JOC Article

β-Lactam-Forming Photochemical Reactions of *N*-Trimethylsilylmethyl- and *N*-Tributylstannylmethyl-Substituted α-Ketoamides

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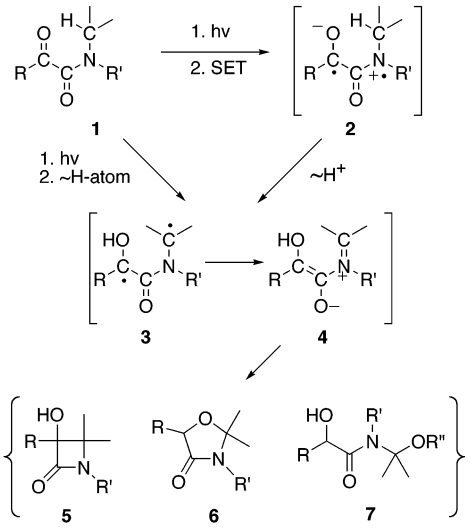
Two mechanisms have been proposed for the β-lactam-forming photochemical reactions of α-ketoamides. One, suggested by Aoyama, involves excited-state H-atom abstraction while the other, put forth by Whitten, follows a sequential SET-proton-transfer route. The photochemical properties of *N*-trimethylsilylmethyl- and *N*-tributylstannylmethyl-substituted α-ketoamides were explored in order to gain information about the mechanism of this process and to develop a regioselective method for β-lactam formation. The results of this effort show that (1) photoreactions of *N*-trimethylsilylmethyl-substituted α-ketoamides proceed by competitive H-atom abstraction and sequential SET-desilylation pathways and (2) a sequential SET-destannylation pathway is preferentially followed in photochemical reactions of the tributylstannylmethyl-substituted α-ketoamides.

Introduction

Far too seldom has the long-range goal of mechanistic photochemical studies been the development of synthetically useful reactions. As a result, the synthetic potential of exited-state reactions has often gone unnoticed. An example of this is found in studies of photoinduced reactions of α-ketoamides **1** that produce β-lactams **5** (Scheme 1). Following a number of earlier studies,[2−6] Aoyama and co-workers[7−10] conducted a series of exploratory investigations that focused on the scope and mechanism of this process. This group proposed that this reaction is initiated by hydrogen atom abstraction by the carbonyl oxygen of the excited ketone from an amide α-carbon. The initially formed intermediate in this pathway is either a triplet 1,4-biradical **3** or a singlet 1,4-dipole **4**, depending upon the multiplicity of the reacting excited state of **1**. Electrocyclic ring closure of the dipole then produces the β-lactam **5** along with other products,

SCHEME 1



including oxazolidinone **6** that derives from intramolecular addition of the hydroxyl group to the iminium cation. Additional evidence for the intermediacy of dipole **4** in this process comes from the observation that α-hydroxamides **7** are produced by photoreactions conducted in MeOH. As with other photochemical reactions promoted by carbonyl H-atom abstraction, this process proceeds in high yields when the amide nitrogen contains identical alkyl substituents. Although an insufficient number of examples exist[8] to conclusively prove the point, one expects that α-ketoamides which possess two different

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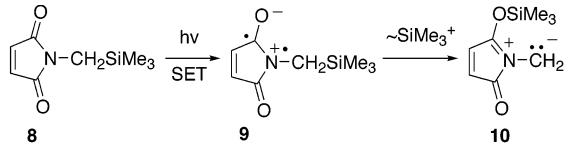
SCHEME 2

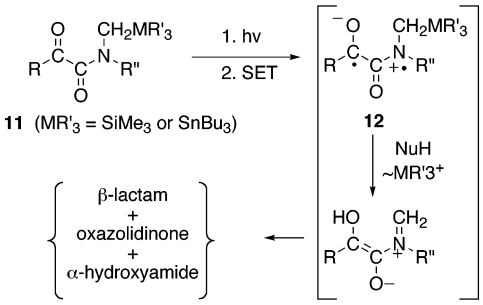


alkyl groups on nitrogen would be transformed to mixtures of *β*-lactams by this pathway.

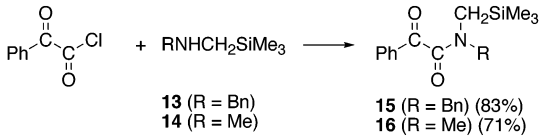
In a later discussion of this novel photochemical process, Chesta and Whitten[11] suggested that a single electron transfer (SET) mechanism is operable. In the SET pathway, intramolecular proton transfer from the amide cation radical in zwitterionic biradical **2** to the ketone anion radical generates the same intermediates, **3** and **4**, that are produced by the H-atom abstraction route. However, Chesta and Whitten's proposal[11] was not supported by any conclusive experimental observations, and consequently, it cannot be used reliably to predict the behavior of unsymmetric and/or structurally complex systems.

The interrelated issues of mechanism and synthetic application of the *β*-lactam forming photoreactions of α-ketoamides were of interest to us as result of earlier investigations carried out in our laboratories in the area of SET photochemistry. In particular, our earlier studies focusing on the kinetics of aminium radical reactions[12,13] and the excited-state reactions of *N*-silylmethylimides[14,15] seemed to be related to these issues. By using a combination of product distribution and laser flash photolysis methods, we showed that the rates of silophile induced desilylation of α-silylamide cation radicals far exceed those of base-induced α-deprotonation.[12,13] An example of this kinetic preference is found in the photochemical generation of azomethine **10** from the *N*-silymethylmaleimide **8**, formed by a pathway involving the intermediacy of zwitterionic biradical **9** (Scheme 2). In this process, transfer of trimethylsilyl group to the oxyanion center occurs more rapidly than does proton transfer. Other efforts in our laboratories demonstrated that the rates of α-destannylation reactions of cation radicals exceeds those of α-desilylation.[16,17] In another pertinent investigation, Yoshida and co-workers[18,19] observed that α-trialkylsilyl and α-tributylstannyl substitution dramatically increases the thermodynamic stability of amine and amide cation radicals. These effects, seen in the oxidation potentials of the corresponding nitrogen containing electron donors, makes SET from α-silyl- and α-stannylamines and α-silyl- and α-stannylamides thermodynamically/kinetically more favorable.

SCHEME 3



SCHEME 4



Based on these observations, we anticipated that zwitterionic biradicals **12**, formed by intermolecular SET in the excited states of *N*-trimethysilylmethyl- or *N*-tributylstannylmethyl-substituted α-ketoamides **11** would preferentially participate in either intermolecular or intermolecular silyl or stannyl group transfer rather than proton-transfer processes (Scheme 3). In addition, we believed that this selectivity might serve as the foundation for regioselective and, thus synthetically useful, *β*-lactam-forming photochemical reactions.

The proposal presented above guided the current studies, in which product distributions, arising from photoreactions of α-silyl- and α-stannyl-substituted α-ketoamides, were determined and translated into conclusions about the mechanism(s) for *β*-lactam formation. Results emanating from this effort demonstrate that (1) *β*-lactam forming photoreactions of α-silyl-substituted α-ketoamides are not regioselective because they occur by competitive H-atom abstraction and sequential SET-desilylation pathways and (2) *N*-tributylstannylmethyl-substituted α-ketoamides undergo regioselective photoreactions to produce *β*-lactams through the near exclusive operation of a sequential SET- destannylation route.

Results and Discussion

Four α-ketoamides, containing *N*-trimethylsilylmethyl or *N*-tributylstannylmethyl substituents, were prepared in order to investigate the issues discussed above. Reactions of the in situ prepared benzoylformic acid chloride with commercially available *N*-benzyl- (**13**) and *N*-methyl-*N*-trimethylsilylmethylamine (**14**) were used to produce the corresponding α-silylketoamides **15** and **16** (Scheme 4). An alternate approach, involving N-alkylation of the anion, formed by sodium hydride treatment of the secondary ketoamides **17** and **18**, with tributylstannylmethyl iodide,[20] was employed to prepare the analogous tin-containing substrates **19** and **20** (Scheme 5).

Preparative photochemical reactions of the ketoamides were explored next. Solutions of **15**, **16**, **19**, and **20** in MeOH and MeCN were irradiated with Pyrex glass filtered light (λ > 290 nm) for time periods required to

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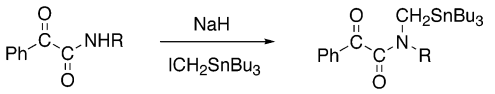
SCHEME 5



17 (R = Bn)
18 (R = Me)

19 (R = Bn) (84%)
20 (R = Me) (93%)

TABLE 1. Products and Yields of Photoreactions of α-Ketoamides 15, 16, 19, and 20

keto-amide	Solvent	products (% yield)
15	MeOH	21 (6), 22 (14), 23 (3), 27 (3), 28 (10), 29 (7), 32 (11), 33 (5), 37 (10)
15	MeCN	21 (10), 22 (22), 23 (6), 27 (3), 38 (8), 39 (4), 40 (22)
16	MeOH	24 (4), 25 (3), 30 (5), 35 (6), 35 (10) 36 (23)
16	MeCN	24 (14), 25 (7), 31 (6), 41 (6), 42 (22)
19	MeOH	21 (37), 26 (3), 27 (10), 32 (25), 37 (8)
19	MeCN	21 (42), 26 (3), 27 (7)
20	MeOH	24 (40, 31 (9), 36 (3)
20	MeCN	24 (44), 31 (5)

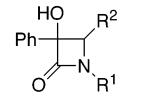
promote >90% conversion of the substrates. Products were separated from each of the mixtures by using preparative TLC. Structural assignments to all previously uncharacterized photoproducts were made by using a combination of spectrophotometric and X-ray crystallographic techniques. As can be seen by viewing the data in Table 1, the mass balances of products generated in these photochemical reactions are less than 100%. In each case, the remaining material is comprised of a mixture of very minor (<1%), uncharacterized substances.

The results of the preparative photochemical studies are summarized in Table 1 and Scheme 6. Irradiation of the *N*-benzyl-*N*-trimethylsilylmethyl ketoamide **15** in MeOH results in the generation of a highly complex mixture of products, including substances which do (*β*-lactams **22** and **23**, oxazolidinones **28** and **29**) and do not contain TMS groups (*β*-lactam **21**, oxazolidinone **27**, α-hydroxyamides **22** and **23**, ester **37**). Photoreaction of **15** in MeCN also produces a complex product mixture comprised of TMS-containing (**22**, **23**, **38**) and non-TMS-containing (**21**, **27**, **39**, **40**) substances. Similar observations were made in studies of the *N*-methyl-substituted α-silylketoamide **16**. Irradiation of **16** in MeOH or MeCN brings about formation of products that contain (in MeOH **25**, **30**, **35**; in MeCN **25**) and do not contain TMS groups (in MeOH **24**, **34**, **36**; in MeCN **24**, **31**, **41**, **42**).

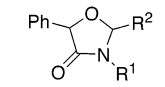
In contrast to the behavior of the TMS-substituted substrates, photoreactions of the tributylstannyl-ketoamides **19** and **20** produce less complex product mixtures. For example, irradiation of the *N*-benzyl analogue **19** in both MeOH and MeCN leads to formation of the tin-containing product **26** along with those that do not contain the tributyl-stannyl group (in MeOH **21**, **27**, **32**; in MeCN **21**, **27**). The *N*-methyl-*N*-tributylstannylmethyl ketoamide **20** participates in the most chemoselective photoreactions observed in this series. Irradiation of MeOH and MeCN solutions of **20** in each case leads to exclusive production of the nontributylstannyl containing *β*-lactam **24**, oxazolidinone **31**, and α-hydroxyamide **36**.

It seems reasonable to conclude that the major products generated in the photoreactions described above arise by secondary reactions of 1,4-dipolar intermediates,

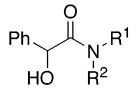
SCHEME 6



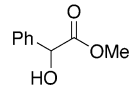
21 (R^1 = Bn, R^2 = H)
22 (R^1 = CH_2SiMe_3, R^2 = Ph)
23 (R^1 = Bn, R^2 = $SiMe_3$)
24 (R^1 = Me, R^2 = H)
25 (R^1 = Me, R^2 = $SiMe_3$)
26 (R^1 = CH_2SnBu_3, R^2 = Ph)



27 (R^1 = Bn, R^2 = H)
28 (R^1 = CH_2SiMe_3, R^2 = Ph)
29 (R^1 = Bn, R^2 = $SiMe_3$)
30 (R^1 = CH_2SiMe_3, R^2 = H)
31 (R^1 = Me, R^2 = H)



32 (R^1 = Bn, R^2 = CH_2OMe)
33 (R^1 = Bn, R^2 = H)
34 (R^1 = Me, R^2 = H)
35 (R^1 = CH_2SiMe_3, R^2 = CH_2OMe)
36 (R^1 = Me, R^2 = CH_2OMe)



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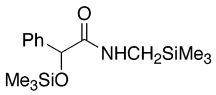

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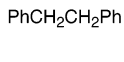

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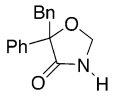

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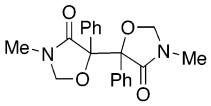

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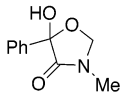

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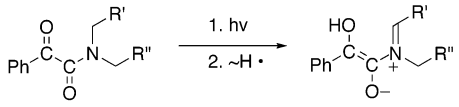
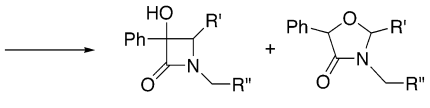
SCHEME 7



15-16, 19-20
(R' = H or Ph
and
R" = $SiMe_3$ or $SnBu_3$)

43
(R' = H or Ph; R" = $SiMe_3$ or $SnBu_3$
or
R' = $SiMe_3$ or $SnBu_3$R")



44 **45**

produced by H-atom abstraction and/or SET pathways. As shown in Scheme 7, H-atom transfer from α-positions of the *N*-alkyl or *N*-trialkylmetal groups to the phenone excited state gives rise to Si- or Sn-containing dipolar intermediates **43**. Electrocyclic ring closure of these intermediates leads to *β*-lactams **44** while oxazolidinones arise by intramolecular addition of the alcohol group to the iminium cation moiety in **43**. Also, hydrolysis (by adventitious water) and MeOH addition reactions of **43** yield α-hydroxyamide products. We suggest that in contrast sequential SET-demetalation pathways are responsible for formation of the *β*-lactams, oxazolidinones and α-hydroxyamide that do not contain either Me_3Si or

SCHEME 8

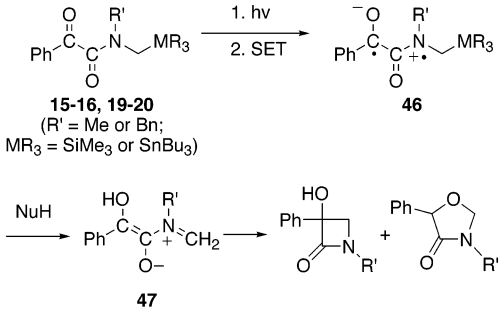


TABLE 2. Total Yields of Products Containing and Not Containing Me_3Si or Bu_3Sn Groups from Photoreactions of α-Ketoamides 15, 16, 19, and 20

ketoamide	solvent	total yield of MR_3-containing products (%)	total yield of non-MR_3-containing products (%)
15	MeOH	34	25
15	MeCN	36	39
16	MeOH	18	33
16	MeCN	7	48
19	MeOH	3	61
19	MeCN	3	49
20	MeOH	0	52
20	MeCN	0	49

Bu_3Su groups. In these cases, SET from the amide nitrogen to the excited ketone carbonyl gives rise to zwitterionic biradicals **46** (Scheme 8), which undergo nucleophile (H_2O or MeOH) induced demetalation to form the dipolar intermediates **47**.

On the basis the mechanistic proposals made above, the relative contributions of the H-atom abstraction and sequential SET-demetalation pathways to photoreactions of the Si- and Sn-substituted α-ketoamides can be approximated by evaluating the ratios of products that contain Me_3Si and Bu_3Sn groups to those in which these groups are absent. The ratios (Table 2) clearly demonstrate that (1) H-atom abstraction and SET-demetalation routes operate with nearly equal efficiencies in photoreactions of the *N*-benzyl-*N*-trimethylsilylmethyl substrate **15,** (2) the SET-demetalation pathway is favored over the H-atom abstraction route in the reaction of the *N*-methyl TMS-containing ketoamide **16**, and (3) photochemical reactions of the Bu_3Sn-substituted substrates **19** and **20** follow the SET-demetalation route nearly exclusively.

Several interesting conclusions come from the observations summarized above. First, since H-atom abstraction is competitive with sequential SET-desilylation (as expected, more so in reactions of the *N*-benzyl substrate) in substrates where the latter pathway is facilitated by lower oxidation potentials of the α-silyl amide moiety, it is reasonable to conclude that the photoreactions of *N*,*N*-dialkyl-substituted α-ketoamides studied earlier by Aoyama[7−10] are also initiated by ketone carbonyl H-atom abstraction. Thus, Aoyama's original mechanistic explanation[11] of these photoreactions appears to be correct. Second, photoreactions of the Bu_3Sn-substituted substrates, which follow the SET-destannylation pathway nearly exclusively, are highly regioselective because a single dipolar intermediate is selectively formed in these processes.

Experimental Section

***N*-(Trimethylsilyl)methyl-*N*-benzyl α-Ketoamide 15.** To the in situ prepared benzoylformic acid chloride (2.5 g, 15 mmol) in CH_2Cl_2 was added triethylamine (1.1 g, 11 mmol) followed by dropwise addition of *N*-(trimethylsilylmethyl)-benzylamine (2.0 g, 10.3 mmol) at 0 °C. The resulting mixture was warmed to 25 °C, stirred overnight, washed with water, dried, and concentrated in vacuo, giving a residue which was subjected to flash chromatography (silica gel, 1:9 EA−hexane) to yield **15** (2.8 g, 83%) as a solid: mp 66−69 °C; ^{1}H NMR (mixture of rotamers) 7.93−7.90 (m, 2H), 7.50−7.45 (m, 1H), 7.39−7.33 (m, 2H), 7.29−7.16 (m, 5H), 4.67 (s, 0.33H), 4.28 (s, 1.67H), 2.86 (s, 1.67H), 2.64 (s, 0.33H), 0.05 (s, 7.5H), −0.02 (s, 1.5H); ^{13}C NMR 191.2, 191.0, 166.2, 166.0, 135.5, 134.8, 134.1, 133.0, 129.2, 129.1, 128.5, 128.4, 128.3, 128.0, 127.7, 127.6, 53.0, 48.5, 37.5, 35.6, −1.6, −2.0; IR 1679, 1630; HRMS (FAB) *m*/*z* 326.1587 (calcd for $C_{19}H_{24}NO_2Si$, 326.1576).

***N*-(Trimethylsilyl)methyl-*N*-methyl α-Ketoamide 16.** To the in situ prepared benzoylformic acid chloride (3.4 g, 20 mmol) in CH_2Cl_2 was added *N*-(trimethylsilylmethyl)-*N*-methylamine (1.17 g, 10 mmol) at 0 °C. The temperature was raised to 25 °C, and the resulting mixture was stirred overnight and concentrated in vacuo affording a residue which was subjected to flash chromatography (silica gel, 1:3 EA−hexane) giving **16** (1.7 g, 71%): ^{1}H NMR (mixture of rotamers) 7.94−7.90 (m, 2H), 7.66−7.58 (m, 1H), 7.50−7.45 (m, 2H), 3.08 (s, 2H), 2.93 (s, 2.4H), 2.77 (s, 0.6H), 0.15 (s, 6.2H), 0.05 (s, 2.8H); ^{13}C NMR 191.9, 166.0, 134.5, 133.3, 129.6, 128.9, 41.4, 39.0, 37.5, 34.1, −1.5, −1.8; IR 1674, 1634; HRMS (FAB) *m*/*z* 250.1275 (calcd for $C_{13}H_{20}NO_2Si$ 250.1263).

***N*-(Tri-*n*-butylstannyl)methyl-*N*-benzyl α-Ketoamide 19.** Sodium hydride (95%, 280 mg, 11.1 mmol) was added to a solution of α-oxo-*N*-benzylbenzeneacetamide (2.66 g, 11.1 mmol) in DMF (25 mL). When evolution of hydrogen ceased (ca.15−30 min), tri-*n*-butylstannylmethyl iodide[20] (4.7 g, 10.8 mmol) was added, and the resulting mixture was stirred for 1 h at room temperature, poured into water, and extracted with ethyl ether. The organic layers were washed with water, dried, and concentrated in vacuo giving a residue which was subjected to flash chromatography (silica gel, 1:10 EA−hexane) to give **19** (4.94 g, 84%): ^{1}H NMR (mixture of rotamers) 7.99−7.95 (m, 2H), 7.62−7.58 (m, 1H), 7.51−7.44 (m, 2H), 7.35−7.24 (m, 5H), 4.63 (s, 0.23H), 4.37 (s, 1.77H), 2.91 (s, 0.23H), 2.88 (m, J = 14.3 Hz, 1.77H), 1.41−1.51 (m, 7H), 1.20−1.35 (m, 7H), 0.81−0.94 (m, 13H); ^{13}C NMR 191.4, 166.3, 136.1, 135.4, 134.5, 133.6, 129.8, 129.7, 129.0, 128.9, 128.7, 128.2, 128.1, 128.0, 54.7, 49.9, 33.4, 31.0, 29.0, 27.3, 13.7, 10.6; IR 1679, 1630; HRMS (FAB) *m*/*z* 550.2307 (calcd for $C_{28}H_{41}NO_2$-$Li^{120}Sn$ 550.2319), *m*/*z* 548.2297 (calcd for $C_{28}H_{41}NO_2Li^{118}Sn$ 548.2313), *m*/*z* 546.2304 (calcd for $C_{28}H_{41}NO_2Li^{116}Sn$ 546.2315).

***N*-(Tri-*n*-butylstannyl)methyl-*N*-methyl α-Ketoamide 20.** Sodium hydride (95%, 96 mg, 3.8) was added to the solution of α-oxo-*N*-methylbenzeneacetamide (615 mg, 3.8 mmol) in DMF (15 mL). When the evolution of hydrogen ceased (ca. 10−20 min), tri-*n*-butylstannylmethyl iodide (1.3 g, 3 mmol) was added and the resulting mixture was stirred for 1 h, poured into water, and extracted with ethyl ether. The organic layers were washed with water, dried, and concentrated in vacuo affording a residue which was subjected to flash chromatography (silica gel, 1:10 EA−hexane) giving **20** (1.3 g, 93%): ^{1}H NMR (mixture of rotamers) 7.90−7.87 (m, 2H), 7.60−7.53 (m, 1H), 7.45−7.39 (m, 2H), 3.06 (s, 2H), 3.01 (s, 0.4H), 2.91 (s, 2.6H), 1.54−1.44 (m, 7H), 1.40−1.19 (m, 7H), 1.00−0.79 (m, 13H); ^{13}C NMR 191.5, 165.6, 134.3, 133.3, 129.5, 128.7, 38.3, 35.8, 34.3, 33.6, 28.9, 27.3, 13.5, 10.4; IR: 1687, 1630; HRMS (FAB) *m*/*z* 470.1964 (calcd for $C_{22}H_{37}NO_2Li^{116}Sn$ 470.2002), 472.2034 (calcd for $C_{22}H_{37}NO_2Li^{118}Sn$ 472.2000), 474.2026 (calcd for $C_{22}H_{37}NO_2Li^{120}Sn$ 474.2006).

Irradiation of 15 in MeOH. A solution of **15** (400 mg, 1.23 mmol) in 100 mL of MeOH was irradiated for 4 h (100% conversion). Concentration of the photolysate in vacuo followed by preparative TLC of the resulting residue gave **21** (19 mg,

6%), **27** (6 mg, 3%), **22** (58 mg, 14%), **23** (13 mg, 3%), **28** (39 mg, 10%), **29** (28 mg, 7%), **32** (38 mg, 11%), **33** (15 mg, 5%), and **37** (20 mg, 10%).

Irradiation of 15 in MeCN. A solution of **15** (400 mg, 1.23 mmol) in 100 mL of MeCN was irradiated for 3 h (100% conversion). Concentration of the photolysate in vacuo followed by preparative TLC of the resulting residue gave **21** (30 mg, 10%), **22** (89 mg, 22%), **23** (23 mg, 6%), **27** (9 mg, 3%), and **38** (30 mg, 8%), **39** (9 mg, 4%), **40** (68 mg, 22%).

Irradiation of 16 in MeOH. A solution of **16** (300 mg, 1.21 mmol) in 100 mL of MeOH was irradiated for 3 h (100% conversion). Concentration of the photolysate in vacuo followed by preparative TLC of the resulting residue gave **24** (8 mg, 4%), **25** (9 mg, 3%), **30** (15 mg, 5%), **35** (34 mg, 10%), **36** (58 mg, 23%) **34** (11 mg, 6%), and **37** (14 mg, 7%).

Irradiation of 16 in MeCN. A solution of **16** (353 mg, 1.42 mmol) in 100 mL of MeCN was irradiated for 2 h (100% conversion). Concentration of the photolysate in vacuo followed by preparative TLC of the resulting residue gave **24** (35 mg, 14%), **25** (24 mg, 7%), **31** (15 mg, 6%), **41** (29 mg, 6%), and **42** (6 mg, 2%).

Irradiation of 19 in MeOH. A solution of **19** (400 mg, 0.74 mmol) in 100 mL of MeOH was irradiated for 3 h (100% conversion). Concentration of the photolysate in vacuo followed by preparative TLC of the resulting residue gave **21** (70 mg, 37%), **26** (11 mg, 3%), **27** (18 mg, 10%), **32** (52 mg, 15%), and **37** (10 mg, 8%).

Irradiation of 19 in MeCN. A solution of **19** (310 mg, 0.57 mmol) in 100 mL of MeCN was irradiated for 2.5 h (100% conversion). Concentration of the photolysate in vacuo followed by preparative TLC of the resulting residue gave **21** (60 mg, 42%), **26** (10 mg, 3%), and **27** (10 mg, 7%).

Irradiation of 20 in MeOH. A solution of **20** (393 mg, 0.84 mmol) in 100 mL of MeOH was irradiated for 4 h (100% conversion). Concentration of the photolysate in vacuo followed by preparative TLC of the resulting residue gave **24** (60 mg, 40%), **31** (13 mg, 9%), and **36** (54 mg, 31%).

Irradiation of 20 in MeCN. A solution of **20** (385 mg, 0.83 mmol) in 100 mL of MeCN was irradiated for 4 h (100% conversion). Concentration of the photolysate in vacuo followed by preparative TLC of the resulting residue gave **24** (65 mg, 44%) and **31** (8 mg, 5%).

Spectroscopic Data for Photoproducts.

21: mp 107−109 °C; ^{1}H NMR 7.46−7.22 (m, 10H), 5.22 (s, 1H), 4.47, 4.38 (ABq, J = 15.0 Hz, 2H), 3.50, 3.38 (ABq, J = 5.5 Hz, 2H); ^{13}C NMR 170.0, 138.5, 134.7, 128.8, 128.5, 128.2, 128.0, 127.8, 125.4, 85.4, 57.0, 45.8; IR 3338, 1724; HRMS (FAB) m/z 254.1194 (calcd for $C_{16}H_{16}NO_2$ 254.1181).

22: ^{1}H NMR 7.52−7.25 (m, 10H), 4.63 (s, 1H), 4.05 (s, 1H), 3.06, 2.35 (ABq, J = 15.4 Hz, 2H), 0.06 (s, 9H); ^{13}C NMR 169.5, 139.5, 133.6, 128.8, 128.6, 128.5, 128.2, 128.1, 125.5, 87.5, 72.9, 31.8, −1.7; IR 3305, 1728; HRMS (FAB) m/z 326.1570 (calcd for $C_{19}H_{24}NO_2Si$ 326.1576).

23: ^{1}H NMR 7.43−7.19 (m, 10H), 4.99, 4.02 (ABq, J = 15.3 Hz, 2H), 3.51 (s, 1H), 3.13 (s, 1H), 0.12 (s, 9H); ^{13}C NMR 169.8, 140.5, 135.5, 128.7, 128.7, 128.1, 128.1, 127.7, 125.2, 87.8, 61.2, 45.8, −1.9; IR 3305, 1728; HRMS (FAB) m/z 326.1586 (calcd for $C_{19}H_{24}NO_2Si$ 326.1576).

24. Three earlier reports[21−23] of this compound exist in which no spectroscopic data is given. The spectroscopic data for this substance given in a more recent publication matches the data accumulated in this effort:[24] mp 107−108 °C (lit.[24] mp 102−103 °C); ^{1}H NMR 7.45−7.27 (m, 5H), 4.85 (s, 1H), 3.56, 3.47 (ABq, J = 5.3 Hz, 2H), 2.85 (s, 3H); ^{13}C NMR 170.3, 138.5, 128.5, 128.3, 125.5, 86.1, 59.3, 28.4; IR 1736; HRMS (FAB) m/z 177.0779 (calcd for $C_{10}H_{11}NO_2$ 177.0790).

25: mp 135−137 °C; ^{1}H NMR 7.41−7.27 (m, 5H), 3.88 (s, 1H), 3.10 (s, 1H), 2.90 (s, 3H), 0.19 (s, 9H); ^{13}C NMR 169.7, 140.7, 128.6, 128.0, 125.2, 87.9, 63.1, 28.3, −2.1; IR 3305, 1732; HRMS (FAB) m/z 250.1257 (calcd for $C_{13}H_{20}NO_2Si$ 250.1263).

26: ^{1}H NMR 7.54−7.10 (m, 10H), 4.65 (s, 1H), 3.05, 2.53 (ABq, J = 13.3 Hz, 2H), 1.48−1.21 (m, 14H), 0.96−0.82 (m, 13H); ^{13}C NMR 169.5, 139.2, 133.8, 129.0, 128.7, 128.5, 127.9, 127.4, 125.7, 87.5, 73.7, 29.0, 27.3, 23.1, 13.6, 10.5. The instability of this compound prevented the accumulation of additional spectroscopic data.

27. The spectroscopic data accumulated for this substance matched those previously reported:[25] ^{1}H NMR 7.45−7.24 (m, 10H), 5.29 (s, 1H), 5.10, 5.04 (ABq, J ≈ 15.0 Hz, 2H), 4.55, 4.50 (ABq, J = 15.0 Hz, 2H); ^{13}C NMR 169.6, 136.3, 135.0, 128.9, 128.6, 128.5, 128.1, 127.9, 126.2, 79.9, 79.3, 44.5; IR HRMS (FAB) m/z 254.1189 (calcd for $C_{16}H_{16}NO_2$ 254.1181).

28. The spectroscopic data accumulated for this substance matched those previously reported:[26] ^{1}H NMR 7.50−7.33 (m, 10H), 5.96 (d, J = 2.0 Hz, 1H), 5.35 (d, J = 1.8 Hz, 1H), 2.87, 2.21 (ABq, J = 15.2 Hz, 2H), 0.03 (s, 9H); ^{13}C NMR 169.5, 136.4, 136.3, 130.3, 129.0, 128.5, 128.4, 128.1, 126.7, 92.3, 79.3, 32.1, −1.3; IR 1699; HRMS (FAB) m/z 324.1407 (calcd for $C_{19}H_{22}NO_2Si$ 324.1420), m/z 326.1561 (calcd for $C_{19}H_{24}NO_2Si$ 326.1576).

29: ^{1}H NMR 7.50−7.23 (m, 10H), 5.18 (d, J = 2.8 Hz, 1H), 4.96 (d, J = 2.9 Hz, 1H), 5.04, 4.13 (ABq, J = 15.5 Hz, 2H), 0.13 (s, 9H); ^{13}C NMR 171.7, 136.5, 135.7, 128.7, 128.4, 128.1, 127.8, 127.6, 126.9, 85.9, 79.3, 44.9, −3.8; IR 1695; HRMS (FAB) m/z 324.1424 (calcd for $C_{19}H_{22}NO_2Si$ 324.1420).

30: ^{1}H NMR 7.43−7.30 (m, 5H), 5.20−5.09 (m, 3H), 2.89, 2.72 (ABq, J = 15.4 Hz, 2H), 0.10 (s, 9H); ^{13}C NMR 168.9, 136.7, 128.6, 128.4, 126.3, 82.0, 79.0, 31.5, −1.8; IR 1699; HRMS (FAB) m/z 250.1270 (calcd for $C_{13}H_{20}NO_2Si$ 250.1263).

31. ^{1}H NMR spectroscopic data has been reported previously for this compound:[27] ^{1}H NMR 7.44−7.27 (m, 5H), 5.20−5.10 (m, 3H), 2.89 (s, 3H); ^{13}C NMR 169.6, 136.3, 128.5, 128.4, 126.2, 81.7, 78.9, 26.5; IR 1707; HRMS (FAB) m/z 248.1112 (calcd. for $C_{13}H_{18}NO_2Si$ 248.1107), m/z 250.1270 (calcd for $C_{13}H_{20}NO_2Si$ 250.1263).

32: ^{1}H NMR (mixture of rotamers) 7.34−6.95 (m, 10H), 5.34 (d, J = 6.5 Hz, 0.5H), 5.19 (d, J = 6.4 Hz, 0.5H), 5.09−4.95 (m, 1H), 4.61−4.20 (m, 4H), 3.26 (s, 1H), 3.08 (s, 2H); ^{13}C NMR 174.4, 173.6, 129.2, 129.1, 128.9, 128.9, 128.7, 128.6, 128.1, 127.8, 127.6, 127.4, 127.4, 126.6, 77.5, 76.1, 72.0, 71.8, 56.3, 55.3, 48.6, 47.7; IR 3415, 1646; HRMS (FAB) m/z 286.1448 (calcd for $C_{17}H_{20}NO_3$ 286.1443).

35: ^{1}H NMR (mixture of rotamers) 7.33−7.29 (m, 5H), 5.27, 4.69 (ABq, J = 6.6 Hz, 1H), 4.59, 4.18 (ABq, J = 10.7 Hz, 2H), 3.21, 2.83 (ABq, J = 15.1 Hz, 2H), 3.22 (s, 0.8H), 3.12 (s, 2.2H), 0.01 (s, 6.5H), −0.07 (s, 2.5H); ^{13}C NMR 172.4, 139.6, 129.0, 128.6, 127.4, 79.7, 77.8, 71.9, 71.7, 56.2, 55.2, 38.2, 36.1, −1.5, −1.9; IR 1646; HRMS (FAB) m/z 282.1537 (calcd for $C_{14}H_{24}NO_3Si$ 282.1525).

36. This substance has been reported previously,[28] but no spectroscopic data was given: ^{1}H NMR (mixture of rotamers) 7.42−7.30 (m, 5H), 5.26 (d, J = 6.1 Hz, 0.5H), 5.18 (d, J = 5.8 Hz, 0.5H), 4.85, 4.76 (ABq, J = 9.9 Hz, 1H), 4.67−4.60 (m, 1H), 4.58, 4.24 (ABq, J = 10.7 Hz, 1H), 3.18 (s, 1.7H), 3.05 (s, 1.3H), 3.00 (s, 1.3H), 2.72 (s, 1.7H); ^{13}C NMR 173.9, 173.3, 139.2, 138.6, 128.9, 128.6, 128.4, 127.5, 127.3, 126.1, 79.7, 78.5, 71.7, 71.6, 55.9, 55.1, 33.5, 32.6; IR 1711, 1650; HRMS (FAB) m/z 210.1143 (calcd for $C_{11}H_{16}NO$ 210.1130).

38: ^{1}H NMR 7.49−7.21 (m, 5H), 4.49 (s, 1H), 3.03 and 2.36 (ABq, J = 15.3 Hz, 2H), 0.06 (s, 9H); ^{13}C NMR 168.4, 134.6,

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128.5, 127.5, 126.0, 73.2, 31.9, 0.9, −1.6. The instability of this compound prevented the accumulation of additional spectroscopic data.

40: mp 134−135 °C; ^{1}H NMR 8.01 (s, 1H), 4.93, 4.65 (ABq, J = 2.7 Hz, 2H), 3.39, 3.13 (ABq, J = 13.9 Hz, 2H); ^{13}C NMR 174.6, 139.5, 135.4, 130.5, 128.7, 128.2, 127.8, 126.7, 125.2, 83.8, 75.5, 44.9; IR 3207, 1703; HRMS (FAB) m/z 254.1175 (calcd for $C_{16}H_{16}NO_2$ 254.1181)

41: mp 244−246 °C; ^{1}H NMR 7.60−7.20 (m, 10H), 4.79, 4.68 (ABq, J = 2.2 Hz, 4H), 2.62 (s, 6H); ^{13}C NMR 167.7, 134.5, 128.3, 127.6, 127.2, 82.7, 80.4, 26.5; IR 1699; HRMS (FAB) m/z 353.1490 (calcd for $C_{20}H_{21}N_2O_4$ 353.1501).

42: ^{1}H NMR 7.68−7.36 (m, 5H), 5.20, 5.05 (ABq, J = 3.2 Hz, 2H), 2.90 (s, 3H); ^{13}C NMR 167.7, 135.3, 129.7, 128.4, 126.0, 99.5, 79.3, 27.1; IR 3297, 1695; HRMS (FAB) m/z 194.0815 (calcd for $C_{10}H_{12}NO_3$ 194.0817).

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for all previously uncharacterized or not fully characterized compounds prepared in this study and Chem-3D plots of X-ray crystallographically determined atomic coordinates for and a summary of crystallographic parameters of **40**−**42**. This material is available free of charge via the Internet at http://pubs.acs.org.

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