Investigations of Novel Azomethine Ylide-Forming Photoreactions of *N*-Silylmethylimides

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The scope of a recently discovered (Yoon, E. C. et al. *J. Am. Chem. Soc.* **1995**, *117*, 2698), azomethine ylide-forming photoreaction has been explored by probing the excited state chemistry of several *N*-trimethylsilylmethyl substituted cyclic and acyclic imides and amide analogs. Photolysis of *N*-[(trimethylsilyl)methyl]maleimide (**4**) in acetonitrile leads to efficient production of the tricyclic product **16**, formed by trapping of the photogenerated azomethine ylide intermediate **15** through cycloaddition with **4**. Irradiation **4** in solutions containing high concentrations of the dipolarophiles, acrylonitrile or fumaronitrile, results in production of the products (**19–21** and **23–24**, respectively) arising by cycloaddition of the ylide **15** with the added dipolarophiles. In contrast, photolysis of the nonconjugated cyclic imide, *N*-[(trimethylsilyl)methyl]succinimide (**5**), brings about *N*-acyl migration resulting in the exclusive production of the unstable, iminolactone **30**. On the other hand, acyclic, *N*-trimethylsilylmethyl aroyl imides **6–8** undergo the excited state C to O silyl migration reaction to produce azomethine ylide intermediates **35**. Both in the presence or absence of added dipolarophiles, these ylides undergo electrocyclization to form transient aziridine intermediates **36** which react further by ring opening to generate *N*-phenacylamide products **32–34**. In contrast, the nonconjugated imide, *N*-[(trimethylsilyl)methyl]-*N*-acetylacetamide (**9**), is unreactive upon irradiation. Similarly, simple *N*-[(trimethylsilyl)methyl] amides **10–13**, while being photochemically labile, do not react to form "trappable" ylide intermediates upon irradiation. The results outlined above are presented and discussed in terms of the scope and limitations of the new, azomethine ylide-forming photoreaction of silylmethyl imides.

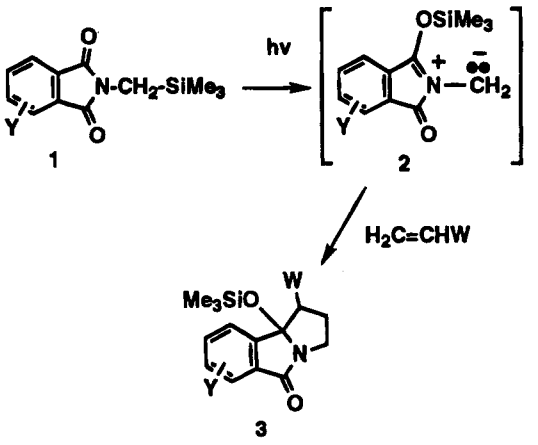
Introduction

In a recent publication,[1] we described the results of an investigation in which a novel, azomethine ylide-forming, photoreaction of *N*-(silylmethyl)phthalimides **1** and related *N*-phthaloyl α-amino acid and phthalimidophenylethanol derivatives was discovered. As shown in Scheme 1 for the silyl analogs, this process involves excited state C to O migration of a TMS-group to generate azomethine ylides **2**. Dipolarophile trapping of these intermediates results in efficient production of pyrrolizidine ring-containing adducts of general structure **3**. The cycloaddition processes are attended by high degrees of regiochemical and stereochemical control. Our continuing studies of this new photochemical reaction have led to observations which demonstrate its generality, limitations, and synthetic potential. Below are presented the results of this investigation in which the photochemistry of several *N*-trimethylsilylmethyl imides including cyclic unsaturated and saturated systems (**4** and **5**), symmetric and unsymmetric acyclic analogs (**6–9**), potentially related silylmethyl amides (**10–13**), and carboxylic acid derivative **14** have been explored.

Results and Discussion

Photochemistry of Silylmethyl-Succinimide and -Maleimide Systems. The silylmethyl imides **4** and **5** were subjected to photochemical study to determine if

Scheme 1



the azomethine ylide-forming silyl migration reaction uncovered for phthalimide analogs (Scheme 1)[1] would occur in cyclic nonaromatic and/or nonconjugated imides. These substances were prepared by two different procedures. In the first, silylmethylation of succinimide was efficiently (64%) performed by reaction with NaH/MeCN and $TMSCH_2I$ to furnish the desired saturated cyclic imide **5**. When maleimide is subjected to these same reaction conditions, the target imide **4** is not generated but instead extensive decomposition of the starting material occurs. However, an alternative approach involving Mitsunobu[2] coupling (Ph_3P/DEAD/THF) of maleimide with $TMSCH_2OH$ does provide the cyclic unsaturated imide **4** in high (71%) yield.

[⊗] Abstract published in *Advance ACS Abstracts*, April 1, 1995.

(1) 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*, 2698.

(2) Mitsunobo, O. *Synthesis* **1981**, 1.

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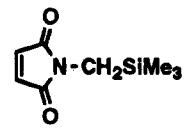

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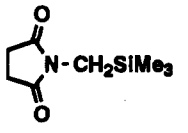

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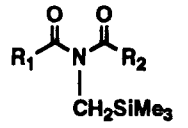
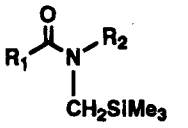
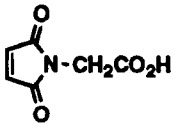


6 (R_1=R_2=Ph)
7 (R_1=Ph, R_2=Me)
8 (R_1=p-MeOC$_6$H$_4$, R_2=Me)
9 (R_1=R_2=Me)

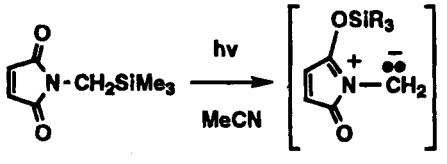


10 (R_1=Ph, R_2=Me)
11 (R_1=Ph, R_2=Bn)
12 (R_1=R_2=Me)
13 (R_1=R_2=Ph)



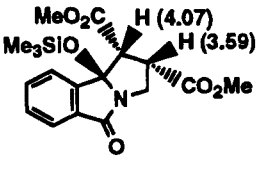
14

Direct irradiation (λ > 290 nm) of silylmethyl-maleimide **4** (0.01 M in MeCN) leads to efficient production of the tricyclic product **16** (92%, isolated, mp 150–152 °C). This substance is formed as a single diastereomer to which the cis-syn stereochemistry is assigned. This assignment is founded on the highly endo-selective nature noted for dipolar cycloaddition reactions of analogous ylides and on comparisons of spectroscopic data for closely related substances (*e.g.*, the adduct **17A** formed by photoreaction of the silylmethylphthalimide **1** (Y = H) in the presence of dimethyl maleate).[1]

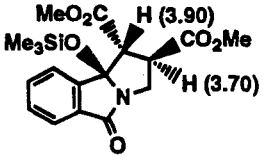


4 15

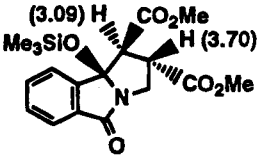
16



17A

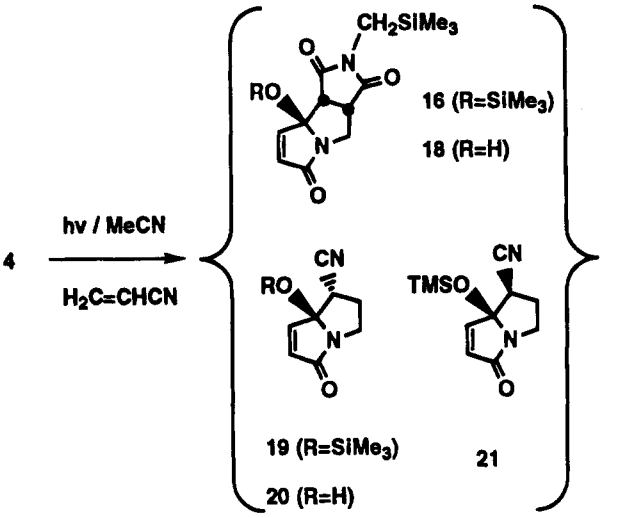


17B



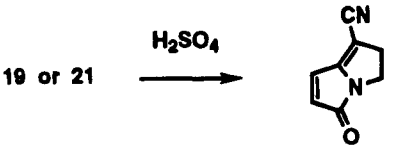
17B

The tricyclic product **16** arises in this photoreaction by cycloaddition of the dipolarophilic starting maleimide **4** to the intermediate ylide **15**, formed by the excited state silyl-migration process. The intermediate ylide **15** can be trapped by cycloaddition with other dipolarophiles. For example, preparative irradiation of maleimide **4** (0.013 M) in an MeCN solution containing 2.3 M acrylonitrile followed by silica gel chromatography results in the isolation of tricyclic adduct **16** (6%) and its desilylated derivative **18** (4%) along with the crossed cycloaddition products **19**–**21** (43%, *ca.* 8:1:1 ratio). ^{1}H NMR analysis of crude photolysates arising by irradiation of CD_3CN solutions of **4** (0.013 M) containing 0.13, 1.3 and 13 M acrylonitrile shows that **16**, **19**, and **21** are produced in respective ratios of 2.6, 0.2, and 0.04.



16 (R=SiMe$_3$)
18 (R=H)
19 (R=SiMe$_3$)
20 (R=H)
21

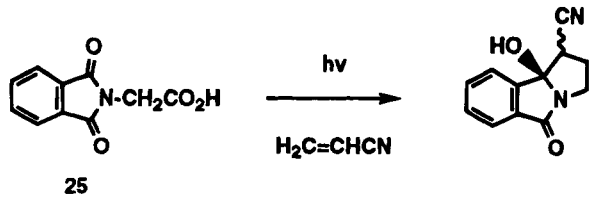
The above results indicate that the desilylated products **18** and **20** must arise in the preparative process by hydrolysis of the primary adducts during chromatographic separation. In accord with this proposal is the observation that **19** is transformed to **20** by acid treatment (1 N H_2SO_4, THF, 25 °C). Also, the epimeric nature of adducts **19** and **21** is evidenced by both their ^{1}H NMR spectroscopic properties and their independent conversion to the same unsaturated pyrrolizidine **22** upon treatment with concentrated sulfuric acid.



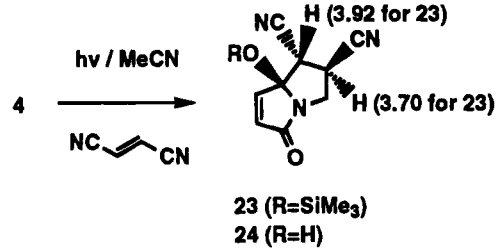
22

The observations described above clearly demonstrate that the cyclic, unsaturated silylmethyl imide **4**, like the related phthalimides,[1] undergoes photoinduced C to O silyl migration efficiently. In addition, the results show that the highly electron deficient maleimide **4** is more reactive than acrylonitrile in dipolar cycloaddition reactions with azomethine ylide intermediate **15**. Further information about the dipolarophile reactivity of **15** has come from an exploration of the photoreaction of maleimide **4** with fumaronitrile. Irradiation of an MeCN solution of **4** (4 mM) and fumarontrile (0.06 M) followed by silica gel chromatography affords the crossed adducts **23** and **24** (83%, *ca.* 1:1.8 ratio), exclusively, both as single stereoisomers. The stereochemical assignment to **23** is based on the previously observed, highly endo-stereose-

Scheme 2

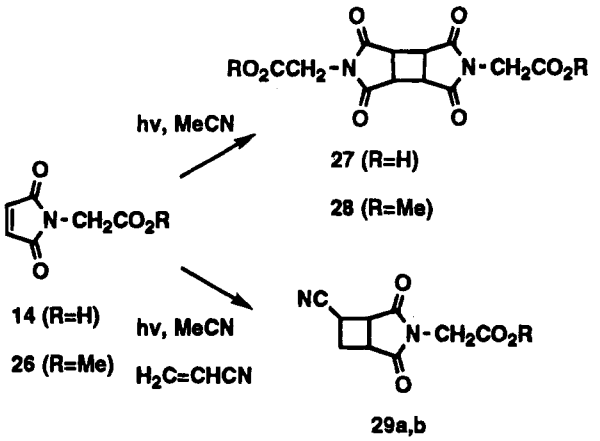


lective and stereospecific (retention) nature of these azomethine ylide cycloaddition reactions in the related phthalimide series.[1] In addition, comparisons of the ^1H and ^{13}C NMR spectroscopic properties of **23** with those of closely related adducts produced by dimethyl fumarate and maleate trapping of a corresponding silylmethylphthalimide-derived ylide[1] provide further evidence for the assignment. As seen by viewing the ^1H NMR data shown next to the CN (for **23**) and CO_2Me (for **17A** and **17B**) substituted pyrrolidine ring, methine protons, hydrogens located on the exo-face of these substances, resonate at lower fields than those disposed on the endo-face. This is due to the anisotropic shielding effects associated with the olefin/arene moieties in these substances.



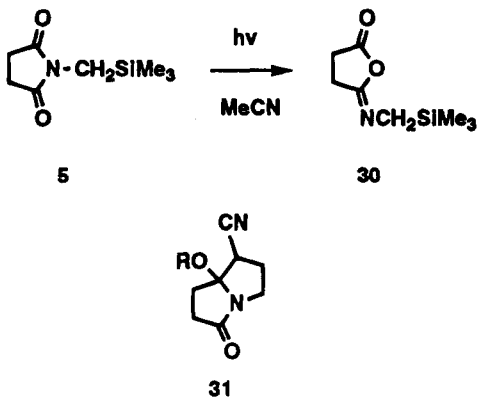
In our earlier investigations, we showed that *N*-phthaloyl α-amino acids undergo decarboxylative azomethine ylide forming photoreactions.[1] This process is exemplified by the phototransformation of phthaloylglycine **25** to the corresponding dipolar adduct (Scheme 2). To determine if this photochemical reactivity pattern is generalizable to more simply structured, conjugated α-imido carboxylic acids, we have explored the excited state chemistry of the maleimide-acetic acid derivative **14**.

Preparation of this substance was accomplished by a known[3] method involving condensation of glycine with maleic anhydride. Irradiation (λ > 290 nm) of an MeCN solution of **14** (5.8 mM) leads to production of a mixture of a cyclobutane-containing 2 + 2 dimer **27** as the major product (67%). Careful analysis of the crude photolysate does not reveal the presence of any azomethine ylide-derived products related to **16** (with H and CH_2CO_2H instead of TMS and CH_2TMS). In addition, a mixture of maleimide-acetic acid **14** (5.8 mM) and acrylonitrile (0.09 M) in MeCN is transformed upon irradiation to a mixture of the stereoisomeric 2 + 2 adducts **29a,b**. One of the stereoisomeric adducts, **29a**, could be isolated (74%) in pure form by silica gel chromatography. Here again, no evidence can be gained for the formation of substances arising by dipolar cycloaddition to an ylide intermediate related to **15** (with H instead of TMS). Structural assignment to the sparingly soluble dimer **27** is facilitated by conversion to its diester **28**, which is independently prepared (94%) by irradiation of the maleimido ester **26**.



Thus, unlike the phthalimidoglycine **25**, maleimide-acetic acid **14** does not undergo photoinduced decarboxylation to form an azomethine ylide intermediate. Instead, the excited state of this substance, like those of its *N*-alkyl and *N*-aryl relatives,[4] reacts exclusively by 2 + 2 cycloaddition pathways. Under comparable conditions (*i.e.*, maleimide and acrylonitrile concentrations), the silylmethyl analog **4** rearranges in a highly chemoselective manner by TMS group transfer to form the corresponding ylide. We can conclude from these observations that the excited state C to O TMS-migration process in **4** is more efficient/rapid than 2 + 2 cycloaddition of **4** with itself or acrylonitrile even when the concentrations of the latter substance are exceptionally high (*e.g.*, 2.3 M acrylonitrile). These qualitative results show that the kinetic heirarchy for excited state reactions of the α-substituted maleimides (and perhaps for the related phthalimides) is silyl transfer > 2 + 2 cycloaddition > decarboxylation.

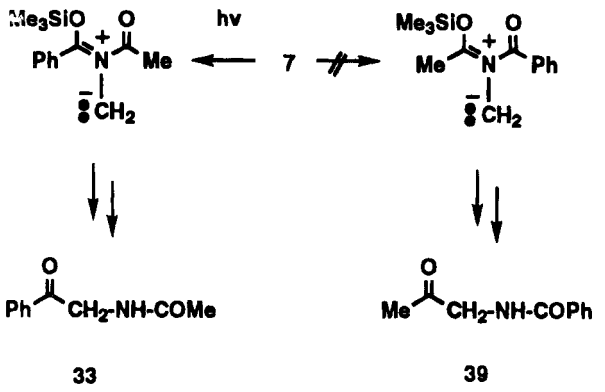
The photoreactivity of the saturated, cyclic silylmethyl imide **5** contrasts sharply with that of its unsaturated analog **4**. Specifically, irradiation (λ > 220 nm) of the **5** in MeCN solutions, with and without added acrylonitrile, results in clean production of the modestly stable iminolactone **30**. This substance, identified by ^1H and ^{13}C NMR spectroscopic methods, reconverts to **5** upon standing in $CDCl_3$ solution at 25 °C for 1 day. ^1H NMR monitoring of the progress of photoreaction of **5** in the presence of acrylonitrile indicates that no ylide trapping product(s) related to **31** are produced. These observations suggest that succinimide **5** undergoes exclusive N to O acyl migration upon irradiation. Thus, the ylide forming, silyl migration process appears to be restricted to silylmethyl imides having conjugated carbonyl moieties (see below).



(3) Rich, D. H.; Gegellschen, B.; Tong, A.; Cheung, A.; Buckner, C. K. *J. Med. Chem.* **1975**, *18*, 1004.

(4) Schenck, G. O.; Hartmann, W.; Mannsfeld, S. P.; Metzner, W.; Krauch, *Chem. Ber.* **1962**, *95*, 1642.

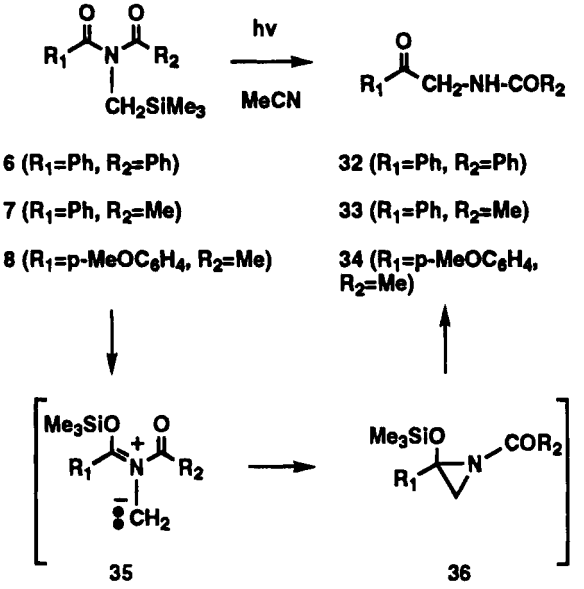
Scheme 3



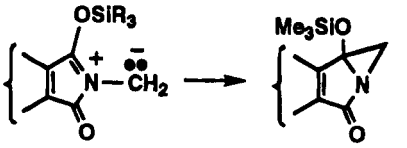
The difference observed in excited state reactivity of conjugated unsaturated silylmethyl imides (*e.g.*, phthalimides and maleimide **4**) vs their saturated analog **5** most probably reflects the effects of conjugation on the electronic characteristics of the excited imide chromophore. Simple aliphatic imides are known to participate in several photochemical reaction pathways initiated by C–C or C–N bond cleavage α to the carbonyl functions.[5] The latter route, resulting in photo-Fries type rearrangement, is documented in the photochemistry of *N*-phenyl imides.[6] This pathway is responsible for imino-lactone **30** formation in the photochemistry of succinimide **5**. In contrast, phthalimide excited states, having the imide chromophore directly conjugated to an aryl grouping, typically participate in photochemical processes initiated by H-atom abstraction, single electron transfer, or σ_{C-N} bond cycloaddition.[5] As mentioned earlier,[1] the electronic properties that drive these reaction types are those which may also be responsible for the C to O silyl migration process leading to azomethine ylide formation.

Photochemistry of Acyclic Silylmethyl Imides. To further explore the scope and limitations of the new azomethine ylide-forming process, the photochemistry of the acyclic silylmethyl imides **6–9** was probed. These substances were prepared starting with the known NH-imide analogs by alkylation with NaH and $TMSCH_2I$. Irradiation ($\lambda > 290$ nm) of the benzoyl imide **6** in MeCN, in both the absence and presence of added acrylonitrile, leads to clean production of a single product, identified as the *N*-phenacylbenzamide **32**. In a similar fashion, the aroyl-acetyl analogs **7** and **8** are transformed upon irradiation to the respective phenacylacetamides **33** and **34**.

In order to elucidate the mechanistic pathway responsible for the photoinduced chain extension process occurring in these systems, low temperture (−32 °C) irradiations of CD_3CN solutions of **6** and **7** were carried out, and the crude photolysates were analyzed at 0 °C by ^1H NMR spectroscopy. The spectra showed that each photolysate contained the respective aziridine intermediates **36** (R_1 = Ph, R_2 = Ph or Me). For example, for irradiation of **6** new resonances are observed at 0.18 ppm (s, $OSi(CH_3)_3$), 7.3–7.7 ppm (m, non-carbonyl conjugated aryl-H), and 3.96 and 4.13 ppm (ABq, J = 16.3 Hz, aziridine CH_2) and for irradiation of **7** at 0.10 ppm (s, $OSi(CH_3)_3$), 7.5–7.8 ppm (m, non-carbonyl conjugated aryl-H), and 3.67 and 3.84 ppm (ABq, J = 15.4 Hz, aziridine CH_2). Warming of each photolysate to 25 °C promotes rapid ($t_{1/2}$ *ca.* 1 h) conversion of the intermediate aziridine to the corresponding phenacyl amide **32** or **33**.



It is clear from these results that the mono- and diaryl substituted silylmethyl imides also participate in the general excited state C to O silyl-migration reaction. However, unlike the azomethine ylide intermediates derived from the phthalimide and maleimide counterparts, those produced in photoreactions of **6–8** undergo rapid 4π-electrocyclizations to form aziridines.[7] The reason why the cyclic azomethine ylides **37** do not electrocyclize rapidly may be due to ring strain developing in the bicyclic aziridines **38** which would be formed in this route.



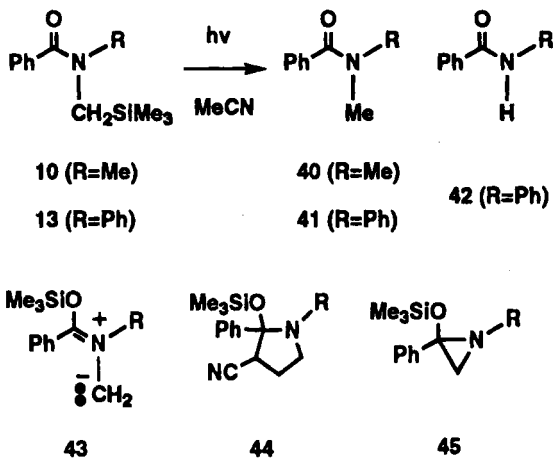
Another important aspect of these photoreactions concerns the C to O silyl migration regioselectivity. Specifically, the exclusive formation of *N*-phenacylamide **33** rather than the acetonylamide **39** indicates that the photochemical silyl-migration reaction of **7** (and **8**) occurs selectively in the direction of the aroyl rather than acetyl grouping (Scheme 3). Thus, silyl migration occurs to the oxygen in the carbonyl chromophore which has the lowest singlet and triplet excitation energy.

A final pertinent observation made in this investigation has come from a study of the photochemistry of the nonconjugated, acylic imide **9**. Specifically, irradiation of MeCN solutions of this substance with or without added acrylonitrile fails to promote any observable reaction. Thus, as with the cyclic systems, imide carbonyl conjugation appears to be a necessary requirement for the efficient operation of the photochemical C to O silyl-migration reaction.

Photochemistry of Silylmethyl Amides. The last series of compounds subjected to study in this effort are the silylmethyl amides **10–13**. These substances were prepared by acylation reactions of the appropriate sec-

(5) Coyle, J. D. In *Synthetic Organic Photochemistry*; Horspool, W. M., Ed., Plenum Press: New York, 1984, Chap. 4, pp 259–280.
(6) Katsuhara, Y.; Maruyama, H.; Shigemitsu, Y.; Odaira, Y. *Tetrahedron Lett.* **1973**, *16*, 1323.
(7) Huisgen, R.; Scheer, W.; Huber, H. *J. Am. Chem. Soc.* **1967**, *89*, 1753.

ondary silylmethyl amines with the corresponding acid chlorides. Irradiation ($\lambda > 220$ nm) of the *N*-methylbenzamide **10** in MeCN in the presence or absence of acrylonitrile leads to exclusive formation of the dimethylbenzamide **40**. Although the desilylation process observed here is reminiscent of that occuring in the photochemistry of the *N*-(silylmethyl)phthalimides,[1] the absence of dipolarophile-trapping or aziridine-derived products (*e.g.* **44** or **45**) suggests that the conversion of **10** to **40** does not occur by an excited state C to O silyl-migration pathway to form an intermediate azomethine ylide **43** (R = Me) followed by hydrolytic Si–O bond cleavage and C-protonation. Similarly, the *N*-phenylbenzamide **13** is converted into a mixture of the amides **41** and **42** when irradiated in MeCN. Here again, no evidence (*i.e.*, dipolarophile trapping or aziridine ring formation) has been gained for the existence of an ylide-forming pathway in these reactions. Finally, the *N*-benzylbenzamide **11** and *N*-methylacetamide **12** also do not react by excited state C to O silyl migration pathways. In the former case, irradiation leads to formation of *N*-benzyl-*N*-methylbenzamide and benzamide while in the latter case no photoreaction occurs. Thus, it appears that the generality for azomethine ylide formation cannot be extended to *N*-silylmethyl amides.



Summary

The results reported above suggest that the photochemical pathway involving C to O silyl migration and leading to azomethine ylide formation is ubiquitous for cyclic and acyclic, conjugated silylmethyl imides. However, this process is not generalizable to saturated imide and amide analogs. Despite these latter limitations, the new azomethine ylide-forming photochemical reaction discovered in our investigations has proven to have a reasonably wide scope and mechanistically intriguing features, and it is possible to forecast that it will have preparative value in the area of N-heterocycle synthesis.

Experimental Section

General. NMR spectra are recorded by using $CDCl_3$ solutions unless otherwise noted. Chemical shifts are reported in ppm relative to $SiMe_4$ or $CHCl_3$ as internal standards. ^{13}C NMR assignments are aided by INEPT or DEPT results for determining the number of attached hydrogens. Infrared spectral bands are reported in cm^{-1} units. Mass spectra (MS and HRMS) were recorded using electron impact ionization unless specified as chemical ionization (CI). All compounds were obtained as oils (unless specified otherwise by giving recorded melting points) and in purities of >90% as judged by ^1H and ^{13}C NMR. All preparative irradiations were conducted by using and immersion apparatus (Hanovia 450 Watt, medium pressure lamp) at a solution temperature of *ca.* 20 °C and using cutoff filters (Vycor $\lambda > 220$ nm, Pyrex $\lambda > 290$ nm).

Preparation of *N*-[(Trimethylsilyl)methyl]maleimide (4). To a solution of commercial maleimide (2.0 g, 21 mmol), triphenylphosphine (5.4 g, 21 mmol), and trimethylmethanol (2.6 mL, 21 mmol) in THF (50 mL) was added diethyl azodicarboxylate (4.0 g, 23 mmol). After stirring for 6 h at 25 °C, the solution was concentrated *in vacuo* giving a residue which was subjected to chromatography (silica gel 1:1 ether/hexane) to provide a solid which was crystallized (CH_2Cl_2) to yield 2.7 g (71%, mp 80–81 °C) of *N*-[(trimethylsilyl)methyl]-maleimide (**4**): ^1H NMR δ 0.04 (s, 9 H), 2.97 (s, 2 H), 6.63 (s, 2 H); ^{13}C NMR δ −2.0, 28.9, 133.9, 170.9; MS *m/z* (rel intensity) 183 (M^+, 20.4), 168 (73), 155 (33), 154 (30), 140 (31), 85 (26), 83 (39), 73 (100); HRMS *m/z* 183.0722 ($C_8H_{13}NO_2Si$ requires 183.0716).

Preparation of *N*-[(Trimethylsilyl)methyl]succinimide (5). This substance was prepared from the commercial succinimide (2.0 g, 20 mmol) by silylmethylation with NaH (20 mmol) and (iodomethyl)trimethylsilane (3 mL, 20 mmol) in 30 mL of DMF at 105 °C. The crude product was subjected to chromatography (silica gel, 1:1 ether/hexane) to provide a solid which was crystallized ($CHCl_3$) to yield 2.3 g (64%, mp 46–46.5 °C) of *N*-[(trimethylsilyl)methyl]succinimide (**5**): ^1H NMR δ 0.05 (s, 9 H), 2.68 (s, 2 H), 3.03 (s, 4 H); ^{13}C NMR δ −2.0, 27.9, 29.9, 176.9; MS *m/z* (rel intensity) 185 (M^+, 72.1), 170 (100), 156 (35), 143 (20), 142 (11), 73 (79); HRMS *m/z* 185.0859 ($C_8H_{15}NO_2Si$ requires 185.0872).

Preparation of *N*-[(Trimethylsilyl)methyl]-*N*-benzoylbenzamide (6). A solution of 1.4 g (6.2 mmol) of dibenzoyl imide[8] and NaH (6.2 mmol) in 30 mL of DMSO containing 1 mL (6.2 mmol) of (trimethylsilyl)methyl iodide was stirred for 4 h at 110 °C. The resulting solution was diluted with a CH_2Cl_2–ice–water mixture. The organic layer was concentrated *in vacuo* giving a residue which was subjected to chromatography (silica gel, 2:1 hexane/ether) to provide a solid which was crystallized (hexane/CH_2Cl_2) to yield 0.7 g (38%, mp 80–83 °C) of the benzamide **6**: ^1H NMR δ 0.16 (s, 9 H), 3.64 (s, 2 H), 7.10 (t, J = 7.4 Hz, 4 H), 7.18 (t, J = 7.4 Hz, 2 H), 7.35 (d, J = 7.4 Hz, 4 H); ^{13}C NMR δ −1.2, 39.5, 128.1, 128.9, 131.5, 136.9, 174.4; MS *m/z* (rel intensity) 311 (M^+, 13.9), 297 (15), 296 (63), 206 (81), 117 (29), 106 (15), 105 (100), 77 (65), 73 (26); HRMS *m/z* 311.1330 ($C_{18}H_{21}NO_2Si$ requires 311.1342).

Preparation *N*-[(Trimethylsilyl)methyl]-*N*-benzoylacetamide (7). A mixture of *N*-acetylbenzamide[9] (3.0 g, 18.4 mmol), $TMSCH_2I$ (4.3 g, 20.0 mmol), and K_2CO_3 (2.5 g, 18.1 mmol) in MeCN (40 mL) was stirred at reflux for 2 h. The reaction mixture was extracted with $CHCl_3$ and the organic layer was concentrated *in vacuo*. The residue was subjected to column chromatography (ethyl acetate:hexane = 1:4) to give *N*-[(trimethylsilyl)methyl]-*N*-benzoylacetamide (**7**) (1.8 g, 40%): ^1H NMR δ 0.32 (s, 9H), 2.06 (s, 3H), 3.33 (s, 2H), 7.40–7.63 (m, 5H); ^{13}C NMR δ −1.63, 26.0, 38.4, 128.4, 128.6, 132.2, 135.8, 172.8, 174.2; IR (neat) 1680, 1650 cm^{-1}; MS *m/z* (rel intensity) 249 (M^+, 9), 248 ($M^+ - 1$, 9), 234 (8), 221 (1), 206 (8), 192 (10), 144 (14), 128 (4), 105 (100), 102 (20), 77 (38), 55 (9), HRMS *m/z* 249.1190 ($C_{13}H_{19}NO_2Si$ requires 249.1185).

Preparation *N*-[(Trimethylsilyl)methyl]-*N*-(*p*-methoxyphenyl)acetamide (8). A mixture of commercial 4-methoxybenzamide (4.0 g, 26 mmol), acetic anhydride (3.2 g, 31 mmol), and 0.1 mL of concentrated sulfuric acid was heated at 100 °C with stirring for 2 h. After cooling, 5% aqueous $NaHCO_3$ was added and the resulting crystalline solid was separated and recrystallized from ethanol to give *N*-acetyl-4-methoxybenzamide (3.4 g, 67%, mp 117–118 °C): ^1H NMR 2.60 (s, 3H), 3.88 (s, 3H), 6.93 (d, 2H, J = 9.0 Hz), 7.89 (d, 2H, J = 9.0 Hz), 9.50 (s, 1H); ^{13}C NMR 25.5, 55.4, 113.9, 130.0, 124.6, 163.4, 165.3, 174.3; IR (KBr) 3240, 1715, 1695 cm^{-1}; MS *m/z* (rel intensity) 193 (40), 136 (12), 135 (100), 92 (13), 77 (14); HMRS *m/z* 193.0738 ($C_{10}H_{11}NO_3$ requires 193.0739).

A mixture of the above benzamide (2.0 g, 10 mmol), $TMSCH_2I$ (2.4 g, 11 mmol), and K_2CO_3 (1.4 g, 10 mmol) in CH_3-

(8) Tithebley, A. W. *J. Chem. Soc.* **1901**, *79*, 395.
(9) Blagoeva, I.; Kurtev, B. J.; Pojarlieff, I. G. *J. Chem. Soc.* **1970**, *13*, 232.

CN (30 mL) was stirred at reflux for 4 h. The mixture was extracted with $CHCl_3$, and the organic layer was concentrated *in vacuo*. The residue was subjected to column chromatography (ethyl acetate:hexane = 1:4) to give *N*-[(trimethylsilyl)-methyl]-*N*-(p-methoxyphenyl)acetamide (**8**) (1.8 g, 62%): ^{1}H NMR δ 0.04 (s, 9H), 2.05 (s, 3H), 3.34 (s, 2H), 3.86 (s, 3H), 6.94 (d, 2H, J = 9.0 Hz), 7.62 (d, 2H, J = 9.0 Hz); ^{13}C NMR δ −1.5, 25.8, 38.8, 55.4, 114.1, 131.2, 127.7, 163.2, 172.6, 174.0; IR (neat) 1680, 1650 cm^{-1}; MS *m/z* (rel intensity) 279 (1), 144 (18), 135 (100); HRMS *m/z* 279.1291 ($C_{14}H_{21}NO_3Si$ requires 279.1291).

Preparation of *N*-[(Trimethylsilyl)methyl]-*N*-acetylacetamide (9). A mixture of acetamide (5.0 g, 85 mmol) and acetic anhydride (9 mL, 93 mmol) containing 0.5 mL of concd H_2SO_4 was heated at 100 °C for 1 h, diluted with saturated $NaHCO_3$, and extracted with $CHCl_3$. The organic layer was dried and concentrated *in vacuo* to yield 2.0 g (21 mmol, 25%) of diacetimide. A solution of 1.9 g (19 mmol) of the above crude acetimide and NaH (19 mmol) in 20 mL of DMSO containing 3 mL (20 mmol) of (trimethylsilyl)methyl iodide was stirred for 4 h at 100 °C. The resulting solution was extracted with a CH_2Cl_2−ice−water mixture. The organic layer was concentrated *in vacuo* giving a residue which was subjected to chromatography (silica gel, 1:1 hexane/ether) to yield 0.96 g (28%) of the imide **9**: ^{1}H NMR δ 0.04 (s, 9 H), 2.35 (s, 6 H), 3.16 (s, 2 H); ^{13}C NMR δ −1.5, 26.6, 36.8, 173.2; MS *m/z* (rel intensity) 187 (M^+, 0.05), 172 (2), 144 (4), 130 (11), 87 (40), 75 (52), 73 (83), 56 (65), 55 (100); HRMS *m/z* 187.1022 ($C_8H_{17}NO_2Si$ requires 187.1029).

Preparation of *N*-Methyl-*N*-[(trimethylsilyl)methyl]-benzamide (10). A solution of commercial *N*-methylbenzamide (2.0 g, 15 mmol) and 0.6 g (15 mmol) of NaH in 20 mL of THF was stirred at reflux for 2 h. $TMSCH_2I$ (3.2 g, 15 mmol) was added, and the resulting mixture was stirred at reflux for 4 h, cooled to 25 °C, poured into water, and extracted with $CHCl_3$. The $CHCl_3$ layers were dried and concentrated *in vacuo* to give a residue which was subjected to column chromatography (silica gel, ethyl acetate-hexane, 2:1) to yield 2.8 g (85%) of **10** as a crystalline solid, mp 38−40 °C: ^{1}H NMR δ 0.14 (s, 9 H), 2.94 (s, 3 H), 3.08 (s, 2 H), 7.35 (s, 5 H); ^{13}C NMR δ −1.3, 40.0, 40.2, 126.9, 128.3, 129.2, 136.9, 170.3; MS *m/z* (rel intensity) 221 (M^+, 3.9), 206 (15), 133 (4), 105 (100); HRMS *m/z* 221.1236 ($C_{12}H_{19}NOSi$ requires 221.1236).

Preparation of *N*-Benzyl-*N*-[(trimethylsilyl)methyl]-benzamide (11). A mixture of commercial *N*-benzylbenzamide (2.0 g, 13 mmol) and sodium hydride (0.5 g, 13 mmol) in THF (30 mL) was stirred at reflux under for 2 h. $TMSCH_2I$ (3.0 g, 14 mmol) was added, and the mixture was stirred at reflux for 4 h. The reaction mixture was extracted with $CHCl_3$, and the organic layer was dried and concentrated *in vacuo* to give a residue which was subjected to column chromatography (ethyl acetate:hexane = 1:3) to yield 2.0 g (65%) of the amide **11** as a crystalline substance (mp 50−53 °C): ^{1}H NMR δ −0.16 (s, 9H), 2.97 (s, 2H), 4.51 (s, 2H), 7.15−7.42 (m, 10H); ^{13}C NMR δ −1.2, 17.2, 55.0, 126.5, 126.7, 127.4, 128.3, 128.6, 129.1, 136.5, 136.6, 171.0; IR (KBr) 1610 cm^{-1}; MS *m/z* (rel intensity) 297 (17), 296 (63), 282 (31), 206 (14), 105 (100), 91 (95), 77 (33); HRMS *m/z* 297.1535 ($C_{18}H_{23}NOSi$ requires 297.1549).

Preparation of *N*-Methyl-*N*-[(trimethylsilyl)methyl]-acetamide (12). A mixture of commercial *N*-methylacetamide (2.0 g, 27 mmol) and sodium hydride (1.1 g, 27 mmol) in THF (30 mL) was stirred at reflux for 2 h. To the reaction mixture was added $TMSCH_2I$ (6.0 g, 28 mmol), and reflux was continued for 4 h. After filtration and concentration *in vacuo* the residue was subjected to column chromatography (ethyl acetate) to yield 2.0 g (46%) of the amide **12**: ^{1}H NMR δ 0.008, 0.01 (two s, 9H), 1.99, 2.01 (two s, 3H), 2.80, 2.86 (two s, 2H), 2.94 (s, 3H); ^{13}C NMR δ −2.1, −1.9, 21.1, 21.2, 35.2, 38.2, 39.5, 42.1, 168.9, 169.6; IR (neat) 1640 cm^{-1}; MS *m/z* (rel intensity) 159 (M^+, 25), 144 (100), 116 (7), 102 (9), 59 (4); HRMS *m/z* (rel intensity) 159.1087 ($C_7H_{17}ONSi$ requires 159.1079).

Preparation of *N*-Phenyl-*N*-[(trimethylsilyl)methyl]-benzamide (13). A mixture of 3.7 g (21 mmol) of *N*-phenyl-*N*-[(trimethylsilyl)methyl]amine,[10] 11.3 g (82 mmol) of K_2CO_3, and 2.2 mL (19 mmol) of benzoyl chloride in 50 mL of CH_3CN was stirred for 12 h at 25 °C and filtered. The filtrate was concentrated *in vacuo* giving a residue which was partitioned between ether and water. The ethereal layer was dried and concentrated *in vacuo* to give a residue which was subjected to chromatography (silica gel 1:1 ether/hexane) to yield 4.1 g (78%) of benzamide **13** as an oil: ^{1}H NMR δ 0.03 (s, 9 H), 3.52 (s, 2 H), 6.95−7.23 (m, 10 H); ^{13}C NMR δ −1.4, 43.2, 126.3, 145.2, 169.5; IR 3090, 2960, 2900, 1650, 1600, 920, 850; MS *m/z* (rel intensity) 283 (M^+, 25.7), 282 (100), 268 (70), 267 (3), 105 (60), 77 (60), 73 (67); HRMS *m/z* 283.1373 ($C_{17}H_{21}NOSi$ requries 283.1393).

Preparation of Methyl α-[*N*-Maleimido]acetate (26). To a mixture of maleimide (1.0 g, 0.01 mol), triphenylphospine (2.6 g, 0.01 mol), and methyl glycolate (0.8 mL, 0.01 mol) in 50 mL of anhydrous THF was added dropwise a solution of diethyl diazodicarboxylate (1.9 g, 0.01 mol) in 10 mL of THF. The mixture was allowed to stir for 12 h at 25 °C. The resulting solution was concentrated *in vacuo* and the residue obtained was subjected to flash chromatography on silica gel (6:4 Et_2O−hexane) to yield 0.9 g (53%) of **26**: ^{1}H NMR ($CDCl_3$) δ 6.74 (2H, s), 4.21 (2H, s), 3.68 (3H, s); ^{13}C NMR δ 169.67, 167.56, 134.38, 52.52, 38.32; IR (film) 1732, 1694, 1220, 1160; UV (MeCN) 216 (8800), 285 (600) nm; CIMS *m/z* (rel intensity) 170 (M^+ + 1, 3), 169 (M^+, 26), 109 (100), 82 (47), 58 (26), 56 (31); HRMS(CI) *m/z* 170.0453 (M + 1 $C_7H_7NO_4$ requires 170.0452).

Preparation of *N*-Phenacylacetamide (33). The known[11] acetamide **33** was independently prepared starting with N-acylation of 2-amino-1-phenylethanol followed by Jones oxidation. A solution of 1.8 g (13 mmol) of K_2CO_3 and 1.0 g (7.3 mmol) of 2-amino-1-phenylethanol in 20 mL of CH_3CN containing 0.5 mL of acetyl chloride was stirred at 65 °C for 12 h and filtered. The residue obtained by concentration of the filtrate was subjected to chromatography (silica gel, 3:1 ether/hexane) to yield 0.6 g (47%) of the acetamidophenylethanol as an oil: ^{1}H NMR δ 1.97 (s, 3 H), 3.29 (m, 1 H), 3.65 (m, 1 H), 4.80 (dd, J = 8, 3.3 Hz, 1 H), 6.04 (br s, 1 H), 7.33 (m, 5 H).

This substance (40 mg, 0.2 mmol) in 15 mL of acetone was oxidized by excess Jones reagent to afford acetamide **33** (mp 83−84 °C) in a quantitative yield. The physical properties of the synthesized **33** were identical to those of the isolated photoproduct.

Irradiation of *N*-[(Trimethylsilyl)methyl]maleimide (4). A solution of 203 mg (1.1 mmol) of the maleimide **4** in 100 mL of CH_3CN was irradiated with Pyrex filtered-light for 34 h (>99% conversion). The photolysate was concentrated *in vacuo* giving a solid which was crystallized (CH_2Cl_2−hexane) to yield 190 mg (92%, mp 150−152 °C) of the adduct **16**: ^{1}H NMR δ −0.04 (s, 9 H), 0.09 (s, 9 H), 2.90 (AB_q, J = 14.7 Hz, 2 H), 3.43−3.65 (m, 3 H), 4.19 (d, J = 12.6 Hz, 1 H), 5.89 and 7.24 (d, J = 5.8 Hz, 2 H); ^{13}C NMR δ −2.1, 1.3, 31.0, 43.2, 49.5, 56.0, 99.7, 119.7, 149.7, 170.7, 173.5, 177.1; MS *m/z* (rel intensity) 366 (M^+, 51.8), 351 (39), 197 (23), 182 (21), 168 (23), 121 (22), 73 (100); HRMS *m/z* 366.1439 ($C_{16}H_{26}N_2O_4Si_2$ requires 366.1431).

Irradiation of *N*-[(Trimethylsilyl)methyl]maleimide (4) with Acrylonitrile. A solution of 232 mg (1.3 mmol) of the maleimide **4** and 15 mL (0.23 mol) of acrylonitrile in 100 mL of CH_3CN was irradiated with Pyrex-filtered light for 45 h (55% conversion). The photolysate was concentrated *in vacuo* giving a residue which was subjected to column chromatography (silica gel, 1:1 ether/hexane) to yield 15 mg (6%) of the tricyclic adduct **16**, 49 mg (30%) of the acrylonitrile adduct **19**, 8 mg (5%) of the isomeric acrylonitrile adduct **21**, 8 mg (4%) and 9 mg (8%) of the desilylated adducts, **18** and **20**, respectively, and 104 mg of the recovered starting material **4**.

18: ^{1}H NMR δ −0.04 (s, 9 H), 2.71 (br s, 1 H, OH), 2.93 (AB_q, J = 14.6 Hz, 2 H), 3.52−3.68 (m, 3 H), 4.16 (d, J = 12.2 Hz, 1 H), 5.89, 7.26 (d, J = 5.8 Hz, 2 H); ^{13}C NMR δ −2.1, 33.0, 42.9, 49.6, 53.0, 98.5, 127.0, 148.3, 170.3, 173.2, 176.9;

(10) Kim, J.-M. Ph.D. Dissertation, University of Maryland−College Park, 1994, p 36.

(11) Although reported previously (Saito, K.; Hayakawa, K.; Yoshita, S. *J. Chem. Soc. Perkin 1*, **1976**, *787*), no spectroscopic data have been recorded for this substance.

MS *m/z* (rel intensity) 294 (M^+, 5.2), 279 (24), 197 (25), 184 (62), 182 (47), 168 (22), 75 (29), 73 (100); HRMS *m/z* 294.1057 ($C_{13}H_{18}N_2O_4Si$ requires 294.1036).

19: ^{1}H NMR δ 0.07 (s, 9 H), 2.51 and 2.78 (m, 2 H), 3.15 (d, J = 6.8 Hz, 1 H), 3.33 and 3.67 (m, 2 H), 6.15 and 7.08 (d, J = 5.8 Hz, 2 H); ^{13}C NMR δ 0.9, 32.7, 39.1, 41.2, 99.9, 117.3, 129.1, 147.9, 173.4; MS *m/z* (rel intensity) 236 (M^+, 21.8), 183 (32), 126 (36), 75 (100), 73 (65); HRMS *m/z* 236.0977 ($C_{11}H_{16}N_2O_2Si$ requires 236.0981).

20: ^{1}H NMR δ 2.48 and 2.82 (m, 2 H), 3.29 and 3.53 (m, 2 H), 4.55 (br s, 1 H, OH), 6.10 and 7.16 (d, J = 5.8 Hz, 2 H); ^{13}C NMR δ 33.1, 36.9, 40.9, 98.8, 117.2, 129.5 and 146.9, 173.1; CIMS *m/z* (rel intensity) 165 ($M^+ + 1$, 14.9), 110 (25), 78 (66), 75 (100); HRMS (CI) *m/z* 165.0665 ($C_8H_9N_2O_2$ requires 165.0664).

21: ^{1}H NMR δ 0.12 (s, 9 H), 2.46 (dd, J = 12.3, 7.3 Hz, 1 H), 2.69 (m, 1 H), 2.79 (m, 1 H), 3.34 and 3.49 (m, 2 H), 6.04 and 7.15 (d, J = 5.8 Hz, 2 H); ^{13}C NMR δ 0.9, 32.8, 38.6, 41.1, 97.8, 116.9, 127.9, 148.7, 173.0; MS *m/z* (rel intensity) 236 (M^+, 17.5), 221(82), 183 (45), 155 (20), 154 (21), 147 (30), 126 (48), 73 (100); HRMS *m/z* 236.0985 ($C_{11}H_{16}N_2O_2Si$ requires 236.0981).

Elimination Chemistry of Pyrrolizidines 19 and 21. A solution of 5 mg (0.02 mmol) of **19** and 0.5 mL of concd H_2SO_4 in 1 mL of THF was stirred at 80 °C for 2 h. Standard workup gave 3 mg of **22** as an oil in >80% purity. The instability of this substance prevented its further purification. Also, **21** (5 mg) was transformed to **22** (2 mg) under identical reaction conditions.

22: ^{1}H NMR δ 3.33 (t, J = 8.0 Hz, 2 H), 3.85 (t, J = 8.0 Hz, 2 H), 6.53 (d, J = 5.8 Hz, 1 H), 7.12 (d, J = 5.8 Hz, 1 H); MS *m/z* (rel intensity) 146 (M^+, 100), 145 (37), 118 (45), 91 (42), 80 (7); HRMS *m/z* 146.0483 ($C_8H_6N_2O$ requires 146.0480).

Irradiation of *N*-[(Trimethylsilyl)methyl]maleimide (4) with Fumaronitrile. A solution of 73 mg (0.4 mmol) of maleimide **4** and 0.5 g (6.4 mM) of fumaronitrile in 100 mL of MeCN was irradiated with Pyrex-filtered light for 20 h. The concentrated photolysate was subjected to preparative TLC (silica gel 1:1 ether/hexane) to provide 30 mg (30%) of the adduct **23** and 40 mg (53%) of desilylated adduct **24**.

23: ^{1}H NMR δ 0.15 (s, 9 H), 3.52–3.59 (m, 2 H), 3.68 (m, 1 H), 4.21 (dd, J = 12.2, 8.4 Hz, 1 H), 6.24 and 7.13 (d, J = 5.8 Hz, 2 H); ^{13}C NMR δ 0.7, 35.9, 43.5, 44.3, 99.5, 114.3, 116.7, 129.1, 147.1, 171.4; MS *m/z* (rel intensity), 261 (M^+, 1.4), 246 (43), 183 (27), 145 (100), 102 (21), 75 (88), 73 (35); HRMS *m/z* 261.0924 ($C_{12}H_{15}N_3O_2Si$ requires 261.0934).

24: ^{1}H NMR δ 3.51 (dd, J = 12.1, 4.5 Hz, 1 H), 3.71 (d, J = 4.0 Hz, 1 H), 3.92 (m, 1 H), 4.05 (dd, J = 12.1 8.4 Hz, 1 H), 6.24 and 7.21 (d, J = 5.8 Hz, 2 H); ^{13}C NMR δ 37.1, 42.6, 45.1, 99.6, 116.6, 119.1, 129.7, 148.3, 173.0; MS *m/z* (rel intensity) 189 (M^+, 1.4), 111 (38), 110 (100), 83 (23), 82 (37), 54 (51), 52 (36); HRMS *m/z* 189.0541 ($C_9H_7N_3O_2$ requires 189.0538).

Irradiation of *N*-[(Trimethylsilyl)methyl]succinimide (5). A solution of 237 mg (1.3 mmol) of the succinimide **5** with or without 6 mL of acrylonitrile added in 200 mL of MeCN or acetone was irradiated with Vycor-filtered light for 3 h. The photolysate was concentrated *in vacuo* giving a residue which was characterized by NMR spectroscopy as the iminolactone **30**. Upon standing in the $CDCl_3$ solvent in the dark for 24 h at 25 °C, **30** reverts nearly quantitatively to the succinimide **5**.

30: ^{1}H NMR δ 0.03 (m, 9 H), 2.79 (m, 2 H), 2.89 (m, 2 H), 3.10 (s, 2 H); ^{13}C NMR δ −2.7, 26.4, 27.9, 41.3, 149.6, 173.0.

Irradiation of *N*-[(Trimethylsilyl)methyl]-*N*-benzoylbenzamide (6). A solution of 70 mg (0.23 mmol) of the imide **6** with or without 8 mL of acrylonitrile added in 100 mL of MeCN was irradiated with Pyrex filtered-light for 8 h (60% conversion of **6**). The photolysate was concentrated *in vacuo* giving a residue which was subjected to preparative TLC (silica gel 1:1 ether/hexane) to yield 25 mg (46%) of N-phenacylbenzamide **32** and 28 mg of recovered **6**.

32: ^{1}H NMR δ 4.83 (d, J = 5.4 Hz, 2 H), 7.30 (br s, 1 H, NH), 7.40–7.67 (m, 6 H), 7.84 (d, J = 7.1 Hz, 2 H), 8.02 (d, J = 7.7 Hz, 2 H); ^{13}C NMR δ 46.9, 127.1, 128.0, 128.6, 129.0, 131.8, 134.3, 128.2, 133.9, 167.4, 194.2; MS *m/z* (rel intensity) 239 (M^+, 7.4), 211 (11), 134 (9), 105 (100), 76 (40), 68 (16); HRMS *m/z* 239.0948 ($C_{15}H_{13}NO_2$ requires 239.0946).

A solution of 10 mg (0.03 mmol) of the imide **6** in 0.6 mL of anhydrous CD_3CN in a sealed NMR tube was irradiated with Pyrex-filtered light at −32 °C (ethylene glycol−CO_2) for 20 h. ^{1}H-NMR spectroscopic analysis at 0 °C showed the presence of resonances (see above) characteristic of the aziridine **36** (R_1, R_2 = Ph).

Irradiation of *N*-[(Trimethylsilyl)methyl]-*N*-benzoylacetamide (7). A solution of *N*-acetyl-*N*-[(trimethylsilyl)-methyl]benzamide (**7**) was irradiated through a Pyrex filter under N_2 purging. Removal of solvent and column chromatography (ethyl acetate) of the resulting residue gave phenacyl amide **33**. Reaction conditions, reaction times, % conversion of **7**, and product **33** yields in acetone and MeCN are as follows: acetone, **7** (300 mg, 1.2 mmol) in 100 mL, 1 h, 50%, **33** (100 mg, 95%); in CH_3CN, **7** (600 mg, 2.4 mmol) in 200 mL, 9 h, 50%, **33** (180 mg, 86%).

33: ^{1}H NMR δ 2.08 (s, 3 H), 4.74 (d, J = 4.3 Hz, 2 H), 6.62 (br s, 1 H), 7.47 (t, J = 7.6 Hz, 2 H), 7.59 (t, J = 7.4 Hz, 1 H), 7.96 (d, J = 7.6 Hz, 2 H); ^{13}C NMR δ 23.0, 46.5, 127.9, 128.9, 134.1, 134.3, 170.3, 194.2.

A solution of 7 mg (0.029 mmol) of the imide **7** in 0.6 mL of CD_3CN solution in a sealed NMR tube was irradiated with Pyrex-filtered light at −32 °C (ethylene glycol−CO_2) for 16.5 h. H-NMR spectroscopic analysis at 0 °C showed the presence of resonances (see above) characteristic of the aziridine **36** (R_1=Ph, R_2=Me).

Irradiation of *N*-[(Trimethylsilyl)methyl]-*N*-acetylacetamide (8). Solutions of *N*-acetyl-*N*-[(trimethylsilyl)-methyl]-4-methoxybenzamide (**8**) in 100 mL of acetone and CH_3CN were irradiated through a Pyrex filter under N_2 purging. Concentration of the photolysates *in vacuo* and preparative TLC (ethyl acetate) of the resulting residues gave the phenacyl amide **34**. Reaction conditions, reaction times, % conversion of **8**, and product yields in acetone and MeCN are as follows: acetone, **8** (200 mg, 0.72 mmol), 6 h, 50%, **34** (60 mg, 81%); in CH_3CN, **8** (130 mg, 0.46 mmol), 5 h, 61%, **34** (31 mg, 53%).

34: mp 111–113 °C; ^{1}H NMR δ 2.07 (s, 3H), 3.85 (s, 3H), 4.68 (d, 2H), 6.72 (br s, 1H, NH), 6.93 (d, 2H, J = 8.8 Hz), 7.92 (d, 2H, J = 8.8 Hz); ^{13}C NMR δ 22.9, 46.0, 55.4, 114.0, 127.3, 130.1, 164.2, 170.2, 192.5; IR (KBr) 3320, 1700, 1640 cm^{-1}; MS *m/z* (rel intensity) 207 (2), 135 (100), 92 (11), 83 (12), 77 (18); HRMS *m/z* 207.0890 ($C_{11}H_{13}NO_3$ requires 207.0895).

Irradiation of *N*-Methyl-*N*-[(trimethylsilyl)methyl]-benzamide (10). A solution of 200 mg (0.9 mmol) of the benzamide **10** in 100 mL of MeCN was irradiated with Vycor-filtered light for 4 h (80% conversion of **10**). The concentrated photolysate was subjected to chromatography (silica gel 1:1 ether/hexane) to yield 43 mg (17%) of *N*,*N*-dimethylbenzamide (**40**).

Irradiation of *N*-Benzyl-*N*-[(trimethylsilyl)methyl]-benzamide (11). Solutions of *N*-benzyl-*N*-[(trimethylsilyl)-methyl]benzamide (**11**) (200 mg, 0.82 mmol) in 100 mL of acetone and CH_3CN were irradiated through a Pyrex filter under N_2 purging. Removal of solvent *in vacuo* and preparative TLC (ethyl acetate:hexane = 1:3) of the resulting residues gave *N*-methyl-*N*-benzylbenzamide and benzamide. Reaction times, % conversion of **11**, and respective product yields in acetone and CH_3CN are as follows: acetone, 4 h, 90%, (78 mg, 61% and 12 mg, 13.4%); in CH_3CN, 8 h, 85%, (50 mg, 42% and 9 mg, 11%).

Irradiation of *N*-Phenyl-*N*-[(trimethylsilyl)methyl]-benzamide (13). A solution (MeCN, 100 mL) containing 200 mg (0.7 mmol) of benzamide **13** was irradiated (Pyrex filter) for 74 h (30% conversion of **13**). The concentrated photolysate was subjected to chromatography (silica gel 1:1 ether/hexane) giving 12 mg (20%) of *N*-methyl-*N*-phenylbenzamide (**41**) and 3 mg (8%) of *N*-phenylbenzamide (**42**).

Irradiation of α-[*N*-Maleimido]acetic Acid 14. In MeCN. A solution of **14** (100 mg, 0.6 mmol) in 110 mL of MeCN was irradiated through a Pyrex filter under nitrogen for 2 h (100% conversion of **14**). The solvent was removed under reduced pressure yielding 85 mg of a sparingly soluble white solid. Analysis of this solid by ^{1}H NMR reveals that it contains the dimer **27** (67%, using triphenylmethane as standard reference). The white solid was then dissolved in 5 mL of $SOCl_2$ and stirred under a nitrogen atmosphere at reflux

for 3 h. The thionyl chloride was then removed by distillation. To the resulting solid was added 5 mL of anhydrous MeOH, and the mixture was stirred for 3 h at 25 °C. The solvent was removed *in vacuo*, and the crude residue was subjected to column chromatography on silica gel (Et_2O–hexane 4:1). The white solid (49 mg) obtained was identified as the dimer diester **28**, by comparison of its properties with that of an authentic sample (see below).

In Acetone. A solution of **14** (100 mg, 0.6 mmol) in 110 mL of acetone was irradiated through a Pyrex filter under nitrogen for 6 h (100% conversion of **14**, 100% yield). The solvent was removed in vacuo, and the residue was subjected to flash chromatography on silica gel (Et_2O) giving 60 mg (60%) of **27** (mp 200 °C dec, from MeOH): ^{1}H NMR (D_2O) δ 4.02 (4H, s, $2CH_2$), 3.48 (4H, s, 4CH).

With Acrylonitrile in MeCN. A solution of **14** (100 mg, 0.6 mmol) and acrylonitrile (0.7 mL, 0.01 mmol) in 110 mL of MeCN was irradiated through a Pyrex filter under nitrogen for 2 h (100% of conversion of **14**). The solvent was removed in vacuo yielding 130 mg (98%) of a white solid that was identified as a mixture of two diasteroisomers **29a,b** (^{1}H NMR ratio *ca.* 65:35). Chromatography on silica gel (Et_2O–hexane 4:1) gave 98 mg (74%) of the major isomer **29a** (mp 200 °C dec, MeOH) and 26 mg of a mixture of **29a** and **29b**: ^{1}H NMR (D_2O) δ 4.0 (2H, s), 3.85 (1H, m), 3.65 (1H, dd, J = 10.2 Hz, J = 6.2 Hz), 3.35 (1H, d, J = 6.2 Hz), 2.9 (1H, m), 2.4 (1H, m); ^{13}C NMR (D_2O–*p*-dioxane as reference) δ 180.59, 177.89, 173.00, 119.25, 42.14, 41.09, 36.48, 26.94, 21.33; IR (KBr) 3615, 2244, 1718, 1685; CIMS *m/z* (rel intensity) 164 (52), 163 (100), 110 (74), 79 (82), 68 (35), 55 (30), 52 (46); HRMS (CI) *m/z* 209.0562 (M + 1, $C_9H_8N_2O_4$ requires 209.0569).

Irradiation of Methyl α-[*N*-Maleimido]acetate (26). A solution of **26** (100 mg, 0.6 mmol) in 110 mL of MeCN was irradiated through a Pyrex filter under nitrogen for 2 h (100% conversion of **26**). The solvent was removed in vacuo yielding 94 mg (94%) of a white solid that was identified as **28**, mp > 200 °C dec, from MeOH; ^{1}H NMR (acetone-d_6) δ 4.31 (4H, s), 3.75 (6H, s), 3.57 (4H, s); ^{13}C NMR (DMSO-d_6) δ 179.33, 175.99, 174.95, 167.29, 52.54, 42.60, 41.04; IR (KBr) 1747, 1709, 1314, 1223, 1170 cm^{-1}; MS *m/z* 338 (M^+, 13), 279 (43), 184 (34), 125 (59), 111 (33), 109 (61), 82 (31), 80 (68), 59 (43), 56 (49), 52 (100); HRMS *m/z* 338.0750 ($C_{14}H_{14}N_2O_8$ requires 338.0750).

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Supplementary Material Available: Copies of ^{1}H and/or ^{13}C NMR spectra for compounds **4–11**, **13**, **14**, **16**, **18–24**, **26–34**, and **36** (60 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 ACS. See any current masthead for ordering information.

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