Applications of Phthalimide Photochemistry to Macrocyclic Polyether, Polythioether, and Polyamide Synthesis

Ung Chan Yoon,*,† Sun Wha Oh,† Jae Ho Lee,† Jong Hoon Park,† Kyung Tae Kang,† and Patrick S. Mariano‡

Department of Chemistry and the Chemistry Institute for Functional Materials, Pusan National University, Pusan 609-735, Korea, and Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131

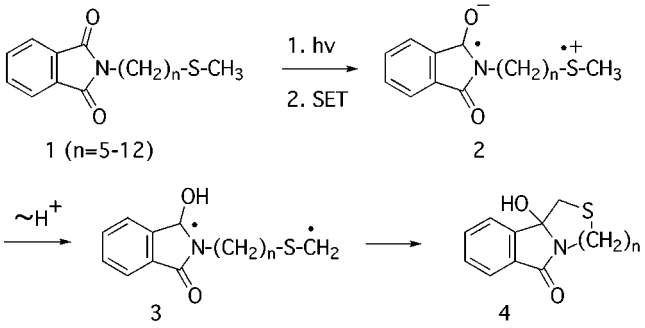
ucyoon@hyowon.pusan.ac.kr

Received October 10, 2000

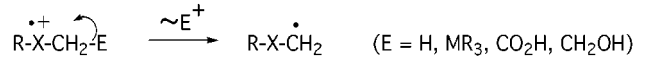
Irradiation of phthalimides which contain N-linked ω-trimethylsilylmethyl-substituted polyether, polythioether, and polysulfonamide chains results in efficient production of the corresponding macrocyclic polyether, polythioether, and polysulfonamide products. These photocyclization reactions follow sequential single electron transfer (SET)−desilylation pathways. Only in the cases of phthalimides, bearing mixed ether-thioether N-substituents, do these excited-state cyclization reactions proceed with lower degrees of regioselectivity. This is a result of competitive desilylation and α-to-sulfur deprotonation reactions of the zwitterionic diradical intermediates formed by initial SET.

Owing to their high singlet and triplet excited-state reduction potentials, phthalimides participate in photoinduced single-electron transfer (SET) reactions with a wide variety of electron donors.[1] Photocyclizations promoted by initial intramolecular excited-state SET have been observed in phthalimides having N-tethered-ether, -thioether, -silane, -arene, and -carboxylate electron donor groups.[2] Early examples of this reactivity profile are found in the photochemistry of the *N*-(methylthioalkyl)phthalimides **1** (Scheme 1).[3] In these cases, the excited-state SET pathway is dominant over H-atom abstraction processes, which are common in the photochemistry of *N*-alkylphthalimides.[4] The zwitterionic intermediates **2**, generated by intramolecular SET, undergo proton transfer to form diradicals **3**, precursors of the macrocyclic thioether photoproducts **4**.

Scheme 1



Scheme 2



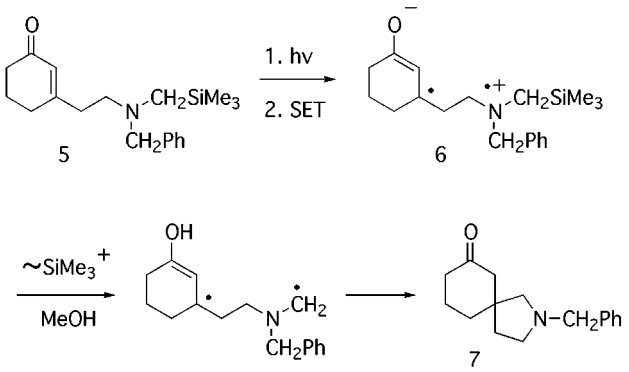
Cation radicals, arising by one-electron oxidation of *n*-electron donors, are known to participate in a number of different secondary reactions, which lead to formation of heteroatom-stabilized, carbon-centered radicals.[5] Examples of these α-heterolytic fragmentation reactions are deprotonation, decarboxylation, retro-aldol-type cleavage, and demetalation (Scheme 2). By using available rate data for these processes,[6] it is possible to design substrates that will undergo sequential SET-α-fragmentation reactions to furnish radical intermediates in a regioselective fashion. For example, both product distribution[7] and laser flash photolysis data[6] show that nucleophile-induced α-desilylation of α-silyl-substituted, heteroatom-centered, cation radicals is a faster process than α-deprotonation. Numerous observations made in studies of photoaddition and photocyclization reactions of systems composed of α-silylamines and α,β-unsaturated ketones,[8] α-diketones,[9] and phthalimides[10] show that the rate data can be used reliably to predict the nature of SET-promoted photochemical reactions. An early example is found in the photochemistry of the aminoenone **5** (Scheme 3),[11] where irradiation in MeOH leads

* To whom correspondence should be addressed.
† Pusan National University.
‡ University of New Mexico.

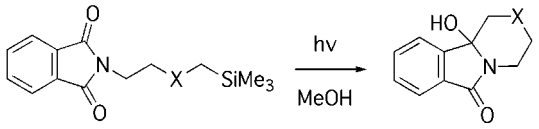
(1) Coyle, J. D. In *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum Press: New York, 1984; pp 259−284.
(2) *Cf.* Kanaoka, Y.; Migita, Y. *Tetrahedron Lett.* **1974**, 3693. Lee, Y. J.; Ling, R.; Mariano, P. S.; Yoon, U. C.; Kim, D. U.; Oh, S. W. *J. Org. Chem.* **1996**, *61*, 3304. Griesbeck, A. G. *Chimia* **1998**, *52*, 272.
(3) Sato, Y.; Nakai, H.; Ogiwara, H.; Mizoguchi, T.; Migata, Y.; Kanaoka, Y. *Tetrahedron Lett.* **1973**, 4565.
(4) Kanaoka, Y.; Migita, Y.; Koyama, K.; Sato, Y.; Nakai, H.; Mizoguchi, T. *Tetrahedron Lett.* **1973**, 1193. Kanaoka, Y. *Acc. Chem. Res.* **1978**, *11*, 407.
(5) Cf. Mariano, P. S.; Stavinoha, J. L. In *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum Press: New York, 1984; pp 145−258.
(6) Zhang, X. M.; Yeh, S. R.; Hong, S.; Freccero, M.; Albini, A.; Falvey, D. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1994**, *116*, 4211. Su, Z.; Falvey, D. E.; Yoon, U. C.; Oh, S. W.; Mariano, P. S. *J. Am. Chem. Soc.* **1998**, *120*, 10676.
(7) d'Alessandro, N.; Albini, Al; Mariano, P. S. *J. Org. Chem.* **1993**, *58*, 937.
(8) Yoon, U. C.; Mariano, P. S. *Acc. Chem. Res.* **1992**, *25*, 233.
(9) Yoon, U. C.; Kim, Y. C.; Choi, J. J.; Kim, D. U.; Mariano, P. S.; Cho, I. S.; Jeon, Y. T. *J. Org. Chem.* **1992**, *57*, 1422.
(10) Yoon, U. C.; Kim, J. W.; Ryu, J. Y.; Cho, S. J.; Oh, S. W.; Mariano, P. S. *J. Photochem. Photobiol. A: Chem.* **1997**, *106*, 145.

10.1021/jo001457u CCC: $20.00
Published on Web 01/12/2001

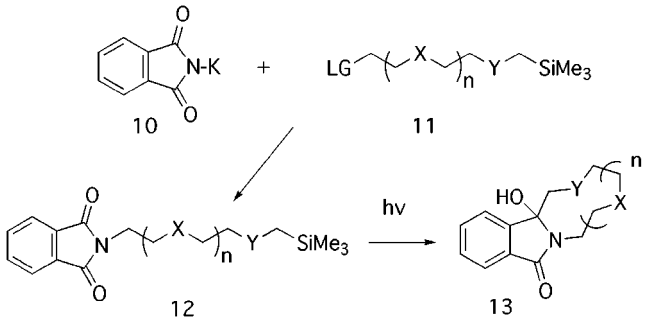
Scheme 3



Scheme 4



Scheme 5

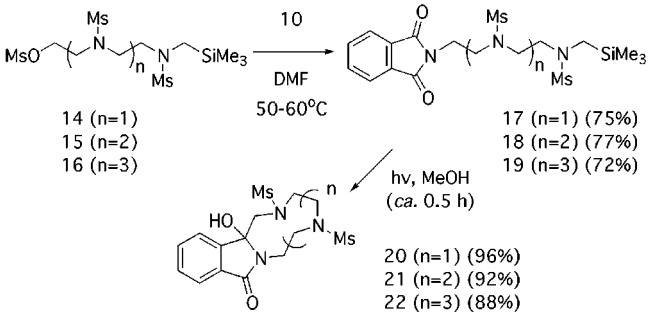


to exclusive generation of the spirocyclic aminoketone **7**. In this case, the initially formed zwitterionic diradical **6** undergoes MeOH-induced desilylation in preference to proton transfer from the reasonably acidic[12] α-benzylic site.

In a series of related studies, we have shown how knowledge of the rates of cation radical α-desilylation can be used to design efficient photocyclization reactions of α-silylamine-, -amide-, -ether-, and -thioether-tethered phthalimides (**8** → **9**, Scheme 4).[10,13] More recently, we have found that this excited-state SET chemistry can be used in efficient and selective methods to prepare a variety of macrocyclic polyethers, -thioethers, and -sulfonamides. In this paper, we describe the results of our studies with phthalimide derivatives of general structure **12**, which have led to the development of efficient photomacrocyclization reactions (**12** → **13**, Scheme 5).

The phthalimides, used in this investigation, are prepared by use of N-alkylation reactions of potassium phthalimide (**10**) with the corresponding polyamide or polyether-linked mesylates or halides (**11**, LG = OMS, Cl, or Br). For example, the α-silyl polysulfamidophthalimides **17**−**19** are efficiently (72−77%) generated in

Scheme 6



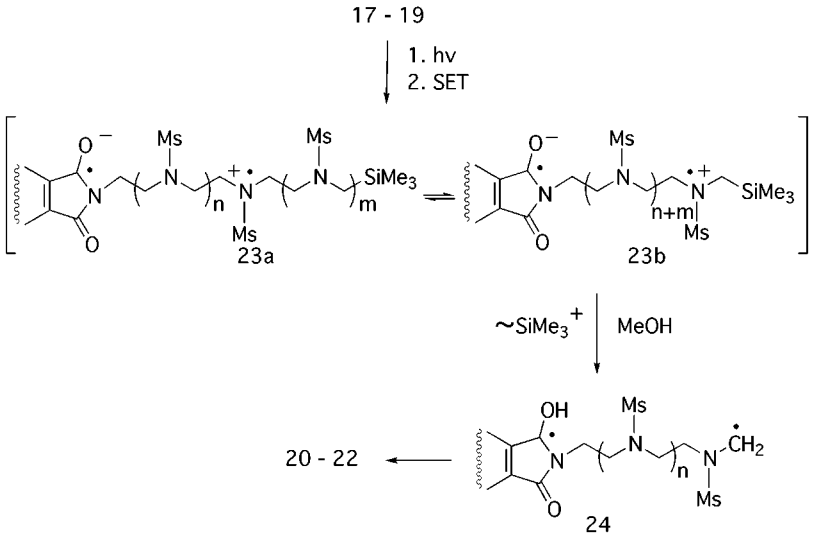
reactions of the mesylates **14**−**16** with **10** in DMF at 50−60 °C (Scheme 6). As observed with more simply structured substrates (Scheme 4),[10,13] irradiation ($\lambda > 290$ nm) of MeOH solutions (ca. 8mM) of the phthalimides **17**−**19** results in high-yielding (88−96%) formation of the macrocyclic polyamides **20**−**22** (Scheme 6). The high chemical yields associated with these photocyclizations are, in part, a consequence of the fast rates of intramolecular SET from the amide donor sites to the phthalimide singlet excited states. This makes other excited-state reaction pathways, like hydrogen-atom abstraction, uncompetitive. This most likely produces a mixture of equilibrating zwitterionic diradicals **23** (Scheme 7) whose population is governed by the oxidation potentials of the individual amide moieties. Because the rates of amide cation radical α-desilylation far exceed those of α-deprotonation,[6] MeOH-induced desilylation of **23b** occurs selectively to produce 1,ω-diradicals **24**, the precursors of the aza-crowns **20**−**22**.

In a similar manner, the phthalimido-polythioethers **25**−**26** undergo efficient photocyclization when irradiated in MeOH solutions (Scheme 8). These processes are accompanied by low-yielding formation of the benzazepinedione **29**, which results from a complex multiphoton pathway, initiated by competitive α-deprotonation of the proximal cation radical **30** and terminated by a Norrish type II photocleavage reaction (Scheme 9).[14]

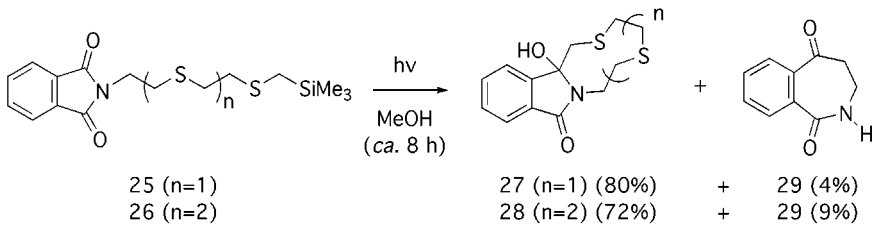
Previously, we described the results of a preliminary study of the photocyclization reactions of the phthalimido-α-silyl-polyethers **31** ($n = 1-5$).[15] Like their thia-analogues, these substrates also produce the corresponding crown ethers **32** upon irradiation in MeOH (Scheme 10). To determine if this photochemical methodology can be used to prepare mixed, oxygen−sulfur substituted macrocyclic polyethers, the phthalimides **33**, **34**, **37**, **39**, and **41**, differing in the relative positions of the ether and thioether moieties, were prepared and subjected to photochemical study. As seen by inspecting the results summarized in Scheme 11, irradiation of MeOH solutions of these substances leads in all but one case to predominant formation of the macrocyclic product arising by operation of the sequential SET-desilylation pathway.[16] The single exception is reaction of the phthalimide **41** where the macrocycle **43**, arising by an SET-proton-transfer route, is generated in a slight excess over the SET-desilylation derived product **42**.

(11) Wu, W.; Zhang, X. M.; Mariano, P. S. *J. Am. Chem. Soc.* **1991**, *113*, 8847.
(12) Xu, W.; Mariano, P. S. *J. Am. Chem. Soc.* **1991**, *113*, 1431.
(13) Yoon, U. C.; Lee, S. J.; Lee, K. J.; Cho, S. J.; Lee, C. W.; Mariano, P. S. *Bull. Kor. Chem. Soc.* **1994**, *15*, 154. Yoon, U. C.; Cho, S. J.; Oh, J. H.; Lee, J. G.; Kang, K. T.; Mariano, P. S. *Bull. Kor. Chem. Soc.* **1991**, *12*, 241.
(14) Griesbeck, A. G.; Henz, A.; Kramer, W.; Wamser, P.; Peters, K.; Peters, E. M. *Tetrahedron Lett.* **1998**, *39*, 1549.
(15) Yoon, U. C.; Oh, S. W.; Mariano, P. S. *Heterocycles* **1995**, *41*, 2665.
(16) Wada, M.; Nakai, H.; Sato, Y.; Hatanaka, Y.; Kanaoka, Y. *Chem. Pharm. Bull.* **1983**, *31*, 429.

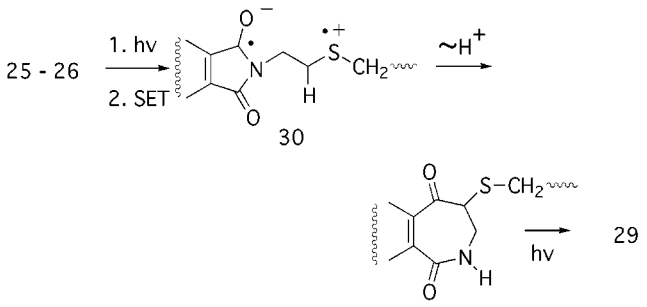
Scheme 7



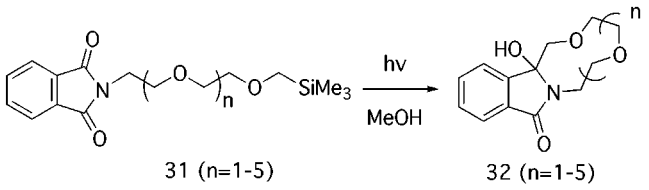
Scheme 8



Scheme 9



Scheme 10



The results presented above clearly show that SET-promoted photochemical reactions of substances containing phthalimide acceptors and α-silyl substituted donors serve as key steps in efficient methods for macrocyclic polyether, -thioether, and -amide synthesis. Accordingly, the presence of the trialkylsilyl group in these substrates governs reactions of intermediate zwitterionic diradicals, which lead to highly selective formation of photocyclization products. Only in the cases where sulfur is present in nonterminal positions of mixed ether-thioether side chains do sequential SET-proton transfer pathways become competitive. The high predictability of this cation radical chemistry suggests that it may be more widely applied to the design of synthetically relevant ground and excited-state SET-oxidation processes.

Experimental Section

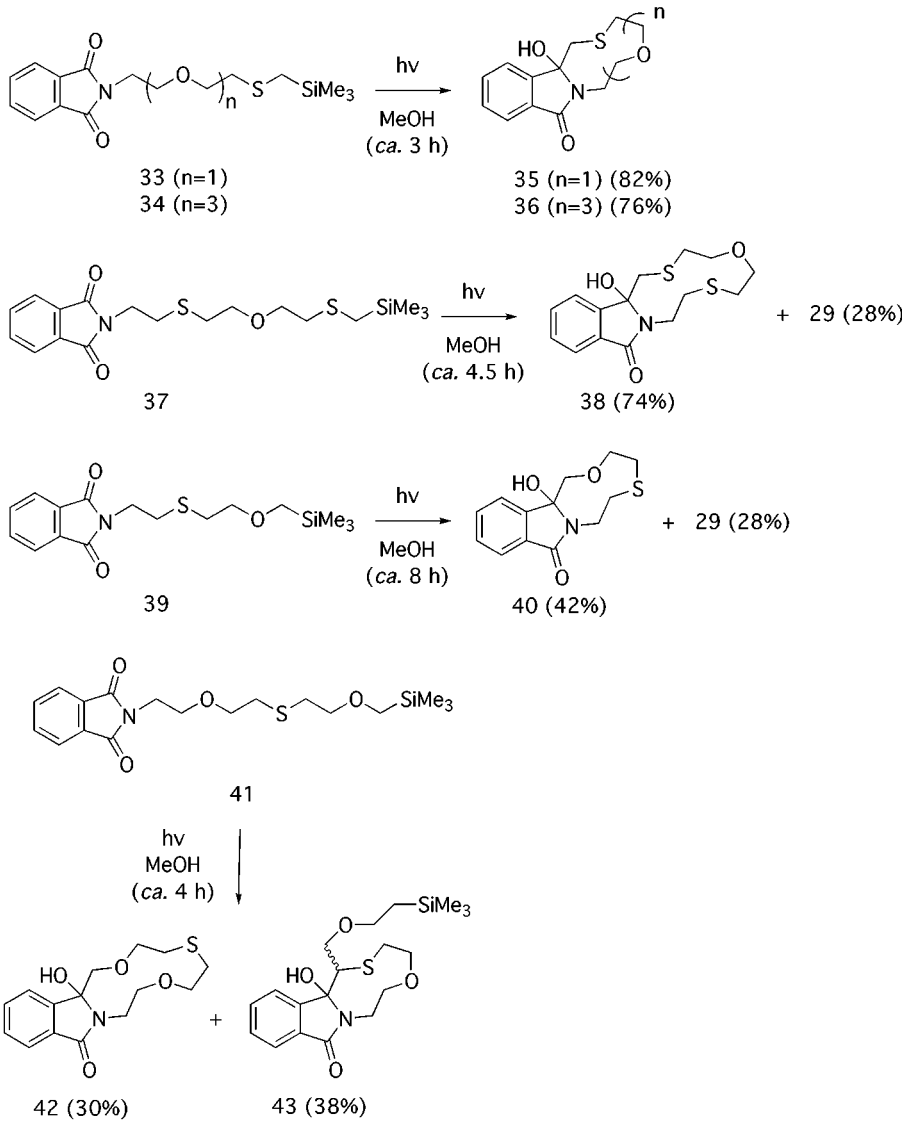
General Methods. ^{1}H and ^{13}C NMR chemical shifts are presented below in ppm relative to tetramethylsilane and chloroform, respectively. The purities of all compounds characterized in this study are >90% (determined by use of ^{1}H and ^{13}C NMR spectroscopy). All compounds are isolated as oils except in the cases where mp and crystallization solvents are given. All photochemical reactions are conducted in a preparative apparatus by using Pyrex glass filtered-light emitted by a 450-W medium-pressure Hg-lamp and N_2-purged MeOH solutions of the substrates. Photoreaction times needed to bring about 86−100% conversions of ca. 0.75 mmol of amides **20**−**22** in 100 mL of MeOH are ca. 0.5 h and to bring about 60−95% conversions of ca. 1.75 mmol of ethers **25**, **26**, **33**, **34**, **37**, **39**, and **41** in 200 mL of MeOH are ca. 2−9 h.

Preparation of the *N*-Trimethylsilylmethylpolymethansulfonamido Phthalimides 17−19. Solutions of the α-trimethylsilylpolymethansulfonamido mesylates **14** (3.00 g, 7.00 mmol), **15** (3.82 g, 7.00 mmol), and **16** (4.66 g, 7.00 mmol) in DMF (15 mL), each containing potassium phthalimide (1.94 g, 10.5 mmol), were stirred for 4 h at 50−60 °C. The residues obtained by concentration in vacuo were dissolved in CH_2Cl_2 and filtered. Concentration of the filtrates and column chromatography (silica, ethyl acetate/hexane = 1:3) gave 2.49 g (75%) of **17**, 3.21 g (77%) of **18**, and 3.11 g (62%) of **19**.

17: ^{1}H NMR ($CDCl_3$) 0.16 (s, 9H), 2.71 (s, 2H), 2.82 (s, 3H), 2.93 (s, 3H), 2.93−3.45 (m, 2H), 3.47−3.51 (m, 2H), 3.52−3.56 (m, 2H), 3.92 (t, 2H, J = 8.0 Hz), 7.74−7.69 (m, 2H), 7.83−7.86 (m, 2H); ^{13}C NMR ($CDCl_3$) −1.9, 34.0, 36.6, 37.4, 40.5 (CH_2SiMe_3), 46.9, 47.9, 49.8, 123.1 and 133.8, 131.7, 168.1; IR (KBr) 1720 cm^{-1}; MS(CI) *m*/*z* (rel intensity) 476 (M^+ + 1, 1), 460 (63), 396 (91), 281 (73), 194 (100), 174 (84), 137 (70); HRMS(CI) *m*/*z* 475.1267 ($C_{18}H_{29}N_3O_6S_2Si$ requires 475.1269).

18: ^{1}H NMR ($CDCl_3$) 0.15 (s, 9H), 2.71 (s, 2H), 2.87, 2.94 and 2.95 (3 s, 9H), 3.39−3.53 (m, 10H), 3.90 (t, 2H, J = 6.3

Scheme 11



Hz), 7.81−7.87 (m, 4H); ^{13}C NMR ($CDCl_3$) −1.8, 35.0, 36.4, 36.8, 39.7, 37.5, 46.8, 47.8, 47.9, 48.2, 49.3, 123.1 and 133.9, 131.8, 168.0; IR (KBr) 1710 cm^{-1}; MS(FAB) *m*/*z* (rel intensity) 597 ($M^+ + 1$, 2), 324 (19), 237 (13), 221 (15), 217 (10), 208 (28), 174 (100); HRMS(FAB) *m*/*z* 597.1541 ($C_{21}H_{37}N_4O_8S_3Si$ requires 597.1543).

19: ^{1}H NMR ($CDCl_3$) 0.15 (s, 9H), 2.72 (s, 2H), 2.84, 2.87, 2.91 and 2.95 (4 s, 12H) 3.43−3.56 (m,14H), 3.91 (t, 2H, J = 5.3 Hz), 7.69−7.87 (m, 4H); ^{13}C NMR ($CDCl_3$) −1.3, 34.5, 35.5, 36.7 and 38.0, 39.9, 47.3, 47.7, 48.1, 49.5, 50.0, 51.2, 123, 133.7, 132.1, 168.3; IR (KBr) 1710 cm^{-1}; MS(FAB) *m*/*z* (rel intensity) 719 ($M^+ + 1$,9), 605 (40), 549 (44), 460 (57), 398 (48), 329 (25), 295 (34), 238 (48), 208 (100), 203 (71); HRMS(FAB) *m*/*z* 718.1723 ($C_{24}H_{44}N_5O_{10}S_4Si$ requires 718.1740).

Irradiation of the *N*-Trimethylsilylmethylpolymethansulfonamido Phthalimides 17−19. Solutions of **17** (355 mg, 0.75 mmol), **18** (393 mg, 0.66 mmol), and **19** (587 mg, 0.82 mmol) in 100 mL of methanol were irradiated with Pyrex glass filtered light under a N_2 atmosphere. The residues obtained by concentration in vacuo of each photolysate were crystallized (CH_3OH) yielding 266 mg (96%) of **20**, 318 mg (92%) of **21**, and 400 mg (88%) of **22**, respectively.

20: mp 245−246 °C (ethanol); ^{1}H NMR (DMSO-d_6) 2.63 and 2.98 (2 s, 6H), 3.21−3.36 (m, 2H), 3.40−3.49 (m, 2H), 3.69−3.87 (m, 2H), 3.92−4.11 (m, 2H), 4.24 and 4.30 (two d, 2H, J = 14.7 Hz), 6.78 (s, 1H), 7.51−7.76 (m, 4H); ^{13}C NMR (DMSO-d_6) 35.5, 39.6, 40.7, 41.9, 47.5, 48.6, 49.3, 88.4, 122.7, 123.6, 129.9, 132.5, 131.1, 146.2, 167.4; IR (KBr) 3200−3530 (br), 1700 cm^{-1}; MS(FAB) *m*/*z* (rel intensity) 405 ($M^+ + 1$,13), 225 (18), 192 (17), 133 (30), 100 (100); HRMS (FAB) *m*/*z* 404.4097 ($C_{15}H_{22}N_3O_6S_2$ requires 404.0950).

21: mp 233−234 °C (ethanol); ^{1}H NMR (DMSO-d_6), 2.59 (s, 3H), 2.61 and 2.67 (two s, 6H), 3.33−3.92 (m, 12H), 4.21 and 4.27 (two d, 2H, J = 14.4 Hz), 6.76 (s, 1H), 7.56−7.81 (m, 4H); ^{13}C NMR (DMSO-d_6) 33.7, 35.4, 36.6, 42.6, 47.7, 50.8, 51.2, 51.6, 53.5, 54.2, 91.2, 122.5, 123.4, 132.2, 139.6, 136.6, 139.6, 172.6; IR (KBr) 3200−3600 (br), 1700 cm^{-1}; MS(FAB) *m*/*z* (rel intensity) 527 ($M^+ + 1$, 21), 525 (11), 446 (53), 428 (83), 337 (46), 292 (56), 279 (100), 239 (45); HRMS(FAB) *m*/*z* 525.1132 ($C_{18}H_{29}N_4O_8S_3$ requires 525.1147).

22: mp 257−258 °C (ethanol); ^{1}H NMR (DMSO-d_6) 2.47, 2.48, 2.59 and 2.94 (4 s, 12H), 3.11−3.58 (m, 12H), 3.62−3.77 (m, 4H), 4.15 and 4.25 (2 d, 2H, J = 13.9 Hz), 6.72 (s, 1H), 7.49−7.70 (m, 4H); ^{13}C NMR (DMSO-d_6) 34.5, 35.3, 36.7, 37.7, 41.9, 47.5−59.1 (4), 88.8, 122.6, 123.5, 129.8, 132.5, 126.6, 146.2, 163.7; IR (KBr) 3150−3500 (br), 1700 cm^{-1}.

Irradiation of the Trimethylsilylmethyl-Polyoxathioalkyl Phthalimides 25, 26, 33, 34, and 37. Solutions of the trimethylsilylmethyl-polyoxathioalkyl phthalimides **25** (578 mg, 1.64 mmol), **26** (700 mg, 1.69 mmol), **33** (586 mg, 1.74 mmol), **34** (748 mg, 1.76 mmol), and **37** (373 mg, 0.94 mmol) in 200 mL of methanol were irradiated with Pyrex glass filtered-light under a N_2 atmosphere. The residues obtained by concentration in vacuo of each photolyzate were subjected to column chromatography (silica, ethyl acetate/*n*-hexane = 1:1) yielding the respective macrocyclized products **27** (295 mg,

80%), **28** (274 mg, 72%), **35**[16] (265 mg, 82%), **36** (449 mg, 76%), and **38** (199 mg, 74%).

27: mp 142−144 °C (acetone); ^{1}H NMR ($CDCl_3$) 2.41−2.78 (m, 2H), 2.80−3.12 (m, 4H), 3.29 and 4.61 (two d, 2H, J = 14.2 Hz), 3.60−3.78 (m, 1H), 3.80−3.92 (m, 1H), 7.81−8.42 (m, 4H); ^{13}C NMR ($CDCl_3$) 30.6, 32.8, 38.5, 38.6, 42.6, 90.9, 122.6, 123.6, 130.2, 133.1, 131.1, 147.1, 169.4; IR (KBr) 3200−3600 (br), 1690 cm^{-1}; MS(CI) *m*/*z* (rel intensity) 282 (M^+ + 1, 2), 263 (29), 203 (39), 174 (63), 160 (100), 74 (78); HRMS(CI) *m*/*z* 282.0625 ($C_{13}H_{16}NO_2S_2$ requires 282.0622).

28: mp 160−161 °C (acetone); ^{1}H NMR (acetone-d_6) 2.74−3.41 (m, 12H), 3.70 and 3.74 (2 d, 2H, J = 7.2 Hz), 5.72 (s, 1H), 7.48−7.78 (m, 4H); ^{13}C NMR ($CDCl_3$−CD_3OD) 30.0, 30.1, 31.1, 33.2, 35.1, 39.9, 40.7, 91.6, 123.5, 124.4, 131.3, 134.3, 131.1, 147.1, 170.0; IR (KBr) 3200−3600 (br), 1670 cm^{-1}; MS-(FAB) *m*/*z* (rel intensity) 342 (M^+ + 1, 11), 324 (31), 279 (12), 206 (32), 174 (50), 147 (43), 105 (49), 63 (100); HRMS(FAB) *m*/*z* 342.0669 ($C_{15}H_{20}NO_2S_3$ requires 342.0656).

36: ^{1}H NMR ($CDCl_3$) 2.60−2.71 (m, 1H), 2.89−3.02 (m, 1H), 3.37 and 3.56 (2 d, 2H, J = 13.7 Hz), 3.61−3.83 (m, 12H), 3.84−3.95 (m, 1H, 4.19−4.28 (m, 1H), 5.64 (s, 1H), 7.45−7.57 (m, 3H), 7.75−7.86 (m, 1H); ^{13}C NMR ($CDCl_3$), 39.3, 32.7, 40.5, 69.9, 70.2, 70.9, 71.0, 71.1, 72.9, 89.9, 122.9, 123.0, 129.3, 131.9, 130.6, 145.9, 167.2; IR (KBr) 3200−3600 (br), 1690 cm^{-1}; MS-(EI) *m*/*z* (rel intensity), 353 (M^+, 0.5), 335 (M^+ − H_2O, 23), 272 (4), 202 (16), 174 (100), 130 (31); HRMS(EI) *m*/*z* 353.1304 ($C_{17}H_{23}NO_5$ requires 353.1297).

38: mp 193−195 °C (acetone); ^{1}H NMR ($CDCl_3$) 2.58−2.69 (m, 2H), 2.82−2.97 (m, 2H), 3.11−3.17 (m, 1H), 3.27−3.43 (m, 1H) 3.51 and 3.67 (2 d, 2H, J = 12.7 Hz), 3.77−3.92 (m, 4H), 4.02−4.12 (m, 2H), 7.41−7.72 (m, 4H); ^{13}C NMR ($CDCl_3$) 29.9, 31.4, 32.4, 40.0, 40.3, 73.5, 75.6, 90.2, 122.2, 123.7, 130.4, 132.9, 131.3, 146.2, 168.1; IR (KBr) 3200−3600 (br), 1670 cm^{-1}; MS-(FAB) *m*/*z* (rel intensity) 326 (M^+ + 1, 12), 308 (52), 285 (13), 239 (17), 185 (25), 174 (28), 147 (60), 93 (67), 52 (100); HRMS-(FAB) *m*/*z* 326.0878 ($C_{15}H_{20}NO_3S_2$ requires 326.0884).

Irradiation of the Trimethylsilylmethyl-Polyoxathioalkyl Phthalimides 39 and 41. Solutions of the trimethylsilylmethyl-polyoxathioalkyl phthalimides **39** (640 mg, 1.90 mmol) and **41** (663 mg, 1.74 mmol) in 200 mL of methanol were irradiated with Pyrex glass filtered-light under a N_2 atmosphere. The residues obtained by concentration in vacuo of each photolysate were subjected to column chromatography (silica, ethyl acetate/*n*-hexane = 1:1) yielding the respective macrocyclic products **40** (27 mg, 42%) and **29** (56 mg, 28%), and **42** (153 mg, 30%) and **43** (239 mg, 38%).

40: mp 128−129 °C (acetone); ^{1}H NMR ($CDCl_3$) 1.26 (s, 1H), 2.56−2.70 (m, 1H), 2.77−2.96 (m, 2H), 3.19−3.34 (m, 1H), 3.49−3.61 (m, 1H), 3.69−3.91 (m, 2H), 3.95−4.10 (m, 1H), 4.24 and 4.56 (2 d, 2H, J = 9.8 Hz), 7.27−7.59 (m, 3H), 7.73−7.77 (m, 1H); ^{13}C NMR ($CDCl_3$) 30.2, 34.0, 36.1, 41.5, 71.3, 89.4, 122.5, 123.8, 130.6, 132.7, 132.1, 144.9, 168.6; IR (KBr) 3200−3550 (br), 1660 cm^{-1}; MS(EI) *m*/*z* (rel intensity) 265 (M^+, 2), 247 (M^+ − H_2O, 7), 233 (87), 174 (48), 160 (100), 105 (28); HRMS(EI) *m*/*z* 265.0772 ($C_{13}H_{15}NO_3S$ requires 265.0773).

42: ^{1}H NMR ($CDCl_3$) 2.56−2.66 (m, 1H), 2.79−2.86 (m, 2H), 2.96−3.50 (m, 1H), 3.47−3.59 (m, 2H), 3.86 and 3.95 (2 d, 2H, J = 11.0 Hz), 3.71−4.05 (m, 4H), 4.05−4.20 (m, 2H), 6.10 (s, 1H), 7.48−7.58 (m, 3H), 7.75−7.79 (m, 1H); ^{13}C NMR ($CDCl_3$) 32.2, 33.6, 38.2, 67.5, 71.3, 73.1, 75.9, 89.6, 122.1, 123.3, 129.7, 132.1, 131.5, 144.2, 167.5; IR (KBr) 3200−3600 (br.), 1700 cm^{-1}; MS(EI) *m*/*z* (rel intensity) 309 (M^+, 0.5), 291 (M^+ − H_2O, 31), 262 (16), 234 (100), 190 (24) 89 (27); HRMS(EI) *m*/*z* 309.1030 ($C_{15}H_{19}NO_4S$ requires 309.1034).

43: ^{1}H NMR ($CDCl_3$) 0.14 (s, 9H), 2.25−2.40 (m, 1H), 2.60−2.80 (m, 1H), 3.40 (s, 2H), 3.41−3.52 (m, 1H), 3.60−3.78 (m, 2H), 3.93 (d, 2H, J = 3.7 Hz), 3.98 (s, 1H), 4.03−4.20 (m, 1H), 4.22−4.24 (m, 4H) 4.32−4.42 (m, 1H), 7.34−7.38 (m, 1H), 7.45−7.55 (m, 2H), 7.78−7.82 (m, 1H); ^{13}C NMR ($CDCl_3$) −3.2, 32.9, 41.5, 49.6, 66.6, 72.4, 77.2, 77.5, 92.7, 121.8, 122.9, 129.3, 131.6, 132.5, 145.4, 168.4; IR (KBr) 3200−3600 (br), 1680 cm^{-1}; MS(EI) *m*/*z* (rel intensity) 381 (M^+, 0.2), 364 (M^+ − H_2O, 0.4), 160 (7), 86 (100), 73 (18); HRMS(EI) *m*/*z* 381.1439 ($C_{18}H_{27}NO_4SiS$ requires 381.1430).

Acknowledgment. This study was financially supported by grants from the Korea Research Foundation (KRF-99-015-DI-0064 to U.C.Y.), the National Institutes of Health (GM-27251 to P.S.M.) and the National Science Foundation International Program (INT-9796064 to P.S.M.).

Supporting Information Available: Experimental procedures for the preparation of silyl-polysulfonamides **14**−**16** and phthalimides **25**, **26**, **33**, **34**, **37**, **39**, and **41** and ^{1}H and ^{13}C NMR spectra for **14**−**22**, **25**−**28**, **33**, **34**, and **36**−**43**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO001457U