DOI 10.5012/bkcs.2010.31.9.2453

Articles

Studies of Silyl-Transfer Photochemical Reactions of *N*-[(Trimethylsilyl)alkyl]saccharins

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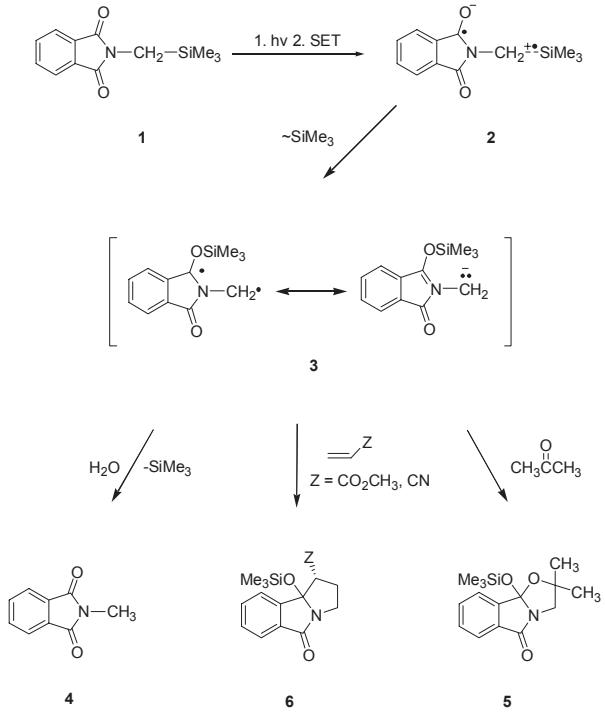
Received June 14, 2010, Accepted July 1, 2010

Photochemical studies of *N*-[(trimethylsilyl)alkyl]saccharins were carried out to investigate their photochemical behavior. Depending on the nature of the substrate and the solvent system employed, reactions of these substances can take place by either SET-promoted silyl migration from carbon to either the amide carbonyl or sulfonyl oxygen or by a *N*-*S* homolysis route. The results of the current studies show that an azomethine ylide, arising from a SET-promoted silyl migration pathway, is generated in photoreactions of *N*-[(trimethylsilyl)methyl]saccharin and this intermediate reacts to give various photoproducts depending on the conditions employed. In addition, irradiation of *N*-[(trimethylsily)ethyl]saccharin produces an excited state that reacts through two pathways, the relative importance is governed by solvent polarity and protic nature . Finally, photoirradiation of *N*-[(trimethylsilyl)propyl]saccharin in a highly polar solvent system comprised of 35% aqueous MeOH gives rise to formation of a tricyclic pyrrolizidine and saccharin that generated *via* competitive SET-promoted silyl transfer and γ-hydrogen abstraction pathways.

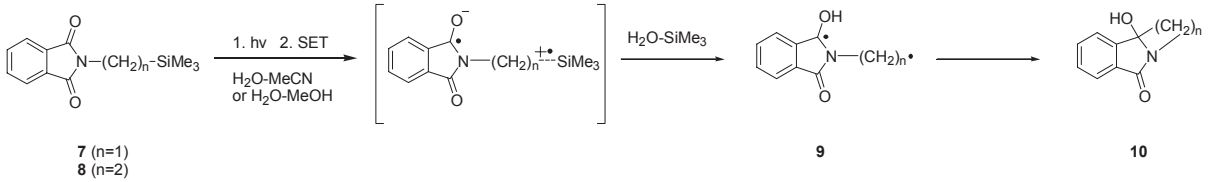
Key Words: Single electron transfer, Photochemistry, *N*-[(Trimethylsilyl)alkyl]saccharin, Silyl transfer

Introduction

The photochemistry of imides has been extensively investigated in the past.[1-3] Phthalimides, one subclass of this broad family, participate in a variety of excited state reactions including photoreduction, photoaddition, photocyclization, and Norrish type I and II reactions.[1-6] The results of our recent studies have shown that the single electron transfer (SET) photochemistry of imides containing α-silyl terminated electron donor/polydonor systems serves as efficient and regioselective method for the constructions of highly functionalized heteromacrocyclic systems.[1-3,6-8] Investigations aimed at gaining information about the factors governing the efficiencies of SET-promoted photocyclization reactions of linked acceptor-polydonor systems have shown that photocyclization reactions of the polyethylenoxy-linked phthalimides take place in higher chemical yields and quantum efficiencies than those of analogs containing polymethylene tethers of near equal length.[3a,7b] The findings suggest that internal donor sites in the tethers facilitate both initial SET to acceptor excited states and ensuing intrachain SET, resulting in migration of the cation radical center to the terminal, reactive α-trimethylsilyl electron donor position. Moreover, exploratory studies have demonstrated that photochemical reactions of *N*-[(trimethylsilyl)alkyl]phthalimides[1,6b,9-10] are promoted by competitive hydrogen atom abstraction and SET-promoted



Scheme 1



7 (n=1)
8 (n=2)

9 **10**

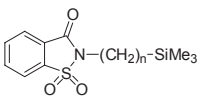
Scheme 2

C-to-*O* silyl transfer pathways. Interestingly, photoreaction of *N*-[(trimethylsilylmethyl]phthalimide **1** proceeds *via* a pathway involving the intermediacy of the azomethine ylid **3**, generated *via* an SET-promoted *C*-to-*O* silyl transfer pathway.[1,9-10] Protodesilylation or dipolar cycloaddition reactions of the azomethine ylid lead to formation of the respective *N*-methylphthalimide **4** and 1,3-dipolar adducts **5** and **6** (Scheme 1).

Photoreactions of the longer trimethylsilylalkyl chain containing phthalimides, exemplified by the *N*-silylethyl- and *N*-silylpropyl-phthalimide analogs **7-8**, occur to generate biradical intermediates **9** through SET-promoted silyl group transfer pathways when protic-polar solvent systems (e.g., H_2O-MeCN or H_2O-MeOH) are employed. These processes generate cyclized products **10** (Scheme 2). While the SET-silyl transfer processes are observed to dominate reactions in protic-polar solvents, intramolecular hydrogen atom abstraction processes take place when less polar non-protic solvents are used.[9-10]

In contrast to the many reports describing the photochemistry of imides including phthalimides, many less exist chronicling the photochemistry of sufonimide derivatives (e.g., saccharin). One example is found in the report by Kamigata[11] and Ono,[12] which showed that *N*-alkylsaccharins undergo photochemical reactions *via* homolytic *N*-*S* bond cleavage pathways. Our previous study of intermolecular photoreactions of saccharin with α-silylamine revealed that photoproducts are generated *via* pathways involving SET from a silylamine donor to the triplet excited state of the saccharins.[13] These results suggest that the presence of a sulfonyl group in saccharins can result in different photoreaction profiles as compared to those of related phthalimides.

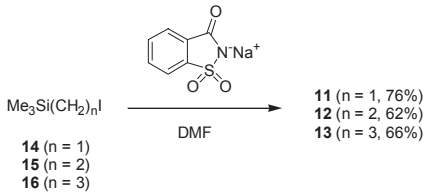
In exploratory efforts focusing on the development of new SET-promoted photochemical reactions, we have investigated photochemical reactions of *N*-[(trimethylsilyl)alkyl]saccharins **11-13**. Below is described the results of studies of the photochemical reactions of *N*-[(trimethylsilyl)alkyl]saccharins **11-13**, which demonstrate that the excited states of these substrates participate in novel competitive SET-promoted silyl group transfer, homolytic *N*-*S* bond cleavage, and hydrogen abstraction processes.



11 (n = 1)
12 (n = 2)
13 (n = 3)

Results and Discussion

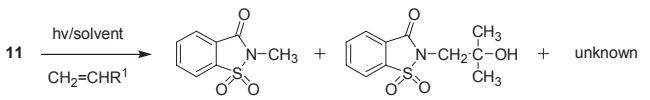
Synthesis of *N*-[(trimethylsilyl)alkyl]saccharins 11-13. The



14 (n = 1)
15 (n = 2)
16 (n = 3)

11 (n = 1, 76%)
12 (n = 2, 62%)
13 (n = 3, 66%)

Scheme 3



20 (R^1 = $COCH_3$)
21 (R^1 = CN)

17 **18** **19**

Scheme 4

Table 1. Photoreaction of *N*-[(trimethylsilyl)methyl]saccharin **11**[a]

Entry	Reactant	Solvent	Reaction Time (h)	Conversion (%)	Product (% yield)[b]
1	**11**	acetone	5	85	**17** (37), **18** (12), **19**
2	**11**	MeCN	32	71	**17** (69)
3	**11**	MeOH	7.5	86	**17** (89)
4	**11** + **20**	MeCN	16	55	**17** (89)
5	**11** + **21**	MeCN	7	40	**17** (85)

[a]Concentrations of reactant **11** is 5-6 mM. [b]Yields are determined based on consumed reactant.

N-[(trimethylsilyl)alkyl]saccharins **11-13** were efficiently prepared by using *N*-alkylation reactions of the saccharin sodium salt with (trimethylsilyl)alkyl iodides **14-16**[8b,10a] (Scheme 3).

Photochemical reactions of *N*-[(trimethylsilyl)alkyl]saccharins 11-13. Photoreactions of *N*-[(trimethylsilyl)methyl]saccharin **11** were carried out in solutions of various solvents in the presence-/absence of additives, such as methyl acrylate or acrylonitrile (Scheme 4 and Table 1). Irradiation of an acetone solution of **11** gave rise to *N*-methyl saccharin **17**[13] (37%) and the solvent-incorporated tertiary alcohol **18** (12%), along with an unidentified substance **19**[14] (entry 1 in Table 1). Structural assignment to photoproduct **18** was made on the basis of spectroscopic data. For example, the ^{1}H-NMR spectrum of **18** contains singlets at 1.32 ppm (6H) and 3.82 ppm (2H) and a multiple between 7.86 - 8.07 that correspond to the respective methyl, methylene and arene protons. In addition, the ^{13}C-NMR spectrum of this substance contains resonances that correspond to primary (methyl, 26.9 ppm), secondary (methylene, 51.5 ppm),

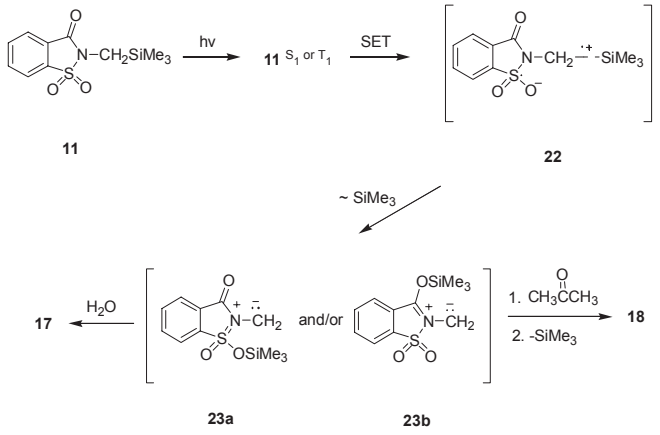
quaternary (70.7 ppm), carbonyl carbon (160.2 ppm), and aromatic (120 - 137 ppm) carbons.

When MeCN was used as the solvent for photoreaction of **11**, only *N*-methylsaccharin **17** (69%) was produced (entry 2 in Table 1). Moreover, irradiation of a MeOH solution containing **11** without any additives also brought about formation of **17** (89%) (entry 3 in Table 1). The presence of dipolarophiles such as methyl acrylate (**20**) or acrylonitrile (**21**) in the irradiated MeCN solutions of **11** did not appreciably affect the photoproduct distribution (entries 4-5 in Table 1) which contrasts with pathways followed in photoreactions of the corresponding *N*-silylmethylphthalimide (Scheme 1).

Based on the product distributions observed in photoreactions of the *N*-silylmethylsaccharine **11** and the results of our previous work,[10] the plausible mechanistic pathways given in Scheme 5 can be used to explain the formation of **17** and **18**. Single electron transfer (SET) from the $\sigma_{C\text{-}Si}$ bond in the excited state of **11** to the saccharin chromophore ($E^*_{1/2(-)} = ca. +2.2$ V *vs* $Ag/AgNO_3$)[13,15] is followed by silyl migration (~$SiMe_3^+$) to either the sulfonyl or amide oxygen takes place to generate azomethine ylid intermediates **23a** and/or **23b**, which can undergo protodesilyation to form **17** or addition to acetone to generate products **18**. In polar solvents, such as MeCN and MeOH, the protodesilyation pathway dominates even over 1,3-dipolar cycloadditions to methyl acrylate and acrylonitrile.

Irradiation of *N*-[(trimethylsilylethyl]saccharin **12**, interestingly, gave different type of product distributions depending on the solvent employed. While photoreaction of **12** in acetone led to simultaneous sulfur dioxide elimination and formation of benzamide **24** (48%), in MeCN solution of **12** reacts to generate saccharin **25** (57%). Finally, photoreaction of **12** in the highly polar solvent MeOH produced a mixture of **24** and **25** (Scheme 6 and Table 2). Structural assignment to **24** was based on a combination of characteristic ^{1}H-NMR, ^{13}C-NMR, IR and EI mass spectroscopic data (see experimental section).

As can be seen by viewing the pathways given in Scheme 7, two excited state decay processes occur competitively in the excited state of **12**. These include sequential SET-desilylation-*C*-*N* bond cleavage and *S*-*N* bond homolytic cleavage, which lead to formation of saccharin (**25**) and benzamide (**24**) respec-

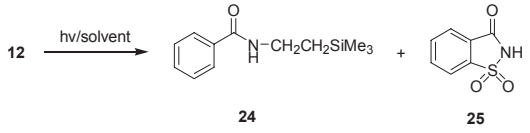


Scheme 5

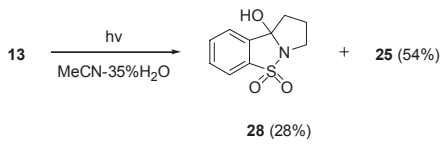
Table 2. Photoreaction of *N*-[(trimethylsilyl)ethyl]saccharin **12**[a]

Entry	Reactant	Solvent	Reaction Time (h)	Conversion (%)	Product (% yield)[b]
1	**12**	acetone	35	59	**24** (48)
2	**12**	MeCN	27	44	**25** (57)
3	**12**	MeOH	22	55	**24** (24), **25** (23)

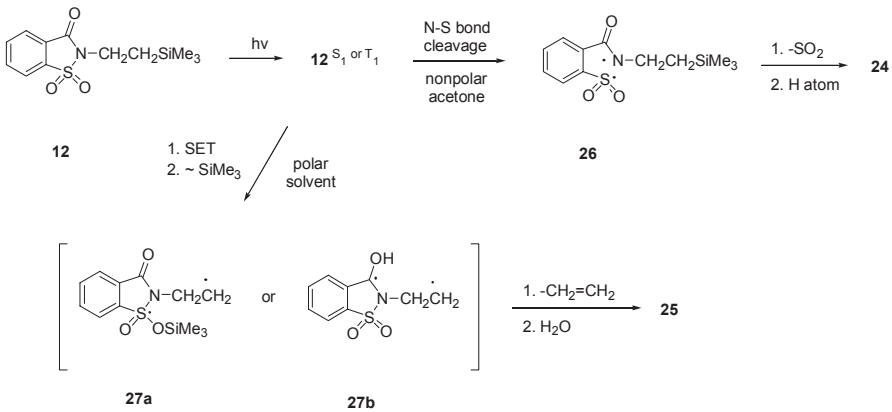
[a]Concentrations of reactant **12** is 3 - 4 mM. [b]Yields are determined based on consumed reactant.



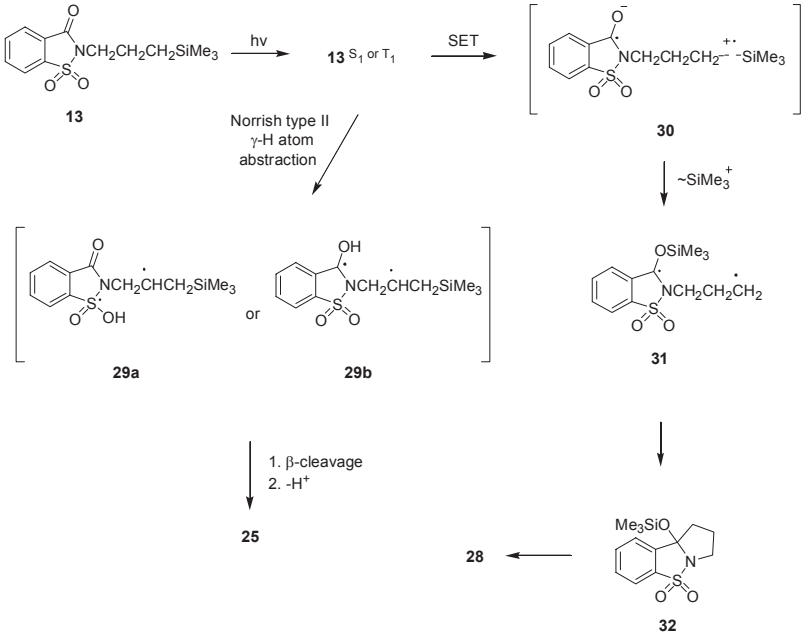
Scheme 6



Scheme 8



Scheme 7



Scheme 9

tively. Solvent polarity and protic nature appear to govern the relative rates of reactions by these two routes.

Comparable observations were made in studies of the photochemical reactions of the *N*-silylpropyl tethered saccharin derivative **13**. Contrary to the homologs **11**-**12**, **13** remained unreactive when irradiated in either acetone, MeCN or MeOH solution. Interestingly, irradiation of a 35% H_2O-MeCN solution of **13** led to production of pyrrolizidine **28** (28%) and saccharin **25** (54%) (Scheme 8).

This interesting observation indicates that in the presence of a highly protic and polar solvent the excited state of **13** is reactive *via* a Norrish-type II γ-hydrogen abstraction reaction pathway[4,15b] which forms intermediate **29a** and/or **29b** that undergo *C*-*C* bond cleavage following β-cleavage and H_2O-assisted reduction to give saccharin **25**. In addition, SET-promoted silyl transfer from the $\sigma_{C\text{-}Si}$ bond to amide carbonyl oxygen in excited state of **13** results in generation of biradical intermediate **31** which undergoes cyclization to form **28**. Thus, it appears that in 35% H_2O-MeCN, SET promoted silyl transfer processes *via* a zwitterionic biradical intermediates **30** are favorable.

Conclusion

In this study aimed at an investigation of the photochemical behaviors of silyl terminated electron donor chain linked saccharin systems, saccharin derivatives were prepared and their photochemical reactions were probed. The results show that depending on the alkyl chain length and solvent polarity, either SET-promoted silyl migration from carbon to the sulfonyl or carbonyl oxygens, or *N*-*S* bond homolysis occurs in the excited states of the saccharin derivatives. Mechanistic analyses of these processes, in terms of knowledge gained in previous efforts, were made in order to rationalize product distribution and their dependence on the nature of the solvent.

Experimental

General procedure. ^{1}H- and ^{13}C-NMR (400 MHz) spectra were recorded using $CDCl_3$ solutions and chemical shifts are reported in parts per million relative to $CHCl_3$ (7.24 ppm) or $CDCl_3$ (77.0 ppm) respectively. IR spectral bands are reported in cm^{-1}. Preparative photochemical reactions were conducted using an apparatus consisting of a 450 W Hanovia medium vapor pressure mercury lamp surrounded by a Vycor (> 220 nm) glass filter in a water-cooled quartz immersion well surrounded by the solution being irradiated. The photolysis solutions were purged with nitrogen before and during irradiation. The photolysates were concentrated under reduced pressure giving residues which were subjected to silica gel column chromatography. High resolution mass spectra (HRMS) were obtained by using electron impact ionization (EI) unless otherwise noted. All new compounds described are isolated as oils in > 90% purity (by NMR analysis) unless noted otherwise.

Preparation of *N*-(trimethylsilylalkyl)saccharin 11-13. Solutions containing the trimethylsilylalkyl iodide (3 g, 14 mmol of **14**, 1.5 g, 7 mmol of **15**, 1.1 g, 4.5 mmol of **16**) and saccharin sodium salt hydrate (4 g, 19 mmol for **14**, 2.7 g, 13 mmol for **14**, 0.9 g, 4.4 mmol for **15**) in 30 mL of DMF were stirred at 80 - 90 ^{o}C for 5 h. Concentration of solutions in vacuo gave residues which were diluted with ether and extracted with water. The ether layers were dried with Na_2SO_4, filtered and concentrated in vacuo to afford residues which were subjected to silica gel column chromatography (1:4 EtOAc-hexane) to afford **11** (3.4 g, 76%), **12** (1.5 g, 62%) and **13** (1 g, 66%).

11: ^{1}H-NMR($CDCl_3$) δ 0.15 (s, 9H, $SiMe_3$), 3.0 (s, 2H, CH_2-$SiMe_3$), 7.71-7.99 (m, 4H, aromatic) ; ^{13}C-NMR($CDCl_3$) δ −1.7, 29.0, 120.8, 124.8, 127.7, 134.2, 134.3, 137.7, 158.8; IR (KBr) 1710 (C=O), 1350 (SO_2, asymmetric), 1190 (SO_2, asymmetric); MS (CI) *m*/*z* (rel. intensity) 267 (M^+ + H, 1), 254 (M+- CH_3,

100); HRMS (CI) *m/z* ($M^+ + 1$) 270.0609 ($C_{11}H_{16}NO_3SSi$ requires 270.0620).

12: mp 73 - 74 °C; ^{1}H-NMR ($CDCl_3$) δ 0.08 (s, 9H, $SiMe_3$), 1.18-1.23 (m, 2H, $C\underline{H}_2SiMe_3$), 3.77-3.82 (m, 2H, NCH_2), 7.76-7.89 (m, 3H, aromatic), 8.00-8.03 (m, 1H, aromatic); ^{13}C-NMR ($CDCl_3$) δ −1.9, 17.0, 36.5, 120.7, 124.9, 127.5, 134.1, 134.5, 137.9, 170.3; IR (KBr) 1725 (C=O), 1325 (SO_2, asymmetric), 1160 (SO_2, asymmetric); MS (CI) *m/z* (rel. intensity), 283 (M^+, 1), 282 (M^+- H, 4), 268 (M+- CH_3, 76), 240 (98), 218 (55), 179 (17), 166 (53), 73 (73); HRMS (CI) *m/z* 283.0698 ($C_{12}H_{17}NO_3SSi$ requires 283.0699).

13: mp 62 - 63 °C; ^{1}H-NMR ($CDCl_3$) δ −0.02 (s, 9H, $SiMe_3$), 0.52-0.61 (m, 2H, $C\underline{H}_2SiMe_3$), 1.73-1.89 (m, 2H, $NCH_2C\underline{H}_2$), 3.73 (t, 2H, J = 7.6 Hz, $NC\underline{H}_2$), 7.76-8.04 (m, 4H, aromatic); ^{13}C-NMR ($CDCl_3$) δ −1.9, 13.6, 23.1, 42.2, 120.7, 124.9, 134.2, 134.5, 127.3, 137.6, 158.8; IR (KBr) 1730 (C=O stretching), 1330 (asymmetric SO_2 stretching), 1180 (symmetric SO_2 stretching); LRMS (EI), *m/z* (rel. intensity) 297 (M+, 3), 282 (43), 202 (32), 166 (9), 104 (8), 74 (100); HRMS (EI) *m/z* 297.0865 ($C_{13}H_{19}NO_3SSi$ requires 297.0855).

Irradiation of *N*-(trimethylsilylmethyl)saccharin (11).

In Acetone: A solution of *N*-(trimethylsilylmethyl)saccharin **11** (400 mg, 1.2 mmol) in 200 mL of acetone was irradiated by using Vycor filtered light for 5 h (*ca.* 85% conversion of **11**). Concentration in vacuo gave a residue, which was subjected to silica gel column chromatography (1:1 EtOAc-hexane) to give **17** (114 mg, 37%), **18** (48 mg, 12%) and 102 mg of an uncharacterized substance.

In MeCN: A solution of *N*-(trimethylsilylmethyl)saccharin **11** (400 mg, 1.2 mmol) in 200 mL of MeCN was irradiated by using Vycor filtered light for 32 h (*ca.* 71% conversion of **11**). Concentration in vacuo gave a residue, which was subjected to silica gel column chromatography (1:2 EtOAc-hexane) to give **17** (115 mg, 69%).

In MeOH: A solution of *N*-(trimethylsilylmethyl)saccharin **11** (400 mg, 1.2 mmol) in 200 mL MeOH was irradiated by using Vycor filtered light 7.5 h (*ca.* 86% conversion of **11**). Concentration in vacuo gave a residue, which was subjected to silica gel column chromatography (1:2 EtOAc-hexane) to give **17** (176 mg, 89%).

17: ^{1}H-NMR ($CDCl_3$) δ −3.22 (s, 3H, CH_3), 7.79-8.05 (m, 4H, aromatic); ^{13}C-NMR ($CDCl_3$) δ 23.2, 120.9, 125.1, 127.5, 134.3, 134.6, 137.6, 158.6

18: mp 85 - 86 °C; ^{1}H-NMR ($CDCl_3$) δ 1.32 (s, 6H, $C(C\underline{H}_3)_2$-OH), 3.82 (s, 2H, NCH_2), 7.86-7.96 (m, 3H, aromatic), 8.05-8.07 (m, 1H, aromatic); ^{13}C-NMR ($CDCl_3$) δ 26.9, 51.5, 70.7, 121.2, 125.4, 127.0, 134.5, 135.1, 137.6, 160.2; IR(neat) 3700-3200 (OH), 1720 (C=O), 1340 (SO_2, asymmetric), 1190 (SO_2, symmetric); MS (CI) *m/z* (rel. intensity) 256 (M^+ + H, 7), 238 (M^+- OH, 45), 197 (M^+- $C(CH_3)OH$, 23), 133 (100), 132 (46), 105 (37); HRMS (CI) *m/z* ($M^+ + 1$) 256.0650 ($C_{11}H_{14}NO_4S$ requires 256.0644).

Irradiation of a MeCN solution of *N*-(trimethylsilylmethyl) saccharin 11 and methyl acrylate. A solution of *N*-(trimethylsilylmethyl)saccharin **11** (300 mg, 0.9 mmol) containing methyl acrylate **20** (1.1 g, 13 mmol) in 200 mL of MeCN was irradiated by using Vycor filtered light 16 h (*ca.* 55% conversion of **11**). Concentration in vacuo gave a residue, which was subjected to silica gel column chromatography (1:2 EtOAc-hexane) to give **17** (90 mg, 89%).

Irradiation of a MeCN solution of *N*-(trimethylsilylmethyl)-saccharin 11 and acrylonitrile. A solution of *N*-(trimethylsilylmethyl)saccharin **11** (300 mg, 0.9 mmol) containing acrylonitrile **21** (790 mg, 15 mmol) in 200 mL of MeCN was irradiated by using Vycor filtered light for 7 h (*ca.* 40% conversion of **11**). Concentration in vacuo gave a residue, which was subjected to silica gel column chromatography (1:2 EtOAc-hexane) to give **17** (60 mg, 85%).

Irradiation of *N*-(trimethylsilylethyl)saccharin 12.

In Acetone: A solution of *N*-(trimethylsilylethyl)saccharin **12** (200 mg, 0.6 mmol) in 200 mL of acetone was irradiated by using Vycor filtered light for 35 h (*ca.* 59% conversion of **12**). Concentration in vacuo gave a residue, which was subjected to silica gel column chromatography (1:2 EtOAc-hexane) to give **24** (37 mg, 48%).

In MeCN: A solution of **12** (220 mg, 0.7 mmol) in 200 mL of MeCN was irradiated by using Vycor filtered light for 27 h (*ca.* 44% conversion of **12**). Concentration in vacuo gave a residue, which was subjected to silica gel column chromatography (1:3 EtOAc-hexane) to give **25** (30 mg, 57%).

In MeOH: A solution of **12** (200 mg, 0.6 mmol) in 200 mL of MeOH was irradiated by using Vycor filtered light for 22 h (*ca.* 55% conversion of **12**). Concentration in vacuo gave a residue, which was subjected to silica gel column chromatography (1:2 EtOAc-hexane) to give **24** (14 mg, 23%) and **25** (18 mg, 24%).

24: ^{1}H-NMR ($CDCl_3$) δ 0.05 (s, 9H, $SiMe_3$), 0.88 (t, 2H, J = 8.6 Hz, $C\underline{H}_2SiMe_3$), 3.46-3.51 (m, 2H, $NHC\underline{H}_2$), 6.10 (s, 1H, NH), 7.38-7.48 (m, 3H, aromatic), 7.71-7.74 (m, 2H, aromatic); ^{13}C-NMR ($CDCl_3$) δ −1.6, 17.9, 36.5, 126.7, 128.5, 128.8, 131.2, 134.9, 167.2; IR (KBr) 3500-3200 (NH), 1650 (C=O); MS (EI) *m/z* (rel. intensity), 221 (M^+, 11), 220 (M+- H, 53), 206 (M^+- CH_3, 19), 178 (22), 167 (38), 149 (100), 105 (53), 75 (53); HRMS (EI) *m/z* 221.1241 ($C_{12}H_{19}NOSi$ requires 221.1236).

Irradiation of *N*-(trimethylsilylpropyl)saccharin 13. Solutions of *N*-(trimethylsilylpropyl)saccharin **13** (400 mg, 1.1 mmol) in 200 mL of acetone, MeCN or MeOH were irradiated by using Vycor filtered light for 23-39 h. TLC (EtOAc) monitoring showed that no photoproduct formed in these reactions.

In MeCN-35% H_2O: A solution of **13** (300 mg, 0.9 mmol) in 65 mL MeCN and 35 mL H_2O was irradiated by using Vycor filtered light for 37 h, (*ca.* 82% conversion of **13**). Concentration in vacuo gave a residue, which was subjected to silica gel column chromatography (1:2 EtOAc-hexane) to give **28** (44 mg, 28%) and **25** (91 mg, 54%).

28: mp 108-109 °C; ^{1}H-NMR ($CDCl_3$) δ 1.86-1.94 (m, 1H, $NCH_2C\underline{H}_2$), 2.09-2.21 (m, 1H, $NCH_2C\underline{H}_2$), 2.34-2.50 (m, 2H, $C(OH)C\underline{H}_2$), 3.12 (s, 1H, OH), 3.48-3.58 (m, 1H, NCH_2), 3.72-3.84 (m, 1H, NCH_2), 7.56-7.74 (m, 4H, aromatic); ^{13}C-NMR ($CDCl_3$) δ 26.6, 38.4, 46.2, 98.4, 121.3, 124.3, 130.9, 133.9, 133.8, 133.9; IR (KBr) 3200-3600 (br, OH stretching), 1290 (asymmetric SO_2), 1160 (symmetric SO_2); LRMS (EI) *m/z* (rel. intensity) 225 (M^+, 1), 207 (M^+-H_2O, 92), 151 (14), 143 (36), 115 (100); HRMS (EI) *m/z* 225.0463 ($C_{10}H_{11}NO_3S$ requires 225.0460).

Acknowledgments. This works was supported by National

Research Foundation of Korea Grant funded by the Korean Government (2009-0072585).

References

1. Yoon, U. C.; Mariano, P. S. *Acc. Chem. Res*. **2001**, *34*(7), 523.
2. (a) Yoon, U. C.; Jin, Y. X.; Oh, S. W.; Park, C. H.; Park, J. H.; Campana, C. F.; Cai, X.; Duesler, E. N.; Mariano, P. S. *J. Am. Chem. Soc.* **2003**, *125*, 10664. (b) Yoon, U. C.; Oh, S. W.; Lee, C. W. *Heterocycles* **1995**, *41*(2), 2665.
3. (a) Yoon, U. C.; Kwon, H. C.; Hyung, T. G.; Choi, K. H.; Oh, S. W.; Yang, S.; Zhao, Z.; Mariano, P. S. *J. Am. Chem. Soc.* **2004**, *126*, 1110. (b) Oh, S. W., Kim, J. Y.; Cho, D. W.; Choi, J. H.; Yoon, U. C. *Bull. Korean Chem. Soc*. **2007**, *28*(9), 629. (c) Cho, D. W.; Lee, H.-Y.; Oh, S. W.; Choi, J. H.; Park, H. J.; Mariano, P. S.; Yoon, U. C. *J. Org. Chem*. **2008**, *73*(12), 4539.
4. (a) Kanaoka, Y.; Koyama, K. *Tetrahedron Lett*. **1972**, 4517. (b) Coyle, J. D. *Chem. Rev*. **1978**, *78*, 97. (b) Kanaoka, Y.; Yoshida, K.; Hatanaka, Y. *J. Org. Chem*. **1979**, *44*, 664. (c) Kanaoka, Y. *Acc. Chem. Res.* **1978**, *11*, 407. (d) Kanaoka, Y.; Koyama, K.; Flippen, J. L.; Karle, I. L.; Witkoo, B. *J. Am. Chem. Soc*. **1974**, *96*, 4719. (e) Coyle, J. D.; Haniman, A,; Newport, G. L. *J. Chem. Soc., Perkin Trans. 2* **1979**, 799.
5. (a) Oelgemoller, M.; Griesbeck, A. G. *J. Photochem. Photobiol. C: Photochem. Rev.* **2002**, *3*, 109. (b) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. R.; Mattes, S. L. *J. Am. Chem. Soc*. **1989**, *111*, 8973.
6. (a) Yoon, U. C.; Mariano, P. S. *Bull. Korean Chem. Soc.* **2006**, *27*, 1099. (b) Yoon, U. C.; Oh, S. W.; Lee, S. M.; Cho, S. J.; Gamlin, J.; Mariano, P. S. *J. Org. Chem.* **1999**, *64*, 4411
7. (c) Sung, N. K.; Cho, D. W.; Choi, J. H.; Choi, K, W.; Yoon, U. C.; Maeda, H.; Mariano, P. S. *J. Org. Chem.* **2007**, *72*, 8831. (b) Cho, D. W.; Choi, J. H.; Oh, S. W.; Quan, C.; Yoon, U. C.; Wang, R.; Yang, S.; Mariano, P. S. *J. Am. Chem. Soc.* **2008**, *130* (7), 2276. (c) Cho, D. W.; Quan, C.; Park, H. J.; Choi, J. H.; Kim, S. R.; Hyung, T. G.; Yoon, U. C.; Kim, S. H.; Jin, Y. X.; Mariano, P. S. *Tetrahedron* **2010**, *66*, 3173.
8. (b) Maeda, H.; Tierney, D. L.; Mariano, P. S.; Banerjee, M.; Cho, D. W.; Yoon, U. C. *Tetrahedron* **2008**, *64*(22), 5268.
9. (a) Yoon, U. C.; Oh, J. H.; Lee, S. J.; Kim, D. U.; Lee, J. G.; Kang, K.-T.; Mariano, P. S. *Bull. Korean Chem. Soc*. **1992**, *13*(2), 166. (b) Yoon, U. C.; Kim, D. U.; Lee, C. W.; Choi, Y. S.; Lee, Y.-J.; Ammon, H. L.; Mariano, P. S. *J. Am. Chem. Soc.* **1995**, *177*, 2698. (c) Yoon, U. C.; Cho, S. J.; Lee, Y. -J.; Mancheno, M. J.; Mariano, P. S. *J. Org. Chem.* **1995**, *60*, 2353.
10. (a) Lee, Y. J.; Ling, R.; Mariano, P. S.; Yoon, U. C.; Kim, D. U.; Oh, S. W. *J. Org. Chem.* **1996**, *61*, 3304. (b) 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. (c) Yoon, U. C.; Lee, C. W.; Oh, S. W.; Mariano, P. S. *Tetrahedron* **1999**, *55*, 11997.
11. Kamigata, N.; Saegusa, T.; Fujie, S.; Kobayashi, M. *Chem. Lett*. **1997**, *1*, 9.
12. Ono, I.; Sato, S.; Fukuda, K.; Inayoshi, T. *Bull. Chem. Soc. Jpn.* **1997**, 70, 2051
13. Yoon, U. C.; Koh, Y. S.; Kim, H. J.; Jung, D. Y.; Kim, D. U.; Cho, S. J.; Lee, S. J. *Bull. Korean Chem. Soc*. **1994**, *15*(9), 743.
14. The simplicity of the ^{1}H and ^{13}C NMR data for this substance contrasts with the complexity suggested by its mass spectrometric data prevent an unambiguous structural assignment.
15. (a) Cooper, B. E.; Owen, W. J. *J. Organomet. Chem*. **1971**, *29*, 33. (b) Cowan, D. O.; Drisko, R. L. *Elements of Organic Photochemistry*; Plenum Press: New York, USA 1976; Chapter 5, pp 205-266.