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Single electron transfer-induced photocyclization reactions of *N*-[(*N*-trimethylsilylmethyl)aminoalkyl]phthalimides

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Abstract

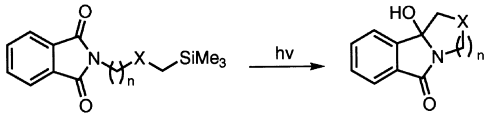
Studies have been conducted to explore single electron transfer (SET) induced photocyclization reactions of *N*-[(*N*-acetyl-*N*-trimethylsilylmethyl)amidoalkyl]phthalimides (alkyl ≡ ethyl, *n*-propyl, *n*-pentyl and *n*-hexyl) and *N*-[(*N*-mesyl-*N*-trimethylsilylmethyl)amidoethyl]phthalimide. Photocyclizations occur on irradation of these substances in methanol in modest to high yields to produce cyclized products in which the phthalimide carbonyl carbon has become bonded to the carbon of the side chain in place of the trimethylsilyl group. A mechanism for these photocyclization reactions involving intramolecular SET from nitrogen in the α-silylamido group to the singlet excited state of the phthalimide followed by desilylation of the intermediate α-silylamido cation radical and cyclization by radical coupling is proposed. Furthermore, photoreactivity of *N*-[(*N*-methyl-*N*-trimethylsilylmethyl)aminoethyl]phthalimide differs from the other members of this series. Here a route involving triplet hydrogen atom abstraction predominates over that involving sequential singlet SET-desilylation. A relationship between the quantum efficiencies for reactions of the phthalimides with various α-silyl-*n*-electron donors and the oxidation potentials of the electron donors has been noted. The results suggest that the rate of desilylation of the cation radical intermediate is an important factor in determining the quantum efficiency of the SET-induced photoreaction and that the desilylation rates are directly proportional to the oxidation potentials of the donors. The efficient and regioselective cyclization reactions observed for photolyses in methanol represent synthetically useful processes for construction of medium and large ring heterocyclic compounds. © 1997 Elsevier Science S.A.

Keywords: Single electron transfer; Photocyclizations; *N*-[(*N*-trimethylsilylmethyl)aminoalkyl]phthalimides; Quantum efficiencies; α-Silyl electron donors

1. Introduction

Recently, there have been a number of reports on photocyclization reactions of N-substituted phthalimides leading to new heterocycles with either nitrogen and oxygen, nitrogen and sulfur or nitrogen and nitrogen atoms in the newly formed rings [1]. However the photocyclization reactions operated by a mechanistic route involving intramolecular hydrogen abstraction by excited phthalimide carbonyls or sequential single electron transfer (SET)-deprotonation and they suffered from both low regioselectivities and low product yields.

Our recent studies of SET photochemistry using α-silyl electron donors have shown that photoinduced sequential SET-desilylation serves as an efficient and highly regioselective pathway for carbon centered radical generation [2]. Phthalimides have been found to undergo smooth photoaddition reactions in methanol with α-silyl electron donors to generate 3-substituted products via mechanistic routes which involve sequential SET-desilylation [3]. Similarly phthalimides tethered with α-silyl ether or thioether groups (**1**, X ≡ O or S) undergo efficient and high yielding photocyclization reactions to provide medium and large ring heterocycles **2** [4,5].



1. X=O or S **2**

In a continuation of our investigations aimed at developing new SET-induced photochemical reactions of synthetic utility, we have explored photocyclization reactions of a series of *N*-[(*N*-trimethylsilylmethyl)aminoalkyl]phthalimides (**3**).

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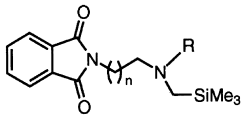


3a (n = 1, R = Me) **3d** (n = 4, R = Ac)
3b (n = 2, R = Ac) **3e** (n = 5, R = Ac)
3c (n = 3, R = Ac) **3f** (n = 1, R = Ms)

The results of this effort, reported below, show that *N*-[(*N*-acetyl-*N*-trimethylsilylmethyl)amidoalkyl)]phthalimides (**3b**–**3e**) and *N*-[(*N*-mesyl-*N*-trimethylsilylmethyl)amidoethyl]phthalimide (**3f**) undergo efficient and regioselective photocyclization reactions exclusively via sequential SET-desilylation pathways. On the other hand *N*-[(*N*-methyl-*N*-trimethylsilylmethyl)aminoethyl]phthalimide (**3a**) exhibits significantly different reactivity in photocyclization reactions [6].

2. Experimental details

2.1. General procedures

^{1}H nuclear magnetic resonance (NMR) and ^{13}C-NMR spectra were recorded using 200 MHz and 300 MHz spectrometers and chemical shifts are reported in parts per million downfield from tetramethylsilane employed as an internal standard; abbreviations used are s (singlet), d (doublet), t (triplet), and m (multiplet). ^{13}C-NMR resonances were assigned by use of the DEPT technique to determine the number of attached hydrogens. All compounds were obtained as oils (unless specified otherwise by giving a recorded melting point) and in purities of greater than 90% as judged by ^{1}H-NMR and ^{13}C-NMR. Preparative photolyses were conducted with an apparatus consisting of a 450 W medium mercury vapor lamp surrounded by a Pyrex filter in a quartz immersion well under an inert atmosphere. Low and high resolution mass spectral analyses were performed at 70 eV on a Hitachi VG-7070 mass spectrometer.

2.2. Syntheses

2.2.1. N-[N-Methyl-N-trimethylsilylmethyl)aminoethyl]-phthalimides (3a)

To a solution of phthalimide (1.42 g, 9.62 mmol), triphenylphosphine (2.52 g, 9.62 mmol), and 2-(*N*-methyl-*N*-trimethylsilylmethyl)amino-1-ethanol (**4**) (1.55 g, 9.62 mmol) in THF (30 ml) was added diethyl azodicarboxylate (1.68 g, 9.62 mmol). After stirring for 6 h at 25 °C, the solution was concentrated in vacuo giving a residue which was subjected to column chromatographic separation (silica, ethylacetate:hexane = 1:1) to give 1.09 g (39%) of **3a**. Spectral data for **3a**: ^{1}H-NMR ($CDCl_3$) −0.06 (s, 9H, $SiMe_3$), 1.92 (s, 2H, $C\underline{H}_2SiMe_3$), 2.24 (s, 3H, CH_3), 2.56 (t, 2H, J = 6.6 Hz, $C\underline{H}_2NCH_3$), 3.76 (t, 2H, J = 6.6 Hz, $NC\underline{H}_2CH_2$), 7.64–7.84 (m, 4H, aromatic); ^{13}C-NMR ($CDCl_3$) −0.6 ($SiMe_3$), 36.0 ($\underline{C}H_2SiMe_3$), 46.0 (CH_3), 49.7 ($\underline{C}H_2NCH_3$), 58.9 ($N\underline{C}H_2CH_2$), 132.2 and 134.2 (CH, aromatic), 133.8 (C, aromatic), 168.4 (C=O); IR (KBr) 1760 and 1720 cm^{-1} (C=O stretching); MS (EI) m/z (relative intensity) 290 (3), 275 (3), 217 (9), 160 (23), 147 (6), 130 (100), 104 (7), 73 (14); HRMS (EI) m/z 290.1441 ($C_{15}H_{22}N_2O_2Si$ requires 290.1450).

2.2.2. (N-Trimethylsilylmethyl)aminoalcohols (6a–6d)

To a solution of aminoalkyl alcohol (**5a** 10.4 g, 170 mmol; **5b** 4.7 g, 63 mmol; **5c** 10.0 g, 97 mmol; **5d** 5.0 g, 43 mmol) in acetonitrile (50 ml) was added trimethylsilylmethyl iodide (17.8 g, 83 mmol for **5a**; 12.0 g, 56 mmol for **5b**; 18.7 g, 87 mmol for **4c**; 12.0 g, 12 mmol for **5d**) dropwise. After stirring for 3 h at 70 °C the mixture was cooled to room temperature and extracted with ethyl ether. The ether solution was washed with water, dried over anhydrous Na_2SO_4 and concentrated in vacuo to afford a residue. From the residue, 11.3 g (93%) of **6a**, 7.6 g (58%) of **6b** and 2.1 g (86%) of **6d** were obtained respectively [7] by vacuum distillation (**6a** 49–52°/4 Torr; **6b** 60–62°/4 Torr; **6d** 80–82°/4 Torr). The residue for **6c** was subjected to column chromatographic separation (silica, ethyl acetate) to yield 5.6 g (30%) of **6c**. Spectral data for **6c**: ^{1}H-NMR ($CDCl_3$) 0.01 (s, 9H, $SiMe_3$), 1.34–1.57 (m, 7H, $\underline{H}OCH_2(C\underline{H}_2)_3$), 2.02 (s, 2H, $C\underline{H}_2SiMe_3$), 2.58 (t, 2H, J = 6.8 Hz, $C\underline{H}_2NH$), 3.57 (t, 2H, J = 6.4 Hz, $HOC\underline{H}_2$); ^{13}C-NMR ($CDCl_3$) −2.1 ($SiMe_3$), 23.9 ($HOCH_2CH_2C\underline{H}_2$), 29.6 ($\underline{C}H_2CH_2N$), 33.0 ($HOCH_2\underline{C}H_2$), 40.7 ($\underline{C}H_2SiMe_3$), 54.8 ($\underline{C}H_2N$), 62.5 ($HO\underline{C}H_2$); IR (KBr) 3000–3550 cm^{-1} (br, OH stretching); MS (CI) m/z (relative intensity) 190 (100), 174 (12), 116 (55), 101 (19), 74 (17); HRMS (CI) m/z 190.1618 ($C_9H_{24}NOSi$ requires 190.1627)

2.2.3. (N-Acetyl-N-trimethylsilylmethyl)amido alcohols (7a–7d)

To a solution of (*N*-trimethylsilymethyl)aminoalcohol (**6a** 2.70 g, 18.4 mmol; **6b** 2.19 g, 10.8 mmol; **6c** 2.42 g, 15.0 mmol; **6d** 2.19 g, 10.8 mmol) in acetonitrile (120 ml), 5 molar excess of potassium carbonate was suspended and was added acetyl chloride (2.0 ml, 27.6 mmol for **6a**; 1.6 ml, 22.5 mmol for **6b**; 3.1 ml, 44 mmol for **6c**; 1.2 ml, 16.2 mmol for **6d**) dropwise for 2 h at 0 °C. After stirring for 10 h at 0 °C, the mixture was filtered through Celite and extracted with 2 N NaOH solution (50 ml) and chloroform. The chloroform solution was washed with water, dried and concentrated in vacuo to afford a residue. From the residue, 3.10 g (89%) of **7a** [7], 2.36 g (78%) of **7b**, 4.10 g (60%) of **7c** and 1.28 g (4.8%) of **7d** were obtained by column chromatographic separation (silica, ethyl acetate). Spectral data for **7b** (1:2.0 mixture of two rotamers based on ^{1}H-NMR integration): ^{1}H-NMR ($CDCl_3$) of rotamer A 0.05 (s, 9H, $SiMe_3$), 1.24 (s, 1H, OH), 1.74–1.84 (m, 2H, $HOCH_2C\underline{H}_2$), 2.10 (s, 3H, CH_3), 2.81 (s, 2H, $C\underline{H}_2SiMe_3$), 3.34–3.38 (m, 2H, CH_2N), 3.63–3.69 (m, 2H, $HOC\underline{H}_2$), rotamer B 0.13 (s, 9H, $SiMe_3$),

1.24 (s, 1H, OH), 1.74–1.84 (m, 2H, $HOCH_2C\underline{H}_2$), 2.10 (s, 3H, CH_3), 2.81 (s, 2H, $C\underline{H}_2SiMe_3$), 3.42–3.51 (m, 4H, $NC\underline{H}_2CH_2C\underline{H}_2$); ^{13}C-NMR ($CDCl_3$) of rotamer A −1.1 ($SiMe_3$), 21.0 ($CH_3$), 30.9 ($NCH_2\underline{C}H_2$), 38.0 ($\underline{C}H_2SiMe_3$), 47.9 ($NCH_2$), 59.1 ($HOCH_2$), 169.6 (C=O), rotamer B −1.4 ($SiMe_3$), 21.7 (CH_3), 29.3 ($NCH_2\underline{C}H_2$), 39.9 ($\underline{C}H_2SiMe_3$), 43.3 (NCH_2), 58.1 ($HOCH_2$), 171.2 (C=O); IR (KBr) 3200–3600 (br, OH stretching), 1620 cm^{-1} (C=O stretching); MS (CI) m/z (relative intensity) 204 (14), 188 (95), 159 (100), 130 (35), 102 (17), 73 (60); HRMS (CI) m/z 204.1423 ($C_9H_{22}NO_2Si$ requires 204.1420). Spectral data for **7c** (1:2.0 mixture of two rotamers based on ^{1}H-NMR integration): ^{1}H-NMR ($CDCl_3$) of rotamer A 0.12 (s, 9H, $SiMe_3$), 1.33–1.44 (m, 7H, $\underline{H}OCH_2(C\underline{H}_2)_3$), 2.04 (s, 3H, CH_3), 2.84 (s, 2H, $C\underline{H}_2SiMe_3$), 3.19–3.28 (m, 2H, CH_2N), 3.64–3.67 (m, 2H, $HOC\underline{H}_2$), rotamer B 0.12 (s, 9H, $SiMe_3$), 1.54–1.63 (m, 7H, $\underline{H}OCH_2(C\underline{H}_2)_3$), 2.07 (s, 3H, CH_3), 2.82 (s, 2H, $C\underline{H}_2SiMe_3$), 3.19–3.28 (m, 2H, CH_2N), 3.64–3.67 (m, 2H, $HOC\underline{H}_2$); ^{13}C-NMR ($CDCl_3$) of rotamer A −1.2 ($SiMe_3$), 22.3 (CH_3), 23.4 ($HOCH_2CH_2\underline{C}H_2$), 26.8 ($\underline{C}H_2CH_2N$), 32.7 ($HOCH_2\underline{C}H_2$), 40.4 ($\underline{C}H_2SiMe_3$), 47.8 ($\underline{C}H_2N$), 62.3 ($HOCH_2$), 170.3 (C=O), rotamer B −0.8 ($SiMe_3$), 21.2 (CH_3), 23.5 ($HOCH_2CH_2\underline{C}H_2$), 28.5 ($\underline{C}H_2CH_2N$), 32.7 ($HOCH_2\underline{C}H_2$), 38.5 ($\underline{C}H_2SiMe_3$), 51.5 ($\underline{C}H_2N$), 62.2 ($HOCH_2$), 169.6 (C=O); IR (KBr) 3100–3500 (br, OH stretching), 1620 cm^{-1} (C=O stretching); MS (CI) m/z (relative intensity) 232 (24), 216 (100), 159 (89), 130 (75), 116 (34), 73 (80); HRMS (CI) m/z 232.1737 ($C_11H_{26}NO_2Si$ requires 232.1733). Spectral data for **7d** (1:2.5 mixture of two rotamers based on ^{1}H-NMR integration): ^{1}H-NMR ($CDCl_3$) of rotamer A −0.03 (s, 9H, $SiMe_3$), 1.14–1.20 (m, 9H, $\underline{H}OCH_2(C\underline{H}_2)_4$), 1.88 (s, 3H, CH_3), 2.69 (s, 2H, $C\underline{H}_2SiMe_3$), 3.03–3.14 (m, 2H, CH_2N), 3.40–3.48 (m, 2H, $HOC\underline{H}_2$), rotamer B −0.09 (s, 9H, $SiMe_3$), 1.33–1.42 (m, 9H, $\underline{H}OCH_2(C\underline{H}_2)_4$), 1.91 (s, 3H, CH_3), 2.66 (s, 2H, $C\underline{H}_2SiMe_3$), 3.03–3.14 (m, 2H, CH_2N), 3.40–3.48 (m, 2H, $HOC\underline{H}_2$); ^{13}C-NMR ($CDCl_3$) of rotamer A −1.5 ($SiMe_3$), 22.0 (CH_3), 25.4 ($\underline{C}H_2CH_2CH_2N$), 26.5 ($HOCH_2CH_2\underline{C}H_2$), 28.2 ($\underline{C}H_2CH_2N$), 32.5 ($HOCH_2\underline{C}H_2$), 39.9 ($\underline{C}H_2SiMe_3$), 47.2 ($CH_2N$), 62.0 ($HOCH_2$), 169.8 (C=O), rotamer B −1.1 ($SiMe_3$), 20.9 (CH_3), 25.6 ($\underline{C}H_2CH_2CH_2N$), 26.6 ($HOCH_2CH_2\underline{C}H_2$), 28.2 ($\underline{C}H_2CH_2N$), 32.5 ($HOCH_2\underline{C}H_2$), 38.2 ($\underline{C}H_2SiMe_3$), 51.1 ($CH_2N$), 62.0 ($HOCH_2$), 169.2 (C=O); IR (KBr) 3250–3600 (br, OH stretching), 1620 cm^{-1} (C=O stretching); MS (EI) m/z (relative intensity) 245 (2), 230 (100), 214 (27), 159 (68), 130 (50), 116 (24), 73 (79); HRMS (EI) m/z 245.1815 ($C_{12}H_{27}NO_2Si$ requires 245.1811).

*2.2.4. (N-Acetyl-N-trimethylsilylmethyl)amidoalkyl chlorides (**8a–8d**)*

To a stirred solution of (*N*-acetyl-*N*-trimethylsilylmethyl)amidoalcohol (**7a** 1.90 g, 10.1 mmol; **7b** 1.58 g, 7.8 mmol; **7c** 4.15 g, 18.0 mmol; **7d** 1.13 g, 4.6 mmol) in chloroform (30 ml) was added 1.5 molar equivalent of thionyl chloride dropwise at 0 °C and the resulting solution was heated for 5 h at 50 °C. The mixture was extracted with 2 N NaOH solution and chloroform and the chloroform solution was concentrated in vacuo to a residue. From the residue, 1.39 g (67%) of **8a**, 1.13 g (61%) of **8b**, 3.27 g (73%) of **8c** and 1.14 g (94%) of **8d** were obtained by column chromatographic separation (silica, ethyl acetate:hexane = 3:1). Spectral data for **8a** (1:1.3 mixture of two rotamers based on ^{1}H-NMR integration): ^{1}H-NMR ($CDCl_3$) of rotamer A 0.10 (s, 9H, $SiMe_3$), 2.10 (s, 3H, CH_3), 2.91 (s, 2H, $C\underline{H}_2SiMe_3$), 3.48–3.57 (m, 2H, CH_2N), 4.12–4.23 (m, 2H, $ClC\underline{H}_2$), rotamer B 0.05 (s, 9H, $SiMe_3$), 2.05 (s, 3H, CH_3), 2.81 (s, 2H, $C\underline{H}_2SiMe_3$), 3.48–3.57 (m, 2H, CH_2N), 4.12–4.23 (m, 2H, $ClC\underline{H}_2$); ^{13}C-NMR ($CDCl_3$) of rotamer A −1.6 ($SiMe_3$), 21.8 (CH3), 41.1 ($\underline{C}H_2SiMe_3$), 46.2 (CH_2N), 61.6 (CH_2Cl), 170.5 (C=O), rotamer B −1.2 ($SiMe_3$), 21.0 (CH_3), 38.4 ($\underline{C}H_2SiMe_3$), 49.3 (NCH_2), 61.0 (CH_2Cl), 169.6 (C=O); IR (KBr) 1740 cm^{-1} (C=O stretching). Spectral data for **8b** (1:2.0 mixture of two rotamers based on ^{1}H-NMR integration): ^{1}H-NMR ($CDCl_3$) of rotamer A −0.12 (s, 9H, $SiMe_3$), 1.74–1.81 (m, 2H, $ClCH_2C\underline{H}_2$), 1.82 (s, 3H, CH_3), 2.64 (s, 2H, $C\underline{H}_2SiMe_3$), 3.14–3.22 (m, 2H, $CH_2C\underline{H}_2N$), 3.27–3.35 (m, 2H, $ClCH_2$), rotamer B −0.19 (s, 9H, $SiMe_3$), 1.74–1.81 (m, 2H, $ClCH_2C\underline{H}_2$), 1.85 (s, 3H, CH_3), 2.55 ($C\underline{H}_2SiMe_3$), 3.14–3.22 (m, 2H, $CH_2C\underline{H}_2N$), 3.27–3.35 (m, 2H, $ClCH_2$); ^{13}C-NMR ($CDCl_3$) of rotamer A −2.2 ($SiMe_3$), 21.4 (CH_3), 29.4 ($ClCH_2\underline{C}H_2$), 40.0 ($\underline{C}H_2SiMe_3$), 42.1 ($CH_2\underline{C}H_2N$), 44.6 ($ClCH_2$), 169.3 (C=O), rotamer B −1.7 ($SiMe_3$), 20.4 (CH_3), 30.3 ($ClCH_2\underline{C}H_2$), 37.4 ($\underline{C}H_2SiMe_3$), 41.2 ($NC\underline{H}_2CH_2$), 47.4 ($ClCH_2$), 168.6 (C=O); IR (KBr) 3200–3600 (br, OH stretching), 1620 cm^{-1} (C=O stretching); MS (CI) m/z (relative intensity) 222 (5), 186 (78), 159 (49), 116 (58), 102 (93), 73 (100); HRMS (CI) m/z 222.1074 ($C_9H_{21}ClNOSi$ requires 222.1081). Spectral data for **8c** (1:2.2 mixture of two rotamers based on ^{1}H-NMR integration): ^{1}H-NMR ($CDCl_3$) of rotamer A 0.05 (s, 9H, $SiMe_3$), 1.68–1.78 (m, 6H, $ClCH_2(C\underline{H}_2)_3$), 1.97 (s, 3H, CH_3), 2.78 (s, 2H, $C\underline{H}_2SiMe_3$), 3.14–3.27 (m, 2H, CH_2N), 3.43–3.51 (m, 2H, $ClC\underline{H}_2$), rotamer B 0.00 (s, 9H, $SiMe_3$), 1.34–1.58 (m, 6H, $ClCH_2(C\underline{H}_2)3$), 2.01 (s, 3H, CH_3), 2.74 (S, 2H, $C\underline{H}_2SiMe_3$), 3.14–3.27 (m, 2H, CH_2N), 3.42–3.51 (m, 2H, $ClC\underline{H}_2$); ^{13}C-NMR ($CDCl_3$) of rotamer A −1.5 ($SiMe_3$), 22.1 (CH_3), 24.2 ($ClCH_2CH_2\underline{C}H_2$), 26.1 ($\underline{C}H_2CH_2N$), 32.3 ($ClCH_2\underline{C}H_2$), 40.0 ($\underline{C}H_2SiMe_3$), 44.9 ($CH_2N$), 47.1 ($ClCH_2$), 169.6 (C=O), rotamer B −1.1 ($SiMe_3$), 21.0 (CH_3), 24.1 ($ClCH_2CH_2\underline{C}H_2$), 27.7 ($\underline{C}H_2CH_2N$), 32.2 ($ClCH_2\underline{C}H_2$), 38.2 ($\underline{C}H_2SiMe_3$), 44.7 ($CH_2N$), 61.0 ($ClCH_2$), 169.0 (C=O); IR (KBr) 1640 cm^{-1} (C=O stretching); MS (CI) m/z (relative intensity) 250 (0.5), 214 (81), 159 (27), 130 (23), 116 (20), 73 (100); HRMS (CI) m/z 250.1408 ($C_{11}H_{25}ClNOSi$ requires 250.1394). Spectral data for **8d** (1:2.6 mixture of two rotamers based on ^{1}H-NMR integration): ^{1}H-NMR ($CDCl_3$) of rotamer A −0.30 (s, 9H, $SiMe_3$), 1.52–1.70 (m, 8H, $ClCH_2(C\underline{H}_2)_4$), 1.86 (s, 3H, CH_3), 2.68 (s, 2H, $C\underline{H}_2SiMe_3$), 3.05–3.18 (m, 2H, NCH_2), 3.35–3.42 (m, 2H, $ClCH_2$), rotamer B −0.10 (s, 9H,

$SiMe_3$), 1.05–1.48 (m, 8H, $ClCH_2(C\underline{H}_2)4$), 1.90 (s, 3H, CH_3), 2.64 (s, 2H, $C\underline{H}_2SiMe_3$), 3.05–3.18 (m, 2H, NCH_2), 3.35–3.42 (m, 2H, $ClC\underline{H}_2$); ^{13}C-NMR ($CDCl_3$) of rotamer A −1.5 ($SiMe_3$), 22.0 (CH_3), 26.1 ($\underline{C}H_2CH_2CH_2N$), 26.5 ($ClCH_2CH_2\underline{C}H_2$), 28.1 ($\underline{C}H_2CH_2N$), 32.4 ($ClCH_2\underline{C}H_2$), 39.8 ($\underline{C}H_2SiMe_3$), 44.9 ($NCH_2$), 47.1 ($ClCH_2$), 169.5 (C=O), rotamer B −1.1 ($SiMe_3$), 21.0 (CH_3), 26.0 ($\underline{C}H_2CH_2CH_2N$), 26.5 ($ClCH_2CH_2\underline{C}H_2$), 28.1 ($\underline{C}H_2CH_2N$), 32.4 ($ClCH_2\underline{C}H_2$), 38.1 ($\underline{C}H_2SiMe_3$), 44.8 ($NCH_2$), 50.9 ($ClCH_2$), 168.9 (C=O); IR (KBr) 1640 cm^{-1} (C=O stretching); MS (CI) m/z (relative intensity) 264 (3), 248 (94), 228 (38), 159 (89), 130 (56), 116 (25), 73 (100); HRMS (CI) m/z 264.1561 ($C_{12}H_{27}ClNOSi$ requires 264.1551)

2.2.5. *N-[(N-Acetyl-N-trimethylsilylmethyl)amidoalkyl]-phthalimides (**3b**–**3e**)*

To a solution of (*N*-acetyl-*N*-trimethylsilylmethyl)-amidoalkyl chloride (**8a** 1.40 g, 6.7 mmol; **8b** 1.30 g, 5.9 mmol; **8c** 0.59 g, 2.4 mmol; **8d** 1.62 g, 6.1 mmol) in DMF (20 ml) was added 1.5 molar equivalent of potassium phthalimide (**10**) and the reaction was stirred for 7 h at 70–80 °C. After removal of DMF in vacuo, the residue was dissolved in ethyl acetate and filtered. Concentration of the filtrate and column chromatography (silica, ethyl acetate) gave *N*-[(*N*-acetyl-*N*-trimethylsilylmethyl)amidoalkyl]phthalimides (**3b**–**3e**) respectively (**3b** 0.62 g, 29%; **3c** 1.64 g, 84%; **3d** 0.61 g, 72%; **3e** 2.21 g, 96%). Spectral data for **3b** (1:1.7 mixture of two rotamers based on ^{1}H-NMR integration): mp 104–107 °C; ^{1}H-NMR ($CDCl_3$) of rotamer A 0.12 (s, 9H, $SiMe_3$), 1.95 (s, 3H, CH_3), 2.90 (s, 2H, $C\underline{H}_2SiMe_3$), 3.50–3.66 (m, 2H, $C\underline{H}_2NAc$), 3.84–3.91 (m, 2H, $CONC\underline{H}_2$), 7.68–7.90 (m, 4H, aromatic), rotamer B 0.08 (s, 9H, $SiMe_3$), 2.11 (s, 3H, CH_3), 2.93 (s, 2H, CH_2SiMe_3), 3.50–3.66 (m, 2H, $C\underline{H}_2NAc$), 3.84–3.91 (m, 2H, $CONC\underline{H}_2$), 7.68–7.90 (m, 4H, aromatic); ^{13}C-NMR ($CDCl_3$) of rotamer A −1.5 ($SiMe_3$), 21.8 (CH_3), 35.1 ($CONC\underline{H}_2$), 40.3 ($\underline{C}H_2SiMe_3$), 45.5 ($\underline{C}H_2NAc$), 123.4 and 134.0 (CH, aromatic), 132.2 (C, aromatic) 168.1 (C=O), 169.5 ($\underline{C}OCH_3$), rotamer B −1.1 ($SiMe_3$), 20.9 (CH_3), 35.4 ($CONC\underline{H}_2$), 38.2 ($\underline{C}H_2SiMe_3$), 48.5 ($\underline{C}H_2NAc$), 123.6 and 134.4 (CH, aromatic), 131.9 (C, aromatic), 168.1 (C=O), 169.5 ($\underline{C}OCH_3$); IR (KBr) 1710 and 1630 cm^{-1} (C=O stretching); MS (EI) m/z (relative intensity) 318 (2), 303 (13), 247 (100), 189 (14), 145 (17), 101 (63), 59 (41); HRMS (EI) m/z 318.1396 ($C_{16}H_{22}N_2O_3Si$ requires 318.1399). Spectral data for **3c** (1:2.1 mixture of two rotamers based on ^{1}H-NMR integration): ^{1}H-NMR ($CDCl_3$) of rotamer A 0.06 (s, 9H, $SiMe_3$), 1.88–1.99 (m, 2H, $NCH_2C\underline{H}_2$), 2.01 (s, 3H, CH_3), 2.84 (s, 2H, $C\underline{H}_2SiMe_3$), 3.25–3.41 (m, 2H,$C\underline{H}_2NAc$), 3.62–3.71 (m, 2H, $CONC\underline{H}_2$), 7.68–7.86 (m, 4H, aromatic), rotamer B 0.01 (s, 9H, $SiMe_3$), 1.88–1.99 (m, 2H, $NCH_2C\underline{H}_2$), 2.04 (s, 3H, CH_3), 2.78 (s, 2H, $C\underline{H}_2SiMe_3$), 3.25–3.41 (m, 2H, $C\underline{H}_2NAc$), 3.62–3.71 (m, 2H, $CONC\underline{H}_2$), 7.68–7.86 (m, 4H, aromatic); ^{13}C-NMR ($CDCl_3$) of rotamer A −1.5 ($SiMe_3$), 22.1 (CH_3), 26.1 ($NCH_2\underline{C}H_2$), 35.9 ($CONC\underline{H}_2$), 39.9 ($\underline{C}H_2SiMe_3$), 44.8 ($\underline{C}H_2NAc$), 123.3 and 134.0 (CH, aromatic), 132.2 (C, aromatic), 169.1 (C=O), 169.9 ($\underline{C}OCH_3$), rotamer B −1.1 ($SiMe_3$), 21.1 (CH_3), 27.4 ($NCH_2\underline{C}H_2$), 35.6 ($CONC\underline{H}_2$), 38.2 ($\underline{C}H_2SiMe_3$), 48.8 ($\underline{C}H_2NAc$), 123.5 and 134.3 (CH, aromatic), 132.0 (C, aromatic), 168.3 (C=O), 170.0 ($\underline{C}OCH_3$); IR (KBr) 1630 and 1710 cm^{-1} (C=O stretching); MS (CI) m/z (relative intensity) 333 (7), 317 (48), 289 (3), 232 (3), 189 (14), 160 (43), 102 (29), 73 (100); HRMS (Cl) 333.1644 ($C_{17}H_{25}N_2O_3Si$ requires 333.1634). Spectral data for **3d** (1:2.2 mixture of two rotamers based on ^{1}H-NMR integration): ^{1}H-NMR ($CDCl_3$) of rotamer A 0.06 (s, 9H, $SiMe_3$), 1.28–1.32 (m, 6H, $NCH_2(C\underline{H}_2)_3$), 1.98 (s, 3H, CH_3), 2.79 (s, 2H, $C\underline{H}_2SiMe_3$), 3.12–3.20 (m, 2H, $C\underline{H}_2NAc$), 3.62–3.69 (m, 2H, $CONC\underline{H}_2$), 7.65–7.82 (m, 4H, aromatic), rotamer B 0.00 (s, 9H, $SiMe_3$), 1.54–1.67 (m, 6H, $NCH_2(C\underline{H}_2)_3$), 2.03 (s, 3H, CH_3), 2.76 (s, 2H $C\underline{H}_2SiMe_3$), 3.12–3.20 (m, 2H, $C\underline{H}_2NAc$), 3.62–3.69 (m, 2H, $CONC\underline{H}_2$), 7.65–7.82 (m, 4H, aromatic); ^{13}C-NMR ($CDCl_3$) of rotamer A −1.1 ($SiMe_3$), 22.4 (CH_3), 24.5 ($NCH_2CH_2\underline{C}H_2$), 26.7 ($CONCH_2\underline{C}H_2$), 28.7 ($\underline{C}H_2CH_2NAc$), 38.2 ($CONC\underline{H}_2$), 40.3 ($\underline{C}H_2SiMe_3$), 47.5 ($\underline{C}H_2NAc$), 123.5 and 134.3 (CH, aromatic), 132.5 (C, aromatic), 168.8 (C=O), 170.7 ($\underline{C}OCH_3$), rotamer B −0.7 ($SiMe_3$), 21.4 (CH_3), 24.4 ($NCH_2CH_2\underline{C}H_2$), 26.7 ($CONCH_2\underline{C}H_2$), 28.1 ($\underline{C}H_2CH_2$-NAc), 38.0 ($CONC\underline{H}_2$), 38.5 ($\underline{C}H_2SiMe_3$), 51.3 ($\underline{C}H_2NAc$), 123.6 and 134.4 (CH, aromatic), 132.4 (C, aromatic), 168.7 (C=O), 169.4 ($\underline{C}OCH_3$); IR (KBr) 1720 and 1640 cm^{-1} (C=O stretching); MS (EI) m/z (relative intensity) 360 (4), 345 (90), 200 (76), 159 (78), 130 (58), 73 (100); HRMS (EI) m/z 360.1848 ($C_{19}H_{28}N_2O_3Si$ requires 360.1869). Spectral data for **3e** (1:2.7 mixture of two rotamers based on ^{1}H-NMR integration): ^{1}H-NMR ($CDCl_3$) of rotamer A −0.02 (s, 9H, $SiMe_3$), 1.22–1.60 (m, 8H, $NCH_2(C\underline{H}_2)_4$), 1.89 (s, 3H, CH_3), 2.71 (s, 2H, $C\underline{H}_2SiMe_3$), 3.04–3.16 (m, 2H, $C\underline{H}_2NAc$), 3.49–3.58 (m, 2H, $CONC\underline{H}_2$), 7.56–7.72 (m, 4H, aromatic), rotamer B −0.08 (s, 9H, $SiMe_3$), 1.22–1.60 (m, 8H, $NCH_2(C\underline{H}_2)_4$), 1.93 (s, 3H, CH_3), 2.67 (s, 2H, $C\underline{H}_2SiMe_3$), 3.04–3.16 (m, 2H, $C\underline{H}_2NAc$), 3.49–3.58 (m, 2H, $CONC\underline{H}_2$), 7.56–7.72 (m, 4H, aromatic); ^{13}C-NMR ($CDCl_3$) of rotamer A −1.8 ($SiMe_3$), 21.8 (CH_3), 26.1 ($CONCH_2CH_2\underline{C}H_2$), 26.3 ($CON(CH_2)_3\underline{C}H_2$), 27.8 ($CONCH_2\underline{C}H_2$), 28.1 ($\underline{C}H_2CH_2NAc$), 37.5 ($CONC\underline{H}_2$), 39.5 ($\underline{C}H_2SiMe_3$), 46.8 ($\underline{C}H_2NAc$), 122.8 and 133.5 (CH, aromatic), 131.7 (C, aromatic), 167.9 (C=O), 169.1 ($\underline{C}OCH_3$), rotamer B −1.4 ($SiMe_3$), 20.7 (CH_3), 26.0 ($CONCH_2CH_2\underline{C}H_2$), 26.2 ($CON(CH_2)_3\underline{C}H_2$), 27.8 ($CONCH_2\underline{C}H_2$), 28.1 ($\underline{C}H_2CH_2NAc$), 37.4 ($CONC\underline{H}_2$), 37.7 ($\underline{C}H_2SiMe_3$), 50.7 ($\underline{C}H_2NAc$), 122.8 and 133.6 (CH, aromatic), 131.7 (C, aromatic), 167.9 (C=O), 168.5 ($\underline{C}OCH_3$); IR (KBr) 1710 and 1630 cm^{-1} (C=O stretching); MS (EI) m/z (relative intensity) 359 (100), 259 (4), 214 (70), 186 (26), 159 (98), 73 (100); HRMS (EI) m/z 359.1770 ($C_{19}H_{27}N_2O_3Si$ requires 359.1791).

2.2.6. N-(Mesyl-N-trimethylsilylmethyl)amidoethyl mesylate (9)

To a solution of 2-(*N*-trimethylsilylmethyl)amino-1-ethanol (**6a** 3.08 g, 20.8 mmol) in acetonitrile (100 ml) was suspended potassium carbonate (14.4 g, 100 mmol) and was added mesyl chloride (4.0 ml, 50 mmol) in acetonitrile (20 ml) dropwise for 1 h at 0 °C. After stirring for 20 h at 20 °C, the mixture was filtered through Celite and extracted with ether. Concentration of the ether solution and column chromatography (silica, ethyl acetate:hexane = 1:1) gave the mesylate **9** (4.44 g, 70%). Spectral data for **9**: mp 56–57 °C; ^{1}H-NMR ($CDCl_3$) 0.14 (s, 9H, $SiMe_3$), 2.74 (s, 2H, $C\underline{H}_2SiMe_3$), 2.86 (s, 3H, $NSO_2C\underline{H}_3$), 3.05 (s, 3H, $OSO_2C\underline{H}_3$), 3.51 (t, 2H, J = 5.8 Hz, $CH_2C\underline{H}_2N$), 4.36 (t, 2H, J = 5.8 Hz, $MsOC\underline{H}_2$); ^{13}C-NMR ($CDCl_3$) −2.2 ($SiMe_3$), 35.1 ($\underline{C}H_2SiMe_3$), 36.8 ($NSO_2\underline{C}H_3$), 39.0 ($OSO_2\underline{C}H_3$), 48.4 ($CH_2\underline{C}H_2N$), 66.7 ($MsO\underline{C}H_2$); IR (KBr) 1360 (OSO_2CH_3, S=O asymmetric stretching), 1310 (NSO_2CH_3, S=O asymmetric stretching), 1170 (OSO_2CH_3, S=O symmetric stretching), 1140 cm^{-1} (NSO_2CH_3, S=O symmetric stretching); MS (CI) m/z (relative intensity) 354 (0.2), 288 (M^+-CH_3, 8), 224 (M^+-Ms, 5), 208 (M^+-OMs, 4), 192 (M^+-CH_2OMs, 7), 137 (56); HRMS (CI) m/z 354.0714 ($C_8H_{22}NO_5S_2Si$ requires 354.0709).

2.2.7. N-[(N-Mesyl-N-trimethylsilylmethyl)amidoethyl]-phthalimide (3f)

A solution of (*N*-mesyl-*N*-trimethylsilylmethyl)-amidoethyl mesylate (**9**, 4.44 g, 14.6 mmol) and potassium phthalimide (**10**, 3.52 g, 19.0 mmol) in DMF was stirred for 3 h at 60–70 °C. After removal of DMF in vacuo, the residue was dissolved in methylene chloride and filtered. Concentration of the filtrate and column chromatography (silica, ethyl acetate:chloroform = 1:5) gave **3f** (3.83 g, 74%). Spectral data for **3f**: mp 125–126 °C; ^{1}H-NMR ($CDCl_3$) 0.18 (s, 9H, $SiMe_3$), 2.79 (s, 3H, $C\underline{H}_3$), 2.81 (s, 2H, $C\underline{H}_2SiMe_3$), 3.48 (t, 2H, 6.4 Hz, $CH_2C\underline{H}_2NMs$), 3.92 (t, 2H, J = 6.4 Hz, $CONCH_2$), 7.70–7.78 (4H, aromatic); ^{13}C-NMR ($CDCl_3$) −1.7 ($SiMe_3$), 36.0 ($\underline{C}H_3$), 36.4 ($\underline{C}H_2SiMe_3$), 39.2 ($CH_2\underline{C}H_2NMs$), 47.7 ($CON\underline{C}H_2$), 123.3 and 134.0 (CH, aromatic), 132.0 (C, aromatic), 168.0 (C=O); IR (KBr) 1720 (C=O stretching), 1330 (S=O asymmetric stretching), 1150 cm^{-1} (S=O symmetric stretching); MS (EI) m/z (relative intensity) 354 (0.25), 281 (M^+-$SiMe_3$, 0.6), 275 (M^+-Ms, 46), 267 (M^+-CH_2SiMe_3, 0.3), 202 (12), 174 (17), 160 (17), 87 (CH_2SiMe_3, 3), 73 (100); HRMS (EI) m/z 354.1079 ($C_{15}H_{22}N_2O_4SSi$ requires 354.1070).

2.3. Photoreactions

2.3.1. Irradiation of N-[(N-methyl-N-trimethylsilylmethyl)-aminoethyl]phthalimide (3a)

A solution of *N*-[(*N*-methyl-*N*-trimethylsilylmethyl)-aminoethyl]phthalimide (**3a** 400 mg, 1.38 mmol) in 200 ml of methanol was irradiated with Pyrex-filtered light under N_2 for 7 h (88% conversion of **3a**). Concentration of the photolyzate gave a residue which was subjected to column chromatography (silica, ethyl acetate) yielding 58 mg (22%) of cyclized product **11**, 98 mg (28%) of azetidinol **13**, and 75 mg (21%) of reduction product **14**. Spectral data for **11**: mp 143–144 °C; ^{1}H-NMR ($CDCl_3$) 1.84–1.98 (m, 2H, $C\underline{H}_2NCH_3$), 2.31 (s, 3H, CH_3), 2.76 and 2.81 (two d, 1H, J = 3.8 Hz, $C(OH)C\underline{H}_2$), 3.21–3.35 (m, 2H, $C\underline{H}_2CH_2NCH_3$), 4.05 and 4.12 (two d, 1H, J = 3.0 Hz, $C(OH)C\underline{H}_2$), 7.43–7.74 (m, 4H, aromatic); ^{13}C-NMR ($CDCl_3$) 36.0 ($\underline{C}H_2CH_2NCH_3$), 45.7 ($CH_3$), 54.1 ($\underline{C}H_2NCH_3$), 64.0 ($C(OH)\underline{C}H_2$), 84.9 (COH), 121.9, 123.6, 129.9 and 132.0 (CH, aromatic), 130.1 and 144.7 (C, aromatic), 170.3 (C=O); IR (KBr) 3600–3200 (br, OH stretching), 1690 cm^{-1} (C=O stretching); MS (EI) m/z (relative intensity) 218 (0.2), 130 (2), 105(4), 77 (5), 58 (100); HRMS (EI) m/z 218.1056 ($C_{12}H_{14}N_2O_2$ requires 218.1055). Spectral data for **13**: mp 188–189 °C; ^{1}H-NMR ($CDCl_3$) −0.05 (s, 9H, $SiMe_3$), 2.10 (s, 2H, $C\underline{H}_2SiMe_3$), 2.49 (s, 3H, CH_3), 2.77 (t, 1H, J = 11.9 Hz, CH), 4.30–4.59 (m, 2H, $CONC\underline{H}_2$), 7.11–7.39 (m, 4H, aromatic); ^{13}C-NMR ($CDCl_3$) −0.8 ($SiMe_3$), 39.4 ($\underline{C}H_2SiMe_3$), 45.5 (CH_3), 52.2 ($CON\underline{C}H_2$), 61.6 (CH), 92.2 (COH), 122.5, 123.0, 129.2 and 132.3 (CH, aromatic), 131.8 and 146.4 (C, aromatic), 168.6 (C=O); IR (KBr) 3600–3200 (br, OH stretching), 1700 cm^{-1} (C=O stretching); MS (CI) m/z (relative intensity) 291 (35), 275 (12), 217 (23), 203 (8), 174 (49), 160 (18), 147 (8), 130 (100), 104 (11), 87 (6), 73 (34); HRMS (EI) m/z 290.1431 ($C_{15}H_{22}N_2O_2Si$ requires 290.1450). Spectral data for **14**: ^{1}H-NMR ($CDCl_3$) 0.06 (s, 9H, $SiMe_3$), 1.90 (d, 1H, J = 14.4 Hz, $C\underline{H}_2SiMe_3$), 2.16 (d, 1H, J = 14.4 Hz, $C\underline{H}_2SiMe_3$), 2.33 (s, 3H, $C\underline{H}_3$), 2.37–2.42 (m, 1H, $C\underline{H}_2NCH_3$), 2.69–2.75 (m, 1H, $C\underline{H}_2NCH_3$), 3.17–3.24 (m, 1H, $CONC\underline{H}_2$), 4.21–4.26 (m, 1H, $CONC\underline{H}_2$), 5.68 (s, 1H, methine), 7.39–7.72 (m, 4H, aromatic); ^{13}C-NMR ($CDCl_3$) −1.3 ($SiMe_3$), 39.6 ($\underline{C}H_2SiMe_3$), 44.6 ($\underline{C}H_3$), 50.0 ($\underline{C}H_2NCH_3$), 62.0 ($CON\underline{C}H_2$), 82.5 (COH), 123.1, 123.2, 129.1 and 132.1 (CH, aromatic), 131.2 and 144.3 (C, aromatic), 167.5 (C=O); IR (KBr) 3600–3150 (br, OH strectching), 1710 cm^{-1} (C=O stretching); MS (EI) m/z (relative intensity) 292 (10), 217 (23), 176 (10), 160 (8), 130 (100), 105 (10), 77 (12), 59 (28); HRMS (EI) m/z 292.1570 ($C_{15}H_{24}N_2O_2Si$ requires 292.1607).

A solution of **3a** (900 mg, 3.1 mmol) in 200 ml of methanol–acetone (2:1) was irradiated for 3 h (82% conversion of **3a**) and subjected to work up and purification all as described above yielding 60 mg (11%) of **11**, 250 mg (34%) of **13**, and 250 mg (34%) of **14**.

2.3.2. Oxygen quenching of photoreaction of N-[(N-methyl-N-trimethylsilylmethyl)aminoethyl]phthalimide (3a)

Two solutions of *N*-[(*N*-methyl-*N*-trimethylsilylmethyl)-aminoethyl]phthalimide (**3a** 50 mg, 0.17 mmol) in 20 ml of methanol or methanol–acetone (2:1) were irradiated simultaneously in a Rayonet reactor with RUL-3000 lamps while one was purged with a stream of N_2 and the other with a stream of O_2. During irradiation, the two reaction mixtures

were intermittently analyzed and compared by TLC (silica, ethyl acetate).

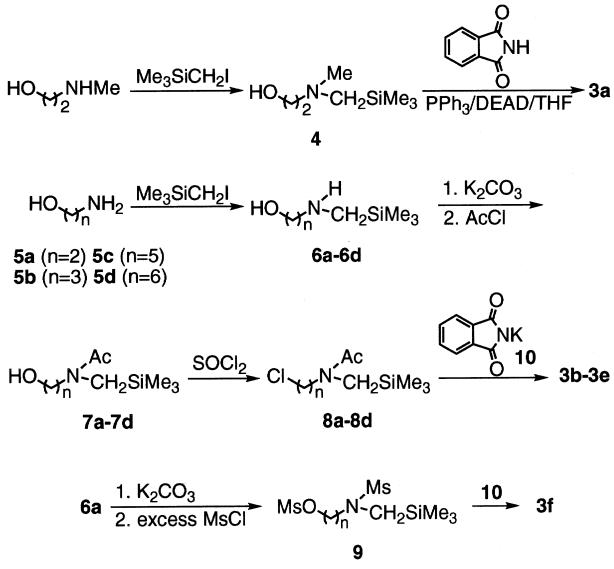
The formation of products **13** and **14** was completely quenched by O_2 while the formation of **11** was not quenched.

2.3.3. Irradiations of N-[(N-acetyl-N-trimethylsilylmethyl)-amidoalkyl]phthalimides (3b–3e)

A solution of *N*-[(*N*-acetyl-*N*-trimethylsilylmethyl)-amidoalkyl]phthalimide (**3b** 300 mg, 0.94 mmol; **3c** 500 mg, 1.51 mmol; **3d** 500 mg, 1.39 mmol; **3e** 500 mg, 1.34 mmol) in 100 ml of methanol was irradiated with Pyrex-filtered light under N_2 (irradiation time, percentage conversion: 3 h, 100% for **3b**; 5 h, 96% for **3c**; 2 h, 82% for **3d**; 3 h, 80% for **3e**). Concentration of the photolyzate gave a residue which was subjected to chromatogrophy (silica, ethyl acetate for **3b**, **3c** and **3d**, ethyl acetate:hexane = 3:1 for **3e**) yielding cyclized product (**15a** 155 mg, 67%; **15b** 222 mg, 59%; **15c** 236 mg, 72%; **15d** 216 mg, 67%). Spectral date for **15a** (1:1.6 mixture of two rotamers based on ^{1}H-NMR integration): mp 170–173 °C; ^{1}H-NMR ($CDCl_3$) of rotamer A 2.05 (s, 1H, OH), 2.19 (s, 3H, CH_3), 3.05–3.33 (m, 4H, $C\underline{H}_2C\underline{H}_2NAc$), 4.12 and 4.64 (two d, 2H, J = 14.0 Hz, $HOCC\underline{H}_2$), 7.45–7.70 (m, 4H, aromatic), rotamer B 2.05 (s, 1H, OH), 2.23 (s, 3H, CH_3), 3.05–3.33 (m, 4H, $C\underline{H}_2C\underline{H}_2NAc$), 4.28 and 5.21 (two d, 2H, J = 13.5 Hz, $HOCC\underline{H}_2$), 7.45–7.70 (m, 4H, aromatic); ^{13}C-NMR ($CDCl_3$) of rotamer A 21.7 (CH_3), 36.4 ($\underline{C}H_2CH_2NAc$), 46.0 ($CH_2\underline{C}H_2NAc$), 55.1 ($C(OH)\underline{C}H_2$), 85.3 (COH), 121.9, 123.7, 130.1 and 132.4 (CH, aromatic), 131.0 and 145.1 (C, aromatic), 165.4 (C=O), 170.7 ($\underline{C}OCH_3$), rotamer B 21.5 (CH_3), 36.2 ($\underline{C}H_2CH_2NAc$), 41.6 ($CH_2\underline{C}H_2NAc$), 55.2 ($C(OH)\underline{C}H_2$), 85.3 (COH), 122.0, 123.8, 130.2 and 132.6 (CH, aromatic), 131.1 and 145.1 (C, aromatic), 165.4 (C=O), 171.1 ($\underline{C}OCH_3$); IR (KBr) 3600–3150 (br, OH stretching), 1690 and 1630 cm^{-1} (C=O stretching); MS (CI) m/z (relative intensity) 247 (9), 229 (19), 228 (100), 186 (94), 129 (13), 103 (16), 77 (9); HRMS (CI) 247.1077 ($C_{13}H_{15}N_2O_3$ requires 247.1083). Spectral data for **15b** (1:1.3 mixture of two rotamers based on ^{1}H-NMR integration): mp 152–155 °C; ^{1}H-NMR ($CDCl_3$) 1.82 (CH_3-A), 2.10 (CH_3-B), 1.90–2.06 (m, 2H, $AcNCH_2C\underline{H}_2$), 3.11–3.31 (m, 2H, $CH_2C\underline{H}_2NAc$), 3.98–4.08 (m, 2H, $CONC\underline{H}_2$), 3.48 and 4.50 (two d, 2H, J = 14.3 Hz, $C(OH)C\underline{H}_2$), 5.18 (s, 1H, OH), 7.42–7.70 (m, 4H, aromatic); ^{13}C-NMR ($CDCl_3$) of rotamer A 20.9 (CH_3), 25.8 ($AcNCH_2\underline{C}H_2$), 35.6 ($CON\underline{C}H_2$), 47.5 ($CH_2\underline{C}H_2NAc$), 58.2 ($C(OH)\underline{C}H_2$), 89.8 (COH), 121.8, 123.3, 129.8 and 132.5 (CH, aromatic), 130.4 and 146.0 (C, aromatic), 167.2 (C=O), 170.9 ($\underline{C}OCH_3$), rotamer B 21.0 (CH_3), 26.9 ($AcNCH_2\underline{C}H_2$), 36.3 ($CON\underline{C}H_2$), 49.7 ($CH_2\underline{C}H_2NAc$), 55.3 ($C(OH)\underline{C}H_2$), 89.8 (COH), 122.2, 129.5 and 132.5 (CH, aromatic), 130.8 and 146.0 (C, aromatic), 167.0 (C=O), 172.2 ($\underline{C}OCH_3$); IR (KBr) 3200–3550 (br, OH stretching), 1700 and 1610 cm^{-1} (C=O stretching); MS (EI) m/z (relative intensity) 242 (M^+-H_2O, 100), 200 (78), 171 (40); HRMS (EI) m/z 260.1157 ($C_{14}H_{16}N_2O_3$ requires 260.1161). Spectral data for **15c**: mp 168–170 °C; ^{1}H-NMR ($CDCl_3$) 1.52–1.66 (m, 4H, $CONCH_2C\underline{H}_2C\underline{H}_2$), 1.76–1.94 (m, 2H, $C\underline{H}_2CH_2NAc$), 2.03 (s, 1H, OH), 2.27 (s, 3H, CH_3), 2.34–2.47 (m, 1H, $CONC\underline{H}_2$), 3.14–3.28 (m, 1H, $CONC\underline{H}_2$), 3.68–3.87 (m, 2H, $C\underline{H}_2NAc$), 2.89 and 4.76 (two d, 2H, J = 14.6 Hz, $C(OH)C\underline{H}_2$), 7.41–7.57 (m, 3H, aromatic), 7.72–7.78 (m, 1H, aromatic); ^{13}C-NMR ($CDCl_3$) 22.3 (CH_3), 25.1 ($NCH_2CH_2\underline{C}H_2$), 26.9 ($CONCH_2\underline{C}H_2$), 27.1 ($\underline{C}H_2CH_2NAc$), 41.0 ($CON\underline{C}H_2$), 55.2 ($\underline{C}H_2NAc$), 60.0 ($C(OH)\underline{C}H_2$), 90.6 (COH), 121.6, 123.4, 129.7 and 132.4 (CH, aromatic), 131.1 and 147.5 (C, aromatic), 169.6 (C=O), 176.3 ($\underline{C}OCH_3$); IR (KBr) 3200–3450 (br, OH stretching), 1690 and 1610 cm^{-1} (C=O stretching); MS (EI) m/z (relative intensity) 270 (100), 229 (8), 197(90), 185 (65), 132 (30), 89 (36), 70 (49); HRMS (EI) m/z 270.1377 (M^+-H_2O, $C_{16}H_{18}N_2O_2$ requires 270.1368). Spectral data for **15d**: mp 161–163 °C; ^{1}H-NMR ($CDCl_3$) 1.44–1.73 (m, 9H, $C(O\underline{H})CH_2NCH_2(C\underline{H}_2)4$), 2.24 (s, 3H, CH_3), 2.31–2.46 (m, 1H, $CONC\underline{H}_2$), 3.20–3.32 (m, 1H, $CONC\underline{H}_2$), 3.61–3.77 (m, 2H, $C\underline{H}_2NAc$), 3.05 and 4.65 (two d, 2H, J = 14.7 Hz, $C(OH)C\underline{H}_2$), 7.43–7.57 (m, 3H, aromatic), 7.74–7.78 (m, 1H, aromatic); ^{13}C-NMR ($CDCl_3$) 22.3 (CH_3), 23.1 ($CONCH_2CH_2\underline{C}H_2$), 25.0 ($CON(CH_2)_3\underline{C}H_2$), 26.0 ($CONCH_2\underline{C}H_2$), 26.1 ($\underline{C}H_2CH_2NAc$), 41.0 ($CON\underline{C}H_2$), 53.0 ($\underline{C}H_2NAc$), 61.2 ($C(OH)\underline{C}H_2$), 90.6 (COH), 121.6, 123.2, 129.5 and 132.2 (CH, aromatic), 130.9 and 147.9 (C, aromatic), 170.5 (C=O), 176.6 ($\underline{C}OCH_3$); IR (KBr) 3200–3550 (br, OH, stretching), 1660 and 1640 cm^{-1} (C=O stretching); MS (EI) m/z (relative intensity) 302 (21), 287 (100), 259 (53), 160 (13), 142 (10), 87 (16); HRMS (EI) m/z 302.1625 ($C_{17}H_{22}N_2O_3$ requires 302.1631).

2.3.4. Irradiation of N-[(N-mesyl-N-trimethylsilylmethyl)-amidoethyl]phthalimide (3f)

A solution of *N*-[(*N*-mesyl-*N*-trimethylsilylmethylamidoethyl]phthalimide (**3f** 800 mg, 2.26 mmol) in 150 ml of methanol was irradiated with Pyrex-filtered light under N_2 for 3 h (100% conversion of **3f**). Concentration of the photolyzate gave a crystalline product which was recrystallized in chloroform yielding 590 mg (92%) of cyclized product **12**. Spectral data for **12**: mp 213–214 °C; ^{1}H-NMR (DMSO-d_6) 2.76–2.86 (m, 1H, $C\underline{H}_2CH_2NMs$), 2.99 (s, 3H, $C\underline{H}_3$), 3.28–3.37 (m, 1H, $C\underline{H}_2CH_2NMs$), 3.68–3.73 (m, 1H, $CH_2C\underline{H}_2NMs$), 4.06–4.11 (m, 1H, $CH_2C\underline{H}_2NMs$), 2.74 and 4.14 (two d, 2H, J = 12.4 Hz, $C(OH)C\underline{H}_2$), 7.56–7.75 (m, 4H, aromatic); ^{13}C-NMR (DMSO-d_6) 35.2 ($\underline{C}H_2CH_2NMs$), 36.7 (CH_3), 44.3 ($CH_2\underline{C}H_2NMs$), 53.3 ($C(OH)\underline{C}H_2$), 83.7 (OH), 122.4, 122.8, 129.8 and 132.2 (CH, aromatic), 131.0 and 145.9 (C, aromatic), 163.8 (C=O); IR (KBr) 3600–3200 (OH stretching), 1680 (C=O stretching), 1340 (S=O asymmetric stretching), 1170 cm^{-1} (S=O symmetric stretching); MS (EI) m/z (relative intensity) 264 (M^+-H_2O, 1), 203 (M^+-SO_2CH_3, 100), 185 (8), 171 (1), 161 (3), 147 (7), 79 (SO_2CH_3, 2); HRMS (EI) m/z 203.0825 (M^+-SO_2CH_3, $C_{11}H_{11}N_2O_2$ requires 203.0820).



Scheme 1.

2.4. Quantum yields for photoreactions of phthalimides with α-silyl electron donor (*3a*, *3b*, *3f*, *16* and *17*)

Quantum yields were measured using a Rayonet photoreactor with 3000 Å light and a 0.10 M benzophenone–benzhydrol mixture was employed as actinometer. The sealed solutions containing phthalimide (**3a** 30.0 mg, 0.10 mmol; **3b** 76.8 mg, 0.24 mmol; **3f** 61.0 mg, 0.17 mmol; **16** 66.9 mg, 0.24 mmol; **17** 50.5 mg, 0.17 mmol) in methanol (18 ml) were simultaneously irradiated for 20 min in a merry-go-round apparatus (ca. 10%–20% conversions). From the crude photolyzates obtained after concentration in vacuo, unreacted phthalimides were separated and recovered by preparative thin layer chromatography (silica), and analyzed in methanol by UV spectroscopy at 292–294 nm to determine recovery of phthalimides **3a**, **3b**, **3f**, **16** and **17**.

2.5. Oxidation potentials of α-silyl electron donors

Pt electrodes were employed as a working electrode and a counter electrode. Before each experiment, a Pt electrode was prepared by cycling between -2.0 and $+2.0$ vs. a saturated calomel electrode (SCE) in 0.1 M H_2SO_4. All potentials were measured versus a saturated calomel electrode. A solution containing 2×10^{-3} M of 2-(*N*-methyl-*N*-trimethylsilylmethyl)amino-1-ethanol (**4**), 2-(*N*-acetyl-*N*-trimethylsilylmethyl)amino-1-ethanol (**7a**), *N*-(mesyl-*N*-trimethylsilylmethyl)aminoethyl mesylate (**9**), 2-trimethylsilylmethoxy-1-ethanol (**18**) and 2-trimethylsilylmethylthio-1-ethanol (**19**) in 0.1 M tetra-*n*-butyl ammonium perchlorate (TBAP)–acetonitrile, was purged with purified nitrogen and kept under atmosphere of nitrogen throughout the experiment. In all cases the scan rate was 50 mV s^{-1}. The measured oxidation potentials for the compounds are as follows: $+0.59$ V for **4**, $+1.72$ V for **7a**, $+2.01$ V for **9**, $+2.05$ V for **18** and $+1.71$ V for **19**.

3. Results

3.1. Preparation of N-[(N-trimethylsilylmethyl)aminoalkyl]phthalimides

For the photochemical studies, six *N*-[(*N*-trimethylsilylmethyl)aminoalkyl]phthalimide derivatives **3a**–**3f** were prepared in modest to good yields starting with 2-(*N*-methylamino)ethanol or the longer chain aminoalkyl alcohols **5a**–**5d** by use of the general reaction sequences outlined in Scheme 1.

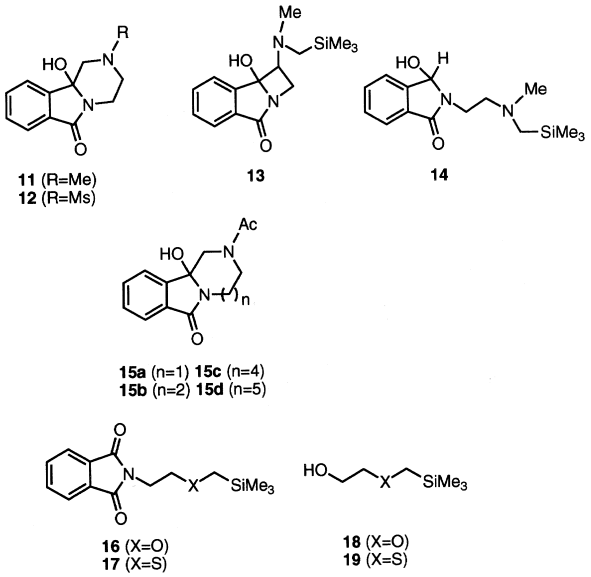
3.2. Photocyclizations of N-[(N-trimethylsilylmethyl)-aminoalkyl]phthalimides (*3a*–*3f*)

Photocyclization reactions of *N*-[(*N*-trimethylsilylmethyl)aminoalkyl]phthalimides (**3a**–**3f**) were explored. Preparative photocyclization reactions were performed by irradiation of methanol or methanol–acetone solutions of phthalimides (6.9–15.5 mM) by using Pyrex-filtered light ($\lambda > 290$ nm). Products were separated by use of silica gel chromatography. Product distributions and yields along with the reaction conditions employed are given in Table 1.

Table 1
Photochemical reactions of *N*-[(*N*-trimethylsilylmethyl)aminoalkyl]phthalimides

Phthalimide	Concentration (mM)	Solvent	Reaction time (h)	Conversion (%)	Products (yield %) [a]
3a	6.9	Methanol	7	88	**11** (22%), **13** (28%), **14** (21%)
3a	15.5	Methanol–acetone (2:1)	3	82	**11** (11%), **13** (34%), **14** (34%)
3b	9.4	Methanol	3	100	**15a** (67%)
3c	15.1	Methanol	5	96	**15b** (59%)
3d	13.9	Methanol	2	82	**15c** (72%)
3e	13.4	Methanol	3	80	**15d** (67%)
3f	15.1	Methanol	3	100	**12** (92%)

[a] Yields are based on consumed phthalimides **3a**–**3f**.



Irradiation of *N*-[*N*-methyl-*N*-trimethylsilylmethyl)-aminoethyl]phthalimide (**3a**) in methanol leads to production of a complex mixture of products including the six and four membered ring containing amidols **11** (22%) and **13** (28%) along with the reduced phthalimide **14** (21%). The same products are produced but via a more efficient reaction (i.e. shorter irradation time) when **3a** is irradiated in methanol–acetone (2:1). In contrast to this result, irradiation of *N*-[(*N*-acetyl-*N*-trimethylsilylmethyl)amidoalkyl]phthalimides (**3b**–**3e**) and *N*-[(*N*-mesyl-*N*-trimethylsilylmethyl)-amidoethyl]phthalimides, **3b**–**3f**, all of which contain N-electron withdrawing substituents, in methanol leads to rapid and high yielding production of the cyclized products **15a**–**15d** and **12** exclusively.

Structural assignments to the photoproducts were made on the basis of spectroscopic data. IR spectra of cyclized products **11**, **12**, **15a**, **15b**, **15c** and **15d** show characteristic absorption bands for hydroxy groups at 3150–3600 cm^{-1} and amide carbonyl group at 1610–1700 cm^{-1}. The ^{13}C-NMR spectra of these substances contain resonances which correspond to C-3 quarternary carbon at 83.7–90.6 ppm and methylene carbons α to nitrogen atom at 53.3–61.2 ppm. ^{1}H-NMR and ^{13}C-NMR spectra of the *N*-acetyl cyclized products **15a**–**15b** show that **15a**–**15b** exist as amide rotamers in ca. 2 to 3 ratios. Along with the disappearance of resonances for the trimethylsilyl (TMS) group in the ^{1}H-NMR and ^{13}C-NMR spectra found in the starting materials, the spectral features of the cyclization products are consistent with carbon–carbon bond formation between the phthalimide carbonyl carbons and carbons α to nitrogen formerly occupied by the silicon substituents. The ^{1}H-NMR spectrum of product **13** contains singlets at -0.05 ppm and 2.10 ppm for the TMS and methylene hydrogens α to nitrogen in addition to a triplet at 2.77 ppm for the methine hydrogen and multiplet at 4.30–4.59 for the methylene hydrogens of the azetidine ring, all of which are consistent with the assigned structure.

3.3. Oxygen quenching of the photoreaction of N-[(N-methyl-N-trimethylsilylmethyl)aminoethyl]phthalimide

As described above, photoreaction of *N*-[(*N*-methyl-*N*-trimethylsilylmethyl)aminoethyl]phthalimide (**3a**) produces azetidinol **13** and amidol **14** as major photoproducts. These substances are believed to be generated via intra- and inter-molecular hydrogen abstraction pathways. The photoreactivity observed in the reaction of **3a** is largely different from those observed in reactions of *N*-[(*N*-acetyl-*N*-trimethylsilylmethyl)amidoalkyl]phthalimides (**3b**–**3e**) and *N*-[(*N*-mesyl-*N*-trimethylsilylmethyl)amidoethyl]phthalimide (**3f**) in methanol which produce cylized products **15a**–**15d** and **12** exclusively in methanol. Noticeable changes occur in the product distribution and reaction rate when acetone is used as a cosolvent of the mixed solvent, methanol–acetone (2:1) in the photoreaction of **3a**. The product yields for **13** and **14** significantly increase while that of cyclized product **11** decreases. Moreover, the reaction rate increases by ca. 5 times for the reaction in the mixed solvent, methanol–acetone, as compared with that in methanol. These observations suggest that (1) the excited state of phthalimide **3a** responsible for formation of products **13** and **14** is a triplet while that for formation of cyclized product **11** is a singlet, and (2) reaction pathways via triplet excited state predominate over that via singlet excited state in reaction of **3a** in methanol. These results imply that singlet excited states are responsible for photoreactions of **3b**–**3f** which afford cyclized products **15a**–**15d** and **12**.

In order to obtain further information about the reactive excited states of **3a**–**3b**, oxygen quenching experiments were performed. Oxygen was not found to affect the efficiency of formation of **15a** and the conversion rate in reaction of **3b** in methanol, while oxygen results in almost no quenching of the formation of **11** and complete quenching of the production of **13** and **14** in the reaction of **3a** in methanol or in a mixed solvent, methanol–acetone.

3.4. Quantum yields for photoreactions of phthalimdes with α-silyl electron donor and oxidation potentials of α-silyl electron donors

Our previous investigations revealed that *N*-(trimethylsilylmethoxyalkyl)phthalimides (**1**, X≡O) [4] and *N*-(trimethylsilylmethylthioalkyl)phthalimides (**1**, X≡S) [5] undergo rapid and highly regioselective photocyclization reactions in methanol via sequential SET-desilylation pathways to give cyclized products **2** in high yields. As described above, *N*-[(*N*-acetyl-*N*-trimethylsilylmethyl)amidoalkyl]-phthalimides and *N*-[(*N*-mesyl-*N*-trimethylsilylmethyl)-amidoalkyl]phthalimides (**3a**–**3f**) undergo similar photocyclization reactions to give cyclized products **15a**–**15d** and **12**. However, photoreaction of *N*-[(*N*-methyl-*N*-trimethylsilylmethyl)aminoethyl)phthalimde (**3a**) exhibits completely different photoreactivity. Here an SET pathway leading to cyclized product **11** is not efficient and it competes unfavorably with hydrogen abstraction leading to **13** and **14**.

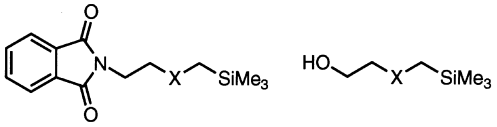
Table 2
Quantum yields for photoreactions of phthalimides with α-silyl electron donor and oxidation potentials of α-silyl electron donors

Phthalimide	Quantum yield [a]	Oxidation potential $E_{1/2(+)}$ [b] vs. SCE (eV)	Free energy for SET ΔG_{SET} [c] (eV)
3a	0.05	+0.59	−1.49
3b	0.22	+1.72	−0.36
3f	0.12	+2.01	−0.07
16	0.22	+2.05	−0.03
17	0.11	+1.71	−0.37

[a] Quantum yields for disappearance of phthalimides.
[b] Measured oxidation potentials of α-silyl electron donors (see Section 2).
[c] Reported reduction potential $E_{1/2(-)} = 1.37$ eV (vs. SCE) [8] and excited singlet energy $E_s = 3.45$ eV [9] of *N*-methylphthalimide were used for calculations [10].

Further, photoreaction of *N*-[(*N*-methyl-*N*-trimethylsilylmethyl)aminoethyl]phthalimide (**3a**) is observed to be much more sluggish than those of *N*-[(*N*-acetyl-*N*-trimethylsilylmethyl)amidoalkyl)phthalimides (**3b**–**3e**), *N*-[(*N*-mesyl-*N*-trimethylsilylmethyl)amidoethyl]phthalimide (**3f**), *N*-(trimethylsilylmethylthioalkyl)phthalimides (**1**, X≡S) and *N*-(trimethylsilylmethoxyalkyl)phthalimides (**1**, X≡O). Photocyclization of *N*-(trimethylsilylmethylthioalkyl)phthalimides (**1**, X≡S) are ca. 5–10 times less efficient than those of *N*-(trimethylsilylmethoxyalkyl)phthalimides (**1**, X≡O) [4,5].

Considering the fact that the oxidation potential of the donor side chain in this phthalimides should increase in the series tertiary amine < thioether < amide < ether, the observed reactivity of phthalimides tethered with these various α-silyl electron donors in SET-induced photocyclization reactions seems to be counterintuitive. In order to obtain more detailed information about the relationship between photoreactivities of phthalimides with various α-silyl electron donor side chains and oxidation potentials of the α-silyl electron donors, quantum yields for photoreactions of phthalimides with various electron donor **3a**–**3b**, **3f**, **16** [4], **17** [5] were determined. In addition, oxidation potentials of model α-silyl electron donors **4**, **7a**, **9**, **18** [4] and **19** [5] were measured. The data gained from these studies are compiled in Table 2 along with calculated free energy changes ΔG_{SET} [10] for SET from the α-silyl electron donors to singlet excited phthalimide [9].



16 (X=O)
17 (X=S)

18 (X=O)
19 (X=S)

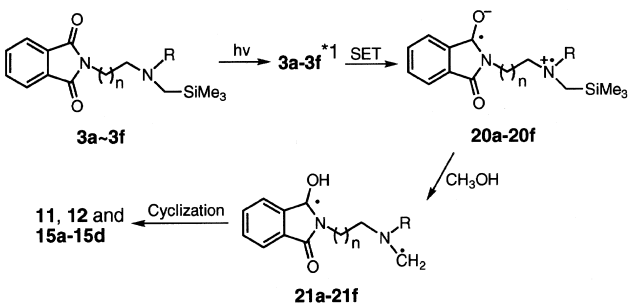
The data indicate that singlet state intramolecular SET is energetically favorable and, thus, rapid in photoreactions of all of the phthalimides **3a**–**3b**, **3f**, **16** and **17** ($\Delta G_{SET} < 0$). The quantum efficiencies of the photoreactions, however, are roughly directly related to the oxidation potential of the corresponding electron donor. Phthalimide **3a**, which has a tertiary α-silylamine with the lowest oxidation potential ($E_{1/2(+)} = +0.59$ V), exhibits the lowest quantum efficiency (0.05) and **17**, containing an α-silyl ether of the highest oxidation potential, has the largest quantum yield (0.22) for reaction. *N*-[(*N*-Acetyl-*N*-trimethylsilylmethyl)amidoethyl]phthalimide (**3b**) and *N*-[(*N*-mesyl-*N*-tri-methylsilylmethyl)amidoethyl]phthalimide (**3f**) have ca. 2–4 times larger quantum yields than *N*-[(*N*-methyl-*N*-trimethylsilylmethyl)aminoethyl)phthalimide (**3a**).

4. Discussion

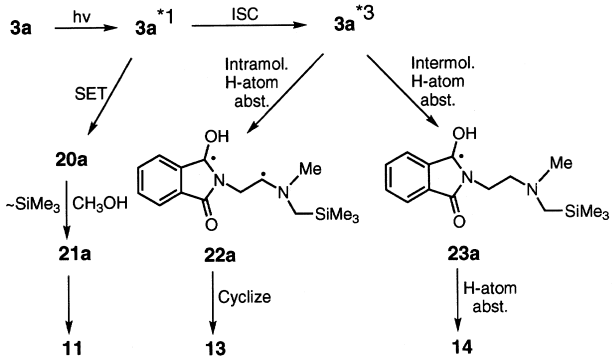
The observations presented above show that *N*-[(*N*-acetyl-*N*-trimethylsilylmethyl)amidoethyl]phtalimides and *N*-[(*N*-mesyl-*N*-trimethylsilylmethyl)amidoalkyl]phtalimides undergo photocyclization in methanol with high quantum efficiencies and high degrees of chemoselectivity and regioselectivity to generate cyclized products of various ring sizes (six to ten membered). The process formally involves bond formation between the phthalimide carbonyl carbon and the α-nitrogen carbon in place of the trimethylsilyl group. Results obtained in this study and those of our earlier investigations [3–5] of photoinduced SET reactions of phthalimide-α-silyl-*n*-electron donor systems in methanol suggest that photocyclizations leading to **11**, **12** and **15a**–**15d** occur via excited singlet state SET pathways (shown in Scheme 2). Accordingly, intramolecular SET in singlet excited phthalimides (**3a**–**3f**^{*1}) results in generation of zwitterionic radical intermediates **20a**–**20f** which undergo exclusive desilylation leading to biradicals **21a**–**21f**.

Biradicals **21a**–**21f** then undergo cyclization to produce cyclized products **11**, **12** and **15a**–**15d**. Further observations made in our study of the photoreactions of *N*-[(*N*-methyl-*N*-trimethylsilylmethyl)aminoethyl)phthalimide (**3a**) in methanol and a mixed solvent, methanol–acetone (2:1), and oxygen quenching suggest that phthalimide singlet excited states follow SET-desilylation pathways to produce cyclized products **11** whereas reaction of the triplet phthalimides involves intra- and inter-molecular hydrogen atom abstraction exclusively to form biradicals **22a** and **23a** which undergo cyclization or a second intermolecular hydrogen atom abstraction to produce products **13** and **14** respectively (Scheme 3).

As described above, our observations show that intersystem crossing followed by triplet reaction of **3a** (i.e. H-atom



Scheme 2.



Scheme 3.

abstraction) predominates over singlet state SET despite the fact that the tertiary amine is an excellent electron donor (i.e. low oxidation potential). In contrast, photoreactions of the phthalimides which contain poorer electron donor sites (i.e. amides, sulfonamides, ethers) are dominated by singlet state SET pathways. This suggests the interesting conclusion that singlet state SET-photoreactions in these phthalimides become less efficient with better electron donor substitution in the side chain. Two factors are probably responsible for this curious behavior. First, it is well known [11] that the rates of ion radical pair decay by back electron transfer are a function of the exothermicity. These processes in singlet ion radical pairs often fall in the Marcus-inverted region and thus have rates which are inversely dependent upon the thermodynamic driving force. Translated into the current topic, back electron transfer between radical ion pairs, formed by highly exothermic excited state SET (i.e. between phthalimide singlets and donors with low oxidation potentials), should be less exothermic than that between ion radical pairs formed by less exothermic excited state SET (i.e. from amides). Thus, in the former case back electron transfer should be faster. The second factor operating in controlling the efficiencies of singlet state reactions promoted by SET relates to the chemical reactivity of the α-silyl cation radical intermediates. The competition between desilylation and back electron transfer in these intermediates also governs the reaction quantum efficiencies. It has been reported that the rates of α-deprotonation of tertiary amine cation radicals directly depend on their oxidation potentials [12]. Recent unpublished results [13] show that this trend also holds for the methanol induced desilylation reactions of amine and amide cation radicals. Specifically, α-silylamide cation radicals undergo methanol induced desilylation ca. 10 times faster than do their α-silylamine derived counterparts.

There have been earlier studies on the photocyclization reactions of *N*-(aminoalklyl)phthalimides [14–17]. In these studies, acetone was employed as reaction solvent and, as a result, a mechanistic route involving triplet intramolecular hydrogen atom abstraction was the source of the observed reactivity of these systems. The photocyclization reactions were observed to suffer from low quantum efficiencies, low regioselectivities, and low product yields. However the photocyclization reactions of *N*-[(*N*-acetyl-*N*-trimethylsilylmethyl)aminoalkyl]phthalimides in methanol observed in the current work produce cyclized products, diazaheterocyclic compounds, in high chemical and quantum yields with high chemoselectivity and regioselectivity. Thus, they might hold synthetic utility for construction of medium to large ring heterocyclic compounds.

Acknowledgements

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References

[1] Y. Kanaoka, *Acc. Chem. Res., 11* (1978) 407. J.D. Coyle, in W.M. Horsepool (ed.), *Synthetic Organic Photochemistry*, Plenum, New York, 1984, p. 259. P.H. Mazzocchi, in A. Padwa (ed.), *Organic Photochemistry*, Vol. 5, Marcel Dekker, New York, 1981, p. 421.
[2] M.A. Brumfield, S.L. Quillen, U.C. Yoon and P.S. Mariano, *J. Am. Chem. Soc., 106* (1984) 6855. K. Ohga, U.C. Yoon and P.S. Mariano, *J. Org. Chem., 49* (1984) 213. M.A. Brumfield, U.C. Yoon, E. Hasegawa and P.S. Mariano, *J. Org. Chem., 53* (1988) 5435. U.C. Yoon, J.U. Kim, E. Hasegawa and P.S. Mariano, *J. Am. Chem. Soc., 109* (1987) 4421. E. Hasegawa, W. Xu, P.S. Mariano, U.C. Yoon and J.U. Kim, *J. Am. Chem. Soc., 110* (1988) 8099. U.C. Yoon, Y.C. Kim, J.J. Choi, D.U. Kim, P.S. Mariano, I.S. Cho and Y.T. Jeon, *J. Org. Chem., 57* (1992) 1422. U.C. Yoon and P.S. Mariano, *Acc. Chem. Res., 25* (1992) 233. U.C. Yoon, P.S. Mariano, R.S. Givens and B.W. Atwater, in P.S. Mariano (ed.), *Advances in Electron Transfer Photochemistry*, Vol. 4, JAI Press, Connecticut, 1994, p. 117.
[3] U.C. Yoon, H.J. Kim and P.S. Mariano, *Heterocycles, 29* (1989) 1041.
[4] U.C. Yoon, J.H. Oh, S.J. Lee, D.U. Kim, J.G. Lee, K.T. Kang and P.S. Mariano, *Bull. Korean Chem. Soc., 13* (1992) 166.
[5] U.C. Yoon, S.J. Lee, S.J. Cho, C.W. Lee and P.S. Mariano, *Bull. Korean Chem. Soc., 15* (1994) 154.
[6] Preliminary results are reported. U.C. Yoon, S.J. Cho, J.H. Oh, K.T. Kang, J.G. Lee and P.S. Mariano, *Bull. Korean Chem. Soc., 12* (1991) 241.
[7] Y.T. Jeon, C.P. Lee and P.S. Mariano, *J. Am. Chem. Soc., 113* (1991) 8847.
[8] O.W. Leedy and D.L. Muck, *J. Am. Chem. Soc., 93* (1971) 4264.
[9] J.D. Coyle, G.L. Newport and A. Harriman, *J. Chem. Soc. Perkin Trans. II*, (1978) 133.
[10] D. Rehm and A. Weller, *Isr. J. Chem., 8* (1970) 259.
[11] K.S. Peters, in P.S. Mariano (ed.), *Advances in Electron Transfer Chemistry*, Vol. 4, JAI Press, Connecticut, 1994, p. 27.
[12] X. Zhang, S.R. Yeh, S. Hong, M. Freccero, A. Albini, D.E. Falvey and P.S. Mariano, *J. Am. Chem. Soc., 116* (1994) 4211.
[13] P.S. Mariano, Z. Su and D.E. Falvey, unpublished results.
[14] M. Machida, H. Takechi and Y. Kanaoka, *Chem. Pharm. Bull., 30* (5) (1982) 1579.
[15] M. Machida, H. Takechi and Y. Kanaoka, *Heterocycles, 14* (1980) 1255.
[16] M. Machida, H. Takechi and Y. Kanaoka, *Synthesis*, (1982) 1078.
[17] J.D. Coyle and G.L. Newport, *Synthesis*, (1979) 381.