Exploratory Studies of H-Atom Abstraction and Silyl-Transfer Photoreactions of Silylalkyl Ketones and (Silylalkyl)phthalimides

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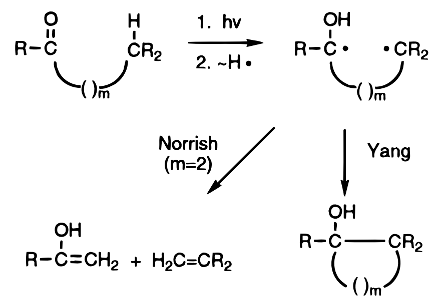
Exploratory studies have been conducted to probe competitive H-atom abstraction and SET-promoted, silyl-transfer reactions of excited states of silylalkyl ketones and (silylalkyl)phthalimides. Photochemical investigations with the (silylalkyl)phthalimides have demonstrated that typical γ-H atom abstraction reactions occur upon irradiation in less polar and less silophilic solvents. In contrast, irradiation of these substances in polar−protic−silophilic solvents results in product formation via pathways involving SET-induced desilylation. Photoreactions of silylamido−aryl ketones in either nonsilophilic or silophilic solvents take place almost exclusively by sequential SET silyl-transfer routes to produce azetidine products. Finally, the chemical selectivities of photochemical reactions of silylpropyl−aryl ketones appear to depend on medium polarity and silophilicity. Irradiation of these substrates in less polar−nonsilophilic solvents leads to almost exclusive formation of acetophenone and vinyltrimethylsilane in essentially equal yields by a reaction pathway initiated by γ-H atom abstraction and 1,4-biradical fragmentation. However, irradiation of these substances in polar−silophilic solvents produces acetophenone and vinyltrimethylsilane in an *ca.* 1.7:1 ratio reflecting the fact that a silyl-transfer pathway competes with H-atom abstraction under these conditions.

Introduction

Perhaps the most general and certainly the most well-explored reactions in organic photochemistry are initiated by intramolecular hydrogen−atom abstraction by an excited state of a carbonyl compound.[1] This process serves as the key chemical step in the familiar Norrish Type II fragmentation and Yang cyclization reactions,[2] both of which proceed via the intermediacy of 1,*n*-diradicals (Scheme 1). A number of comprehensive reviews of these photoreactions have appeared[1] and in these can be found thorough summaries of the vast number of mechanistically intriguing features of the carbonyl excited state H-atom abstraction process as well as the chemical and physical characteristics of intermediate 1,*n*-diradicals. Since it is pertinent to the investigation described below, a discussion of a few of the features of excited state carbonyl H-atom abstraction reactions will be briefly presented here. First, the process occurs efficiently from carbonyl n−π* triplet states owing to their electron-deficient, oxy radical nature. Second, in structurally unconstrained systems, intramolecular H-atom abstractions display strong regiochemical preferences for γ-hydrogens as a result of transition state oxygen−hydrogen distances[3] and conformational issues.[4] Third, as expected for the radical nature of the processes, C−H bond dissociation energies are also influential in determining regiochemistry. Last, a number of studies in recent years have demonstrated that an indirect, excited-state electron transfer (SET) pathway can be followed in bringing about formal H-atom migration.[1,5] This is the case for systems in which the carbonyl excited state has a sufficiently high reduction potential and/or in which a donor site of low oxidation potential is present in the appended alkyl chain. As a result, SET can occur to generate zwitterionic diradicals **1** (Scheme 2). Proton transfer in **1** then yields the same types of 1,*n*-diradicals that would have arisen by H-atom abstraction routes.

Scheme 1



It is clear that the efficiencies of hydrogen migration reactions proceeding by the sequential SET−proton-

⊗ Abstract published in *Advance ACS Abstracts,* May 1, 1996.

(1) Wagner, P. J. *Top. Curr. Chem.* **1976**, *66*, 1. Wagner, P. J. *Rearrangements in Ground and Excited States*; deMayo, P., Ed., Academic Press: New York, 1980; Vols. 42 and 43. Wagner, P. J.; Park, B.-S. *Organic Photochemistry*; Padwa A., Ed.; Marcel Dekker,: New York, 1991; Vol. 11.

(2) Yang, N. C.; Morduchowitz, A.; Yang, D.-D. H. *J. Am. Chem. Soc.* **1963**, *85*, 1017.

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(6) Yoon, U. C.; Mariano, P. S. *Acc. Chem. Res.* **1992**, *25*, 233. Mariano, P. S. *Acc. Chem. Res.* **1983**, *16*, 130. Zhang, X.-M.; Yeh, S.-R.; Hong, S.; Freccaro, M.; Albini, A.; Falvey, D. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1994**, *116*, 4211. d'Alessandro, N.; Albini, A.; Mariano, P. S. *J. Org. Chem.* **1993**, *58*, 937.

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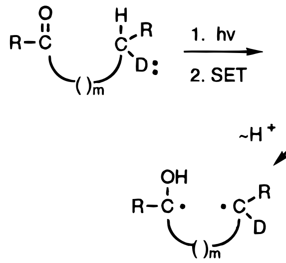
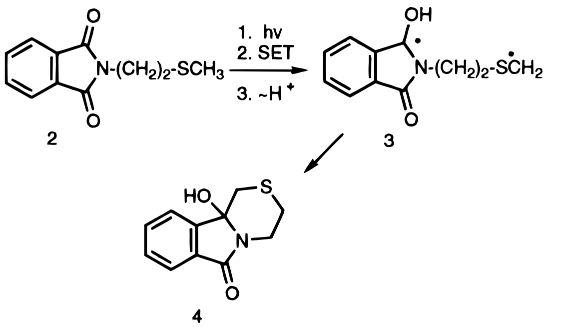
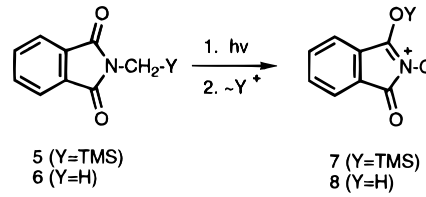
Scheme 2



Scheme 3



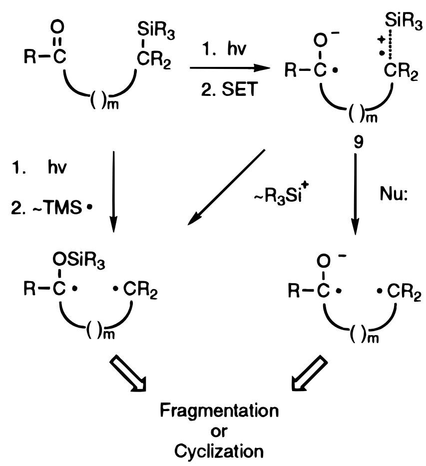


transfer pathway are governed by the redox properties of the excited carbonyl group and not its configuration or multiplicity. Also, regiochemical preferences in photoreactions of this type are determined by the location of donor sites in the alkyl chain and the resultant kinetic α-C−H acidities of cation radicals. Good examples of the latter control are found in photoreactions of phthalimides which contain arene, ether, thioether, or amine functions in *N*-alkyl appendages.[5] As demonstrated by the selective formation of the tricyclic amidol **4** from phthalimide **2** (Scheme 3), diradicals **3** formed by the photoinduced sequential SET−proton-transfer sequence can be quite different from those expected in direct H-atom abstraction reactions.

Studies in our laboratories during recent years have concentrated on a number of SET-photochemical reactions which are driven by nucleophile- or base-promoted α-fragmentation reactions of cation radicals.[6] One specific aim of our efforts in this area has been to gain an understanding of factors which govern the nature and dynamics of cation radical α-desilylation processes. This work has led to the development of preparatively useful SET photoreactions of allyl-, benzyl-, and aminosilanes.[7] Recent observations made in these studies have given rise to thoughts about potentially general and interesting photoreactions of silicon substituted carbonyl compounds, especially those which mimic the familiar Norrish Type II and Yang cyclization processes. A specific, provocative example is seen in the photochemistry of *N*-[(trimethylsilyl)methyl]phthalimide (**5**) in which the transient azomethine ylide **7** is produced by a route formally involving excited-state carbon-to-oxygen migration of the TMS group.[8] This efficient process is quite unique in that it does not have a "non-silicon" counterpart (*i.e.*, *N*-methylphthalimide (**6**) does not produce ylide **8** upon irradiation).

This and other observations led us to think about the potential viability of silicon versions of excited-state H-atom migration reactions. As depicted in Scheme 4, TMS migration reactions of this type can be envisaged as occurring directly by O−Si bonding in the carbonyl excited states or by sequential SET−silyl-transfer routes. In addition, under conditions where oxygen of the carbonyl anion radical is complexed to a Lewis acid or H-bonded and where an alternate silophile is present in the medium, another potential pathway open to the zwitterionic diradical intermediates **9** is desilylation followed by cyclization of the resultant diradical anion. The latter process would represent a silicon analog of the Yang photocyclization reaction.

Scheme 4



Simple bond energy considerations suggest the thermodynamic feasibility of excited-state reactions involving simultaneous cleavage of a C−Si and formation of an O−Si bond.[9] Moreover, a few examples of related intermolecular reactions are known in which a TMS group is transferred from a disilane to oxygen in quinone triplet excited states.[10] In addition, Ohashi[11] has demonstrated that alkylsilanes undergo photoreactions with polycyanoarenes by pathways involving SET from the σ_{C-Si} bond to the arene singlet excited states followed by nucleophile-induced C−Si bond cleavage and radical coupling to the arene anion radical. When combined, these findings lend credence to the possibilities embodied in Scheme 4, and they suggest that a study of the photochemistry of silicon-substituted carbonyl compounds might be a fruitful avenue to new reaction discovery. With this in mind we have conducted exploratory photochemical investigations with selected substances in this class including the phthalimides **10** and **11**, α-amido ketones **12** and **13**, and phenones **14**−**16**.

(7) Ahmed-Schofield, R.; Mariano, P. S. *J. Org. Chem.* **1987**, *52*, 1478. Ho, G. D.; Mariano, P. S. *J. Org. Chem.* **1988**, *53*, 5113. Jung, Y. S.; Mariano, P. S. *Tetrahedron Lett.* **1993**, *34*, 4611.

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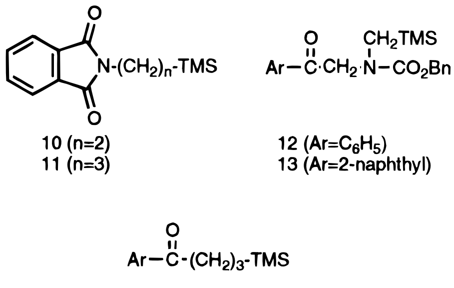
(9) Clovin, E. *Silicon in Organic Synthesis*; Butterworth: London, 1981; Chapter 2.

(10) Alberti, A.; Dellonte, S.; Paradisi, C.; Roffia, S.; Pedulli, G. F. *J. Am. Chem. Soc.* **1990**, *112*, 1123. Sakamoto, K.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 1466.

(11) Krushin, S.; Masuda, Y.; Matsushita, K.; Nakadaira, Y.; Ohashi, M. *Tetrahedron Lett.* **1990**, *31*, 6395.

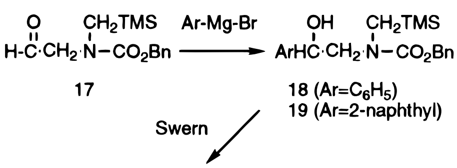
The results of this investigation are presented and discussed below.[12]



10 (n=2)
11 (n=3)
12 (Ar=C6H5)
13 (Ar=2-naphthyl)
14 (Ar=C6H5)
15 (Ar=2-naphthyl)
16 (Ar=p-CN-C6H4)

Results and Discussion

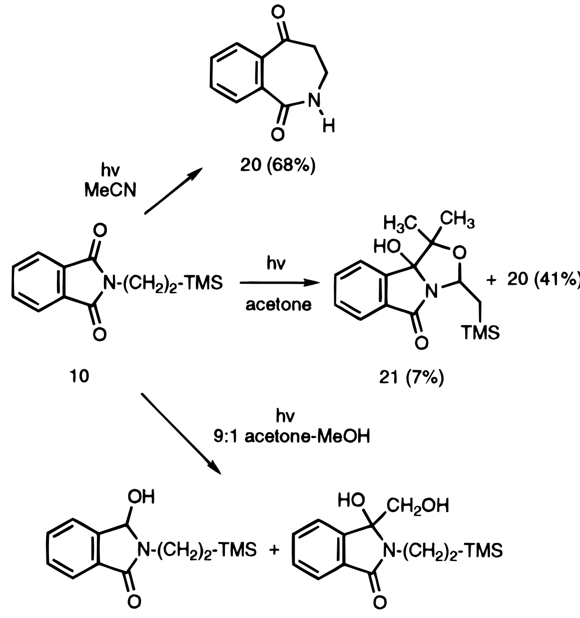
Synthetic Issues. The photochemical substrates employed in this investigation were prepared by using simple synthetic sequences (see Experimental Section and below). For example, phthalimide **10** was synthesized by a two-step route starting with conversion of 2-(trimethylsilyl)ethanol to its chloride followed by alkylation with potassium phthalimide. Similarly, phthalimidation of the 3-(trimethylsilyl)-1-propyl iodide, prepared from the corresponding alcohol, provides **11**. Preparative routes to the silylamidophenones **12** and **13** began with the respective additions of phenyl and 2-naphthylmagnesium bromide to the known[13] amido aldehyde **17**. The alcohols, **18** and **19**, formed in this way were then subjected to Swern oxidation to produce the ketones **12** and **13**.



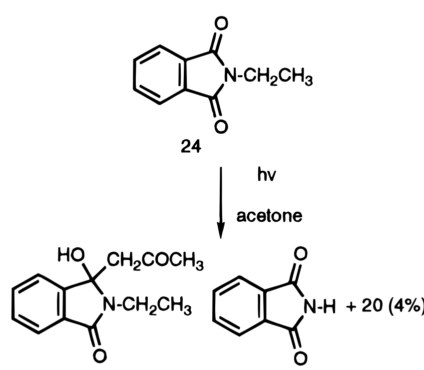
γ-(Trimethylsilyl)butyrophenone (**14**) was made by using the route described previously by Kuivila.[14] In an analogous fashion, reaction of 4-(trimethylsilyl)butyronitrile with 2-naphthylmagnesium bromide followed by aqueous NH_4Cl hydrolysis provided the naphthone **15**. Finally, 4-cyanobenzoic acid was converted to the *p*-cyanobutyrophenone **16** by treatment of the corresponding acid chloride with [3-(trimethylsilyl)-1-propyl]magnesium bromide.

Silylalklyl Phthalimide Photochemistry. Exploratory photochemical studies were initiated with the (silylalkyl)phthalimides **10** and **11**. Preparative irradiation (λ > 220 nm) of an MeCN solution (10 mM) of the silylethyl analog **10** followed by chromatography on silica gel leads to isolation of the benzazepinedione **20** (68%).[15]

Photoproduct **20** (41%) along with the adduct **21** (7%) is produced when an acetone solution of **10** is subjected to otherwise identical irradiation conditions. A dramatic



change occurs in the product profile when photoreaction of **10** is carried out in 9:1 acetone−MeOH. Under these conditions, the benzazepinedione **20** is not produced and instead the reduction and reductive coupling products, **22** and **23**, are generated in respective isolated yields of 16% and 75%. We have also investigated the photochemistry of the non-silicon-containing analog of **10**, *N*-ethylphthalimide (**24**), for comparative purposes. Kanaoka and his co-workers[15] reported earlier that irradiation of **24** in either MeCN or *t*-BuOH solution leads to low yielding (3−6%) generation of benzazepinedione **20**. Inefficient production of **20** is also observed (this work) when an acetone solution of **24** is irradiated under conditions identical to those used for photoreaction of the silicon analog **10** (see above). In this solvent, the major photoproduct of **24** is the acetone adduct **25** (29%) which is formed along with **20** (4%) and phthalimide **26** (2%).



Preparative irradiation of the (silylpropyl)phthalimide **11** in either MeCN or acetone followed by chromatographic separation on silica gel results in isolation of four photoproducts comprised of the (silylmethyl)benzazepinedione **27** (28% in MeCN, 22% in acetone), the bicyclic amidol **28** (21%, 8%), and the (silylpropenyl) amidols **29** (11%, 28%), and **30** (6%, 9%).

The photochemistry of the non-silicon analog of **11**, *N*-propylphthalimide (**31**) has been studied previously by Kanaoka and his co-workers.[15] Irradiation of an MeCN

(12) Lee, Y. J.; Lee, C. P.; Jeon, Y. T.; Mariano, P. S.; Yoon, U. C.; Kim, D. U.; Kim, J. C.; Lee, J. G. *Tetrahedron Lett.* **1993**, *34*, 5855.
(13) Jeon, Y. T.; Lee, C. P., Mariano, P. S. *J. Am. Chem. Soc.* **1991**, *113*, 8847.
(14) Kuivila, H. G.; Maxfield, P. L. *J. Organomet. Chem.* **1967**, *10*, 41.
(15) Kanaoka, Y.; Migita, Y.; Koyama, K.; Sato, Y.; Nakai, H.; Mizoguchi, T. *Tetrahedron Lett.* **1973**, *14*, 1193.

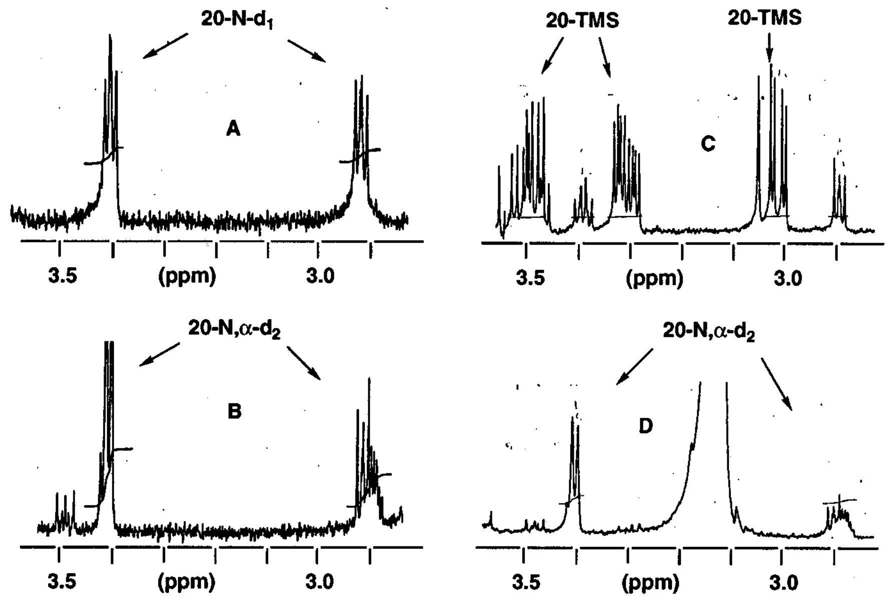
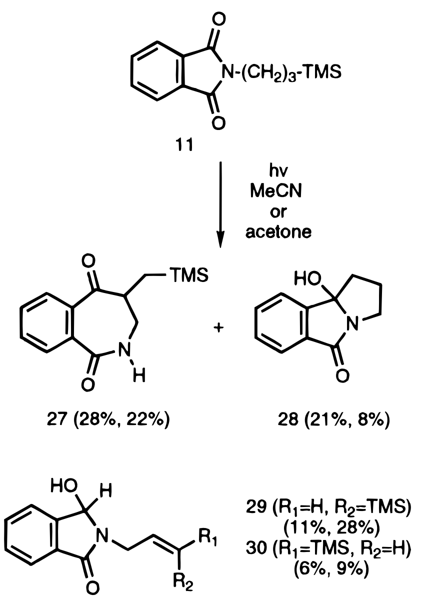
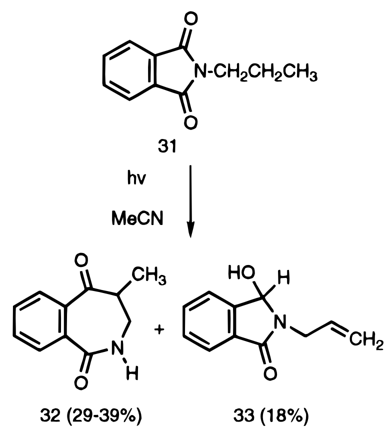


Figure 1. The results of [1]H NMR monitoring experiments following the photoconversion of *N*-(silylethyl)phthalimide **10** to benzazepinediones. Displayed are the 2.8−3.6 ppm regions of [1]H NMR spectra following (A) irradiation of **10** in 35% D_2O in CD_3CN; the resonances at *ca.* 2.9 and 3.4 ppm correspond to the vicinal methylene protons in *N*-deuteriobenzazepinedione (**20-N-d$_1$**); (B) irradiation of **10** in 5% D_2O in CD_3CN; the resonance at *ca.* 2.9 ppm corresponds to the methylene protons (N-CH_2) and that at *ca.* 3.4 ppm to the methine proton in **20-N,α-d$_2$** showing that this solution contains a >5:1 ratio of **20-N,α-d$_2$**: **20-N-d$_1$**; (C) irradiation of **10** in CD_3CN; the resonances at *ca.* 3.05, 3.35, and 3.5 ppm correspond to the methine and diastereotopic methylene protons in **20-TMS**; (D) addition of D_2O to C; the resonances corresponding to the methylene and methine protons of **20-N,α-d$_2$**.





solution of **31** is reported to yield the methylbenzazepinedione **32** (29−39%) and the propenyl amidol **33** (18%).

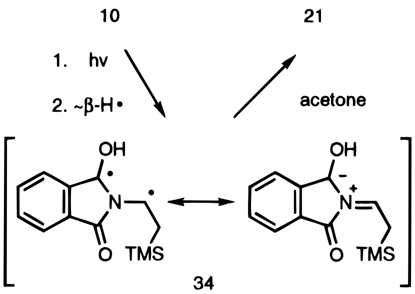
The results outlined above show that a number of features of (silylalkyl)phthalimide photochemistry are quite different from those of their non-silicon analogs. This is true in the case of the (silylethyl)phthalimide **10** which, in contrast to *N*-ethylphthalimide (**24**), undergoes highly efficient photocyclization to produce benzazepinedione **20** even under acetone triplet photosensitization conditions. The inefficient photoreactivity of **24** is most probably associated with a slow rate of γ-H atom abstraction from the primary center by the carbonyl of the singlet or triplet excited phthalimide chromophore. This process becomes more efficient when the γ-position is methyl-substituted, as in the case of the propylphthalimide **31**, owing to radical stabilization (*i.e.*, BDE) effects.

Application of this line of reasoning to understanding the photochemical reactivity of the (silylalkyl)phthalimides is only partially fruitful. For example, β-TMS radical stabilization (expected to be in the range of 2.6−2.9 kcal/mol)[16] appears to be the reason why photolysis of (silylethyl)phthalimide **10** is unique in its generation of the acetone adduct **21**. This substance arises by excited-state β-hydrogen abstraction which yields the stabilized diradical/azomethine ylide (if singlet) **34**. Dipolar cycloaddition to **34** of acetone giving **21** (Scheme 5) has a strong precedence gained in our earlier studies with (silylmethyl)phthalimides.[8]

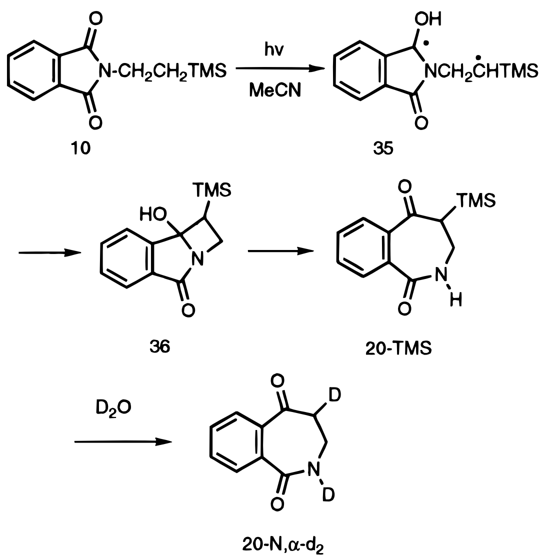
In order to fully understand how silicon substitution in **10** (or **11**) enhances the efficiency of benzazepinedione **20** (or amidol **28**) formation, a significant question must be resolved first; this concerns the mechanistic pathway(s) involved in transformation of **10** (or **11**) to **20** (or **28**). Several experiments, were performed to gain information about this issue. [1]H NMR monitoring of the progress of the photoreaction of **10**, conducted in CD_3CN under rigorously anhydrous conditions, showed that the major

(16) Davidson, J. M. T. *Organometallics* **1987**, *6*, 644.

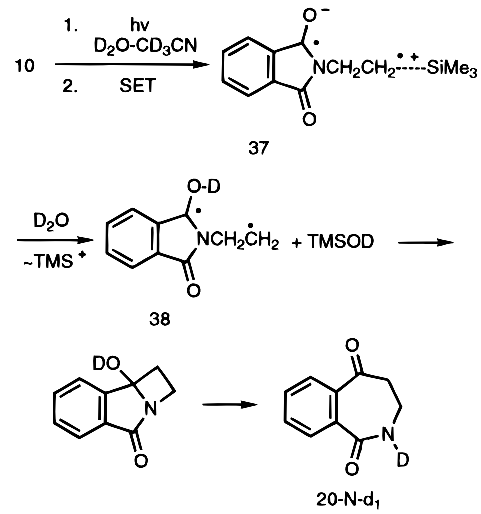
Scheme 5



Scheme 6



Scheme 7



primary product formed in this process is the α-silylbenzazepinone, **20-TMS** (See Figure 1, panel C and Scheme 6). Introduction of D_2O into this photolysate leads to rapid conversion of **20-TMS** to the *N*,α-dideuteriobenzazepinedione, **20-N,α-d₂** (Figure 1, panel D). These observations demonstrate that the major (if not exclusive) pathway followed in photoconversion of **10** to **20** involves initial formation of the diradical intermediate **35** by a γ-hydrogen-atom-transfer process (see below) followed by sequential cyclization, producing the transient azetidinol **36**, and amidol ring opening yielding **20-TMS** (Scheme 6). As an α-silyl ketone, **20-TMS** undergoes rapid protonolysis of the C−Si bond (with adventitious water to form **20** in the ^{1}H NMR experiment) as indicated by production of **20-N,α-d₂** when **20-TMS** is exposed to D_2O.

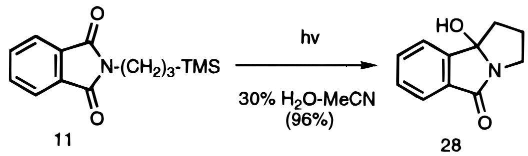
Another observation which provides additional information about the source of the unique reactivity of the *N*-(silylethyl)phthalimide **10** has come from a study of the photoreaction of this substance in aqueous MeCN. Specifically, ^{1}H NMR analysis (Figure 1, panel A) shows that irradiation of **10** in 35% D_2O-CD_3CN efficiently produces the *N*-deuteriobenzazepinedione **20-N-d₁** exclusively. Thus, in a protic and highly silophilic solvent system **10** is transformed to **20** by a mechanism which does not involve the intermediacy of the silicon-containing benzazepinedione **20-TMS**. Instead, **20** appears to form directly from the excited state of **10** via a pathway most likely involving direct production of diradical **38** through desilylation of the zwitterionic diradical **37** (Scheme 7).

The effect of the protic−silophilic solvent is reminiscent of similar observations made in our earlier studies of the photoreactivity of silylamino enones.[17] The previous and current results enable us to construct a reasonable mechanistic framework to understand the unusual photoreactivity of the (silylethyl)phthalimide **10** (as compared to its non-silicon analogs **24** and **31**) and the nature of its photochemistry in solvent systems which differ in their protic and silophilic character. Accordingly, we suggest that the initial step in the sequence for photoreactions of **10** involves intramolecular SET from the σ_{C-Si} bond to the phthalimide singlet (or triplet in the case of acetone sensitization). This process finds precedence in the work of Ohashi with silylalkanes and cyanoarenes (see above). In aprotic−nonsilophilic solvents (*e.g.* MeCN), proton transfer then occurs in the zwitterionic diradical **37** from the acidic C−H (α to TMS) to the oxy anionic center to produce the diradical **35** (Scheme 6) which serves as the precursor to the TMS-substituted benzazepinedione **20-TMS**. However, in protic solvents (35% $H_2O-MeCN$) where the basicity of the oxy anion center is reduced by a H-bonding interaction and where a silophile (H_2O) is present in high concentration, desilylation of **37** predominates (Scheme 7) leading to diradical **38** and eventually to direct production of the benzazepinedione.

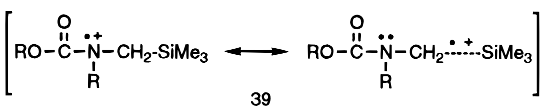
Observations which both support these mechanistic proposals and demonstrate their synthetic consequences have come from further studies with the (silylpropyl)phthalimide **11**. As discussed above, irradiation of **11** in MeCN results in the production of a complex product mixture. Formation of the benzazepinedione **27**, amidol **28**, and silylpropenyl amidols **29** and **30** in this solvent system by competitive excited-state β- and γ-H-atom abstraction reactions, parallels the behavior of the silylethyl analog **10**. A remarkable change in the product profile occurs when a protic−silophilic solvent system is used for this reaction. Thus, preparative irradiation of a 30% $H_2O-MeCN$ solution of **11** leads to exclusive generation of the tricyclic amidol **28** in a 96% yield. ^{1}H NMR monitoring of this photoreaction (30% D_2O-CD_3CN) shows that **11** is cleanly converted to the O−D analog of **28**. Importantly, **28**, formed under these conditions, does not contain C−D incorporation, showing that TMS group loss does not occur by protodesilylation of a homolog of the α-silyl ketone **20-TMS**. Clearly, the

(17) (a) Hasegawa, E.; Xu, W.; Mariano, P. S.; Yoon, U. C.; Kim, S. U. *J. Am. Chem. Soc.* **1988**, *109*, 8089. (b) Xu, W.;Mariano, P. S. *J. Am. Chem. Soc.* **1991**, *113*, 1431.

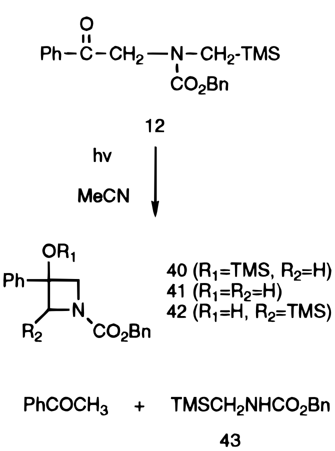
efficient production of **28** by irradiation of **11** in 30% H_2O−MeCN is a consequence of selective desilylation of an intermediate zwitterionic diradical formed by photoinduced SET. In addition, this mechanistic alteration promoted by a change in the solvent system transforms an unselective process into one that is selective has preparative potential.



Silylamido Ketone Photochemistry. The generality of the mechanistic conclusions outlined above is also demonstrated by the photochemistry of the α-silylamido ketones **12** and **13**. Both of these substances contain an *n*-electron donor site within the alkyl chain connecting the σ_{C-Si} bond and phenone groupings. Moreover, cation radicals derived by SET oxidation of the α-silylamido functions in **12** and **13** are delocalized (*i.e.*, they have two contributing resonance representations **39**). As a consequence of this feature, the oxidation potentials of α-silylamides are lower than those of simple alkylsilane analogs. Therefore, it is expected that SET pathways will dominate the photochemistry of these substances.

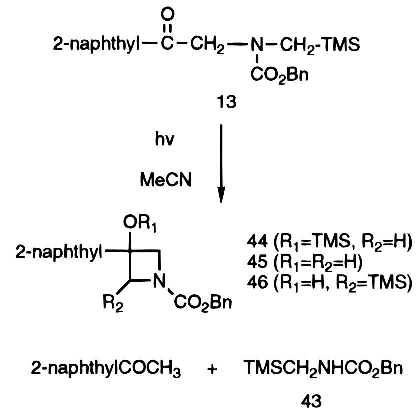


Irradiation (λ > 280 nm) of an MeCN solution of the phenone **12** followed by alumina chromatography results in the isolation of the azetidines **40** (22%), **41** (13%), and **42** (9%). ^{1}H NMR monitoring of this photoreaction shows that the crude photolysate (CD_3CN) contains azetidines **40** and **42** only (29% and 18%, respectively) along with acetophenone (6%) and benzyl *N*-(trimethylsilyl)carbamate (**43**, 6%). In a similar manner, the 2-naphthyl ketone

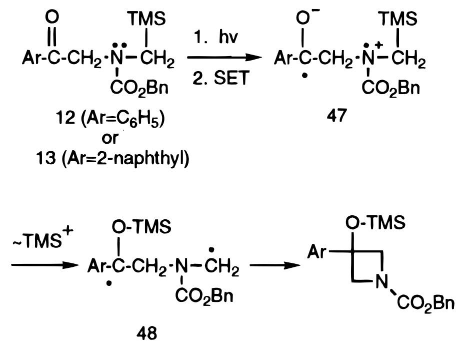


13 reacts upon irradiation to give azetidines **44**−**46** (6%, 15%, and 1% isolated, 37%, 0%, and 5% by ^{1}H NMR), 2-acetonaphthone (14%), and carbamate **43** (5%).

The major primary products generated in photoreactions of the phenyl and 2-naphthyl silylamido ketones **12** and **13** are the siloxyazetidines **40** and **44**, respectively. These substances are produced with near equal efficiencies (see below) by routes involving intramolecular silyl transfer in the intermediate zwitterionic diradicals **47**, themselves being formed by excited-state SET (Scheme



Scheme 8



8). The diradicals **48** formed in this fashion undergo selective cyclization rather than fragmentation, a characteristic observed previously in photochemical studies of amido ketones.[18] Hydrogen migration (yielding **42** or **46**) and β-cleavage photoprocesses (yielding the respective acylarenes and **43**) occur to a lesser extent in the excited-state chemistry of these substances.

Another interesting observation is that the phenyl and 2-naphthyl ketones **12** and **13** react with near equal quantum efficiencies (0.40 and 0.33, respectively). This is an expected characteristic of reaction by SET pathways where, unlike H-atom abstractions, only the redox properties (and not electronic configurations or multiplicities) of the excited aryl ketone chromophores govern reaction efficiencies.

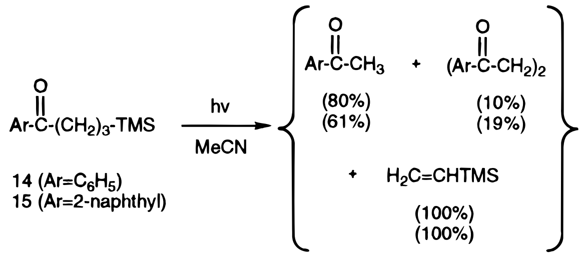
Silylalkyl Ketone Photochemistry. Both the (silylalkyl)phthalimides and silylamido ketones, whose photochemical properties are described above, contain structural features which encourage the operation of excited-state SET processes. Accordingly, the excited phthalimide function is a good acceptor and the silylamido grouping is a good SET donor. Simple silylalkyl ketones such as the phenone **14** and 2-naphthone **15**, at first sight seem to lack these driving forces for excited-state SET, and therefore, they would be expected to mimic simple aryl ketones in their photochemical reactivity.

In line with this expectation, both **14**[19] and **15** react cleanly when irradiated in MeCN to produce products resulting from the operation of Norrish Type II (acylarenes and vinyl trimethylsilane) and/or β-cleavage (vinyl trimethylsilane and diketones) pathways. The results of these photoreactions are summarized in Scheme 9.

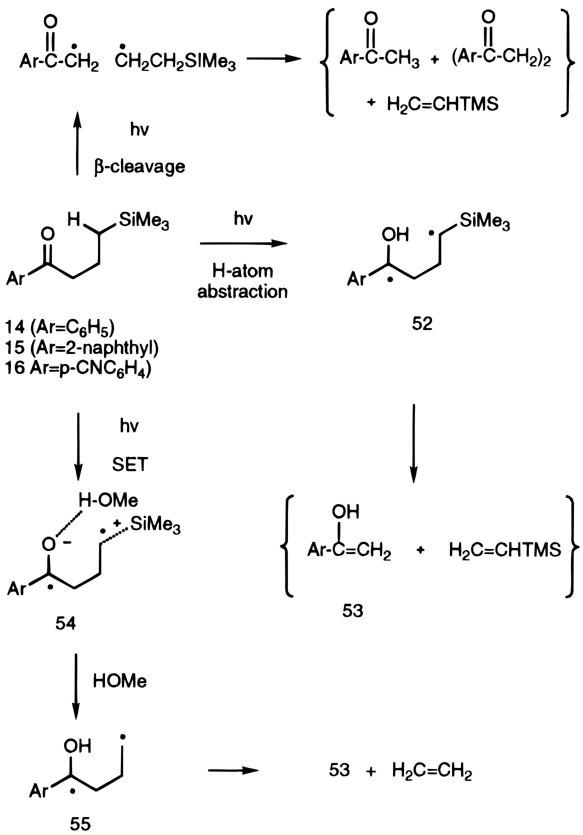
(18) Gold, E. H. *J. Am. Chem. Soc.* **1971**, *93*, 2793. Allworth, K. L.; El-Hamamy, A. A.; Hesabi, M. M.; Hill, J. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1671.

(19) The results of the current study with **14** match those found earlier by Kuivila (ref 14).

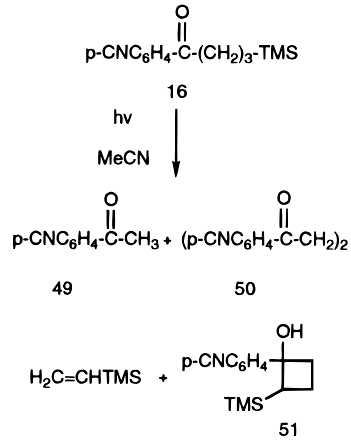
Scheme 9



Scheme 10



In the absence of additional information, it is difficult to determine what fraction of the products formed in the photoreactions of **14** and **15** derive from the Norrish Type II and β-cleavage processes. As can be seen by viewing Scheme 10, the β-cleavage reaction could yield all three of the observed products, the acylarenes and vinyltrimethylsilane arising by disproportionation in the initially formed radical pair and the diketone by out-of-cage combination. However, a more careful study of the photoreaction of the *p*-cyano analog **16** provides important information on this issue. For example, preparative irradiation of **16** in MeCN leads to production of the acylarene **49** (91%), vinyltrimethylsilane (92%), 1,4-diketone **50** (1%), and cyclobutanol **51** (7%). ^{1}H NMR monitoring of the photoreaction of **16** in anhydrous CD_3CN shows that the enol **53** (Scheme 10, Ar = *p*-CN-C_6H_4) is the major primary product (terminal vinyl protons at 4.45 and 4.80 ppm) formed simultaneously with and in near equal amounts to vinyltrimethylsilane. The stable (due to the *p*-CN substituent)[20] enol **53** tautomerizes over a 12 h period at 25 °C to generate the ketone **49**. It is important to note that the intermediate **53** detected by this analysis is not the silyl enol ether which has different spectroscopic properties and solution lifetimes.



Thus, in the case of **16** and most probably in photoreactions of the related ketones **14** and **15**, the major reaction pathway in MeCN is γ-hydrogen atom abstraction leading to formation of the 1,4-diradical **52** (Scheme 10). Bond scission then generates the enol and the vinylsilane. As anticipated for operation of a H-atom abstraction route, the quantum efficiencies for photoreactions of the phenyl and 2-naphthyl ketones differ greatly; *i.e.*, 0.90 (MeCN) for reaction of **14** with a lowest energy n$-\pi^*$ triplet and 0.01 (MeCN) for reaction of **15** with a lowest $\pi-\pi^*$ triplet state.[21]

An observation, which suggests that another mechanistic route can become competitive with H-atom abstraction in the excited state chemistry of the silylalkyl ketones, relates to the effect of protic/silophilic solvents on the nature of the products produced. As indicated above, ^{1}H NMR analysis shows that irradiation of **16** in CD_3CN leads to production of the enol **53** (Ar = *p*-CNC_6H_4) and vinylsilane in near equal amounts. In contrast, photolysis of **16** in CD_3OD, monitored by ^{1}H NMR, again gives enol **53** and the vinylsilane but this time in a ratio of 1.6:1. In a similar manner, photoreaction of the phenyl ketone **14** in CD_3OD gives acetophenone and vinyltrimethylsilane in a 1.8:1 ratio as compared to the 0.8:1 ratio of these products when **14** is irradiated in CD_3CN.

A full interpretation of the latter results is difficult to formulate. However, the observations suggest that two mechanism are responsible for generation of the acylarene products in the photoreactions of the aryl ketone **14**$-$**16**. The major pathway in MeCN involves initial γ-hydrogen abstraction by the carbonyl n$-\pi^*$ triplet and generates the acylarene and vinylsilane products in equal amounts (Scheme 10). Another route operates competitively for photoreactions of **14**$-$**16** in the protic$-$silophilic solvent MeOH and it appears to lead to generation of the acylarenes but not vinyltrimethylsilane. A reasonable proposal to explain this outcome would invoke methanol-induced desilylation of CT complexes or even a zwitterionic diradical **54** formed by interaction of the σ_{C-Si} and excited carbonyl moieties (Scheme 10). This process would produce the non-silicon-containing diradical **55**, the precursor of the acylarenes and ethylene. Clearly, if this proposal were to be correct, a close link would exist between the excited-state reaction profiles of the (silyl-

(20) Kresge, A. J. *Pure Appl. Chem.* **1991**, *63*, 213.

(21) See: Cohen, S. G.; Davis, G. A.; Clark, W. D. K. *J. Am. Chem. Soc.* **1972**, *94*, 869 and references therein.

alkyl)phthalimide, silylamido ketone, and silylalkyl ketone systems.

Summary

The studies outlined above have provided a broad overview of the types of photochemical processes that occur in substances which possess tethered silylalkane or amide and aryl ketone or phthalimide groups. The accumulated results demonstrate that classical Norrish Type II or Yang photoreactivity, initiated by carbonyl excited-state H-atom abstraction, dominates in these systems when photoreactions occur in less polar, aprotic, and nonsilophilic solvents. However, clear evidence has been gathered to show that CT or SET interactions between excited carbonyl and ground state σ_{C-Si} groupings doe occur and that in silophilic solvents this can lead to cleavage of the C–Si bond and to activation of unique excited -state reaction pathways. Finally, the observation that silicon substitution in alkylphthalimides enhances the efficiencies of their photocyclization reactions brings synthetic significance to the results of this investigation.

Experimental Section

General. ^{1}H NMR and ^{13}C NMR spectra were recorded using $CDCl_3$ solutions and chemical shifts are reported in ppm relative to $CHCl_3$ (δ 7.24 ppm for ^{1}H and δ 77.0 ppm for ^{13}C) which was used as a chemical shift internal standard for samples in $CDCl_3$; ^{13}C NMR resonance assignments were aided by the use of the DEPT technique to determine numbers of attached hydrogens. IR spectra vibrational frequencies are expressed in wave numbers (cm^{-1}). Column chromatography was performed with either Merck-EM type 60 (230–400 mesh) or Alcoa type F-20 alumina (neutral, 80–200 mesh) absorbants. Preparative TLC was performed on 20 × 20 cm plates coated with Merck-EM type 60 GF-254 silica gel. Gas chromatographic analyses were conducted on a chromatograph with a flame ionization detector. Mass spectra were recorded by using electron impact ionization unless specified as chemical ionization by CI. All reactions were run under a dry N_2 atmosphere unless otherwise noted. Organic extracts obtained following workup of reaction mixtures were dried over anhydrous Na_2SO_4 or $MgSO_4$. All compounds prepared in this study were oils and were judged by NMR to be >90% pure unless otherwise noted.

Preparative photochemical reactions were conducted with an apparatus consisting of a 450 W Hanovia medium-pressure mercury lamp surrounded by a glass filter (for wavelength band selection) immersed in the photolysis solution. The photolysis solutions were purged with N_2 both before and during irradiation. The progress of each preparative photochemical reaction was monitored by UV absorption spectrometry, gas chromatography, TLC, and/or ^{1}H NMR spectroscopy. Sealed NMR tubes were devoided of air by using N_2 purging before irradiations.

3-(Trimethylsilyl)-1-propanol, 2-(trimethysilyl)-1-ethanol, and 4-(trimethylsilyl)butyronitrile were purchased from Petrarch, and sodium phthalimide and 4-cyanobenzoic acid were purchased from Aldrich.

Preparation of *N*-[2-(Trimethylsilyl)ethyl]phthalimide (10). A solution of 1.50 g (11 mmol) of 2-(chloroethyl)-trimethylsilane (prepared from the corresponding alcohol by reaction with $SOCl_2$) and 2.03 g (12 mmol) of sodium phthalimide in 20 mL of DMF was stirred at 85 °C for 7 h and concentrated in vacuo. The residue was diluted with Et_2O, filtered, and then subjected to column chromatography (silica, 1:4 EtOAc–hexane) to give 1.51 g (56%) of the phthalimide **10** (mp 64–65 °C): ^{1}H NMR 0.05 (s, 9 H, $SiMe_3$), 0.99 (t, J = 7.3 Hz, 2 H, CH_2Si), 3.70 (t, J = 7.3 Hz, 2 H, CH_2N), 7.64–7.83 (m, 4 H, arom); ^{13}C NMR −1.8 ($SiMe_3$), 17.1 (CH_2Si), 34.4 (CH_2N), 123.0, 132.3, 132.3, 133.7 (arom), 168.2 (C=O); IR 1710; LRMS m/z 247 (M, 25), 246 (100), 232 (65), 204 (66), 160 (27), 130 (43); HRMS m/z 247.1037 ($C_{13}H_{17}NO_2Si$ requires 247.1029).

Preparation of *N*-[3-(Trimethylsilyl)propyl]phthalimide (11). To a solution of 3-(trimethylsilyl)-1-propanol (5.0 g, 38 mmol) and Et_3N (4.1 g, 41 mmol) in 40 mL of Et_2O at 0 °C was added a solution of MsCl (3.0 mL, 39 mmol) in 20 mL of ether dropwise. The resulting mixture was stirred at 25 °C for 18 h and filtered. The filtrate was concentrated in vacuo giving a residue which was vacuum distilled to give 8.0 g (*ca.* 100%) of the mesylate derivative (125 °C, 3 mm): ^{1}H NMR −0.04 (s, 9 H, $SiMe_3$), 0.48 (m, 2 H, CH_2Si), 1.63 (q, J = 7.2 Hz, CH_2), 2.96 (s, 3 H, S-Me), 4.12 (t, J = 7.2 Hz, 2 H, CH_2O); ^{13}C NMR −2.0 ($SiMe_3$), 11.4 (CH_2Si), 23.8 (CH_2), 37.2 (SMe), 72.5 (OCH_2); IR 1352, 1170.

A solution of NaI (23 g, 0.15 mol) and the mesylate (8.0 g, 0.038 mol) in 40 mL of acetone was stirred at reflux for 18 h and then extracted with pentane. The pentane layer was concentrated in vacuo and distilled to give 9.1 g (99%) of the corresponding iodide (59 °C, 3 mm): ^{1}H NMR −0.04 (s, 9 H, $SiMe_3$), 0.55 (m, 2 H, CH_2Si), 1.78 (m, 2 H, CH_2), 3.14 (t, 2 H, J = 7.3 Hz, CH_2I); ^{13}C NMR −1.7 ($SiMe_3$), 11.1 (CH_2Si), 18.7 (CH_2), 28.9 (CH_2I).

A solution of 1.74 g (7.2 mmol) of the iodide and 1.30 g (7.7 mmol) of sodium phthalimide in DMF was subjected to the reaction work up and purification conditions described for preparation of **10** above. This gave 1.76 g (96%) of the phthalimide **11** (mp 60–61 °C): ^{1}H NMR −0.04 (s, 9 H, $SiMe_3$), 0.50 (m, 2 H, CH_2Si), 1.65 (quintet, J = 7.4 Hz, 2 H, CH_2), 3.64 (t, J = 7.4 Hz, 2 H, CH_2N), 7.67–7.84 (m, 4 H, arom); ^{13}C NMR −1.8 ($SiMe_3$), 13.8 (CH_2Si), 23.6 (CH_2), 41.1 (N-CH_2), 123.1, 132.2, 133.8 (arom), 168.5 (C=O); IR 1711; LRMS m/z 261 (M, 16); 246 (33), 232 (49), 204 (33), 131 (77), 130 (17), 119 (100), 100 (14); HRMS m/z 261.1185 ($C_{14}H_{19}NO_2Si$ requires 261.1186).

Preparation of α-Silylamidoacetophenone 12. To a solution of 0.76 g (2.7 mmol) of the known[13] amidoaldehyde **17** in 20 mL of anhydrous THF was added a THF solution of 1.4 mL (4.1 mmol) of phenylmagnesium bromide (Aldrich) at −78 °C. The resulting solution was stirred for 3 h at −15 °C, quenched by addition of saturated aqueous NH_4Cl and extracted with ether. The ethereal extracts were dried over Na_2SO_4 and then concentrated in vacuo to give a residue which was subjected to Florisil column chromatography (20% Et_2O/cyclohexane) to yield 0.76 g (2.1 mmol, 79%) of the amido alcohol **18**: ^{1}H NMR −0.02 (broad, 9H, $SiCH_3$), 2.71–2.88 (broad, $SiCH_2$), 3.20–3.73 (broad, 2 H, H-2), 4.06 (broad, 1 H, H-1), 5.08 (s, 2 H, benzylic), 7.30 broad, 10 H, aromatic); ^{13}C NMR −1.60 ($SiCH_3$), 40.6 ($SiCH_2$), 58.0 (C-2), 67.5 (benzylic), 73.5 (C-1), 125.8, 127.9,128.1, 128.2, 128.5, 136.5 and 142.3 (aromatic), 158.0 (NCO); IR 3560–3250, 3020, 2975, 2895, 1600, 1520, 1475, 1420, 1155, 1095, 925; LRMS m/z 358 (M^+ + 1, 26), 341, (5), 340 (19), 280 (16), 266 (11), 250 (26), 206 (25), 116 (9), 104 (17), 91 (100), 73 (25); HRMS m/z 358.1846 (M^+ + 1, $C_{20}H_{28}NO_3Si$ requires 358.1839).

The amido alcohol **18** (0.29 g, 8.2 × 10^{-1} mmol) was oxidized by the procedure of Swern using 0.18 mL (2.0 mmol) of oxalyl chloride and 0.28 mL (4.0 mmol) of DMSO and 2 mL of triethylamine. Concentration gave amidophenone **12** (0.29 g, 8.2 × 10^{-1} mmol, >98%) which was used without further purification. ^{1}H NMR 0.02 and 0.08 (s, 9 H, $SiCH_3$), 2.89 and 2.93 (s, 2 H, $SiCH_2$), 4.65 and 4.74 (s, 2 H, H-2), 5.08 and 5.16 (s, 2 H, benzylic), 7.21–7.94 (m, 10 H, aromatic); ^{13}C NMR −1.69 ($SiCH_3$), 39.9 and 41.1 ($SiCH_2$), 55.9 (C-2), 67.4 (benzylic), 127.8, 128.3, 128.7, 133.3, 135.6 and 136.8 (aromatic), 156.8 (NCO), 194.5 (C-1); IR 3070, 3020, 2980, 2960, 2900, 1700, 1450, 1405, 1220, 1110, 860; LRMS m/z 355 (M^+, 0.08), 340 (2), 310 (1), 264 (4), 248 (2), 220 (7), 206 (4), 192 (10), 177 (4), 105 (9), 91 (100), 73 (25); HRMS m/z 356.1674 (M^+ + 1, $C_{20}H_{26}NO_3Si$ requires 356.1682).

Preparation of α-Silylamido-2-acetonaphthone 13. To a solution of the known amido aldehyde **17** (2.79 g, 0.010 mol) in 20 mL of anhydrous THF at −78 °C was added a solution of 0.013 mol of 2-naphthylmagnesium bromide in THF (15 mL). The resulting solution was stirred at 25 °C for 24 h, quenched by adding saturated aqueous NH_4Cl (6 mL), and extracted with ether. The ethereal extracts were dried and concentrated *in vacuo* to give 4.3 g (100%) of the naphthyl alcohol **19** which was used without further purification. ^{1}H NMR −0.04 (br s, 9 H, $SiCH_3$), 2.77 (br s, 2 H, $SiCH_2$), 2.86 (br s, 1 H, OH), 3.30−3.70 (m, 2 H, H-2), 4.20 (br s, 1 H, H-1), 5.15 (br s, 2 H, $PhCH_2$), 7.06−7.83 (m, 12 H, aromatic).

The alcohol **19** (4.0 g, 9.8 mmol) was oxidized by the procedure of Swern using 2.14 mL (0.02 mol) of oxalyl chloride and 2.79 mL (0.04 mol) of DMSO. The reaction was quenched by adding 6.85 mL of triethylamine, and the mixture was extracted with CH_2Cl_2. The CH_2Cl_2 extracts were washed with water and concentrated *in vacuo* to give a residue which was subjected to column chromatography (Florisil, 20% ether/hexane) to yield 1.79 g (45%) of the amido naphthone **13**: ^{1}H NMR (rotamer mixture) 0.05 and 0.13 (s, 9 H, $SiCH_3$), 2.95 and 2.98 (s, 2 H, $SiCH_2$), 4.81 and 4.86 (s, 2 H, H-2), 5.12 and 5.19 (s, 2 H, $PhCH_2$) 7.27−8.08 (m, 11 H, aromatic), 8.39 and 8.49 (s, 1 H, H-1-naphthyl); ^{13}C NMR (a 1:1 rotamer mixture) −1.7 and −1.6 ($SiCH_3$), 39.8 and 41.1 ($SiCH_2$), 56.0 (C-2), 67.3 and 67.6 ($PhCH_2$), 123.5, 123.6, 126.9, 127.8, 128.0, 128.2, 128.4, 128.7, 129.4, and 129.6 (aromatic, CH), 132.5, 132.6, 135.8, and 136.7 (aromatic, *ipso*), 156.5 (NC═O), 194.7 (C-1); IR 3062, 2953, 1700, 1457, 1248, 856; LRMS (CI) *m/z* 406 (M + 1,20), 390 (23), 360 (13), 314 (40), 298 (11), 270 (40), 242 (100), 241 (29), 227 (33), 206 (40), 155 (45), 141 (24), 127 (22); HRMS (CI) *m/z* 406.1847 (M + 1, $C_{24}H_{28}NO_3Si$ requires 406.1838).

Preparation of 4-(Trimethylsilyl)-2-butyronaphthone (15). To a solution of (3-cyanopropyl)trimethylsilane (1.90 g, 0.014 mol) in 30 mL of anhydrous THF was added 0.15 mol of 2-naphthylmagnesium bromide in 25 mL of THF dropwise at 25 °C over a 0.5 h period. The mixture was then stirred at reflux for 3 days, quenched by addition of saturated aqueous NH_4Cl, and extracted with ether. The ethereal extracts were dried and concentrated *in vacuo* to give a residue which was subjected to column chromatography (silica gel, 20% ether/hexane) to yield 1.06 g (28%) of the naphthyl ketone **15**: ^{1}H NMR 0.00 (s, 9 H, $SiCH_3$), 0.56−0.65 (m, 2 H, H-4), 1.80 (m, 2 H, H-3), 3.11 (t, J = 7.3 Hz, 2 H, H-2), 7.50−8.04 and 8.45 (m, 7 H, aromatic); ^{13}C NMR −2.0 ($SiCH_3$), 14.0 (C-4), 16.6 (C-3), 42.2 (C-2), 123.8, 126.6, 127.6, 128.2, 128.3, 129.4, and 129.5 (aromatic, CH), 132.5, 134.4, and 135.4 (aromatic, *ipso*), 200.3 (C-1); IR 3059, 2951, 1682, 1248, 862, 837, 749; LRMS (CI) *m/z* 271 (M + 1, 32), 270 (39), 255 (100), 242 (56), 241 (47), 170 (34), 165 (8), 155 (67), 127 (30), 73 (49); HRMS *m/z* 270.1429 ($C_{17}H_{22}OSi$ requires 270.1440).

Preparation of [4-(Trimethylsilyl)butyryl]-*p*-cyanophenone (16). A solution of 4-cyanobenzoic acid (2.0 g, 0.014 mol) in thionyl chloride (40 mL) was stirred at reflux for 4 h. Solvent was evaporated *in vacuo*. The solid residue, 4-cyanobenzoyl chloride (mp 66−67 °C), was then dissolved in 20 mL anhydrous THF. [3-(Trimethylsilyl)-1-propyl]magnesium chloride (0.027 mol in 14 mL of THF) was added and the resulting mixture was stirred at −78 °C for 1.5 h. The reaction was quenched by adding 3 N HCl and the mixture extracted with ether. The ethereal extracts were washed with 0.5 N KOH, dried, and concentrated *in vacuo* to give a residue which was subjected to column chromatography (silica gel, 10% ether/hexane) to yield 1.0 g (30%) of the cyanophenone **16**: ^{1}H NMR −0.02 (s, 9 H, $SiCH_3$), 0.49−0.58 (m, 2 H, H-4), 1.71 (m, 2 H, H-2), 2.98 (t, J = 7.2 Hz, 2 H, H-3), 7.74 and 8.01(AB q, J = 8.5 Hz, 4 H, aromatic); ^{13}C NMR −1.9 ($SiCH_3$), 16.5 (C-4), 18.7 (C-3), 42.4 (C-2), 116.1 (CN), 128.3 and 132.2 (aromatic, CH), 117.8 and 140.0 (aromatic, *ipso*), 198.9 (C-1); IR 3068, 2953, 2230, 1693, 1404, 1248, 1215, 838, 750; LRMS *m/z* 245 (M, 5), 231 (14), 230 (68), 218 (15), 217 (71), 216 (50), 203 (28), 202 (100), 130 (43); HRMS *m/z* 245.1237 ($C_{14}H_{19}NOSi$ requires 245.1236).

Photochemistry of *N*-[2-(Trimethylsilyl)ethyl]phthalimide (10). Irradiation in MeCN. A solution of 500 mg (2.02 mmol) of the (silylethyl)phthalimide **10** in 200 mL of MeCN under N_2 was irradiated with Vycor-filtered light for 7.5 h (31% conversion of **10**). Chromatography (silica, EtOAc) of the residue obtained by concentration of the photolysate gave 75 mg (68% based on 31% conversion) or 389 mg (66% based on 31% conversion) of the known[15] benzazepinedione **20** (mp 161−162 °C).

Irradiation in Acetone. A solution of **10** (500 mg, 2.02 mmol) in 200 mL of acetone under N_2 was irradiated with Vycor-filtered light for 24 h (51% conversion of **10**). Chromatography under the conditions described above gave 74 mg (41% based on recovered **10**) of benzazepinedione **20** and 22 mg (7%) of the acetone adduct **21**: ^{1}H NMR 0.11 (s, 9 H, $SiMe_3$), 0.68 (s, 3 H, Me), 1.24 (dd, J = 14.0, 6.8 Hz, 1 H, CH_2-Si), 1.33 (dd, J = 14.0, 6.8 Hz, 1 H, CH_2Si), 1.53 (s, 3 H, Me), 2.63 (s, 1 H, OH), 5.36 (t, J = 6.8 Hz, 1 H, CHN), 7.43−7.73 (m, 4 H, arom); ^{13}C NMR −1.0 ($SiMe_3$), 21.9 (Me), 22.9 (Me), 27.2 (CH_2Si), 82.1 (CMe_2), 84.9 (N-C), 96.3 (CO), 122.0, 124.0, 130.3, 133.0, 133.3, 144.3 (arom), 170.4 (C═O); IR 3450, 1695; LRMS (CI) *m/z* 306 (M + 1, 17), 290 (20), 262 (15), 247 (73), 246 (100), 218 (74), 190 (40); HRMS (CI) *m/z* M + 1, 306.1525 ($C_{16}H_{24}NO_3Si$ requires 306.1526).

Irradiation in Acetone−Methanol. A solution of **10** (500 mg, 2.02 mmol) in 200 mL of acetone containing 10% CH_3OH was irradiated with Vycor-filtered light under N_2 purging for 7 h (100% conversion of **10**). The residue obtained by concentration of the photolysate was subjected to column chromatography (silica, EtOAc) to give 80 mg (16%) of the reduction product **22** and 425 mg (75%) of the addition product **23**.

22: ^{1}H NMR −0.01 (s, 9 H, TMS), 0.68−0.77 (m, 1 H, CH_2-TMS), 0.84−0.93 (m, 1 H, CH_2TMS), 3.03−3.12 (m, 1 H, NCH_2), 3.28−3.37 (m, 1 H, NCH_2), 3.81 (d, J = 12.0 Hz, 1 H, NCHOH), 5.73 (d, J = 12.0 Hz, 1 H, OH), 7.37−7.61 (m, 4 H, aromatic); ^{13}C NMR −1.7 (TMS), 16.3 (CH_2TMS), 35.1 (NCH_2), 80.9 (NCH), 123.1, 123.3, 129.6, 131.8, 132.0, 144.0 (aromatic), 166.9 (C═O); IR 3650−3200, 1698; LRMS *m/z* 249 (M, 7), 234 (21), 206 (18), 133 (23), 75 (34), 73 (43), HRMS *m/z* 249.1185 ($C_{13}H_{19}NO_2Si$ requires 249.1186).

23: Mp 138−139°C; ^{1}H NMR −0.03 (s, 9 H, TMS), 0.64−0.73 (m, 1 H, CH_2TMS), 0.88−0.97 (m, 1 H, CH_2TMS), 2.14 (t, J = 6.8 Hz, OH), 2.73−2.82 (m, 1 H, NCH_2), 3.04−3.12 (m, 1 H, NCH_2), 3.74 (dd, J = 11.6, 6.8 Hz, 1 H, CH_2O), 3.92 (dd, J = 11.6, 6.8 Hz, 1 H, CH_2O), 4.68 (s, 1H, OH), 7.38−7.63 (m, 4 H, aromatic); ^{13}C NMR −1.8 (TMS), 17.6 (CH_2TMS), 34.9 (NCH_2), 65.4 (CH_2O), 89.9 (COH), 122.6, 123.1, 129.7, 131.4, 132.2, 145.5 (aromatic), 167.8 (C═O); IR 3700−3300, 1695; LRMS (CI) *m/z* 279 (m, 0.4), 264 (20), 248 (42), 232 (100), 224 (57), 204 (84), 160 (31), 130 (33); HRMS *m/z* 279.1290 ($C_{14}H_{21}$-NO_3Si requires 279.1291).

Sealed-Tube Irradiation. A solution of 5 mg (0.021 mmol) of **10** in 0.5 mL of CD_3CN was irradiated for 2 h in a degassed (freeze−thaw) sealed NMR tube. NMR analysis of the photolysate indicated that it contained a mixture of the benzazepinedione **20** and its α-silyl analog **20-TMS** in a 1:6 ratio. Partial spectroscopic data for **20-TMS**: ^{1}H NMR (CD_3CN) 3.02 (dd, J = 12.0, 4.0 Hz, 1 H, CHSi), 3.33 (ddd, J = 15.0, 7.0, 4.0 Hz, 1 H, NCH_2), 3.54 (ddd, J = 15.0, 12. 0, 7.0 Hz, 1 H, CH_2N); ^{13}C NMR 39.5 (NCH_2), 54.3 (CHSi).

Photochemistry of *N*-Ethylphthalimide (24). A solution of phthalimide **24** (350 mg, 2.0 mmol) in 200 mL of acetone was irradiated with Vycor-filtered light with N_2 purging for 20 h (51% conversion of **24**). The residue obtained by concentration *in vacuo* was subjected to column chromatography (silica, EtOAc−$CHCl_3$) to give 15 mg (8%) of **20**, 68 mg (29%) of **18**, and 5 mg (3%) of **26**.

25: ^{1}H NMR 1.22 (t, J = 6.7 Hz, 3 H, CH_3), 2.15 (s, 3 H, $COCH_3$), 2.96 (d, J = 16.6 Hz, 1 H, CH_2-CO), 3.21 (d, J = 16.6 Hz, 1 H, CH_2−CO), 3.25−3.36 (m, 1 H, CH_2), 3.48−3.59 (m, 1 H, CH_2), 5.05 (s, 1 H, OH), 7.39−7.69 (m, 4 H, aromatic); ^{13}C NMR 14.5 (CH_3), 31.5 ($COCH_3$), 33.8 (CH_2CO), 49.1 (CH_2), 88.5 (COH), 121.6, 123.3, 129.6, 131.0, 132.2, 146.7 (aromatic), 166.9 (NC═O), 207.8 (C═O); IR 3650−3200, 1695; LRMS *m/z* 233 (M, 6), 232 (8), 216 (6), 191 (7), 190 (12), 177 (20), 176 (100), 175 (35), 172 (39), 160 (68), 148 (30), 147 (25); HRMS *m/z* 233.1052 ($C_{13}H_{15}NO_3$ requires 233.1053).

Photochemistry of *N*-[3-(Trimethylsilyl)propyl]phthalimide (11). In MeCN. Irradiation of a MeCN (200 mL) solution containing the (silylpropyl)phthalimide **11** (550 mg, 2.10 mmol) was conducted by using Vycor-filtered light for 6 h (55% conversion of **11**). Chromatography (silica, 1:4 EtOAc−

CH_2Cl_2) of the residue obtained by concentration of the photolysate gave 85 mg (28%) of **27** (mp 54−55 °C), 46 mg (21%) of **28** (mp 123−125 °C); 34 mg (11%) of **29** (mp 84−85 °C), and 20 mg (6%) of **30** (mp 70−71 °C).

27: ^{1}H NMR 0.07 (s, 9 H, $SiMe_3$), 0.72 (dd, J = 14.9, 9.2 Hz, 1 H, CH_2Si), 1.03 (dd, J = 14.9, 5.8 Hz, 1 H, CH_2Si), 2.96 (m, 1 H, CH−), 3.33 (m, 1 H, NCH_2), 3.44 (m, 1 H, NCH_2), 6.84 (s, 1 H, NH), 7.5−7.9 (m, 4 H, arom); ^{13}C NMR −0.8 ($SiMe_3$), 18.0 (CH_2Si), 44.3 (CH_2N), 52.1 (CH), 128.4, 129.7, 131.2, 132.0, 132.1, 136.8 (arom), 171.1, 207.0 (C═O); IR 1678; LRMS *m*/*z* 262 (M + 1, 5), 229 (5), 217 (20), 195 (21), 160 (27); HRMS (CI) *m*/*z* 262.1263 ($C_{14}N_{20}NO_2Si$ requires 262.1264).

28: ^{1}H NMR 1.45 (m, 1 H), 2.24 (m, 2 H), 2.58 (m, 1 H), 3.23 (m, 1 H, CHN), 3.49 (m, 1 H, CHN), 3.88 (s, 1 H, OH), 7.32−7.53 (m, 4 H, arom); ^{13}C NMR 27.6 (CH_2), 34.6 (CH_2), 41.2 (NCH_2), 96.4 (quart. C), 122.5, 123.4, 129.5, 131.6, 132.6, 147.3 (arom), 170.1 (C═O); IR 3300 (br), 1684; LRMS *m*/*z* 189 (M, 100), 174 (14), 172 (67), 170 (38), 161 (80); HRMS *m*/*z* 189.0790 ($C_{11}H_{11}NO_2$ requires 189.0790).

29: ^{1}H NMR −0.01 (s, 9 H, $SiMe_3$), 1.62 (s, 1 H, OH), 3.74 (dd, J = 15.7, 5.8 Hz, 1 H, NCH_2), 4.12 (dd, J = 15.7, 3.4 Hz, 1 H, NCH_2), 5.68 (s, 1 H, NCH), 5.74 (d, J = 9.2 Hz, 1 H, ═CHSi), 5.90 (ddd, J = 9.2, 5.8, 3.4 Hz, 1 H, HC═), 7.40−7.82 (m, 4 H, arom); ^{13}C NMR −1.4 ($SiMe_3$), 43.5 (NCH_2), 81.3 (NCH), 123.3 (HC═), 123.4 (HC═), 129.9, 131.5, 132.3, 133.2, 139.9, 143.9 (arom), 167.1 (C═O); IR 3300 (br), 1683; LRMS *m*/*z* 261 (m, 14), 246 (10), 232 (100), 204 (26), 177 (10), 133 (12), 130 (11); HRMS *m*/*z* 261.1185 ($C_{14}H_{19}NO_2Si$ requires 261.1186).

30: ^{1}H NMR 0.02 (s, 9 H, $SiMe_3$), 2.87 (s, 3 H, CH_3O), 3.75 (dd, J = 15.7, 6.0 Hz, 1 H, NCH_2), 4.52 (dd, J = 15.7, 3.8 Hz, 1 H, NCH_2), 5.81 (d, J = 18.7 Hz, 1 H, ═CHSi), 5.82 (s, 1 H, NCHO), 5.96 (ddd, J = 18.7, 6.0, 3.8 Hz, 1 H, CH═), 7.47−7.86 (m, 4 H, aromatic); ^{13}C NMR −1.3 ($SiMe_3$), 43.9 (NCH_2), 49.3 (CH_3O), 85.9 (NCH), 123.5 (═CHSi), 123.6 (CH═), 129.9, 132.0, 133.1, 133.4, 139.7, 140.5 (arom), 167.4 (C═O); IR 1697; LRMS *m*/*z* 275 (M, 15), 261 (21), 260 (100), 244 (19), 224 (12), 205 (12), 202 (35); HRMS *m*/*z* 275.1347 ($C_{15}H_{21}NO_2Si$ requires 275.1342).

In Acetone. Irradiation of a solution of (silylpropyl)-phthalimide **11** (500 mg, 1.91 mmol) in 200 mL of acetone with Vycor-filtered light under N_2 for 20 h (58% conversion of **11**) gave after concentration in vacuo and chromatography of the residue (silica, 1:4 EtOAc−CH_2CH_2) 63 mg (22%) of **27**, 16 mg (8%) of **28**, 82 mg (28%) of **29**, and 27 mg (9%) of **30**.

In 30% H_2O−MeCN. A solution of **11** (220 mg, 0.84 mmol) in a solution of 65 mL of MeCN and 35 mL of H_2O was irradiated with Vycor-filtered light under N_2 for 20 min. The photolysate was conentrated in vacuo to give 153 mg (96%) of **28**, a crystalline solid (mp 121−124 °C). One recrystallization from acetone−hexane gave 144 mg (91%) of pure **28** (mp 123−125 °C).

Photochemistry of α-Silylamidoacetophenone 12. A solution (75 mL) of CH_3CN containing 327 mg (0.92 mmol) of the amido phenone **12** was irradiated with Corex glass-filtered light under N_2 for 1 h (>90% conversion). The photolysate was concentrated *in vacuo* giving a residue which was subjected to column chromatography (Alumina, 20% ether−cyclohexane) to yield 31 mg (9%) of recovered amidophenone **12**, 73 mg (22%) of 1-[(benzyloxy)carbonyl]-3-phenyl-3-[(trimethylsilyl)oxy]azetidine (**40**), 35 mg (13%) of 1-[(benzyloxy)-carbonyl]-3-hydroxy-3-phenylazetidine (**41**), 29 mg (9%) of 1-[(benzyloxy)carbonyl]-2-(trimethylsilyl)-3-hydroxy-3-phenylazetidine (**42**), and trace quantities of acetophenone and benzyl N-[(trimethylsilyl)methyl]carbamate (**43**). The product **40** was converted to **41** with the treatment by 1.0 N aqueous H_2SO_4 in THF at 25 °C.

40: ^{1}H NMR 0.00 (s, 9 H, $SiCH_3$), 4.28 (s, 4 H, H-2, and H-4), 5.10 (s, 2 H, $PhCH_2$), 7.21−7.43 (m, 10 H, aromatic); ^{13}C NMR 1.3 ($SiCH_3$), 64.5 (C-2 and C-4), 66.7 ($PhCH_2$), 73.0 (C-3), 124.9, 127.7, 127.9, 128.0, 128.4, and 128.6 (aromatic, CH), 136.5 and 143.7 (aromatic, *ipso*), 156.4 (NC═O); IR 3018, 2959, 1693, 1216, 1116, 769; LRMS (CI) *m*/*z* 356 (M + 1, 3), 266 (5), 264 (3), 193 (22), 192 (100), 191 (62), 190 (6), 179 (7), 178 (9), 177 (57), 130 (8); HRMS (CI) *m*/*z* 356.1693 (M + 1, $C_{20}H_{26}NO_3Si$ requires 356.1682).

41: ^{1}H NMR 2.60 (br s, 1 H, OH), 4.23 and 4.35 (AB q, J = 9.5 Hz, 4 H, H-2, and H-4), 5.11 (s, 2 H, $PhCH_2$), 7.28−7.49 (m, 10 H, aromatic); ^{13}C NMR 64.4 (C-2 and C-4), 66.9 ($PhCH_2$), 71.9 (C-3), 124.5, 128.0, 128.1, 128.1, 128.5, and 128.8 (aromatic, CH), 136.5 and 142.8 (aromatic, *ipso*), 156.6 (NC═O); IR 3500−3400, 1685, 1451, 1357, 757, 698; LRMS (CI) *m*/*z* 284 (M + 1, 10), 224 (5), 220 (7), 178 (15), 148 (23), 134 (31), 120 (90), 105 (100); HRMS *m*/*z* 283.1212 ($C_{17}H_{17}NO_3$ requires 283.1208).

42: ^{1}H NMR 0.17 (br s, 9 H, $SiCH_3$), 4.17 (d, J = 9.8 Hz, 1 H, H-4), 4.23 (s, 1 H, H-2), 4.56 (d, J = 9.8 Hz, 1 H, H-4), 5.09 (s, 2 H, $PhCH_2$), 7.25−7.45 (m, 10 H, aromatic); ^{13}C NMR −1.7 ($SiCH_3$), 64.9 (C-4), 66.8 ($PhCH_2$), 69.3 (C-2), 75.1 (C-3), 124.5, 127.8, 128.0, 128.2, 128.4, and 128.8 (aromatic, CH), 136.7 and 144.7 (aromatic, *ipso*), 156.5 (NC═O); IR 3500−3400, 3030, 2951, 1684, 845, 698; LRMS *m*/*z* 355 (M, 0.65), 340 (12), 264 (10), 236 (30), 220 (100), 206 (25), 192 (99.98), 177 (34), 130 (21), 120 (30), 105 (35); HRMS *m*/*z* 355.1599 ($C_{20}H_{25}NO_3Si$ requires 355.1604).

43: ^{1}H NMR 0.04 (s, 9 H, $SiCH_3$), 2.66 (d, J = 5.5 Hz, 2 H, $SiCH_2$), 4.51 (br s, 1 H, NH), 5.08 (s, 2 H, $PhCH_2$), 7.34 (m, 5 H, aromatic); ^{13}C NMR −2.87 ($SiCH_3$), 26.9 ($SiCH_2$), 66.8 ($PhCH_2$), 128.1, 128.2, and 128.5 (aromatic, CH), 136.7 (aromatic, *ipso*), 157.3 (NC═O); IR 3400−3300, 3034, 2955, 1700, 1540, 1273, 858; LRMS *m*/*z* 237 (M, 0.18), 236 (0.92), 220 (23), 178 (7), 146 (13), 102 (48), 91 (100), 73 (96), 59 (5); HRMS *m*/*z* 237.1162 ($C_{12}H_{19}NO_2Si$ requires 237.1185).

Photochemistry of α-Silylamidoacetonaphthone 13. A solution of the amidonaphthone **13** (53 mg, 0.13 mmol) in CH_3CN (100 mL) was irradiated with Pyrex glass-filtered light under N_2. The reaction progress was followed by UV, TLC, and ^{1}H NMR which showed that >90% of **13** consumed after 3 h. The photolysate was concentrated *in vacuo* to give a residue which was subjected to column chromatography (Alumina, 20% ether/cyclohexane) to yield 6 mg (11%) of recovered amidonaphthone **13**, *ca.* 2 mg (5%, ^{1}H NMR integration) of benzyl carbamate **43,** 3 mg (6%) of 1-[(benzyloxy)-carbonyl]-3-(2-naphthyl)-3-[(trimethylsilyl)oxy]azetidine (**44**), 6 mg (15%) of 1-[(benzyloxy)carbonyl]-3-hydroxy-3-(2-naphthyl)azetidine (**45**), 0.5 mg (1%) of 1-[(benzyloxy)carbonyl]-2-(trimethylsilyl)-3-hydroxy-3-(2-naphthyl)azetidine (**46**), and 3 mg (14%) of 2-acetonaphthone.

44: ^{1}H NMR 0.03 (s, 9 H, $SiCH_3$), 4.35 (m, 4 H, H-2 and H-4), 5.13 (s, 2 H, $PhCH_2$), 7.29−7.91 (m, 12 H, aromatic); ^{13}C NMR 1.44 ($SiCH_3$), 64.4 (C-2 and C-4), 66.9 ($PhCH_2$), 73.3 (C-3), 123.5, 123.5, 126.3, 126.4, 127.6, 128.0, 128.1, 128.2, 128.5, and 128.7 (aromatic, CH), 132.8, 132.9, 136.6, and 141.0 (aromatic, *ipso*), 156.6 (NC═O); IR 3059, 2955, 1709, 1420, 1356, 1252, 1105, 843, 750; LRMS *m*/*z* 405 (M, 1.24), 390 (22), 314 (10), 299 (13), 243 (12), 242 (43), 241 (20), 227 (28), 171 (13), 170 (100), 155 (32), 141 (16), 128 (22), 127 (18); HRMS *m*/*z* 405.1727 ($C_{24}H_{27}NO_3Si$ requires 405.1760).

45: ^{1}H NMR 3.23 (s, 1 H, OH), 4.29 and 4.41 (AB q, J = 9.3 Hz, 4 H, H-2 and H-4), 5.11 (s, 2 H, $PhCH_2$), 7.31−7.90 (m, 12 H, aromatic); ^{13}C NMR 64.3 (C-2 and 4), 67.0 ($PhCH_2$), 71.9 (C-1), 122.7, 123.3, 126.4, 126.5, 127.6, 128.0, 128.1, 128.2, 128.5, and 128.8 (aromatic, CH), 132.8, 133.0, 136.5, and 140.1 (aromatic, *ipso*), 156.7 (NC═O); IR 3392, 3055, 2952, 1684, 1429, 1356, 1185, 1105, 748; LRMS *m*/*z* 333 (M, 0.5), 242 (15), 198 (8), 178 (11), 171 (38), 170 (100), 156 (12), 155 (84), 142 (15), 141 (54), 134 (18), 128 (74), 127 (44); HRMS *m*/*z* 333.1360 ($C_{21}H_{19}NO_3$ requires 333.1365).

46: ^{1}H NMR 0.2 (br s, 9 H, $SiCH_3$), 4.24 (d, J = 8.8 Hz, 1 H, H-4), 4.34 (br s, 1 H, H-2), 4.68 (br s, 1 H, H-4), 5.11 (s, 2 H, $PhCH_2$), 7.29−7.86 (m, 12 H, aromatic); IR 3500−3400, 1694, 1682, 1417, 845, 748; LRMS *m*/*z* 405 (M, 4.96), 404 (5), 391 (12), 390 (38), 314 (28), 299 (17), 282 (23), 270 (34), 252 (10), 242 (24), 241 (100), 236 (25), 227 (30), 206 (19), 192 (52), 170 (98), 155 (70), 141 (19), 128 (32), 127 (41), 107 (22); HRMS *m*/*z* 405.1775 ($C_{24}H_{27}NO_3Si$ requires 405.1760).

Photochemistry of γ-(Trimethylsilyl)butyrophenone (14). A 0.5 mL CD_3CN solution containing 5 mg (0.024 mmol) of the phenyl ketone **14** was irradiated with Corex glass-filtered light for 35 min. The reaction progress was monitored by ^{1}H NMR. The yield of the photoproducts, acetophenone, 1,4-diphenyl-1,4-butanedione, and vinyltrimethylsilane, were determined to be 80%, 10%, and 100% (based on conversion 80%), respectively, by ^{1}H NMR integration.

Photochemistry of γ-(Trimethylsilyl)butyro-2-naphthone (15). A 0.5 mL CD_3CN solution containing 5 mg (0.018 mmol) of the naphthyl ketone **15** was irradiated with Vycor glass-filtered light for 100 h. The yield of photoproducts, 2-acetonaphthone, 1,4-di(2-naphthyl)-1,4-butanedione, and vinyltrimethylsilane, were determined to be 61%, 100%, and 19%, respectively as determined by ^{1}H NMR integration.

Photochemistry of [γ-(Trimethylsilyl)butyryl]-*p*-cyanophenone (16). A solution of CH_3CN (100 mL) containing 71 mg (0.028 mmol) of the cyano ketone **16** was irradiated with Corex glass-filtered light for 30 min (90% conversion). The photolysate was concentrated *in vacuo* to give a residue which was subjected to preparative TLC (Silica gel, 30% ether−hexane) separation to yield 27 mg (67%) of 4-cyanoacetophenone (**49**), a trace of 1,4-bis(4-cyanophenyl)-1,4-butanedione (**50**), 8 mg (11%) of 1-(4-cyanophenyl)-2-(trimethylsilyl)-1-cyclobutanol (**51**), and 5 mg (7%) of recovered 4-cyano ketone **16**.

A 0.5 mL CD_3CN solution in a NMR tube containing 7 mg (0.028 mmol) of the cyano ketone **16** was irradiated with Corex glass-filtered light for 20 min. The yield of photoproducts, **49**−**51** and vinyltrimethylsilane, were 91%, 1%, 7%, and 91%, respectively.

51: ^{1}H NMR 0.09 (s, 9 H, $SiCH_3$), 1.85 (br s, 1 H, OH), 1.91 (m, 2 H, H-3), 2.02 (m, 1 H, H-4), 2.35 (m, 1 H, H-2), 2.68 (m, 1 H, H-4), 7.63 (s, 4 H, aromatic); ^{13}C NMR −1.8 ($SiCH_3$), 14.3 (C-3), 37.5 (C-4), 37.8 (C-2), 78.6 (C-1), 110.6 (CN), 118.9 and 153.8 (aromatic, *ipso*), 125.2 and 132.3 (aromatic, CH); IR 3480, 2950, 2229, 1246, 836; LRMS *m/z* (relative intensity) 245 (M, 14.2), 230 (39), 217 (34), 216 (19), 202 (75), 169 (13), 154 (10), 146 (10), 145 (100), 131 (21), 130 (52), 127 (18), 119 (17); HRMS *m/z* 245.1215 ($C_{14}H_{19}NOSi$ requires 245.1236).

Quantum Yield Measurements for Photoreactions of Ketones 12−15. Quantum yields for photoreactions of the 2-naphthyl ketones **13** and **15** were determined by use of the 2-acetonaphthone and triethylamine photoreduction reaction[21] as an actinometer. The Norrish Type II cleavage of butyrophenone[22] was used as the actinometer in quantum yield determinations of the photoreactions of the phenyl ketones **12** and **14**. All photoreactions were conducted to low conversions (4−17%) and quantitative analyses of products and/or starting materials was carried out by use of ^{1}H NMR spectroscopic methods.

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Supporting Information Available: Copies of spectra for new compounds characterized in this work (52 pages). This material is contained in 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.

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