 (C-3), 51.4 (C-1), 122.6, 123.8, 126.2, 127.2, 127.4, 127.7, 128.3, 130.3 (aromatic CH), 124.0, 128.0, 130.1, 132.8, 142.3 (aromatic C), 169.5 (NCO), 194.3 (CO), rotamer B δ 21.4 (CH_3), 42.0 (C-1), 55.5 (C-3), 122.6, 123.4, 125.1, 127.2, 127.4, 127.7, 128.3, 130.3 (aromatic CH), 124.0, 128.0, 130.1, 132.8, 142.3 (aromatic C), 169.5 (NCO), 193.0 (CO); IR (CCl_4) 3190, 2927, 1654 cm^{-1}; EIMS *m/e* (rel intensity) 289 (M^+, 56), 246 (70), 245 (75), 228 (100); HRMS calcd for $C_{19}H_{15}NO_2$ 289.1103, found 289.1103.

76: ^1H NMR δ 2.22 (s, 3 H, $COCH_3$), 3.20 (s, 3 H, NCH_3), 4.88 (s, 2 H, NCH_2), 7.62–7.79 (m, 5 H, H-1, H-2, H-5, H-6, and H-7), 7.95–7.99 (m, 1 H, H-8), 8.21 (s, 1 H, H-10), 8.56–8.74 (m, 2 H, H-4 and H-5); ^{13}C NMR δ 21.4 ($COCH_3$), 37.6 (NCH_3), 56.7 (CH_2CO), 122.7, 122.9, 126.4, 127.2, 127.7, 129.0, 129.7, 129.9 (aromatic CH), 126.3, 127.2, 128.3, 130.4 (aromatic C), 173.4 (NCO), 199.1 (CO); IR ($CHCl_3$) 2930, 1645, 1425 cm^{-1}; EIMS *m/e* (rel intensity) 291 (M^+, 100), 246 (9), 218 (9), 205 (66); HRMS calcd for $C_{19}H_{17}NO_2$ 291.1259, found 291.1265.

77 (1:2.4 mixture of two rotamers based on ^1H NMR integration): ^1H NMR of rotamer A δ 2.02 (s, 3 H, CH_3), 4.69 (s, 2 H, H-4), 4.87 (s, 2 H, H-6), 7.50–7.80 (m, 4 H, H-2, H-3, H-10, and H-11), 8.00 (d, J = 7.9 Hz, 1 H, H-9), 8.26 (s, 1 H, H-8), 8.68 (d, J = 8.5 Hz, 1 H, H-1), 8.76 (d, J = 7.8 Hz, 1 H, H-12), rotamer B δ 2.09 (s, 3 H, CH_3), 4.85 (s, 2 H, H-4), 4.88 (s, 2 H, H-6), 7.50–7.80 (m, 4 H, H-2, H-3, H-10, and H-11), 8.00 (d, J = 7.9 Hz, 1 H, H-9), 8.24 (s, 1 H, H-8), 8.68 (d, J = 8.5 Hz, 1 H, H-1), 8.76 (d, J = 7.8 Hz, 1 H, H-12); ^{13}C NMR of rotamer A δ 18.1 (CH_3), 50.9 (C-6), 61.9 (C-4), 122.9, 123.8, 126.3, 127.4, 128.6, 129.4, 130.4, 133.0 (aromatic CH), 127.0, 135.9 (aromatic C), 170.0 (NCO), 202.8 (CO), rotamer B δ 18.1 (CH_3), 53.9 (C-4), 58.9 (C-6), 122.9, 123.8, 126.3, 127.7, 128.6, 129.4, 130.4, 133.3 (aromatic CH), 127.0, 135.9 (aromatic C), 170.0 (NCO), 202.8 (CO); IR (CCl_4) 3000, 2940, 2880, 1650, 1420 cm^{-1}; EIMS *m/e* (rel intensity) 289 (M^+, 100), 246 (72), 231 (63), 189 (34); HRMS calcd for $C_{19}H_{15}NO_2$ 289.1103, found 289.1085.

Direct Irradiation of the Amido Enone 70. A 1.5-mL CD_3CN solution containing 4.0 mg (0.01 mmol) of the amido enone **70** was irradiated in an NMR tube with uranium glass filtered light for 45 min. The amido enone reaction was monitored by ^1H NMR spectroscopy, and only the starting amido enone **70** and azetidine silyl ether **73** were observed in the mixture.

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Supplementary Material Available: Synthetic sequences for the preparation of aldehydes **8–15**, **53**, **54**, and **66** used in this study (18 pages). Ordering information is given on any current masthead page.

Single Electron Transfer Promoted Photocyclization Reactions of (Aminoalkyl)cyclohexenones. Mechanistic and Synthetic Features of Processes Involving the Generation and Reactions of Amine Cation and α-Amino Radicals

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Abstract: Mechanistic and synthetic aspects of the SET-induced photocyclization reactions of a series of α-, β-, and γ-(aminoethyl)cyclohexenones have been explored. These investigations have provided results that demonstrate that both direct (in MeOH) and SET-sensitized photocyclization reactions of members of this series containing *N*-(trimethylsilyl)methyl substituents serve as highly efficient methods for preparation of both fused and spiro N-heterobicyclic systems. In addition, as observed earlier, the solvent has been shown to play an important role in governing the chemoselectivity (i.e., amine cation radical desilylation vs deprotonation) of these photocyclizations. Specifically, desilylation is preferred in the polar protic solvent MeOH while deprotonation is favored in the aprotic MeCN. The results also show that the kinetic acidities of amine cation radicals, as judged by photoproduct distributions from reactions conducted in MeCN, are governed in a predictable way by substituents that control the stabilities of the resulting α-amino radical intermediates. Finally, the SET-sensitized reactions of these (aminoethyl)cyclohexenones that proceed via the radical cyclization mechanism are shown to display modest-to-low degrees of stereoselectivity.

Introduction

In the preceding paper,[1] we have described several single electron transfer (SET) promoted photocyclization reactions of trimethylsilyl-substituted aminoalkyl α,β-unsaturated ketone and ester systems. The results of those studies pointed out a number of unique features of the SET-photosensitized processes of these systems, which are driven by efficient desilylation reactions of intermediate silylmethylamine cation radicals and by intramolecular conjugate additions of the resulting α-amino radical intermediates to unsaturated ester and ketone groupings (Scheme I). In addition, comparisons of the SET-sensitized (path a in Scheme I) and direct-irradiation (path b in Scheme I) induced photoprocesses of these systems demonstrated how the former method is superior in promoting photocyclization reactions in cases where the α,β-unsaturated ester and ketone excited states are too reactive to be quenched by intramolecular SET from the tethered amine donors or where diradicals produced as intermediates in the direct-irradiation processes undergo alternative fragmentation reactions rather than cyclization. These investigations also showed that problems encountered with the use of the SET-photosensitization methodology and associated with the ready oxidation of slowly cyclizing α-amino radical intermediates can be avoided by the proper selection of photosensitizer and substituents on the amine functions. Finally, the synthetic potential of the SET-

(1) Jeon, Y. T.; Lee, C.-P.; Yoon, U. C.; Mariano, P. S. *J. Am. Chem. Soc.*, preceding paper in this issue.

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