STEREOCHEMICAL CHARACTERISTICS OF SET-PROMOTED PHOTOCHEMICAL REACTIONS OF DIHYDROISOQUINOLINIUM SALTS

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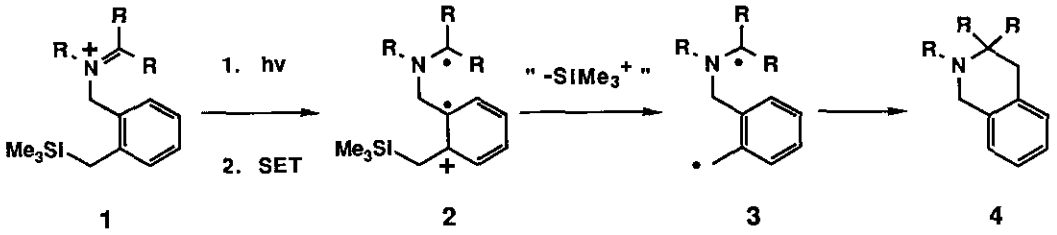
Abstract- Single electron transfer (SET) promoted photocyclization reactions of a series of silylbenzyl- and silylalkenyl-dihydroisoquinolinium perchlorates have been explored in order to evaluate the extent and source of stereochemical control in these *N*-heterocycle forming, diradical cyclization processes.

INTRODUCTION

In earlier reports,[1] we have described the results of exploratory and mechanistic studies which have led to the development of a new class of photocyclization reactions operating *via* excited state single electron transfer (SET) pathways. These efforts demonstrated for example that transformations of *N*-silylbenzyliminium salts (**1**) to the benzo-fused *N*-heterocyclic products (**4**) occur through mechanistic routes involving sequential excited state SET, cation diradical (**2**) desilylation, and diradical (**3**) coupling (Scheme 1). We also showed that related photocyclizations of the silylmethallyl-substituted iminium salts (**5**) follow analogous sequences in their transformation to azacyclic products (**6**) (Scheme 2).

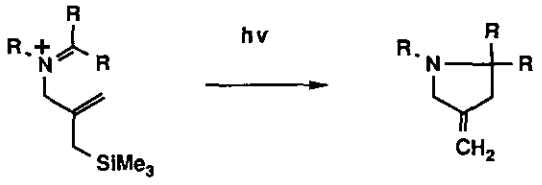
The high chemical efficiencies of these processes coupled with their unique structural outcomes suggested their use in the area of alkaloid synthesis. Investigations testing this proposal have successfully demonstrated how these photocyclizations of this type can be applied as key ring building steps in approaches to selected members of the protoberberine,[2] erythrina,[3] and harringtonine[4] families. We recognize that, as with other organic transformations, the synthetic value of this chemistry would be enhanced if the photocyclization reactions were to display predictable and

Scheme 1.



1 2 3 4

Scheme 2.



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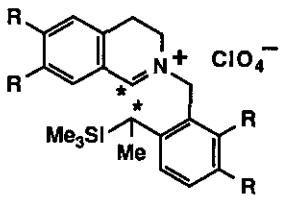
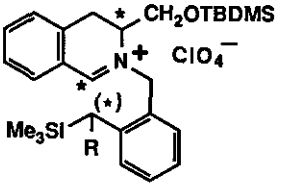
degrees of stereochemical control. This is a particularly intriguing issue since bond formation in the photoreactions exemplified by (**1**) → (**4**) and (**5**) → (**6**) occurs by diradical (*eg.* (**3**)) cyclization. Even though the stereochemistry of diradical cyclization and related radical pair coupling reactions has been probed in the past, the main focus has been the exploration of *reaction mechanism*[5] *and medium effects on chain* dynamics.[6] Thus, while isolated examples of high stereoselectivities have been noted for cyclizations of some diradicals produced by intramolecular triplet carbonyl H-atom abstraction,[7] a general understanding of the factors governing the stereochemical outcome of these processes is not yet at hand.

One aim of our continuing program to develop synthetically useful SET-photochemical reactions is to gain information about the issue of diradical cyclization stereochemistry.[8] One effort concerns the photocyclization reactions of a series of dihydroisoquinolinium salts (**7** - **11**) which contain chiral and/or prochiral centers marked by asterisks. Stereoselectivities in the reactions of these salts are reflected in the diastereomeric products formed via the mechanistic pathways shown in Schemes 1 and 2. Studies with these substances have provided us with the opportunity to explore three classes of diradical cyclizations, generalized in Scheme 3, where stereochemistry is embodied in (1) adjacent chiral centers formed at the site of C-C bond formation, (2) non-adjacent chiral centers one of which is external to the formed ring, and (3) non-

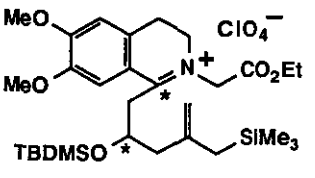
adjacent chiral centers one of which is within the cyclizing chain. Below we describe the preparative and photochemical aspects of this investigation and the preliminary conclusions we have drawn about stereochemistry.[9]



7 (R=OMe)
8 (R=H)



9 (R=H)
10 (R=Me)



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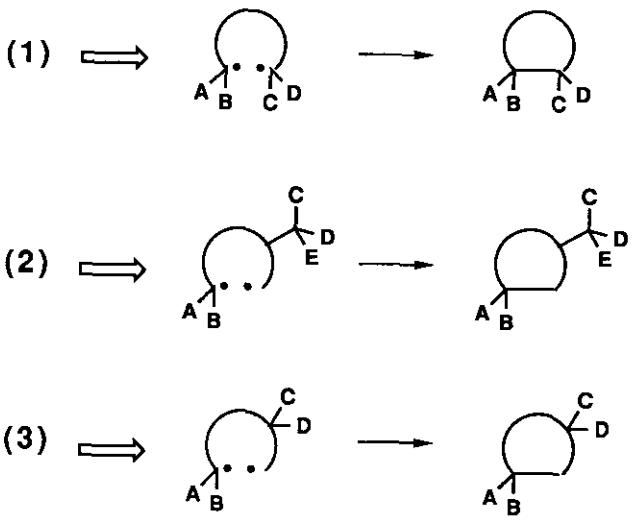
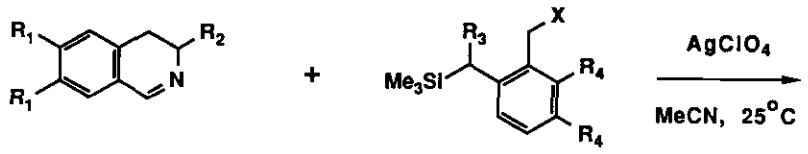
Scheme 3.



RESULTS

Syntheses of the Dihydroisoquinolinium Perchlorates (7-11). The silylbenzyldihydroisoquinolinium salts (**7-10**) employed in this effort were synthesized by *N*-alkylations of the 3,4-dihydroisoquinolines (**12-14**) with the appropriate benzylic halides (**15-17**) as shown in Scheme 4. The benzylic halides were either known (for (**17**))[2] or

Scheme 4.



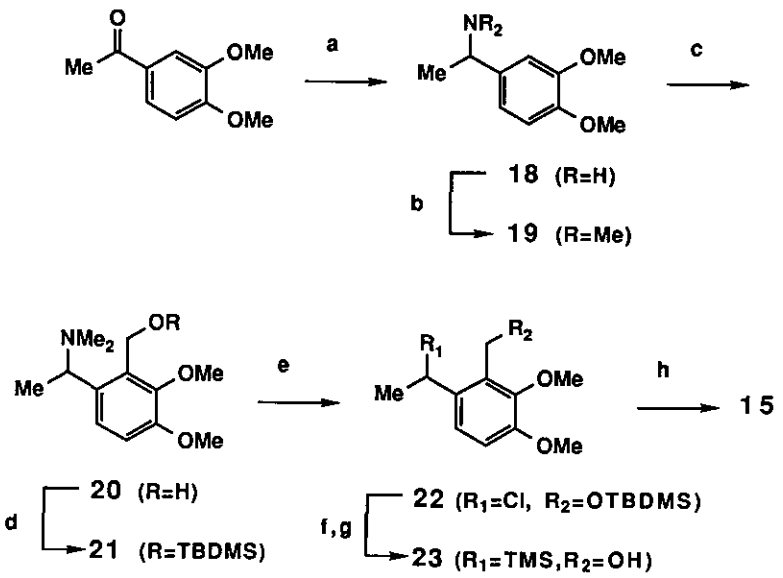
12 (R_1=OMe, R_2=H) + 15 (R_3=Me, R_4=OMe, X=I) ⟶ 7 (60%)

13 (R_1=R_2=H) + 16 (R_3=Me, R_4=H, X=Br) ⟶ 8 (70%)

14 (R_1=H, R_2=CH_2OTBDMS) + 17 (R_3=R_4=H, X=I) ⟶ 9 (71%)

14 + 16 ⟶ 10 (91%)

Scheme 5.



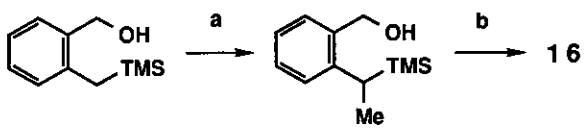
(a) $NaBH_3CN$, NH_4OAc, (b) HCO_2H, HCHO, (c) BuLi; HCHO, (d) TBDMSCl, DIEPA, (e) $ClCO_2Et$, (f) Mg; TMSCl, (g) 0.5% H_2SO_4, (h) TMSCl, NaI

*prepared (for (**15**) and (**16**)) by the sequences outlined in Schemes 5 and 6 (see Experimental Section for details).* While the dihydroisoquinolines ((**12**) and (**13**)) used were commercially available, the 3-siloxymethyl analog (**14**) required

preparation from the known[10] methyl tetrahydroisoquinoline-3-carboxylate (**26**) by the route depicted in Scheme 7. These alkylation reactions employed silver perchlorate as both a catalyst and a stoichiometric reagent thereby allowing direct generation of the crystalline (except for the diastereomer mixture (**10**)) perchlorate[11] salts.

The procedure used to generate the silylalkenyldihydroisoquinolinium perchlorate (**11**) (Scheme 8) involved addition of the metalloenamine, derived from reaction of the commercially available 1-methyl-6,7-dimethoxy-3,4-dihydroisoquinoline with butyllithium, to the silylmethyl butenal (**30**) with *in situ* trapping of the intermediate alkoxide by TBDMSCl to form (**31**). The silicon-substituted aldehyde (**30**) was produced by Cornforth-oxidation of the known[12] alcohol (**29**). Finally, silver perchlorate promoted alkylation of **31** with ethyl iodoacetate then gave the desired salt (**11**).

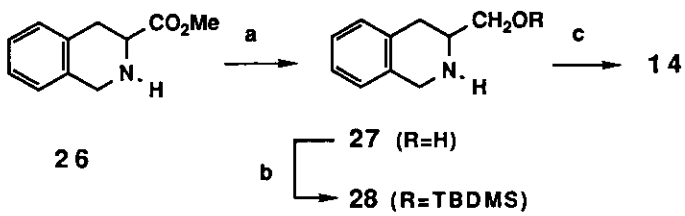
Scheme 6.



24 **25**

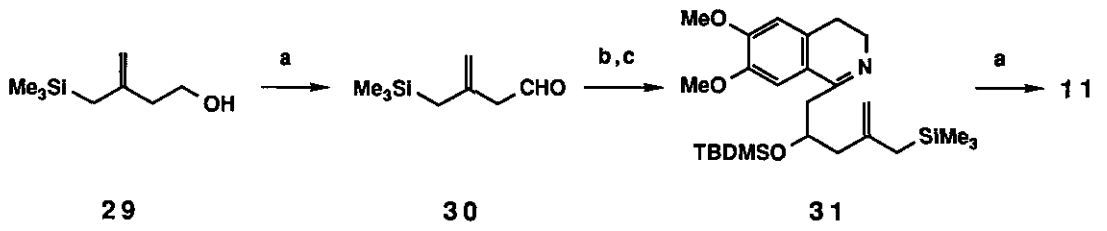
(a) BuLi; MeI, (b) Ph_3P, CBr_4

Scheme 7.



(a) $LiAlH_4$, (b) TBDMSCl, (c) NCS; KOH

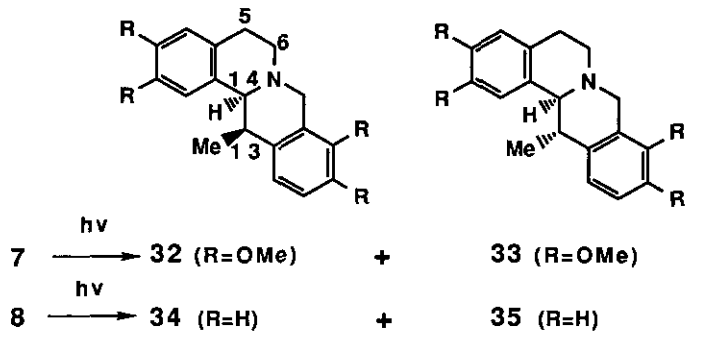
Scheme 8.



(a) DMSO, H_3PO_4, DCC, (b) lithio-6,7-dimethoxy-1-methyl-3,4-dihydroisoquinoline; TBDMSCl, (c) ICH_2CO_2Et, $AgNO_3$

Photochemistry of the Dihydroisoquinolinium Salts (7-11). Our studies began with an investigation of the photochemistry of the methoxy-substituted silylbenzyldihydroisoquinolinium perchlorate (**7**). SET-promoted diradical cyclization of this salt would result in generation of two adjacent chiral centers flanking the forming C-C bond. As anticipated,[2] direct irradiation ($\lambda > 280$ nm) of a MeOH solution of this substance at 25°C led to efficient production of the diastereomeric protoberberines, corydaline (**32**) and mesocorydaline (**33**), in isolated (chromatography) yields of 54% and 33%, respectively (Scheme 9). Stereochemical assignments to these natural products were made by comparisons of their spectroscopic and physical properties to those previously reported.[13]

Scheme 9.



Observations made in further studies with **7** quickly suggested several limitations of the use of this substance in efforts planned to investigate the influence of factors (*e.g.* solvent, multiplicity, *etc.*) on diradical cyclization stereochemistry (see below). Thus, although conversion of **7** to **32** and **33** occurs efficiently when promoted by direct irradiation in MeOH, it

does not occur upon either direct irradiation in MeCN or xanthone triplet sensitized irradiation. The negative effects of alkoxy group substitution on photocyclizations of closely related silylbenzyldihydroisoquinolinium salts have been reported and discussed earlier.[14] Based on these observations, we turned our attention to studies with non-alkoxysubstituted systems.

In contrast to **7**, its desmethoxy analog (**8**) undergoes smooth conversion to the isomeric berbines, (**34**) (33%) and (**35**) (35%), upon direct irradiation ($\lambda > 270$ nm) in MeCN. Moreover, photocyclization of **8** could also be promoted by direct irradiation in either MeOH or CF_3CH_2OH or by xanthone triplet sensitization in MeCN or CF_3CH_2OH. The berbine product ratios, **34**:**35**, arising in these processes were accurately determined by ^1H nmr spectroscopic analyses of the crude photolysates (see Experimental Section) and are recorded in Table 1. The structural and stereochemical assignments to the known berbines (**34**) and (**35**) were again made by comparisons of spectroscopic data to those reported[13d,e] earlier.

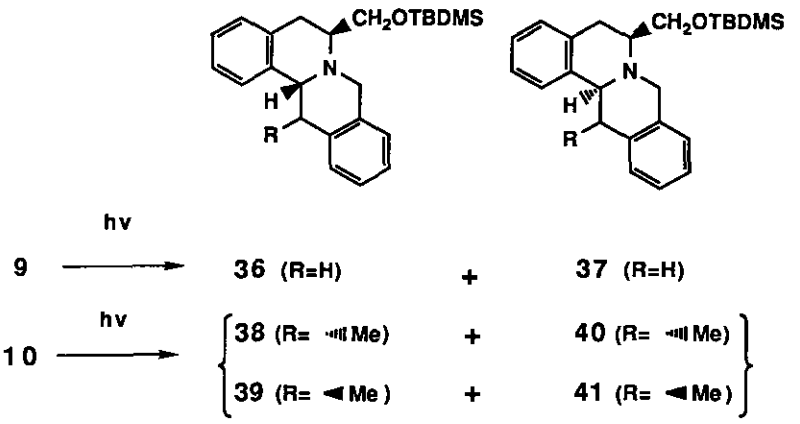
Table 1. Berbine Product Ratios (**34**:**35**) from Photocyclizations of the Silylbenzyldihydroisoquinolinium Salt (**8**).

Solvent	Conditions Method[a] / Temp. (°C)	Stereoisomer Distributions (%) (**34**)	(**35**)
MeCN	Direct / 20	48	52
MeCN	Sensitized / 20	60	40
MeOH	Direct / 20	58	42
MeOH	Direct / - 50	55	45
CF_3CH_2OH	Direct / 20	50	50
CF_3CH_2OH	Sensitized / 20	58	42

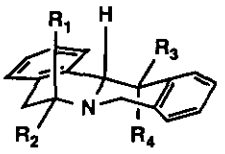
(a) Direct irradiations employed Corex glass filtered-light ($\lambda > 270$ nm) and sensitized irradiations used xanthone as a triplet sensitizer and Uranium glass filtered-light ($\lambda > 320$ nm).

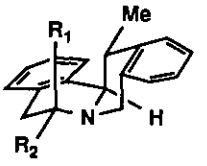
The photochemistry of the silylbenzyldihydroisoquinolinium salt (**9**) was explored next. In this system, the issue of photocyclization stereochemistry relates to configurational preferences at a chiral center created in the diradical cyclization process relative to a pre-existing external (to the forming ring) chiral center. Direct irradiation ($\lambda>270$ nm) of an MeCN solution of **9** followed by chromatographic purification led to isolation of the diastereomeric siloxymethylberbines (**36**) (52%) and (**37**) (30%)(Scheme 10).

Scheme 10.



The relative stereochemistry and quinolizidine ring conformation of **36** and **37** were determined by spectroscopic methods and by comparing key data with those for closely related substances.[13] For example, strong Bohlmann bands[15] between 2800 cm^{-1} and 2780 cm^{-1} are present in the ir spectra of **36** and **37**, indicating that both exist as *trans*-BC-quinolizidine ring conformers (**36A** and **37A**). The C-6 configuration assignments derive from ^{1}H nmr and ^{13}C nmr data. The observation that the ^{13}C nmr resonances for the C-14, C-6 and $CH_2OTBDMS$ carbons of **36** (55.6, 57.8 and 60.4 ppm) occur further upfield than the corresponding resonances for **37** (60.2, 60.6 and 66.0 ppm) is a characteristic result of the γ-gauche effects associated with the axial siloxymethyl group in **36**. The diastereomer ratios, **36**:**37**, were determined (see Experimental Section) for photoreactions of **9** conducted under a variety of conditions. The results are summarized in Table 2.





36A (R_1=$CH_2OTBDMS$, R_2=R_3=R_4=H)

37A (R_2=$CH_2OTBDMS$, R_1=R_3=R_4=H)

38A (R_1=$CH_2OTBDMS$, R_2=R_3=H, R_4=Me)

41A (R_1=R_3=H, R_2=$CH_2OTBDMS$, R_4=Me)

39A (R_1=H, R_2=$CH_2OTBDMS$)

40A (R_1=$CH_2OTBDMS$, R_2=H)

Table 2. Berberine Product Ratios (**36**:**37**) from Photocyclizations of the Silylbenzyl-Dihydroisoquinolinium Salt (**9**).

Solvent	Conditions Method[a]/Temp.(°C)	Stereoisomer Distributions (%) (**36**)	(**37**)
MeCN	Direct / 20	63	37
MeCN	Sensitized / 20	57	43
MeOH	Direct / 20	64	36
MeOH	Direct / - 50	66	34
CF_3CH_2OH	Direct / 20	63	37
CF_3CH_2OH	Sensitized / 20	71	29

(a) Direct irradiations employed Corex glass filtered-light ($\lambda > 270$ nm) and sensitized irradiations used xanthone as a triplet sensitizer and Uranium glass filtered-light ($\lambda > 320$ nm).

The silylbenzyldihydroisoquinolinium perchlorate (**10**) combines the stereochemical features of both **8** and **9**. As a result, studies with this substance could lead to a dissection of the sources of stereochemical control in these SET-promoted diradical cyclizations and to determining whether or not synergistic substituent effects on stereoselectivities are possible in these processes. Indeed the four possible diastereomeric berbines (**38**-**41**) were formed upon direct irradiation (λ>270 nm) of **10** in MeCN in respective yields of 28%, 21%, 12% and 4% (Scheme 10). Photoreactions of **10** conducted under a variety of conditions gave the product ratios recorded in Table 3. Finally, the assignments of relative stereochemistry and conformational preferences (**38A**-**41A**) to the berbine stereoisomers (**38**-**41**) were made by use of characteristic spectroscopic parameters. This was aided by the existence of data for closely related substances (**34**-**37**).

The final stereochemical issue probed in this effort concerns the influence of a remote chiral center, located within the forming ring, on the configurational preference at a chiral center generated in the diradical cyclization process. Photocyclization of the silylalkenyldihydroisoquinolinium perchlorate (**11**) appeared to be ideally suited for this purpose.[16] Irradiation (λ>320 nm) of a MeOH solution of **11** followed by chromatographic separation led to isolation of the diastereomeric spirocyclic amines, (**42**) and (**43**), along with the tetracyclic amino ester (**44**) of unassigned stereochemistry which arises by a [2+2] cycloaddition pathway[3] (Scheme 11). The isolated yields of **42** and **43** are exceptionally low (4% and 1%) despite the fact that ^{1}H nmr analysis of the crude photolysate suggests that a modestly

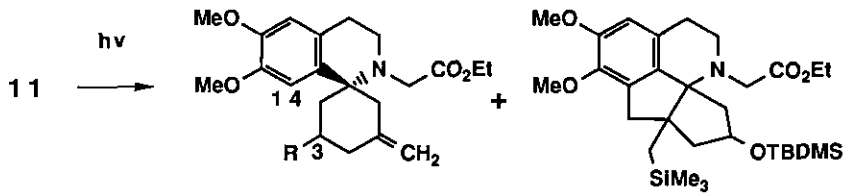
efficient (*ca.* 40%) conversion of **11** to these substances occurred. The low recovery is due to an unanticipated[17] instability of these materials to the silica gel chromatographic conditions. Consequently, product ratios for reactions conducted under a variety of conditions were determined by ^{1}H nmr methods (see Experimental Section) on the crude photolysates (Table 4).

Table 3. Product Ratios (**38**:**41**) from Photoreactions of the Silylbenzyldihydroisoquinolinium Salt (**10**).

Solvent	Conditions[a]	Stereoisomer Distributions (%)			
		(38)	**(39)**	**(40)**	**(41)**
MeCN	Direct	39	34	22	6
MeCN	Sensitized	37	38	15	10
MeOH	Direct	34	27	24	15
CF_3CH_2OH	Direct	31	37	18	14
CF_3CH_2OH	Sensitized	33	42	19	6

(a) Direct irradiations employed Corex glass filtered-light ($\lambda > 270$ nm) and sensitized irradiations used acetophenone as a triplet sensitizer and Uranium glass filtered-light ($\lambda > 320$ nm)and both were at 20°C.

Scheme 11.



42 (R= ◀ OTBDMS)

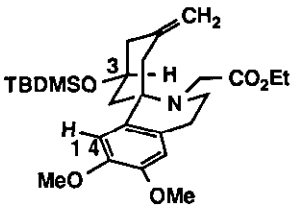
43 (R= ··· OTBDMS)

44

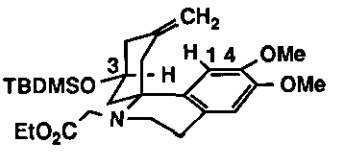
Table 4. Product (**42-44**) Distributions from Photoreactions of the Silylalkenyldihydroisoquinolinium Perchlorate (**11**).

Solvent	Temp. (°C)	Stereoisomer Distributions (%) (**42**)	(**43**)
MeCN	20	67	33
MeOH	20	83	17

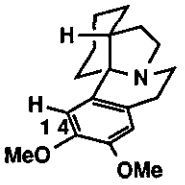
Stereochemical assignments to the spirocyclic products (**42**) and (**43**) were based upon characteristic spectroscopic parameters. For example, the significant difference between the H-14 chemical shifts (6.68 ppm for **42** and 7.12 ppm for **43**) parallel those observed earlier[18] for related protons in the erythrinanes (**45**; 6.51 ppm) and (**46**; 7.18 ppm). This is due to the fact that H-14 in the preferred conformers of both **43** and **46** (see **43A** and **46A**) exist in a sterically crowded region of a cyclohexane ring. In addition, the ^{1}H nmr chemical shift of the H-3 methine proton in **42** is higher (4.19 ppm) than that of the corresponding proton in **43** (3.68 ppm) attributable to the existence of H-3 in **43** in the shielding region of the aromatic residue (see **43A**).



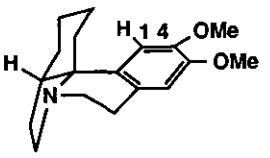
42A



43A



45A



46A

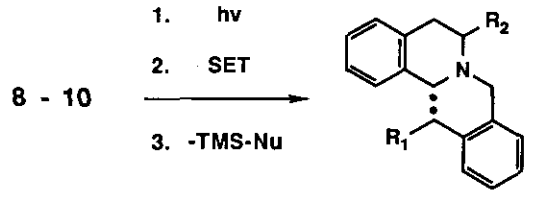
DISCUSSION

Mechanistic Features. The silylbenzyldihydroisoquinolinium salt (**8-10**) photocyclization reactions described above proceed via mechanistic pathways involving the intermediacy of benzyldihydroisoquinolin-1-yl diradicals (**47**). Our

previous studies[2] have shown that these species are generated by intramolecular SET from the electron rich benzylsilane moieties to the singlet (direct)[2] or triplet (sensitized)[1b] excited states of the dihydroisoquinolinium cations. Solvent (MeCN or ROH) promoted nucleophilic displacement of the trimethylsilyl group in the derived diradical cations should be exceptionally fast processes with pseudo first order rate constants in the range of 10^8 s^{-1}.[19]

Diradicals (**47**) produced by direct irradiation will have singlet multiplicity since it is known[2] that intersystem crossing (ISC) converting singlet to triplet excited states of 2-benzyl-3,4-dihydroisoquinolinium salts is slow relative to intramolecular SET. However, these diradicals could have triplet multiplicity in the triplet sensitized processes if the rates of SET and desilylation are fast compared to ISC.[20] Cyclization of diradicals (**47**) then produces the berbine products. For those reactions which proceed *via* triplet diradicals, ICS is required to produce singlet diradicals prior to final bond formation.

Stereochemical Features. Perhaps the most striking features of the photocyclization reactions of dihydroisoquinolinium salts (**8-10**) are their low to modest stereoselectivities. Clearly, from a synthetic viewpoint these low stereochemical preferences detract from what otherwise is a generally efficient methodology for construction of the heterocyclic framework of the berbine related alkaloids. Attempts to understand the factors which are responsible for governing stereochemistry in these photocyclization processes are complicated by a number of issues. For example, their stereochemical course could be regulated by steric effects which govern diradical (**47**) conformer populations in the cases where diradical conformer interconversion is slow relative to bond formation. This could apply to the direct irradiation reactions where **47** is delivered with singlet multiplicity since it is known[21] that singlet diradicals can undergo fast cyclization compared to conformational equilibration. Alternatively, stereochemical controls could reside in the relative energies of diradical cyclization transition states in the events where cyclizations are slow. Finally, the origins of stereoselectivity might be found in stereoelectronic effects which determine the rates of triplet to singlet diradical interconversion by intersystem crossing (ISC). This view which suggests that certain triplet diradical conformations might favor ISC to produce reactive singlets, arises from the studies of Scaiano[22a] and Doubleday[22b] which have shown that ISC rates in diradicals can be influenced by the distance between and orientation of the odd electron centers.[23]



47

Conformational preferences in singlet diradicals (**47**) produced exclusively in the direct irradiation reactions could be related to those found in their precursor salts if the intervening mechanistic sequence (hv, SET, $-TMS^+$) occurs fast relative

to bond rotations. We have inspected the preferred conformations of the precursor dihydroisoquinolinium salts by both crystallographic and molecular mechanics techniques. The X-ray structure of salt (7) (Figure 1) shows that in the solid state the silylbenzyl moiety resides in a perpendicular conformation relative to the dihydroisoquinolinium salt grouping. More importantly, the TMS-substituent in 7 is oriented parallel to the arene-ring π-orbitals and the benzylic methyl group occupies a less crowded anti position. Macromodel calculations (MM2) show that this and a related structure having the *N*-benzylic rotated *ca.* 180° represent low energy conformers of these substances.

Obviously, major conformational changes would be required of a singlet diradical directly generated from these salt conformations in order to orient the odd electron centers in the manner required for bond formation. These reactive diradical conformers, (**48**-**51**), are portrayed below using labelling patterns which refer to the orientation at the benzylic radical center (endo *vs.* exo) and to the direction of approach to the dihydroisoquinolin-1-yl radical center (axial *vs.* equatorial). The relative stereochemistry at C-6 and C-14 in the berbine products would reflect the axial *vs.* equatorial diradical closure preference. Information about this preference derives from photocyclizations of the 3-substituted

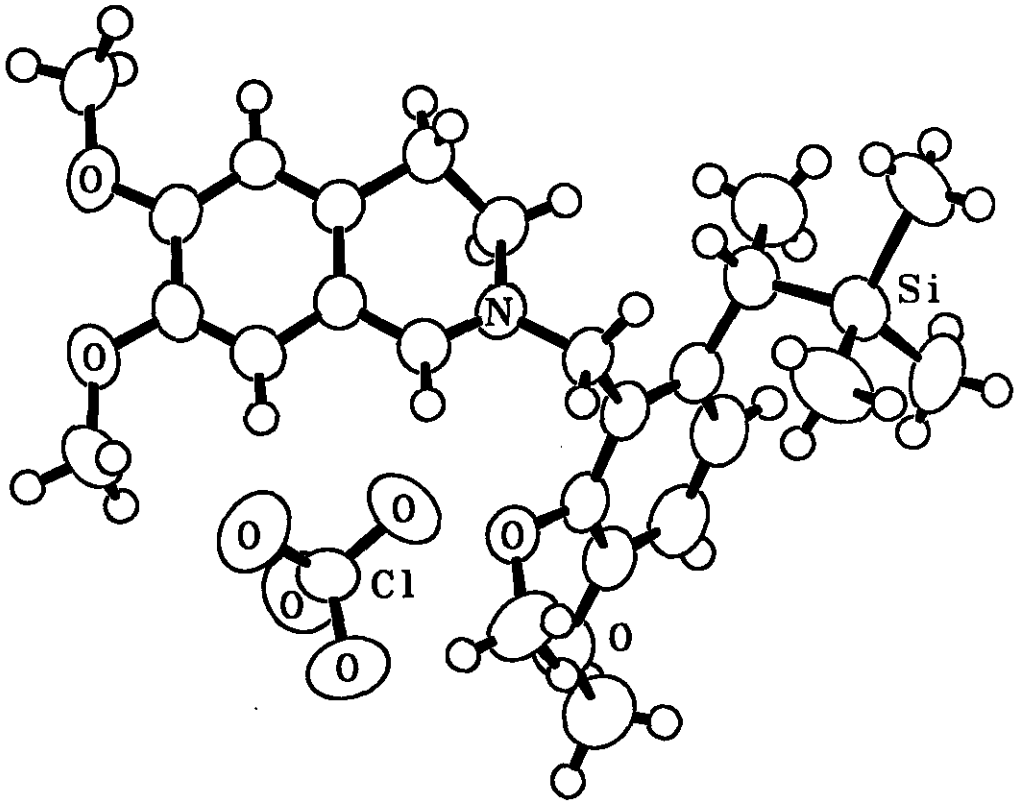
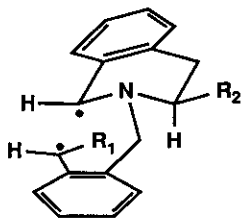
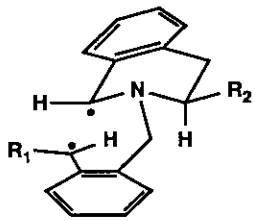


Figure 1. An Ortep plot of the X-ray structure of dihydroisoquinolinium perchlorate (7).

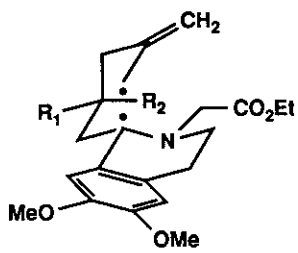
Scheme 12.



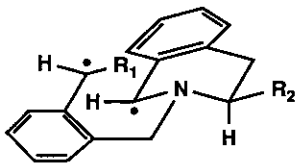
48 axial-endo



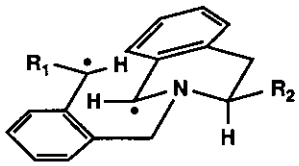
49 axial-exo



52 (R_1=OTBDMS, R_2=H)



50 equatorial-endo



51 equatorial-exo

dihydroisoquinolinium salts (**9**; axial/equatorial = **36/37**) and (**10**; axial/equatorial = (**38**+**40**)/(**39**+**41**)). The relativ stereochemistry at C-13 and C-14 corresponds to the endo *vs.* exo preferences and can be seen in reactions of th benzylic methyl substituted salts (**8**; endo/exo = **34/35**) and (**10**; endo/exo = (**38**+**41**)/(**39**+**40**)).

If transition state energetics contributes to determining the stereoselectivities of these diradical cyclization processes, th distributions of product stereoisomers should correlate with predictions based upon evaluations of the diradical structure shown in Scheme 12. This is only partially successful. Accordingly, a preference for axial over equatorial bonding at th dihydroisoquinolin-1-yl radical center is both observed (*eg.* **36/37** ratios range from 1.7 to 2.5 and the (**38**+**40**)/(**39**+**4** ratios vary from 1.6 to 3.0) and anticipated on the basis of maximization of transition state orbital overlap. However, diradic cyclizations *via* the endo-methyl modes should be of higher energy owing to bad steric interactions with the adjace benzylic center and dihydroisoquinolin ring. Yet in reactions of salt (**8**) products resulting from endo cyclizatio predominate (*eg.* **34/35** range from 0.9 to 1.5) while in photocyclizations of (**10**) they do not (*eg.* (**38**+**41**)/(**39**+**4** range from 0.6 to 1.0).

The highest stereoselectivities we have observed in our studies have been with photocyclizations of t silylakenyldihydroisoquinolinium perchlorate (**11**). In this system, the transition state for diradical cyclization (**52**) havi axial bonding to the dihydroisoquinolin-1-yl radical center and the TBDMSO-substituent oriented equatorially leads to t major (**42/43** from 2.0 to 4.8) spirocyclic amine stereoisomer (**42**).

SUMMARY

It is evident from the observations presented above that the SET-promoted photocyclizations of silylbenzyl- and silylalkenyldihydroisoquinolinium salts represent viable methods for preparation of a variety of *N*-heterocyclic ring systems found in isoquinoline alkaloid families. However, the stereoselectivities of these processes, although in some cases reaching the modest level, are generally low and difficult to predict.

EXPERIMENTAL SECTION

General. ^1H Nmr and ^{13}C nmr spectra were recorded on 500, 400 and 200 MHz instruments with $CDCl_3$ solutions and chemical shifts are reported in ppm relative to tetramethylsilane as an internal standard. Infrared absorption bands are reported in cm^{-1}. Column chromatography was performed with either Merck-EM Type 60 (230-400 mesh) Silica gel (flash) or Florisil (100-200 mesh). Preparative tlc was performed on 20 x 20 cm plates coated with Merck-EM Type 60 GF-254 silica gel. Melting points are reported uncorrected. All reactions were performed under a N_2 atmosphere. Drying of organic layers obtained following work up of reaction mixtures was performed with anhydrous Na_2SO_4. All new compounds were isolated as oils or crystalline solids and were judged to be >90% pure by ^{13}C and ^1H nmr analysis or >95% pure by elemental analysis (Galbraith).

Preparative photochemical reactions were conducted by using an apparatus consisting of a 450W medium pressure, mercury lamp surrounded by a glass filter (for wavelength band selection; Corex, λ>270 nm; Pyrex, λ>290 nm; Uranium, λ>320 nm) and within a quartz, water-cooled well which was immersed in the photolysis solution. The photolysis solutions were purged with O_2 free N_2 both before and during irradiation. Analytical photochemical reactions were conducted in sealed quartz tubes (10 ml) containing solutions purged with Ar or N_2 prior to irradiation. Preparative photochemical reaction progress was monitored by uv and irradiations were stopped at *ca.* 95% completion. The crude photolysates were subjected to a general work-up procedure involving the addition of satd. aqueous $NaHCO_3$, concentration *in vacuo* to give a residue which was subjected to the indicated chromatographic condition. Yields from preparative photochemical reactions were determined by mass of isolated materials while those for analytical photochemical reactions were determined by the indicated technique.

2-[2,3-Dimethoxy-6-(1'-trimethylsilylethyl)benzyl]-6,7-dimethoxy-3,4-dihydroisoquinolinium Perchlorate (7). A solution of the benzyl iodide (**15**) (511 mg, 1.35 mmol), 6,7-dimethoxy-3,4-dihydroisoquinoline (**12**) (284 mg, 1.48 mmol) in 20 ml of acetonitrile containing silver perchlorate (294 mg, 1.42 mmol) was stirred at 25 °C for

24 h. The mixture was filtered and the filtrate was concentrated *in vacuo* giving after trituration with hexane 720 mg (68%) of the perchlorate salt (7) (mp 218-219°C, MeOH). Uv (MeOH) λmax (ε) 369 nm (8.4 x 10^3), 314 nm (8.0 x 10^3); ^{1}H-nmr -0.09 (s, 9H, $Si(CH_3)_3$), 1.33 (d, J=7.3 Hz, 3H), 2.42 (q, J=7.3 Hz, IH), 3.09 (m, 2H, H4), 3.62-3.99 (m, 14H, 4 OCH_3 and H-3), 5.09, 5.18 (ABq, J=14.4 Hz, 2H, $ArCH_2N$), 6.80 (s, IH), 6.87 (d, J=8.8 Hz, IH), 6.96 (d, J=8.8 Hz, IH), 7.35 (s, IH), 8.86 (s, IH); ^{13}C-nmr -3.2 ($Si(CH_3)_3$), 16.3 (CH_3), 24.1 (ArCHSi), 25.4, 46.8 ($ArCH_2CH_2N$), 55.3 ($ArCH_2N$), 55.8, 56.5, 56.7, 61.0 (4 OCH_3's), 110.9, 114.6, 115.7, 122.8, 117.1, 121.4, 132.2, 139.3, 148.5, 149.0, 149.3, 157.7 (aromatic), 164.4 (C=N); ir ($CHCl_3$) 1650, 1600, 1570, 1300, 1090, 840; Elms, m/z (relative intensity) 442 (M^+-ClO_4, 10), 441 (M^+-$HClO_4$, 16), 427 (M^+-ClO_4-TMS, 6), 251 (35), 191 (17), 178 (100), 73 (TMS, 100); HRms, m/z 442.2411 ($C_{25}H_{36}NO_4Si$ requires 442.2414). Anal. Calcd for $C_{25}H_{36}NO_8ClSi$: C, 55.39; H, 6.69; N, 2.59. Found : C, 55.50; H, 6.67; N, 2.31.

X-Ray Crystal Structure of 7. White crystals from MeOH, 0.008 x 0.26 x 0.43 mm specimen; Enraf-Nonius CAD4 diffractometer with Cu radiation (graphite monochromator, CuKα, λ = 1.5418 Å); cell parameters and crystal orientation from 29 automatically centered reflections in the range $18.3 < \theta < 39.1^0$; triclinic P-1; a = 10.692(2), b = 11.702(1), c = 13.154(2) Å, α = 11.02(1), β = 100.42(1), γ = 106.16(1)°, V = 1510(1) Å^3; $_{calcd}$ = 1.192 g cm^{-3} for Z = 2 ($C_{25}H_{36}NO_8SiCl$, mol wt 542.1); 2θ–θ scans over Δθ range of 1.5(1.1 + 0.14 tan θ) at θ scan speed of 16.48^0 min^{-1}; each scan recorded in *ca.* 0.01° steps; reflection profiles processed on-line; diffractometer controlled with NRCCAD system;[24] 6 standard reflections monitored at 1 h. intervals of X-ray exposure, -2.7 to 0.1% intensity variation, -1.3% average, correction applied; $2 < \theta < 65^0$, hkl range for data collection of h = -12 to 11, k = 0 to 12, l = -14 to 13; 4998 total data measured including standards, 4828 unique data, 3066 data with $I > 3\sigma(I)$; R_{int} = 0.01 for 74 twice-measured data. All crystallographic calculations performed with the TEXSAN program system[25] on D. E. C. MicroVax II or VaxStation II computers; structure solved with the MITHRIL[26] direct methods program incorporated in TEXSAN. Full-matrix least-squares refinement, $\Sigma[w(F_o - F_c)^2]$ minimized with $w = 1/\sigma^2(F_o)$, reflections with $I < 3\sigma(I)$ excluded from refinement; correction for secondary isotropic extinction[27] applied, g = 0.115(4)x10^{-5}; absorption correction with the DIFABS[28] subprogram of TEXSAN following a full isotropic structure refinement, transmission factor range of 0.418-1.338, average of 0.952; C, N, O, Si and Cl refined with anisotropic temperature factors; H atoms positioned from the C-N-O-Si-atom framework and individual isotropic temperature factors refined; 362 total variables; atomic scattering factors from International Tables for X-ray Crystallography;[29] minimum and maximum Δρ of -0.30 and 0.44 e Å^{-3}; maximum Δ/σ in final l.s. cycle of 0.03; R, wR and S of 0.072, 0.087 and 2.78. Atomic coordinates, bond lengths and angles and torsion angles are given in the supplementary material. The PLOTMD program[30] was used to display the ORTEP drawing[31] on a VaxStation II monitor, label the drawing, and prepare a print file for a Hewlett-Packard Laser-Jet II printer.

2-[2-(1-Trimethylsilylethyl)benzyl]-3,4-dihydroisoquinolinium Perchlorate (8). The dihydroisoquinolinium perchlorate (**8**) was prepared from 3,4-dihydroisoquinoline (**13**) (580 mg, 4.43 mmol), benzyl bromide (**16**) (928 mg, 3.42 mmol) and silver perchlorate (918 mg, 4.43 mmol) by the procedure used for preparation of **7**. This gave 1.08 g (75%) of the crystalline perchlorate (**8**) (mp 122-125°C, CH_2Cl_2-BuOH). ^{1}H-Nmr -0.06 (s, 9H, $Si(CH_3)_3$), 1.31 (d, J= 7.3 Hz, 3H), 2.37 (q, J= 7.3 Hz, 1H), 3.23 (m, 2H), 3.97 (m, 2H), 5.16, 5.42 (ABq, J=15 Hz, 2H, $ArCH_2N$), 7.09-7.86 (m, 8H, ArH), 9.00 (s, 1H, ArCH=N); ^{13}C-nmr -3.0 ($Si(CH_3)_3$), 16.2 (CH_3), 24.7 (ArCHSi), 25.3 ($ArCH_2CH_2N$), 48.3 ($ArCH_2CH_2N$), 61.6 ($ArCH_2N$), 124.6, 125.7, 126.8, 128.0, 128.4, 128.7, 130.2, 131.2, 134.6, 136.4, 138.4, 146.8; ir ($CHCl_3$) 2940, 1650 (ArC=N), 1600, 1250, 1150, 840; uv (MeCN) λ_{max} (ε) 286 nm (1.3 x 10^4); Elms, m/z (relative intensity) 321 (M^+-ClO_4, 1), 247 (M^+-ClO_4-TMS, 3), 132 (11), 130 (12), 118 (3), 73 (23); HRms, m/z 321.1922 ($C_{21}H_{27}NSi$ requires 321.1913). Anal. Calcd for $C_{21}H_{28}NO_4ClSi$: C, 59.77; H, 6.69; N, 3.32. Found: C,59.80; H, 6.75; N, 3.16.

2-(2'-Trimethylsilylmethyl)benzyl-3-*tert*-butyldimethylsiloxymethyl-3,4-dihydroisoquinolinium Perchlorate (9). A solution of silver perchlorate (673 mg, 3.24 mmol) in 20 ml of MeCN was slowly added to a solution of 2-trimethylsilylmethylbenzyl iodide (**17**) (0.987 g, 3.24 mmol) , which was prepared by a sequence previously described,[2] and dihydroisoquinoline (**14**) (0.894 g, 3.24 mmol) in MeCN (15 ml) at 0°C. After stirring for 1 h, the reaction mixture was diluted with CH_2Cl_2 and filtered through celite. The filtrate was concentrated in vacuo and the residue obtained was triturated with hexane. The residue was subjected to silica gel column chromatography (1% MeOH in $CHCl_3$) giving 1.28 g (71%) of the hydroscopic, crystalline dihydroisoquinolinium salt (**9**), (mp 43-45°C, Et_2O). ^{1}H-Nmr -0.09 and -0.05 (s, 6H, $Si(CH_3)_2$), 0.02 (s, 9H, $Si(CH_3)_3$), 0.70 (s, 9H, $SiC(CH_3)_3$), 2.10 and 2.23 (ABq, J=13.8 Hz, 2H, $TMSCH_2Ar$), 3.14 (d, J=17.4 Hz, 1H, H-4 equatorial), 3.72 (dd, J=7.9, 17.4 Hz, 1H, H-4 axial), 3.79 and 3.82 (d of ABq, J=5.2, 12.4 Hz, 2H, CH_2O), 4.38 (dt, J=7.9, 5.2 Hz, 1H, H-3), 5.24 and 5.36 (ABq, J=15.4 Hz, 2H, NCH_2Ar), 7.10-7.76 (m, 8H, aromatic), 8.74 (s, 1H, H-1); ^{13}C-nmr -5.8 ($Si(CH_3)_2$), -1.7 ($Si(CH_3)_3$), 17.9 ($SiC(CH_3)_3$), 23.7 ($SiCH_2Ar$), 25.6 ($SiC(CH_3)_3$), 28.5 (C-4), 60.2 (C-3), 60.9 (NCH_2Ar), 63.0 (CH_2O), 125.8, 128.4, 130.0, 130.3, 130.8, 134.6, 138.6, 124.3, 126.8, 135.7, 140.8 (aromatic), 166.5 (C-1); ir($CHCl_3$) 2960, 1650, 1605, 1470, 1250, 1095, 845; Elms m/z (relative intensity) 452 (M^+, 18), 322 (5), 308(67), 234 (21), 218 (100), 177 (76); HRms m/z 452.2850 ($C_{27}H_{42}NOSi_2$ requires 452.2805).

2-[2'-(1-Trimethylsilylethyl)benzyl]-3-*tert*-butyldimethylsiloxymethyl-3,4-dihydroisoquinolinium Perchlorate (10). A solution of silver perchlorate (650 mg, 3.13 mmol) in 20 ml of MeCN was slowly added to a solution of 2-[1-(trimethylsilylethyl)benzyl] iodide (**16**) (1.125 g, 3.5 mmol) and dihydroisoquinoline (**14**) (0.860 g, 3.12 mmol) in MeCN (15ml) at 0°C. After stirring for 12 h at 25°C, the mixture was diluted with CH_2Cl_2 and filtered. The filtrate was

concentrated *in vacuo*. The residue was subjected to Florisil column chromatography (1% MeOH in $CHCl_3$) to yield 1.601g (91%) of the dihydroisoquinolinium salt (**10**) as an oil consisting of a mixture of two diastereomers in a 1:1.8 ratio (^{1}H nmr integration).

(10a): ^{1}H-Nmr -0.19 and -0.14 (s, 6H, $Si(CH_3)_2$), -0.06 (s, 9H, $Si(CH_3)_3$), 0.63 (s, 9H, $SiC(CH_3)_3$), 1.32 (d, J=7.4 Hz, 3H, CH_3), 2.27 (q, J=7.4 Hz, 1H, $CHCH_3$), 3.18 (d, J=17.6 Hz, H-4), 1H 3.51 (dd, J=7.1, 17.6 Hz, 1H, H-4), 3.63 and 3.74 (d of ABq, J=4.4, 11.2 Hz, 2H, CH_2O), 4.38 (m, 1H, H-3), 5.22 and 5.44 (ABq, J=15.2 Hz, 2H, NCH_2Ar), 7.01-7.82 (m, 8H, aromatic), 8.76 (s, 1H, H-1); ^{13}C-nmr -5.9 ($Si(CH_3)_2$), -3.1 ($Si(CH_3)_3$), 16.1 (CH_3), 17.9 ($SiC(CH_3)_3$), 24.8 ($SiCH_2Ar$), 25.5 ($SiC(CH_3)_3$), 28.5 (C-4), 60.4 (C-3), 60.9 (NCH_2Ar), 63.0 (CH_2O), 125.8, 127.9, 128.3, 130.2, 130.5, 131.8, 134.3, 138.5, 124.3, 126.6, 135.8, 146.5 (aromatic), 166.3 (C-1); ir ($CHCl_3$) 3090, 3015, 2960, 1860, 1640, 1610, 1580, 1470, 1250, 1100, 910, 840; Elms m/z (relative intensity) 466 (M^+, 100), 320 (14), 218 (16), 191 (51); HRms m/z 466.2987 ($C_{28}H_{44}NOSi_2$ requires 466.2961).

(10b): ^{1}H-Nmr -0.16 and -0.11 (s, 6H, $Si(CH_3)_2$), -0.07 (s, 9H, $Si(CH_3)_3$), 0.74 (s, 9H, $SiC(CH_3)_3$), 1.36 (d, J=7.4 Hz, 3H, CH_3), 2.42 (q, J=7.4 Hz, 1H, $CHCH_3$), 3.16 (d, J=17.6 Hz, 1H, H-4), 3.51 (dd, J=7.1, 17.6 Hz, 1H, H-4), 3.63 and 3.74 (d of ABq, J=4.4, 11.2 Hz, 2H, CH_2O), 4.27 (m, 1H, H-3), 5.19 and 5.50 (ABq, J=15.2 Hz, 2H, NCH_2Ar), 7.01-7.82 (m, 8H, aromatic), 8.96 (s, 1H, H-1); ^{13}C-nmr -5.9 ($Si(CH_3)_2$), -3.2 ($Si(CH_3)_3$), 16.0 (CH_3), 17.9 ($SiC(CH_3)_3$), 24.6 ($SiCH_2Ar$), 25.6 ($SiC(CH_3)_3$), 28.2 (C-4), 60.0 (C-3), 60.6 (NCH_2Ar), 62.7 (CH_2O), 125.7, 128.3, 128.6, 130.15, 130.25, 131.8, 134.7, 138.7, 124.0, 127.2, 135.4, 146.5 (aromatic), 166.3 (C-1); ir ($CHCl_3$) 3090, 3015, 2960, 1860, 1640, 1610, 1580, 1470, 1250, 1100, 910, 840; Elms m/z (relative intensity) 466 (M^+, 100), 320 (14), 218 (16), 191 (51); HRms m/z 466.2987 ($C_{28}H_{44}NOSi_2$ requires 466.2961).

2-Carbethoxymethyl-6,7-dimethoxy-1-[2-*tert*-butyldimethylsilyloxy-4-trimethylsilylmethyl-4-pentenyl]-3,4-dihydroisoquinolinum Perchlorate (11). A solution of the silyloxydihydroisoquinoline (**31**) (0.495 g, 1.04 mmol) and ethyl iodoacetate (0.222 g, 1.04 mmol) in 15 ml of anhydrous MeCN was stirred at 25°C for 4 h. Silver perchlorate (0.236 g, 1.14 mmol) in 10 ml of MeCN was added. The reaction mixture was stirred at 25°C in the dark for 18 h and then filtered. The filtrate was concentrated in vacuo giving a residue which was subjected to column chromatography (Florisil, 1% MeOH in $CHCl_3$) yielding 0.628 g (91%) of the crystalline perchlorate salt (**11**) (mp 131-135°C, MeOH-CH_2Cl_2). ^{1}H-Nmr -0.30 (s, 3H, CH_3SiO), -0.02 (s, 3H, CH_3SiO), 0.01 (s, 9H, $Si(CH_3)_3$), 0.72 (s, 9H, $(CH_3)_3CSiO$), 1.32 (t, J=7.1 Hz, 3H, CH_3), 1.44 and 1.60 (ABq, J=13.0 Hz, 2H, CH_2Si), 2.15 (dd, J=9.9, 13.1 Hz, 1H, allylic CH_2), 2.35 (dd, J=3.5, 13.1 Hz, 1H, allylic CH_2), 3.07 (d, J=14.4 Hz, 1H, H-4), 3.16-3.26 (m, 2H, $CH_2C=N$), 3.41 (d, J=14.4 Hz, 1H, H-4), 3.89 (s, 3H, OCH_3), 4.01 (s, 3H, OCH_3),3.80-4.06 (m, 3H, H-3 and CH-OSi), 4.26 (dq, J=7.1 Hz, 2.1Hz, 2H, CO_2CH_2-),

4.74 (s, 2H, vinyl CH_2), 4.84 and 5.10 (ABq, J = 18.1 Hz, 2H, C=NCH_2CO_2-), 6.90 (s, 1H, H-5), 7.27 (s, 1H, H-8); ^{13}C-nmr -5.0 (CH_3SiO), -4.9 (CH_3SiO), -1.6 ($Si(CH_3)_3$), 14.0 (CH_3), 17.6 ($(CH_3)_3CSiO$), 25.6 (C-SiO), 25.8 (CH_2Si), 27.5 (C-4), 38.2 (CH_2C=N), 48.0 (allylic CH_2), 52.7 (C-3), 56.4 (OCH_3), 56.9 (OCH_3), 57.5 (CO_2CH_2), 63.2 (C=NCH_2CO_2), 71.8 (CH-OSi), 110.9 (C-8), 112.2 (vinyl CH_2), 114.1 (C-5), 119.3 (C-9), 135.2 (C-10), 143.0 (vinyl), 148.6 (C-6), 157.5 (C-7), 166.3 (C=N), 178.2 (C=O); ir ($CDCl_3$) 2930, 1735, 1590, 1250, 860; uv (MeOH), λ_{max} 374.8 (7032), 317.0 nm (7208); Elms m/z (relative intensity) 489(M^+-$Si(CH_3)_3$-ClO_4, 14), 434(100), 218(13), 147(19), 73(65); HRms m/z 489.2902 ($C_{27}H_{43}NO_5Si$ (M^+-Si)$CH_3)_3$-ClO_4) requires 489.2910).

3-*tert*-Butyldimethylsiloxymethyl-3,4-dihydroisoquinoline (14). A mixture of the siloxyamine (**28**) (2.00 g, 7.21 mmol) and *N*-chlorosuccinimide (1.44 g, 10.8 mmol) in 100 ml of ether was stirred at 25°C for 20 min and then concentrated in vacuo. A methanolic KOH (5%, 25 ml) solution of the residue was stirred for 20 min at 25°C and then poured into water. The solution was extracted with CH_2Cl_2. The organic layers were combined, dried, and concentrated in vacuo . The residue was subjected to silica gel column chromatography ($CHCl_3$) to yield 1.69 g (85%) of the desired imine (**14**) as an oil. ^{1}H-Nmr 0.05 (s, 6H, $Si(CH_3)_2$), 0.88 (s, 9H, $SiC(CH_3)_3$), 2.66 (dd, J=10.7, 16.2 Hz, 1H, H-4), 2.89 (dd, J=5.3, 16.2 Hz, 1H, H-4), 3.66 (m, 2H, CH_2O), 4.04 (m, 1H, H-3), 7.12-7.34 (m, 4H, aromatic), 8.29 (d, J=2.1 Hz, 1H, H-1); ^{13}C-nmr -5.4 ($Si(CH_3)_2$), 18.3 ($SiC(CH_3)_3$), 25.7 ($SiC(CH_3)_3$), 27.7 (C-4), 58.9 (C-3), 66.5 (CH_2O), 126.9, 127.1, 127.8, 131.1, 128.6, 136.0 (aromatic), 160.2 (C-1); ir ($CHCl_3$) 2950, 1625, 1470, 1260, 1110, 835; Elms m/z (relative intensity) 275 (M^+, 4), 260 (9), 218 (100), 132 (78), 130 (12); HRms m/z 275.1711 ($C_{16}H_{25}NOSi$ requires 275.1705).

6-(1'-Trimethylsilylethyl)-2,3-dimethoxybenzyl Iodide (15). To a solution of 6-(1'-trimethylsilylethyl)-2,3-dimethoxybenzyl alchol (**23**) (326 mg, 1.22 mmol) and sodium iodide (364 mg, 2.43 mmol) in 10 ml of MeCN was added dropwise trimethylsilyl chloride (264 mg, 2.43 mmol). The mixture was stirred for 30 min at 25°C, poured into water, and extracted with ethyl acetate. The combined organic extracts were washed with saturated $NaHCO_3$ and sodium thiosulfate, dried, and concentrated *in vacuo*. The residue was subjected to flash column chromatography (hexane) to afford 428 mg (93%) of the benzyl iodide (**15**): ^{1}H-Nmr -0.05 (s, 9H, $Si(CH_3)_3$), 1.34 (d, J=7.4 Hz, 3H), 2.28 (q, J=7.4 Hz, 1H), 3.81 (s, 3H), 3.96 (s, 3H), 4.20, 4.82 (ABq, J=9.0 Hz, 2H, $ArCH_2I$), 6.72 (d, J=8.6 Hz, IH), 6.81 (d, J=8.6 Hz, IH); ^{13}C-nmr -2.9 ($Si(CH_3)_3$), -0.9 ($ArCH_2I$), 15.8 (CH_3), 24.0 (ArCHSi), 55.7, 59.7 (2 OCH_3), 112.6, 122.5, 130.1, 138.2, 146.8, 149.3 (aromatic); ir ($CHCl_3$) 2920, 1600, 1575, 1485, 1450,1260, 1160, 1090, 840; Elms, m/z (relative intensity) 378 (M^+, 5), 363 (M^+-CH_3, 6), 251 (M^+-I, 100), 236 (64), 221 (33), 206 (76), 178 (60), 163 (32), 73 (TMS, 100); HRms, m/z 378.0491 ($C_{14}H_{23}O_2ISi$ requires 378.0512).

2-(1-Trimethylsilylethyl)benzyl Bromide (16). To a stirred solution of triphenylphosphine (1.9 g, 7.3 mmol) and carbon tetrabromide (2.4 g, 7.3 mmol) in 8 ml of anhydrous ether was added benzyl alcohol (**25**) (1 g, 4.85 mmol). The solution was allowed to stir for 5 h at 25°C. Heptane (20 ml) was added and the solution was stirred at 25°C for 30 min before filtering through celite. The filtrate was concentrated in vacuo giving a residue which was subjected to column chromatographic separation on silica gel (heptane) to yield 1.2 g (92%) of the bromide (**16**). ^{1}H-Nmr -0.02 (s, 9H, $Si(CH_3)_3$), 1.43 (d, J= 7.4 Hz, 3H), 2.53 (q, J= 7.4 Hz, 1H), 4.46, 4.59 (ABq, J=10.1 Hz, 2H, $ArCH_2Br$), 7.04-7.32 (m, 4H, ArH); ^{13}C-nmr -2.8 ($Si(CH_3)_3$), 16.1 (CH_3), 24.5 (ArCHSi), 32.8 ($ArCH_2Br$), 124.6, 127.5, 128.9, 130.4, 134.3, 146.0; ir (neat) 2940, 1600, 1480, 1450, 1240, 820; Elms, m/z (relative intensity) 272 (M^++2, 0.8), 270 (M^+, 0.8), 191 (M^+-Br, 10), 118 (100), 73 (TMS, 58); HRms, m/z 272.0439, 270.0449 ($C_{12}H_{19}Br$ requires 272.0419, 270.0439).

1-(3',4'-Dimethoxyphenyl)ethylamine (18). A solution of 3,4-dimethoxyacetophenone (25.9 g, 144 mmol), ammonium acetate (59.0 g, 76.5 mmol), and $NaBH_3CN$ (9.0 g, 14.3 mmol) in 200 ml of MeOH was stirred for 48 h at 25°C. Concentrated HCl was added until the pH of the solution was < 2 and the mixture was concentrated *in vacuo*. The residue was dissolved in water and washed with ether. To the aqueous solution was added solid KOH until the pH was > 10. Extraction with ether gave ethereal extracts which were dried and concentrated *in vacuo* to give a residue which was subjected to molecular distillation (95°C, 0.05 torr) to yield 19.3 g (74%) of the known benzyl amine (**18**).[32] Spectroscopic data not previously reported: ^{1}H-Nmr 1.35 (d, J=7.0 Hz, 3H), 1.50 (br s, 2H), 3.83 (s, 3H), 3.87 (s, 3H), 4.05 (q, J=7.0 Hz, 1H), 6.75-6.90 (m, 3H); ^{13}C-nmr 25.8 (CH_3), 51.0 (ArCHN), 55.8, 55.9 (2 OCH_3), 109.0, 111.1, 117.5, 140.5, 147.8, 149.0 (aromatic); Elms, m/z (relative intensity) 181 (M^+, 44), 166 (100), 150 (M^+-CH_3NH_2, 26); HRms, m/z 181.1104 ($C_{10}H_{15}NO_2$ requires 181.1 103).

***N,N*-Dimethyl-*N*-(1-(3',4'-dimethoxyphenyl)ethyl)amine (19).** To a solution of 1-(3',4'-dimethoxyphenyl)ethylamine (**18**) (5.9 g, 32.5 mmol) was added 4.48 g (97.4 mmol) of 98 % formic acid followed by 5.3 g (64.9 mmol) of 37 % formaldehyde. After heating at 80°C for 24 h, the mixture was cooled to 25°C and ca. 15 ml of 6 N HCl was added. The mixture was extracted with ether. The aqueous solution was made basic with 5 % aqueous NaOH and extracted with ether. The ethereal extracts were washed with water, dried and concentrated *in vacuo* giving an oil which was subjected to molecular distillation (92°C, 0.10 torr) to produce 5.17 g (76%) of tertiary amine (**19**). ^{1}H-Nmr 1.31 (d, J=6.9 Hz, 3H), 2.12 (s, 6H), 3.13 (q, J=6.9 Hz, lH), 3.81 (s, 3H), 3.85 (s, 3H), 6.71 (s, 2H), 6.81 (s, 1H); ^{13}C-nmr 20.5 (CH_3), 43.4 ($N(CH_3)_2$), 55.9 (ArCHN), 65.8 (2 OCH_3), 110.4, 111.7, 119.5, 137.1, 147.9, 148.9 (aromatic); ir (neat) 2940,

2810, 2755, 1600, 1585, 1510, 1460, 1410, 1255, 1230, 1140, 1025, 755; Elms, m/z (relative intensity) 209 (M^+, 20), 194 (100), 165 (M^+-$N(CH_3)_2$, 88), 164 (13); HRms, m/z 209.1411 ($C_{12}H_{19}NO_2$ requires 209.1416).

***N,N*-Dimethyl-*N*-[1-(2'-hydroxymethyl-3',4'-dimethoxyphenyl)ethyl]amine (20).** To a solution of *N,N*-dimethyl-*N*-[1-(3',4'-dimethoxyphenyl]ethyl)amine (**19**) (2.59 g, 11.0 mmol) in 20 ml of THF was added BuLi (0.94 ml, 10.0 M, 22.0 mmol) at -78°C. The mixture was stirred at 0°C for 1 h and cooled to -78°C before being transfered to a cooled (-78°C) solution of paraformaldehyde (0.994 g, 11.0 mmol) in 5 ml of THF. The mixture was then stirred at 25° C for 24 h, poured into water, and extracted with ether. The ethereal extracts were dried, concentrated *in vacuo*, and the residue obtained was subjected to flash column chromatography on silica gel (1-3 % MeOH- $CHCl_3$) to give 2.47 g (83%) of benzyl amine (**20**). ^{1}H-Nmr 1.32 (d, J=6.8 Hz, 3H), 2.16 (s, 6H), 3.81 (s, 3H), 3.82 (s, 3H), 4.00 (q, J=6.8 Hz, 1H), 4.54, 4.88 (ABq, J=12.0 Hz, 2H), 6.76 (d, J=8.5 Hz, 1H), 6.96 (d, J=8.5 Hz, 1H); ^{13}C-nmr 9.6 (CH_3), 39.7 ($N(CH_3)_2$), 55.7 (ArCHN), 56.0 ($ArCH_2O$), 60.3, 61.5 (2 OCH_3), 110.5, 122.8, 135.1, 135.5, 147.7, 152.1 (aromatic); ir ($CHCl_3$) 3250 (br, OH), 2940, 1600, 1580, 1485, 1445, 1300, 1265, 1220, 1020; Elms, m/z (relative intensity) 239 (M^+, 6), 224 (11), 222 (30), 194 (M^+-$HN(CH_3)_2$), 179 (62), 161 (15); HRms, m/z 239.1508 ($C_{13}H_{21}NO_3$ requires 239.1521).

***N,N*-Dimethyl-*N*-[1-(2'-*t*-butyldimethylsilyloxymethyl-3',4'-dimethoxyphenyl)ethyl]amine (21).** A solution of *t*-butyldimethylsilyl chloride (5.20 g, 34.5 mmol) in 5 ml of DMF was added to a solution of *N,N*-dimethyl-*N*-[1-(2'-hydroxymethyl-3',4'-dimethoxyphenyl)ethyl]amine (**20**) (5.50 g, 23.0 mmol) and diisopropylethylamine (3.60 g, 27.8 mmol) in 15 ml of DMF. The mixture was stirred at 25 °C for 2 h, poured into saturated $NaHCO_3$ solution, and extracted with ether. The ethereal extracts were dried, concentrated in *vacuo* giving an oil which was subjected to molecular distillation (122°C, 0.10 torr) to yield 6.60 g (81%) of the desired *t*-butyldimethylsilyl ether (**21**). ^{1}H-Nmr 0.08 (s, 3H $SiCH_3$), 0.10 (s, 3H, $SiCH_3$), 0.87 (s, 9H, $C(CH_3)_3$), 1.27 (d, J=6.5 Hz, 3H), 2.16 (s, 6H), 3.50 (q, J=6.5 Hz, 1H), 3.79 (s, 3H), 3.80 (s, 3H), 4.71, 4.84 (ABq, J=10.5 Hz, 2H), 6.83 (d, J=8.6 Hz, 1H), 7.19 (d, J=8.6 Hz, 1H); ^{13}C-nmr -5.4 ($SiCH_3$), -5.3 ($SiCH_3$), 18.2 ($SiC(CH_3)_3$), 21.0 (CH_3), 25.9 ($Si(CH_3)_3$), 43.7 ($N(CH_3)_2$), 55.6 (ArCHN), 55.7 ($ArCH_2O$), 60.8, 61.4 (2 OCH_3), 112.0, 122.4, 132.1, 138.4, 147.2, 150.9 (aromatic); ir ($CHCl_3$) 2960, 1600, 1580, 1490, 1280, 1220, 1060, 840; Elms, m/z (relative intensity) 353 (M^+, 1), 338 (4), 308 (M^+- $HN(CH_3)_2$, 100), 296 (M^+-$C(CH_3)_3$, 5), 236 (13), 222 (8), 206 (11), 177 (13); HRms, m/z 353.2373 ($C_{19}H_{35}NO_3Si$ requires 353.2386).

1-[3',4'-Dimethoxy-2'-(*t*-butyldimethylsilyloxymethyl)phenyl]ethyl Chloride (22). A solution of *N,N*-dimethyl-*N*-[1-(2'-*t*-butyldimethylsilyloxymethyl-3',4'-dimethoxyphenyl)ethyl]amine (**21**) (1.75 g, 4.94 mmol) in 10 ml of

THF was added slowly to a solution of ethyl chloroformate (1.20 g, 6.43 mmol) in 15 ml of THF at 0°C. The mixture was stirred at 0°C for 3 h, poured into water, and extracted with methylene chloride. The organic extracts were dried, concentrated in *vacuo* giving 1.63 g (96%) of the desired chloride (**22**) which was sufficiently pure to be used without further purification. ^{1}H-Nmr 0.07 (s, 3H, $SiCH_3$), 0.13 (s, 3H, $SiCH_3$), 0.89 (s, 9H, $C(CH_3)_3$), 1.83 (d, J=6.7 Hz, 3H), 3.80 (s, 3H), 3.84 (s, 3H), 4.74, 4.95 (ABq, J=11.2 Hz, 2H), 5.60 (q, J=6.7 Hz, 1H), 6.89 (d, J=8.7 Hz, 1H), 7.34 (d, J=8.7 Hz, 1H); ^{13}C-nmr -5.5 ($SiCH_3$), -5.4 ($SiCH_3$), 18.2 ($SiC(CH_3)_3$), 25.8 ($Si(CH_3)_2$), 26.4 (CH_3), 54.7, 55.7 (2 OCH_3's), 55.8 ($ArCH_2O$), 61.5 (ArCHCl), 111.9, 122.5, 131.7, 135.6, 146.5, 152.2 (aromatic); ir ($CHCl_3$) 2940, 1600, 1580, 1515, 1280, 1220, 1030, 840; Elms, m/z (relative intensity), 287 (M^+ - $C(CH_3)_3$, 39), 251 (M^+-$C(CH_3)_3$-HCl, 69), 177 (100), 146 (47); HRms, m/z 287.0874 ($C_{13}H_{20}O_3ClSi$ requires 287.0870).

6-(1'-Trimethylsilylethyl)-2,3-dimethoxybenzyl Alcohol (23). A solution of 1-[3',4'-dimethoxy-2'-(*t*-butyldimethylsilyloxymethyl)phenyl]ethyl chloride (**22**) (1.63 g, 4.72 mmol) in 60 ml of THF was slowly added dropwise to a solution of magnesium turning (1.15 g, 47.2 g-at) and trimethylsilyl chloride (2.57 g, 23.6 mmol) in 20 ml of THF. The mixture was stirred for 12 h at 25°C, and then was filtered. The filtrate was poured into water and extracted with ether. The ethereal extracts were dried and concentrated *in vacuo* giving a residue which was added to a mixture of 0.50 ml of sulfuric acid, 10.0 ml of MeOH, and 10 ml of ether. The resultant two-phase mixture was then stirred vigorously for 2 h at 25° C, poured into saturated $NaHCO_3$, and extracted with ethyl acetate. The organic extracts were dried and concentrated *in vacuo* to yield a residue which was subjected to preparatory thin layer chromatography on silica gel ($CHCl_3$). This gave 0.37 g (31%) of the crystalline benzyl alcohol (**23**) (mp 56-57°C, hexane).^{1}H-Nmr -0.08 (s, 9H, $Si(CH_3)_3$), 1.32 (d, J=7.5 Hz, 3H), 2.09 (br s, IH, OH), 2.46 (q, J=7.5 Hz, 1H), 3.83 (s, 3H), 3.86 (s, 3H), 4.67 (s, 2H), 6.79 (d, J=8.7 Hz, 1H), 6.84 (d, J=8.7 Hz, 1H); ^{13}C-nmr -3.1 ($Si(CH_3)_3$), 16.2 (CH_3), 23.6 (ArCHSi), 55.6, 61.1 (2 OCH_3's), 57.0 ($ArCH_2O$), 112.7, 122.7, 131.5, 137.9, 147.5, 149.1 (aromatic); ir ($CHCl_3$) 3500 (br, OH), 2950, 1565, 1485, 1470, 1270, 1080, 1000, 840; Elms, m/z (relative intensity) 268 (M^+, 1), 235 (12), 195 (M^+-TMS, 3), 178 (M^+-TMSOH, 100), 163 (34), 73 (TMS, 46); HRms, m/z 268.1507 ($C_{14}H_{24}O_3Si$ requires 268.1495). Anal. Calcd for $C_{14}H_{24}O_3Si$: C, 62.64; H, 9.01. Found : C,62,82; H, 8.92.

2-(1-Trimethylsilylethyl)benzyl Alcohol (25). To a stirred solution of *o*-(trimethylsilylmethyl)benzyl alcohol (**24**)[2] (2 g, 10.4 mmol) in 6 ml of anhydrous ether was added BuLi (3.1 ml, 10 M, 31.0 mmol) at -78°C. After stirring for 40 h at 25°C, the reaction mixture was cooled to -78°C and methyl iodide (4.43 g, 31.25 mmol) was added. The solution was stirred at 25°C for an additional 1 h before pouring into water and extracting with ether. The ethereal extracts were dried and concentrated *in vacuo* giving a residue which was subjected to flash column chromatographic separation on silica gel

(30% ether-hexane) to provide 1.53 g (71%) of the benzyl alcohol (**25**). ^{1}H-Nmr -0.06 (s, 9H, $Si(CH_3)_3$), 1.35 (d, J= 7.4 Hz, 3H, $ArCH(CH_3)Si$), 1.51 (br s, 1H, OH), 2.49 (q, J=7.4 Hz, 1H, $ArCH(CH_3)Si$), 4.55, 4.74 (ABq, J= 12.5 Hz, 2H, $ArCH_2O$), 7.05-7.32 (m, 4H, ArH); ^{13}C-nmr -2.9 ($Si(CH_3)_3$), 16.2 (CH_3), 23.7 (ArCHSi), 63.7 ($ArCH_2O$), 124.4, 127.0, 127.9, 128.3, 137.2, 145.0; ir (neat) 3300 (br, OH), 2940, 1600, 1240, 840 ; Elms, m/z (relative intensity) 208 (M^+, 4), 192 (20), 191 (4), 177 (48), 73 (TMS, 100); HRms, m/z 135.0805 ($C_9H_{11}O$ (M^+-TMS) requires 135.0810).

3-Hydroxymethyl-1,2,3,4-tetrahydroisoquinoline (27). A solution of 3-carbomethoxymethyl-1,2,3,4-tetrahydroisoquinoline (**26**) (5.11 g, 26.7 mmol), which was prepared by a sequence previously described,[10] in ether (100ml) was slowly added to a solution of lithium aluminium hydride (2.03 g, 53.4 mmol) in 200 ml of ether and the resulting mixture was stirred at 25°C for 12h. Ten ml of a 2N sodium hydroxide solution was then added and the reaction mixture was filtered. The precipitate was washed with chloroform. The chloroform solution and the ether filtrate were combined, dried, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (2% MeOH in $CHCl_3$) giving 2.92g (67%) of the crystalline amino alcohol (**27**), (mp 76-78°C, Et_2O). ^{1}H-Nmr 2.55 (dd, J=10.6, 16.5 Hz, 1H, H-4 axial), 2.67 (dd, J=4.9, 16.5 Hz, 1H, H-4 equatorial), 2.99 (m, 1H, H-3), 3.17 (br s, 2H, NH and OH), 3.49 (dd, J=7.6, 10.9 Hz, 1H, CH_2O), 4.02 (br s, 2H, H-1), 6.96-7.16 (m, 4H, aromatic); ^{13}C nmr 30.9 (C-4), 47.8 (C-1), 55.1 (C-3), 65.6 (CH_2O), 125.8, 126.0, 126.2, 129.3, 134.0, 135.4 (aromatic); ir ($CHCl_3$) 3310 (br), 2930, 1495, 1455, 1430, 1320, 1220, 1035; Elms m/z (relative intensity) 163 (M^+, 0.1), 132 (100), 130 (35); HRms m/z 163.0990 ($C_{10}H_{13}NO$ requires 163.0997). Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58. Found : C, 73.73; H, 7.94; N, 8.46.

3-*tert*-Butyldimethylsilloxymethyl-1,2,3,4-tetrahydroisoquinoline (28). A mixture of amino alcohol (**27**) (1.44 g, 8.83 mmol), *tert*-butyldimethylsilylmethyl chloride (2.66 g, 19.9 mmol) and triethylamine (2.68 g, 26.5 mmol) in 30 ml of MeCN was stirred at 25°C for 15h. The reaction mixture was then diluted with CH_2Cl_2 and washed with 2% NaOH solution and brine. The organic layer was dried and concentrated in vacuo. The residue was subjected to silica gel column chromatography ($CHCl_3$) to yield 2.00 g (82%) of the desired silyl ether (**28**) as an oil. ^{1}H-Nmr 0.08 (s, 6H, $Si(CH_3)_2$), 0.91 (s, 9H, $SiC(CH_3)_3$), 2.25 (br s, 1H, NH), 2.62 and 2.65 (s, 2H, H-4), 3.00 (m, 1H, H-3), 3.60 (dd, J=6.7, 9.8 Hz, 1H, CH_2O), 3.76 (dd, J=4.0, 9.8 Hz, 1H, CH_2O), 4.07 (br s, 2H, H-1), 7.01-7.14 (m, 4H, aromatic); ^{13}C-nmr -5.4 ($Si(CH_3)_2$), 18.3 ($SiC(CH_3)_3$), 26.0 ($SiC(CH_3)_3$), 31.1 (C-4), 48.2 (C-1), 55.0 (C-3), 67.0 (CH_2O), 125.6, 126.0, 126.2, 129.3 , 134.4, 135.7 (aromatic); ir ($CHCl_3$) 3330 (br), 2940, 1470, 1255, 1105, 1075, 835; Elms m/z (relative intensity) 277 (M^+, 3), 262 (8), 222 (38), 144 (10), 132 (100), 130 (17); HRms m/z 277.1859 ($C_{16}H_{27}NOSi$ requires 277.1862)

Synthesis of 3-Trimethylsilylmethyl-3-buten-1-al (30). This compound was prepared by oxidation of 3-trimethylsilylmethyl-3-buten-1-ol (**29**), which was prepared from 3-methyl-3-buten-1-ol by a sequence previously described,[12] in 67% yield. A solution of *ortho*-phosphoric acid (0.917 g, 9.39 mmol) in 15 ml of anhydrous dimethyl sulfoxide (DMSO) was added dropwise to a solution of 1,3-dicyclohexylcarbodiimide (11.582 g, 56 mmol), and 3-trimethylsilylmethyl-3-buten-1-ol (2.966 g, 19 mmol) in 50 ml of anhydrous DMSO and 5 ml of anhydrous benzene. After the reaction mixture was stirred at 25°C for 4 h, 200 ml of ether was added, and the crystalline dicyclohexylurea was removed by filtration. The filtrate was washed with cold water. The organic layer was separated, dried and concentrated *in vacuo* followed by molecular distillation (25°C, 0.025 torr) to give 1.523 g (51%) of the desired aldehyde (**30**) as a colorless oil. ^{1}H-Nmr 0.00 (m, 9H, $Si(CH_3)_3$), 1.54 (d, J=0.9 Hz, 2H, $-CH_2Si$), 2.98 (dd, J=0.9 Hz, 2.6 Hz, 2H, allylic CH_2), 4.73 and 4.79 (AB q, J=1.0 Hz, 2H, vinyl CH_2), 9.59 (t, J=2.6 Hz, 1H, CHO); ^{13}C-nmr -1.5 ($Si(CH_3)$), 27.6 (CH_2Si), 52.9 (allylic CH_2), 112.6 (vinyl CH_2), 138.5 (vinyl C), 199.8 (CHO); ir (neat) 3065, 2805, 2710, 1720, 1630; Elms m/z (relative intensity), 156 (M^+,12), 141(10), 116(37), 101(59), 73(100), 61(10); HRms m/z 156.0967 ($C_8H_{16}OSi$ requires156.0970).

6,7-Dimethoxy-1-(2-*tert*-butyldimethylsilyloxy-4-trimethylsilylmethyl-4-pentenyl)-3,4-dihydroisoquinoline (31). To a -78°C solution of 6,7-dimethoxy-1-methyl-3,4-dihydroisoquinoline (2.023 g, 8.08 mmol) in 75 ml of anhydrous THF was added slowly 8.08 mmol of an anhydrous hexane solution of butyllithium and *N,N,N',N'*-tetramethylethylenediamine (0.908 g, 7.82 mmol). The solution was stirred at -78°C for 0.5 h. A solution of 3-trimethylsilylmethyl-3-buten-1-al (**30**) (1.28 g, 8.21 mmol) in 2 ml of anhydrous THF was added. The mixture was stirred at 0°C for 1 h. A solution of *tert*-butyldimethylsilyl chloride (1.941 g, 12.88 mmol) in 15 ml of anhydrous THF was then added. The mixture was stirred at 25°C for 40 h. Pyridine(0.489 g, 6.18 mmol) was added and the resulting mixture was stirred for 1 h before being poured into cold (0°C) ether and washed with cold (0°C) saturated aqueous ammonium chloride and cold (0°C) water. The organic layer was dried and concentrated in vacuo. The residue was subjected to flash alumina column chromatography (5% ethyl acetate in hexanes) to afford the desired product (**31**) (1.772 g, 46%) as an oil. ^{1}H-Nmr -1.54 (s, 3H, CH_3SiO), -0.24 (s, 12H, $(CH_3)Si$ and CH_3SiO), 0.78 (s, 9H, *t*-butyl-SiO), 1.54 (s, 2H, CH_2Si), 2.12 and 2.23(ABq, J=6.6, 13.5 Hz, 2H, allylic CH_2), 2.57 (m, 2H, H-4), 2.75 (d, J=6.6 Hz, 2H, CH_2C=N), 3.48 (dd, J=10.0, 15.3 Hz, 1H, H-3), 3.74 (dd, J=6.7, 15.3 Hz, 1H, H-3), 3.88 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 4.28 (tt, J=6.6, 6.6 Hz, 1H, CHOSi), 4.57 and 4.65 (ABq, J=1.8 Hz, 2H, vinyl CH_2), 6.64 (s, 1H, H-5), 7.04 (s, 1 H, H-8); ^{13}C-nmr -4.6(CH_3SiO), -4.5(CH_3SiO), -1.5 ($Si(CH_3)_3$), 17.9 (CSiO), 25.8 (*tert*-butyl-SiO), 27.0(C-4 and CH_2Si), 43.2 (allylic CH_2), 46.8 (CH_2C=N), 47.0 (C-3), 55.8 (OCH_3), 56.0 (OCH_3), 70.5 (CHOSi), 109.4 (C-8), 110.1 (C-5), 110.2 (vinyl CH_2), 122.6 (C-9), 131.2 (C-10), 144.0

(vinyl C), 147.2 (C-6), 150.5 (C-7), 165.1 (C=N); ir (neat) 2905, 1610, 1280, 890; Elms m/z (relative intensity) 475(M^+, 16), 460(8), 402(39), 348(37), 205(87), 73(100); HRms m/z 475.2974 ($C_{26}H_{45}NO_3Si_2$ requires 475.2938).

Irradiation of 2-[2,3-Dimethoxy-6-(1'-trimethylsilylethyl)benzyl]-6,7-dimethoxy-3,4-dihydroisoquinolinium Perchlorate (7). Preparation of Corydaline (32) and Mesocorydaline (33). A solution of the dihydroisoquinolinium perchlorate (7) (113 mg, 0.21 mmol) in 100 ml of MeOH was irradiated with Pyrex glass filtered-light for 24 h. The crude photolysate was subjected to the general work-up procedure and flash column chromatographic separation on silica gel ($CHCl_3$) to provide corydaline (**32**) (42 mg, 54%) and mesocorydaline (**33**) (17 mg, 33%). Spectroscopic data for these substances matched those previously reported.[13]

32: ^{1}H-Nmr 0.92 (d, J=6.9 Hz, 3H, CH_3), 2.58 (m, 2H), 3.09 (m, 2H), 3.18 (m, 2H). 3.67 (br s, 1H, H-14), 3.48, 4.18 (ABq, J= 15.9 Hz, 2H, H-8), 3.84-3.87 (four s, OCH_3), 6.59 (s, 1H), 6.66 (s, 1H), 6.80 (d, J=8.4 Hz, 1H), 6.89 (d, J=8.4 Hz, 1H); ^{13}C-nmr 18.3 (CH_3), 29.3 (C-5), 38.3 (C-13), 51.4 (C-6), 54.4 (C-8), 55.75, 55.8, 56.0, 60.0 (4 OCH_3), 63.0 (C-14), 108.6, 110.9, 111.1, 123.9, 128.3, 128.4, 134.9, 144.8, 147.1, 147.6, 150.0 (aromatic).

33: ^{1}H-Nmr 1.45 (d, J=6.8 Hz, 3H, CH_3), 2.77 (m, 1H), 2.90 (m, 2H), 3.05 (m, 2H), 3.58 (d, J=8.4 Hz, 1H, H-14), 3.80, 3.825, 3.83, 3.85 (four s, OCH_3), 3.97, 4.10 (ABq, J=16.4 Hz, 2H, H-8), 6.60 (s,1H), 6.72 (s, 1H), 6.78 (d, J=8.5 Hz, 1H), 6.93 (d, J=8.5 Hz, 1H); ^{13}C-nmr 22.3 (CH_3), 28.1 (C-5), 34.4 (C-13), 46.8 (C-6), 51.0 (C-8), 55.8, 56.1, 60.4 (4 OCH_3), 64.0 (C-14), 130.5, 132.7, 145.2, 146.4, 147.8, 150.0 (aromatic).

Irradiation of 2-[2-(1-Trimethylsilylethyl)benzyl]-3,4-dihydroisoquinolinium Perchlorate (8). Preparation of the Berberines (34) and (35). A solution of dihydroisoquinolinium perchlorate (8) (144 mg, 0.34 mmol) in 90 ml of MeCN was irradiated with Corex glass filtered-light for 30 min. The crude photolysate was subjected to the general work-up procedure giving a residue which was subjected to flash column chromatography on silica gel ($CHCl_3$-1% MeOH-$CHCl_3$) to provide cis-13-methylberbine (**34**) (28 mg, 33%) and trans-13-methylberbine (**35**) (30 mg, 35%).

34 : ^{1}H-Nmr 0.95 (d, J=6.8 Hz, 3H, CH_3), 2.65 (m, 2H, H-5), 3.15 (m, 2H, H-6), 3.35 (td, J=6.8, 3.4 Hz, 1H, H-13), 3.69 and 4.04 (ABq, J=7.0, Hz, 2H, H-8), 3.84 (d, J=3.3 Hz, H-14), 7.09-7.30 (m, 8H, ArH); ^{13}C-nmr 18.2 (CH_3), 29.7 (C-5), 38.8 (C-13), 51.1 (C-6), 58.9 (C-8), 63.5 (C-14), 125.6, 125.7, 126.0, 126.1, 128.6, 128.9, 134.1, 136.0, 136.7, 141.5 (aromatic); ir ($CHCl_3$) 2900, 2890, 2740, 1450, 740; Elms, m/z (relative intensity) 249 (M^+, 78), 248 (40), 234 (M^+-CH_3, 51), 132 (44), 118 (100); HRms, m/z 249.1518 ($C_{18}H_{19}N$ requires 249.1517).

35 : ^{1}H-Nmr 1.49 (d, J=6.9 Hz, 3H, CH_3), 2.81 (m, 1H, H-5), 3.29 (m, 2H), 3.10 (m, 2H), 3.&3 (d, J=8.3 Hz, 1H, H-14), 3.80 and 4.18 (ABq, J=15.0, Hz, 2H, H-8); 7.09-7.31 (m, 8H, ArH); ^{13}C-nmr 22.5 (CH_3), 28.4 (C-5), 35.2 (C-13), 47.1 (C-6),

56.6 (C-8), 65.1 (C-14), 125.2, 125.7, 126.5, 126.7, 126.9, 127.8, 129.2, 133.4, 134.1, 138.5, 139.7 (aromatic); ir ($CHCl_3$) 2900, 2800 (w), 2740 (w), 1500, 900, 730; Elms, m/z (relative intensity) 249 (M^+, 58), 248 (28), 234 (M^+-CH_3, 38), 132 (33), 130 (28), 118 (100); HRms, m/z 249.1511 ($C_{18}H_{19}N$ requires 249.1517).

Product ratios (**34** : **35**) from reactions of **8** conducted under a variety of conditions were measured by integrations of the ^1H nmr resonances for the H-8 and 13'CH_3 protons in **34** (3.69 and 4.04 (ABq), 0.95 ppm) and **35** (3.80 and 4.18 (ABq), 1.49 ppm). The results are recorded in Table 1.

Irradiation of 2-(2'-Trimethylsilylmethyl)benzyl-3-*tert*-butyldimethylsiloxymethyl-3,4-dihydroisoquinolinium Perchlorate (9). Preparation of Berberines (36) and (37). A N_2-purged solution of the dihydroisoquinolinium salt (**9**) (100 mg, 0.18 mmol) in 120 ml of MeCN was irradiated for 45 min with Corex glass filtered light. Work up by the general procedure gave a residue which was subjected to flash column chromatography on silica gel ($CHCl_3$) yielding the cis-6-*t*-butyldimethylsiloxymethylberbine (**37**) (20 mg, 30%) and *trans*-6-*t*-butyldimethylsiloxymethylberbine (**36**) (35 mg, 52%) as oils. Analytical irradiations under various conditions were performed in a similar manner and the (**36** : **37**) products ratios from these were determined by comparing integrations of ^1H nmr resonances of the respective H-8 and CH_2O protons (4.37, 3.50 and 3.91 ppm for (**36**) and 4.29, 3.60 and 3.96 ppm for **37**). The results are recorded in Table 2.

36: ^1H-Nmr -0.072 and -0.066 (s, 6H, $Si(CH_3)_2$), 0.82 (s, 9H, $SiC(CH_3)_3$), 2.86 (dd, J=3.3, 15.9 Hz, 1H, axial H-5), 2.87 (dd, J=10.9, 16.1 Hz, 1H, axial H-13), 3.14 (dd, J=5.3, 15.9 Hz, 1H, equatorial H-5), 3.22 (dd, J=4.0, 16.1 Hz, 1H, equatorial H-13), 3.32 (m, 1H, H-6), 3.50(dd, J=7.3, 10.1 Hz, 1H, CH_2O), 3.91 (dd, J=4.7, 10.1 Hz, 1H, CH_2O), 4.00 (d, J=15.4 Hz, 1H, axial H-8), 4.07 (dd, J=4.0, 10.9 Hz, 1H, H-14), 4.35 (d, J=15.4 Hz, 1H, equatorial H-8), 7.01-7.18 (m, 8H, aromatic); ^{13}C-nmr -5.52 and -5.46 ($Si(CH_3)_2$), 18.2 ($SiC(CH_3)_3$), 25.9 ($SiC(CH_3)_3$), 32.2 (C-5), 37.2 (C-13), 54.4 (C-8), 55.6 (C-14), 57.8 (C-6), 60.4 (CH_2O), 125.5, 125.8, 126.10, 126.17, 126.21, 128.8, 129.4, 133.1, 134.4, 135.1, 138.1 (aromatic); ir ($CHCl_3$) 3020, 2930, 2860, 2800, 1470, 1100, 840; Elms, m/z (relative intensity) 379 (M^+, 1), 234 (100), 130 (10), 104 (7); HRms, m/z 379.2305 ($C_{24}H_{33}NOSi$ requires 379.2331).

37: ^1H-Nmr 0.07 and 0.09 (s, 6H, $Si(CH_3)_2$), 0.92 (s, 9H, $SiC(CH_3)_3$), 2.75 (m, 1H, H-6), 2.84 and 2.85 (br s, 2H, H-5), 2.95 (dd, J=11.1, 16.1 Hz, 1H, axial H-13), 3.37 (dd, J=3.5, 16.1 Hz, 1H, equatorial H-13), 3.60 (dd, J=5.6, 10.3 Hz, 1H, CH_2O), 3.74 (d, J=15.1 Hz, 1H, axial H-8), 3.79 (dd, J=3.5, 11.1 Hz, 1H, H-14), 3.96 (dd, J=5.5, 10.3 Hz, 1H, CH_2O), 4.31 (d, J=15.1 Hz, 1H, equatorial H-8), 7.05-7.28 (m, 8H, aromatic); ^{13}C-nmr -5.3 ($Si(CH_3)_2$), 18.3 ($SiC(CH_3)_3$), 25.9 ($SiC(CH_3)_3$), 32.8 (C-5), 37.3 (C-13), 55.2 (C-8), 60.2 (C-14), 60.6 (C-6), 66.0 (CH_2O), 125.1, 125.8, 126.0, 126.1, 126.2, 126.4, 128.5, 128.6, 134.3, 134.7, 134.9, 137.9 (aromatic); ir ($CHCl_3$) 3020, 2930, 2860, 2780, 1470, 1100,

840; Elms, m/z (relative intensity) 379 (M^+, 0.3), 234 (100), 130 (10), 104 (11); HRms, m/z 379.2331 ($C_{24}H_{33}NOSi$ requires 379.2331).

Irradiation of 2-[2'-(1-Trimethylsilylethyl)benzyl]-3-*tert*-butyldimethylsiloxymethyl-3,4-dihydroisoquinolinium Perchlorate (10). Preparation of Berberines (38-41). A N_2-purged solution of the dihydroisoquinolinium salt (**10**) (266 mg, 0.47 mmol) in 100 ml of MeCN was irradiated with Corex glass filtered-light. The reaction was monitored by uv and was stopped when >95% of the starting iminium salt (**10**) was consumed. The photolysate was subjected to the general work up procedure giving a residue which was subjected to flash column chromatography on silica gel (4% ether in cyclohexane) yielding pure cis-6-*tert*-butyldimethylsiloxymethy-cis-13-methylberbine (**41**) (7 mg, 4%), trans-6-*tert*-butyldimethylsiloxymethy-*cis*-13-methylberbine (**38**) (51 mg, 28%), cis-6-*tert*-butyldimethylsiloxymethy-trans-13-methylberbine (**40**) (22 mg, 12%), and trans-6-*tert*-butyldimethylsiloxymethy-trans-13-methylberbine (**39**) (38 mg, 21%) as oils.

38: ^{1}H-Nmr -0.78 and -0.76 (s, 6H, $Si(CH_3)_2$), 0.84 (s, 9H, $SiC(CH_3)_3$), 0.89 (d, J=6.8 Hz, 3H, CH_3), 2.87 (d, J=15.4 Hz, 1H, H-5), 3.12 (dd, J=4.0, 15.4 Hz, 1H, H-5), 3.20 (dq, J=3.3, 6.8 Hz, 1H, H-13), 3.36-3.43 (m, 2H, H-6 and CH_2O), 3.92 (dd, J=8.8, 14.1 Hz, 1H, CH_2O), 3.99 and 4.38 (ABq, J=15.1 Hz, 2H, H-8), 4.15 (d, J=2.9 Hz, 1H, H-14), 7.05-7.24 (m, 8H, aromatic); ^{13}C-nmr -5.54 and -5.50 ($Si(CH_3)_2$), 17.8 (CH_3), 18.2 ($SiC(CH_3)_3$), 25.9 ($SiC(CH_3)_3$), 32.3 (C-5), 40.2 (C-13), 54.9 (C-8), 58.4 (C-14), 58.9 (CH_2O), 59.0 (C-6), 125.6 (two peaks), 125.8, 125.9, 126.0 (two peaks), 129.1, 129.3, 134.0, 134.9, 136.8, 141.4 (aromatic); ir ($CHCl_3$) 3010, 2930, 2789, 1472, 1258, 1107, 1090, 838 cm^{-1}; Elms, m/z (relative intensity) 393 (M^+, 11), 348 (14), 330 (80), 290 (66), 274 (100), 248 (98); HRms, m/z 393.2488 ($C_{25}H_{35}NOSi$ requires 393.2488).

39: ^{1}H-Nmr 0.01 and 0.02 (s, 6H, $Si(CH_3)_2$), 0.87 (s, 9H, $SiC(CH_3)_3$), 1.43 (d, J=6.8 Hz, 1H, CH_3), 2.72 (dd, J=5.7, 15.2 Hz, 1H, H-5), 2.93 (dddd, J=4.4, 5.7, 6.7, 7.3 Hz, 1H, H-6), 2.98 (dd, J=6.7, 15.2 Hz, 1H, H-5), 3.16 (dq, J=6.6, 6.8 Hz, 1H, H-13), 3.44 (dd, J=7.3, 9.8 Hz, 1H, CH_2O), 3.61 and 3.96 (ABq, J=16.0 Hz, 2H, H-8), 3.70 (dd, J=4.4, 9.8 Hz, 1H, CH_2O), 3.79 (d, J=6.6 Hz, 1H, H-14), 6.93-7.22 (m, 8H, aromatic); ^{13}C-nmr -5.3 and -5.2 ($Si(CH_3)_2$), 18.3 ($SiC(CH_3)_3$), 22.3 (CH_3), 26.0 ($SiC(CH_3)_3$), 30.5 (C-5), 34.0 (C-13), 53.3 (C-8), 57.0 (C-6), 62.7 (C-14), 66.1 (CH_2O), 125.4, 125.5, 126.0, 126.5, 126.6 (two peaks), 128.1, 128.5, 133.9, 135.0, 139.1, 140.0 (aromatic); ir ($CHCl_3$) 3016, 2957, 2930, 1472, 1258, 1098, 838; Elms, m/z (relative intensity) 393 (M^+, 0.6), 352 (3), 336 (2), 248 (100); HRms, m/z 393.2454 ($C_{25}H_{35}NOSi$ requires 393.2454).

40: ^{1}H-Nmr 0.03 (s, 6H, $Si(CH_3)_2$), 0.90 (s, 9H, $SiC(CH_3)_3$), 1.51 (d, J=6.6 Hz, 3H, CH_3), 2.85 (dd, J=5.8, 16.0 Hz, 1H, H-5), 3.01 (dd, J=7.9, 16.0 Hz, 1H, H-5), 3.21 (dddd, J=5.3, 5.8, 7.8, 7.9 Hz, 1H, H-6), 3.40 (dd, J=7.8, 10.1 Hz, 1H, CH_2O),

3.58 (dq, J=5.3, 6.6 Hz, 1H, H-13), 3.72 (dd, J=5.3, 10.1 Hz, 1H, CH_2O), 3.74 (d, J=5.3 Hz, 1H, H-14), 3.78 and 3.84 (ABq, J=14.9 Hz, 2H, H-8), 6.92-7.28 (m, 8H, aromatic); ^{13}C-nmr -5.4 and -5.3 ($Si(CH_3)_2$), 18.3 ($SiC(CH_3)_3$), 23.9 (CH_3), 25.9 ($SiC(CH_3)_3$), 27.8 (C-5), 35.4 (C-13), 50.1 (C-8), 61.5 (C-6), 64.3 (C-14), 65.5 (CH_2O), 124.3, 125.3, 126.0, 126.28, 126.33, 126.4, 128.4, 128.8, 134.4, 136.3, 137.2, 139.2 (aromatic); ir ($CHCl_3$) 3020, 2930, 1472, 1254, 1105, 1075; Elms. m/z (relative intensity) 393 (M^+, 0.3), 336 (3), 262 (1), 148 (100); HRms, m/z 393.2497 ($C_{25}H_{35}NOSi$ requires 393.2488).

41: ^{1}H-Nmr 0.086 and 0.093 (s, 6H, $Si(CH_3)_2$), 0.92 (s, 9H, $SiC(CH_3)_3$), 0.94 (d, J=6.8 Hz, 3H, CH_3), 2.63-2.73 (ddd, J=5.0, 5.0, 11.7 Hz, 3H, H-6), 2.75, 2.77 (d of ABq, J=10.3, 11.7 Hz, 2H, H-5), 3.28 (dq, J=3.0, 6.8 Hz, 1H, H-13), 3.65 and 4.31 (ABq, J=15.1 Hz, 2H, H-8), 3.68 and 4.00 (d of ABq, J=5.0, 10.2 Hz, 2H, CH_2O), 3.93 (d, J=3.0 Hz, 1H, H-14), 7.05-7.20 (m, 8H, aromatic); ^{13}C-nmr -5.3 ($Si(CH_3)_2$), 17.8 (CH_3), 18.2 ($SiC(CH_3)_3$), 25.9 ($SiC(CH_3)_3$), 33.6 (C-5), 39.9 (C-13), 55.0 (C-8), 59.8 (C-14), 64.2 (C-6), 66.2 (CH_2O), 125.5, 125.6 (two peaks), 125.99, 126.05, 126.4, 128.3, 128.7, 134.7, 135.9, 136.8, 141.5 (aromatic); ir ($CHCl_3$) 3020, 2930, 2800, 1472, 1257, 1107, 1089, 839; Elms, m/z (relative intensity) 393 (M^+, 3), 290 (10), 248 (100), 234 (16); HRms, m/z 393.2480 ($C_{25}H_{35}NOSi$ requires 393.2488).

Analytical irradiations under various conditions were performed in a similar manner and the product ratios from these were determined by comparing integrations of ^{13}C nmr resonances of the respective C-13 and C-14 carbons by use of the NONOE technique. The results are recorded in Table 3.

Irradiation of 2-Carbethoxymethyl-6,7-dimethoxy-1-[2-(*tert*-butyldimethyl-silyloxy)-4-(trimethylsilyl-methyl)-4-pentenyl)]-3,4-dihydroisoquinolinum Perchlorate (11). Preparation of Spiroisoquinolines (42) and (43) and Photoproduct (44). A N_2-purged solution of the dihydroisoquinolinum salt (**11**) (104 mg, 0.16 mmol) in 110 ml of methanol was irradiated for 1 h with Uranium glass filtered light. The photolysate was subjected to the general work up procedure giving a residue which was subjected to flash column chromatography on silica (17% ethyl acetate in hexanes) yielding the the spiroisoquinolines (**42**) (3 mg, 4%) and (**43**) (1 mg, 1%) and the tetracyclic product (**44**) (3 mg, 3%) as oils.

42: ^{1}H-Nmr 0.05 (s, 3H, CH_3SiO), 0.07 (s, 3H, CH_3SiO), 0.87 (s, 9H, *t*-butylSiO), 1.20 (t, J=7.1 Hz, 3H, CH_3), 1.77 (dd, J=10.6 , 13.7 Hz, 1H, axial H-2), 2.10 (dd, J=12.5, 12.5 Hz, 1H, axial H-4), 2.26 (d, J=13.7 Hz, 1H, equatorial H-2), 2.35 and 2.57 (ABq, J=14.4 Hz, 2H, H-6), 2.64 (dd, J=12.5, 5.0 Hz, 1H, equatorial H-4), 2.68 and 2.75 (ABq, J=6.8H, 17.5Hz, 2H, H-11), 3.14 (dd, J=6.8, 15.1 Hz, 1H, H-10), 3.20 (dd, J=6.8, 15.1 Hz, 1H, H-10), 3.22 and 3.30 (ABq, J=16.0 Hz, 2H, NCH_2CO_2-), 3.82 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 4.09 (q, J=7.1 Hz, 2H, CO_2CH_2-), 4.19 (ddd, J=5.0, 10.6, 12.5 Hz, 1H, CH-OSi), 4.69 and 4.82 (ABq, J=1.5 Hz, 2H, vinyl CH_2), 6.53 (s, 1H, H-17), 6.68 (s, 1H, H-14); ^{13}C-nmr -4.6

$(CH_3)_2SiO$), 14.2 (CH_3), 18.1 (C-SiO), 21.6 (C-11), 25.9 (*t*-butyl-SiO), 41.3 (C-4), 44.4 (C-2), 44.6 (C-6), 45.1 (C-10), 48.8 (NCH_2CO_2), 55.8 (OCH_3), 56.1 (OCH_3), 59.9 (C-5), 60.2 (CO_2CH_2), 67.7 (CH-OSi), 108.4 (C-12), 110.8 (vinyl CH_2), 112.2 (C-17), 126.2 (C-12), 133.5 (C-13), 143.5 (C-1), 147.4 (C-16), 147.6 (C-15), 171.9 (C=O); ir ($CHCl_3$) 3060, 2930, 1745, 1600, 1250, 860; Elms, m/z (relative intensity) 489(M^+, 14), 434(100), 416(10), 73(43); HRms, m/z 489.1260 ($C_{27}H_{43}NO_5Si$ requires 489.2910).

43: ^{1}H-Nmr -0.12 (s, 6H, $(CH_3)_2SiO$), 0.76 (s, 9H, $(CH_3)_3CSiO$), 1.22 (t, J=7.2 Hz, 3H, CH_3), 1.77 (dd, J=11.7, 11.7 Hz, 1H, axial H-4), 2.17 (dd, J=11.7, 11.7 Hz, 2H, equatorial H-4 and axial H-2), 2.46 (d, J=14.4 Hz, 1H, H-6), 2.53-2.64 (m, 1H, equatorial H-11), 2.59-2.63 (m, 1H, equatorial H-2), 2.65 (d, J=14.4 Hz, 1H, equatorial H-6), 2.91 (ddd, J=8.4, 8.4, 17.4Hz, 1H, axial H-11), 3.04 (ddd, J=2.0, 8.4, 14.8 Hz, 1H, equatorial H-10), 3.11 and 3.32 (ABq, J=16.7 Hz, 2H, NCH_2CO_2), 3.56 (ddd, J=8.4, 8.4, 14.8 Hz, 1H, axial H-10), 3.64-3.72 (m, 1H, CH-OSi), 3.69 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 4.14 (dq, J=1.9, 7.2Hz, 2H, CO_2CH_2-), 4.91 (s, 2H, vinyl CH_2), 6.53 (s, 1H, H-17), 7.12 (s, 1H, H-14); ^{13}C-nmr -4.7 ($(CH_3)_3SiO$), 14.2 (CH_3), 18.1 (C-SiO), 23.5 (C-11), 25.8 (*t*-butyl-SiO), 43.6 (C-4), 44.2 (C-2), 44.3 (C-6), 46.5 (C-10), 51.4 (NCH_2CO_2), 55.8 (OCH_3), 55.9 (OCH_3), 59.4 (C-5), 60.6 (CO_2CH_2-), 68.1 (CH-OSi), 110.9 (C-14), 111.1 (vinyl CH_2), 112.0 (C-17), 125.8 (C-12), 134.6 (C-13), 146.2 (C-15), 146.6 (C-16), 147.2 (vinyl), 172.2 (-CO_2); ir ($CHCl_3$) 2920, 1745, 1500, 1240, 850; Elms, m/z (relative intensity) 489(M^+, 14), 434(100), 416(9), 73(43); HRms, m/z 489.2908 ($C_{27}H_{43}NO_5Si$ requires 489.2910).

44: ^{1}H-Nmr -0.01 (s, 12H, $Si(CH_3)_3$ and $(CH_3)_2SiO$), 0.60 and 0.73 (ABq, J=15.0 Hz, 2H, CH_2Si), 0.83 (s, 9H, *t*-butyl-SiO), 1.25 (t, J=7.2 Hz, 3H, CH_3), 1.67 (dd, J=5.8, 15.5 Hz, 1H, H-3'), 2.05-2.09 (m, 2H, H-1'), 2.58 (dd, J=8.2, 15.5Hz, 1H, H-3'), 2.74-3.00 (m, 6H, H-5' and -CH_2CH_2N-), 3.21 and 3.28 (ABq, J=8.6 Hz, 2H, NCH_2CO_2), 3.78 (s, 6H, OCH_3), 4.18 (q, J=7.2 Hz, 2H, CO_2CH_2), 4.46 (m, 1H, H-2'), 6.42 (s, 1H, H-5); ^{13}C-nmr -4.7 (CH_3SiO), -4.6 (CH_3SiO), 0.9 ($(CH_3)_3Si$), 14.3 (CH_3), 17.9 (CSiO), 20.3 (CH_2Si), 25.9 (*t*-butyl-SiO), 27.0 (C-4), 42.3 (C-1'), 42.6 (C-3'), 47.9 (C-5'), 49.1 (C-3), 53.9 (NCH_2CO_2), 56.2 (OCH_3), 60.5 (OCH_3), 60.7 (CO_2CH_2), 62.6 (C-4'), 74.3 (CH-OSi), 79.0 (C-1), 109.4 (C-5), 126.9 (C-9), 130.4 (C-8), 138.9 (C-10), 144.4 (C-6), 151.7 (C-7), 171.2 (C=O); ir ($CHCl_3$) 2940, 1740, 1240; Elms, m/z (relative intensity) 561(M^+, 1), 429((7), 356(22), 342(10), 75(100); HRms, m/z 561.3299 ($C_{30}H_{51}O_5NSi_2$ requires 561.3306).

Product ratios (**42**:**43**:**44**) from reactions carried out under a variety of conditions were measured by integration of ^{1}H nmr resonances of the respective H-14 and H-17 aromatic protons. The results are recorded in Table 4.

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