matic), 7.81 (1 H, s, vinylic); ^{13}C NMR ($CDCl_3$) δ 46.46 (CH_2), 51.51 (OCH_3), 51.94 (OCH_3), 72.82 ()C(), 126.50, 127.40, 127.59, 127.90, 128.54, 128.87, 129.06, 130.93, 131.13, 136.70, 136.89, 140.78, 143.00, 160.76, 166.71 (C=O), 167.09 (C=O); mass spectrum m/e (rel intensity) 427 (M^+, 1), 396 ($M^+ - OCH_3$, 1) 335 ($M^+ - CH_2C_6H_5$, - H, 100).

Anal. Calcd for $C_{27}H_{25}NO_4$: C, 75.88; H, 5.85; N, 3.28. Found: C, 75.41; H, 5.48; N, 3.62.

Further elution with a mixture (1:4) of ethyl acetate and benzene gave 120 mg (33%) of **10d**, mp 215–216 °C, after recrystallization from a mixture (1:1) of chloroform and methanol: IR ν_{max} (KBr) 3150 (NH), 3060, 2960 (CH), 1720, 1680 (C=O), 1610 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 216 nm (ϵ 39 300), 264 (25 300); ^1H NMR ($CDCl_3$) δ 3.80 (2 H, dd, CH_2, J = 12 Hz), 3.81 (3 H, s, OCH_3), 6.50 (1 H, s, vinylic), 7.05–7.68 (10 H, m, aromatic), 7.75 (1 H, broad, NH, D_2O-exchangeable); ^{13}C NMR ($CDCl_3$) δ 41.87 (CH_2), 52.23 (OCH_3), 69.72 ()C(), 126.37, 127.23, 128.23, 128.81, 130.36, 133.27, 135.03, 138.58, 153.58, 162.48 (C=O), 170.84 (C=O); mass spectrum m/e (rel intensity) 307 (M^+, 28), 216 ($M^+ - C_6H_5CH_2$, 100), 91 ($C_6H_5CH_2^+$, 38), 77 ($C_6H_5^+$, 24).

Anal. Calcd for $C_{19}H_{17}NO_3$: C, 74.26; H, 5.53; N, 4.56. Found: C, 73.92; H, 5.62; N, 4.45.

Conversion of 6d to 10d. A mixture of **6d** (50 mg, 0.11 mmol) in methanol (15 mL) and concentrated hydrochloric acid (1 mL) was stirred at ca. 35 °C for 3 h. Removal of the solvent under vacuum and extraction with methylene dichloride gave 33 mg (92%) of **10d**, mp 215–216 °C (mixture mp), after recrystallization from a mixture (1:1) of chloroform and methanol.

X-ray Crystallographic Analysis of 8a, 12a, and 10d. Single crystals of **8a**, **12a**, and **10d** with appropriate dimensions were subjected to X-ray crystallographic analysis, employing a Siemens R3 automated four-circle diffractometer. Summary of crystal data are presented in Table S-I in the supplementary material. Data reduction and structure solution was achieved by SHELXTL-Plus structure solution software package.[14] All calculations were carried out on a VAX station II GPX computer using SHELXTL-Plus software.

Laser Flash Photolysis. For laser flash photolysis, the laser excitation was carried out at the following wavelengths: 248 nm (KrF) and 308 nm (XeCl) (Lambda Physik EMG 101 MCS excimer laser; 50 mJ, 10 ns), 266 nm (fourth harmonic) and 355 nm (third harmonic) (Quanta-Ray Nd-YAG laser; 5–20 mJ, 6 ns), and 337.1 nm (Molectron UV-400 nitrogen laser; 2–3 mJ, ~8 ns). The outputs from the laser sources were suitably attenuated to ~20 mJ $pulse^{-1}$ or less and defocused to minimize multiphoton processes. The details of the kinetic spectrophotometer and the data collection system have been given earlier.[15,16] Unless oxygen effects were to be studied, the solutions were deoxygenated by purging with pure argon. For transient absorption spectra requiring wavelength-by-wavelength measurements with a large number of laser shots, use was made of a flow system, in which the solution was allowed to drain from a reservoir through the cell.

Acknowledgment. We thank the Council of Scientific and Industrial Research and the Department of Science and Technology, Government of India, Regional Research Laboratory Trivandrum, Jawarlal Nehru Centre for Advanced Scientific Research, and the Office of Basic Energy Sciences of the U.S. Department of Energy for financial support of this work. The authors thank Drs. S. Pratapan, K. R. Gopidas, and C. V. Kumar for partial experimental assistance.

Supplementary Material Available: X-ray data for **8a**, **12a**, and **10d** (21 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(14) Sheldrick, G. M. Siemens Analytical X-Ray Division, Madison, WI, 1989.

(15) Das, P. K.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965–6970.

(16) Nagarajan, V.; Fessenden, R. W. *J. Phys. Chem.* **1985**, *89*, 2330–2335.

Exploratory Studies of α-Silylamino and α-Silylamido 2,5-Cyclohexadien-1-one SET Photochemistry. Methodology for Synthesis of Functionalized Hydroisoquinolines

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The electron-transfer (SET) photochemistry of selected α-silylamino and α-silylamido 2,5-cyclohexadienones has been explored with the intent of developing a novel and potentially efficient method for functionalized hydroisoquinoline synthesis. These substances, prepared by Birch reduction–alkylation–oxidation sequences, were found to undergo 9,10-dicyanoanthracene-SET-sensitized radical cyclization to form hydroisoquinolines in a highly regio- and stereoselective fashion and in modest to good yields. In contrast, the major direct irradiation reaction pathway followed by the α-silylamido-substituted systems involves type A rearrangement to bicyclic cyclohexenones or phenols. Direct irradiation of the α-silylamino analogs, on the other hand, brings about near-exclusive conversion to the corresponding hydroisoquinolines. The synthetic and mechanistic features of this study are described.

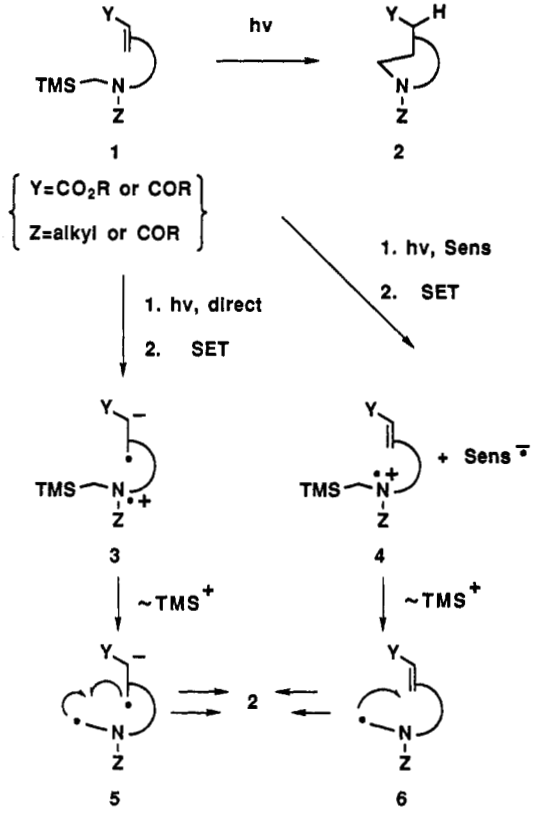
Introduction

In recent reports,[1] we have described the results of mechanistic and exploratory studies from one of our laboratories that have led to the development of novel electron transfer (SET) promoted photocyclization processes applicable to the synthesis of N-heterocycles. These efforts have shown that photoreactions of α-silylamine- or α-silylamide-substituted α,β-unsaturated esters or ketones of general structure **1** (Scheme I), induced by direct and/or SET-sensitized irradiation methods, generate the cyclic amino or amido esters or ketones **2**. The combined

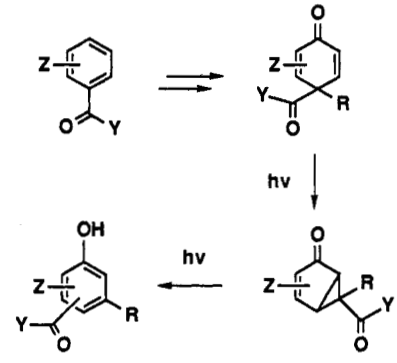
(1) (a) Hasegawa, E.; Xu, W.; Mariano, P. S.; Yoon, U. C.; Kim, J. U. *J. Am. Chem. Soc.* **1988**, *110*, 8099. (b) Jeon, Y. T.; Lee, C. P.; Mariano, P. S. *Ibid.* **1991**, *113*, 8847. (c) Xu, W.; Zhang, X. M.; Mariano, P. S. *Ibid.* **1991**, *113*, 8863. (d) Yoon, U. C.; Mariano, P. S. *Acc. Chem. Res.*, in press.

0022-3263/92/1957-6037$03.00/0

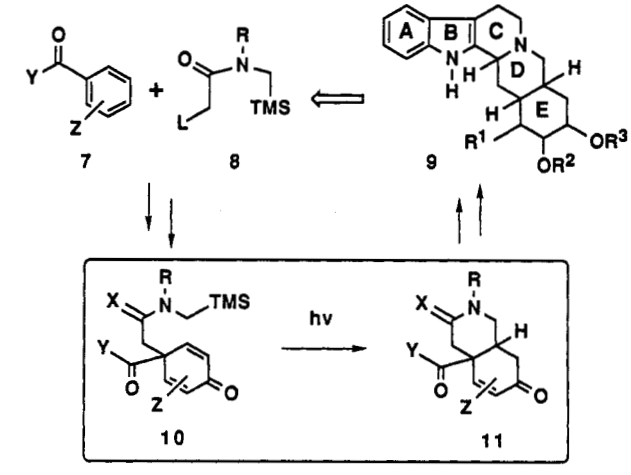
Scheme I



Scheme II



Scheme III



structural and functional features of these reactions appear to make them compatible with strategies for N-heterocycle and alkaloid synthesis.

Several of the mechanistic characteristics of these photocyclization processes have an important bearing on their preparative potential. The direct irradiation reactions involve SET from the amine or amide donor sites to the excited unsaturated ester or ketone chromophores and produce zwitterionic diradicals **3** and then diradicals **5** as precursors to the cyclization products (Scheme I). In contrast, the SET-sensitized process follows pathways in which α-amino or α-amido radical cations **4** are formed by SET to the excited sensitizers. Desilylation of these intermediates then gives N-substituted carbon-centered radicals which undergo intramolecular conjugate additions to the unsaturated esters and ketones. Thus, the major distinguishing features of these two methods are (1) the nature of the excited state (ester or ketone vs sensitizer) serving as the electron acceptor and (2) the reaction type (diradical coupling vs radical cyclization) involved in the carbon–carbon bond formation step. As a consequence, the processes promoted by direct irradiation generally will be inefficient unless the SET step is fast relative to alternative modes of decay of the unsaturated ester or ketone excited states. Experimental observations[1b] coupled with evaluations of SET-thermodynamics/kinetics and excited-state properties suggest that the direct irradiation methodology will be applicable only for systems in which α-silylamines (not amides) are linked to α,β-unsaturated ketones (not esters) which lack rapid excited state decay modes (e.g., small ring systems to block cis–trans isomerization).[1b] In addition, in cases where the intermediate diradicals (**3** or **5**) are prone to fragmentation (e.g., 1,4-biradicals), photocyclizations promoted by direct irradiation will be inefficient.[1b] Finally, since intramolecular diradical coupling reactions,[2] as compared to their radical cyclization counterparts,[3] can be nonstereoselective, lower degrees of stereochemical control are both expected and observed in the direct irradiation reactions.[1c]

Another area which has recently received detailed scrutiny in one of our laboratories[4] concerns the synthesis and photochemistry of 2,5-cyclohexadienones. From these recent efforts have come novel and practical methods for the preparation of a variety of substituted cyclohexadienones based on Birch reduction–alkylation–oxidation sequences (Scheme II).[4a] These synthetic routes are enantioselective when chiral auxiliaries are used to control alkylation diastereoselectivities.[4b] The availability of a wide variety of substituted 2,5-cyclohexadienones by these methods has facilitated an investigation of dienone photoreactions (Scheme II) with the intent of delineating the effects of substituents on photoreactivity and developing new procedures for building complex organic structures.[4c]

While seemingly unrelated, the areas of silylamine SET-photochemistry and dienone synthesis and photochemistry overlap extensively when thought about in the context of a new and potentially efficient and enantioselective strategy for yohimbane alkaloid synthesis. Members of this alkaloid family, structurally generalized by **9** (Scheme III), share a common pentacyclic skeleton with imbedded indole (A–B) and functionalized hydroisoquinoline (D–E) ring systems. As shown in Scheme III,

(2) Cho, I. S.; Lee, C. P.; Chang, S. S.; Ho, C.; Ammon, H. L.; Mariano, P. S. *Heterocycles* **1991**, *31*, 3910.

(3) Cf. Curran, D. P.; Morgan, T. M.; Schwartz, C. E.; Snider, B. B. *J. Am. Chem. Soc.* **1991**, *113*, 6607. Mohan, R.; Kates, S. A.; Dombroski, M. A.; Snider, B. B. *Tetrahedron Lett.* **1987**, *28*, 845.

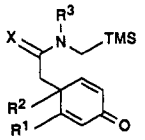
(4) (a) Schultz, A. G. *Pure Appl. Chem.* **1988**, *60*, 981. (b) Schultz, A. G. *Acc. Chem. Res.* **1990**, *23*, 207. (c) For a recent example, see: Schultz, A. G.; Green, N. J. *J. Am. Chem. Soc.* **1992**, *114*, 1824.

the proposed route to the yohimbane alkaloids takes advantage of the Birch reduction methodology to prepare the intermediate silylamino or silylamido 2,5-cyclohexadienones **10** from aromatic and α-haloamide precursors, **7** and **8**. In the cases where a cyclohexadienone Z-substituent is present, this chemistry is capable of furnishing **10** in an enantioselective fashion.[4b] SET-promoted photocyclizations of the cyclohexadienones **10**, paralleling photoreactions developed by Mariano and his co-workers, gives the functionalized hydroisoquinolines **11**. The success of these excited-state processes depends heavily on the avoidance of the often efficient type A photorearrangement[5] of the cyclohexadienone groupings. Consequently, this suggests that the SET-sensitization procedure would be most efficient. Finally, when the C=X position and R group in **11** are carbonyl and tryptophyl, respectively, one could employ Bischler–Napieralski chemistry to complete construction (C-ring formation) of the highly substituted yohimbane skeleton in a regioselective fashion.

Several key issues about this strategy have been addressed in a recent collaborative effort. Specifically, we have investigated methods to prepare a variety of substituted α-silylamino and α-silylamido 2,5-cyclohexadienones related to **10** and we have explored the direct and SET-sensitized photochemistry of these substances. Below is reported the results of this preliminary work which has demonstrated the viability of key features of the proposed yohimbane synthetic design.

Results and Discussion

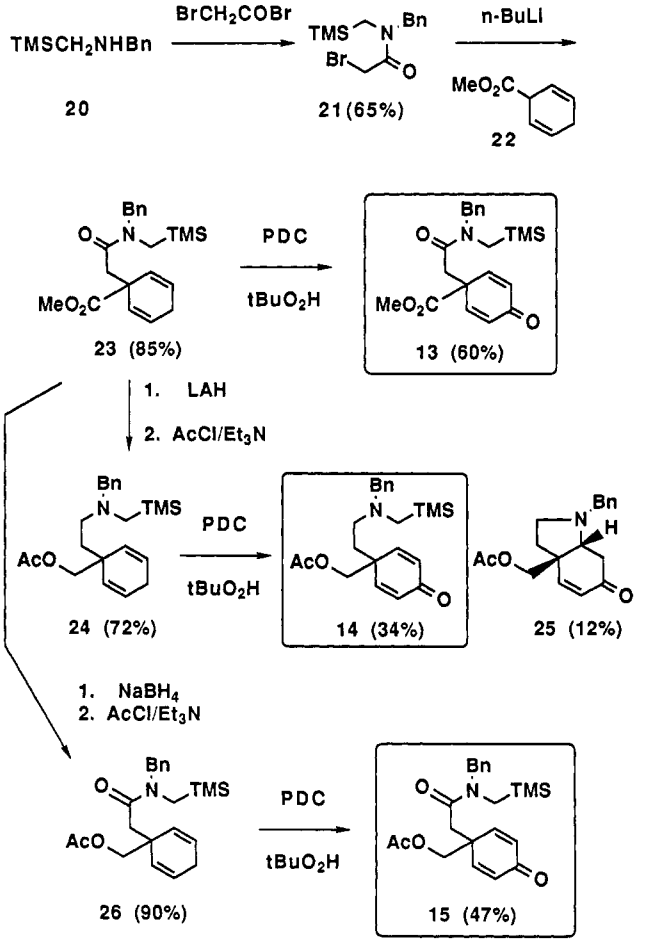
Preparation of 2,5-Cyclohexadienones. The current efforts focused on the synthesis and photochemistry of the silylamido and silylamino cyclohexadienones **12–19**. These



	R^1	R^2	R^3	X	UV (MeCN) λ_{max} (nm) (ε) (Other λ)
12	H	pyrrolidine-C=O	Bn	O	252 (10500) (300 (108), 320 (100))
13	H	CO_2Me	Bn	O	230 (15900) (300 (49), 320 (30))
14	H	CH_2OAc	Bn	H_2	227 (17500) (300 (769), 320 (385))
15	H	CH_2OAc	Bn	O	260 (3800) (300 (110))
16	OMe	CO_2Me	Bn	O	255 (5880) (300 (96), 320 (40))
17	OMe	CH_2OAc	Bn	H_2	266 (5250) (300 (829), 320 (415))
18	OMe	CH_2OAc	Bn	O	269 (5080) (300 (900), 320 (120))
19	H	pyrrolidine-C=O	CO_2Et	H_2	257 (8710) (300 (337))

substances contain various dienone C-4 and C-3 substituents as well as amine, amide, and carbamate environments for the TMS–CH_2N group which are required for a full investigation of synthetic and photochemical issues. The sequences used to prepare **12–19** utilize the general Birch reduction–alkylation–oxidation methodology described earlier.[4a] An example of the application of this chemistry is given by the synthesis of cyclohexadienones **13–15** from the dihydrobenzoate **22**[6] and (silylmethyl)benzylamine **20**,[7] as outlined in Scheme IV. Accordingly, **20** is converted to the bromoamide derivative **21** which is then used to alkylate the lithium enolate of **22** to provide amide ester **23**. Allylic oxidation of **23** gives the silylamido cyclohexadienone **13**. The related dienone **14** is obtained by first transforming **23** into the silylamino acetoxymethyl-

Scheme IV



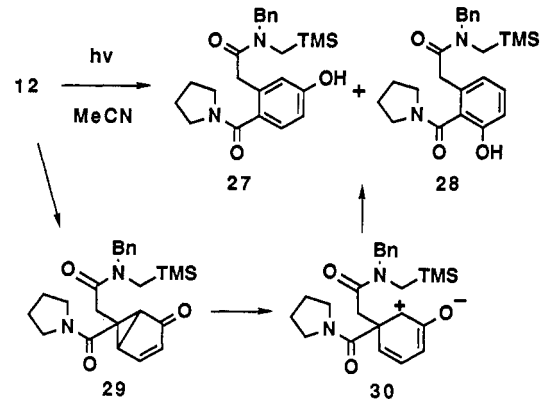
substituted cyclohexadiene **24** and then by allylic oxidation. In this case, oxidation to form **14** is complicated by competitive, oxidative desilylmethylation[8] which produces the hydroindolinone **25**. Finally, **23** is converted to the acetoxymethyl silylamide **15** by selective reduction, esterification, and allylic oxidation. An outline of the schemes used to prepare the other cyclohexadienones along with detailed experimental procedures are included in the supplementary material. In general, the yields for reactions used in these sequences are modest except for the diene to dienone conversions which, especially in the case of the tertiary amine systems (e.g., **24** → **14**), are less efficient.

Photochemistry of Cyclohexadienones 12–19. General Procedures. Exploratory studies were conducted to determine the nature and efficiency of both the direct and SET-sensitized photoreactions of cyclohexadienones **12–19**. The direct irradiation reactions were conducted on either MeCN or MeOH solutions (ca. 2×10^{-3} M) by using Uranium glass (λ > 320 nm) filtered light. For the SET-sensitized processes, 9,10-dicyanoanthracene (DCA) was used as the sensitizer ($1–4 \times 10^{-4}$ M) in MeCN or MeOH solutions. Under these conditions, DCA absorbs >85% of the incident light so that in some cases these processes are complicated by competitive direct irradiation reactions. The progress of the photoreactions was monitored by UV and TLC or GLC, and irradiations were terminated when >95% of the starting dienones had been consumed. Photoproducts were purified by chromatographic tech-

(5) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1962**, *84*, 4527.
(6) Kuehne, M. E.; Lambert, B. F. *Organic Synthesis*; Wiley: New York, 1972; Collect. Vol. V, p 400.
(7) Padwa, A.; Dent, W. *Org. Synth.* **1988**, *67*, 133.

(8) This oxidation proceeds by formation and hydrolysis of an intermediate iminium cation. Similar observations have been made in our general study of oxidative desilylmethylations of tertiary α-silylamines.

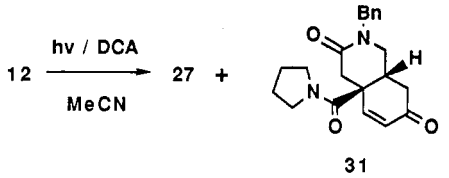
Scheme V



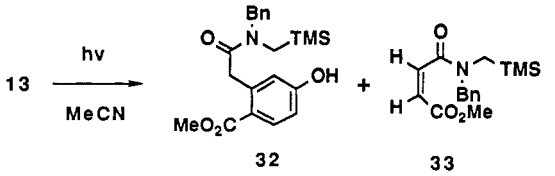
niques and fully characterized by spectroscopic methods. Isolated yields are given along with accurate yields of photoproducts determined by ^1H NMR and/or GLC analysis of crude photolysates.

Direct irradiation of the silylamido cyclohexadienone pyrrolidine **12** in MeCN, as anticipated, leads to production of the regioisomeric phenols, **27** and **28**, in respective isolated yields of 40% and 29%. These substances arise by typical type A rearrangement[5] pathways via the intermediate bicyclohexenones **29** (Scheme V). Migration of the amide group in the zwitterion **30**, generated by photolysis of **29**, to either the 4- or 2-positions gives the phenols. In this system, SET from the silylamide function to the cyclohexadienone is slow[9] relative to type A rearrangement.

In contrast, DCA-sensitized irradiation of cyclohexadienone **12** in MeCN results in efficient (65% by NMR and 59% isolated) production of the hydroisoquinoline along with a lesser amount (13%) of the major phenol **27** formed by a competitive direct irradiation reaction. Only one stereoisomer of **31** is produced in the SET-sensitized photocyclization of **12**, and it is assigned as having the cis ring-fusion stereochemistry on the basis of arguments presented below.

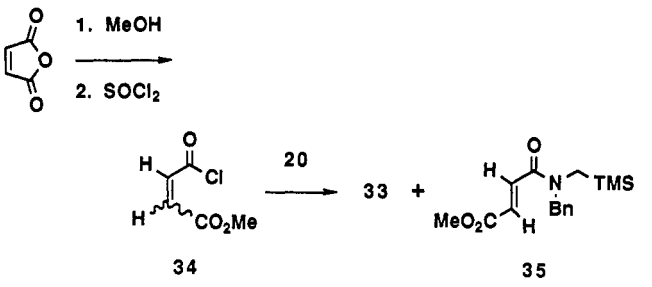


The direct and SET-sensitized photochemistries of the closely related cyclohexadienone ester **13** are surprisingly more complicated. Accordingly, the phenol **32** (37%) is



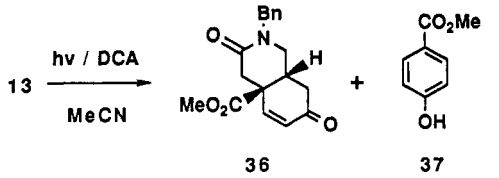
formed in the direct irradiation reaction in MeCN along with the maleate ester amide **33** (33%) while only **32** is generated in a 25% yield when the solvent is changed to MeOH. The unexpected production of **33** dictated an

Scheme VI



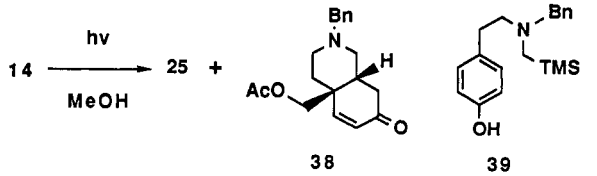
unambiguous structural assignment which was accomplished by its independent synthesis from maleic anhydride through the sequence shown in Scheme VI.

The DCA-sensitized photocyclization of silylamido cyclohexadienone **13** in MeCN to generate hydroisoquinoline **36** (one stereoisomer, 21%) is also made complex by the



simultaneous formation of the phenol **37** (3%) which arises by a fragmentation reaction pathway. Interestingly, the phenol becomes the major product (52%) when DCA is irradiated in a 25% MeCN–75% C_6H_6 solution containing **13**.

It is clear from the results summarized thus far that subtle changes in the C-4 dienone substituent can have a significant impact on the yields and nature of both the direct and SET-sensitized photoreactions of the silylamido cyclohexadienones. Further exploratory work has uncovered a number of other relationships between substituents and reactivity and, as a result, has enhanced understanding of the scope of the process and the factors that influence hydroisoquinoline yields. For example, the direct irradiation reaction of cyclohexadienone **14**, which contains a tethered silylamine rather than silylamide function, in MeOH gives a mixture of products including the cis-fused hydroisoquinoline **38**, hydroindolidenone **25** (see Scheme IV), and aminophenol **39** in yields of 43%, 3%, and 24%, respectively.[10] Type A rearrangement products are not observed in this mixture, presumably as a consequence of the higher rate of SET from the easily oxidized[9] α-silylamine donor which now dominates over triplet-state rearrangement.

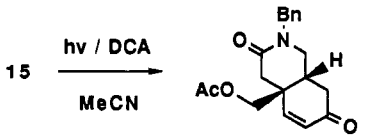


DCA-sensitization of the photocyclization reaction of **14** results in improved yields. Thus, the hydroisoquinoline **38** and hydroindolinone **25** are obtained in isolated yields of 56% and 16%, respectively, when DCA is irradiated in a MeOH solution containing **14**. Likewise, DCA-promoted photocyclization of **14** in MeCN occurs to form **38** (51% by NMR) and **25** (9%). Finally, the silylamide analog **15** upon DCA-sensitized irradiation is converted to the related

(9) (a) Oxidation potentials of α-silylamines and α-silylamides fall in the ranges of +1 and +1.5 V, respectively (ref 9b) while the reduction potential of the triplet excited states of dienones are estimated to be ca. +1 V. (b) Yoshida, J.; Maekawa, T.; Murata, T.; Matsunaga, S.; Isoe, S. *J. Am. Chem. Soc.* **1990**, *112*, 1962. Cooper, B. E.; Owen, W. J. *J. Organomet. Chem.*, **1971**, *29*, 33.

(10) A complicated product mixture containing two TMS-substituted hydroisoquinolines and bicyclic dienone was obtained.

fused bicyclic amide **40** (33% isolated, 60% NMR), again as a single diastereomer assigned the cis-stereochemistry.



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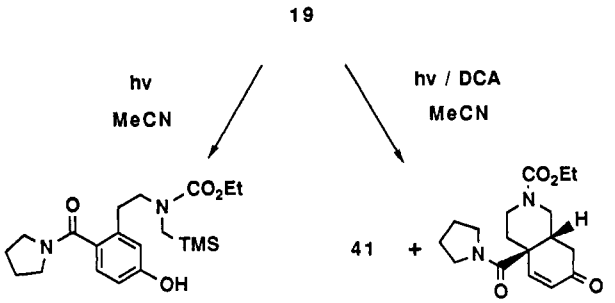
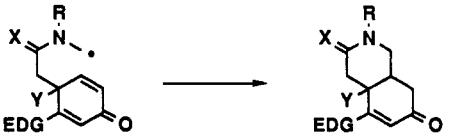
The photochemistry of the silylcarbamate **19** parallels that of the silylamide-containing dienones described above. Upon direct irradiation in MeCN this substance is transformed by the typical type A pathway to the disubstituted phenol **41** (40%), whereas DCA sensitization in MeCN gives a mixture of **41** (formed by competitive direct irradiation) and the hydroisoquinoline **42** in low respective yields of 5% and 20%.



41 42

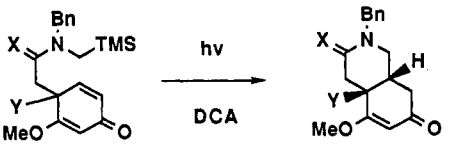
The final issue addressed in this exploratory effort concerns the effect of cyclohexadienone C-3 electron-donating substituents (EDG) on the regiochemistry and efficiency of the SET-promoted cyclization reactions of both silylamido and silylamino systems. Our initial thoughts, guided by steric and electronic considerations, suggested that addition reactions in tethered α-amino radical 3-EDG-substituted cyclohexadienones of general structure **43** should favor the unsubstituted π-bond. Thus, we predicted that the processes would be highly regioselective and, consequently, that they might serve as useful methods for generating hydroisoquinolines **44** with high and well-positioned (for yohimbane syntheses) functionality.



43 44

Studies with the 3-methoxy-substituted cyclohexadienones **16–18** have provided results which support this prediction about substituent control of radical cyclization regiochemistry. For example, DCA-sensitized reactions of these substances in each case result in formation of the corresponding hydroisoquinolines **45–47** (Scheme VII) in yields which depend on solvent (MeCN or MeOH) and the nature of the other substituents. Thus, the silylamido esters **16** and **18** undergo cyclization to form **45** and **47** in very low isolated yields (2% and 10%, respectively) in MeCN as solvent while the corresponding silylamine is converted into hydroisoquinoline **46** with modest efficiency (25%) in MeOH. In addition, other products are formed in these DCA-sensitized reactions. Along with the hydroisoquinoline ester **45**, for example, is formed the bicyclic cyclohexenones **48** and **49**. These enones, of unassigned stereochemistry,[11] are products of direct-irradiation promoted rearrangement of dienone **16** (e.g., $h\nu$ in MeCN gives **48** and **49** in respective yields of 23% and 61%). Related

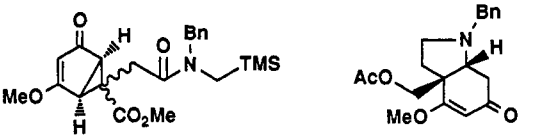
Scheme VII



16 (Y=CO_2Me, X=O) 45

17 (Y=CH_2OAc, X=H_2) 46

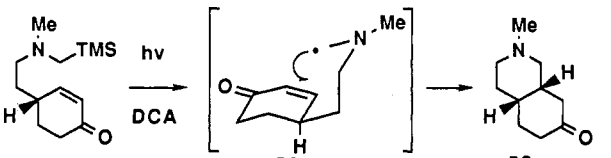
18 (Y=CH_2OAc, X=O) 47



48 & 49 50

substances are known to be formed by type A rearrangements of 3-methoxy-2,5-cyclohexadienones and to resist further photochemical conversion to phenols.[12] Finally, DCA-sensitized reaction of **17** in MeOH gives hydroindolinone **50** (22%) in addition to **46**.

Stereochemical Assignments to the Hydroisoquinolines. As stated above, SET-sensitized photocyclizations of the silylamino and silylamido 2,5-cyclohexadienones give hydroisoquinolines as single stereoisomers. The cis-ring fusion has been assigned to each of these substances by use of the following reasoning. Precedence for this stereochemical outcome can be found in our earlier studies[1c] of the related radical cyclization reaction of the 4-[(α-silylamino)ethyl]cyclohexenone **51**. Here we noted that a strong (ca. 7:1) preference exists for formation of the cis-product **53**. This result demonstrates



51 52 53

that cyclization of the intermediate α-amino radical **52**, through a 6-exo transition state with β-addition to the cyclohexenone group from a pseudoaxial direction, is favored. This is anticipated owing to both the steric and electronic preferences associated with radical cyclization reactions.[13] The driving force for production of cis-ring-fused products should be even greater in the radical intermediates derived from the corresponding 2,5-cyclohexadienones since the planar dienone geometry[14] should strongly enforce cyclization by addition from the syn face (i.e., transition state **54** > transition state **55**).

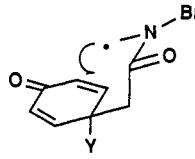
^{1}H NMR analysis of the hydroisoquinolines provides supportive evidence for their cis-ring-fusion stereochemistry. It should be noted that the large number of sp^2-centers in these substances causes them to exist in conformations which are more planar than that expected for

(11) (a) The stereochemistry of these substances is not readily assigned on the basis of chemical shift differences as has been done for related substances (ref 12). However, preliminary NOE results suggest that **48** is the stereoisomer having an endo CO_2Me group.

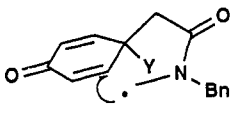
(12) Schultz, A. G.; Lavieri, F. P.; Macielag, M.; Plummer, M. *J. Am. Chem. Soc.* **1987**, *109*, 3991.

(13) Giese, B. *Radicals in Organic Synthesis*; Baldwin, J. E., Ed.; Organic Chemistry Series; Pergamon: Oxford, 1986.

(14) Schultz, A. G.; Harrington, R. E. *J. Org. Chem.* **1991**, *56*, 6391.



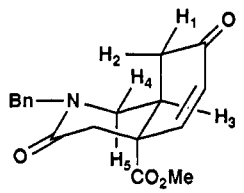
54



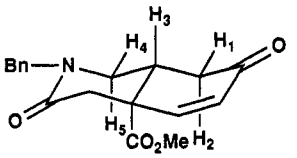
55

idealized decalins. As a consequence, coupling constant differences between pseudoaxial and pseudoequatorial protons should be less pronounced. Despite this, the absence of a large pseudoaxial–axial coupling constant between H_3 and either H_4 or H_5 (for example, in **36** 5.5 and 5.7 Hz observed) and the presence of a large pseudoaxial–axial coupling between H_2 and H_3 (for example, in **36** 9.0 Hz observed) are characteristic of both the cis-stereochemistry and conformational preference depicted by *cis*-**36** in **36** as well as the other hydroisoquinolines formed by the SET-photocyclization process.

It should be noted that the stereochemistry resulting from the photocyclization reactions should not have a major influence on the stereochemistry at these centers in the overall yohimbane strategy (Scheme III) since removal of acyl-blocking function COY (**11** → **9**) by vinylogous β-keto ester decarboxylation or retro-Claisen methodologies would generate dienolic E-ring intermediates. Protonation of these intermediates at C-15 (yohimbane numbering) would then govern the DE ring-fusion stereochemistry of the target.



36-cis



trans

Mechanistic and Synthetic Issues. This exploratory study has provided a number of observations which substantiate the proposal made initially about the synthetic potential of the SET-sensitized photocyclization strategy for functionalized hydroisoquinoline preparation. The accumulated results clearly show that by use of this method, silylamino and silylamido cyclohexadienones of general structure **10** (Scheme III) can be transformed into the corresponding functionalized hydroisoquinolines in modest yields. Moreover, in the case of the mono-β-methoxy-substituted systems **16–18**, regiochemical control is seen in the formation of hydroisoquinolines via radical addition to the unsubstituted β-dienone center. The significance of this selectivity, which presumably is a consequence of steric and electronic effects,[15] is in the demonstration that this methodology will be applicable to the preparation of hydroisoquinolines having substituents properly positioned for further elaboration into functionality commonly found in members of the yohimbane alkaloid family. In addition, since these photocyclizations can be performed with unsymmetrically substituted cyclohexadienones, which themselves can be made enantioselectively,[4b] it should be possible to carry out asymmetric syntheses of hydroisoquinolines and/or yohimbanes.

It is important to mention that the sensitized processes are sometimes complicated by competitive direct irradiation reactions owing to the low solubility of the cyanoarene, DCA, in solvents (e.g., MeCN or MeOH) which are compatible[1b] with the nature of the reaction pathways followed. When the photocyclization substrates are α-silylamines (e.g., **14** and **17**) rather than amides or carbamates, the DCA-sensitized reactions are generally more efficient owing to the fact that both the direct and sensitized pathways lead to formation of hydroisoquinolines predominantly. The comparative direct irradiation reactivity of the silylamino vs silylamido cyclohexadienones is easy to understand on the basis of the expected rates of SET from amine vs amide donors to cyclohexadienone triplet acceptors. The experimentally determined and estimated redox potentials for these donor–acceptor pairs[9] are such that SET is expected to be thermodynamically (thus, kinetically)[16] feasible only when the donor is a silylamine. Thus, in the direct irradiation reaction of **14**, the sequential intramolecular SET-diradical coupling mechanism for cyclization depicted in Scheme I must be followed. The observed effects of C-4 substitution on the photocyclization efficiencies are more difficult to understand.

One problem associated with the DCA-sensitized photocyclization reactions of silylamino-cyclohexadienones is seen in the competitive formation of hydroindolinones (e.g., **25** from **14** and **50** from **17**). These materials arise through oxidation of the intermediate α-amino radicals ($E_{1/2}$ (+) = ca. −1 V)[17] by DCA ($E_{1/2}$ (−) = −0.89 V)[18] followed by formaldiminium cation hydrolysis.[1b,c,8]

Finally, the interesting and, in some cases, unprecedented direct irradiation chemistry of the silylamido cyclohexadienones observed in this study is worthy of brief mention. The cyclohexadienones **16**, **12**, and **19** undergo typical type A photorearrangements to generate either bicyclohexenones (e.g., **48** and **49** from **16**) or phenols (e.g., **27** and **28** from **12**) upon direct irradiation. In contrast, **13**, although having a closely related structure, is transformed to the unique fragmentation product, maleate amide ester **33**, along with the phenol **32**. The mechanistic origins of **33** as well as those of other unusual products observed from some of these photoreactions are sufficiently interesting to warrant a further study of this chemistry.

Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded by using 200-, 400-, and 500-MHz spectrometers on $CDCl_3$ solutions, and chemical shifts are recorded in δ units. ^{13}C NMR resonances were assigned by use of the DEPT technique to determine numbers of attached hydrogens. For substances comprised of amide rotamers, NMR spectroscopic data are given for both rotamers only when all resonances for both rotamers are discernible. IR spectra were recorded on CH_2Cl_2 solutions. Melting points were recorded uncorrected. Analytical GLC employed either 10% OV-101 or 30% SE-30 packed, 10-ft × $^1/_8$-in. columns. Column chromatography was performed with either Merck-EM Type 60 (230–400 mesh) silica gel (flash), Florisil (100–200 mesh), or Merck-Alcoa Type F-20 (80–200 mesh) alumina. Preparative TLC was performed on 20- × 20-cm plates coated with Merck-EM Type-60 GF-254 silica gel. All the solvents were purified before use. Drying of organic layers obtained following workup of reaction mixtures was performed with anhydrous Na_2SO_4. All reactions were run under a N_2 atmosphere unless otherwise noted. All compounds were isolated as oils unless otherwise noted and judged to be >90% pure by ^{13}C and ^1H NMR or elemental analysis.

Preparative photochemical reactions were conducted by using an apparatus consisting of a 450-W Hanovia medium-pressure

(15) The intramolecular 2 + 2 photocycloaddition of 4-(3′-butenyl)-3-methoxy-2,5-cyclohexadien-1-ones also shows high regioselectivity for cyclization at C(5) rather than C(3); see: Schultz, A. G.; Plummer, M.; Taveras, A. G.; Kullnig, R. K. *J. Am. Chem. Soc.* **1988**, *110*, 5547.

(16) Rehm, D.; Weller, A. *Isr. J. Chem.*, **1970**, *8*, 259.

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

(18) Chanon, M.; Eberson, L. *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: New York, 1988; Part A, Chapter 1.11.

mercury lamp (ACE) surrounded by a uranium glass filter (for wavelength band selection) and within a quartz, water-cooled well which was immersed in the photolysis solution. For photochemical reactions on which accurate product yields analyses were performed, irradiations were conducted in sealed quartz tubes (25 or 12 mL) using an APQ 40 merry-go-round photoreactor. The photolysis solutions were purged with N_2 before and during irradiation. The solutions used in the photoreactions were spectrograde CH_3CN (Baker) or CH_3OH (Baker). 9,10-Dicyanoanthracene (Eastman Kodak) was recrystallized prior to use.

Preparation of (Silylmethyl)bromoacetamide 21. To a solution of the *N*-benzyl-*N*-(trimethylsilyl)methylamine (**20**) (14.08 g, 72.8 mmol) (prepared from (iodomethyl)trimethylsilane and benzylamine)[7] and Et_3N (15 mL) in CH_2Cl_2 (200 mL) was added dropwise bromoacetyl bromide (8.2 mL, 94 mmol) over a 1-h period at 0 °C. The reaction mixture was warmed to 25 °C and stirred for 8 h, sequentially washed with water, saturated aqueous $NaHCO_3$, and brine, dried, and concentrated in vacuo. The residue was subjected to silica gel chromatography (deactivated with 2% Et_3N in hexanes, EtOAc:hexanes = 1:10) to give 14.96 g (65%) of the bromoamide **21**: (rotamer A:B = 0.76:0.24) ^1H NMR 0.07 (rotamer A) and 0.11 (rotamer B) (s, 9 H, $SiMe_3$), 2.85 (rotamer B) and 2.90 (rotamer A) (s, 2 H, NCH_2Si), 3.80 (rotamer A) and 3.87 (rotamer B) (s, 2 H, CH_2Br), 4.57 (rotamer A) and 4.58 (rotamer B) (s, 2 H, NCH_2Ph), 7.14–7.37 (m, 5 H, ArH); ^{13}C NMR −1.3 (rotamer A) and −1.5 (rotamer B) ($SiMe_3$), 26.0 (rotamer A) and 26.5 (rotamer B) (CH_2Br), 39.1 (rotamer A) and 41.0 (rotamer B) (NCH_2Si), 50.2 (rotamer B) and 54.1 (rotamer A) (NCH_2Ph), 126.2, 127.4, 127.7, 127.8, 128.6, 129.0 (rotamer A and B) (aromatic para, ortho, meta), 136.0 (ipso), 166.1 (C=O); IR 3030, 2953, 1648, 1451, 1249, 854 cm^{-1}; EIMS *m/e* (rel intensity) 313 (M^+, 0.02), 298 (16), 234 (100), 91 (79), 73 (25); HRMS (CI) *m/e* 314.0571 (MH^+, $C_{13}H_{21}BrNOSi$ requires 314.0575).

Preparation of Silylamido (Methoxycarbonyl)cyclohexadiene 23. To a solution of the cyclohexadiene ester **22** (6.76 g, 48.9 mmol) (prepared from benzoic acid by Birch reduction and methylation)[6] in THF (450 mL) was added *n*-BuLi (1.6 M solution in hexanes, 35 mL, 56 mmol) at −78 °C over 30 min. The mixture was stirred for 1.5 h. The bromoamide **21** (15.57 g, 49.5 mmol) was added, and the mixture was warmed to 25 °C and stirred for 12 h. After addition of saturated aqueous $NaHCO_3$ solution, the mixture was extracted with CH_2Cl_2. The organic extract was washed with brine, dried, and concentrated in vacuo. The residue was subjected to Florisil chromatography (ether:hexane = 1:1) to give the amido cyclohexadiene ester **23** (15.4 g, 85%) as a solid (mp 78–80 °C): (rotamer A:B = 0.64:0.36) ^1H NMR 0.00 (rotamer A) and 0.07 (rotamer B) (s, 9 H, $SiMe_3$), 2.58–2.78 (m, 2 H, diene CH_2), 2.68 (rotamer B) and 2.78 (rotamer A) (s, 2 H, CH_2C=O), 2.75 (rotamer B) and 2.83 (rotamer A) (s, 2 H, NCH_2Si), 3.68 (rotamer A) and 3.69 (rotamer B) (s, 3 H, CO_2CH_3), 4.43 (rotamer A) and 4.54 (rotamer B) (s, 2 H, NCH_2Ph), 5.80–5.90 (m, 4 H, diene H-2, H-3, H-5, H-6), 7.10–7.34 (m, 5 H, ArH); ^{13}C NMR −1.4 ($SiMe_3$), 26.0 (rotamer A) and 26.1 (rotamer B) (CH_2C=O), 37.8, 37.9 (rotamer A and B) 43.9, 44.6 (rotamers A and B) (diene CH_2, NCH_2Si), 45.8 (diene C-1), 52.2 (CO_2CH_3), 49.8 (rotamer B) and 52.9 (rotamer A) (NCH_2Ph), 125.6, 125.7, 126.2, 127.1, 127.4, 127.6, 127.6, 127.8, 128.4, 128.7 (rotamer A and B) (aromatic para, ortho, meta, diene) 136.3, 137.1 (rotamer A and B) (ipso), 168.5 (amide C=O), 174.5 (ester C=O); IR 3030, 2953, 1725, 1633, 1466, 1451, 908, 854 cm^{-1}; EIMS *m/e* (rel intensity) 372 (M^+, 100), 308 (61), 252 (5), 236 (8), 137 (16); HRMS (EI) *m/e* 371.1906 (M^+, $C_{21}H_{29}NO_3Si$ requires 371.1916).

Preparation of Silylamino (Acetoxymethyl)cyclohexadiene 24. To a solution of the amido cyclohexadiene **23** (0.332 g, 0.89 mmol) in THF (10 mL) was added $LiAlH_4$ (34 mg, 0.9 mmol) at 0 °C. The resulting suspension was stirred at reflux for 10 min, cooled to 25 °C, quenched with water, and extracted with CH_2Cl_2. The organic extract was dried and concentrated in vacuo to give a crude alcohol. To a solution of the crude alcohol in CH_2Cl_2 was added Et_3N (0.2 mL, 1.4 mmol) and acetyl chloride (0.1 mL, 1.4 mmol) at 25 °C. The mixture was stirred for 1 h, diluted with CH_2Cl_2, washed with aqueous $NaHCO_3$ and brine, and concentrated in vacuo. The residue was subjected to silica gel chromatography (deactivated with 2% Et_3N in hexane, ether:hexane = 1:1) to give the silylamino (acetoxymethyl)cyclohexadiene **24** (0.295 g, 72%): ^1H NMR −0.03 (s, 9 H, $SiMe_3$), 1.46–1.54 (m, 2 H, CH_2CH_2N), 1.83 (s, 2 H, NCH_2Si), 1.98 (s, 3 H, CH_3CO_2), 2.22–2.30 (m, 2 H, CH_2CH_2N), 2.47–2.56 (m, 2 H, diene CH_2), 3.41 (s, 2 H, CH_2OAc), 3.82 (s, 2 H, NCH_2Ph), 5.31 (dt, J = 10.0, 1.9 Hz, 2 H, diene H-2 and H-6), 5.75 (dt, J = 10.0, 3.3 Hz, 2 H, diene H-3 and H-5), 7.16–7.26 (m, 5 H, ArH); ^{13}C NMR −1.3 ($SiMe_3$), 20.9 (CH_3CO_2, 26.4 (CH_2CH_2N), 34.2 (diene CH_2), 39.6 (diene C-1), 46.2 (NCH_2Si), 52.9 (CH_2CH_2N), 62.1 (NCH_2Ph), 71.2 (CH_2OAc), 126.2, 126.5, 127.9, 128.6, 129.0 (aromatic para, ortho, meta, and diene), 140.3 (ipso), 171.0 (C=O); IR 3025, 2951, 2893, 1743, 1453, 1421, 1372, 1247, 1033, 854 cm^{-1}; EIMS *m/e* (rel intensity) 371 (M^+, 27), 356 (3), 298 (23), 293 (14), 220 (19), 206 (100); HRMS (EI) *m/e* 371.2300 (M^+, $C_{22}H_{33}NO_2Si$ requires 371.2280).

Preparation of Silylamido (Acetoxymethyl)cyclohexadiene 26. To a solution of the silylamido cyclohexadiene ester **23** (2.86 g, 7.7 mmol) in ethanol (60 mL) was added $NaBH_4$ (1.6 g, 42 mmol) at 25 °C. The mixture was stirred at reflux for 10 h. More $NaBH_4$ (2 g × 3) was added portionwise, and stirring was continued for 36 h. The mixture was cooled, quenched with water, and extracted with CH_2Cl_2. The organic extract was concentrated in vacuo to give the crude alcohol. To a solution of the crude alcohol in CH_2Cl_2 solution was added Et_3N (1.3 mL, 9.3 mmol) and acetyl chloride (0.6 mL, 8.3 mmol) at 25 °C. The mixture was stirred for 1 h, diluted with CH_2Cl_2, washed with aqueous $NaHCO_3$ solution and brine, and concentrated in vacuo. The residue was subjected to Florisil chromatography (EtOAc:hexane = 1:6) to give the cyclohexadiene **26** (2.66 g, 90%): (rotamer A:B = 0.70:0.30) ^1H NMR −0.01 (rotamer A) and 0.02 (rotamer B) (s, 9 H, $SiMe_3$), 1.89 (rotamer A) and 1.91 (rotamer B) (s, 3 H, CH_3CO_2), 2.43 (s, 2 H, CH_2C=O), 2.54 (m, 2 H, diene CH_2), 2.71 (rotamer B) and 2.79 (rotamer A) (s, 2 H, NCH_2Si), 4.07 (rotamer A) and 4.10 (rotamer B) (s, 2 H, CH_2OAc), 4.43 (rotamer A) and 4.49 (rotamer B) (s, 2 H, NCH_2Ph), 5.60–5.78 (m, 4 H, diene), 7.04–7.27 (m, 5 H, ArH); ^{13}C NMR −1.6 (rotamer B) and −1.5 (rotamer A) ($SiMe_3$), 20.4 (CH_3CO_2), 25.7 (rotamer B) and 25.9 (rotamer A) (CH_2C=O), 38.0, 38.4 (rotamer A and B) 39.7, 40.0 (rotamer A and B) (NCH_2Si and diene CH_2), 39.1 (rotamer A) and 39.2 (rotamer B) (diene C-1), 49.5 (rotamer B) and 53.5 (rotamer A) (NCH_2Ph), 69.4 (rotamer A) and 69.6 (rotamer B) (CH_2OAc), 125.4, 125.8, 125.9, 126.8, 127.1, 127.5, 127.6, 128.0, 128.4, 128.6 (rotamer A and B) (aromatic para, ortho, meta, and diene), 136.3 (ipso), 168.8 (amide C=O), 170.2 (ester C=O); IR 3054, 2986, 1738, 1630, 1421, 1265, 738, 704 cm^{-1}; EIMS *m/e* (rel intensity) 386 (M^+, 12), 370 (25), 326 (28), 312 (34), 234 (100), 220 (38), 108 (31); HRMS (EI) *m/e* 386.2101 (M^+, $C_{22}H_{32}NO_3Si$ requires 386.2151).

General Procedure for 2,5-Cyclohexadienone Preparation. A general procedure was used for transformations of 2,5-cyclohexadienes into cross-conjugated dienone analogs.[4a] To a solution of the cyclohexadiene in benzene was added Celite and PDC at 25 °C. The mixture was stirred for 5 min, after which *tert*-butyl hydroperoxide was added, and the resulting suspension was stirred for 7 h. After filtration through Celite, the filtrate was concentrated in vacuo giving a residue which was subjected to chromatography to give the 2,5-cyclohexadienone and, in some cases, side products.

Preparation of Silylamido (Methoxycarbonyl)cyclohexadienone 13. Oxidation of cyclohexadiene **23** (0.917 g, 2.47 mmol) gave a residue which was subjected to Florisil chromatography (EtOAc:hexane = 1:6–1:3) to give the dienone **13** (0.568 g, 60%): (rotamer A:B = 0.73:0.27) ^1H NMR 0.00 (rotamer A) and 0.05 (rotamer B) and (s, 9 H, $SiMe_3$), 2.65 (rotamer B) and 2.86 (rotamer B) (s, 2 H, CH_2C=O), 2.84 (rotamer B) and 2.86 (rotamer A) (s, 2 H, NCH_2Si), 3.69 (rotamer A) and 3.70 (rotamer B) (s, 3 H, CO_2CH_3), 4.41 (rotamer A) and 4.52 (rotamer B) (s, 2 H, NCH_2Ph), 6.22–6.33 (m, 2 H, dienone α-H), 7.05–7.34 (m, 7 H, ArH and dienone β-H); ^{13}C NMR −1.5 ($SiMe_3$), 38.0 (rotamer B) and 38.4 (rotamer A) (NCH_2Si), 41.0 (rotamer A) and 41.7 (rotamer B) (CH_2C=O), 49.9 (rotamer A) and 50.0 (rotamer B) (NCH_2Ph), 52.9 (rotamer B) and 53.0 (rotamer A) (CO_2CH_3), 126.0, 127.3, 127.6, 128.4, 128.8 (rotamer A and B) (aromatic para, ortho, meta), 129.0, 130.0 (rotamer A and B) (dienone α-C), 135.5, 136.4 (rotamer A and B) (ipso), 147.7 (dienone β-C), 167.1, 167.4 (rotamer A and B) (amide C=O), 170.5 (ester C=O), 184.8 (dienone C=O); IR 3030, 2952, 1737, 1671, 1640, 1249, 859 cm^{-1}; EIMS *m/e* (rel intensity) 385 (M^+, 0.2), 370 (14), 326 (10), 234 (61), 91 (100),

73 (60); HRMS (EI) m/e 385.1713 (M^+, $C_{21}H_{27}NO_4Si$ requires 385.1709).

Preparation of Silylamino (Acetoxymethyl)cyclohexadienone 14. Oxidation of cyclohexadiene **24** (55 mg, 0.15 mmol) gave a residue which was subjected to F-20 alumina chromatography (ether:hexane = 2:1) to give the dienone **14** (19 mg, 34%) as a solid (mp 64–66 °C) and the hydroindolinone **25** (5 mg, 12%).

14: ^{1}H NMR 0.00 (s, 9 H, $SiMe_3$), 1.72–1.80 (m, 2 H, CH_2CH_2N), 1.86 (s, 2 H, NCH_2Si), 1.95 (s, 3 H, CH_3CO_2), 2.04–2.19 (m, 2 H, CH_2CH_2N), 3.40 (s, 2 H, CH_2OAc), 4.06 (s, 2 H, NCH_2Ph), 6.26 (d, J = 10.1 Hz, 2 H, dienone α-H), 6.64 (d, J = 10.1 Hz, 2 H, dienone β-H), 7.21–7.25 (m, 5 H, ArH); ^{13}C NMR –1.3 ($SiMe_3$), 20.6 (CH_3CO_2), 32.8 (CH_2CH_2N), 45.2 (dienone C-4), 46.5 (NCH_2Si), 52.1 (CH_2CH_2N), 62.2 (NCH_2Ph), 67.8 (CH_2OAc), 127.0, 128.2, 128.7 (aromatic para, ortho, meta), 131.1 (dienone α-C), 139.6 (ipso), 150.6 (dienone β-C), 170.4 (ester C=O), 185.8 (dienone C=O); IR 3040, 2955, 1750, 1675, 1635, 1250, 1225, 1045, 860 cm^{-1}; EIMS m/e (rel intensity) 385 (M^+, 40), 370 (7), 312 (100), 294 (19), 252 (10), 222 (62); HRMS (EI) m/e 385.2043 (M^+, $C_{22}H_{31}NO_3Si$ requires 385.2073).

25: ^{1}H NMR 1.71–1.82 (m, 2 H, H-7), 2.04 (s, 3 H, CH_3CO_2), 2.19–2.32 (m, 1 H, H-7a), 2.69–2.74 (m, 2 H, CH_2CH_2N), 2.81–2.96 (m, 2 H, CH_2CH_2N), 3.14 and 4.02 (AB quart, J = 13.1 Hz, 2 H, CH_2OAc), 4.05 and 4.27 (AB quart, J = 11.0 Hz, 2 H, NCH_2Ph), 5.99 (d, J = 10.2 Hz, 1 H, H-5), 6.48 (dd, J = 10.2, 1.4 Hz, 1 H, H-4), 7.17–7.29 (m, 5 H, ArH); ^{13}C NMR 20.8 (CH_3CO_2), 33.2 (C-3), 37.9 (C-7), 46.7 (C-3a), 51.3 (C-2), 57.0 (NCH_2Ph), 65.3 (C-7a), 68.4 (CH_2OAc), 127.0, 128.2, 128.3, 128.7 (aromatic para, ortho, meta, and C-5), 138.4 (ipso), 151.1 (C-4), 170.7 (ester C=O), 197.6 (enone C=O); IR 3030, 2960, 1743, 1680, 1365, 1235, 1039 cm^{-1}; EIMS m/e (rel intensity) 299 (M^+, 10), 239 (5), 226 (5), 208 (4), 198 (4), 148 (9), 104 (5), 91 (100), 65 (10); HRMS (EI) m/e 299.1529 (M^+, $C_{18}H_{21}NO_3$ requires 299.1521).

Preparation of Silylamido (Acetoxymethyl)cyclohexadienone 15. Oxidation of cyclohexadiene **26** (1.66 g, 4.3 mmol) gave a residue which was subjected to Florisil chromatography (ether:hexane = 1:1) to give the dienone **15** (0.80 g, 47%): (rotamer A:B = 0.68:0.32) ^{1}H NMR 0.00 (rotamer A) and 0.06 (rotamer B) (s, 9 H, $SiMe_3$), 1.92 (rotamer A) and 1.96 (rotamer B) (s, 3 H, CH_3CO_2), 2.60 (rotamer A) and 2.62 (rotamer B) (s, 2 H, CH_2C=O), 2.69 (rotamer B) and 2.89 (rotamer A) (s, 2 H, NCH_2Si), 4.31 (rotamer A) and 4.36 (rotamer B) (s, 2 H, CH_2OAc), 4.43 (rotamer A) and 4.50 (rotamer B) (s, 2 H, NCH_2Ph), 6.27 (d, J = 10.3 Hz, 2 H, dienone α-H), 6.98 (d, J = 10.3 Hz, 2 H, dienone β-H), 7.03–7.32 (m, 5 H, ArH); ^{13}C NMR –1.5 (rotamer B) and –1.4 (rotamer A) ($SiMe_3$), 20.5 (CH_3CO_2), 37.4 (rotamer A) and 37.9 (rotamer B) (CH_2C=O), 38.7 (rotamer B) and 39.0 (rotamer A) (NCH_2Si), 43.9 (rotamer A) and 44.0 (rotamer B) (dienone C-4), 50.0 (rotamer B) and 53.6 (rotamer A) (NCH_2Ph), 66.6 (rotamer A) and 66.7 (rotamer B) (CH_2OAc), 125.9, 127.4, 127.7, 127.8, 128.5, 128.9 (rotamer A and B) (aromatic para, ortho, meta), 130.3 (rotamer A) and 130.4 (rotamer B) (dienone α-C), 135.9 (ipso), 150.0 (rotamer B) and 150.1 (rotamer A) (dienone β-C), 167.3 (amide C=O), 170.1 (ester C=O), 185.4 (dienone C=O); IR 3055, 2955, 1743, 1668, 1628, 1451, 1265, 1249, 736 cm^{-1}; EIMS m/e (rel intensity) 400 (M^+, 50), 384 (92), 340 (51), 326 (80), 234 (100), 218 (38); HRMS (EI) m/e 400.1942 (M^+, $C_{22}H_{30}NO_4Si$ requires 400.1944).

Properties of Cyclohexadienones 12, 16–19 Whose Preparations Are Described in Supplementary Material.

12: (rotamer A:B = 0.70:0.30) ^{1}H NMR 0.00 (rotamer A) and 0.06 (rotamer B) (s, 9 H, $SiMe_3$), 1.69–1.80 (m, 4 H, pyrrolidine CH_2), 2.74 (rotamer B) and 2.85 (rotamer A) (s, 2 H, NCH_2Si), 2.83 (s, 2 H, CH_2C=O), 3.18–3.21 (m, 2 H, pyrrolidine CH_2NCH_2), 3.45–3.51 (m, 2 H, pyrrolidine CH_2NCH_2), 4.47 (rotamer A) and 4.54 (rotamer B) (s, 2 H, NCH_2Ph), 6.35 (rotamer A) and 6.40 (rotamer B) (d, J = 10.3 Hz, 2 H, dienone α-H), 7.39 (rotamer A) and 7.43 (rotamer B) (d, J = 10.3 Hz, 2 H, dienone β-H); ^{13}C NMR –1.4 ($SiMe_3$), 23.3, 26.6 (pyrrolidine CH_2), 38.3 (CH_2C=O), 42.6, 46.7 (pyrrolidine CH_2NCH_2), 48.3 (NCH_2Si), 52.4 (dienone C-4), 53.2 (NCH_2Ph), 126.2, 127.5, 128.8 (aromatic para, ortho, meta), 129.9 (dienone α-C), 136.1 (ipso), 150.1 (dienone β-C), 166.0, 168.0 (amides C=O), 185.1 (dienone C=O); IR 3057, 2953, 1776, 1666, 1633, 1449, 1409, 1249, 858 cm^{-1}; EIMS m/e (rel intensity) 424 (M^+, 2), 409 (16), 326 (8), 234 (55), 120 (5), 91 (100), 73 (71); HRMS (EI) m/e 424.2183 (M^+, $C_{24}H_{32}N_2O_3Si$ requires 424.2182).

16: (rotamers A:B = 0.71:0.29) ^{1}H NMR 0.03 (rotamer A) and 0.13 (rotamer B) (s, 9 H, $SiMe_3$), 2.76 and 3.57 (AB quart, J = 16.1 Hz, 2 H, CH_2CO), 2.76 (rotamer B) and 2.87 (rotamer A) (d, J = 1.7 Hz, 2 H, NCH_2Si), 3.69 (s, 3 H) and 3.70 (s, 3 H) (rotamer A, CH_3O and CO_2CH_3), 3.72 (s, 3 H) and 3.74 (s, 3 H) (rotamer B, CH_3O and CO_2CH_3), 4.51 (s, 2 H, NCH_2Ph), 5.63 (rotamer A) and 5.67 (rotamer B) (s, 1 H, H-2), 6.27 (dd, J = 10.0, 1.3 Hz, 1 H, H-6), 7.13–7.38 (m, 6 H, ArH and H-5); ^{13}C NMR –1.6 ($SiMe_3$), 38.2 (CH_2CO), 38.9 (NCH_2Si), 52.5 (C-4), 53.0 (NCH_2Ph), 53.2 (CO_2CH_3), 56.0 (CH_3O), 103.5 (C-2), 126.1, 127.6, 128.6, 128.8 (aromatic para, ortho, meta, and C-6), 135.9 (ipso), 167.3 (C-3), 167.7 (amide C=O), 171.7 (ester C=O), 187.2 (dienone C=O); IR 3035, 2955, 1743, 1665, 1640, 1600, 1450, 1220, 855 cm^{-1}; EIMS m/e (rel intensity) 415 (M^+, 5), 400 (64), 384 (15), 356 (100), 234 (95), 218 (12); HRMS (EI) m/e 415.1801 ($C_{22}H_{29}NO_5Si$ requires 415.1815).

17: ^{1}H NMR –0.02 (s, 9 H, $SiMe_3$), 1.61–1.68 (m, 1 H, CH_2CH_2N), 1.85 (d, 2 H, NCH_2Si), 1.90 (s, 3 H, CH_3CO_2), 1.93–2.14 (m, 3 H, CH_2CH_2N), 3.34 and 3.42 (AB q, J = 13.5 Hz, 2 H, CH_2OAc), 3.55 (s, 3 H, CH_3O), 4.17 and 4.22 (AB q, J = 10.6 Hz, 2 H, NCH_2Ph), 5.53 (d, J = 1.5 Hz, 1 H, H-2), 6.17 (dd, J = 10.0, 1.5 Hz, 1 H, H-6), 6.39 (d, J = 10.0 Hz, 1 H, H-5), 7.17–7.27 (m, 5 H, ArH); ^{13}C NMR –1.5 ($SiMe_3$), 20.5 (CH_3CO_2), 31.1 (CH_2CH_2N), 46.3 (NCH_2Si), 47.2 (C-4), 51.5 (CH_2CH_2N), 55.0 (CH_3O), 62.0 (NCH_2Ph), 67.1 (CH_2OAc), 104.6 (C-2), 126.8, 128.0, and 128.6 (aromatic para, ortho, meta), 130.2 (C-6), 139.7 (ipso), 146.8 (C-5), 170.3 (C-3), 174.4 (ester C=O), 188.0 (dienone C=O); IR 2953, 1746, 1662, 1627, 1597, 1222, 1045, 855 cm^{-1}; EIMS m/e (rel intensity) 415 (M^+, 30), 400 (8), 342 (100), 324 (29), 270 (19), 241 (31), 206 (67); HRMS (EI) m/e 415.2166 ($C_{23}H_{33}NO_4Si$ requires 415.2178).

18: (rotamer A:B = 0.70:0.30) ^{1}H NMR –0.06 (rotamer A) and 0.05 (rotamer B) (s, 9 H, $SiMe_3$), 1.84 (rotamer A) and 1.90 (rotamer B) (s, 3 H, CH_3CO_2), 2.62 and 2.87 (AB quart, J = 15.4 Hz, 2 H, CH_2CO), 2.62 and 2.87 (AB quart, J = 14.9 Hz, 2 H, NCH_2Ph), 3.61 (rotamer B) and 3.63 (rotamer A) (s, 3 H, CH_3O), 4.12 and 4.32 (AB quart, J = 10.5 Hz, 2 H, CH_2OAc), 4.37 and 4.47 (AB quart, J = 17.0 Hz, 2 H, NCH_2Ph), 5.56 (rotamer A) and 5.58 (rotamer B) (d, J = 1.5 Hz, 1 H, H-2), 6.19 (rotamer A) and 6.21 (rotamer B) (dd, J = 10.0, 1.5 Hz, 1 H, H-6), 6.68 (rotamer A) and 6.75 (rotamer B) (d, J = 10.0 Hz, 1 H, H-5), 7.03–7.31 (m, 5 H, Ar-H); ^{13}C NMR –1.6 ($SiMe_3$), 20.4 (CH_3CO_2), 36.7 (CH_2CO), 38.6 (NCH_2Si), 46.4 (C-4), 53.3 (NCH_2Ph), 55.6 (CH_3O), 66.8 (CH_2OAc), 103.9 (C-2), 126.0, 128.4, 128.8, 129.6 (aromatic para, ortho, meta, C-6), 146.1 (C-5), 167.3, 170.0 and 174.4 (amide and ester C=O and C-3), 187.6 (dienone C=O); IR 3030, 2951, 1746, 1662, 1629, 1598, 1452, 1222, 854 cm^{-1}; EIMS m/e (rel intensity) 429 (M^+, 7), 414 (72), 370 (40), 356 (57), 234 (100); HRMS (EI) m/e 429.1968 ($C_{23}H_{31}NO_5Si$ requires 429.1971).

19: ^{1}H NMR (rotational isomers) 6.93 (m, 2 H), 6.51 (d, 2 H, J = 10.1 Hz), 4.06 (q, 2 H, J = 7.1 Hz), 3.51 (t, 2 H, J = 6.3 Hz), 3.20 (t, 2 H, J = 6.3 Hz) overlapped by 3.2–3.01 (m, 2 H), 2.72 (s, 2 H), 2.29 (t, 2 H, J = 7.9 Hz), 1.89–1.69 (m, 4 H), 1.23 (t, 3 H, J = 7.1 Hz), 0.05 (s, 9 H); IR (film) 1700, 1665, 1625 cm^{-1}; CIMS m/z (relative intensity) 393 (M^+ + 1, 50), 296 (10), 98 (100); ^{13}C NMR 185, 165 and 159 (C=O), 148 (C-3), 131 (C-2), 77 (CH_2O), 61 and 52 (CH_2), 45 (C-4), 44, 34, 26 and 23 (CH_2), 14 (CH_3), –2 (CH_3Si). Anal. Calcd for $C_{20}H_{32}N_2O_4Si$: C, 61.19; H, 8.22. Found: C, 61.26; H, 8.23.

General Procedure for Photoreactions of the 2,5-Cyclohexadienones. MeCN or MeOH solutions containing the appropriate dienone (ca. 2×10^{-3} M) were irradiated with Uranium glass filtered light using the apparatus described in the General section above. In DCA-sensitized irradiations, solutions of the dienones (ca. 2×10^{-3} M) in MeCN containing DCA (ca. 4×10^{-4} M) or MeOH containing DCA (ca. 1×10^{-4} M) were irradiated with Uranium glass filtered light. Reactions were monitored by TLC and UV (or GLC) and terminated when >95% of starting material was consumed. The photolysates were concentrated in vacuo and subjected to chromatography (flash column or preparative TLC) to provide pure photoproducts. Accurate yields of photoproducts were determined by ^{1}H NMR (triphenylmethane as an internal standard) and/or GLC (pyrene as an internal standard) methods.

Irradiation of the 2,5-Cyclohexadienone 12. A solution of **12** (90 mg, 0.21 mmol) in MeCN (95 mL) was irradiated for 1.5 h. Concentration of the photolysate followed by silica gel chromatography (EtOAc:hexane = 1:2–2:1) gave phenols **27** (30 mg, 40%) and **28** (21 mg, 29%) and starting dienone **12** (16 mg). A solution of the dienone **12** (48 mg, 0.11 mmol) in MeCN (55 mL) containing DCA (4×10^{-4} M) was irradiated for 1.5 h. Solvent removal followed by preparative TLC (silica gel, EtOAc:hexane = 2:1) gave phenol **27** (6 mg, 13%), hydroisoquinoline **31** (22 mg, 59%), and starting dienone **12** (4 mg).

27: (rotamer A:B = 0.69:0.31) ^{1}H NMR –0.01 (rotamer A) and 0.08 (rotamer B) (s, 9 H, $SiMe_3$), 1.71–1.87 (m, 4 H, pyrrolidine CH_2), 2.85 (s, 2 H, NCH_2Si), 3.19–3.25 (m, 2 H, pyrrolidine CH_2NCH_2), 3.44–3.53 (m, 2 H, pyrrolidine CH_2NCH_2), 3.79 (rotamer B) and 3.81 (rotamer A) (s, 2 H, $CH_2C{=}O$), 4.54 (rotamer A) and 4.57 (rotamer B) (s, 2 H, NCH_2Ph), 6.58 (rotamer A) and 6.60 (rotamer B) (dd, J = 8.3, 2.3 Hz, 1 H, H-6), 6.81 (rotamer A) and 6.84 (rotamer B) (d, J = 2.3 Hz, 1 H, H-2), 7.02 (rotamer A) and 7.01 (rotamer B) (d, J = 8.3 Hz, 1 H, H-5), 7.07–7.33 (m, 5 H, ArH), 9.13 (br s, 1 H, OH); ^{13}C NMR –1.4 (rotamer B) and –1.1 (rotamer A) ($SiMe_3$), 24.5, 26.0, 37.2, 38.7, 45.6, 49.0, 53.5 (rotamer A), 126.8, 127.2, 127.5, 127.8, 128.0, 128.5, 128.7 (rotamer A and B) (aromatic), 128.1, 133.3, 133.7, 136.2, 126.8, 158.0 (rotamer A and B) (aromatic quaternary), 170.0, 170.7 (rotamer A) (amides C=O); IR 3404, 3054, 2954, 1735, 1620, 1436, 1265, 737 cm^{-1}; EIMS m/e (rel intensity) 424 (M^+, 4), 409 (19), 385 (4), 353 (7), 326 (43), 299 (15), 232 (23), 199 (21), 91 (100); HRMS (EI) m/e 424.2197 (M^+, $C_{24}H_{32}N_2O_3Si$ requires 424.2182).

28: (rotamer A:B = 0.68:0.32) ^{1}H NMR 0.00 (rotamer A) and 0.09 (rotamer B) (s, 9 H, $SiMe_3$), 1.63–1.88 (m, 4 H, pyrrolidine CH_2), 2.81 (rotamer B) and 2.85 (rotamer A) (s, 2 H, NCH_2Si), 3.24–3.25 (m, 2 H, pyrrolidine CH_2NCH_2), 3.50 (rotamer A) and 3.53 (rotamer B) (s, 2 H, $CH_2C{=}O$), 3.57–3.71 (m, 2 H, pyrrolidine CH_2NCH_2), 4.47 (rotamer A) and 4.55 (rotamer B) (s, 2 H, NCH_2Ph), 6.62 (d, J = 8.1 Hz, 1 H, H-6), 6.69 (d, J = 7.4 Hz, 1 H, H-4), 6.98 (dd, J = 8.1, 7.4 Hz, 1 H, H-5), 7.09–7.36 (m, 5 H, Ar-H), 8.39 (br s, 1 H, OH); ^{13}C NMR –1.4 (rotamer B) and –1.2 (rotamer A) ($SiMe_3$), 24.5, 25.9, 37.4, 38.7, 45.8, 50.2, 53.5 (rotamer A), 115.0, 121.0, 126.5, 127.5, 127.8, 128.4, 128.7, 129.7 (rotamer A and B) (aromatic), 125.1, 133.2, 136.5, 153.0 (rotamer A) (aromatic quarternary), 167.9, 170.0 (rotamer A) (amides C=O); IR 3191, 3060, 2953, 1712, 1633, 1451, 1290, 1248, 853 cm^{-1}; EIMS m/e (rel intensity) 424 (M^+, 4), 409 (22), 326 (58), 232 (17), 192 (16), 91 (100); HRMS (EI) m/e 424.2174 (M^+, $C_{24}H_{32}N_2O_3Si$ requires 424.2182).

31: ^{1}H NMR 1.77–1.90 (m, 4 H, pyrrolidine CH_2), 2.44–2.57 (m, 2 H, H-8 and H-8a), 2.49 (d, J = 17.2, 1 H, H-4), 2.84–2.93 (m, 2 H, H-8 and H-1), 3.06 (d, J = 17.2 Hz, 1 H, H-4), 3.28–3.35 (m, 2 H, H-1 and pyrrolidine CH_2NCH_2), 3.42–3.48 (m, 2 H, pyrrolidine CH_2NCH_2), 3.51–3.56 (m, 1 H, pyrrolidine CH_2NCH_2), 4.48 and 4.68 (AB quart, J = 14.8 Hz, 2 H, NCH_2Ph), 6.06 (d, J = 10.1 Hz, 1 H, H-6), 6.95 (d, J = 10.1 Hz, 1 H, H-5), 7.18–7.32 (m, 5 H, ArH); ^{13}C NMR 23.1, 26.9 (pyrrolidine CH_2), 34.0 (C-8a), 38.2, 38.9, 47.6, 48.1, 48.3 (C-1, C-4, C-8, and pyrrolidine CH_2NCH_2), 47.9 (C-4a), 49.8 (NCH_2Ph), 127.5, 127.9, 128.6 (aromatic para, ortho, meta), 129.0 (C-6), 136.4 (ipso), 149.4 (C-5), 167.2, 169.2 (amides C=O), 196.8 (enone C=O); IR 3054, 2982, 1732, 1681, 1633, 1420, 1312, 1265, 737 cm^{-1}; EIMS m/e (rel intensity) 352 (M^+, 53), 324 (16), 254 (100), 206 (48), 91 (20); HRMS (EI) m/e 352.1775 (M^+, $C_{21}H_{24}N_2O_3$ requires 352.1786).

Irradiation of 2,5-Cyclohexadienone 13. A solution of **13** (66 mg, 0.17 mmol) in MeCN (100 mL) was irradiated for 4 h. Product yields were determined by the ^{1}H NMR method. Concentration of the photolysate followed by preparative TLC (silica gel, EtOAc:hexane = 1:3) separation gave the maleic acid derivative **33** (17 mg, 33%) and phenol **32** (18 mg, 27%). A solution of the dienone **13** (71 mg, 0.18 mmol) in MeCN (100 mL) containing DCA (4×10^{-4} M) was irradiated for 4 h. Concentration of the photolysate followed by preparative TLC (silica gel, EtOAc:hexane = 1:3) separation gave hydroisoquinoline **36** (12 mg, 21%) and methyl *p*-hydroxybenzoate **37** (1 mg, 3%). A solution of dienone **13** (14 mg, 0.036 mol) in MeOH (12 mL) was irradiated for 4 h. Concentration of the photolysate followed by preparative TLC (silica gel, EtOAc:hexane = 1:3) separation gave phenol **32** (4 mg, 25%). A solution of the dienone **13** (75 mg, 0.19 mmol) in MeOH (100 mL) containing DCA (1×10^{-4} M) was irradiated for 4 h. Concentration of the photolysate followed by preparative TLC (silica gel, EtOAc:hexane = 1:3) separation gave benzoate **37** (3 mg, 9%).

32: (rotamer A:B = 0.68:0.32) ^{1}H NMR 0.04 (rotamer A) and 0.14 (rotamer B) (s, 9 H, $SiMe_3$), 2.91 (rotamer B) and 2.95 (rotamer A) (s, 2 H, NCH_2Si), 3.75 (rotamer A) and 3.76 (rotamer B) (s, 3 H, CO_2CH_3), 4.04 (rotamer A) and 4.11 (rotamer B) (s, 2 H, $CH_2C{=}O$), 4.64 (rotamer B) and 4.71 (rotamer A) (s, 2 H, NCH_2Ph), 6.50 (rotamer A) and 6.58 (rotamer B) (dd, J = 8.6, 2.5 Hz, 1 H, H-6), 6.59 (rotamer A) and 6.70 (rotamer B) (d, J = 2.5 Hz, 1 H, H-2), 7.24–7.39 (m, 5 H, ArH), 7.81 (rotamer A) and 7.85 (rotamer B) (d, J = 8.6 Hz, 1 H, H-5), 8.54 (br s, 1 H, OH); ^{13}C NMR –1.1 ($SiMe_3$), 38.9 (NCH_2Si), 39.4 ($CH_2C{=}O$), 51.3 (CO_2CH_3), 53.9 (NCH_2Ph), 114.5, 120.0, 126.8, 127.2, 127.5, 128.0, 128.5, 128.8, 133.3, 139.3 (aromatic), 161 (amide C=O), 171 (ester C=O); IR 3441, 3054, 2985, 1731, 1709, 1605, 1572, 1452, 1265, 738 cm^{-1}; EIMS m/e (rel intensity) 385 (M^+, 9), 370 (72), 358 (52), 326 (100), 220 (23), 165 (41); HRMS (EI) m/e 385.1683 (M^+, $C_{21}H_{27}NO_4Si$ requires 385.1709).

33: (rotamer A:B = 0.78:0.22) ^{1}H NMR 0.07 (rotamer B) and 0.08 (rotamer A) (s, 9 H, $SiMe_3$), 2.27 (rotamer B) and 2.87 (rotamer A) (s, 2 H, NCH_2Si), 3.64 (rotamer B) and 3.73 (rotamer A) (s, 3 H, CO_2CH_3), 4.47 (rotamer A) and 4.65 (rotamer B) (s, 2 H, NCH_2Ph), 5.98 (d, J = 12.0 Hz, 1 H, $CHC{=}O$), 6.54 (d, J = 12.0 Hz, 1 H, $CHCO_2$), 7.14–7.35 (m, 5 H, ArH); ^{13}C NMR –1.4 (rotamer B) and –1.2 (rotamer A) ($SiMe_3$), 37.1 (rotamer A) and 38.4 (rotamer B) (NCH_2Si), 49.1 (rotamer B) and 53.9 (rotamer A) (NCH_2Ph), 51.8 (CO_2CH_3), 123.1 (rotamer B) and 123.2 (rotamer A) ($CHCO_2$), 127.0, 127.3, 127.6, 128.4, 128.5, 128.8 (rotamer A and B) (aromatic para, ortho, meta), 136.2, 136.4 (rotamer A and B) (ipso), 165.0 (amide C=O), 165.8 (ester C=O); IR 3031, 2952, 1731, 1632, 1452, 1248, 1219, 1174, 855 cm^{-1}; EIMS m/e (rel intensity) 305 (M^+, 4), 290 (58), 246 (8), 214 (12), 113 (36), 91 (100); HRMS (EI) m/e 305.1440 (M^+, $C_{16}H_{23}NO_3Si$ requires 305.1447).

36: ^{1}H NMR 2.41 (dd, J = 17.4, 9.0 Hz, 1 H, H-8), 2.53 (dd, J = 17.4, 4.6 Hz, 1 H, H-8), 2.63 (d, J = 17.7 Hz, 1 H, H-4), 2.86–2.90 (m, 1 H, H-8a), 2.96 (dd, J = 13.1, 5.7 Hz, 1 H, H-1), 3.04 (d, J = 17.7 Hz, 1 H, H-4), 3.37 (dd, J = 13.1, 5.5 Hz, 1 H, H-1), 3.73 (s, 3 H, CO_2CH_3), 4.50 and 4.64 (AB quart, J = 14.6 Hz, 2 H, NCH_2Ph), 6.05 (d, J = 10.0 Hz, 1 H, H-6), 6.80 (d, J = 10.0 Hz, 1 H, H-5), 7.17–7.32 (m, 5 H, ArH); ^{13}C NMR 34.1, 37.7, 38.5, 46.9, 48.5, 50.0, 53.2, 127.6, 127.7, 128.0, 128.7, 129.5, (aromatic para, ortho, meta, and C-6), 136.2 (ipso), 148.0 (C-5), 172.7 (ester C=O), 196.1 (enone C=O); IR 3060, 2953, 1731, 1650, 1495, 1250, 734 cm^{-1}; EIMS m/e (rel intensity) 313 (M^+, 100), 285 (14), 254 (22), 169 (32), 118 (59); HRMS (EI) m/e 313.1318 (M^+, $C_{18}H_{19}NO_4$ requires 313.1314).

Irradiation of 2,5-Cyclohexadienone 14. A solution of dienone **14** (37 mg, 0.096 mmol) in MeCN (45 mL) containing DCA (4×10^{-4} M) was irradiated for 2 h. Concentration of the photolysate followed by preparative TLC (silica gel, EtOAc:hexane = 1:2) separation gave hydroisoquinoline **38** (9 mg, 30% isolated, 51% NMR) and hydroindole **25** (3 mg, 11% isolated, 9% NMR). A solution of dienone **14** (66 mg, 0.17 mmol) in MeOH (90 mL) was irradiated for 2 h. Concentration of the photolysate followed by preparative TLC (silica gel, EtOAc:hexane = 1:2) separation gave hydroisoquinoline **38** (18 mg, 34% isolated, 43% NMR), hydroindole **25** (3% NMR), and phenol **39** (24% NMR). A solution of dienone **14** (17.4 mg, 0.045 mmol) in MeOH (20 mL) containing DCA (1×10^{-4} M) was irradiated for 2 h. Concentration of the photolysate followed by preparative TLC (silica gel, EtOAc:hexane = 1:2) separation gave **38** (8 mg, 56% isolated, 60% NMR), **25** (16% NMR), and **39** (5% NMR).

38: ^{1}H NMR 1.73–1.76 (m, 2 H, H-4), 2.04 (s, 3 H, CH_3CO_2), 2.17–2.28 (m, 1 H, H-8a), 2.28–2.38 (m, 2 H, H-8), 2.50–2.67 (m, 4 H, H-1 and H-3), 3.42 and 3.47 (AB quart, J = 13.1 Hz, 2 H, CH_2OAc), 4.11 and 4.21 (AB quart, J = 11.2 Hz, 2 H, NCH_2Ph), 6.03 (d, J = 10.1 Hz, 1 H, H-6), 6.53 (d, J = 10.1 Hz, 1 H, H-5), 7.20–7.30 (m, 5 H, ArH); ^{13}C NMR 20.8 (CH_3CO_2), 31.9 (C-4a), 36.1 (C-8a), 38.8, 39.0, 49.4, 54.4 (C-1, C-3, C-4, C-8), 62.7 (NCH_2Ph), 68.0 (CH_2OAc), 127.1, 128.2, 128.8 (aromatic para, ortho, meta), 130.3 (C-6), 138.0 (ipso), 153.1 (C-5), 170.7 (ester C=O), 198.9 (enone C=O); IR 3028, 2943, 1744, 1681, 1453, 1380, 1232, 665 cm^{-1}; EIMS m/e (rel intensity) 313 (M^+, 100), 270 (10), 254 (68), 240 (32), 91 (2); HRMS (EI) m/e 313.1681 (M^+, $C_{19}H_{23}NO_3$ requires 313.1677).

39: ^{1}H NMR 0.00 (s, 9 H, $SiMe_3$), 1.99 (s, 2 H, NCH_2Si), 2.53–2.56 (m, 2 H, $ArCH_2CH_2N$), 2.64–2.68 (m, 2 H, $ArCH_2CH_2N$), 3.54 (s, 2 H, NCH_2Ph), 6.69 (d, J = 8.5 Hz, 2 H, H-2 and H-6), 6.95 (d, J = 8.5 Hz, 2 H, H-3 and H-5), 7.20 (br s, 1 H, OH), 7.24–7.27 (m, 5 H, ArH); ^{13}C NMR –1.3 ($SiMe_3$), 32.4 ($ArCH_2CH_2N$), 45.9, 59.2 ($ArCH_2CH_2N$ and NCH_2Si), 62.0 (NCH_2Ph), 115.0, 126.6, 128.1, 128.7, 129.9, 133.0, 140.2, 153.6 (aromatic); IR 3378, 3026, 2950, 2789, 1612, 1514, 1452, 1247, 855 cm^{-1}; EIMS m/e (rel intensity) 313 (M^+, 2), 298 (22), 240 (8), 206 (100), 91 (1); HRMS (EI) m/e 313.1884 (M^+, $C_{19}H_{27}NOSi$ requires 313.1861).

Irradiation of 2,5-Cyclohexadienone 15. A solution of dienone **15** (76 mg, 0.19 mmol) in MeCN (95 mL) containing DCA (4×10^{-4} M) was irradiated for 4.5 h. Product yields were determined by the ^{1}H NMR method. Concentration of the photolysate followed by preparative TLC (silica gel, EtOAc:hexane = 1:1) separation gave hydroisoquinoline **40** (20 mg, 33% isolated, 60% NMR): ^{1}H NMR 2.04 (s, 3 H, CH_3CO_2), 2.39 (dd, J = 18.3, 10.2 Hz, 1 H, H-8), 2.49 (dd, J = 18.3, 4.4 Hz, 1 H, H-8), 2.5 (m, 1 H, H-8a), 2.53 and 2.62 (AB quart, J = 17.9 Hz, 2 H, H-4), 3.00 (dd, J = 12.9, 5.3 Hz, 1 H, H-1), 3.41 (dd, J = 12.9, 5.2 Hz, 1 H, H-1), 4.05 and 4.16 (AB quart, J = 11.5 Hz, 2 H, CH_2OAc), 4.52 and 4.61 (AB quart, J = 14.5 Hz, 2 H, NCH_2Ph), 6.04 (d, J = 10.1 Hz, 1 H, H-6), 6.70 (d, J = 10.1 Hz, 1 H, H-5), 7.18–7.33 (m, 5 H, Ar-H); ^{13}C NMR 20.6 (MeC=O), 33.1 (C-8a), 37.3 (C-4), 38.1 (C-8), 39.4 (C-4a), 48.3 (C-1), 49.9 (NCH_2Ph), 67.3 (CH_2Ph), 127.8, 128.1, 128.8 (aromatic para, ortho, meta), 130.3 (C-6), 136.2 (ipso), 151.1 (C-5), 166.8 (amide C=O), 170.4 (ester C=O), 196.5 (enone C=O); IR 3061, 2928, 1741, 1691, 1643, 1232, 732 cm^{-1}; EIMS m/e (rel intensity) 327 (M^+, 100), 299 (7), 254 (20), 240 (17), 160 (13), 133 (15); HRMS (EI) 327.1481 ($C_{19}H_{21}NO_4$ requires 327.1471).

Irradiation of 2,5-Cyclohexadienone 16. A solution of the cyclohexadienone **16** (15 mg, 0.04 mmol) in MeCN (10 mL) was irradiated for 8 h (conversion 40%). Product yields were determined by ^{1}H NMR. Concentration of the photolysate followed by preparative TLC (silica gel, EtOAc:hexane = 1:3) separation gave bicyclic hexenones **48** (23%) and **49** (61%). A solution of the cyclohexadienone **16** (15 mg, 0.04 mmol) in MeCN (10 mL) containing DCA (4×10^{-4} M) was irradiated for 8 h (conversion 79%). Concentration of the photolysate followed by preparative TLC (silica gel, EtOAc:hexane = 1:3) separation gave hydroisoquinoline **45** (2%), **48** (24%), and **49** (38%). A solution of the dienone **16** (16 mg, 0.04 mmol) in MeOH (10 mL) was irradiated for 8 h (conversion 55%). Concentration of the photolysate followed by preparative TLC (silica gel, EtOAc:hexane = 1:3) separation gave **48** (22%) and **49** (51%). A solution of the dienone **16** (15 mg, 0.04 mmol) in MeOH (10 mL) containing DCA (1×10^{-4} M) was irradiated for 8 h (conversion 45%). Concentration of the photolysate followed by preparative TLC (silica gel, EtOAc:hexane = 1:3) separation gave **48** (24%) and **49** (38%).

45: ^{1}H NMR 2.37–2.39 (m, 2 H, H-8), 2.76 and 3.18 (AB quart, J = 17.8 Hz, 2 H, H-4), 2.85–2.93 (m, 1 H, H-8a), 2.98 (dd, J = 13.2, 4.6 Hz, 1 H, H-1), 3.24 (dd, J = 13.2, 5.4 Hz, 1 H, H-1), 3.71 (s, 3 H) and 3.72 (s, 3 H) (CH_3O and CO_2CH_3), 4.56 (s, 2 H, NCH_2Ph), 5.38 (s, 1 H, H-6), 7.16–7.32 (m, 5 H, ArH); ^{13}C NMR 34.4 (C-8a), 35.0 (C-4), 37.7 (C-8), 48.1 (C-1), 49.9 (NCH_2Ph), 53.3 (CO_2CH_3), 54.6 (C-4a), 56.8 (OCH_3), 102.2 (C-6), 127.7, 128.0, 128.7 (aromatic para, ortho, meta), 136.2 (ipso), 166.3, 170.5, 175.0 (amide C=O, ester C=O, C-5), 195.7 (enone C=O); IR 2924, 1737, 1650, 1608, 1349, 1256, 1221 cm^{-1}; EIMS m/e (rel intensity) 343 (M^+, 100), 328 (15), 300 (14), 284 (92), 192 (13), 161 (32), 133 (54); HRMS (EI) m/e 343.1422 ($C_{19}H_{21}NO_5$ requires 343.1420).

48: (rotamers A:B = 0.74:0.26) ^{1}H NMR 0.02 (rotamer A) and 0.09 (rotamer B) (s, 9 H, $SiMe_3$), 2.46 (rotamer A) and 2.51 (rotamer B) (dd, J = 5.5, 1.1 Hz, 1 H, H-6), 2.57 and 3.18 (AB quart, J = 16.9 Hz, 2 H, CH_2CO), 2.87 and 2.95 (AB quart, J = 15.0 Hz, 2 H, NCH_2Ph), 3.21 (rotamer A) and 3.26 (rotamer B) (dd, J = 5.5, 0.9 Hz, 1 H, H-4), 4.78 (rotamer A) and 4.96 (rotamer B) (d, J = 0.9 Hz, 1 H, H-2), 7.10–7.35 (m, 5 H, ArH); ^{13}C NMR –1.5, 32.1, 35.4, 38.6, 39.0, 45.3, 52.4, 53.1, 59.7, 100.5, 126.1, 127.8, 129.0, 136.2, 167.5, 168.8, 185.5, 197.6; IR 2951, 1732, 1693, 1644, 1586, 1438, 1245, 854 cm^{-1}; EIMS m/e (rel intensity) 415 (M^+, 9), 400 (100), 384 (46), 372 (26), 356 (43), 267 (28), 220 (49); HRMS (EI) m/e 415.1811 ($C_{22}H_{29}NO_5Si$ requires 415.1815).

49: (rotamers A:B = 0.75:0.25) ^{1}H NMR 0.02 (rotamer A) and 0.09 (rotamer B) (s, 9 H, $SiMe_3$), 2.24 (rotamer A) and 2.35 (rotamer B) (d, J = 4.9 Hz, 1 H, H-6), 2.55 (d, J = 4.9 Hz, 1 H, H-4), 2.66–2.69 (m, 2 H, NCH_2Si), 2.83 and 3.00 (AB quart, J = 15.0 Hz, 2 H, CH_2CO), 3.63 (rotamer A, s, 3 H) and 3.79 (rotamer A, s, 3 H) (CH_3O and CO_2CH_3), 3.68 (rotamer B, s, 3 H) and 3.82 (rotamer B, s, 3 H) (CH_3O and CO_2CH_3), 4.42 (s, 2 H, NCH_2Ph), 4.85 (rotamer A) and 4.87 (rotamer B) (s, 1 H, H-2), 7.07–7.50 (m, 5 H, ArH); ^{13}C NMR –1.4, 32.1, 35.4, 38.7, 39.0, 45.3, 52.4, 53.2, 59.0, 100.5, 136.2, 167.5, 168.8, 185.5, 197.6; IR 2951, 1735, 1686, 1637, 1589, 1450, 1244, 853 cm^{-1}; EIMS m/e (rel intensity) 415 (M^+, 8), 400 (100), 386 (24), 356 (71), 304 (48), 267 (56); HRMS (EI) m/e 415.1814 ($C_{22}H_{29}NO_5Si$ requires 415.1815).

Irradiation of 2,5-Cyclohexadienone 17. A solution of the cyclohexadienone **17** (19 mg, 0.04 mmol) in MeCN (80 mL) containing DCA (4×10^{-4} M) was irradiated for 6 h (conversion >95%). Solvent evaporation followed by preparative TLC (silica gel, EtOAc:hexane = 1:3) separation gave hydroisoquinoline **46** (4 mg, 25%), and hydroindolenone **50** (3 mg, 22%).

46: ^{1}H NMR 1.64 (br s, 1 H, H-4), 2.00 (s, 3 H, CH_3CO_2), 2.11–2.18 (m, 3 H, H-4, H-8a, and H-3), 2.21–2.34 (m, 2 H, H-8), 2.60–2.69 (m, 3 H, H-3 and H-1), 3.46 (br s, 2 H, CH_2OAc), 3.67 (s, 3 H, CH_3O), 4.16 and 4.32 (AB quart, J = 11.1 Hz, 2 H, NCH_2Ph), 5.41 (s, 1 H, H-6), 7.24–7.30 (m, 5 H, ArH); ^{13}C NMR 20.8 (CH_3CO_2), 29.0, 35.8, 38.7, 42.5, 49.9, 55.0, 56.1 (CH_3O), 62.9 (NCH_2Ph), 67.2 (CH_2OAc), 103.8 (C-6), 126.2, 128.3, and 129.0 (aromatic para, ortho, meta), 138.0 (ipso), 170.6 (ester C=O), 177.5 (C-5), 198.3 (enone C=O); IR 2940, 1743, 1656, 1603, 1367, 1220, 1172, 1040 cm^{-1}; EIMS m/e (rel intensity) 343 (M^+, 10), 328 (50), 300 (4), 268 (6), 228 (10), 146 (29), 91 (100); HRMS (EI) m/e 343.1788 ($C_{20}H_{25}NO_4$ requires 343.1784).

50: ^{1}H NMR 1.72 (ddd, J = 13.4, 8.6, 3.2 Hz, 1 H, H-3), 2.03 (s, 3 H, CH_3CO_2), 2.04–2.13 (m, 1 H, H-3), 2.22 (dd, J = 17.9, 8.6 Hz, 1 H, H-2), 2.70 (dd, J = 16.8, 4.7 Hz, 1 H, H-7), 2.77 (dd, J = 16.8, 2.7 Hz, 1 H, H-7) 2.85–2.91 (m, 2 H, H-2 and H-7a), 3.14 and 4.05 (AB quart, J = 13.0 Hz, 2 H, CH_2OAc), 3.70 (s, 3 H, CH_3O), 4.05 and 4.52 (AB quart, J = 10.8 Hz, 2 H, NCH_2Ph), 5.45 (s, 1 H, H-5), 7.20–7.31 (m, 5 H, ArH); ^{13}C NMR 20.7 (CH_3CO_2), 31.6 (C-1), 37.2 (C-7), 49.3 (C-3a), 51.5 (C-2), 55.9 (CH_3O), 56.9 (NCH_2Ph), 65.5 (C-7a), 67.8 (CH_2OAc), 102.4 (C-5), 126.9, 128.1, 128.7 (aromatic para, ortho, meta), 138.2 (ipso), 170.2 (C-4), 176.3 (ester C=O), 197.1 (enone C=O); IR 3027, 2939, 1745, 1666, 1614, 1454, 1366, 1220 cm^{-1}; EIMS m/e (rel intensity) 329 (M^+, 61), 314 (100), 270 (10), 252 (23), 238 (28); HRMS (EI) m/e 329.1620 ($C_{19}H_{23}NO_4$ requires 329.1627).

Irradiation of 2,5-Cyclohexadienone 18. A solution of the cyclohexadienone **18** (99 mg, 0.23 mmol) in MeCN (160 mL) containing DCA (4×10^{-4} M) was irradiated for 15 h (conversion >95%). Solvent evaporation followed by preparative TLC (silica gel, EtOAc:hexane = 1:3) separation gave hydroisoquinoline **47** (8 mg, 10% isolated, 33% NMR): ^{1}H NMR 2.02 (s, 3 H, CH_3CO_2), 2.24–2.30 (m, 1 H, H-8), 2.49 and 2.90 (AB quart, J = 18.0 Hz, 2 H, H-4), 2.46–2.61 (m, 2 H, H-8 and H-8a) 3.02 (dd, J = 13.2, 7.1 Hz, 1 H, H-1), 3.33 (dd, J = 13.2, 5.6 Hz, 1 H, H-1), 3.69 (s, 3 H, CH_3O), 4.08 and 4.34 (AB quart, J = 11.5 Hz, 2 H, CH_2OAc), 4.47 and 4.60 (AB quart, J = 14.5 Hz, 2 H, NCH_2Ph), 5.35 (s, 1 H, H-6), 7.16–7.33 (m, 5 H, ArH); ^{13}C NMR 20.7 (CH_3CO_2), 32.5 (C-8a), 34.9 (C-4), 37.5 (C-8), 42.7 (C-4a), 48.2 (C-1), 49.8 (NCH_2Ph), 56.6 (CH_3O), 65.7 (CH_2OAc), 103.0 (C-6), 127.8, 128.0, 128.8 (aromatic para, ortho, meta), 136.3 (ipso), 166.9 (C-5), 170.2 (amide C=O), 175.4 (ester C=O), 195.9 (enone C=O); IR 2940, 1742, 1652, 1601, 1454, 1368, 1223, 1039 cm^{-1}; EIMS m/e (rel intensity) 357 (M^+, 6), 300 (5), 284 (10), 194 (9), 137 (18), 91 (100); HRMS (EI) m/e 357.1561 ($C_{20}H_{23}NO_5$ requires 357.1576).

Irradiation of 2,5-Cyclohexadienone 19. A solution of **19** (0.10 g, 0.25 mmol) in MeCN (20 mL) was irradiated for 2 h. Concentration of the crude photolysate followed by silica gel chromatography (ethyl acetate:ammonium hydroxide = 200:1) gave the phenol **41** (0.04 g, 40%) and starting **19** (0.011 g, 11%). An analytical sample of **41** was prepared by recrystallization (ether–ethanol, mp 146 °C). A solution of **19** (73 mg, 0.19 mmol) in MeCN (115 mL) containing DCA (4×10^{-4} M) was irradiated for 2 h. Concentration of the photolysate followed by preparative TLC (silica gel, EtOAc:hexane = 4:1) separation gave hydroisoquinoline **42** (12 mg, 20%). Product yield determined by the ^{1}H NMR method at low photoconversion (1 h irradiation, 13%

conversion) was 60%.

41: ^{1}H NMR (60 °C) 7.01 (d, 1 H, J = 8.4 Hz), 6.7–6.5 (m, 1 H), overlapped by 6.67 (dd, 1 H, J = 8.4, 1.8 Hz), 4.11 (q, 2 H, J = 7.2 Hz), 3.7–3.55 (m, 2 H), 3.41 (t, 2 H, J = 7.8 Hz), 3.3–3.15 (m, 2 H), 2.79 (t, 2 H, J = 7.8 Hz) overlapped by 2.72 (s, 2 H), 2.1–1.7 (m, 4 H), 1.27 (t, 3 H, J = 7.2 Hz), 0.07 (s, 9 H); IR (film) 3200, 1670, 1600, 1570; CIMS m/z (relative intensity) 393 (M^+ + 1, 100), 294 (10); ^{13}C NMR ($CDCl_3$) 170 (e), 157 (e), 156 (e), 147 (o), 137 (e), 129 (e), 127 (o), 117 (o), 113 (o), 61 (e), 51 (e), 50 (e), 45 (e), 26 (e, 2 carbons), 24 (e), 14 (o), −2 (o, 3 carbons). Anal. Calcd for $C_{20}H_{32}N_2O_4Si$: C, 61.19; H, 8.22. Found: C, 61.18; H, 8.25.

42: ^{1}H NMR 1.23 (rotamer A) and 1.26 (rotamer B) (t, J = 6.9 Hz, 3 H, OCH_2CH_3), 1.72–1.94 (m, 5 H, $CH_2CH_2NCH_2CH_2$ and H-4), 2.07–2.11 (m, 1 H, H-4), 2.37–2.44 (m, 1 H, H-8), 2.64 (dd, J = 17.7, 4.8 Hz, 1 H, H-8), 2.86–2.90 (m, 1 H, H-8a), 3.33–3.45 (m, 1 H, H-1), 3.46–33.52 (m, 6 H, CH_2NCH_2 and H-3), 3.77–3.81 (m, 1 H, H-1), 4.06–4.14 (m, 2 H, OCH_2CH_3), 6.09 (d, J = 10.1 Hz, 1 H, H-6), 6.78 (d, J = 10.1 Hz, 1 H, H-5); ^{13}C NMR 14.6 (OCH_2CH_3), 23.1, 27.0, 31.6, 38.7, 44.1, 44.7, 47.7, and 48.2 (CH_2 peaks), 36.0 (C-8a), 47.3 (C-4a), 61.5 (OCH_2CH_3), 129.5 (C-6), 150.1 (C-5), 155.7 (carbamate C=O), 170.0 (amide C=O), 198.0 (enone C=O); IR 2974, 2874, 1694, 1627, 1453, 1344, 1243, 1141 cm^{-1}; EIMS m/e (rel intensity) 320 (M^+, 28), 222 (34), 205 (22), 192 (100), 129 (33), 121 (14); HRMS (EI) m/e 320.1757 (M^+, $C_{17}H_{24}O_4N_2$ requires 320.1736).

Preparation of Maleate and Fumarate Derivatives 33 and 35. A solution of maleic anhydride (0.91 g, 9.2 mmol) in MeOH (20 mL) was stirred at reflux for 1 h, cooled, and concentrated in vacuo to give an oil. To a solution of the oil in benzene (20 mL) was added thionyl chloride (1.0 mL, 13.6 mmol). The mixture was stirred at reflux for 2 h, cooled, and concentrated in vacuo to give the acid chloride **34**.[19] To a solution of the acid chloride **34** in CH_2Cl_2 (20 mL) was added Et_3N (2.3 mL, 17 mmol) and *N*-benzyl-*N*-(trimethylsilyl)methylamine (**20**) (3.0 g, 15 mmol). The reaction mixture was stirred at 25 °C for 1 h, washed with aqueous $NaHCO_3$ and brine, dried, and concentrated in vacuo. The residue was subjected to preparative TLC (silica gel, EtOAc:hexane = 1:6) to give a 1:1 mixture of the maleate **33** and fumarate **34** isomers (33% overall).

35: (rotamer A:B = 0.75:0.25) ^{1}H NMR 0.04 (rotamer A) and 0.07 (rotamer B) (s, 9 H, $SiMe_3$), 2.88 (rotamer B) and 2.92 (rotamer A) (s, 2 H, NCH_2Si), 3.73 (rotamer A) and 3.77 (rotamer B) (s, 3 H, CO_2CH_3), 4.57 (rotamer A) and 4.64 (rotamer B) (s, 2 H, NCH_2Ph), 6.82 (rotamer A) and 6.88 (rotamer B) (d, J = 15.2 Hz, 1 H, $CHCO_2$), 7.11–7.35 (m, 5 H, ArH), 7.41 (rotamer B) and 7.42 (rotamer A) (d, J = 15.2 Hz, 1 H, CHC=O); ^{13}C NMR −1.6 (rotamer B) and −1.2 (rotamer A) ($SiMe_3$), 38.7 (rotamer B) and 39.1 (rotamer A) (NCH_2Si), 52.0 (rotamer A) and 52.1 (rotamer B) (CO_2CH_3), 50.9 (rotamer B) and 53.6 (rotamer A) (NCH_2Ph), 126.6, 127.6, 127.9, 128.0, 128.6, 128.9 (rotamer A and B) (aromatic para, ortho, meta), 130.7 (rotamer A) and 131.0 (rotamer B) ($CHCO_2$), 133.8 (rotamer A) and 134.1 (rotamer B) (CHC=O), 136.0 (rotamer A) and 136.6 (rotamer B) (ipso), 163.9 (rotamer A) and 164.0 (rotamer B) (amide C=O), 166.2 (ester C=O); IR 3031, 2952, 1726, 1649, 1621, 1440, 1400, 1294, 1249, 1166, 854 cm^{-1}; EIMS m/e (rel intensity) 305 (M^+, 2), 290 (3), 274 (5), 246 (7), 214 (4), 91 (100); HRMS (EI) m/e 305.1446 (M^+, $C_{16}H_{23}NO_3Si$ requires 305.1447).

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Supplementary Material Available: Procedures for the preparation and spectroscopic data for intermediates in the syntheses of the 2,5-cyclohexadienones used in this study and ^{1}H NMR spectra for all compounds listed in the Experimental Section (44 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from ACS; see any current masthead page for ordering information.

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Reactions of Positively Charged Chlorine Species in the Gas Phase

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The mechanism of chlorine addition to aromatic compounds in the gas phase is probed using an ion trap mass spectrometer (ITMS). Chloronium ion (Cl^+) and chlorine radical cation ($Cl_2^{\bullet+}$) are formed and trapped in the mass spectrometer and then reacted with a variety of aromatic compounds. The data are consistent with a two-step mechanism involving formation of a radical cation of the aromatic compound through single-electron transfer (SET) to Cl^+ followed by quenching of the resulting radical cation by neutral chlorine. Although $Cl_2^{\bullet+}$ reacts with aromatic compounds through SET, the aromatic cation formed gives the chlorine addition product with only two of the compounds studied. Formation of the chlorine addition product with aromatic compounds can be qualitatively related to the thermodynamics of the reaction and the stability of the aromatic cation radical. There appears to be a similarity between chlorine addition in the gas phase and the intermediate formed in electrophilic aromatic substitution. The structure of the chlorine addition product is probed using MS/MS and by studying the reaction of the chlorine addition in the presence of pyridine. The results suggest that the chlorine addition product is a σ-complex.

Introduction

Electrophilic aromatic halogenation reactions have been well studied in solution.[1,2] Mechanistically, they have been shown to proceed by a π-complex, a σ-complex (cyclohexadienyl carbocation), or single-electron transfer (SET) depending on the experimental conditions. In this study, we prepared chlorine electrophiles in the gas phase and have investigated their reaction with aromatic compounds. The ion that is formed is compared with that which results

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