Single electron transfer promoted photocyclization reactions of (aminoalkyl)cyclohexenones. Mechanistic and synthetic features of processes involving the generation and reactions o...

ARTICLE *in* CHEMINFORM · NOVEMBER 1991

Impact Factor: 0.74 · DOI: 10.1021/ja00023a039

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= 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.

Acknowledgment. Support for this research by the National Science Foundation (CHE-8917725 and INT-87-17290) and the National Institutes of Health (GM-27251) is greatly appreciated.

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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Contribution from the Department of Chemistry and Biochemistry, University of Maryland at College Park, College Park, Maryland 20742. *Received May 1, 1991. Revised Manuscript Received June 26, 1991*

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.

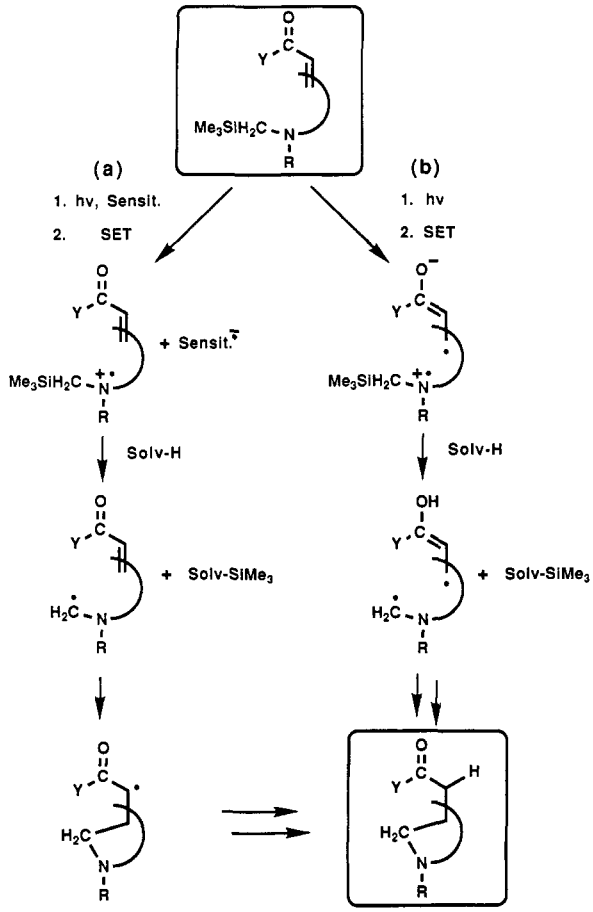
Introduction

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-

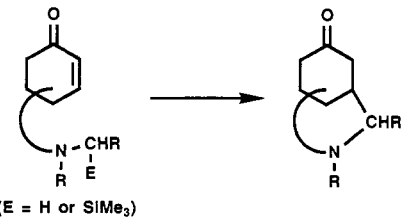
(1) Jeon, Y. T.; Lee, C.-P.; Yoon, U. C.; Mariano, P. S. *J. Am. Chem. Soc.*, preceding paper in this issue.

0002-7863/91/1513-8863$02.50/0

Scheme I



Scheme II

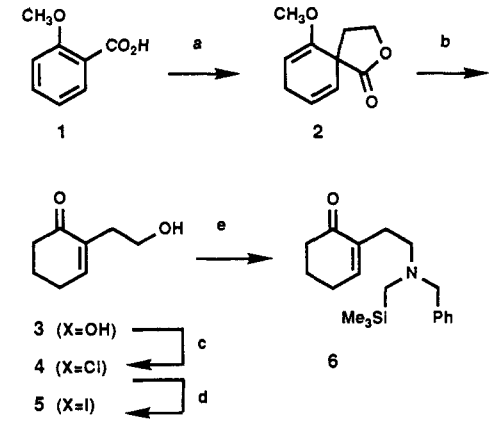


sensitized photocyclization reactions was demonstrated by applications to the preparation of a number of nitrogen heterocyclic systems by pathways involving either exo- or endo-type cyclization of α-amino radical intermediates.

Our continuing efforts in this area have focused on an exploration of mechanistic and synthetic features of SET-promoted photocyclization reactions of selected tertiary (aminoalkyl)-cyclohex-2-en-1-ones (Scheme II). These investigations have provided results that show that (1) photoreactions of members of this series containing α-silyl amine groups serve as highly efficient methods for the preparation of both fused and spiro N-heterobicyclic systems, (2) as observed earlier,[2] solvent plays an important role in governing the chemoselectivity (i.e., amine cation radical desilylation vs deprotonation) of these photocyclizations, (3) kinetic acidities of amine cation radicals are governed in a predictable way by substituents that control the stabilities of the resulting α-amino radical intermediates, and (4) both direct-irradiation and SET-photosensitized methods are useful in promoting photocyclization reactions in these systems with different levels of chemo- and stereoselectivity. The experimental observations that serve as the basis for these conclusions are presented and discussed below.

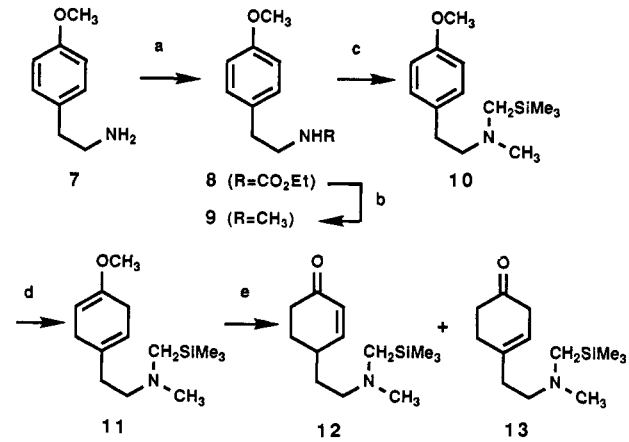
(2) Hasegawa, E.; Xu, W.; Mariano, P. S.; Yoon, U. C.; Kim, J. U. *J. Am. Chem. Soc.* **1988**, *110*, 8099.

Scheme III[a]



[a] (a) Li/NH_3, THF, −78 °C; $BrCH_2CH_2Cl$ (40%). (b) 0.1 N HCl, MeOH–H_2O reflux (85%). (c) Ph_3P, CCl_4, CH_2Cl_2, 40 °C (88%). (d) NaI, acetone, 25 °C (85%). (e) $PhCH_2NHCH_2TMS$, MeCN (35%).

Scheme IV[a]



[a] (a) $ClCO_2Et$, K_2CO_3, THF, 25 °C (99%). (b) $LiAlH_4$, THF, reflux (99%). (c) ICH_2TMS, MeCN, reflux (88%). (d) Na/NH_3, EtOH, THF, −78 °C (94%). (e) $HClO_4$, MeOH–H_2O, reflux (95%).

Results

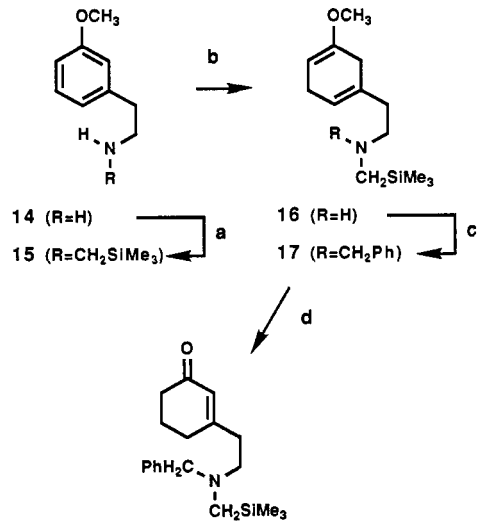
Preparation of the (Aminoethyl)cyclohexenones. The sequences used to prepare the (aminoethyl)cyclohex-2-en-1-ones whose photochemistry was explored in this study are all based upon substituted anisole, Birch reduction methodologies. Representative examples of the routes employed are given in Schemes III–VI below and in sequences A–M in the supplementary material.

The α-linked, silylmethyl-substituted amino cyclohexenone **6** was synthesized by a sequence (Scheme III) initiated by Birch reduction–alkylation of the *o*-anisic acid **1** with 1-bromo-2-chloroethane. This process provides the spirocyclic lactone **2**, which is then converted to the enone alcohol **3** by acid hydrolysis. In the final step of the sequence, iodide **5** derived from **3** is transformed to **6** by reaction with the known[3] *N*-benzyl-*N*-(trimethylsilyl)methylamine. While other methods can be envisaged for the preparation of this cyclohexenone, the one shown in Scheme III is modestly efficient, short, and potentially flexible.

The γ-linked silyl amino cyclohexenone **12** was obtained by a route starting with p-methoxyphenethylamine **7** (Scheme IV), involving sequential introduction of the *N*-methyl and *N*-(trimethylsilyl)methyl groups followed by Birch reduction and hydrolysis of the resulting cyclohexadiene **11**. Under optimal conditions (i.e., sufficient time to allow full equilibration of the double bond isomers), the hydrolysis step provides a 3.5:1 mixture of the desired cyclohex-2-en-1-one **12** along with the minor cyclohex-

(3) Padwa, A.; Chen, Y.-Y.; Chiacchio, U.; Dent, W. *Tetrahedron* **1985**, *41*, 3529.

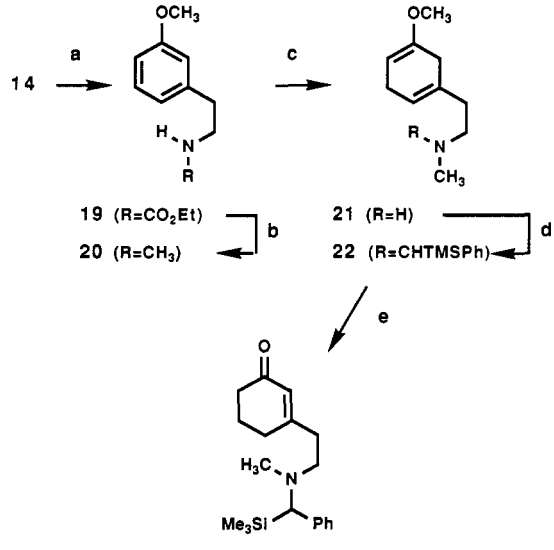
Scheme V[a]



18

[a](a) ICH_2TMS, MeCN, reflux (90%). (b) Na/NH_3, EtOH, THF, −78 °C (95%). (c) ICH_2Ph, Et_3N, MeCN, 25 °C (75%). (d) $HClO_4$, $MeOH-H_2O$, 25 °C (94%).

Scheme VI[a]



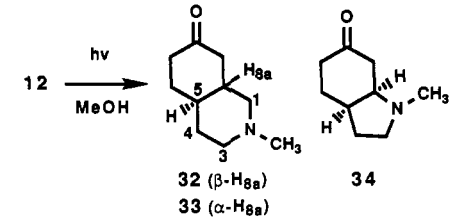
23

[a](a) $ClCO_2Et$, K_2CO_3, THF, 25 °C (98%). (b) $LiAlH_4$, THF, 25 °C (94%). (c) Li/NH_3, THF, EtOH (90%). (d) PhCH (TMS) Br, DIEA, MeCN, 25 °C (30%). (e) $HClO_4$, $MeOH-H_2O$, 25 °C (90%).

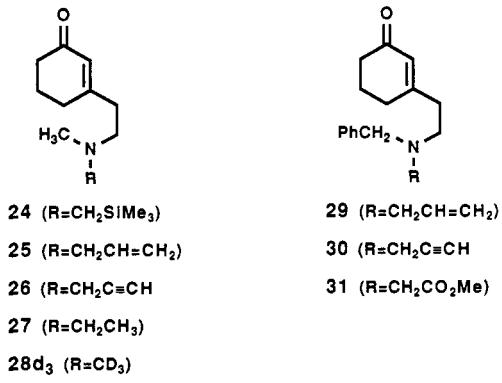
3-en-1-one **13** isomer. This mixture, reflecting the typical equilibrium phenomenon for 4-alkylcyclohexenones, is used in the photochemical studies described below.

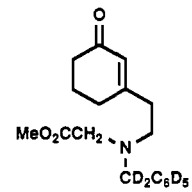
Two general procedures, differing in the order used for the introduction of N-substituents and for Birch reduction, were implemented to prepare the series of β-linked (aminoethyl)-cyclohex-2-en-1-ones probed in these investigations. Representative of these are the sequences presented in Schemes V and VI, which were employed in the synthesis of the respective enones **18** and **23**. In the first, *m*-anisylethylamine **14** is transformed into the silylmethyl derivative **15**. Birch reduction followed by N-benzylation and enol ether hydrolysis then converts **15** into the target silyl amine enone **18**. For the preparation of enone **23**, arylethylamine **14** is N-methylated, and the resulting secondary amine **20** is reduced under the Birch conditions to give cyclohexadiene **21**. Alkylation of this substance with the known α-(trimethylsilyl)benzyl bromide[4] followed by hydrolysis gives enone

Scheme VII



23. The other 3-[(*N*,*N*-disubstituted)aminoethyl]cyclohex-2-en-1-ones **24**–**31** required as part of these efforts are prepared by closely related procedures.





31d7

Photochemistry of the (Aminoethyl)cyclohexenones. General Methodology. The direct and SET-sensitized irradiation induced photochemistry of the (aminoethyl)cyclohexenones, prepared by the above procedures, was explored next. Direct-irradiation reactions employing uranium glass filtered light (λ > 320 nm) were conducted on ca. 1×10^{-3} M solutions of the enones in nitrogen-purged MeOH and MeCN. The sensitized processes involved the use of 9,10-dicyanoanthracene (DCA) and 1,4-dicyanonaphthalene (DCN), typical[5,6] SET sensitizers with long-lived, readily reduced singlet excited states.[6] Irradiations of ca. 10^{-3}–10^{-4} M solutions of DCA or DCN and the aminoethyl enones with uranium glass filtered light results in >ca. 80–90% light absorption by the sensitizers.

The products of these photoreactions were isolated by chromatographic methods and characterized as pure materials by use of spectroscopic and chemical methods. Accurate analyses of product yields and ratios were performed by use of both GLC and ^{13}C NMR spectroscopy techniques.

Photochemistry of the γ-(Aminoethyl)cyclohexenone 12. Direct irradiation of a MeOH solution of the γ-(aminoethyl)cyclohexenone **12** leads to clean formation of the separable diastereomeric hydroisoquinolones **32** (51%) and **33** (40%) (Scheme VII). A minor product (ca. 1%) possessing the hydroindolone structure **34** is also isolated from the photoreaction mixture. The yield of **34**, a substance arising by photoinduced oxidative desilylmethylation of **12**, is enhanced when direct irradiation of **12** is conducted on an air-saturated MeOH solution. In this case,

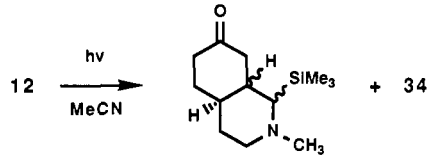
(4) Tsuge, O.; Tanaka, J.; Kanemasa, S. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1991.
(5) Maroulis, A. J.; Shigemitsu, Y.; Arnold, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 534.
(6) Mattes, S. L.; Farid, S. *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, pp 233–326.

Table I. Selected ^{13}C NMR Chemical Shifts for Hydroisoquinolones **32** and **33** and Related 2-Methyldecahydroisoquinolines (NMDI)

substance	^{13}C NMR chemical shifts[a]			
	C-1	C-3	C-4	C-5
32	62.2	55.8	32.4	31.9
33	58.7	53.9	28.9	26.9
trans-NMDI[b]	62.8	56.6	33.0	33.3
cis-NMDI[b]	59.9	54.7	28.0	29.1

[a] Assignments for **32** and **33** are aided by ^{13}C NMR analysis of the 6,6,8,8-tetradeuterio analogues of **32** and **33** prepared by exchange in NaOH in CD_3OD–D_2O. [b] Data taken from ref 7.

Scheme VIII

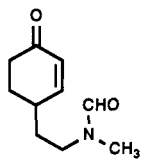


35 a, b and c

32, **33**, and **34** are generated in respective yields of 31%, 15%, and 34%.

Differentiation between the trans- and cis-fused hydroisoquinolines **32** and **33** proved to be straightforward on the basis of characteristic differences between their ^{13}C NMR spectroscopic properties and comparisons with ^{13}C NMR data for the known[7] *trans*- and *cis*-2-methyldecahydroisoquinolines (NMDI). Significant in this regard is the ca. 3–5 ppm downfield shift displayed by the methylene C-1, C-3, C-4, and C-5 carbons of the trans isomer **32** as compared to those of the cis-fused isomer **33** (Table I). The γ-gauche effects on the axial methylene carbons in **33** are nearly identical with those that influence the ^{13}C NMR chemical shifts of related carbons in the *cis*-NMDI model.

The key evidence for assignment of the cis-ring-fusion stereochemistry in hydroindolone **34** is found in the ^1H NMR coupling pattern for the bridghead proton H-7a in the 5,5,7,7-tetradeuterio analogue, **34***d*$_4$, formed by base-catalyzed exchange in CD_3OD–D_2O. In the spectrum of **34***d*$_4$, the H-7a proton appears as a dd (J = 2.0 and 2.3 Hz) as a result of vicinal equatorial–axial coupling to H-3a and long-range W coupling to H-4eq. This demonstrates the equatorial deposition of H-7a as is expected for the cis stereochemistry of **34** and its existence in the conformation portrayed in **34***d*$_4$.



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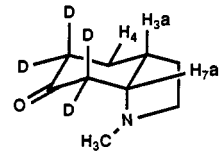
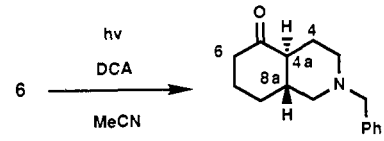


34d$_4$

The nature of the excited-state chemistry of **12** changes when it is induced by direct irradiation in MeCN rather than MeOH. Chromatographic separation of the product mixture formed in this fashion affords three stereoisomeric TMS-containing hydroisoquinolones **35a–c** (50%, 3:3:2 ratio) (Scheme VIII) along with a minor amount of hydroindolone **34**. Although the stereoisomers **35a–c** are separable, their individual spectroscopic properties are not sufficiently characteristic to make stereochemical diagnosis possible. Presumably, these substances have both the cis- and trans-ring-fusion stereochemistries and, in one case, both configurations at the TMS-substituted C-2 center.

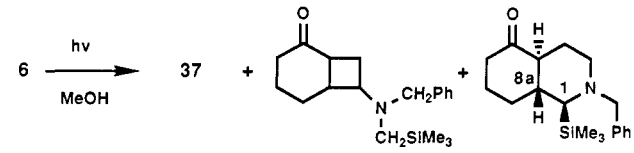
Photocyclization of the γ-(aminoethyl)cyclohexenone **12** can also be promoted by SET sensitization. Thus, irradiation of an MeOH solution of DCA and enone **12** leads to generation of the hydroisoquinolones **32** (13%) and **33** (72%) along with hydroindolone **34** (2%). The ratio of **34**:**32** + **33** increases significantly as the concentration of DCA is increased. Accordingly, a change in [DCA] from 1.1×10^{-4} to 2.3×10^{-4} M for reaction of **12** in 85:15 MeOH–MeCN results in a change of **32**, **33**, and **34** product yields from 9%, 72%, and 2% to 3%, 41%, and 10%, respectively. Although it would have been desirable to determine this ratio over a greater [DCA] range, this is prevented by the low solubility of DCA in the appropriate solvent systems. Halocarbon solvents have an interesting[1] effect on the DCA-sensitized process. Irradiation of a DCA and **12** solution in CH_2Cl_2, for example, provides the hydroindolone **34** exclusively. Oxygen also alters this chemistry as indicated by the observation that irradiation of an air-saturated, 85:15 MeOH–MeCN solution of DCA (1×10^{-4} M) and **12** results in the formation of a mixture of the hydroisoquinolones **32** and **33** (trace), the hydroindolone **34** (23%), and the formamide **36** (41%). Finally, SET sensitization of the reaction of **12** by the cyanoarene DCN in MeCN at high [DCN] (7.7×10^{-3} M) leads to production of the hydroisoquinolones **32** (9%) and **33** (71%) mainly, along with only a minor amount of the hydroindolone **34**.

Scheme IX



37

Scheme X



38 39

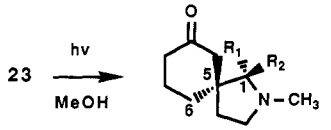
Photochemistry of the α-(Aminoethyl)cyclohexenone 6. Unlike the γ- and β-(aminoethyl)cyclohexenones, the α-analogue **6** has the silyl aminoalkyl side chain positioned close to the carbonyl chromophore. This structural feature could have an impact on the excited-state SET reaction pathways followed by **6**. As a result of this issue and our goal to explore synthetic and mechanistic aspects of (aminoalkyl)cyclohexenone photochemistry, the direct and SET-sensitized photoreactions of **6** were investigated.

We have found that the α-(aminoalkyl)cyclohexenone **6** undergoes an efficient photocyclization reaction to produce the *trans*-hydroisoquinolone **37** (89%) upon DCA-sensitized (3×10^{-4} M) irradiation in MeCN (Scheme IX). The fact that deuterium incorporation does not occur when a CD_3OD–D_2O solution of **37** is stirred for 12 days at 25 °C suggests that epimerization at C-4a does not take place readily under the mild conditions present in the photoreaction mixture and, thus, that the trans stereochemistry in **37** has a kinetic origin. Deuterium exchange does occur when **37** is treated with NaOH in CD_3OD–D_2O to give the 4a,7,7-trideuterio derivative **37***d*$_3$, as attested to by the disappearance of NMR resonances corresponding to the H-4a (1.91 ppm) and H-6 (2.29 and 2.36 ppm) protons and associated carbons (53.4 and 41.5 ppm, respectively). The other ^1H and ^{13}C NMR resonances for **37***d*$_3$ have chemical shifts identical with those for **37**, suggesting that both substances have the thermodynamically more favorable trans-ring-fusion stereochemistry. This conclusion is verified by inspection of the ^1H NMR spectrum of **37** in which H-4a resonates as a ddd with two large (11.6 and 11.7 Hz) axial–axial couplings with H-8a and H-4ax and one small (3.4 Hz) axial–equatorial coupling to H-4eq.

In contrast, the direct-irradiation reactions of the α-(aminoethyl)cyclohexenone **6** are both less efficient and less chemoselective. Accordingly, direct irradiation of **6** in MeOH leads to production of hydroisoquinolone **37** (13%) along with its C-1 TMS analogue **39** (26%) and the [4.2.0]bicyclic amino ketone **38** (12%)

(7) Bailey, J. M.; Booth, H.; Al-Shirayda, H. A. R. Y. *J. Chem. Soc., Perkin 2* **1984**, 583.

Scheme XI



40 (R_1=H, R_2=Ph)

41 (R_1=Ph, R_2=H)

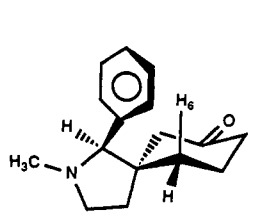
Table II. Characteristic NMR Data for Stereoisomeric Spirocyclic Amino Ketone Pairs

spirocyclic amino ketones	^{13}C NMR (ppm) C-5	C-1	^{1}H NMR (ppm) H-1	H-6ax (m; *J*(Hz))
40	50.5	81.3	2.96	1.5–1.8 (m)
41	49.9	82.3	2.72	0.78 (dt; 14.0, 14.0)
46	50.2	83.7	3.03	1.4–1.5 (m)
47	49.2	84.7	2.79	0.75 (m)
60	49.9	78.8	3.23	1.6–1.8 (m)
61	49.9	79.9	2.97	0.80 (ddd; 4.0, 13.3, 13.4)
65	50.0	75.8	3.47	1.56 (m)
66	49.5	76.7	3.22	0.84 (ddd; 4.1, 13.4, 13.6)
70	49.9	76.9	3.37	1.7–1.8 (m)
71	49.4	78.3	3.30	0.83 (dt; 4.1, 13.3)

(Scheme X). The structures and stereochemistry (**39** only) of these substances were elucidated by use of characteristic spectroscopic data. The same methods employed in assigning the ring-fusion stereochemistry to the non-TMS analogue **37** were used in establishing **39** as the trans diastereomer. The β-TMS orientation at C-1 follows from the appearance of H-1 in the ^{1}H NMR at 2.40 ppm as a doublet with a large axial–axial coupling (11.6 Hz) to H-8a.

Direct irradiation of **6** in MeCN yields the TMS-containing products **38** (23%) and **39** (5%) together with a complex mixture of minor, unidentified products. Importantly, none of the hydroisoquinolone **37** is generated under this condition.

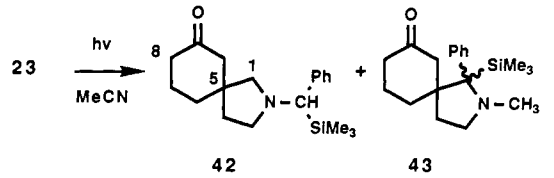
Photochemistry of the TMS-Containing β-(Aminoethyl)cyclohexenones 18, 23, and 24. The excited-state chemistry of several TMS-substituted β-(aminoethyl)cyclohexenones was investigated with the intent of further probing the scope and limitations of amine enone photocyclization reactions and of gaining more information about solvent control of chemoselectivity. The benzylic TMS enone **23** was studied first in order to delineate the profile of reactions that proceed via the intermediacy of α-amino radicals bearing additional stabilizing substituents at the odd electron center. Direct irradiation of **23** in MeOH results in efficient (78%) production of an ca. 1:1 mixture of the separable diastereomeric spirocyclic amino ketones **40** and **41** (Scheme XI). The key to unraveling stereochemistry resides in NMR spectroscopy, which provides characteristic data for these and closely related stereoisomeric spirocyclic amino ketone pairs (Table II). As can be seen by inspecting the preferred conformation **41A** of the syn (C-1 phenyl vs C-6 methylene) stereoisomer **41**, the axial H-6 proton resides in the π-face shielding region of the C-1 phenyl group. As a result, the resonance for H-6ax (and related protons in other syn isomers, Table II) occurs at the unusually upfield position of 0.78 ppm as compared to the 1.5–1.8 region for H-6ax in the anti isomer **40**.



41A

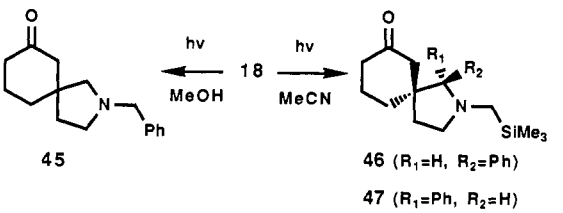
In contrast, irradiation of an MeCN solution of the β-(aminoethyl)cyclohexenone **23** leads to a product mixture that does not contain **40** to **41**. Instead an ca. 1:1 mixture of two related

Scheme XII



42 43

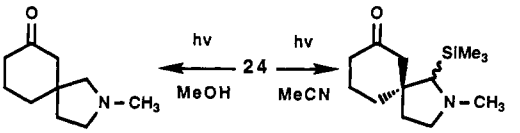
Scheme XIII



45 46 (R_1=H, R_2=Ph)

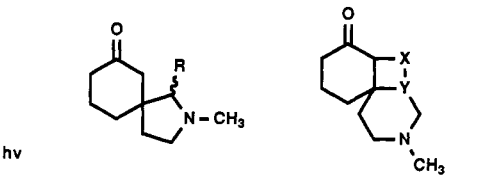
47 (R_1=Ph, R_2=H)

Scheme XIV



48 49 and 50

Scheme XV



25 ⟶ 51 and 52 (R=CH=CH_2) + 53 (X-Y=CH_2-CH)

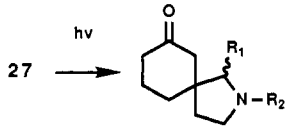
26 ⟶ 54 and 55 (R=C≡CH) + 56 (X-Y=CH=CH)

spirocyclic amino ketones, **42** (6%) and **43** (4%), is formed in low yields (Scheme XII). However, the non-TMS amino ketones **40** and **41** are produced as exclusive products (48%, ca. 3:2 ratio) in the DCA-sensitized (1×10^{-4} M) photocyclization of **23** in 85:15 MeCN–MeOH.

It is clear from the above results that both solvent and reaction type (i.e., direct vs SET-sensitized irradiation) have a pronounced effect upon the nature of the photoreaction pathways followed by the TMS-containing (aminoethyl)cyclohexenones. The trends involving preferential formation of non-TMS products from direct irradiations in MeOH and SET-sensitized irradiations and of TMS products from direct MeCN irradiations are adhered to in the photochemistry of the related silylmethylamino enones **18** and **24**. Accordingly, upon direct irradiation in MeOH **18** efficiently generates the spirocyclic *N*-benzylamino ketone **45** (71%) (Scheme XIII), whereas the separable *N*-silylmethylamino ketones **46** and **47** (65%, ca. 2:3 ratio) arise from photoreaction of **18** in MeCN (Scheme XIV). Stereochemical assignments to **46** and **47** were made by use of similar spectroscopic analyses applied to **40** and **41** (Table II). DCA-sensitized photocyclization of **18** in MeCN leads to generation of a product mixture containing mainly the non-TMS spirocyclic amine **45** (56%) and minor amounts of the TMS analogues **46** and **47** (10%, ca. 2:3 ratio), which most probably derive from a competitive direct-irradiation reaction. In a closely related fashion, direct irradiation of the silylmethylamino enone **24** in MeOH gives spirocyclic amino ketone **48** (72%), while a 4:3 mixture of the TMS-containing products **49** and **50** (76%) is formed by irradiation in MeCN (Scheme XV). Although **49** and **50** are separable, their spectroscopic properties are not sufficiently characteristic to enable assignment of stereochemistry.

Photochemistry of Non-TMS β-(Aminoethyl)cyclohexenones 25–31. The results presented above demonstrate that photo-

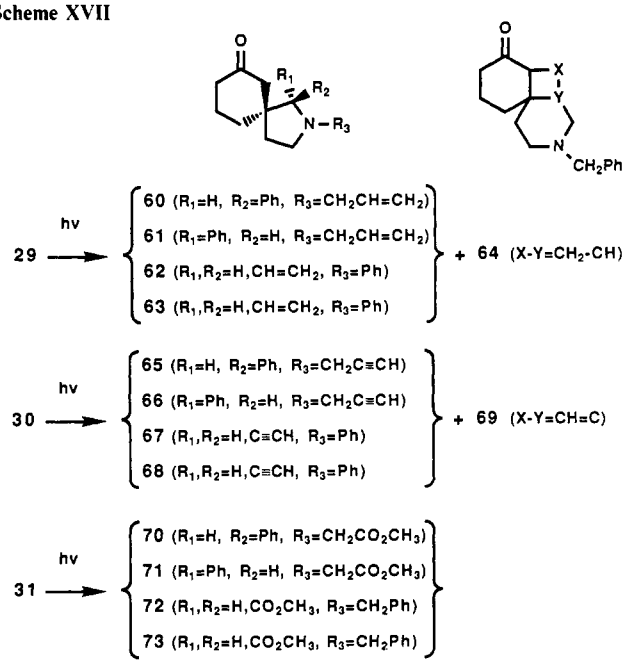
Scheme XVI



57 (R_1=H, R_2=CH_2CH_3)

58 and 59 (R_1=R_2=CH_3)

Scheme XVII

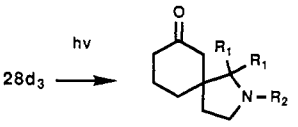


60 (R_1=H, R_2=Ph, R_3=CH_2CH=CH_2)
61 (R_1=Ph, R_2=H, R_3=CH_2CH=CH_2)
62 (R_1,R_2=H,CH=CH_2, R_3=Ph)
63 (R_1,R_2=H,CH=CH_2, R_3=Ph)
+ 64 (X-Y=CH_2-CH)

65 (R_1=H, R_2=Ph, R_3=$CH_2C{\equiv}CH$)
66 (R_1=Ph, R_2=H, R_3=$CH_2C{\equiv}CH$)
67 (R_1,R_2=H,C≡CH, R_3=Ph)
68 (R_1,R_2=H,C≡CH, R_3=Ph)
+ 69 (X-Y=CH=C)

70 (R_1=H, R_2=Ph, R_3=$CH_2CO_2CH_3$)
71 (R_1=Ph, R_2=H, R_3=$CH_2CO_2CH_3$)
72 (R_1,R_2=H,CO_2CH_3, R_3=CH_2Ph)
73 (R_1,R_2=H,CO_2CH_3, R_3=CH_2Ph)

Scheme XVIII



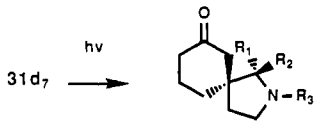
74 (R_1=H, R_2=CD_3)

75 (R_1=D, R_2=CH_3)

cyclization reactions of TMS-containing (aminoethyl)cyclohexenones in MeCN display remarkably high degrees of regioselectivity for bond formation at amine α-carbon centers. The selectivities observed relate to the α-C–H bond kinetic acidity of intermediate amine cation radicals and its control by α-substituents. We deemed that a more complete exploration of this issue was worthwhile. As a result, studies have been performed on a series of tertiary β-(aminoethyl)cyclohexenones **25–31**, each possessing differentially substituted α-amine sites. The spirocyclic amino ketones formed in photocyclization reactions of these substances occurring in both MeCN and MeOH (Schemes XVI–XIX) were isolated and characterized. The product yields were accurately determined by NMR and GLC methods and are listed in Table III.

Additional information about the nature of these reactions has been gained by measurements of *d* isotope effects. These were determined by internal competition in the photocyclization reactions of the *N*-CH_3, *N*-CD_3 derivative **28**d_3 in MeCN and MeOH (Scheme XVIII). The ratios of spirocyclic amino ketones **74** and **75** generated from **28**d_3 were quantitated by ^{13}C NMR analysis by using the NONOE technique to maximize integration accuracy. This gave an observed *d* isotope effect of 2.4 for reaction in MeOH and 5.1 in MeCN. The isotope effects on the photocyclization reaction were also evaluated by external comparison. In this case, the (**70** + **71**):(**72** + **73**) product ratios for MeOH

Scheme XIX



76 (R_1=D, R_2=C_6D_5, R_3=$CH_2CO_2CH_3$)

77 (R_1=C_6D_5, R_2=D, R_3=$CH_2CO_2CH_3$)

78 (R_1,R_2=H, CO_2CH_3, R_3=$CD_2C_6D_5$)

79 (R_1,R_2=H, CO_2CH_3, R_3=$CD_2C_6D_5$)

Table III. Product Yields of Photoreactions of the Non-TMS β-(Aminoethyl)cyclohexenones **25–31**

amino enone	products	percent yields[a] (stereoisomer ratio) MeCN	MeOH
25	**51** + **52**[b]	69 (1)	79 (1)
	53	15	0
26	**54** + **55**[b]	59 (1)	79 (1)
	56	23	5
27	**58** + **59**[c]	34 (1.2)	17 (1.6)
	57	24	17
29	**60**[d]	5	10
	61[d]	7	12
	62 + **63**[c]	25 (1.1)	66 (1.2)
	64	35	0
30	**65**[d]	3	8
	66[d]	4	11
	67 + **68**[c]	24 (1.1)	38 (1.2)
	69	36	10
31	**70**[d]	10	20
	71[d]	13	24
	72 + **73**[e]	12	28

[a] Yields based on recovered starting materials. [b] Mixture of isomers, ratio determined by GLC. [c] Isomers separated, ratio determined by GLC, stereochemistry not determined. [d] Isomers separated, ratio determined by GLC, stereochemistry determined (see Table II). [e] Isomers separated, stereochemistry not determined, ratio cannot be determined by GLC.

and MeCN reactions of the all-protio amino enone **31** (Scheme XVII) are compared to the (**76** + **77**):(**78** + **79**) ratios for cyclizations of its heptadeuterio analogue **31**d_7 (Scheme XIX) to give an observed *d* isotope effect of 2.2 for reaction in MeOH and 6.6 in MeCN.

Discussion

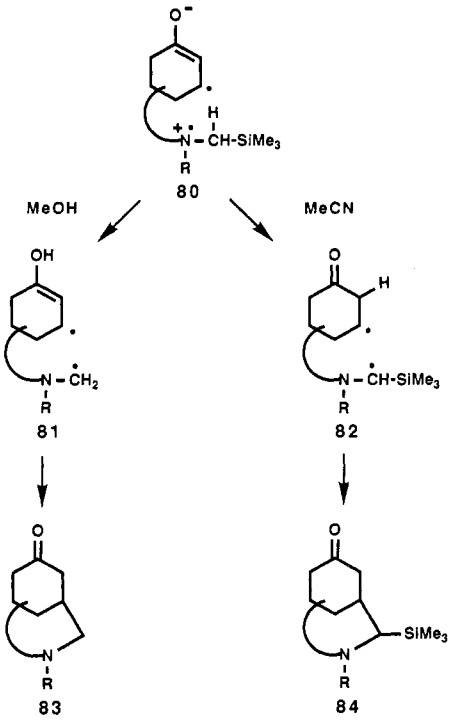
Mechanisms for the Direct and SET-Sensitized Photocyclization Processes. The photocyclization reactions of the TMS-containing (aminoethyl)cyclohexenones described above proceed by SET mechanisms. The direct-irradiation processes are promoted by excitation of the conjugated cyclohexenone chromophore, resulting in initial population of n–π^* singlet excited states. In intermolecular systems explored previously,[2,8] enone π–π^* triplets formed by ISC from singlet precursors were identified as the excited states responsible for SET quenching by tertiary amine donors. However, it is difficult to extend this conclusion about reaction multiplicity to intramolecular amine enone SET processes since the rates of SET could be competitive with or greater than those for ISC.[8b]

Intramolecular SET from the silyl amine donors to the cyclohexenone excited states results in formation of either singlet or triplet zwitterionic diradicals **80**. As we have convincingly demonstrated in our earlier efforts,[2,9] the pathways followed in ensuing

(8) (a) Pienta, N. J. *J. Am. Chem. Soc.* **1984**, *106*, 2704. Pienta, N. J.; McKimmey, J. E. *Ibid.* **1982**, *104*, 5501. Smith, D. W.; Pienta, N. J. *Tetrahedron Lett.* **1984**, 915. Dunn, D. A.; Schuster, D. I.; Bonneau, R. *J. Am. Chem. Soc.* **1985**, *107*, 2802. Schuster, D. I.; Bonneau, R.; Dunn, D. A.; Dubien, J. J. *Ibid.* **1984**, *106*, 2706. Cookson, R. C.; Hudec, J.; Mirza, N. A. *J. Chem. Soc., Chem. Commun.* **1986**, 180. (b) For a discussion of this issue, see: Wagner, P. J.; Kemppainen, P. E.; Jellinek, T. *J. Am. Chem. Soc.* **1972**, *94*, 7512.

(9) Zhang, X.-M.; Mariano, P. S. *J. Org. Chem.* **1991**, *56*, 1655.

Scheme XX

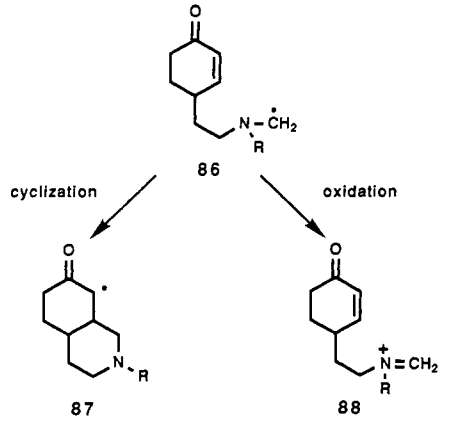


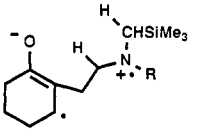
reactions of the ion radical components of intermediates **80** are highly dependent on the medium. In accord with the results of pulse radiolysis studies,[10] our prior investigations[2,9] showed that enone anion radicals are not strongly basic species, especially in polar protic solvents where stabilization by H-bonding interactions with the oxy anionic centers can occur. It is important to emphasize that enone anion radicals are not sufficiently basic to be protonated by water or alcohols (e.g., pK_a's (H_2O) of hydroxyallyl radicals are ca. 10).[10] Even though tertiary amine cation radicals are acidic (pK_a (H_2O) ca. 8),[11] they are not rapidly deprotonated by enone anion radicals when both are formed in polar protic solvents like MeOH. As a result, alternate reaction pathways can be followed. In the case of α-silyl amine cation radicals, an alternate pathway involves desilylation by transfer of the trialkylsilyl group to the solvent or other nucleophiles. Thus, in solvents like MeOH where deprotonation is retarded and desilylation is facilitated, zwitterionic diradicals related to **80** undergo preferential desilylation to produce non-TMS-containing diradicals **81**, which transform to products by diradical coupling (Scheme XX).

The nature and chemistry of enone anion–amine cation radical pairs change dramatically when present in less polar aprotic media. In aprotic solvents like MeCN, proton transfer between these charged radicals existing as contact ion pairs is rapid. Similarly, proton transfer resulting in charge annihilation should also be rapid in intramolecular systems. In zwitterionic diradicals (**80**) derived from the TMS-containing γ- and β-(aminoethyl)cyclohexenones, proton transfer from the silicon-substituted centers (see below) to the anion radical α-carbon rather than to the carbonyl oxygen should be more facile owing to orientation and distance effects (Scheme XX). The diradical intermediates (**82**) generated in this fashion cyclize to produce the corresponding TMS-containing products.

The propensity for proton transfer vs desilylation is not only governed by the solvent but is also dependent on the structure of the zwitterionic diradical. For intermediates of this type derived from the γ- and β-(aminoethyl)cyclohexenones, proton transfer is restricted to occur to the enone anion radical α-carbon, owing to strain developed in transition states for proton transfer to the carbonyl oxygen. In contrast, the zwitterionic diradical intermediate **85**, arising from photoinduced SET in the α-amino enone **6**, has the cation radical side chain positioned close to the oxygen of the anion radical. Consequently, proton transfer to the oxy anionic center can occur via either a 6- or 8-membered transition state and, unlike with the corresponding γ and β systems, proton transfer to the anion radical α-carbon can occur in **85** via a 6-membered transition state. These factors are those that allow proton transfer from the α-carbons in the amine cation radical moiety to be competitive with desilylation in reactions of **6** even in MeOH.

Scheme XXI





The SET-sensitized reactions of silyl (aminoethyl)cyclohexenones are exceptionally clean, providing non-TMS cyclization products in modestly high yields. The mechanistic pathways for product formation in these processes involve endo or exo radical cyclizations rather than diradical coupling. Accordingly, the singlet excited state of DCA ($E_{1/2}$ (−) = ca. 2.9 V)[6] produced by light absorption is capable of rapidly oxidizing the tertiary amine functions ($E_{1/2}$ (+) = ca. 1.0 V) of the amino enones. Owing to the exceptionally low basicity of the DCA anion radical,[12] desilylation rather than deprotonation of the resulting silyl amine cation radical intermediates is the favored process even in MeCN. The formed α-amino radicals **86**, owing to their electron-rich nature (i.e., high energy SOMO), undergo either 6-exo, 5-exo, or 6-endo cyclizations by conjugate addition to the cyclohexenone moieties to efficiently produce α-keto radicals **87** (Scheme XXI). In parallel efforts,[1] we have demonstrated that termination of these radical cyclization reactions occurs by back electron transfer to the α-keto radicals **87** from the DCA anion radical followed by protonation of the resulting enolate anions. This proposal is consistent with the observation that DCA serves only a catalytic role in these sensitized photocyclization reactions, as it is recovered in most instances nearly quantitatively.

The fact that alternative reactions are available to the intermediate α-amino radicals **86** is emphasized by (1) the DCA concentration and halocarbon-dependent formation of hydroindolone **34** from reaction of amino enone **12** and (2) the production of formamide **36** when the DCA-sensitized reaction of **12** is conducted on air-saturated solutions. The first observations are easily understood on the basis of the ready one-electron oxidation of **86**, owing to its predictably low oxidation potential ($E_{1/2}$ (+) = ca. −1.0 V)[13] and the high reduction potentials of DCA

(10) Hayon, E.; Ibata, J.; Lichtin, N. N.; Simic, M. *J. Phys. Chem.* **1972**, *76*, 2072. Lilie, J.; Henglein, A. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 170.

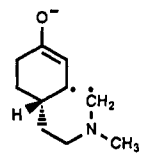
(11) Tertiary amine radical cation α-CH pK_a values have been measured (ref 23) and calculated (ref 25).

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

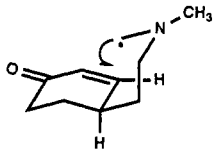
($E_{1/2}$ (−) = −0.89 V) and halocarbons such as CCl_4.[1] The formaldiminium cation **88** produced by oxidation of **86** readily hydrolyzes under the reaction conditions or on workup to give the secondary amine precursor of **34**. It is important to point out that DCN ($E_{1/2}$ (−) = −1.2 V) is not capable of rapidly oxidizing α-amino radicals and, as a result, reaction of **12** sensitized by high concentrations of this cyanoarene yields mainly **32** and **33**.

Stereoselectivity of the SET-Sensitized Reactions. The greater degree of stereoselectivity observed in the SET-sensitized vs direct irradiation induced photocyclizations of the γ-(aminoethyl)-cyclohexenone **12** is consistent with the mechanistic differences outlined above. The direct-irradiation reaction of **12** in MeOH leads to production of an ca. 1:1 mixture of the *cis*- and *trans*-hydroisoquinolines **33** and **32** (see Scheme VII). Ring-juncture stereochemistry in this case is determined in the diradical **89** cyclization step where axial bonding provides the cis product and equatorial bonding gives the trans product. Diradical cyclizations generally have exceedingly low activation energies and, thus, display low stereoselectivities unless the diradical intermediates have triplet multiplicities and large energy differences between conformers, which individually serve as precursors of stereoisomeric products.[14] Apparently, the diradical **89**, which serves as the precursor for **32** and **33**, does not possess any reactive conformer preference and, consequently, it gives the two stereoisomeric products with near-equal facility.

In contrast, the SET-sensitized reaction of **12** displays a modest degree of stereoselectivity favoring the *cis*-hydroisoquinoline **33** by a factor of ca. 6:1 at 20 °C. This outcome is reflective of the radical cyclization mechanism followed in this process and the preference for axial over equatorial addition of the α-amino radical (see **90**) to the cyclohexenone function. Stereoelectronic controls of this type in radical additions to cyclohexenones have been noted earlier.[15]

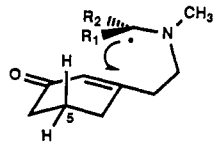


89



90

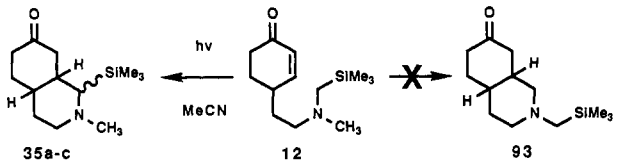
A more subtle stereochemical difference has been observed between the direct and SET-sensitized reactions of the β-silyl-(aminoethyl)cyclohexenone **23**. In these processes, photocyclization leads to the generation of the syn and anti stereoisomeric products, **40** and **41**, respectively, which contain two chiral centers flanking the newly formed carbon–carbon bond. In contrast to the direct-irradiation process in MeOH, which gives an ca. 1:1 ratio of **40** and **41**, the DCA-sensitized reaction of **23** yields a mixture in which the syn isomer **40** predominates by ca. 1.5:1. The small but finite stereoselectivity displayed by the sensitized reaction is associated with the operation of a radical cyclization mechanism in which axial addition of the benzylic α-amino radical is favored. Of the two transition states, **91** and **92**, with this preference, the one having the *syn*-phenyl orientation, i.e. **91**, is of lower energy as expected, owing to the lack of the phenyl–H-5ax interaction present in its anticounterpart **92**.[16]



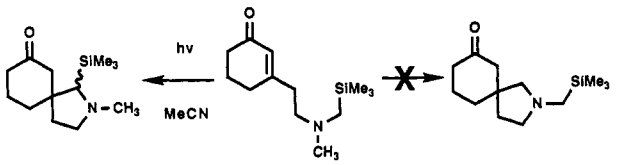
91 (R_1=H, R_2=Ph)

92 (R_1=Ph, R_2=H)

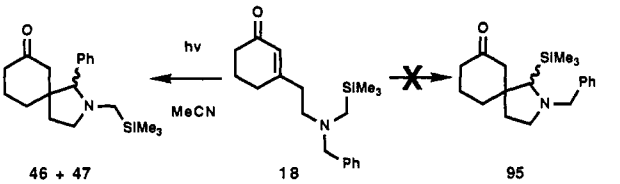
Substituent Effects on Amine Cation Radical Kinetic Acidities. Perhaps the most novel and interesting mechanistic issue arising from the current studies relates to the factors governing photocyclization regioselectivities. Preliminary observations made in our investigations of γ- and β-(aminoethyl)cyclohexenones suggested that substituents at the α-amine carbons have pronounced effects upon the regiochemical course of these photocyclization processes. For example, we noted that direct irradiation in MeCN of the silicon-containing γ-amino enone **12** leads to exclusive production of the diastereomeric ring-TMS-substituted hydroisoquinolines **35a–c** and none of the structurally isomeric *N*-CH_2TMS analogue **93**. Likewise, the epimeric spirocyclic amines, **49** and **50**, and not their TMS-methyl counterpart **94** are generated by irradiation of the β-amino enone **24** in MeCN. In contrast, photocyclization of the closely related, silicon-containing *N*-benzyl-β-amino enone **18** in MeCN occurs to yield the spirocyclic amine products, **46** and **47**, resulting from bond formation at the benzylic center, rather than the *N*-benzyl analogue **95**, arising by bonding at the TMS-substituted amine α-carbon.



35a-c **12** **93**



49 + 50 **24** **94**



46 + 47 **18** **95**

These initial findings were intriguing since they pointed out that the cyclization reactions could be controlled not only by the competition between desilylation vs deprotonation of intermediate zwitterionic diradicals but also by the rates of α-CH deprotonation at the amine cation radical centers. Specifically, amine cation radical kinetic acidity and its control by α-substituents is the source of the regioselectivities seen in these processes, since it governs the relative rates of formation of diradical precursors to the cyclization products.

The issue of amine cation radical acidity is not a new one; it has been addressed in a number of previous photochemical,[2,9,17-20] oxidation,[21] electrochemical,[22] pulse radiolysis,[23] and related[24,25]

(13) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132.

(14) (a) Publications discussing and referencing stereochemical aspects of diradical cyclizations are given in refs 14b and 14c. (b) Cho, I.-S.; Lee, C.-P.; Mariano, P. S. *Tetrahedron Lett.* **1989**, *30*, 799. (c) Wagner, P. J.; Park, B. S. *Ibid.* **1991**, *32*, 165.

(15) Benko, Z.; Fraser-Reid, B.; Mariano, P. S.; Beckwith, A. L. J. *J. Org. Chem.* **1988**, *53*, 2066.

(16) Higher degrees of stereoselectivity have been observed in related radical cyclization; see for example: Hanessian, S.; DiFabio, R.; Marcoux, J.-F.; Prudhomme, M. *J. Org. Chem.* **1990**, *50*, 3436.

(17) Lewis, F. D. *Acc. Chem. Res.* **1986**, *19*, 401. Lewis, F. D.; Ho, T.-I.; Simpson, J. T. *J. Am. Chem. Soc.* **1982**, *104*, 1924. *J. Org. Chem.* **1981**, *46*, 1077.

(18) Xu, W.; Jeon, Y.-T.; Hasegawa, E.; Yoon, U. C.; Mariano, P. S. *Ibid.* **1989**, *111*, 406.

(19) Cohen, S. G.; Stein, N. M. *J. Am. Chem. Soc.* **1971**, *93*, 6542.

(20) Shaefer, C. G.; Peters, K. S. *J. Am. Chem. Soc.* **1980**, *102*, 7566.

(21) Lindsay-Smith, J. R.; Mead, L. A. V. *J. Chem. Soc., Perkin Trans. 2* **1973**, 206.

(22) Smith, P. J.; Mann, C. K. *J. Org. Chem.* **1969**, *34*, 1821. Lindsay-Smith, J. R.; Masheder, P. *J. Chem. Soc., Perkin Trans. 2* **1976**, 47.

Scheme XXII

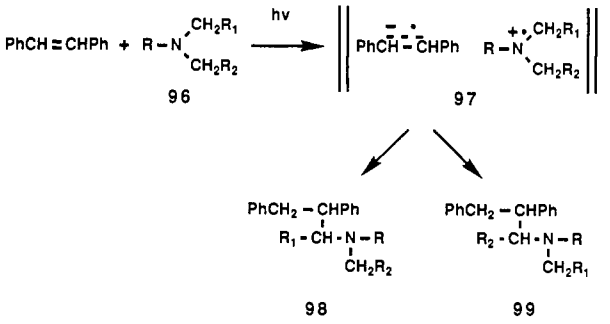
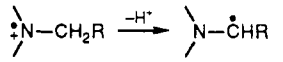


Table IV. Relative Perhydrogen Kinetic Acidities of α-R-substituted Tertiary Amine Cation Radicals



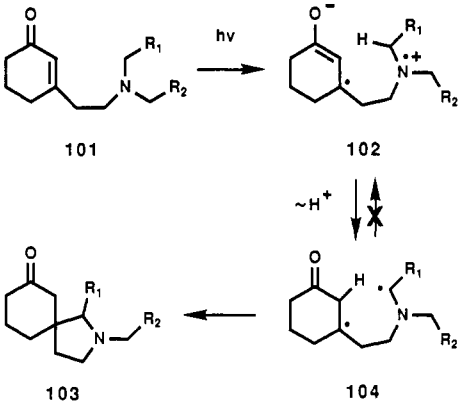
R	this work CH_3CN	this work CH_3OH	Lewis' work[17] CH_3CN	calcd relative pK_a values[d]
H	0.01[b]	0.01[b]	1.1	+16
CH_3	0.02[b]	0.02[b]	0.5	
$Si(CH_3)_3$	0.1[a,b]			
CO_2CH_3	0.5[c]	0.6[c]	2.3	+3
Ph	1.0[c]	1.0[c]	1.0	+1
$CH{=}CH_2$	1.9[c]	3.0[c]	0.5	-1
$C{\equiv}CH$	3.9[c]	2.0[c]	ca. 111	-3

[a] A lower limit based upon product detectability. [b] Comparisons are possible between H and CH_3, but only upper limits are possible in comparisons with others. [c] Comparisons are possible between CO_2CH_3, Ph, $CH{=}CH_2$, and $C{\equiv}CH$, but only lower limits are possible in comparisons with others. [d] Calculated by the methods described previously (ref 27).

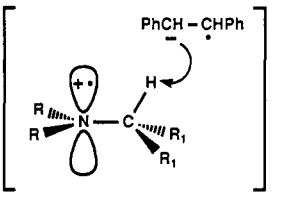
studies. The pK_a values of selected amine cation radicals have been estimated ($[(p\text{-}MeOC_6H_4)_2NCH_3]^{\bullet+}$ ca. 10 in MeCN)[25] and measured ($[Me_3N]^{\bullet+}$ ca. 8 in H_2O).[23] In addition, the rates of deprotonation of these intermediates have been determined. Accordingly, Das and von Sonntag[23] observed by using pulse radiolysis techniques that the trimethylamine cation radical is deprotonated by trimethylamine in H_2O with a bimolecular rate constant of 7.3×10^8 M^{-1} s^{-1} (25 °C). In a careful and thorough study of this issue, Dinnocenzo and Banach[25] have measured rate constants for proton transfer from *N,N*-di-*p*-anisyl-*N*-methylaminium hexafluoroarsenate to quinuclidines (ca. 1×10^5 M^{-1} s^{-1} in MeCN) by use of stopped-flow kinetic techniques. The observed rate constants for the latter reactions were found to vary with the base strength of the quinuclidines (β value from a Bronstead plot of ca. 0.63), to be associated with a small $\Delta H^{\ddagger}$ (ca. 4 kcal/mol) and large negative $\Delta S^{\ddagger}$ (ca. -22 cal/mol·deg), and to have large and base strength dependent kinetic deuterium isotope effects (ca. 6–7).

The dependence of amine cation radical α-CH kinetic acidity on α-substituents has not been explored in this same degree of detail. The only intensive investigation of this issue has been conducted by Lewis and his co-workers[17] in the context of their study on photoadditions of tertiary amines to stilbenes. Product distributions (**98**:**99**) arising from reactions of unsymmetrically substituted amines **96** to stilbene have been converted into relative kinetic acidities of intermediate amine cation radicals (Scheme XXII). The data, in the form of a relative acidity scale (Table IV), shows that in this system the rates of amine cation radical deprotonation by the stilbene anion radical in a contact pair **97** are governed by synergistic steric and stereoelectronic effects. Lewis[17] concluded that steric factors are important in governing the energies of transition states (**100**) for proton removal in a plane parallel to the nitrogen p orbital in the amine cation radical. While

Scheme XXIII



Lewis has emphasized the steric strain associated with internal interactions in the amine cation radical components of these transition states (i.e., between R_1 and R), the energetic consequences of intermolecular interactions (i.e., between stilbene anion and amine cation radical) developed in **100** cannot be ignored.



Likewise, the role of orientation of the charged partners in the contact ion radical pairs **97**, although difficult to assess, could play a role in influencing proton-transfer rates. This would be especially important if, as Dinnocenzo[25] has found, these processes have exceedingly low activation enthalpies and, as a result, rates that are limited by entropic factors. Proton transfers in contact ion radical pairs could be exceedingly rapid and, consequently, selectivities could be a function of sterically controlled orientation of the components in these pairs.

Our observations and methodology have provided us with an opportunity and an ability to investigate the problem of substituent control of amine cation radical kinetic acidity. We have accomplished this through studies with β-(aminoethyl)cyclohexenones of general structure **101** (Scheme XXIII). The distributions of products obtained from photocyclizations of these systems (e.g., **18**, **24–27**, **29–31**), which proceed via the intermediacy of zwitterionic diradicals **102**, reflect the effects of substituents (R_1 vs R_2) on the kinetic acidity of amine cation radicals. Furthermore, the reasonably high yields of these photocyclizations enable their use in this context. The *d* isotope effects of 5.1 and 6.5 (MeCN), and 2.4 and 2.2 (MeOH), determined from analysis of the reactions of the respective substrates **28**d_3 and **31**d_7, are consistent with product-determining α-CH deprotonation. This also shows that the products from reactions of **28**d_3 and **31**d_7 do not have statistical distributions of deuterium at the α-amine centers and proves that equilibration of α-amino radicals by reversible proton transfer (i.e., **104** $\rightleftarrows$ **102**) does not occur in these processes.[26] Thus, product distributions are not governed by α-amino radical stabilities but rather by amine cation radical kinetic acidities.

On the basis of these observations, the product ratios from reactions of the β-(aminoethyl)cyclohexenones can be transformed into perhydrogen relative kinetic acidities. These are given in Table IV together with the comparable data taken from the results of Lewis'[17] studies of amine–stilbene photoadditions. It is important

(23) Das, S.; vonSonntag, C. *Z. Naturforsch.* **1986**, *41b*, 505.
(24) Nelsen, S. F.; Ippoliti, J. T. *J. Am. Chem. Soc.* **1986**, *108*, 4879.
(25) Dinnocenzo, J. P.; Banach, T. E. *J. Am. Chem. Soc.* **1989**, *111*, 8646.

(26) (a) This is a point worth considering in light of the publication by Gardini and Bargon (ref 26b), which reported the results of CIDNP experiments showing that proton exchange interconverting tertiary aminium cation radicals and α-amino radicals can be both rapid and reversible. (b) Gardini, G. P.; Bargon, J. *J. Chem. Soc., Chem. Commun.* **1980**, 757.
(27) Xu, W.; Mariano, P. S. *J. Am. Chem. Soc.* **1991**, *113*, 1431.

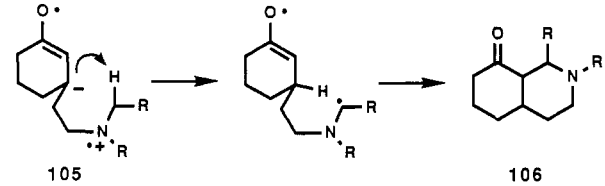
to note that comparisons of the amino enone derived data can only be made within the substituent series H, Me, and TMS and CO_2CH_3, Ph, $CH{=}CH_2$, and $C{\equiv}CH$, owing to the absence of data needed to contrast substituent effects between both series.

Significant differences exist between the substituent effects on amine cation radical acidities determined by Lewis[17] and those arising from the current studies. For example, alkyl substituents decrease the rate of proton transfer in the amine–stilbene ion radical pair **97** (Scheme XXII), while the opposite effect is seen in the amino enone zwitterionic diradical **102** (Scheme XXIII). Also, the kinetic acidity at the methyl and benzyl centers are equivalent in the former process and greatly different favoring the benzylic α-amine position in the latter reactions. The exact source(s) of the differences between these systems is not at all obvious. While steric factors should be important contributors in determining amine cation kinetic radical acidity, electronic factors should also play an important role. Indeed, a simple view of the amine cation radical deprotonation process suggests that radical-stabilizing substituents would enhance the rate, especially if the transition state occurs late. In this situation, the kinetic acidity would parallel the pK_a values of these intermediates. As is highlighted by the treatment of Nicholas and Arnold,[28] the pK_a values of cation radicals are dependent upon the oxidation potentials of donor precursors and the donor CH bond dissociation energies. By using the Nicholas–Arnold equation,[28] electrochemical data for amine analogues,[17] and hydrocarbon bond dissociation energies,[27] we have calculated relative pK_a values for various α-substituted amine cation radicals (Table IV). It is interesting that these values parallel the kinetic acidities determined by use of the β-amino enone photocyclization data.

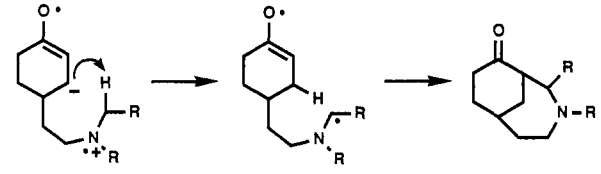
The extent to which radical stabilization vs steric effects of substituents contribute to the kinetic acidities of amine cation radicals should be dependent on the position of the deprotonation transition state. A productlike transition state for this process would involve a greater development of odd electron density on the α-amine carbon and a longer C–H bond length. In this case, stabilization could be more important than steric interactions between the acid–base components.[29] It is interesting in this regard that the *d* isotope effect on proton transfer in the amine–stilbene ion radical pair in MeCN was determined by Lewis[17] to be ca. 1.5, while those for the amine enone system range from 5 to 6 in the aprotic solvent MeCN. The latter values are close to those found by Dinnocenzo[25] for quinuclidine deprotonations of the dianisylmethylaminium hexafluoroarsenate in MeCN. This suggests that the transition states for proton transfer in the amino enone zwitterionic diradical, like in the Dinnocenzo process, occur late.

Caution should be used in applying this reasoning to rationalize the differences between the substituent effects observed by Lewis[17] and us. This is emphasized by inspecting the *d* isotope effects and deprotonation selectivities for the β-amino enone photocyclizations in MeOH. As the data in Table IV indicate, the relative ordering of kinetic acidities is nearly equivalent for proton transfers in MeOH and MeCN, yet the *d* isotope effect is much lower (ca. 2) for the process occurring in the protic solvent MeOH. Thus, a rationalization of the differences based on isotope effects alone is not without ambiguity. The lower *d* isotope effect associated with proton transfer in the amino enone derived zwitterionic diradicals in MeOH compared to MeCN in itself is not difficult to understand. As we have pointed out earlier,[2] the base strength of enone anion radicals, the bases in these intramolecular proton transfer processes, is significantly affected by solvent, base strength being lower in polar protic media where H-bonding interactions exist. As Dinnocenzo has shown,[25] *d* isotope effects for deprotonation of the dianisylmethylaminium cation radical are very sensitive to base strength, increasing from ca. 6 to ca. 9 when the quinuclidine conjugate acid pK_a changes from ca. 15 to ca. 16. Thus, a similar change in enone anion radical base strength induced by a variation in solvent is expected to have an analogous effect on the isotope effect for proton transfer in amino enone zwitterionic diradicals.

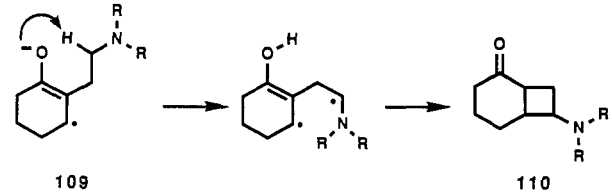
A final issue that requires comment concerns the site in the enone anion radical to which proton transfer occurs in these reactions. For zwitterionic diradicals derived from the β-(aminoethyl)cyclohexenones, proton transfer is required to occur to the α-carbon of the enone anion radical via a 7-membered transition state. Similarly, generation of the hydroisoquinolines in reactions of the γ-(aminoethyl)cyclohexenone **12** also dictates deprotonation by the α-carbon via an 8-membered transition state. In both cases, alternative pathways involving proton transfer to the anion radical oxygen would be highly disfavored owing to distance and transition-state strain factors. While the above conclusions are mandated by product structure and strain considerations, it is not easy to rationalize why other reaction modes are not operable in these systems. For example, proton transfers to the β-carbons in the enone anion radical components[30] of the intermediate zwitterionic diradicals **105** and **107** would proceed via less strained transition states, generate stabilized α-keto radicals, and result in production of reasonable products (e.g., **106** and **108**). We can offer no reasonable explanation for why these photocyclization reactions do not recognize the apparent facility of these alternate pathways.



105 106



107 108



109 110

In contrast, proton transfer in the zwitterionic diradical intermediate formed in the photoreaction of the α-(aminoethyl)-cyclohexenone **6** can occur to the oxygen of the enone anion radical moiety. This feature could be responsible for production of the bicyclo[4.2.0]amino ketone **38** from reaction of **6** in MeCN. Only in this system is a product of this type, **110**, arising by α-CH proton loss from the ethyl tether, seen. The intermediate **109** leading to **110** is unique in that proton transfer from this position to the carbonyl oxygen can occur via a strain-free 6-membered transition state.

(28) Nicholas, A. M. P.; Arnold, D. R. *Can. J. Chem.* **1982**, *60*, 2165.

(29) This is true only if the major steric effects are those associated with interactions between the base and amine cation radical. If, on the other hand, the steric effects are due to substituents at the α-carbon and amine nitrogen centers (i.e., between R_1 and R in **100**) in the forming α-amino radical, their energetic consequences would be expressed more greatly in a late transition state.

(30) (a) Support for the reasonable nature of proton transfers to the β-carbons of enone anion radicals is found in Givens' observations of alkylation (ref 30b) and protonation (ref 30c) of intermediates of this type formed by photoinduced SET methods. (b) Givens, R. S.; Atwater, B. W. *J. Am. Chem. Soc.* **1986**, *108*, 5028. (c) Givens, R. S.; Singh, R.; Xue, J.; Park, Y.-H. *Tetrahedron Lett.* **1990**, *31*, 6793.

Finally, it should be noted that H-atom abstraction rather than sequential SET proton transfer mechanisms could be responsible for the photocyclizations of the non-TMS amino enone systems. However, while this mechanistic alternative would be in accord with the observed regioselectivities, its operation would not be consistent with the wealth of data supporting SET pathways in amine enone photochemistry[8,30] and showing that H-atom abstraction in enone triplet excited states is favored at β- rather than α-positions.[31]

Experimental Section

General. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions by using a Bruker AF-200 or AM-400 spectrometer. ^{1}H NMR spectra were at 200.13 or 400.13 MHz and ^{13}C NMR spectra at 50.32 and 100.62 MHz. Chemical shifts are reported in parts per million relative to Me_4Si as the internal standard. For compounds containing Me_3Si groupings, $CHCl_3$ was used as an internal standard. ^{13}C NMR resonances were assigned by use of the DEPT technique to determine numbers of attached hydrogens. IR spectra were recorded on a Perkin-Elmer 298 spectrometer. UV spectra were obtained on a Perkin-Elmer Lamda-5 UV–vis spectrometer. Mass spectra were recorded by use of Hitachi RMU-6E or VG-7070 instruments with EI sources. Melting points were recorded by use of a Griffin Mel-Temp apparatus and are reported uncorrected. Analytical GLC (10% OV-101 or 30% SE-30 packed, 10 ft × $^1/_8$ in. or methyl 20% phenyl silicone fused silica capillary, 25 m × 0.32 mm, 0.25-m film column) was performed with a Varian-940 (FID) or Perkin-Elmer 8500 chromatograph. Preparative GLC (30% SE-30 packed, 5 ft × $^3/_8$ in. column) was performed with a Varian-3700 chromatograph. Preparative TLC was conducted by using 20 × 20 cm plates coated with Merck-EM Type-60, GF-254 silica gel. Flash chromatography was performed with Merck-EM Type 60 (230–400 mesh) silica gel or (100–200 mesh) Florisil. Drying of organic layers obtained following workup of reaction mixtures was performed with anhydrous Na_2SO_4. All reactions were run under an N_2 atmosphere unless otherwise noted.

Preparative photochemical reactions were conducted by using an apparatus consisting of a 450-W Hanovia medium-pressure, mercury lamp (ACE) 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 solution was purged with N_2 or Ar before and during irradiation, except as noted.

The methoxyphenethylamines, allyl bromide, propargyl bromide, and (iodomethyl)trimethylsilane were purchased from Aldrich. The solvents in photoreactions were spectrograde: MeCN (Baker), MeOH (Baker), cyclohexane (Baker), CH_2Cl_2 (Baker). 9,10-Dicyanoanthracene was purchased from Eastman Kodak and recrystallized ($CHCl_3$) prior to use.

Preparation of (Aminoethyl)cyclohexenones. These substances were prepared by the sequences shown in Schemes III–VI in the Results section and sequences A–M in the supplementary material section. Spectroscopic data for the amino enones are as follows.

6: ^{1}H NMR δ 0.01 (s, 9 H, $SiMe_3$), 1.93 (m, 2 H, H-5), 1.95 (s, 2 H, NCH_2Si), 2.31 (m, 2 H, H-4), 2.36 (m, 2 H, H-6), 3.48 (s, 2 H, NCH_2Ph), 6.62 (t, J = 4.0 Hz, 1 H, C=CH), 7.17–7.30 (m, 5 H, aromatic); ^{13}C NMR δ −1.3 ($SiCH_3$), 23.1 (C-5), 26.0 (C-4), 26.8 (CH_2CH_2N), 38.4 (C-6), 45.8 (NCH_2Si), 56.1 (CH_2CH_2N), 61.8 (NCH_2Ph), 126.6, 128.0, 128.7 (aromatic), 138.2 (C-2), 140.4 (Ar C, ipso), 145.9 (C-3), 199.2 (C-1, C=O); IR 3010, 2940, 2790, 1670, 1495, 1450, 1425, 1375, 1245, 1095, 850 cm^{-1}; CIMS m/e (rel intensity) 316 ((M + 1)$^+$, 7), 242 (10), 206 (78), 123 (33), 91 (100), 73 (15); HRMS (M + 1) m/e 316.2093 $C_{19}H_{30}NOSi$ requires 316.2097).

12: ^{1}H NMR δ 0.02 (s, 9 H, $Si(CH_3)_3$), 1.51–1.58 (m, 1 H), 1.62–1.72 (m, 2 H), 1.86 and 1.90 (AB q, J = 14.4 Hz, 2 H, NCH_2Si), 2.05–2.13 (m, 1 H), 2.21 (s, 3 H, NCH_3), 2.29–2.41 (m, 3 H), 2.44–2.50 (m, 2 H), 5.95 (ddd, J = 10.2, 2.5, 0.5 Hz, 1 H, H-2), 6.86 (ddd, J = 10.2, 2.8, 1.4 Hz, 1 H, H-3); ^{13}C NMR δ −1.3 ($SiCH_3$), 28.8 (CH_2CH_2N), 32.4 (C-5), 34.3 (C-4), 36.9 (C-6), 46.0 (NCH_3), 49.9 (NCH_2Si), 59.3 (CH_2CH_2N), 128.9 (C-2), 155.1 (C-3), 199.2 (C=O); IR (neat) 2930, 2750, 1670, 1450, 1245, 850 cm^{-1}; EIMS m/e (rel intensity) 239 (M$^+$, 9), 224 (4), 180 (30), 166 (35), 130 (100), 122 (18), 116 (16), 73 (40), 58 (74); HRMS of mixture m/e 239.1703 ($C_{13}H_{25}NOSi$ requires 239.1705).

18: ^{1}H NMR δ 0.04 (s, 9 H, $Si(CH_3)_3$), 1.89 (tt, J = 5.8, 7.3 Hz, 2 H, H-5), 1.96 (s, 2 H, NCH_2Si), 2.12 (t, J = 5.8 Hz, H-4), 2.29 (t, J = 7.0 Hz, 2 H, CH_2CH_2N), 2.31 (t, J = 7.0 Hz, 2 H, CH_2CH_2N), 2.50 (t, J = 7.3 Hz, 2 H, H-6), 3.48 (s, 2 H, NCH_2Ar), 5.79 (s, 1 H, H-2), 7.19–7.28 (m, 5 H, ArH); ^{13}C NMR δ −1.4 ($SiCH_3$), 22.6 (C-5), 29.6 (C-4), 35.4 (CH_2CH_2N), 37.2 (C-6), 45.9 (NCH_2Si), 54.7 (CH_2CH_2N), 61.9 (NCH_2Ar), 126.6 (C-2), 126.8 (Ar, para), 128.1 (Ar, ortho), 128.7 (Ar, meta), 139.7 (Ar, ipso), 164.7 (C-3), 199.2 (C=O); IR (neat) 2940, 2790, 1670, 1625, 1450, 1430, 1245, 850, 740, 700 cm^{-1}; EIMS m/e (rel intensity) 315 (M$^+$, 0.1), 242 (2), 206 (30), 91 (100), 73 (12); HRMS m/e 315.2015 ($C_{19}H_{29}NOSi$ requires 315.2018).

23: ^{1}H NMR δ −0.06 (s, 9 H, $Si(CH_3)$), 1.87 (q, J = 6.3 Hz, 2 H, H-5), 2.14 (t, J = 6.3 Hz, 2 H, H-6), 2.29–2.26 (m, 4 H, CH_2N), 2.34 (s, 3 H, NCH_3), 2.40–2.70 (m, 2 H, CH_2CH_2N), 2.95 (s, 1 H, CHPh), 5.78 (s, 1 H, H-2), 7.06–7.26 (m, 5 H, AH); ^{13}C NMR δ −1.2 ($Si(CH_3)_3$), 22.6 (C-5), 29.7 (C-6), 35.2 (C-4), 37.2 (CH_2CH_2N), 42.3 (C-10), 55.0 (C9), 65.2 (CH_2N), 125.7 (C-2), 126.4 (Ar, para), 127.9 (Ar, ortho), 128.4 (Ar, meta), 142.1 (ArCH), 165.1 (C-3), 199.2 (C=O); IR 2952, 2783, 1670, 1624, 1450, 839, 746; EIMS (rel intensity) m/e 315 (M$^+$, 1.8), 300 (2.1), 243 (21), 242 (100), 206 (8.0), 192 (5.0), 135 (18), 132 (64), 120 (14), 91 (32), 77 (16); HRMS m/e 315.2009 ($C_{19}H_{29}NOSi$ requires 315.2018).

24: ^{1}H NMR δ 0.00 (s, 9 H, $Si(CH_3)_3$), 1.84 (s, 2 H, NCH_2Si), 1.93 (tt, J = 5.9, 6.5 Hz, 2 H, H-5), 2.18 (s, 3 H, NCH_3), 2.25–2.38 (m, 6 H), 2.41–2.49 (m, 2 H), 5.83 (s, 1 H, CH=); ^{13}C NMR δ −1.4 ($SiCH_3$), 22.6 (C-5), 29.7 (C-4), 35.8 (CH_2CH_2N), 37.2 (C-6), 45.7 (NCH_3), 49.4 (NCH_2Si), 59.2 (CH_2CH_2N), 126.3 (C-2), 165.0 (C-3), 199.7 (C=O); IR (neat) 2960, 2900, 2800, 1685, 1640, 1470, 1440, 1360, 1260, 1210, 860 cm^{-1}; EIMS m/e (rel intensity) 239 (M$^+$, 1), 224 (2), 166 (6), 130 (100), 109 (2), 73 (31); HRMS m/e 239.1714 ($C_{13}H_{25}NOSi$ requires 239.1705).

25: ^{1}H NMR δ 1.90 (tt, J = 6.2, 6.4 Hz, 2 H, H-5), 2.15 (s, 3 H, NCH_3), 2.20–2.37 (m, 6 H), 2.47 (m, 2 H), 2.93 (d, J = 6.5 Hz, 2 H, NCH_2CH=C), 5.03–5.15 (m, 2 H, C=CH_2), 5.72 (m, 1 H, CH=C), 5.80 (s, 1 H, H-2); ^{13}C NMR δ 22.6 (C-5), 29.7 (C-4), 35.7 (CH_2CH_2N), 37.2 (C-6), 41.8 (NCH_3), 54.4 (NCH_2CH=C), 60.7 (CH_2CH_2N), 117.6 (CH=CH_2), 126.3 (C-2), 135.3 (CH=CH_2), 164.5 (C-3), 199.5 (C=O); IR (neat) 3480, 2970, 2820, 1680, 1640, 1470, 1360, 1270, 1205, 1015, 935, 900, 770 cm^{-1}; EIMS m/e (rel intensity) 193 (M$^+$, 1), 166 (3), 122 (13), 84 (100); HRMS m/e 193.1481 ($C_{12}H_{19}NO$ requires 193.1467).

26: ^{1}H NMR δ 1.86 (tt, J = 4.4, 6.9 Hz, 2 H, H-5), 2.14 (t, J = 2.4 Hz, 1 H, C≡CH), 2.18 (s, 3 H, NCH_3), 2.20 (t, J = 4.4 Hz, 2 H, H-6), 2.33 (t, J = 6.9 Hz, 2 H, H-4), 2.25 (t, J = 7.5 Hz, 2 H, CH_2CH_2N), 2.50 (t, J = 7.5 Hz, 2 H, CH_2CH_2N), 3.25 (d, J = 2.4 Hz, 2 H, CH_2C≡CH), 5.77 (s, 1 H, C=CH); ^{13}C NMR δ 22.4 (C-5), 29.4 (C-6), 35.8 (C-4), 37.0 (CH_2CH_2N), 41.4 (NCH_3), 45.2 (CH_2C≡C), 52.6 (CH_2CH_2N), 73.2 (C-C≡C), 77.9 (C≡CH), 126.2 (C-2), 164.0 (C-3), 199.3 (C=O); IR (neat) 2970, 2900, 2820, 2120, 1680, 1640, 1470, 1440, 1340, 1270, 1210, 1135, 1060, 1040, 980, 900, 770; EIMS m/e (rel intensity) 191 (M$^+$, 15), 166 (11), 134 (9), 122 (54); HRMS m/e 191.1320 ($C_{12}H_{17}NO$ requires 191.1310).

27: ^{1}H NMR δ 0.99 (t, J = 7.2 Hz, 3 H, CH_2CH_3), 1.93 (m, 2 H, H-5), 2.16 (s, 3 H, NCH_3), 2.25 (t, J = 6.4 Hz, 2 H, H-4), 2.29 (t, J = 6.7 Hz, 2 H, H-6), 2.32 (t, J = 7.6 Hz, 2 H, CH_2CH_2N), 2.37 (q, J = 7.2 Hz, 2 H, NCH_2CH_3), 2.48 (t, J = 7.6 Hz, 2 H, CH_2CH_2N), 5.82 (s, 1 H, CH=C); ^{13}C NMR δ 12.2 (CH_2CH_3), 22.6 (C-5), 29.7 (C-6), 35.7 (CH_2CH_2N), 37.2 (C-4), 41.3 (NCH_3), 51.2 (NCH_2CH_3), 54.6 (CH_2CH_2N), 126.2 (C-2), 164.7 (C-3), 199.6 (C=O); IR (neat) 2950, 2800, 1660, 1620, 1450, 1250, 1050, 880 cm^{-1}; CIMS m/e (rel intensity) 182 (MH$^+$, 4), 166 (9), 151 (8), 122 (17), 94 (18), 72 (100); HRMS m/e 181.1475 ($C_{11}H_{19}NO$ requires 181.1467).

28d_3: ^{1}H NMR δ 1.94 (m, 2 H, H-5), 2.18 (s, 3 H, NCH_3), 2.26 (t, J = 6.5 Hz, 2 H, H-4), 2.30 (t, J = 6.6 Hz, 2 H, H-6), 2.23 (t, J = 7.2 Hz, 2 H, CH_2CH_2N), 2.40 (t, J = 7.2 Hz, 2 H, CH_2CH_2N), 5.84 (s, 1 H, H-2, CH=C); ^{13}C NMR δ 22.6 (C-5), 29.7 (C-4), 36.1 (CH_2CH_2N), 37.2 (C-6), 45.2 (NCH_3), 56.9 (CH_2CH_2N), 126.3 (C-2), 164.4 (C-3), 199.5 (C-1, C=O); IR 2943, 2843, 1666, 1625, 1455, 1255, 1192, 886 cm^{-1}; CIMS m/e (rel intensity) 171 (MH$^+$, 42), 169 (41), 155 (5), 135 (7), 123 (100), 122 (88), 121 (15), 112 (11), 111 (11), 110 (19), 107 (12), 105 (12); HRMS m/e 170.1494 ($C_{10}H_{14}D_3NO$ requires 170.1498).

29: ^{1}H NMR δ 1.91 (m, 2 H, H-5), 2.16 (t, J = 5.9 Hz, 2 H, H-4), 2.35 (2 t, J = 7.2 Hz, 4 H, CH_2CH_2N), 2.61 (t, J = 7.3 Hz, 2 H, H-6), 3.07 (d, J = 6.4 Hz, 2 H, NCH_2CH=C), 3.55 (s, 2 H, NCH_2Ph), 5.13 (br d, J = 10.3 Hz, 1 H, CH=CH_2), 5.18 (br d, J = 16.9 Hz, 1 H, CH=CH_2), 5.82 (br s, 1 H, H-2), 5.84 (ddd, J = 6.4, 10.3, 16.9 Hz, 1 H, CH=CH_2), 7.20–7.30 (m, 5 H, aromatic H); ^{13}C NMR δ 22.6 (C-5), 29.5 (C-4), 35.5 (CH_2CH_2N), 37.2 (C-6), 50.7 (CH_2CH_2N), 56.7 (NCH_2C=), 58.1 (NCH_2Ph), 117.5 (C=CH_2), 126.6 (C-2), 126.9, 128.2, 128.7, (aromatic C), 135.5 (CH=CH_2), 139.2 (aromatic C, ipso), 164.9 (C-3), 199.6 (C=O); IR 2930, 2805, 1665, 1620, 1450, 1370, 1345, 1320, 1250, 965, 740 cm^{-1}; EIMS m/e (rel intensity) 269 (M$^+$, 8), 228 (1), 178 (2), 160 (68), 146 (1), 91 (100); HRMS m/e 269.1779 ($C_{18}H_{23}NO$ requires 169.1780).

(31) Cf. Byrne, B.; Wilson, C. A.; Wolff, S.; Agosta, W. C. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1550.

30: ^{1}H NMR δ 1.95 (m, 2 H, H-5), 2.22 (d, J = 2.3 Hz, 1 H, C≡CH), 2.24 (t, J = 6.9 Hz, 2 H, H-4), 2.34 (t, J = 6.5 Hz, 2 H, H-6), 2.39 (t, J = 7.2 Hz, 2 H, CH_2CH_2N), 2.73 (t, J = 7.2 Hz, 2 H, CH_2CH_2N), 3.31 (d, J = 2.3 Hz, 2 H, $NCH_2C{\equiv}C$), 3.61 (s, NCH_2Ph), 5.58 (s, 1 H, H-2, CH=C), 7.22–7.30 (m, 5 H, aromatic H); ^{13}C NMR δ 22.7 (C-5), 29.6 (C-4), 36.1 (C-6), 37.4 (CH_2CH_2N), 41.5 ($NCH_2C{\equiv}C$), 50.6 (CH_2CH_2N), 58.1 (NCH_2Ph), 73.3 (C≡C), 78.2 (C≡CH), 126.8 (C-2), 127.3, 128.4, 129.0, 138.4 (aromatic C), 164.2 (C-3), 199.5 (C-1, C=O); IR (neat) 3028, 2941, 2887, 2827, 2097, 1667, 1624, 1494, 1453, 1427, 1372, 1348, 1325, 1255, 1192, 1120, 1027, 886, 740, 700 cm^{-1}; CIMS m/e (rel intensity) 268 (MH^+, 8), 210 (1), 158 (100), 123 (3); HRMS m/e 267.1632 ($C_{18}H_{21}NO$ requires 267.1623).

31: ^{1}H NMR δ 1.90–1.96 (m, 2 H, H-5), 2.21 (t, J = 5.6 Hz, 2 H, H-4), 2.32 (t, J = 6.5 Hz, 2 H, H-6), 2.38 (t, J = 7.2 Hz, 2 H, CH_2CH_2N), 2.84 (t, J = 7.2 Hz, 2 H, CH_2CH_2N), 3.32 (s, 2 H, NCH_2CO_2Me), 3.67 (s, 3 H, OCH_3), 3.77 (s, 2 H, NCH_2Ph), 5.85 (t, J = 1.1 Hz, 1 H, CH=C), 7.21–7.30 (m, 5 H, aromatic H); ^{13}C NMR δ 22.5 (C-5), 29.3 (C-4), 36.2 (CH_2CH_2N), 37.2 (C-6), 51.0 (CH_2CH_2N), 51.2 (OCH_3), 53.8 (NCH_2CO_2Me), 58.1 (NCH_2Ph), 126.6 (C-2), 127.2, 128.2, 138.4 (aromatic C), 164.3 (C-3), 171.5 (CO_2Me), 199.6 (C=O); IR 3025, 2945, 2865, 1738, 1666, 1620, 1495, 1454, 1428, 1348, 1255, 1195, 1153, 1028, 960, cm^{-1}; EIMS m/e (rel intensity) 301 (M^+, 1), 242 (3), 192 (39), 95 (2), 91 (100); HRMS m/e 301.1682 ($C_{18}H_{23}NO_3$ requires 301.1678).

31d_7: ^{1}H NMR δ 1.90–1.95 (m, 2 H, H-5), 2.20 (t, J = 6.0 Hz, 2 H, H-4), 2.31 (t, J = 6.7 Hz, 2 H, H-6), 2.37 (t, J = 7.2 Hz, 2 H, CH_2CH_2N), 2.28 (t, J = 7.2 Hz, 2 H, CH_2CH_2N), 3.31 (s, 2 H, NCH_2CO_2Me), 3.66 (s, 3 H, OCH_3), 5.84 (s, 1 H, CH=); ^{13}C NMR δ 22.5 (C-5), 29.4 (C-4), 36.2 (CH_2CH_2N), 37.2 (C-6), 51.0 (CH_2CH_2N), 51.2 (OCH_3), 53.7 (NCH_2CO_2Me), 57.2 (quintet, $NCD_2C_6D_5$), 126.6 (C-2), 126.6, 127.7, 128.3 (3 t, aromatic C), 138.1 (aromatic C), 164.2 (C-3), 171.7 (CO_2Me), 199.5 (C-1, C=O); IR 2948, 1737, 1667, 1454, 1430, 1346, 1325, 1252, 1194, 1030, 885 cm^{-1}; EIMS m/e (rel intensity) 308 (M^+, 1), 249 (7), 199 (100), 171 (1), 98 (8); HRMS m/e 308.2103 ($C_{18}H_{16}D_7NO_3$ requires 308.2117).

General Procedure for the Preparative Direct-Irradiation Photoreactions of the (Aminoethyl)cyclohexenones. The general procedures used in the preparative photocyclizations of (aminoethyl)cyclohexenones are as follows. MeOH and/or MeCN solutions containing the appropriate cyclohexenone (2 mM) were irradiated with uranium glass filtered light. (Aminoethyl)cyclohexenone conversions were monitored by GLC. The yields and ratio of cyclization products were determined by GLC (2′-acetonaphthone as an internal standard) and/or ^{13}C NMR techniques. The residues obtained by concentration of the photolysates were dissolved in $CHCl_3$ and extracted with 5% aqueous HCl. The basified (10% aqueous NaOH to pH 14) aqueous extracts were extracted with $CHCl_3$. The $CHCl_3$ extracts were dried and concentrated in vacuo, giving amine-containing residues that were subjected to chromatographic separation (column, TLC, or GLC), providing the photoproducts characterized on the basis of the data given below.

General Procedure for 9,10-Dicyanoanthracene (DCA) or 1,4-Dicyanonaphthalene (DCN) SET-Photosensitized Photoreactions of (Aminoethyl)cyclohexenones. Solutions of the (aminoethyl)cyclohexenones (2 mM) in MeOH (with and without added MeCN) containing DCA (ca. 1×10^{-4} M) were irradiated with uranium glass filtered light. Irradiations were monitored by GLC and UV and terminated when >95% of starting material was consumed. The photolysates were concentrated in vacuo and filtered to remove DCA. The filtrates were subjected to an acid–base extraction procedure to separate the amine products. The amine-containing fractions were subjected to chromatographic (flash column, TLC, or GLC) separation to provide the photoproducts.

Irradiation of the (Aminoethyl)cyclohexenone 6. A solution of 21 mg (6.6×10^{-2} mmol) of silyl (aminoethyl)cyclohexenone **6** in 66 mL of MeOH was irradiated for 6.5 h (78% conversion of **6**). The percent conversion, product ratio, and yields were determined by GC (capillary column) with triphenylene as an internal standard. Workup followed by preparative TLC (silica gel, 1:10 EtOAc–hexanes) separation afforded cyclized products **37**, **38**, and **39**.

Irradiation of an MeCN (66 mL) solution containing 21 mg (6.6×10^{-2} mmol) of silyl amino enone **6** for 6.5 h led to 89% conversion of **6**. Cyclized spirocyclic products **38** and **39** were analyzed and separated as described above.

A solution of the silyl amino enone **6** (1.0 mM) in MeOH or MeCN containing DCA (6.6×10^{-5} M) was irradiated for 4 h. Product yields were determined by GC (capillary column) with triphenylene as an internal standard. Workup followed by preparative TLC (silica gel, 1:5 EtOAc–hexanes) separation afforded cyclized products **37**, **38**, and **39**.

37: ^{1}H NMR δ 1.38 (dddd, J = 13.7, 13.6, 13.5, 3.8 Hz, 1 H, H-8 axial), 1.60 (dddd, J = 13.1, 12.5, 11.7, 3.9 Hz, 1 H, H-4ax), 1.64–1.74 (m, 3 H, H-7ax, H-8eq, H-8a), 1.78 (dd, J = 10.4, 10.5 Hz, 1 H, H-1ax), 1.80 (m, 2 H, H-4eq), 1.91 (ddd, J = 11.7, 11.6, 3.4 Hz, 1 H, H-4), 1.93 (ddd, J = 12.5, 11.3, 2.7 Hz, 1 H, H-3ax), 2.05 (m, 1 H, H-7eq), 2.29 (ddd, J = 13.8, 13.5, 6.6 Hz, 1 H, H-6ax), 2.36 (m, 1 H, H-6eq), 2.89 (br d, J = 10.5 Hz, 1 H, H-1eq), 2.97 (br d, J = 11.3 Hz, 1 H, H-3eq), 3.45 and 3.52 (AB q, J = 13.2 Hz, 2 H, NCH_2Ph), 7.21–7.33 (m, 5 H, aromatic); ^{13}C NMR δ 24.7 (C-4), 26.2 (C-7), 29.6 (C-8), 41.5 (C-6), 43.3 (C-8a), 53.3 (C-3), 53.4 (C-4a), 60.0 (C-1), 63.0 (NCH_2Ph), 127.0, 128.2, 129.0, 138.3 (aromatic), 211.3 (C=O, C-5); IR 2930, 2870, 2800, 2760, 1710, 1495, 1450, 1440, 1465, 1310, 1270, 1165, 1070, 1025, 985 cm^{-1}; EIMS m/e (rel intensity) 243 (M^+, 43), 201 (12), 159 (23), 146 (60), 134 (28), 113 (33), 91 (100); HRMS m/e 243.1620 ($C_{16}H_{21}NO$ requires 243.1623).

38: ^{1}H NMR δ 0.00 (s, 9 H, $SiMe_3$), 1.56–1.63 (m, 3 H, H-5ax, H-6ax, H-6eq), 1.85 (m, 1 H, H-5eq), 1.87 and 1.94 (AB q, J = 14.9 Hz, 2 H, NCH_2Si), 1.96 (ddd, J = 8.4, 9.6, 9.7 Hz, 1 H, H-2), 2.10–2.18 (m, 2 H, H-2, H-4ax), 2.29 (ddd, J = 3.7, 3.9, 14.5 Hz, 1 H, H-4eq), 2.52 (ddd, J = 9.7, 9.7, 9.7 Hz, 1 H, H-2a), 2.83 (m, 1 H, H-6a), 2.92 (ddd, J = 8.3, 8.3, 8.4 Hz, 1 H, H-1), 3.43 and 3.56 (AB q, J = 14.2 Hz, 2 H, NCH_2Ph), 7.16–7.34 (m, 5 H, aromatic); ^{13}C NMR δ −1.4 ($SiCH_3$), 22.7 (C-5), 25.6 (C-6), 27.7 (C-2), 39.2 (C-2a), 41.1 (C-4), 42.1 (NCH_2Si), 42.2 (C-6a), 58.7 (NCH_2Ph), 61.5 (C-1), 126.7 (Ar, para), 128.1, 128.5 (Ar, ortho, meta), 140.2 (Ar, ipso), 215.3 (C-3, C=O); IR 2930, 1700, 1670, 1490, 1450, 1240, 1135, 1090, 1025, 850 cm^{-1}; EIMS m/e (rel intensity) 315 (M^+, 7), 300 (19), 243 (32), 242 (100), 232 (15), 224 (7), 219 (89), 204 (77), 186 (25), 146 (55), 128 (53), 123 (23), 91 (5); HRMS m/e 315.2012 ($C_{19}H_{29}NOSi$ requires 315.2018).

39: ^{1}H NMR δ 0.17 (s, 9 H, $SiMe_3$), 1.28 (br d, J = 13.5 Hz, 1 H, H-4eq), 1.35 (dddd, J = 3.5, 11.3, 12.5, 12.7 Hz, 1 H, H-8ax), 1.65 (m, 1 H, H-7ax), 1.84 (m, 1 H, H-8eq), 1.89 (dddd, J = 4.0, 11.3, 13.0, 13.5 Hz, 1 H, H-4ax), 2.00 (dddd, J = 2.9, 10.9, 11.3, 11.6 Hz, 1 H, H-8a), 2.15 (m, 1 H, H-7eq), 2.20 (ddd, J = 3.5, 11.3, 11.6 Hz, 1 H, H-4a), 2.13–2.39 (m, 2 H, H-6), 2.41 (d, J = 10.9 Hz, 1 H, H-1), 2.53 (br dd, J = 13.0, 13.8 Hz, 1 H, H-3ax), 2.81 (br d, J = 13.8 Hz, 1 H, H-3eq), 3.60 and 3.82 (AB q, J = 13.5 Hz, 2 H, NCH_2Ph), 7.20–7.34 (m, 5 H, aromatic); ^{13}C NMR δ −2.0 ($SiCH_3$), 17.2 (C-4), 26.8 (C-7), 30.6 (C-8), 39.6 (C-8a), 41.6 (C-6), 49.2 (C-3), 53.0 (NCH_2Ph), 56.1 (C-4a), 60.9 (C-1), 126.9, 128.3, 128.4, 139.7 (aromatic), 211.8 (C-5, C=O); IR 2920, 2850, 1705, 1670, 1600, 1490, 1445, 1360, 1345, 1310, 1280, 1245, 1220, 1155, 1110, 1050, 1020, 840 cm^{-1}; EIMS m/e (rel intensity) 315 (M^+, 3), 300 (7), 243 (36), 242 (100), 224 (7), 186 (10), 91 (2), 73 (1); HRMS m/e 315.2004 ($C_{19}H_{29}NOSi$ requires 315.2018).

Irradiation of (Aminoethyl)cyclohexenone 12. The inseparable mixture of isomers **12** and **13** (78:22) was employed in the following experiments. A solution of 360 mg (1.17 mmol) of **12** in 560 mL of MeOH was irradiated for 37 h (95% conversion of **12**). Workup followed by TLC (5:2:1 CH_2Cl_2–2-propanol–hexanes) separation afforded 169 mg (91%) of non-TMS hydroisoquinolone products as a 40:51 mixture of isomers **33** and **32**, and 2 mg (1%) of hydroindolone **34**. Careful separation of the hydroisoquinolone mixture by preparative GLC resulted in a pure sample of **33** and a sample enriched (ca. 70%) in **32**.

Irradiation of an MeCN (570 mL) solution containing 289 mg (0.94 mmol) of **12** for 25 h (95% conversion of **12**) gave, after workup and TLC (96:4 $CHCl_3$–MeOH) separation, 107 mg (50%) of the TMS-containing hydroisoquinolone products **35** as a 3:4:2 mixture of three isomers (**35a**, **35b**, **35c**) as well as 1 mg (1%) of **34**. Careful column chromatographic (silica gel, 98:2 $CHCl_3$–MeOH) separation resulted in pure samples of **35a**, **35b**, and **35c**.

Irradiation of an air-purged MeOH (100 mL) solution containing 47 mg (0.15 mmol) of **12** for 14.5 h (95% conversion of **12**) gave, after workup and TLC separation (see above), 4 mg (15%) of **33**, 8 mg (31%) of **32**, and 8 mg (34%) of **34**.

32 (obtained on mixture of **32** (ca. 75%) and **33**): ^{1}H NMR δ 1.22–1.46 (m, 2 H), 1.59–1.74 (m, 2 H), 1.92–2.05 (m, 3 H), 2.14–2.22 (m, 2 H), 2.25 (s, 3 H, NCH_3), 2.27–2.36 (m, 2 H), 2.37–2.42 (m, 1 H), 2.72–2.75 (m, 1 H), 2.87–2.91 (m, 1 H); ^{13}C NMR δ 31.9 and 32.4 (C-5, C-4), 39.6 (C-4a), 41.4 (C-6), 41.7 (C-8a), 45.4 (C-8), 46.1 (NCH_3), 55.8 (C-3), 62.2 (C-1), 210.6 (C=O); IR (neat) 2925, 2780, 1715, 1680, 1450, 1275, 1265, 1255 cm^{-1}; EIMS m/e (rel intensity) 167 (M^+, 58), 166 (66), 110 (34), 109 (100), 96 (73), 84 (27), 71 (30), 58 (95), 57 (83); HRMS m/e 167.1294 ($C_{10}H_{17}NO$ requires 167.1310).

33: ^{1}H NMR δ 1.50–1.70 (m, 1 H), 1.72–2.05 (m, 4 H), 2.20 (s, 3 H, NCH_3), 2.25–2.45 (m, 7 H), 2.50–2.70 (m, 2 H); ^{13}C NMR δ 26.9 and 28.9 (C-4, C-5), 32.1 (C-4a), 38.0 (C-8a), 38.1 (C-6), 43.3 (C-8), 46.4 (NCH_3), 53.9 (C-3), 58.7 (C-1), 212.4 (C=O); IR (neat) 2915, 2780, 1715, 1470, 1455, 1280, 1135 cm^{-1}; EIMS m/e (rel intensity) 167 (M^+, 53), 166 (57), 109 (100), 96 (61), 84 (18), 71 (19), 70 (19), 58 (44), 57 (37); HRMS m/e 167.1315 ($C_{10}H_{17}NO$ requires 167.1310).

34: ^{1}H NMR 1.53 (m, 1 H), 1.67–1.75 (m, 2 H), 1.87–2.02 (m, 2 H), 2.07–2.21 (m, 2 H), 2.23 (s, 3 H), NCH_3), 2.26–2.51 (m, 4 H), 2.99

(t, 1 H, H-7a); ^{13}C NMR δ 26.6 (C-4), 29.7 (C-3), 35.8 (C-3a), 36.2 (C-5), 39.9 (NCH_3), 41.5 (C-7), 56.3 (C-2), 63.7 (C-7a), 212.1 (C=O); IR (neat) 2920, 2770, 1710, 1675, 1450, 1145, 1025 cm^{-1}; EIMS *m/e* (rel intensity) 153 (M^+, 16), 96 (100), 83 (20), 82 (22); HRMS *m/e* 153.1156 ($C_9H_{15}NO$ requires 153.1154).

35a: ^{1}H NMR δ 0.09 (s, 9 H, $Si(CH_3)_3$), 1.43 (d, J = 11.8 Hz), 1.62–1.74 (m, 2 H), 1.82–1.88 (m, 2 H), 2.07 (br d, J = 10.8 Hz, 2 H), 2.11–2.24 (m, 2 H), 2.29 (s, 3 H, NCH_3), 2.32–2.41 (m, 2 H), 2.88–3.34 (m, 2 H); ^{13}C NMR δ –0.3 ($SiCH_3$), 25.2 (C-5), 30.6 (C-4), 34.8 (C-4a), 36.4 (C-6), 40.6 (C-8a), 41.1 (C-8), 46.9 (NCH_3), 59.9 (C-3), 61.6 (C-1), 212.5 (C=O); IR (neat) 2960, 1720, 1420, 1100, 860 cm^{-1}; EIMS *m/e* (rel intensity) 239 (M^+, 1), 166 (100), 110 (4), 96 (9), 73 (87); HRMS *m/e* 239.1703 ($C_{13}H_{25}NOSi$ requires 239.1705).

35b: ^{1}H NMR δ 0.10 (s, 9 H, $Si(CH_3)_3$), 1.37–1.56 (m, 4 H), 1.85–1.95 (m, 3 H), 2.15 (d, J = 10.3 Hz, 1 H), 2.23–2.41 (m, 3 H), 2.37 (s, 3 H, NCH_3), 2.85–2.99 (m, 2 H); ^{13}C NMR δ –0.5 ($SiCH_3$), 25.9 (C-5), 33.4 (C-4), 36.9 (C-4a), 38.7 (C-8a), 41.4 (C-6), 43.0 (NCH_3), 46.5 (C-8), 56.9 (C-3), 59.8 (C-1), 210.4 (C=O); IR (neat) 2950, 1720, 1440, 1090, 850 cm^{-1}; EIMS *m/e* (rel intensity) 239 (M^+, 1), 224 (4), 166 (100), 96 (5), 73 (70); HRMS *m/e* 239.1700 ($C_{13}H_{25}NOSi$ requires 239.1705).

35c: ^{1}H NMR δ 0.13 (s, 9 H, $Si(CH_3)_3$), 1.30–1.48 (m, 2 H), 1.64–1.73 (m, 1 H), 1.94–2.00 (m, 1 H), 2.11–2.24 (m, 4 H), 2.27–2.48 (m, 3 H), 2.50 (s, 3 H, NCH_3), 2.74–2.78 (m, 1 H), 2.86 (dt, J = 3.4, 13.1 Hz, 1 H); ^{13}C NMR δ 1.6 ($SiCH_3$), 26.1 (C-5), 34.2 (C-4), 37.4 (C-4a), 38.1 (C-6), 43.2 (NCH_3), 46.2 (C-8), 50.9 (C-3), 58.7 (C-1), 210.7 (C=O); IR (neat) 2950, 1720, 1470, 1100, 860 cm^{-1}; EIMS *m/e* (rel intensity) 239 (M^+, 2), 224 (1), 166 (100), 150 (6), 130 (4), 73 (26); HRMS *m/e* 239.1693 ($C_{13}H_{25}NOSi$ requires 239.1705).

A solution of 40 mg (0.16 mmol) of amino enone **12** in 85 mL of MeOH and 15 mL of MeCN containing DCA (1.1×10^{-4} M) was purged with air for 20 min. Irradiation of this solution with air-purging for 2 h (90% conversion of **12**) gave, afer acid–base workup as described above and TLC (5:2:1 CH_2Cl_2–2-propanol–hexanes) separation, 11 mg (41%) of the formamide **36**, 5 mg (23%) of hydroindolone **34**, and trace quantities of hydroisoquinolones **32** and **33**.

An N_2-purged solution of 148 mg (0.62 mmol) of amino enone **12** in 160 mL of MeOH containing DCN (4.7×10^{-3} M) was irradiated for 13 h (95% conversion of **12**). Workup followed by TLC (5:2:1 CH_2Cl_2–2-propanol–hexanes) separation afforded the products **32** (9%), **33** (71%), and **34** (5%).

36: ^{1}H NMR (mixture of anti and syn rotomers) δ 1.45–1.85 (m, 3 H), 2.05–2.16 (m, 1 H), 2.28–2.41 (m, 2 H), 2.47–2.55 (m, 1 H), 2.86, 2.94 (2 s, 3 H, two NCH_3), 3.20–3.50 (m, 2 H), 5.96 and 5.99 (2 overlapping dd, J = 2.4, 10.2 Hz, 1 H, H-3), 6.75 and 6.85 (2 ddd, J = 1.4, 2.7, 10.2 Hz, 1 H, H-2), 8.02 and 8.04 (2 s, 1 H, CHO); ^{13}C NMR (syn isomer) δ 28.5 (CH_2CH_2N), 31.4 (C-5), 33.5 (C-4), 34.4 (NCH_3), 36.6 (C-6), 41.7 (CH_2CH_2N), 129.5 (C-2), 153.6 (C-3), 162.4 (CHO), 199.4 (C=O), (anti isomer) δ 28.4 (CH_2CH_2N), 29.5 (NCH_3), 32.4 (C-5), 33.1 (C-4), 36.5 (C-6), 47.0 (CH_2CH_2N), 129.8 (C-2), 152.6 (C-3), 162.6 (CHO), 198.8 (C=O); IR (neat) 2910, 2850, 1655, 1390, 1065 cm^{-1}; EIMS *m/e* (rel intensity) 181 (M^+, 1), 122 (100), 109 (26), 83 (29), 73 (45), 72 (90), 60 (13), 59 (11); HRMS *m/e* 181.1102 ($C_{10}H_{15}NO_2$ requires 181.1103).

Irradiation of (Aminoethyl)cyclohexenone 18. A solution of 354 mg (1.12 mmol) of amino enone **18** in 560 mL of MeOH was irradiated for 5 h (95% conversion of **18**). Workup followed by TLC (1:8 EtOAc–hexanes) separation afforded 183 mg (71%) of non-TMS cyclized spirocyclic product **45**.

Irradiation of an MeCN (120 mL) solution containing 74 mg (0.24 mmol) of amino enone **18** for 3 h (95% conversion) gave, after workup, 46 mg (65%) of TMS-containing products **46** and **47** (mixture of two diastereomers, ca. 1:1 ratio). Column chromatographic (silica gel, 1:9 EtOAc–hexanes) separation resulted in pure samples of **46** and **47**.

45: ^{1}H NMR δ 1.61 (m, 2 H, H-4), 1.74 (m, 2 H, H-6), 1.80 (m, 2 H, H-7), 2.26 (t, J = 6.7 Hz, 2 H, H-8), 2.31 (d, J = 9.2 Hz, 1 H), 2.32 (d, J = 9.2 Hz, 1 H), 2.36 (d, J = 9.2 Hz, 1 H), 2.37 (d, J = 9.2 Hz, 1 H), 2.57 (m, 2 H, H-3), 3.52 and 3.58 (AB q, J = 13.0 Hz, 2 H, NCH_2Ph), 7.20–7.31 (m, 5 H, ArH); ^{13}C NMR δ 23.4 (C-9), 36.8 (C-10), 36.9 (C-4), 41.1 (C-8), 46.1 (C-5), 53.3 and 53.6 (C-3, C-6), 60.1 (C-1), 65.6 (NCH_2Ph), 126.8 (Ar, para), 128.2 (Ar, ortho), 128.5 (Ar, meta), 139.2 (Ar, ipso), 211.0 (C=O); IR (neat) 2925, 2780, 1710, 1495, 1460, 1350, 1310, 1225, 1145, 1070, 735, 695 cm^{-1}; EIMS *m/e* (rel intensity) 243 (M^+, 59), 185 (30), 172 (32), 132 (41), 91 (100); HRMS *m/e* 243.1624 ($C_{16}H_{21}NO$ requires 243.1623).

46: ^{1}H NMR δ 0.00 (s, 9 H, $Si(CH_3)_3$), 1.35 (d, J = 14.1 Hz, 1 H), 1.52 (d, J = 13.2 Hz, 1 H), 1.57–1.76 (m, 5 H), 1.92–2.07 (m, 2 H), 2.06 (d, J = 14.1 Hz, 1 H), 2.14–2.27 (m, 3 H), 3.03 (s, 1 H, H-1), 3.30 (m, 1 H), 7.26–7.34 (m, 5 H, aromatic); ^{13}C NMR δ –1.4 ($SiCH_3$), 23.3 (C-7), 34.1, 34.8 (C-4 and C-6), 41.1 (C-8), 45.6 (NCH_2Si), 49.7 (C-3), 50.2 (C-5), 53.7 (C-10), 83.7 (C-1), 127.4, 128.0, 128.9, 139.2 (aromatic), 212.6 (C=O); IR (neat) 2980, 2795, 1725, 1425, 1260, 1040, 870, 750 cm^{-1}; EIMS *m/e* (rel intensity) 315 (M^+, 9), 300 (5), 242 (56), 204 (16), 141 (16), 101 (11), 91 (100), 73 (46); HRMS *m/e* 315.2030 ($C_{19}H_{29}NOSi$ requires 315.2018).

47: ^{1}H NMR δ 0.01 (s, 9 H, $Si(CH_3)_3$), 0.75 (m, 1 H, H-6ax), 1.36 (d, J = 14.2 Hz, 1 H), 1.45 (m, 1 H), 1.57–1.71 (m, 4 H), 1.78 (m, 1 H), 2.00 (m, 1 H), 2.08 (d, J = 14.2 Hz, 1 H), 2.16–2.23 (m, 2 H), 2.31 (d, J = 13.0 Hz, 1 H), 2.79 (s, 1 H, H-1), 3.21 (m, 1 H), 7.27–7.37 (m, 5 H, aromatic); ^{13}C NMR δ – 1.4 ($SiCH_3$), 22.2 (C-7), 33.7, 34.6 (C-4 and C-6), 41.3 (C-8), 45.4 (NCH_2Si), 49.2 (C-5), 52.7 (C-3), 54.2 (C-10), 84.7 (C-1), 127.2, 128.0, 129.0, 139.6 (aromatic), 211.7 (C=O); IR (neat) 2970, 2800, 1725, 1455, 1260, 1100, 870 cm^{-1}; EIMS *m/e* (rel intensity) 315 (M^+, 12), 300 (8), 242 (100), 238 (3), 204 (26), 101 (14), 91 (29), 73 (21); HRMS *m/e* 315.2019 ($C_{19}H_{29}NOSi$ requires 315.2018).

Irradiation of (Aminoethyl)cyclohexenone 23. A solution of **23** (50 mg, 0.158 mmol) in 150 mL of MeOH was irradiated for 10 h (95% conversion by GC). Concentration of the photolysate in vacuo gave a residue that was subjected to column chromatographic separation (10% ether–hexane) to afford 15 mg (39%) of photoproduct **40** and an equal amount of diastereoisomer **41**.

40: ^{1}H NMR δ 1.49–1.75 (m, 6 H, H-4, H-6, H-7), 1.91–2.21 (m, 4 H, H-8, H-10), 2.11 (s, 3 H, NCH_3), 2.30 (ddd, J = 9.5, 8.0, 10.5 Hz, 1 H, H-3), 2.96 (s, 1 H, H-1), 3.24 (ddd, J = 4.1, 8.0, 9.5 Hz, 1 H, H-3), 7.26–7.37 (m, 5 H, Ar-H); ^{13}C NMR 23.2 (C-6), 33.6 (C-7), 24.8 (C-4), 41.0 (C-3), 41.1 (NCH_3), 50.5 (C-5), 50.6 (C-8), 54.2 (C-10), 81.3 (C-1), 127.5, 128.1, 128.8, 138.8 (Ar, ortho, para, meta), 212.3 (C=O); IR 2936, 2775, 1708, 1491, 1350, 1312, 1281, 1258, 1226, 705 cm^{-1}; mass spectrum (rel intensity) *m/e* 243 (M^+, 8.3), 186 (2.5), 172 (6.6), 146.9 (9.0), 132 (100), 91 (16.0), 77 (5.0); HRMS *m/e* 243.1618 ($C_{16}H_{21}NO$ requires 243.1623).

41: ^{1}H NMR δ 0.78 (dt, J = 4.0, 14.0 Hz, 1 H, H-6ax), 1.45 (bd, J = 14.0 Hz, H-6eq), 1.50–1.95 (m, 7 H, H-4, H-7, H-8ax, H-10), 1.85–2.11 (dt, J = 6.7, 14.0 Hz, H-8eq), 2.14 (s, 3 H, NCH_3), 2.25 (m, 1 H, H-3), 2.72 (s, 1 H, H-1), 3.17 (m, 1 H, H-3), 7.05–7.40 (m, 5 H, ArH); ^{13}C NMR δ 22.2 (C-6), 34.1 (C-7), 34.3 (C-4), 41.1 (CH_3N), 49.9 (C-5), 52.6 (C-8), 54.9 (C-10), 82.3 (C-1), 127.5, 128.2, 128.7, 138.5 (para, ortho, meta, Ar), 211.6 (C=O); IR 2904, 2776, 1714, 1670, 1491, 1451, 705 cm^{-1}; mass spectrum (rel intensity) *m/e* 243 (M^+, 7.6), 186 (2), 172 (7), 146 (8), 132 (100), 91 (17), 77 (7); HRMS *m/e* 243.1622 ($C_{16}H_{21}NO$ requires 243.1623).

A solution of silyl amino cyclohexenone **23** (113 mg, 0.357 mmol) in 360 mL of MeCN was irradiated for 4.5 h (75% conversion). The photolysate was concentrated in vacuo to give a residue that was subjected to column chromatographic separation (10% ether–hexane) to afford 7 mg (6%) of a 1:1 mixture of the diastereomeric photoproducts **42**, 4 mg (4%) of a 1:1 mixture of diastereomers **43**, and 12 mg (30%) of 3-vinylcyclohexenone.

42 (mixture of diastereomers): ^{1}H NMR δ 0.22 (s, 9 H, $Si(CH_3)_3$), 0.23 (s, 9 H, $Si(CH_3)_3$), 1.0 (m, 1 H, H-6), 1.25 (m, 1 H, H-10), 1.30–1.85 (m, 10 H, H-10, H-4, H-6, H-7), 1.85–2.35 (m, 8 H, H-6, H-7, H-8, H-10), 2.57 (s, 3 H, NCH_3), 2.58 (s, 3 H, NCH_3), 2.50–2.75 (m, 2 H, H-3), 3.18 (dt, J = 5.8, 11.7 Hz, 1 H, H-3), 3.32 (dt, J = 6.7, 13.5 Hz, 1 H, H-3), 7.00–7.35 (m, 10 H, ArH); ^{13}H NMR δ –1.3 ($Si(CH_3)_3$), 22.4 (C-5), 30.1 (C-7), 31.0 (C-4), 40.3, 40.7 (NCH_3), 41.5 (C-8), 46.3 (C-5), 53.1 (C-10), 54.5 (C-3), 59.8, 60.3 (C-1), 125.4, 125.7 (ortho), 127.5, 128.7 (para), 129.6 (meta), 132.4 (C-Ar), 206.1 (C-8); IR 2953, 1708, 1444, 1252, 1071, 753 cm^{-1}; mass spectrum (rel intensity) *m/e* 315 (MH^+, 1.48), 300 (3.6), 256 (9), 242 (100), 159 (22), 132 (23); HRMS (CI) *m/e* 316.2100 ($C_{19}H_{30}NOSi$ requires 316.2096).

43 (mixture of diastereomers): ^{1}H NMR δ –0.88 (s, 18 H, $Si(CH_3)_3$), 0.85 (m, 2 H, H-1), 1.20–2.10 (m, 16 H, H-4, H-6, H-7, H-8), 2.15–2.70 (m, 10 H, H-1, H-3, H-10), 2.73, 2.98 (s, 1 H, N*CH*Ph), 7.05–7.32 (m, 10 H, ArH); ^{13}C NMR δ 23.5 (C-6), 36.4 (C-7), 36.6 (C-4), 45.9 (C-8), 53.5 (C-10), 54.1 (C-3), 64.3, 64.2 (CHPh), 66.4, 67.0 (C-1), 125.3, 127.4, 127.9, 143.5 (ortho, para, meta, Ar), 211.6 (C=O); IR 2948, 2781, 1713, 1654, 1596, 1449, 1132, 917, 861, 840, 702 cm^{-1}; mass spectrum (rel intensity) *m/e* 315 (M^+, 1.4), 300 (2), 242 (100), 170 (2), 135 (2), 91 (14), 73 (11); HRMS *m/e* 315.2010 ($C_{19}H_{29}SiNO$ requires 315.2018).

A solution of silyl (aminoethyl)cyclohexenone **23** (50 mg, 0.16 mmol in 150 mL of 15% MeCN–MeOH, saturated with DCA (ca. 1×10^{-4} M) was irradiated for 6 h. The photolysate was filtered and concentrated in vacuo, giving a residue that was subjected to column chromatographic separation (10% Et_2O–hexane) to afford 18 mg (48%) of a mixture of **40** and **41** (1.5:1 ratio, respectively).

Irradiation of (Aminoethyl)cyclohexenone 24. A solution of 57 mg (0.24 mmol) of amino enone **24** in 120 mL of MeOH was irradiated for 1.5 h (85% conversion). Workup and TLC (3:1 EtOAc–hexanes) sepa-

ration afforded 25 mg (72%) of non-TMS spirocyclic ketone **48**.

Irradiation of an MeCN (120 mL) solution containing 56 mg (0.23 mmol) of amino enone **24** gave, after workup and TLC (5:2 EtOAc–hexanes) separation, 28 mg (76%) of TMS-containing spirocyclic ketones **49** and **50** as an ca. 1:1 mixture of two diastereomers. Careful column chromatographic (5:2 EtOAc–hexanes) separation provided pure samples of the two diastereomers, **49** and **50**.

48: ^{1}H NMR δ 1.54–1.64 (m, 2 H), 1.69–1.72 (m, 2 H), 1.74–1.82 (m, 2 H), 2.16–2.29 (m, 5 H), 2.23 (s, 3 H, NCH_3), 2.35 (d, J = 9.3 Hz, 1 H), 2.43–2.52 (m, 2 H); ^{13}C NMR δ 23.3 (C-7), 36.9, 37.6 (C-4 and C-6), 41.0 (C-8), 42.1 (NCH_3), 46.6 (C-5), (C-10), 55.7 (C-3), 68.0 (C-1), 210.8 (C=O); IR (neat) 2960, 2800, 1725, 1460, 1260, 1240, 1170, 1050, 870 cm^{-1}; EIMS m/e (rel intensity) 167 (M^+, 13), 130 (35), 109 (10), 96 (20), 70 (15), 58 (46), 57 (100); HRMS m/e 167.1311 ($C_{10}H_{17}NO$ requires 167.1310).

49 or **50**: ^{1}H NMR δ 0.23 (s, 9 H, $Si(CH_3)_3$), 1.45–1.55 (m, 2 H), 1.62–2.03 (m, 4 H), 2.07–2.32 (m, 4 H), 2.35–2.46 (m, 2 H), 2.43 (s, 3 H, NCH_3), 3.27 (m, 1 H); ^{13}C NMR δ 0.1 ($SiCH_3$), 22.6 (C-7), 34.5, 35.2 (C-4 and C-6), 41.3 (C-8), 43.6 (NCH_3), 51.5 (C-5), 53.2 (C-10), 58.3 (C-3), 70.2 (C-1), 210.2 (C=O); IR (neat) 2970, 1720, 1420, 1260, 1070, 850 cm^{-1}; EIMS m/e (rel intensity) 239 (M^+, 1), 224 (3), 166 (100), 130 (4), 110 (4), 109 (7), 73 (10); HRMS m/e 239.1720 ($C_{13}H_{25}NOSi$ requires 239.1705).

50 or **49**: ^{1}H NMR δ 0.13 (s, 9 H, $Si(CH_3)_3$), 1.37–1.57 (m, 4 H), 1.62–1.99 (m, 4 H), 2.09 (m, 1 H), 2.25 (m, 2 H), 2.28 (s, 3 H, NCH_3), 2.41 (s, 1 H, H-1), 3.06 (m, 1 H); ^{13}C NMR δ –0.2 ($SiCH_3$), 23.5 (C-7), 35.8, 36.0 (C-4 and C-6), 41.3 (C-8), 44.2 (NCH_3), 51.7 (C-5), 51.8 (C-10), 57.7 (C-3), 69.1 (C-1), 211.4 (C=O); IR (neat) 2870, 2720, 1715, 1460, 1260, 860 cm^{-1}; EIMS m/e (rel intensity) 239 (M^+, 2), 224 (4), 166 (100), 130 (4), 110 (6), 109 (12), 96 (12), 73 (13); HRMS m/e 239.1703 ($C_{13}H_{25}NOSi$ requires 239.1705).

Irradiation of (Aminoethyl)cyclohexenone 25. A solution of 55 mg (0.29 mmol) of amino enone **25** in 120 mL of MeOH was irradiated for 1.5 h (90% conversion). Workup and TLC (4:1 EtOAc–hexanes) separation afforded 45 mg (79%) of the spirocyclic ketones **51** and **52** as an ca. 1:1 mixture of two diastereomers. Careful column chromatographic (silica gel, 5:2 EtOAc–hexanes) separation resulted in pure samples of the two diastereomers, **51** and **52**.

Irradiation of an MeCN (120 mL) solution containing 49 mg (0.25 mmol) of amino enone **25** for 2 h (90% conversion) gave, after workup and flash column chromatographic (silica gel, 5:2 MeOH–EtOAc) separation, 30 mg (60%) of the diastereomeric spirocyclic ketones, **51** and **52**, along with 7 mg (15%) of the tricyclic product **53**.

51 or **52**: ^{1}H NMR δ 1.51 (m, 1 H), 1.56 (dd, J = 3.3, 9.3 Hz, 1 H), 1.64 (t, J = 8.4 Hz, 1 H), 1.65–1.77 (m, 3 H), 1.98 (m, 1 H), 21.6 (s, 3 H, NCH_3), 2.21–2.27 (m, 3 H), 2.29 (d, J = 8.3 Hz, 1 H, H-1), 3.10 (ddd, J = 3.3, 8.4, 9.3 Hz, 1 H), 5.22 (dd, J = 2.1, 17.1 Hz, 1 H, *trans*-CH=CH_2), 5.25 (dd, J = 2.1, 10.3 Hz, 1 H, *cis*-CH=CH_2), 5.45 (ddd, J = 8.3, 10.3, 17.1 Hz, 1 H, CH=CH_2); ^{13}C NMR δ (C-7), 34.5, 35.2 (C-4 and C-6), 40.8 (NCH_3), 41.2 (C-8), 49.8 (C-3), 50.0 (C-5), 54.5 (C-10), 80.2 (C-1), 119.4 (C=CH_2), 137.4 (CH=CH_2), 211.7 (C=O); IR (neat) 2960, 2880, 2810, 1725, 1460, 1440, 1230, 940, 770 cm^{-1}; EIMS m/e (rel intensity) 193 (M^+, 24), 166 (44), 136 (7), 122 (14), 96 (17), 82 (100); HRMS m/e 193.1476 ($C_{12}H_{19}NO$ requires 193.1467).

52 or **51**: ^{1}H NMR δ 1.52 (ddd, J = 2.1, 8.0, 12.7 Hz, 1 H), 1.57–1.75 (m, 3 H), 1.83 (m, 1 H), 1.96 (m, 1 H), 2.05 (d, J = 8.9 Hz, 1 H, H-1), 2.07 (dt, J = 2.2, 13.4 Hz, 1 H), 2.14 (m, 1 H), 2.18 (s, 3 H, NCH_3), 2.23 (m, 1 H), 2.27 (d, J = 13.5 Hz, 1 H), 2.31 (m, 1 H), 3.04 (ddd, J = 2.1, 8.1, 9.7 Hz, 1 H), 5.16 (dd, J = 1.8, 17.1 Hz, 1 H, *trans*-CH=CH_2), 5.26 (dd, J = 1.9, 10.2 Hz, 1 H, *cis*-CH=CH_2), 5.71 (ddd, J = 8.9, 10.1, 17.2 Hz, 1 H, CH=CH_2); ^{13}C NMR δ 22.3 (C-7), 32.9, 34.1 (C-4 and C-6), 40.7 (NCH_3), 41.5 (C-8), 49.7 (C-5), 52.3 (C-3), 54.9 (C-10), 81.3 (C-1), 119.2 (C=CH_2), 137.0 (C=CH_2), 211.4 (C=O); IR (neat) 2970, 2810, 1725, 1460, 1440, 1325, 1250, 1160, 940, 770 cm^{-1}; EIMS m/e (rel intensity) 193 (M^+, 2), 166 (58), 152 (10), 110 (9), 87 (23); HRMS m/e 193.1471 ($C_{12}H_{19}NO$ requires 193.1467).

53: ^{1}H NMR δ 1.41 (m, 1 H), 1.71 (ddd, J = 13.6, 5.7, 3.0 Hz, 1 H), 1.78–1.91 (m, 3 H), 2.13 (ddd, J = 14.0, 10.3, 3.7 Hz, 1 H), 2.19–2.33 (m, 6 H), 2.34 (s, 3 H, NCH_3), 2.36–2.41 (m, 1 H), 2.65 (dd, J = 12.5, 2.2 Hz, 1 H), 2.75 (m, 1 H); ^{13}C NMR δ 21.7 (C-7), 26.2 (C-11), 33.7 and 36.1 (C-4 and C-6), 35.7 (C-12), 40.4 (C-8), 40.5 (C-5), 46.4 (NCH_3), 48.5 (C-10), 52.1 (C-3), 56.5 (C-1), 214.4 (C=O); IR (neat) 2950, 2800, 1715, 1475, 1270, 1160 cm^{-1}; LRMS m/e (rel intensity) 193 (100, M^+), 166 (20), 122 (19), 94 (17); HRMS m/e 193.1451 ($C_{12}H_{19}NO$ requires 193.1467).

Irradiation of (Aminoethyl)cyclohexenone 26. A solution of 51 mg (0.27 mmol) of amino enone **26** in 120 mL of MeOH was irradiated for 2.5 h (90% conversion). Workup and TLC (3:2 EtOAc–hexanes) separation afforded 37 mg (79%) of spirocyclic ketones **54** and **55** (ca. 1:1) and 2 mg (5%) of tricyclic product **56**. Careful flash column chromatographic (silica gel, 1:1 EtOAc–hexanes) separation resulted in pure samples of the diastereomers **54** and **55**.

Irradiation of an MeCN (120 mL) solution containing 66 mg (0.34 mmol) of amino enone **26** for 1.5 h (90% conversion) gave, after workup and TLC (3:2 EtOAc–hexanes) separation, 35 mg (59%) of **54** and **55** (ca. 1:1 mixture of two diastereomers) and 14 mg (23%) of tricyclic product **56**.

54 or **55**: ^{1}H NMR δ 1.54 (ddd, J = 3.6, 8.5, 12.5 Hz, 1 H), 1.63–1.82 (m, 3 H), 1.94–2.05 (m, 2 H), 2.18 (ddd, J = 1.6, 1.8, 13.5 Hz, 1 H, H-6eq), 2.23–2.39 (m, 3 H), 2.35 (s, 3 H, NCH_3), 2.41 (d, J = 2.2 Hz, 1 H, C≡CH), 2.47 (d, J = 13.5 Hz, 1 H, H-6ax), 2.76 (d, J = 2.1 Hz, 1 H H-1), 2.85 (ddd, J = 3.7, 9.0, 9.1 Hz, 1 H); ^{13}C NMR δ 22.6 (C-9), 33.7 and 34.7 (C-4 and C-10), 39.8 (NCH_3), 41.3 (C-8), 49.4 (C-5), 52.4 (C-3), 53.3 (C-6), 67.4 (C-1), 75.4 (*C*≡CH), 79.4 (C≡*C*H), 210.4 (C=Q); IR ($CHCl_3$)2970, 2900, 2820, 1725, 1460, 1330, 1240, 1050, 915, 770 cm^{-1}; EIMS m/e (rel intensity) 191 (M^+, 6), 176 (2), 148 (3), 134 (9), 120 (6); HRMS m/e 191.1322 ($C_{12}H_{17}NO$ requires 191.1310).

55 or **54**: ^{1}H NMR δ 1.53–1.79 (m, 5 H), 1.86 (m, 1 H), 2.00 (m, 1 H), 2.23–2.33 (m, 3 H), 2.35 (s, 3 H, NCH_3), 2.38 (d, J = 2.2 Hz, C≡CH), 2.71 (d, J = 13.8, 1 H, H-10ax), 2.82 (d, J = 2.2 Hz, 1 H, H-1), 2.99 (ddd, J = 4.2, 4.2, 9.1 Hz, 1 H); ^{13}C NMR δ 22.8 (C-7), 34.2, 35.2 (C-4 and C-6), 40.4 (NCH_3), 41.1 (C-8), 49.3 (C-5), 50.4 (C-3), 53.6 (C-10), 67.8 (C-1), 75.4 (*C*≡CH), 80.6 (C≡*C*H), 211.3 (C=O); IR ($CHCl_3$) 2965, 2900, 2870, 2800, 1725, 1460, 1330, 1240, 1065, 925 cm^{-1}; EIMS m/e (rel intensity) 191 (M^+, 5), 176 (1), 148 (2), 134 (7), 120 (3), 94 (6), 86 (61), 84 (100); HRMS m/e 191.1314 ($C_{12}H_{17}NO$ requires 191.1310).

56: ^{1}H NMR δ 1.32 (ddd, J = 4.0, 12.3, 13.9 Hz, 1 H), 1.69–1.78 (m, 2 H), 1.79 (d, J = 3.4 Hz, 1 H), 1.83 (m, 1 H), 2.06–2.17 (m, 2 H), 2.26 (ddd, J = 5.3, 10.0, 12.2 Hz, 1 H), 2.32 (s, 3 H, NCH_3), 2.48–2.56 (m, 2 H), 2.69 (dt, J = 3.3, 12.4 Hz, 1 H), 2.94 (d, J = 1.1 Hz, 1 H), 3.23 (d, J = 11.8 Hz, 1 H), 5.74 (t, J = 1.6 Hz, 1 H, CH=C); ^{13}C NMR δ 18.3 (C-7), 28.8, 37.5 (C-4 and C-6), 40.2 (C-8), 45.5 (C-5), 45.7 (NCH_3), 51.3, 51.9 (C-1 and C-3), 60.5 (C-10), 123.7 (*C*H=C), 152.0 (C-12), 212.3 (C=O); IR (neat) 2950, 1685, 1520, 1440, 1350, 1150, 1020 cm^{-1}; EIMS m/e (rel intensity) 191 (M^+, 19), 162 (17), 155 (38), 148 (22), 134 (24), 129 (34), 120 (38), 91 (98); HRMS m/e 191.1313 ($C_{12}H_{17}NO$ requires 191.1310).

Irradiation of (Aminoethyl)cyclohexenone 27. A solution of 21 mg (0.12 mmol) of amino enone **27** in 60 mL of MeOH was irradiated for 4 h (48% conversion of **27**). The reaction conversion, product ratio, and yields were determined both by GC (capillary column) with 1,4-dicyanobenzene (DCB) as an internal standard and by NONOE ^{13}C NMR technique (for product ratio). Workup followed by column chromatographic (alumina, EtOAc:CH_2Cl_2 = 2:1) separation afforded cyclized spirocyclic products **57**, **58**, and **59** in the yields shown in Table III.

Irradiation of an MeCN (170 mL) solution containing 58 mg (0.32 mmol) of amino enone **27** for 3.3 h led to 58% conversion of **27**. Cyclized spirocyclic products **55–57** were analyzed and separated as described above.

57: ^{1}H NMR δ 1.05 (t, J = 7.2 Hz, 3 H, NCH_2CH_3), 1.55–1.67 (m, 2 H, H-4), 1.73–1.78 (m, 2 H), 1.79–1.86 (m, 2 H), 2.17–2.28 (m, 3 H), 2.30, 2.35 (AB q, J = 13.4 Hz, 2 H, H-1), 2.42 (q, J = 7.2 Hz, 2 H, NCH_2CH_3), 2.45 (d, J = 9.4 Hz, 1 H), 2.52 (ddd, J = 9.2, 7.2, 7.2 Hz, 1 H, H-3), 2.59 (m, 1 H, H-3); ^{13}C NMR δ 13.7 (NCH_2CH_3), 23.4 (C-7), 37.0, 37.1 (C-4 and C-6), 41.2 (C8), 45.9 (C-5), 50.3 (NCH_2CH_3), 53.4 (C-10), 53.7 (C-3), 65.7 (C-1), 211.3 (C=O); IR (neat) 2950, 1700, 1450, 1400, 1300 cm^{-1}; EIMS m/e (rel intensity) 181 (M^+, 43), 166 (100), 152 (3), 100 (42), 71 (93); HRMS m/e 181.1467 ($C_{11}H_{19}NO$ requires 181.1467).

58 or **59**: ^{1}H NMR δ 1.04 (d, J = 6.5 Hz, 3 H, $CHCH_3$), 1.47 (ddd, J = 2.1, 8.1, 12.7 Hz, 1 H), 1.54 (dd, J = 8.1, 9.0 Hz, 1 H), 1.58 (m, 1 H), 1.60 (m, 1 H), 1.66 (q, J = 6.5 Hz, 1 H, $CHCH_3$), 1.72 (m, 1 H), 1.97 (ddd, J = 3.0, 3.4, 6.4 Hz, 1 H), 2.02 (m, 1 H), 2.09 (ddd, J = 8.1, 9.5, 9.6 Hz, 1 H), 2.20 (m, 1 H), 2.24 (s, 3 H, NCH_3), 2.25 (m, 1 H), 2.34 (m, 1 H), 2.99 (ddd, J = 2.1, 8.2, 9.0 Hz, 1 H); ^{13}C NMR δ 13.1 ($CHCH_3$), 22.3 (C-7), 32.2 (C-6), 33.7 (C-4), 40.6 (NCH_3), 41.6 (C-8), 48.4 (C-5), 52.3 (C-10), 55.0 (C-3), 71.3 (C-1), 211.7 (C=O); IR (neat) 2950, 1700, 1450, 1250 cm^{-1}; EIMS m/e (rel intensity) 181 (M^+, 20), 166 (72), 138 (8), 110 (33), 84 (17), 71 (100); HRMS m/e 181.1457 ($C_{11}H_{19}NO$ requires 181.1467).

59 or **58**: ^{1}H NMR δ 0.98 (d, J = 6.4 Hz, 3 H, $CHCH_3$), 1.48 (ddd, J = 3.3, 9.4, 12.9 Hz, 1 H), 1.59 (ddd, J = 8.4, 8.7, 12.9 Hz, 1 H), 1.69 (ddd, J = 3.8, 12.3, 12.4 Hz, 1 H), 1.77 (m, 1 H), 1.88 (q, J = 6.4 Hz, 1 H, $CHCH_3$), 1.95–2.02 (m, 2 H), 2.12 (ddd, J = 8.4, 9.1, 9.4 Hz, 1 H), 2.15–2.30 (m, 3 H), 2.22 (s, 3 H, NCH_3), 2.35 (m, 1 H), 3.06 (ddd, J = 3.3, 8.7, 9.1 Hz, 1 H); ^{13}C NMR δ 13.5 ($CHCH_3$), 23.2 (C-7), 33.8 (C-4), 35.2 (C-6), 40.6 (NCH_3), 41.3 (C-8), 48.8 (C-10), 49.1 (C-5),

54.5 (C-3), 70.4 (C-1), 212.2 (C=O); IR 2940, 1700, 1450 cm^{-1}; EIMS *m/e* (rel intensity) 181 (M^+, 14), 166 (44), 138 (7), 110 (19), 84 (100), 71 (72); HRMS *m/e* 181.1470 ($C_{11}H_{19}NO$ requires 181.1467).

Irradiation of (Aminoethyl)cyclohexenone 28d_3. A solution of 47 mg (0.28 mmol) of amino enone **28**d_3 in 140 mL of MeOH was irradiated for 3.5 h (84% conversion of **28**d_3). The reaction conversion and yields were determined by GC (capillary column) with DCB as an internal standard. The product ratios were determined by NONOE ^{13}C NMR technique. Workup followed by column chromatographic (alumina, EtOAc:CH_2Cl_2 = 1:1) separation afforded a mixture of cyclized spirocyclic isotopomeric products **74** and **75** (41% and 2.4:1.0 ratio by ^{13}C NMR analysis) and starting material **28**d_3.

Irradiation of an MeCN (220 mL) solution containing 77 mg (0.45 mmol) of amino enone **28**d_3 for 4 h led to 90% conversion of **28**d_3. Cyclized spirocyclic products **74** and **75** (21%) were shown by ^{13}C NMR analysis to be present in a 5.1:1.0 ratio.

Irradiation of (Aminoethyl)cyclohexenone 29. A solution of 45 mg (0.17 mmol) of amino enone **29** in 120 mL of MeOH was irradiated for 4 h (90% conversion of **29**). The reaction conversion, product ratio, and yields were determined by GC (capillary column) with triphenylmethane as an internal standard. Workup followed by column chromatographic (silica gel, EtOAc:hexanes = 1:3) separation afforded cyclized spirocyclic products **60**, **61**, **62**, **63**, and **64** in the yields shown in Table III.

Irradiation of an MeCN (120 mL) solution containing 45 mg (0.17 mmol) of amino enone **29** for 3 h led to 72% conversion of **29**. Cyclized spirocyclic products **60–63** and **64** were analyzed and separated as described above.

60: ^1H NMR δ 1.55 (d, J = 13.0 Hz, 1 H, H-10ax), 1.59–1.79 (m, 5 H), 1.97 (m, 1 H), 2.05 (br dd, J = 6.6, 12.6 Hz, 1 H), 2.19 (br d, J = 15.4 Hz, 1 H), 2.23 (ddd, J = 2.2, 2.2, 13.0 Hz, 1 H, H-10eq), 2.29 (ddd, J = 7.0, 9.7, 9.8 Hz, 1 H), 2.52 (dd, J = 7.6, 13.9 Hz, 1 H, NCH_2CH=C), 3.23 (s, 1 H, C*H*Ph), 3.25 (br d, J = 13.9 Hz, 1 H, NCH_2CH=C), 3.30 (m, 1 H), 5.02 (br d, J = 10.2 Hz, 1 H, CH=CH_2), 5.09 (br d, J = 17.2 Hz, 1 H, CH=CH_2), 5.80 (dddd, J = 4.6, 7.6, 10.2, 17.2 Hz, 1 H, CH=C), 7.21–7.34 (m, 5 H, aromatic H); ^{13}C NMR δ 23.2 (C-7), 33.5, 34.6 (C-4 and C-6), 41.1 (C-8), 49.9 (C-5), 49.9, 50.7 (C-3 and C-10), 56.9 (NCH_2CH=C), 78.8 (C-1), 116.2 (C=CH_2), 127.5, 128.1, 128.2 (aromatic C), 135.8 (*C*H=C), 138.7 (aromatic C), 212.4 (C=O); IR 3060, 3010, 2935, 2875, 1705, 1640, 1450, 1420, 920, 750 cm^{-1}; EIMS *m/e* (rel intensity) 269 (M^+, 23), 228 (11), 192 (7), 172 (12), 158 (58), 118 (72), 91 (100); HRMS *m/e* 269.1790 ($C_{18}H_{23}NO$ requires 269.1780).

61: ^1H NMR δ 0.80 (ddd, J = 4.0, 13.3, 13.4 Hz, 1 H, H-6ax), 1.48 (br d, J = 13.4 Hz, 1 H, H-6eq), 1.59–1.71 (m, 3 H), 1.79 (m, 1 H), 2.02 (ddd, J = 6.8, 13.3, 13.5 Hz, 1 H), 2.11–2.31 (m, 3 H), 2.34 (d, J = 13.1 Hz, 1 H, H-10), 2.52 (dd, J = 7.8, 13.7 Hz, 1 H), 2.97 (s, 1 H, C*H*Ph), 3.20–3.32 (m, 2 H), 5.03 (br d, J = 10.2 Hz, 1 H, C=CH_2), 5.06 (br d, J = 17.2 Hz, 1 H, C=CH_2), 5.84 (ddd, J = 4.8, 7.8, 10.2, 17.2 Hz, 1 H, CH=CH_2), 7.18–7.61 (m, 5 H, aromatic H); ^{13}C NMR δ 22.1 (C-7), 33.5, 34.0 (C-4 and C-6), 41.3 (C-8), 49.9 (C-5), 51.3, 52.5 (C-3 and C-10), 57.0 (NCH_2CH=C), 79.9 (C-1), 116.6 (C=CH_2), 127.4, 128.2, 128.9 (aromatic C), 135.7 (*C*H=C), 138.9 (aromatic C), 211.6 (C=O); IR (neat) 2940, 2860, 2790, 1710, 1640, 1450, 1410, 1350, 1305, 1220, 1170, 920 cm^{-1}; EIMS *m/e* (rel intensity) 269 (M^+, 20), 228 (12), 172 (11), 158 (44), 118 (63), 91 (100); HRMS *m/e* 269.1792 ($C_{18}H_{23}NO$ requires 269.1780).

62 or **63**: ^1H NMR δ 1.22–1.65 (m, 3 H), 1.66–1.77 (m, 2 H), 1.97 (m, 1 H), 2.09 (ddd, J = 2.1, 2.1, 13.2 Hz, 1 H, H-10eq), 2.14 (ddd, J = 8.7, 8.7, 9.0 Hz, 1 H), 2.21 (m, 1 H), 2.28 (m, 1 H), 2.33 (d, J = 13.2 Hz, 1 H, H-10ax), 2.43 (d, J = 8.9 Hz, 1 H, C*H*CH=C), 2.84 (dd, J = 2.8, 9.0, 9.0 Hz, 1 H), 3.06 and 3.92 (AB q, J = 13.3 Hz, 2 H, NCH_2Ph), 5.22 (dd, J = 1.7, 17.3 Hz, 1 H, CH=CH_2), 5.29 (dd, J = 1.7, 10.4 Hz, 1 H, CH=CH_2), 5.82 (ddd, J = 8.9, 10.4, 17.3 Hz, 1 H, C*H*=CH_2), 7.19–7.29 (m, 5 H, aromatic H); ^{13}C NMR δ 22.4 (C-7), 32.4, 33.6 (C-4 and C-6), 41.6 (C-8), 49.3 (C-3), 51.3 (C-5), 52.2 (C-10), 57.9 (NCH_2Ph), 78.6 (C-1), 119.1 (C=CH_2), 126.7, 128.1, 128.7 (aromatic C), 137.4 (*C*H=C), 139.3 (aromatic C), 211.7 (C=O); IR 3060, 3025, 2940, 2870, 1710, 1600, 1495, 1450, 1420, 1310, 1230, 1130, 925, 750, 700 cm^{-1}; EIMS *m/e* (rel intensity) 269 (M^+, 11), 242 (3), 228 (1), 178 (11), 159 (44), 91 (100), 68 (85); HRMS *m/e* 269.1780 ($C_{18}H_{23}NO$ requires 269.1780).

63 or **62**: ^1H NMR δ 1.47–1.65 (m, 4 H), 1.68–1.79 (m, 2 H), 2.13 (ddd, J = 7.3, 9.3, 9.3 Hz, 1 H), 2.22–2.34 (m, 3 H), 2.66 (d, J = 8.4 Hz, 1 H, C*H*CH=C), 2.96 (ddd, J = 4.1, 9.3, 9.3 Hz, 1 H), 3.04 and 3.94 (AB q, J = 13.5 Hz, 2 H, NCH_2Ph), 5.27 (dd, J = 1.9, 6.7 Hz, 1 H, CH=CH_2), 5.31 (br s, 1 H, CH=CH_2), 5.69 (m, 1 H, CH=C), 7.17–7.33 (m, 5 H, aromatic H); ^{13}C NMR δ 23.0 (C-7), 33.9, 34.8 (C-4 and C-6), 41.3 (C-8), 49.3 (C-3), 49.6 (C-5), 51.0 (C-10), 57.9 (NCH_2Ph), 77.7 (C-1), 119.5 (C=CH_2), 126.7, 128.1, 128.4 (aromatic C), 137.7 (*C*H=C), 139.6 (aromatic C), 212.3 (C=O); IR 3060, 3025, 2940, 2870, 2790, 1710, 1450, 1420, 1310, 1225, 1130, 925, 750 cm^{-1}; EIMS *m/e* (rel intensity) 269 (M^+, 19), 242 (3), 228 (3), 178 (11), 159 (47), 118 (20), 91 (100), 68 (78); HRMS *m/e* 269.1778 ($C_{18}H_{23}NO$ requires 269.1780).

64: ^1H NMR δ 1.41 (m, 1 H), 1.68 (dd, J = 5.5, 10.8 Hz, 1 H), 1.78–1.91 (m, 3 H), 2.09–2.26 (m, 5 H), 2.29–2.42 (m, 3 H), 2.46 (dd, J = 3.3, 8.6 Hz, 1 H), 2.50 (dd, J = 4.8, 14.0 Hz, 1 H), 2.62 (m, 1 H), 3.46 (s, 2 H, NCH_2Ph), 7.21–7.31 (m, 5 H, aromatic H); ^{13}C NMR δ 21.7 (C-7), 26.0 (C-11), 33.7 (C-4), 35.9 (C-12), 36.6 (C-6), 40.6 (C-8), 41.2 (C-5), 48.8 (C-10), 50.0 (C-3), 54.4 (C-1), 63.2 (NCH_2Ph), 126.9, 128.2, 128.9, 138.8 (aromatic C), 215.3 (C=O); IR 2930, 2800, 1700, 1495, 1450, 1312, 745, 700 cm^{-1}; EIMS *m/e* (rel intensity) 269 (M^+, 16), 228 (2), 192 (5), 185 (5), 1878 (6), 172 (5), 120 (8), 106 (11), 91 (100), 77 (8); HRMS *m/e* 269.1762 ($C_{18}H_{23}NO$ requires 269.1780).

Irradiation of (Aminoethyl)cyclohexenone 30. A solution of 139 mg (0.52 mmol) of amino enone **30** in 260 mL of MeOH was irradiated for 5.8 h (72% conversion of **30**). The reaction conversion, product ratio, and yields were determined both by GC (capillary column) with triphenylmethane as an internal standard and by NONOE ^{13}C NMR technique (for product ratio). Workup followed by column chromatographic (silica gel, EtOAc:hexanes = 1:2) separation afforded cyclized spirocyclic products **65**, **66**, **67**, **68**, and **69** in the yields shown in Table III.

Irradiation of an MeCN (100 mL) solution containing 51 mg (0.20 mmol) of amino enone **30** for 4 h led to 65% conversion of **30**. Cyclized spirocyclic products **65–68** and **69** were analyzed and separated as described above.

65: ^1H NMR δ 1.56 (m, 1 H), 1.66–2.08 (m, 8 H), 2.13 (t, J = 2.3 Hz, 1 H, C≡CH), 2.27 (m, 1 H), 2.79 (ddd, J = 6.5, 9.3, 9.4 Hz, 1 H, H-3), 3.14 (dd, J = 2.3, 17.3 Hz, 1 H, H-11), 3.19 (ddd, J = 4.8, 8.2, 9.3 Hz, 1 H, H-3), 3.41 (dd, J = 2.3, 17.3 Hz, 1 H, H-11), 3.47 (s, 1 H, CHPh), 7.20–7.34 (m, 5 H, aromatic H); ^{13}C NMR δ 32.1 (C-7), 33.5, 34.5 (C-4 and C-6), 40.5 (C-8), 41.0 (NCH_2C≡C), 49.0 (C-3), 50.0 (C-5), 52.3 (C-10), 72.7 (*C*≡C), 75.8 (C-1), 78.7 (C≡*C*H), 127.1, 127.6, 129.0, 137.7 (aromatic C), 212.2 (C=O); IR 3028, 2935, 2872, 2815, 1707, 1604, 1494, 1454, 1427, 1352, 1314, 1287, 1227, 1182, 1126, 743, 701 cm^{-1}; EIMS *m/e* (rel intensity) 267 (M^+, 14), 266 (15), 228 (4), 225 (5), 210 (14), 198 (6), 176 (6), 170 (5), 157 (77), 156 (47), 118 (24), 91 (100), 77 (10), 66 (38); HRMS *m/e* 267.1615 ($C_{18}H_{21}NO$ requires 267.1623).

66: ^1H NMR δ 0.84 (ddd, J = 4.1, 13.4, 13.6 Hz, 1 H, H-6ax), 1.48 (br d, J = 13.6 Hz, 1 H, H-6eq), 1.55–1.59 (m, 1 H), 1.60–1.83 (m, 3 H), 1.88 (ddd, J = 3.9, 10.7, 12.8 Hz, 1 H), 1.97 (m, 1 H), 2.15 (t, J = 2.4 Hz, 1 H, C≡CH), 2.23 (m, 1 H), 2.33 (m, 1 H), 2.72 (m, 1 H), 3.12 (m, 1 H), 3.13 (dd, J = 2.4, 17.2 Hz, 1 H, CH_2C≡C), 3.22 (s, 1 H, C-1), 3.44 (dd, J = 2.4, 17.2 Hz, 1 H, CH_2C≡C), 7.22–7.34 (m, 5 H, aromatic H); ^{13}C NMR δ 22.1 (C-7), 33.5, 33.9 (C-4 and C-6), 40.6 (C-10), 41.2 (NCH_2C≡C), 49.5 (C-5), 49.8 (C-3 and C-10), 73.0 (*C*≡CH), 76.7 (C-1), 78.4 (C≡*C*H), 127.7, 128.1, 128.2, 137.9 (aromatic C), 211.4 (C=O); IR 2932, 2870, 1709, 1653, 1558, 1540, 1495, 1455, 1312, 1228, 1125, 732, 703 cm^{-1}; EIMS *m/e* (rel intensity) 267 (M^+, 14), 266 (8), 228 (7), 2190 (8), 198 (6), 157 (54), 156 (58), 136 (22), 118 (56), 91 (100), 77 (89), 67 (22), 66 (30); HRMS *m/e* 267.1611 ($C_{18}H_{21}NO$ requires 267.1623).

67 or **68**: ^1H NMR δ 1.57 (m, 1 H), 1.65 (m, 1 H), 1.67–1.82 (m, 2 H), 1.85–2.04 (m, 2 H), 2.22 (m, 1 H), 2.29 (m, 1 H), 2.34 (d, J = 13.7 Hz, 1 H, H-10), 2.42 (d, J = 2.2 Hz, 1 H, C≡CH), 2.54 (d, J = 13.7 Hz, 1 H, H-10), 2.63 (br dd, J = 6.9, 7.7 Hz, 2 H, H-3), 3.15 (d, J = 2.2 Hz, 1 H, CHC≡C), 3.55, 3.87 (AB q, J = 13.2 Hz, 2 H, NCH_2Ph), 7.20–7.34 (m, 5 H, aromatic H); ^{13}C NMR δ 22.8 (C-7), 33.4, 34.1 (C-4 and C-6), 41.2 (C-8), 49.2 (C-5), 49.7, 52.6 (C-3 and C-10), 56.3 (NCH_2Ph), 63.4 (C-1), 75.9 (*C*≡CH), 79.2 (C≡*C*H), 126.9, 128.2, 128.7, 138.7 (aromatic C), 211.0 (C=O); IR 3061, 3028, 2935, 2872, 1707, 1603, 1494, 1454, 1313, 1226, 1126, 743, 701 cm^{-1}; EIMS *m/e* (rel intensity) 267 (M^+, 14), 266 (15), 288 (4), 225 (5), 210 (14), 176 (6), 157 (77), 118 (24), 91 (100), 66 (38); HRMS *m/e* 267.1615 ($C_{18}H_{21}NO$ requires 267.1623).

68 or **67**: ^1H NMR δ 1.53–1.64 (m, 3 H), 1.67 (m, 1 H), 1.75 (m, 1 H), 1.88 (ddd, J = 3.6, 10.7, 12.7 Hz, 1 H), 1.96 (m, 1 H), (m, 1 H), 2.29–2.31 (m, 2 H), 2.36 (ddd, J = 6.2, 9.2, 9.5 Hz, 1 H, H-3), 2.42 (d, J = 2.1 Hz, 1 H, C≡CH) 2.45 (dd, J = 1.5, 13.9 Hz, 1 H, H-10eq), 2.70 (d, J = 13.9 Hz, 1 H, H-10ax), 2.79 (ddd, J = 5.1, 9.2, 9.2 Hz, 1 H, H-3), 3.13 (d, J = 2.1 Hz, 1 H, CHC≡C), 3.37 (d, J = 13.2 Hz, 1 H, NCH_2Ph), 4.07 (d, J = 13.2 Hz, 1 H, NCH_2Ph), 7.22 (m, 1 H, aromatic H), 7.26–7.33 (m, 4 H, aromatic H); ^{13}C NMR δ 22.8 (C-7), 33.7, 35.1 (C-4 and C-6), 41.2 (C-8), 49.0 (C-5), 50.0, 50.3 (C-3 and C-10), 56.8 (NCH_2Ph), 64.7 (C-1), 75.8 (*C*≡CH), 80.3 (C≡*C*H), 126.9, 128.1, 128.7, 138.6 (aromatic C), 211.6 (C=O); IR 3027, 2935, 2872, 2849, 2806, 2114, 2708, 1661, 1623, 1582, 1494, 1453, 1427, 1354, 1313, 1287, 1224, 1187, 1128, 750, 770 cm^{-1}; EIMS *m/e* (rel intensity) 267 (M^+, 3),

225 (2), 210 (6), 176 (4), 157 (35), 91 (100), 66 (88); HRMS *m/e* 267.1625 ($C_{18}H_{21}NO$ requires 267.1623).

69: ^{1}H NMR δ 1.33 (ddd, *J* = 4.0, 12.3, 13.9 Hz, 1 H, H-6), 1.71–1.80 (m, 3 H), 1.84 (ddd, *J* = 4.0, 12.6, 12.8 Hz, 1 H, H-4ax), 2.13 (m, 2 H), 2.34 (ddd, *J* = 2.7, 12.4, 12.6 Hz, 1 H, H-3ax), 2.39 (br d, *J* = 19.2 Hz, 1 H), 2.60 (ddd, *J* = 2.2, 2.2, 12.0 Hz, 1 H, H-3ax), 2.80 (br d, *J* = 12.4 Hz, 1 H, H-3eq), 2.98 (br s, 1 H, H-10), 3.23 (d, *J* = 12.0 Hz, 1 H, H-1), 3.58 (s, 2 H, NCH_2Ph), 5.72 (t, *J* = 1.6 Hz, 1 H, CH=C), 7.25–7.31 (m, 5 H, aromatic H); ^{13}C NMR δ 18.4 (C-7), 28.9 (C-6), 37.3 (C-4), 40.3 (C-8), 46.2 (C-5), 49.2, 49.8 (C-1 and C-3), 60.6 (C-10), 62.5 (NCH_2Ph), 123.6 (C-11), 127.2, 128.3, 129.2, 138.0 (aromatic C), 152.2 (C-12), 212.5 (C=O); IR (neat) 2960, 2800, 1690, 1650, 1500, 1450, 1350, 1170, 1040, 920 cm^{-1}; EIMS *m/e* (rel intensity) 267 (M^+, 78), 239 (14), 238 (28), 225 (16), 224 (35), 211 (24), 210 (31), 185 (38), 176 (22), 172 (17), 91 (100); HRMS *m/e* 267.1618 ($C_{18}H_{21}NO$ requires 167.1632).

Irradiation of (Aminoethyl)cyclohexenone 31. A solution of 85 mg (0.28 mmol) of amino enone **31** in 140 mL of MeOH was irradiated for 7 h (81% conversion of **31**). The reaction conversion, product ratio, and yields were determined by GC (capillary column) with pyrene as an internal standard. Workup followed by column chromatographic (silica gel, EtOAc:hexanes = 1:7) separation afforded cyclized spirocyclic products **70**, **71**, **72**, and **73** in the yields shown in Table III.

Irradiation of an MeCN (120 mL) solution containing 70 mg (0.23 mmol) of amino enone **31** for 4 h led to 89% conversion of **31**. Cyclized spirocyclic products **70–73** were analyzed and separated as described above.

70: ^{1}H NMR δ 1.68–1.86 (m, 5 H), 1.95–2.12 (m, 3 H), 2.19–2.32 (m, 2 H), 2.67 (ddd, *J* = 6.5, 9.2, 9.2 Hz, 1 H), 3.01 (d, *J* = 17.0 Hz, 1 H, NCH_2CO_2Me), 3.37 (s, 1 H, H-1), 3.39 (m, 1 H), 3.41 (d, *J* = 17.2 Hz, 1 H, NCH_2CO_2Me), 3.63 (s, 3 H, OCH_3), 7.3 (br s, 5 H, aromatic H); ^{13}C NMR δ 23.1 (C-7), 33.9, 34.4 (C-4 and C-6), 41.0 (C-8), 48.8 (C-10), 49.9 (C-5), 50.2 (C-3), 51.3 (OCH_3), 53.3 (NCH_2CO_2Me), 76.9 (C-1, NCHPh), 127.8, 128.2, 128.3, 138.0 (aromatic C), 171.6 (CO_2Me), 212.3 (C-9, C=O); IR 3024, 2051, 2873, 1738, 1710, 1493, 1447, 1352, 1314, 1222, 1073, 1024, 753, 705 cm^{-1}; EIMS *m/e* (rel intensity) 301 (M^+, 7), 242 (59), 191 (13), 190 (59), 168 (5), 118 (22), 91 (100); HRMS *m/e* 301.1666 ($C_{18}H_{23}NO_3$ requires 301.1678).

71: ^{1}H NMR δ 0.83 (dt, *J* = 4.1, 13.3, 13.3 Hz, 1 H, H-6ax), 1.53 (br d, *J* = 13.3 Hz, 1 H, H-6eq), 1.59–1.71 (m, 2 H), 1.72–1.83 (m, 2 H), 1.96 (m, 1 H), 2.02 (ddd, *J* = 6.5, 13.4, 13.4 Hz, 1 H), 2.18–2.30 (m, 2 H), 2.34 (d, *J* = 13.0 Hz, 1 H), 2.54 (ddd, *J* = 8.4, 8.5, 8.5 Hz, 1 H), 2.95 (d, *J* = 16.8 Hz, 1 H, NCH_2CO_2Me), 3.30 (s, 1 H, H-1), 3.40 (m, 1 H), 3.41 (d, *J* = 16.8 Hz, 1 H, NCH_2CO_2Me), 3.63 (s, 3 H, OCH_3), 7.25–7.34 (m, 5 H, aromatic H); ^{13}C NMR δ 22.1 (C-7), 32.6, 34.1 (C-4 and C-6), 41.2 (C-8), 49.4 (C-5), 51.2 (C-3), 51.4 (OCH_3), 52.3 (C-10), 54.0 (NCH_2CO_2Me), 78.3 (C-1, N-CHPh), 127.7, 128.3, 128.8, 138.2 (aromatic C), 171.4 (CO_2Me), 211.3 (C-10, C=O); IR 3060, 3024, 2950, 2872, 1739, 1709, 1602, 1583, 1493, 1454, 1357, 1312, 1284, 1200, 1174, 1073, 1027, 754, 705 cm^{-1}; EIMS *m/e* (rel intensity) 301 (M^+, 13), 242 (100), 190 (79), 155 (4), 132 (11), 128 (11), 118 (23), 91 (71); HRMS *m/e* 308.1666 ($C_{18}H_{23}NO_3$ requires 301.1678).

72 or **73**: ^{1}H NMR δ 1.50–1.82 (m, 4 H), 1.85–2.06 (m, 2 H), 2.26–2.32 (m, 2 H), 2.38 (m, 1 H), 2.45–2.62 (m, 2 H), 3.03 (m, 1 H), 3.17 (s, 1 H, H-1), 3.52 (d, *J* = 13.0 Hz, 1 H, NCH_2Ph), 3.63 (s, 3 H, OCH_3), 3.77 (d, *J* = 13.0 Hz, 1 H, NCH_2Ph), 7.19–7.32 (m, 5, aromatic H); ^{13}C NMR δ 22.4 (C-7), 35.3, 35.8 (C-4 and C-6), 40.8 (C-8), 49.6 (C-5), 49.7 (C-10), 50.6 (C-3), 51.4 (OCH_3), 57.9 (NCH_2Ph), 74.9 (C-1), 127.2, 128.2, 128.9, 138.2 (aromatic C), 172.3 (CO_2Me), 209.8 (C-9, C=O); IR 3062, 3038, 2950, 2870, 1738, 1713, 1666, 1558, 1540, 1459, 1453, 1436, 1360, 1201, 1176, 1028, 1002, 756, 702 cm^{-1}; EIMS *m/e* (rel intensity) 301 (M^+, 1), 242 (27), 178 (1), 118 (3), 91 (100); HRMS *m/e* 301.1680 ($C_{18}H_{23}NO_3$ requires 301.1678).

73 or **72**: ^{1}H NMR δ 1.55–1.66 (m, 2 H), 1.67–1.80 (m, 3 H), 1.95 (m, 1 H), 2.23–2.33 (m, 2 H), 2.35 (br d, *J* = 13.8 Hz, 1 H, H-10eq), 2.54 (d, *J* = 13.8 Hz, 1 H, H-10ax), 2.55 (m, 1 H), 2.99 (m, 1 H), 3.01 (s, 1 H, H-1), 3.53 (d, *J* = 12.8 Hz, 1 H, NCH_2Ph), 3.69 (s, 3 H, OCH_3), 3.78 (d, *J* = 12.8 Hz, 1 H, NCH_2Ph), 8.20–7.32 (m, 5 H, aromatic H); ^{13}C NMR δ 22.4 (C-7), 32.9, 43.4 (C-4 and C-6), 41.1 (C-8), 49.4 (C-5), 50.7 (C-3), 51.4 (OCH_3), 52.7 (C-10), 57.6 (NCH_2Ph), 75.3 (C-1), 127.2, 128.2, 129.0, 138.2 (aromatic C), 172.3 (CO_2Me), 210.2 (C-9, C=O); IR 3060, 2940, 2865, 1736, 1712, 1500, 1450, 1430, 1350, 1210, 1165, 1010, 760, 705 cm^{-1}; EIMS *m/e* (rel intensity) 301 (M^+, 1), 242 (31), 178 (2), 132 (2), 118 (2), 105 (2), 91 (100); HRMS *m/e* 201.1684 ($C_{18}H_{23}NO_3$ requires 301.1678).

Irradiation of (Aminoethyl)cyclohexenone 31d_7. A solution of 62 mg (0.20 mmol) of amino enone **31d_7** in 100 mL of MeOH was irradiated for 3.5 h (74% conversion of **31d_7**). The reaction conversion, product ratio, and yields were determined by GC (capillary column) with pyrene as an internal standard. Workup followed by column chromatographic (silica gel, EtOAc:hexanes = 1:7) separation afforded cyclized spirocyclic products **76**, **77**, **78**, and **79**. Yields determined by GLC analysis were **76** (12%), **77** (17%), and **78** + **79** (41%).

Irradiation of an MeCN (160 mL) solution containing 100 mg (0.32 mmol) of amino enone **31d_7** for 4.3 h led to 90% conversion of **31d_7**. Cyclized spirocyclic products **76–79** were analyzed and separated as described above, giving **76** (3%), **77** (10%), and **78** + **79** (44%).

76: ^{1}H NMR δ 1.65–1.70 (m, 2 H), 1.71–1.80 (m, 3 H), 1.88–2.08 (m, 3 H), 2.15–2.27 (m, 2 H), 2.68 (ddd, *J* = 6.4, 9.2, 9.2 Hz, 1 H), 3.02 (d, *J* = 17.0 Hz, 1 H, NCH_2CO_2Me), 3.37 (m, 1 H), 3.41 (d, *J* = 17.0 Hz, 1 H, NCH_2CO_2Me), 3.62 (s, 3 H, OCH_3); ^{13}C NMR δ 23.1 (C-7), 33.9, 34.4 (C-4 and C-6), 41.0 (C-8), 48.8 (C-10), 49.9 (C-5), 50.2 (C-3), 51.2 (OCH_3), 53.2 (NCH_2CO_2Me), 171.6 (CO_2Me), 212.2 (C-9, C=O); IR 2932, 2851, 2071, 1732, 1710, 1435, 1315, 1283, 1196, 1174, 758 cm^{-1}; EIMS *m/e* (rel intensity) 307 (M^+, 5), 249 (45), 248 (45), 234 (6), 199 (13), 195 (29), 138 (6), 124 (11), 98 (100), 96 (30); HRMS *m/e* 307.2038 ($C_{18}H_{17}D_6NO_3$ requires 307.2055).

77: ^{1}H NMR δ 0.83 (ddd, *J* = 4.2, 13.3, 13.3 Hz, 1 H, H-6ax), 1.52 (br d, *J* = 13.3 Hz, 1 H, H-6eq), 1.60–1.72 (m, 2 H), 1.73–1.82 (m, 2 H), 1.95–2.08 (m, 2 H), 2.19–2.31 (m, 2 H), 2.55 (ddd, *J* = 8.5, 8.6, 8.6 Hz, 1 H), 3.02 (d, *J* = 16.9 Hz, 1 H, NCH_2CO_2Me), 3.39 (m, 1 H), 3.41 (d, *J* = 16.9 Hz, 1 H, NCH_2CO_2Me), 3.63 (s, 3 H, OCH_3); ^{13}C NMR δ 22.1 (C-7), 32.6, 34.1 (C-4 and C-6), 41.2 (C-8), 48.8 (C-100), 49.8 (C-5), 51.2 (C-3), 52.2 (OCH_3), 53.9 (NCH_2CO_2Me), 172.0 (CO_2Me), 212.2 (C-9, C=O).

78 or **79**: ^{1}H NMR δ 1.60–1.84 (m, 4 H), 1.89–2.00 (m, 2 H), 2.25–2.37 (m, 3 H), 2.46–2.59 (m, 2 H), 3.05 (m, 1 H), 3.17 (s, 1 H, H-1), 3.64 (s, 3 H, OCH_3); ^{13}C NMR δ 22.4 (C-7), 35.3, 35.9 (C-4 and C-6), 40.8 (C-8), 49.6 (C-5), 49.7 (C-10), 50.5 (C-3), 51.4 (OCH_3), 74.8 (C-1), 172.3 (CO_2Me), 209.8 (C-9, C=O); IR 2945, 2872, 2066, 1737, 1711, 1436, 1357, 1318, 1199, 1173, 1011, 841, 752 cm^{-1}; EIMS *m/e* (rel intensity) 308 (M^+, 1), 249 (58), 195 (1), 98 (100), 70 (9); HRMS *m/e* 308.2106 ($C_{18}H_{16}D_7NO_3$ requires 308.2117).

79 or **78**: ^{1}H NMR δ 1.53–1.61 (m, 2 H), 1.63–1.77 (m, 3 H), 1.95 (m, 1 H), 2.25 (m, 1 H), 2.31–2.36 (m, 2 H), 2.52–2.58 (m, 2 H), 2.99 (ddd, *J* = 2.4, 8.9, 8.9 Hz, 1 H), 3.01 (s, 1 H, H-1), 3.69 (s, 3 H, OCH_3); ^{13}C NMR δ 22.4 (C-7), 32.9, 34.4 (C-4 and C-6), 41.1 (C-8), 49.4 (C-5), 50.6 (C-3), 51.4 (OCH_3), 52.7 (C-10), 75.3 (C-1), 137.5 (aromatic C, ipso), 172.4 (CO_2Me), 210.3 (C-9, C=O); IR 2949, 2855, 2067, 1738, 1711, 1434, 1361, 1318, 1197, 1172, 1010, 819, 754, cm^{-1}; EIMS *m/e* (rel intensity) 308 (M^+, 1), 249 (60), 210 (1), 185 (1), 98 (100), 70 (13); HRMS *m/e* 308.2129 ($C_{18}H_{16}D_7NO$ requires 308.2117).

Acknowledgment. Support for this research by the National Science Foundation (CHE-8917725 and INT-8717290) and the National Institutes of Health (GM-27251) is greatly appreciated.

Supplementary Material Available: Synthetic sequences for the preparation of the (aminoethyl)cyclohexenones studied in this effort and the experimental procedures used in these preparations (23 pages). Ordering information is given on any current masthead page.