A Solvent Effect That Influences the Preparative Utility of *N*-(Silylalkyl)phthalimide and *N*-(Silylalkyl)maleimide Photochemistry

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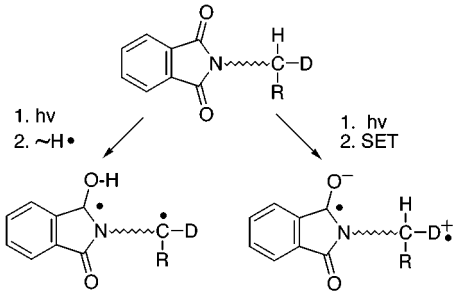
The photochemistry of selected *N*-silylalkyl-substituted phthalimides and maleimides has been investigated with the aim of exploring the generality and preparative consequences of an intriguing solvent effect on excited-state reaction chemoselectivities and quantum efficiencies. An example of this effect is found in the photochemistry of *N*-[(trimethylsilyl)butyl]phthalimide **10**, where irradiation in MeCN leads to production of a mixture of four products that arise by excited-state intramolecular hydrogen-atom abstraction. In contrast, the benzoindolizidine **15** is the sole product produced by a single electron transfer (SET)−desilylation pathway upon irradiation of **10** in 35% H_2O−MeCN. Another example of this solvent effect is found in the photochemistry of the *N*-silylpropyl-maleimide **17**. Irradiation in MeCN results in the production of the 2+2-dimer **19** whereas the pyrrolizidine **18** is generated exclusively by irradiation of **17** in 35% H_2O−MeCN. The results of fluorescence and triplet sensitization experiments suggest that the solvent effect has multiple sources including the control of the nature, reactivity, and intrinsic lifetimes of singlet and triplet excited states of the phthalimide and maleimide systems. The exploratory studies have clearly demonstrated the generality of this solvent effect and how it can be used to enhance the preparative utility of the photochemistry of *N*-(silylalkyl)phthalimides and *N*-(silylalkyl)maleimides.

Introduction

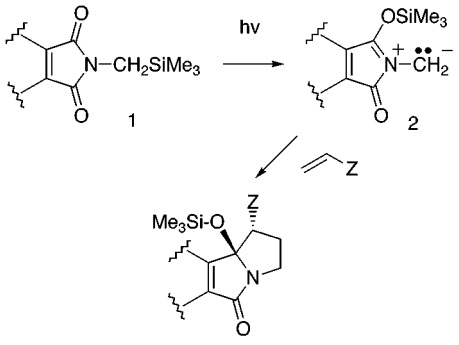
Phthalimides have been the subject of a number of in-depth photochemical[1] and photophysical[2] studies in recent years due to the developing applications of the excited-state chemistry of these substances.[3] Exploratory investigations of preparative aspects of phthalimide photochemistry have uncovered the operation of two major excited-state reaction pathways. These include the sometimes indistinguishable processes initiated by inter- or intramolecular hydrogen-atom abstraction and single electron transfer (SET) (Scheme 1). By virtue of our joint interests in phthalimide photochemistry[4] and organosilane SET chemistry,[5] we became attracted to photochemical studies with linked alkylsilane−phthalimide systems. Our work in this area, thus far, has demonstrated the existence of interesting excited-state reactivity profiles of substances in this family. An example is found in the azomethine ylide **2** forming, excited-state transformations of *N*-(silylmethyl)phthalimides **1** and their maleimide analogues that initiate novel and useful photocycloaddition reactions (Scheme 2).[6]

More pertinent to the studies described below are observations made in our preliminary investigations[7] of the photochemistry of higher homologues of **1**, specifically the *N*-(silylethyl)- and *N*-(silylpropyl)phthalimides **3** and **8**. Particularly intriguing was the finding that irradiation of **3** in MeCN followed by the addition of D_2O leads to production of the benzazepinedione-d_2 **4**. In contrast, the benzazepinedione-d_1 **7** is generated exclusively by photoreaction of **3** in 35% D_2O−MeCN. These observations were rationalized by invocation of a solvent-dependent competition between two mechanistic pathways for ben-

Scheme 1



Scheme 2



† Pusan National University.
‡ University of New Mexico.

(1) Coyle, J. D. In *Synthetic Organic Photochemistry;* Horspool, W. M., Ed.; Plenum Press: New York, 1984.
(2) Aveline, B. M.; Matsuga, S.; Redmond, R. W. *J. Am. Chem. Soc.* **1997**, *119*, 11785.
(3) Brana, M. F.; Castellano, J. M.; Roldan, C. M.; Santos, A.; Vasquez, D.; Jimenez, A. *J. Med. Chem.* **1981**, *16*, 207.
(4) Yoon, U. C.; Kim, H. J.; Mariano, P. S. *Heterocycles* **1989**, *29*, 1041; Yoon, U. C.; Oh, J. H.; Lee, S. J.; Kim, D. U.; Lee, J. G.; Kang, K. T.; Mariano, P. S. *Bull. Korean Chem. Soc.* **1992**, *13*, 166. Yoon, U. C.; Lee, S. J.; Cho, S. J.; Lee, C. W.; Mariano, P. S. *Bull. Korean Chem. Soc.* **1994**, *15*, 154. Yoon, U. C.; Kim, J. W.; Ryu, J. Y.; Cho, S. J.; Oh, S. W.; Mariano, P. S. *J. Photochem. Photobiol.* **1996**, *106*, 145.
(5) Yoon, U. C.; Mariano, P. S. *Acc. Chem. Res.* **1992**, *25*, 233.

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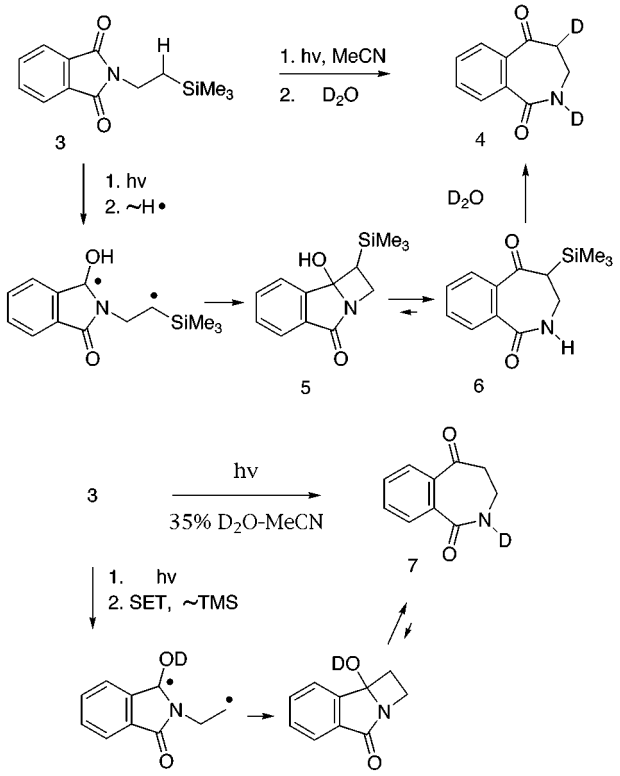
Scheme 3

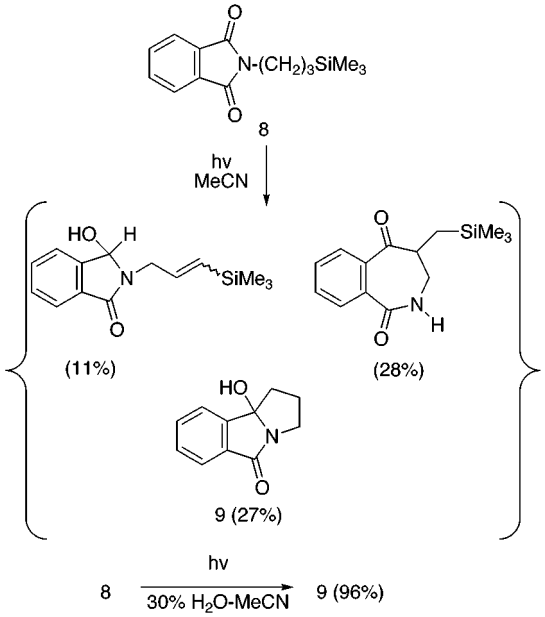


zazepinedione formation (Scheme 3). We proposed that the reactive excited state of **3** in MeCN undergoes H-atom abstraction, giving eventually the equilibrating phthalimido-cyclobutanol **5**−α-silylbenzazepinedione **6**. Deuteriolysis of the labile Si−C bond in **6** upon workup then provides **4**. In the more polar/protic/silophilic solvent, 35% D_2O−MeCN, excitation of **3** is followed by an SET−desilylation process (either concerted or sequential) to yield the mono-*N*-deuteriobenzazepinedione **7**.

Observations made in our early studies[7] with the silylpropyl derivative **8** suggested that the solvent control of mechanistic preferences might have an impact on the preparative potential of phthalimide photochemistry. Specifically, we found that irradiation of an MeCN or acetone solution of **8** promotes nonselective reaction leading to production of a mixture of four photoproducts (Scheme 4) that arise by pathways stemming from the diradical intermediates generated by γ-H-atom abstraction in the excited state of **8**. In contrast, benzopyrrolizidine **9** is the exclusive (96%) product formed in the photoreaction of **8** in 30% H_2O−MeCN. The change in solvent from MeCN to 30% H_2O−MeCN also profoundly alters the quantum efficiency of this process. Thus, irradiation in MeCN for 6 h leads to only 55% conversion of **8**, while a 20 min irradiation of **8** in 30% H_2O−MeCN is sufficient to promote 100% conversion to the benzopyrrolizidine **9**.

The preliminary observations described above suggest that a simple change in solvent can transform an unselective photoreaction of **8** into one that has both a high chemical yield and quantum efficiency. Driven by a desire to determine if this solvent effect is general and applicable in controlling the excited-state reactivity of phthalimides and other conjugated imides, we have conducted exploratory photochemical studies with a variety of *N*-(silylalkyl)phthalimides and -maleimides. Below are presented the results of these investigations, which demonstrate the ubiquitous nature of the solvent effect in controlling the chemoselectivities and efficiencies of the (silylalkyl)phthalimide and -maleimide photoreactions.

Scheme 4



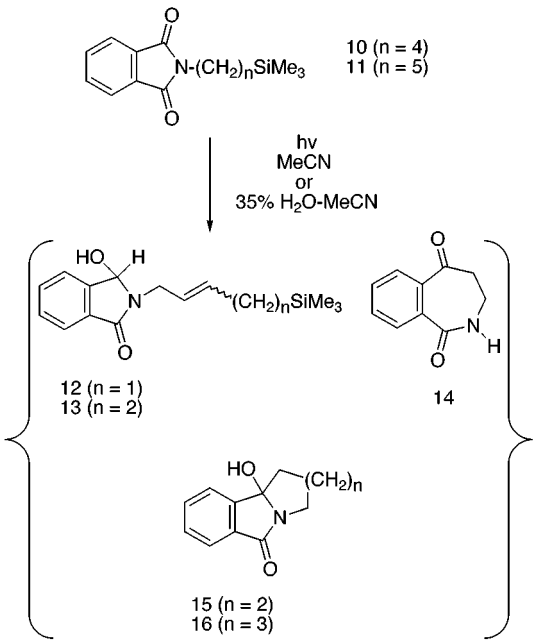
Results

***N*-(Silylalkyl)phthalimide and *N*-(Silylalkyl)maleimide Photochemistry.** Several *N*-(silylalkyl)phthalimides and *N*-(silylalkyl)maleimide analogues were prepared (see Supporting Information for details about the preparation of the substrates) and subjected to exploratory studies in order to probe the magnitude and scope of the solvent effects on the chemoselectivities of their photochemical reactions. As shown in Scheme 5 and Table 1, the nature and efficiencies of the photoreactions of (silylbutyl)phthalimide **10** are dramatically altered by a change in solvent from MeCN to 35% H_2O−MeCN. In MeCN, **10** is photochemically transformed to a mixture of products, including **12**, **14**, and **15**. In contrast, irradiation of a 35% H_2O−MeCN solution of **10** leads to the efficient and exclusive production of the benzoindolizidine **15** (94%). Although this solvent change has a less dramatic effect on the excited-state reactivity of the silylpentylphthalimide **11**, the trend remains in the direction of higher chemoselectivity for reaction in the aqueous solvent system (Scheme 5, Table 1). The influence of solvent on the nature and efficiencies of conjugated imide photoreactions is also seen in the photochemistry of the silylpropyl-maleimide **17**. While irradiation of an MeCN solution of **17** results in quantitative conversion to the 2+2-photodimer **19**, similar treatment of **17** in 35% H_2O−MeCN cleanly produces the functionalized pyrrolizidine **18** (64%) not contaminated with **19** (Scheme 6, Table 1).

(6) Yoon, U. C.; Kim, D. U.; Kim, J. C.; Lee, J. G.; Mariano, P. S.; Lee, Y. J.; Ammon, H. L. *Tetrahedron Lett.* **1993**, *34*, 5859. Yoon, U. C.; Kim, D. U.; Lee, C. W.; Choi, Y. S.; Lee, Y. J.; Ammon, H. L.; Mariano, P. S. *J. Am. Chem. Soc.* **1995**, *117*, 2689. Yoon, U. C.; Cho, S. J.; Lee, Y. J.; Mancheno, M. J.; Mariano, P. S. *J. Org. Chem.* **1995**, *60*, 2353.

(7) Lee, Y. J.; Ling, R.; Mariano, P. S.; Yoon, U. C.; Kim, D. U.; Oh, S. W. *J. Org. Chem.* **1996**, *61*, 3304.

Scheme 5



The magnitude of the solvent effect is somewhat diminished in photoreactions of the allylsilane-containing maleimides **20** and **21**. Photoreactions of these substrates in either MeCN or 35% H_2O−MeCN lead to formation of the respective pyrrolizidine **22** or indolizidines **23** and **24** (Scheme 7). The change to the aqueous solvent system promotes only a slight increase in the yields of both of these photocyclization reactions (Scheme 7, Table 1). Similar observations are made in studies with the *N*-[2-(silylmethyl)benzyl]maleimide **25** (Scheme 7, Table 1) where photoreaction in both MeCN and 35% H_2O−MeCN leads to the benzoindolizidines **26** and **27**.

A greater understanding of how the solvent controls the chemoselectivities of these photoreactions has come from the results of triplet sensitization studies. Benzophenone (50 mM) sensitized irradiation ($\lambda > 310$ nm) of **17** (5 mM) in either MeCN or 35% H_2O−MeCN leads to exclusive formation of the dimer **19**. In addition, acetone triplet sensitized photoreactions of **17** in either neat acetone or 35% H_2O−acetone likewise yield the 2+2-dimer **19**. Thus, the maleimide triplet excited-state undergoes 2+2-photodimerization independent of the solvent system used. By default, pyrrolizidine **18** must arise by an SET−desilylation reaction of a singlet excited state of **17**. Contrastingly different results arise in triplet sensitization studies with the phthalimide analogue **8**. Acetophenone and acetone sensitized reactions of this substrate in MeCN and neat acetone, respectively, lead to production of the same four photoproducts (se Scheme 4) as is obtained by direct irradiation in MeCN. However, the benzopyrrolizidine **9** is generated exclusively in triplet sensitized photoreactions of **8** by both acetophenone in 35% H_2O−MeCN and acetone in 35% H_2O−acetone. Unlike that of the maleimide derivative **17**, the triplet excited-state reactivity of **8** is altered by a change in solvent.

Studies with the *N*-(Silylpropyl)naphthalimide 28 and Benzimide 30. Additional information about the mechanistic origin(s) of the preparatively significant solvent effect described above has come from studies with the naphthalimide derivative **28**. Irradiation of **28** in 30% H_2O−MeCN results in generation of the deceptively complex, dimeric product **29** (unknown stereochemistry) (Scheme 8). Formation of **29** likely occurs via the same type of sequence operating in the photochemistry of (silylalkyl)phthalimides and -maleimides, except in this case the initially formed cyclic amidol undergoes dehydration to form the corresponding enamide. This is followed by enanmide−acyliminium ion coupling and water addition. Interestingly, **29** is also produced by irradiation of an MeCN solution of naphthalimide **28**, but under these conditions the reaction is much less efficient.

In a similar manner, the nature of the photoreaction of (silylpropyl)-*N*-acetylbenzamide **30** is not altered appreciably by a change in the solvent from MeCN to 30% H_2O−MeCN. For example, preparative irradiation of **30** in either MeCN or 30% H_2O−MeCN provides the same products, γ-acetamidopropiophenone **31**, *N*-silylallylamide **32**, and *N*-acetylbenzamide (**33**), albeit in slightly different ratios (Scheme 9). To elucidate the mechanism(s) responsible for generation of the propiophenone derivative **31**, **30** was irradiated in 35% D_2O−MeCN. This leads to formation of **32** and **33**, along with the α-monodeuteriopropiophenone **31D**. Consequently, it is reasonable to conclude that **31** is formed by a mechanistic route involving initial excited-state δ-H-atom abstraction followed by cyclization of the resulting diradical **34**, amidol ring opening, and α-silyl ketone protodesilylation (Scheme 10). Plausible mechanisms for formation of the unsaturated acetamide **32** and imide **33** involve respective sequential acyl cleavage−diradical disproportionation and Norrish Type-II cleavage reactions of the excited state of **30**.

Fluorescence Studies. Information about the possible contribution of excited-state multiplicity to the solvent effects summarized above has come from fluorescence studies with the (silylpropyl)naphthalimide **28** and its *N*-methyl analogue **37**. Unlike simple phthalimides and maleimides, 1,8-naphthalimides are highly fluorescent substances (i.e., they have longer lived and efficiently emitting singlet excited states). As is seen by inspection of the spectra in Figure 1 and data in Table 2, the quantum yields for fluorescence of **28** and **37** increase upon changing the solvent from MeCN to 35% H_2O−MeCN. Since this solvent change does not appreciably alter the absorption spectrum (λ_{max} and extinction coefficient) of the substrates, the enhanced fluorescence efficiencies in the aqueous solvent system are most likely a result of the increased lifetime (slower rate of decay) of the naphthalimide singlet excited states. The data in Table 2 also show that the presence of the silylpropyl tether in 1,8-naphthalimide **28** causes a significant reduction in the emission quantum yield (as compared to **37**), which implicates quenching of the naphthalimide singlet by the Si−C bond containing side chain.

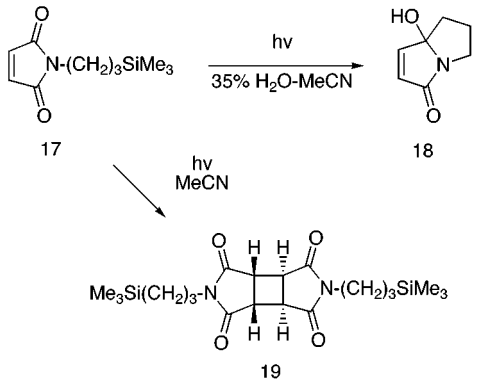
Discussion

Mechanistic Differences. Observations made in this study demonstrate that solvent has a pronounced impact on both the efficiencies and chemical selectivities of (silylalkyl)phthalimide and (silylalkyl)maleimide photoreactions. The most dramatic effects are seen in reactions of substrates that contain simple (trimethylsilyl)alkyl tethers. In these systems, a change in solvent from MeCN to 35% H_2O−MeCN alters their excited-state reactivity from inefficient and often nonselective H-atom abstrac-

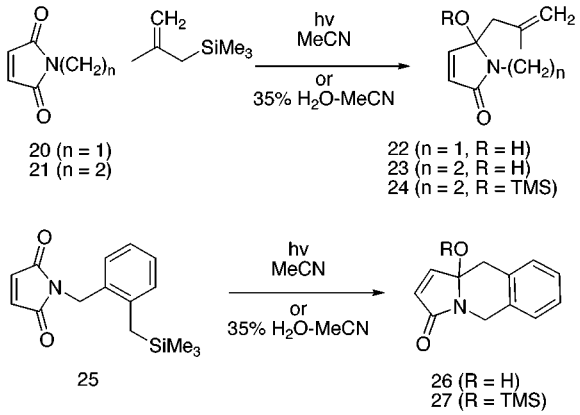
Table 1. Product Distributions and Relative Quantum Efficiencies of Photoreactions of Silylalkyl-Phthalimide and -Maleimide Substrates

	product yields		percent conversion (time)		
substrates	MeCN	35% HOH−MeCN	MeCN	35% HOH−MeCN	$\Phi_{HOH-MeCN}/\Phi_{MeCN}$
10	**12** (14%) **14** (38%) **15** (16%)	**15** (94%)	70% (6 h)	76% (0.3 h)	22
11	**13** (33%) **14** (37%) **16** (4%)	**14** (35%) **16** (58%)	75% (2.5 h)	84% (0.5 h)	6
17	**19** (98%)	**18** (64%)	84% (2 h)	71% (1.6 h)	1.1
20	**22** (68%)	**22** (71%)	63% (27 h)	57% (7 h)	3.5
21	**23** (66%) **24** (11%)	**23** (82%)	100% (3 h)	100% (2 h)	1.5
25	**26** (34%) **27** (37%)	**26** (88%) **27** (3%)	61% (5 h)	54% (4 h)	1.1

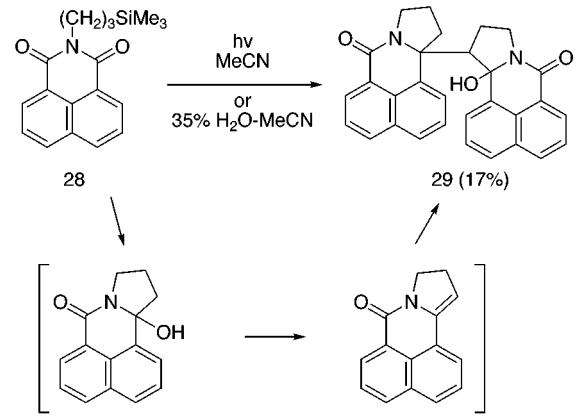
Scheme 6



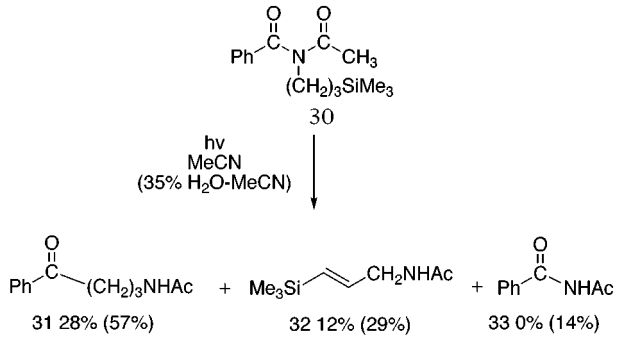
Scheme 7



Scheme 8



Scheme 9



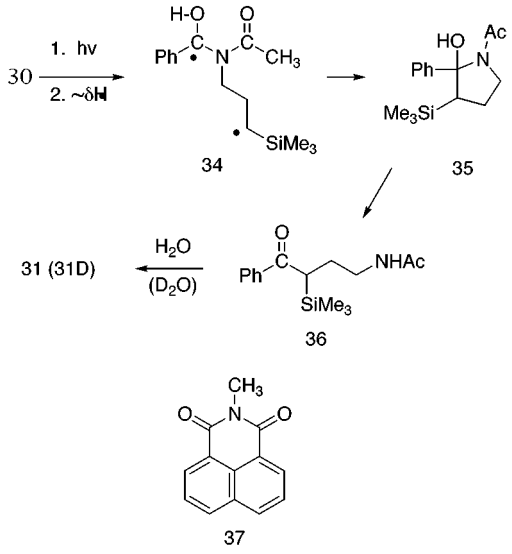
tion and 2+2-dimerization processes into fast and high-yielding SET-promoted photocyclization reactions. Although less pronounced, this solvent change also influences the photoreactivity of substrates in which the TMS moiety is part of an allyl- or benzylsilane function or where the chromophore is a 1,8-naphthalimide or *N*-acetylbenzamide.

The solvent effect on photoreactions of simple (silylalkyl)phthalimides (e.g., **3**, **8**, **10**, and **11**) is associated with a change in reaction mechanism. Excited-state reactions of these substrates in MeCN, like those of other members of the *N*-alkylphthalimide family, follow well-known H-atom abstraction pathways. As illustrated for phthalimide **10** (Scheme 11), competitive γ- and ω-H-atom transfer from the side chain to the excited carbonyl oxygen results in generation of the respective diradical intermediates, **38** and **39**, which serve as precursors of olefins **12** (disproportionation), benzazepinedione **40**, and the silylindolizidine **41**. It is known[8] that substances related to **40**, owing to the extremely high efficiencies of their Norrish-Type II photocleavage reactions, undergo ready secondary photoconversion to benzazepinedione **14**. As a result, it is often difficult to detect these substances as primary photoproducts in phthalimide excited-state reactions. In addition, conversion of the initially formed TMS-substituted indolizidine **41** to **15** occurs by water-induced protodesilylation of the dione tautomer **42** during workup of the photolysate.

In contrast, excited-state reactions of the (silylalkyl)-phthalimides in the aqueous solvent system appear to occur either exclusively or predominantly by an SET−desilylation mechanism. In this route, the phthalimide excited state serves as an electron acceptor and the σ_{C-Si} bond as the donor. Silyl transfer to water can occur either in concert with or following the SET step (Scheme 12).

(8) Kubo, Y.; Tanabe, S. *Bull. Chem. Soc. Jpn*, **1992**, *65*, 2875. Maruyama, K.; Kubo, Y. *J. Org. Chem.* **1985**, *50*, 1426.

Scheme 10



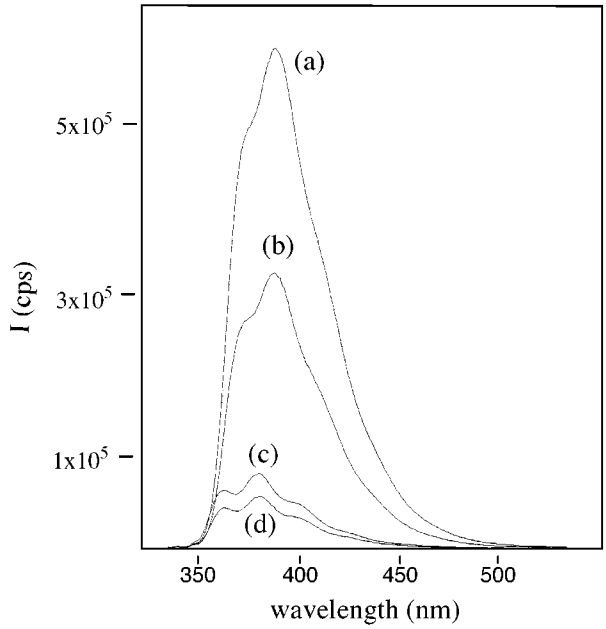


Figure 1. Fluorescence spectra of naphthalimides **28** and **37** in MeCN and 35% H_2O−MeCN at 25 °C: (a) **37** in 35% H_2O−MeCN; (b) **28** in 35% H_2O−MeCN; (c) **37** in MeCN; (d) **28** in MeCN. Excitation is at 311 nm and concentrations (ca. 1 × 10^{-5} M) of all solutions are adjusted to give equal absorbances at this wavelength.

Table 2. Fluorescence Quantum Yields for 1,8-Naphthalimides 28 and 37 at 25 °C

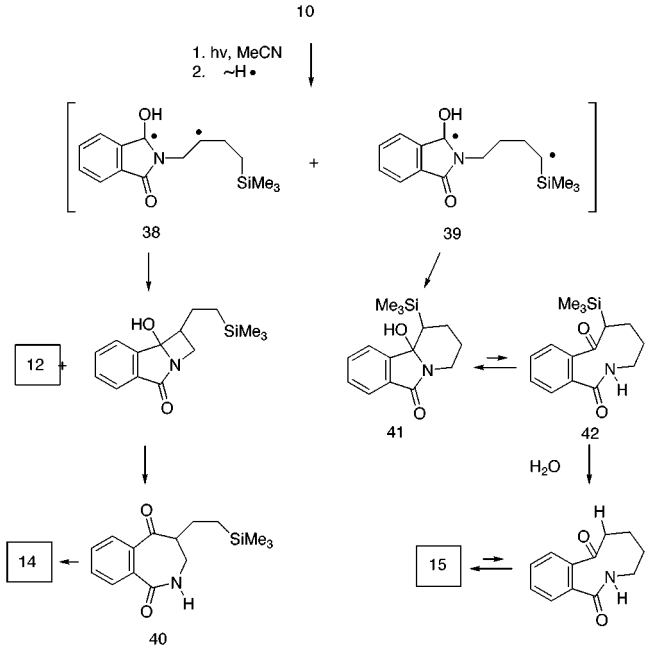
	Φ_f[a]	
naphthalimide	MeCN	35% HOH−MeCN
28	0.01	0.08
37	0.02	0.15

[a] Determined on the basis of the use of **37** (refs 19 and 20) as actinometer.

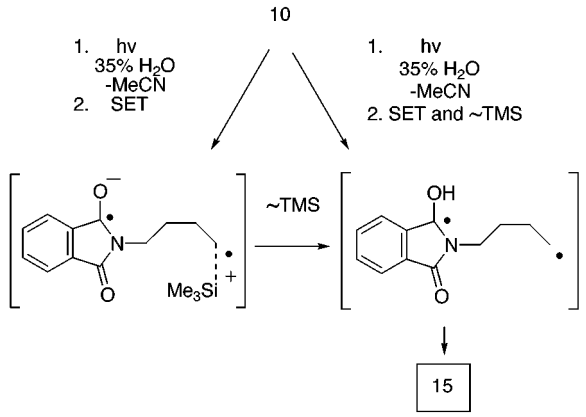
Both pathways lead to formation of the diradical precursor of the non-TMS-containing primary photoproducts (e.g., **10** → **15**).

Possible Sources of the Solvent Effects. A number of plausible arguments can be offered to explain the solvent-dependent mechanistic selectivities of (silylalkyl)-phthalimide photoreactions. For example, it is possible

Scheme 11



Scheme 12



that the role played by water is to control the energetic ordering and rates of interconversion of two differently reactive excited states (e.g., n−π vs π−π*, or singlet vs triplet). It is well-known that H-bonding characteristics of the solvent can influence the relative energies of n−π* and π−π* excited states of aromatic ketones.[9] These energetic priorities, in turn, govern the interrelated singlet excited-state lifetimes and triplet formation efficiencies of carbonyl compounds,[10] since singlet−triplet intersystem crossing (ISC) rates are often strongly dependent on excited-state configurations (S(n−π*) → T(π−π*) fast, while S(π−π*) → T(π−π*) slow).[11]

Some information about the origin(s) of the solvent effect has come from our fluorescence studies with the 1,8-naphthalimides **28** and **37**. The data listed in Table 2 show that the fluorescence quantum efficiencies of these substances are considerably larger in 35% H_2O−MeCN as compared to MeCN, a phenomenon that appears to be associated with naphthalimide π−π* singlet-state lifetimes and not the rate constants for fluorescence (see

(9) Brealey, G. J.; Kasha, M. *J. Am. Chem. Soc.* **1955**, *77*, 4462.
(10) Caldwell, R. A. *Tetrahedron Lett.* **1969**, *26*, 2121. Biszok, L.; Berces, L.; Linschitz, H. *J. Am. Chem. Soc.* **1997**, *119*, 11071.
(11) El-Sayed, M. A. *J. Chem. Phys.* **1963**, *38*, 2834.

above). In addition, fluorescence from the naphthalimide $\pi-\pi^*$ singlet is modestly quenched by intramolecular SET when the σ_{C-Si} bond containing the silylpropyl side chain is present (*i.e.*, **28** vs **37**). Thus, the enhancement seen in the efficiency of photoproduction of **29** in changing the solvent from MeCN to 35% H_2O−MeCN is likely a consequence of a medium effect on the lifetime (longer in 35% H_2O−MeCN) of the SET reactive singlet of **28**.[20]

It has been proposed that $n-\pi^*$ singlet and not triplet excited states of *N*-alkylphthalimides participate in intramolecular hydrogen-atom abstraction reactions.[12] In addition, studies by Coyle[12c] and Davidson[13] have provided convincing evidence for the singlet excited-state origin of intramolecular SET reactions of phthalimides containing electron donor substituted N-substituents. Adding to these observations are the results that show that $\mathbf{8}^{\mathbf{T}}$ reacts by a hydrogen-atom abstraction pathway in MeCN or acetone and an SET−desilylation route in 35% H_2O−MeCN or 35% H_2O−acetone. Together, these observations provide a basis to understand one source of the solvent effects described above. Water may modulate the nature ($n-\pi^*$ vs $\pi-\pi^*$), interconversion rates (k_{ISC}), and thus, selective reactivity (H-atom abstraction vs SET−desilylation) of (silylalkyl)phthalimide excited states. (Silylalkyl)phthalimide $n-\pi^*$ singlets and triplets will likely be of lowest energy in MeCN, while their singlet $\pi-\pi^*$ states could be competitively populated in the aqueous solvent system. If the phthalimide $\pi-\pi^*$ singlets undergo selective SET−desilylation reactions, it would be easy to see how their longer lifetimes (owing to slower ISC) would result in higher reaction quantum yields.

Yet another factor contributing to the observed solvent effect might be associated with alterations in the rates of SET and desilylation. Accordingly, water could function to control the selectivity of these processes by enhancing the rates of intramolecular SET in (silylalkyl)-phthalimide $\pi-\pi^*$ singlets through hydrogen. In addition, if desilylation occurs in concert with one-electron oxidation of the C−Si bond, the greater silophilicity of water would increase the rate[14] of conversion of singlet (silylalkyl)phthalimides to the key diradical intermediates in the cyclization pathways.

A consideration of the energetics of the alkylsilane to phthalimide SET step is germane to this discussion. Calculations based on ground-state reduction potentials and excited-state energies[15] indicate that phthalimide singlet and triplet excited-state reduction potentials in MeCN fall between +2.4 and +1.7 V, respectively, and cyclic voltammetric measurements made on alkylsilanes[16] suggest that these substances are oxidized in MeCN at ca. +2.8 V. On the basis of these values, one can imagine how the aqueous solvent systems, by promoting increases in phthalimide excited-state reduction potentials and decreases in alkylsilane oxidation potentials could cause intramolecular SET to be favorable (i.e., $\Delta G_{SET} < 0$) in the singlet excited states of (silylalkyl)phthalimides. But it is difficult to see how these effects overcome the high (ca. 25 kcal/mol) thermodynamic barrier to SET that exists in the triplet states of these substances.

The results from studies with the (silylpropyl)maleimide **17** clearly demonstrate that the triplet of this substrate undergoes 2+2-photodimerization independent of the solvent used. This suggests that the SET−desilylation reaction occurs in the singlet manifold as a consequence of the control by water of the relative rates of singlet SET−desilylation vs intersystem crossing.

Investigations with the allyl- and benzylsilane-substituted maleimides, **20**, **21**, and **25**, show that the chemical selectivities and efficiencies of these photoreactions are indeed controlled by factors which govern the rates of SET. Accordingly, SET-promoted cyclizations occur exclusively in photoreactions of **20**, **21**, and **25**, independent of the solvent system used. The major difference between these substrates and the (silylpropyl)maleimide **17** resides in the oxidation potentials of their C−Si-containing electron donor group. In contrast to simple alkylsilanes, which have oxidation potentials in the range of +2.8 V,[15] the π-electron donating allyl- and benzylsilanes are more readily oxidized (ca. 1.6−2.0 V).[17] Consequently, thermodynamically driven SET dominates over 2+2-photocycloaddition, H-atom abstraction, and other decay processes available to the excited states of these substrates.

Summary. Although complex in its origin(s), the solvent effects summarized above have an important impact on the preparative utility of (silylalkyl)phthalimide and maleimide excited-state chemistry. Based on the examples provided in this study, it appears to be generally true that a simple change in solvent from MeCN to 35% H_2O−MeCN can be used to alter the photochemical reactivity of these substrates. In the systems probed in the current effort, a change to more protic-silophilic solvent systems transforms less efficient and in some cases less selective hydrogen atom abstraction and 2+2-dimerization type processes into selective, high-yielding SET−desilylation reactions that are potentially applicable to the synthesis of functionalized nitrogen heterocycles.

Experimental Section

General Information. All reported reactions were run under a dried nitrogen atmosphere. Unless otherwise noted, all reagents were obtained from commercial sources and used without further purification. All compounds were isolated as oils and shown to be >90% pure by ^1H and/or ^{13}C NMR unless otherwise noted.

^1H NMR and ^{13}C NMR spectra were recorded by using $CDCl_3$ solutions unless otherwise specified, and chemical shifts are reported in ppm relative to residual $CHCl_3$ at 7.24 ppm (for ^1H NMR) and 77.0 ppm (for ^{13}C NMR). ^{13}C NMR resonance assignments were aided by the use of the DEPT technique to

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determine numbers of attached hydrogens, and ^{1}H NMR coupling constants (*J* values) are reported in Hz. Infrared spectra were obtained using neat liquids unless otherwise specified, and data are reported in units of cm^{-1}. Low (MS) and high (HRMS) mass spectra, reported as *m*/*z* (relative intensity), were recorded by using electron impact ionization (EI) or chemical ionization (CI).

Photochemical reactions were conducted by using an apparatus consisting of a 450-W medium-pressure mercury lamp surrounded by a glass filter and within a quartz, water-cooled well that was purged with O_2-free N_2 both before and during irradiation. Photochemical reaction progress was monitored by gas chromatography, TLC, or ^{1}H NMR.

Irradiation of *N*-[4-(Trimethylsilyl)butyl]phthalimide (10) in CH_3CN. A solution of *N*-[4-(trimethylsilyl)butyl]-phthalimide (**10**) (500 mg, 1.82 mmol) in 200 mL of CH_3CN was irradiated with Vycor-filtered light under N_2 for 6 h (70% conversion of **10**). Concentration of the photolysate gave a residue that was subjected to column chromatography (silica, ethyl actate:hexane = 1:3), yielding 47 mg (14%) of **12**, 41 mg (16%) of **15** and 86 mg (38%) of **14**

12: mp 96−97 °C (CH_2Cl_2; ^{1}H NMR −0.02 (s, 9H, $SiMe_3$), 1.25 (s, 1H, OH), 1.44 (d, 2H, *J* = 8.1, C*H*$_2$SiMe$_3$), 3.64 (dd, 1H, *J* = 8.4 and *J* = 14.6, NCH$_2$), 4.13 (dd, 1H, *J* = 4.9 and *J* = 14.7, NCH$_2$), 5.13−5.26 (m, 1H, NCH$_2$CH=C*H*), 5.62−5.74 (m, 2H, C(OH)*H*NCH$_2$C*H*=CH), 7.36−7.62 (m, 4H, aromatic); ^{13}C NMR −1.5 ($SiMe_3$), 23.3 (*C*H$_2$SiMe$_3$), 41.5 (NCH$_2$), 81.4 (COH), 123.6 and 123.8 (CH, alkenic), 122.7, 130.0, 132.5, and 132.6 (CH, aromatic), 132.0 and 144.5 (C, aromatic), 167.6 (C=O); IR (KBr) 3100−3550 (br OH), 1680 (C=O); MS (EI) *m*/*z* (rel intensity) 275 (M$^+$, 34), 73 (100); HRMS (EI) *m*/*z* 275.1337 ($C_{15}H_{21}NO_2Si$ requires 275.1342).

15: mp 154−155 °C (acetone); ^{1}H NMR 1.19−1.31 (m, 2H, NCH$_2$CH$_2$C*H*$_2$), 1.70−1.77 (m, 2H, NCH$_2$C*H*$_2$), 2.05 (dd, 1H, *J* = 3.2 and *J* = 10.3, C(OH)C*H*$_2$), 2.39 (d, 1H, *J* = 13.2, NCH$_2$), 2.99 (dd, 1H, *J* = 3.1 and *J* = 12.9, C(OH)C*H*$_2$), 3.92 (dd, 1H, *J* = 4.7 and *J* = 12.8, NCH$_2$), 4.11 (s, 1H, OH), 7.28−7.48 (m, 2H, aromatic), 7.51−7.54 (m, 2H, aromatic); ^{13}C NMR 20.1 (NCH$_2$CH$_2$*C*H$_2$), 25.5 (NCH$_2$*C*H$_2$), 36.0 (C(OH)*C*H$_2$), 36.7 (NCH$_2$), 86.8 (COH), 121.8, 123.6, 129.4, and 132.4 (CH, aromatic), 130.7 and 149.1 (C, aromatic), 165.8 (C=O); IR (KBr) 3200−3500 (br OH), 1670 (C=O); MS (EI) *m*/*z* (rel intensity) 203 (M$^+$, 100), 174 (74); HRMS (EI) *m*/*z* 203.0944 ($C_{12}H_{13}NO_2$ requires 203.0946).

Irradiation of *N*-[4-(Trimethylsilyl)butyl]phthalimide (10) in 35% H_2O−CH_3CN. A solution of **10** (150 mg, 0.54 mmol) in a solution of 39 mL of CH_3CN and 21 mL of H_2O was irradiated with Vycor-filtered light under N_2 for 20 min (76% conversion of **10**). Concentration of the photolysate gave a residue that was subjected to column chromatography (silica, ethyl acetate:hexane = 1:3), yielding 79 mg (94%) of **15**.

Irradiation of *N*-[5-(Trimethylsilyl)pentyl]phthalimide (11) in CH_3CN. A solution of *N*-[5-(trimethylsilyl)pentyl)]-phthalimide (**11**) (400 mg, 1.38 mmol) in 200 mL of CH_3CN was irradiated with Vycor-filtered light under N_2 for 2.5 h (75% conversion of **11**). Concentration of the photolysate gave a residue that was subjected to column chromatography (silica, ethyl actate:hexane = 1:3), yielding 99 mg (33%) of **13**, 9 mg (4%) of **16**, and 67 mg (37%) of **14**.[18]

16: mp 136−137 °C (acetone); ^{1}H NMR 0.59−0.71 (m, 1H, NCH$_2$CH$_2$C*H*$_2$), 1.23−1.72 (m, 5H, NCH$_2$(C*H*$_2$)$_3$), 1.98−2.11 (m, 1H, C(OH)C*H*$_2$), 2.50 (dd, 1H, *J* = 7.7 and *J* = 14.6, C(OH)-C*H*$_2$), 2.98 (dd, 1H, *J* = 2.6 and *J* = 10.9, NCH$_2$), 3.27 (d, 1H, *J* = 14.2, NCH$_2$), 4.60 (s, 1H, OH), 7.32−7.58 (m, 4H, aromatic); ^{13}C NMR 22.7 (NCH$_2$CH$_2$*C*H$_2$), 27.5 (C(OH)-CH$_2$*C*H$_2$), 30.2 (NCH$_2$*C*H$_2$), 39.1 (C(OH)*C*H$_2$), 39.2 (NCH$_2$), 91.6 (COH), 122.4, 123.3, 129.6, and 132.9 (CH, aromatic), 131.5 and 148.4 (C, aromatic), 168.3 (C=O); IR (KBr) 3200−3550 (br OH), 1710 (C=O); MS (EI) *m*/*z* (rel intensity) 217 (M$^+$, 85), 160 (100); HRMS (EI) *m*/*z* 217.1107 ($C_{13}H_{15}NO_2$ requires 217.1103).

13: mp 101−102 °C (CH_2Cl_2); ^{1}H NMR −0.05 (s, 9H, $SiMe_3$), 0.50−0.58 (m, 2H, C*H*$_2$SiMe$_3$), 1.94−2.05 (m, 2H, C*H*$_2$CH$_2$-SiMe$_3$), 3.65 (dd, 1H, *J* = 8.0 and *J* = 15.0, NCH$_2$), 3.85 (s, 1H, OH), 4.07 (dd, 1H, *J* = 4.9 and *J* = 14.9 Hz, NCH$_2$), 5.29−5.43 (m, 1H, NCH$_2$CH=C*H*), 5.66−5.79 (m, 2H, C(OH)-*H*NCH$_2$C*H*=CH), 7.37−7.61 (m, 4H, aromatic); ^{13}C NMR −1.2 ($SiMe_3$), 16.5 (CH$_2$SiMe$_3$), 26.9 (*C*H$_2$CH$_2$SiMe$_3$), 41.2 (NCH$_2$), 81.5 (COH), 123.6 and 123.8 (CH, alkenic), 122.9, 130.1, 132.6, and 138.4 (CH, aromatic), 131.9 and 144.5 (C, aromatic), 167.6 (C=O); IR (KBr) 3100−3550 (br OH), 1680 (C=O); MS (EI) *m*/*z* (rel intensity) 289 (M$^+$, 20), 73 (100); HRMS (EI) *m*/*z* 289.1496 ($C_{16}H_{23}NO_2Si$ requires 289.1498).

Irradiation of *N*-[5-(Trimethylsilyl)pentyl]phthalimide (11) in 35% H_2O−CH_3CN. A solution of **11** (250 mg, 0.86 mmol) in 65 mL of CH_3CN and 35 mL of H_2O was irradiated with Vycor-filtered light under N_2 for 30 min (84% conversion of **11**). Concentration of the photolysate gave a residue that was subjected to column chromatography (silica, ethyl acetate: hexane = 1:3), yielding 98 mg (58%) of **16** and 44 mg (35%) of **14**.

Irradiation of *N*-[3-(Trimethylsilyl)propyl]maleimide (17) in CH_3CN. A solution of *N*-[3-(trimethylsilyl)propyl]-maleimide (**17**, 90 mg, 0.43 mmol) in 50 mL of CH_3CN was irradiated with Pyrex-filtered light under N_2 for 2 h (84% conversion of **17**). Concentration of the photolysate gave a residue that was crystallized (CH_2Cl_2), yielding 74 mg (98%) of **19**: mp 244−246 °C (CH_2Cl_2); ^{1}H NMR −0.12 (s, 18H, $SiMe_3$), 0.43−0.52 (m, 4H, C*H*$_2$SiMe$_3$), 1.50−1.66 (m, 4H, NCH$_2$C*H*$_2$), 3.38 (s, 4H, 4CH), 3.56 (t, 4H, *J* = 7.8, 2NCH$_2$); ^{13}C NMR −1.8 ($SiMe_3$), 13.7 (*C*H$_2$SiMe$_3$), 22.3 (NCH$_2$*C*H$_2$), 41.4 (CH), 42.5 (NCH$_2$), 174.8 (C=O); IR (KBr) 1700 (C=O); MS (EI) *m*/*z* (rel intensity) 422 (M$^+$, 3), 105 (100); HRMS (EI) *m*/*z* 422.2059 ($C_{20}H_{34}N_2O_4Si_2$ requires 422.2057).

Irradiation of *N*-[3-(Trimethylsilyl)propyl]maleimide (17) in 35% H_2O−CH_3CN. A solution of *N*-[3-(trimethylsilyl)-propyl]maleimide (**17**) (320 mg, 1.52 mmol) in a solution of 110 mL of CH_3CN and 60 mL of H_2O was irradiated with Pyrex-filtered light under N_2 for 1.6 h (71% conversion of **17**). Concentration of the photolysate gave a residue that was subjected to column chromatography (silica, ethyl acetate: hexane = 1:5), yielding 96 mg (64%) of **18**: mp 122−124 °C (acetone); ^{1}H NMR 1.52−1.68 (m, 1H, NCH$_2$C*H*$_2$), 2.04−2.17 (m, 1H, NCH$_2$C*H*$_2$), 2.22−2.34 (m, 1H, C(OH)C*H*$_2$), 2.49−2.64 (m, 1H, C(OH)C*H*$_2$), 2.74 (s, 1H, OH), 3.26−3.55 (m, 2H, NCH$_2$), 5.93 and 7.10 (two d, 2H, *J* = 5.7, CH=CH); ^{13}C NMR-($CDCl_3$) 28.3 (NCH$_2$*C*H$_2$), 33.9 (C(OH)*C*H$_2$), 41.8 (NCH$_2$), 98.5 (COH), 126.6 and 150.0 (CH=CH), 174.2 (C=O); IR (KBr) 3150−3500 (br OH), 1680 (C=O); MS (EI) *m*/*z* (rel intensity) 139 (M$^+$, 100); HRMS (EI) *m*/*z* 139.0638 ($C_7H_9NO_2$ requires 139.0633).

Irradiation of *N*-[2-((Trimethylsilyl)methyl)prop-2-enyl]maleimide (20) in CH_3CN. A solution of *N*-[(2-((trimethylsilyl)methyl)-2-propenyl]maleimide (**20**) (400 mg, 1.79 mmol) in 200 mL of CH_3CN was irradiated with Pyrex-filtered light under N_2 for 27 h (63% conversion of **20**). Concentration of the photolysate gave a residue that was subjected to column chromatography (silica, ethyl actate:hexane = 1:2), yielding 116 mg (68%) of **22**: mp 104−105 °C (acetone); ^{1}H NMR 2.02 (s, 1H, OH), 2.40 (d, 1H, *J* = 15.5, C(OH)C*H*$_2$), 2.73 (d, 1H, *J* = 15.5, C(OH)C*H*$_2$), 3.80 (d, 1H, *J* = 15.4, NCH$_2$), 4.17 (d, 1H, *J* = 15.4, NCH$_2$), 5.09−5.10 (m, 2H, C=CH$_2$), 5.97 (dd, 2H, *J* = 1.4 and *J* = 5.8, C*H*=CHCO), 7.13 (dd, 1H, *J* = 1.6 and *J* = 5.7, CH=C*H*CO); ^{13}C NMR 41.8 (C(OH)CH$_2$), 46.2 (NCH$_2$), 97.1 (COH), 109.4 (C=*C*H$_2$), 147.8 (*C*=CH$_2$), 126.7 and 149.9 (CH=CH), 172.9 (C=O); IR (KBr) 3100−3550 (br OH), 1700 (C=O); MS (EI) *m*/*z* (rel intensity) 151 (M$^+$, 100), 132 (69); HRMS (EI) *m*/*z* 151.0636 ($C_8H_9NO_2$ requires 151.0633).

Irradiation of *N*-[2-((Trimethylsilyl)methyl)prop-2-enyl]maleimide (20) in 35% H_2O−CH_3CN. A solution of *N*-[(2-(trimethylsilyl)methyl)-2-propenyl]maleimide (**20**, 220 mg, 0.99 mmol) in 65 mL of CH_3CN and 35 mL of H_2O was irradiated with Pyrex-filtered light under N_2 for 7 h (57% conversion of **20**). Concentration of the photolysate gave a residue that was subjected to column chromatography (silica, ethyl acetate:hexane = 1:2), yielding 60 mg (71%) of **22**.

Irradiation of *N*-[3-((Trimethylsilyl)methyl)but-3-enyl]-maleimide (21) in CH_3CN. A solution of *N*-[(3-((trimethylsilyl)methyl)but-3-enyl]maleimide (**21**) (500 mg, 2.11 mmol) in 200 mL of CH_3CN was irradiated with Pyrex-filtered light

under N_2 for 3 h (100% conversion of **21**). Concentration of the photolysate gave a residue that was subjected to column chromatography (silica, ethyl actate:hexane = 1:2), yielding 230 mg (66%) of **23** and 56 mg (11%) of **24**.

23: mp 137−138 °C (acetone); ^{1}H NMR 2.07 (d, 2H, J = 13.2, C(OH)CH_2), 2.32 (d, 1H, J = 12.7, NCH_2CH_2), 2.70 (d, 1H, J = 13.1, NCH_2CH_2), 2.97 (dd, 1H, J = 3.9 and J = 12.6, NCH_2), 3.92 (s, 1H, OH), 4.09 (dd, 1H, J = 5.9 and J = 12.7, NCH_2), 5.02 (d, 2H, J = 9.7, C=CH_2), 6.02 and 7.00 (two d, 2H, J = 5.9, CH=CH); ^{13}C NMR 33.8 (C(OH)CH_2), 37.0 (NCH_2CH_2), 43.9 (NCH_2), 89.2 (COH), 114.5 (C=CH_2), 140.4 (C=CH_2), 126.9 and 150.2 (CH=CH), 167.9 (C=O); IR (KBr) 3100−3500 (br OH), 1670 (C=O); MS (EI) *m*/*z* (rel intensity) 165 (M^+, 64), 110 (100); HRMS (EI) *m*/*z* 165.0794 ($C_9H_{11}NO_2$ requires 165.0790).

24: mp 60−61 °C (acetone); ^{1}H NMR 0.04 (s, 9H, $SiMe_3$), 1.27 (d, 1H, J = 8.3, C($OSiMe_3$)CH_2), 2.01 (d, 1H, J = 13.2, C($OSiMe_3$)CH_2), 2.30 (d, 1H, J = 13.3, NCH_2CH_2), 2.62 (d, 1H, J = 13.3, NCH_2CH_2), 2.89 (dd, 1H, J = 3.4 and J = 12.8, NCH_2), 4.17 (dd, 1H, J = 6.0 and J = 12.8, NCH_2), 4.93 (d, 2H, J = 16.9, C=CH_2), 6.15 and 6.99 (two d, 2H, J = 5.9, CH=CH); ^{13}C NMR 1.9 ($SiMe_3$), 33.8 (C($OSiMe_3$)CH_2), 37.2 (NCH_2-CH_2), 46.4 (NCH_2), 90.6 (C($OSiMe_3$)), 113.6 (C=CH_2), 140.6 (C=CH_2), 127.2 and 150.3 (CH=CH), 167.5 (C=O); IR (KBr) 1700 (C=O); MS (EI) *m*/*z* (rel intensity) 237 (M^+, 72), 74 (100); HRMS (EI) *m*/*z* 237.1175 ($C_{12}H_{19}NO_2Si$ requires 237.1185).

Irradiation of *N*-[3-((Trimethylsilyl)methyl)but-3-enyl]-maleimide (21) in 35% H_2O−CH_3CN. A solution of *N*-[(3-(trimethylsilyl)methyl)-3-butenyl]maleimide (**21**) (300 mg, 1.26 mmol) in 65 mL of CH_3CN and 35 mL of H_2O was irradiated with Pyrex-filtered light under N_2 for 2 h (100% conversion of **21**). Concentration of the photolysate gave a residue that was subjected to column chromatography (silica, ethyl acetate: hexane = 1:2), yielding 172 mg (82%) of **23**.

Irradiation of *N*-[2-((Trimethylsilyl)methyl)benzyl]-maleimide (25) in CH_3CN. A solution of *N*-[2-((trimethylsilyl)methyl)benzyl]maleimide (**25**) (500 mg, 2.11 mmol) in 200 mL of CH_3CN was irradiated with Pyrex-filtered light under N_2 for 5 h (61% conversion of **25**). Concentration of the photolysate gave a residue that was subjected to column chromatography (silica, ethyl acetate:hexane = 1:2), yielding 102 mg (37%) of **27** and 69 mg (34%) of **26**.

26: mp 132−133 °C (acetone); ^{1}H NMR 2.87 (d, 1H, J = 15.9, C(OH)CH_2), 3.22 (d, 1H, J = 15.9, C(OH)CH_2), 4.28 (d, 1H, J = 16.8, NCH_2), 4.94 (d, 1H, J = 16.8, NCH_2), 6.04 (d, 2H, J = 5.9, CH=CH), 7.10−7.26 (m, 4H, aromatic); ^{13}C NMR 38.4 (C(OH)CH_2), 40.0 (NCH_2), 87.7 (COH), 126.9, 127.0, 127.4 and 127.6 (CH, aromatic), 130.2 (CH=CH), 130.3 and 131.1 (C, aromatic); IR (KBr) 3100−3450 (br OH), 1670 (C=O); MS (EI) *m*/*z* (rel intensity) 210 (M^+, 65), 104 (100); HRMS (EI) *m*/*z* 201.0788 ($C_{12}H_{11}NO_2$ requires 201.0799).

27: mp 101−102 °C (acetone); ^{1}H NMR 0.00 (s, 9H, $SiMe_3$), 2.83 (d, 1H, J = 15.5, C($OSiMe_3$)CH_2), 3.18 (d, 1H, J = 15.6, C($OSiMe_3$)CH_2), 4.27 (d, 1H, J = 16.9, NCH_2), 5.05 (d, 1H, J = 16.9, NCH_2), 6.20 (d, 2H, J = 5.9, CH=CH), 7.11−7.25 (m, 4H, aromatic); ^{13}C NMR 1.8 ($SiMe_3$), 40.4 (C($OSiMe_3$)CH_2), 41.1 (NCH_2), 88.9 (C($OSiMe_3$)), 126.7, 127.1, 127.3, and 127.5 (CH, aromatic), 130.0 (CH=CH), 131.0 and 131.4 (C, aromatic); IR (KBr) 1710 (C=O); MS (EI) *m*/*z* (rel.intensity) 273 (M^+, 75), 104 (100); HRMS (EI) *m*/*z* 273.1188 ($C_{15}H_{19}NO_2Si$ requires 273.1185).

Irradiation of *N*-[2-((Trimethylsilyl)methyl)benzyl]-maleimide (25) in 35% H_2O−CH_3CN. A solution of *N*-[2-((trimethylsilyl)methyl)benzyl]maleimide (**64**) (220 mg, 0.81 mmol) in 39 mL of CH_3CN and 21 mL of H_2O was irradiated with Pyrex-filtered light under N_2 for 4 h (54% conversion of **64**). Concentration of the photolysate gave a residue that was subjected to column chromatography (silica, ethyl acetate: hexane = 1:2), yielding 4 mg (3%) of **27** and 77 mg (88%) of **26**.

Irradiation of *N*-[3-(Trimethylsilyl)propyl]-1,8-naphthalimide (28) in 30% H_2O (or D_2O)−MeCN. A solution of *N*-[3-(trimethylsilyl)propyl]-1,8-naphthalimide (**28**) (169 mg, 0.54 mmol) in 40 mL of H_2O and 100 mL of MeCN was irradiated with Vycor-filtered light under N_2 for 6.5 h. The photolysate was concentrated in vacuo, giving a residue that was subjected to preparative TLC (silica, ethyl acetate) to yield 41 mg (17%) of **29**: ^{1}H NMR 0.90 (m, 2H), 1.28 (m, 1H), 1.70 (s, 1H, OH), 1.95 (m, 1H), 2.60 (m, 1H), 3.13 (m, 2H), 3.47 (m, 1H), 3.73 (t, 1H), 4.44 (m 3H), 7.25 (m, 2H), 7.47 (m, 2H), 7.71 (m, 4H), 7.97 (m, 2H), 8.20 (d, 1H), 8.54 (d,1H); ^{13}C NMR 29.7, 30.0, 30.5, 44.3 and 45.9 (CH_2), 48.3 (CH), 70.1 (C), 118.3, 124.9, 125.2, 127.6, 131.8, 132.5, 133.9, 134.6, and 137.1 (Ar C), 119.7, 123.2, 126.3, 126.4, 127.0, 127.2, 128.0, 128.2, 130.5, and 132.1 (Ar CH), 162.4 and 159.3 (C=O); MS (FAB) *m*/*z* 441 (M^+ − H_2O, 71), 440 (49); HRMS (FAB) *m*/*z* 441.1633 ($C_{30}H_{21}N_2O_2$ requires 441.1603).

Irradiation of *N*-Acetyl-*N*-[3-(trimethylsilyl)propyl]-benzamide (30) in 30% H_2O−MeCN and MeCN. A solution of **30** (200 mg, 0.72 mmol) in 200 mL of 30% H_2O−MeCN was irradiated with Corex-filtered light under N_2 for 2 h (72% conversion of **30**). The photolysate was concentrated in vacuo, giving a residue that was subjected to preparative TLC (silica gel, ethyl acetate:hexane = 2:1) to yield 30 mg of **31** (28%), 11 mg of **32** (12%), and 7 mg of **33** (7%).

A solution of **30** (200 mg, 0.72 mmol) in 200 mL of MeCN was irradiated with Corex-filtered light under N_2 for 3 h (63% conversion of **30**). The photolysate was concentrated in vacuo, giving a residue that was subjected to preparative TLC (silica gel, ethyl acetate:hexane = 2:1) to yield 53 mg of **31** (57%), 22 mg of **32** (29%), and 10 mg of **33** (14%).

A solution of **30** (200 mg, 0.72 mmol) in 200 mL of rigorously dried MeCN was irradiated with Corex-filtered light under N_2 for 3 h (80% conversion of **30**). After irradiation, 1.0 mL of D_2O was added. The photolysate was concentrated in vacuo, giving a residue that was subjected to preparative TLC (silica gel, ethyl acetate:hexane = 2:1) to yield 14 mg of **31** (12%), a trace of **32**, 31 mg of a substance that rapidly transforms to **31D**, and 7 mg of **33** (8%).

A solution of **30** (200 mg, 0.72 mmol) in 70 mL of D_2O and 130 mL of MeCN was irradiated with Corex-filtered light under N_2 for 2 h. The photolysate was concentrated in vacuo, giving a residue that was subjected to preparative TLC (silica gel, ethyl acetate:hexane = 2:1) to yield 30 mg of **30** (15%), 29 mg of **32** (12%), 14 mg of **31D** (11%), and 8 mg of **33** (9%).

31: ^{1}H NMR 1.95 (m, CH_3CO and PhCOCH_2), 3.03 (t, J = 5.5, 2H, CH_2), 3.31 (ABq, J = 5.3 and 4.6, CH_2NH), 6.48 (s, 1H, NH), 7.48 (m, 3H, Ar), 7.91 (m, 2H, Ar); ^{13}C NMR 22.9 (CH_2Si), 23.5 (CH_3), 35.9 (CH_2), 39.4 (CH_2N), 128.0, 128.6, 133.2, 136.6, 170.8 (C=O), 200.0 (C=O); IR ($CHCl_3$) 1674, 1643; MS (EI) *m*/*z* 205 (M^+, 0.2), 105 (100); HRMS (EI) *m*/*z* 205.1099 ($C_{12}H_{15}NO_2$ requires 205.1103).

31D: ^{1}H NMR 1.97 (m, CH_3CO and PhCOCH_2), 3.03 (m, 1H, CHD), 3.33 (ABq, 2H, J = 6 Hz, CH_2NH), 5.71 (s, 1H, NH), 7.44 (m, 3H, Ar), 7.94 (d, 2H, Ar).

32: ^{1}H NMR 0.03 (s, 9H, $SiMe_3$), 2.00 (s, 3H, Me), 3.89 (m, 2H, C=CCH_2), 5.52 (s, 1H, NH), 5.77 (d, J = 19, 1H, HC=C), 5.98 (dt, J = 19, 5, 1H, C=CH); ^{13}C NMR −1.4 ($SiMe_3$), 23.3 (CH_3), 44.0 (CH_2), 131.3 (HC=), 141.5 (=CH), 168.9 (C=O); IR ($CHCl_3$) 1744, 1691.

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Supporting Information Available: Experimental procedures are given for preparation of the substrates for the photochemical reactions. Spectroscopic data in the form of ^{1}H and ^{13}C NMR spectra for all previously unreported compounds (**10**−**13** and **15**−**32**) are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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