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Silyl-Tranfer Photoreactions of Trimethylsilylmethyl Substituted Acyclic N-Sulfonylbenzamides

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The azomethine ylide forming photoreaction has been explored by probing the excited state chemistry of several N-trimethylsilylmethyl substituted cyclic and acyclic imides and amide analogs. N-[(Trimethylsilyl)methyl]-N-mesylbenzamide (**5**) undergoes the excited state C to O silyl migration reaction to produce azomethine ylide intermediate **13**. This ylide undergoes electrocyclization to form transient aziridine intermediate **14** which react further by ring opening to generate N-phenacylamine product **10**. On the other hand, photolysis of N-[N-mesyl-N-(trimethylsilyl)methyl]aminoethyl-N-mesylbenzamide (**8**) brings about desilylation resulting in the production of dimer **17**.

Key words: azomethine ylide, N-mesylbenzamide, aziridine intermediate, N-phenacylamine

INTRODUCTION

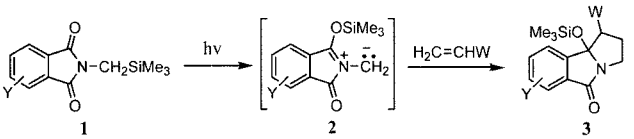
In a previous publication [1-3], it was reported the results of investigation in which a novel, azomethine ylide forming, photoreaction of N-(silylmethyl)phthalimides **1**, related N-phthaloyl a-amino acid and phthalimido-phenylethanol derivatives was discovered. As shown in Scheme 1 for the silyl analogs, this process involves excited state C to O migration of a TMS-group to generate azomethine ylides **2**. Dipolarophile trapping of these intermediates results in efficient production of pyrrolizidine ring-containing adducts of general structure **3**. The cycloaddition processes are attended by high degrees of regiochemical and stereochemical control.

Below are presented the results of this investigation in which the photochemistry of N-trimethylsilylmethyl substituted acyclic N-sulfonylbenzamides have been explored.

MATERIALS AND METHODS

General Procedures

^{1}H nuclear magnetic resonance (NMR) and ^{13}C-NMR spectra were recorded using 200MHz 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), m (multiplet) and br (broad). Infrared spectra were obtained using neat liquids unless otherwise specified, and data are reported in units of cm^{-1}.



1 2 3

Scheme 1.

Preparative photolysis were conducted with an apparatus consisting of a 450 W medium pressure mercury lamp surrounded by a pyrex filter in a quartz immersion well under an inert atmosphere. Photochemical reaction progress was monitored by TLC.

Preparation of N-[(trimethylsilyl)methyl]-N-mesylbenzamide (5)

To a solution of benzamide (4.0 g, 32.0 mmol) and NaH (32.0 mmol) in 100 mL of THF was slowly added methanesulfonyl chloride (4 mL, 34.0 mmol) in 10 mL of THF and refluxed for 18 h. The reaction mixture was cooled to room temperature and extracted with CH_2Cl_2. After concentration of organic layer *in vacuo*, 3.38 g (60%) of 4 was obtained by recrystallization (ethanol).

To a solution of 4 (7.83 g, 39.3 mmol) and NaH (59.0 mmol) in 180 mL of DMF was added trimethylsilylmethyl iodide (7 mL, 47.2 mmol) dropwise and stirred for 18 h at 90°C. The reaction mixture was cooled to room temperature and extracted with ether. The ether solution was washed with water, dried and concentrated to afford a residue which was subjected to column chromatography (silica, ethyl acetate : CH_2Cl_2 : hexane = 1:5:25) yielding 1.12 g (10%) of 5.

4: mp 148-153°C; ^{1}H-NMR ($CDCl_3$) 3.45 (s, 3H, CH_3), 7.46-7.67 (m, 3H, aromatic), 7.85-7.89 (m, 2H, aromatic), 8.90-8.95 (br. s, 1H, NH); ^{13}C-NMR ($CDCl_3$) 40.1 (CH_3), 126.2, 127.4 and 129.3 (CH, aromatic), 132.1 (C, aromatic); IR(KBr) 3200-3400 (br. OH stretching).

5: mp 71-74°C; ^{1}H-NMR ($CDCl_3$) 0.09 (s, 9H, $SiMe_3$), 3.15

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(s, 3H, CH_3), 3.32 (s, 2H, $C\underline{H}_2SiMe_3$), 7.43-7.61 (m, 5H, aromatic); ^{13}C-NMR ($CDCl_3$) –1.7 ($SiMe_3$), 38.9 ($\underline{C}H_2SiMe_3$), 40.4 (CH_3), 127.7, 128.1, 128.4 and 131.6 (CH, aromatic), 135.1 (C, aromatic), 172.2 (C=O); IR(KBr) 1670 (C=O stretching).

Preparations of N-[N-mesyl-N-(trimethylsilyl)methyl] aminoethyl-N-mesyl-benzamide (8) and –benzimidate (9)

To a solution of 2-aminoethanol (2.44 mL, 40.4 mmol) in 100 mL of CH_3CN was added trimethylsilylmethyl iodide (2 mL, 13.5 mmol) dropwise and stirred for 6 h at 60°C. The reaction mixture was extracted with ether, washed with 0.1N NaOH solution and dried over Na_2SO_4. The removal of solvent *in vacuo* yielded **6**.

To a solution of 6 (1.19 g, 8.10 mmol) and $NaHCO_3$ (0.53 g, 13.5 mmol) in 100 mL of CH_3CN was added methanesulfonyl chloride (4 mL, 34.0 mmol) dropwise in 5 mL of CH_3CN for 1 h at 0°C. After stirring for 17 h at 25°C, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with water, dried and concentrated to afford a residue which was subjected to column chromatography (silica, ethyl acetate : hexane = 1:1) yielding 1.15 g (38%) of 7.

To a THF solution of N-mesylbenzamide (**4**, 4.57 g, 23.0 mmol), triphenylphosphine (6.02 g, 23.0 mmol) and silyl alcohol (**7**, 5.55 g, 23.0 mmol) at 25°C was added a THF solution of diisopropyl azodicarboxylate (4.52 mL, 23.0 mmol). After stirring for 24 h at 25°C, the solution was concentrated *in vacuo* giving a residue which was subjected to column chromatography (silica, ethyl acetate : hexane = 1:3) yielding 0.28 g (3%) of **8** and 3.73 g (40%) of **9**.

7: ^{1}H-NMR ($CDCl_3$) 0.07 (s, 9H, $SiMe_3$), 2.67 (s, 2H, $C\underline{H}_2SiMe_3$), 2.84 (s, 3H, CH_3), 3.29 (t, 2H, J = 5.7 Hz, $HOCH_2C\underline{H}_2$), 3.68 (t, 2H, J = 5.7 Hz, $HOC\underline{H}_2$), 3.65-3.67 (br. s, 1H, OH); ^{13}C-NMR ($CDCl_3$) –1.8 ($SiMe_3$), 35.4 (CH_3), 39.1 ($\underline{C}H_2SiMe_3$), 52.2 ($HOCH_2\underline{C}H_2$), 59.8 ($HO\underline{C}H_2$); IR(KBr) 3200-3600 (br. OH stretching).

8: mp 130-132°C; ^{1}H-NMR ($CDCl_3$) 0.09 (s, 9H, $SiMe_3$), 2.57 (s, 2H, $C\underline{H}_2SiMe_3$), 2.72 (s, 3H, $N(CH_2SiMe_3)SO_2C\underline{H}_3$), 3.34 (s, 2H, $C\underline{H}_2N(CH_2SiMe_3)SO_2CH_3$), 3.41 (s, 3H, $N(CO)SO_2C\underline{H}_3$), 4.50 (t, 2H, J = 6.6 Hz, $C\underline{H}_2CH_2N(CH_2SiMe_3)SO_2CH_3$), 7.46-7.60 (m, 5H, aromatic); ^{13}C-NMR ($CDCl_3$) –1.7 ($SiMe_3$), 35.7 ($\underline{C}H_2SiMe_3$), 39.9 ($N(CH_2SiMe_3)SO_2\underline{C}H_3$), 42.9 ($\underline{C}H_2N(CH_2SiMe_3)SO_2CH_3$), 45.3 ($N(CO)SO_2\underline{C}H_3$), 49.7 ($\underline{C}H_2CH_2N(CH_2SiMe_3)SO_2CH_3$), 127.4 and 128.6 (CH, aromatic), 171.7 (C=O); IR(KBr) 1680 (C=O stretching).

9: mp 69-72°C; ^{1}H-NMR ($CDCl_3$) 0.13 (s, 9H, $SiMe_3$), 2.75 (s, 2H, $C\underline{H}_2SiMe_3$), 2.77 (s, 3H, $N(CH_2SiMe_3)SO_2C\underline{H}_3$), 3.12 (s, 3H, NSO_2CH_3), 3.61 (t, 2H, J = 6.0 Hz, $OCH_2C\underline{H}_2N$), 4.48 (t, 2H, J = 6.0 Hz, $OC\underline{H}_2CH_2N$), 7.42-7.57 (m, 3H, aromatic), 7.84-7.88 (m, 2H, aromatic); ^{13}C-NMR ($CDCl_3$) –1.8 ($SiMe_3$), 35.7 ($\underline{C}H_2SiMe_3$), 39.4 ($N(CH_2SiMe_3)SO_2\underline{C}H_3$), 43.2 ($NSO_2CH_3$), 48.1 ($OCH_2\underline{C}H_2N$), 66.1 ($O\underline{C}H_2CH_2N$), 128.1 and 129.1 (CH, aromatic), 169.2 (C=O); IR(KBr) 1620 (C=N stretching).

Irradiation of N-[(trimethylsilyl)methyl]-N-mesylbenzamide (5) in CH_3CN

A solution of N-[(trimethylsilyl)methyl]-N-mesylbenzamide (**5**, 764 mg, 2.67 mmol) in 200 mL of CH_3CN was irradiated with Pyrex-filtered light under N_2 for 9 h (80% conversion of **5**). Concentration of the photolysate gave a residue that was subjected to column chromatography (silica, ethyl acetate : hexane = 1:4) yielding 40 mg (9%) of **10**, 170 mg (60%) of **11** and 15 mg (4%) of **12**.

10: mp 178-180°C; ^{1}H-NMR ($CDCl_3$) 2.94 (CH_3), 4.77 (d, 2H, J = 6.9 Hz, CH_2), 7.38-7.62 (m, 3H, aromatic), 7.72-7.87 (m, 2H, aromatic); ^{13}C-NMR ($CDCl_3$) 38.4 (CH_2), 58.3 (CH_3), 125.6, 126.9, 127.2, 130.4 and 130.5 (CH, aromatic), 131.1 (C, aromatic); IR(KBr) 3200-3400 (br. NH stretching), 1660 (C=O stretching).

11: mp 210-211°C; ^{1}H-NMR ($CDCl_3$) 5.05 (t, 2H, J = 6.2 Hz, CH_2), 7.28-7.58 (m, 3H, aromatic), 7.60 (s, 1H, NH), 7.77-7.86 (m, 2H, aromatic); ^{13}C-NMR ($CDCl_3$) 43.9 (CH_2), 125.5, 126.9 and 130.0 (CH, aromatic), 131.8 (C, aromatic), 166.8 (C=O); IR(KBr) 3200-3400 (br. NH stretching), 1630 (C=O stretching).

12: mp 99-100°C; ^{1}H-NMR ($CDCl_3$) 0.13 (s, 9H, $SiMe_3$), 2.96 (s, 2H, $C\underline{H}_2SiMe_3$), 5.90 (s, 1H, NH), 7.42-7.71 (m, 5H, aromatic); ^{13}C-NMR ($CDCl_3$) –1.4 ($SiMe_3$), 28.8 ($\underline{C}H_2SiMe_3$), 125.2, 126.6 and 129.2 (CH, aromatic), 133.5 (C, aromatic), 166.1 (C=O); IR(KBr) 3200-3400 (br. NH stretching), 1620 (C=O stretching).

Irradiation of N-[N-mesyl-N-(trimethylsilyl)methyl]aminoethyl-N-mesylbenzamide (8) in 35% H_2O-CH_3CN

A solution of N-[N-mesyl-N-(trimethylsilyl)methyl]aminoethyl-N-mesylbenzamide (**8**, 580 mg, 1.34 mmol) in a solution of 70 mL of H_2O and 130 mL of CH_3CN was irradiated with Pyrex-filtered light under N_2 for 4 h (87% conversion of **8**). Concentration of the photolysate gave a residue that was subjected to column chromatography (silica, ethyl acetate : hexane = 1:1) yielding 195 mg (60%) of **17**.

17: mp 167-168°C; ^{1}H-NMR ($CDCl_3$) 2.63 ($CONCH_2CH_2NC\underline{H}_2$), 2.76 (s, 3H, $CONCH_2CH_2NSO_2C\underline{H}_3$), 3.23 (t, 2H, J = 5.5 Hz, $CONCH_2C\underline{H}_2$), 3.49 (s, 3H, $CONSO_2CH_3$), 4.08 (t, 2H, J = 5.1 Hz, $CONC\underline{H}_2$), 7.46-7.60 (m, 5H, aromatic); ^{13}C-NMR ($CDCl_3$) 33.3 ($CONCH_2CH_2NSO_2\underline{C}H_3$), 35.4 ($CONSO_2\underline{C}H_3$), 41.8 ($CONCH_2CH_2N\underline{C}H_2$), 42.8 ($CONCH_2\underline{C}H_2$), 47.9 ($CON\underline{C}H_2$), 125.9, 126.9 and 129.6 (CH, aromatic), 132.7 (C, aromatic), 169.9 (C=O);); IR(KBr) 1680 (C=O stretching).

Irradiation of N-[N-mesyl-N-(trimethylsilyl)methyl]aminoethyl-N-mesylbenzimidate (9) in CH_3CN

A solution of N-[N-mesyl-N-(trimethylsilyl)methyl]aminoethyl-N-mesylbenzimidate (**9**, 1.03 g, 2.45 mmol) in 200 mL of CH_3CN was irradiated with Pyrex-filtered light under N_2 for 25 h (91 conversion of **9**). Concentration of the photolysate gave a residue that was subjected to column chromatography (silica, ethyl acetate : hexane = 1:1) yielding 268 mg (55%) of

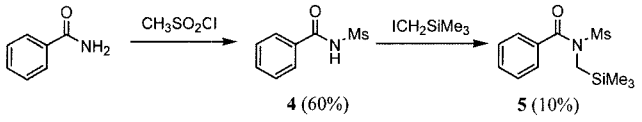
4 and 68 mg (23%) of **18**.

RESULTS AND DISCUSSION

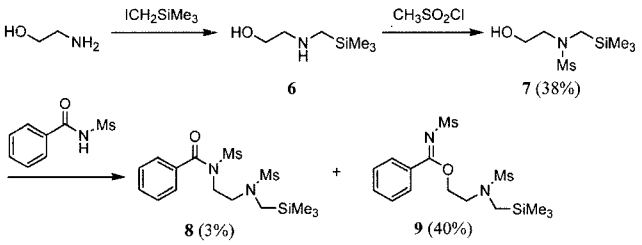
To further explore the scope and limitations of the new azomethine ylide forming process, the photochemistry of the N-trimethylsilylmethyl substituted acyclic N-sulfonylbenzamides was probed. The photochemical substrates for this study was prepared by using the routes outlined in Scheme 2 and Scheme 3. N-Sulfonylbenzamide **5** was synthesized by a two-step route starting with conversion of benzamide to N-mesyl-benzamide followed by silylation with trimethylsilylmethyl iodide. Similarly, N-mesyl-benzamide **8** and -benzimidate **9** were prepared by using Misunobu coupling of silyl alcohol **7** with N-sulfonylbenzamide **5**.

Irradiation of N-sulfonylbenzamide **5** in CH_3CN leads to the production of N-mesyl-N-phenacyl amine **10**, phenacyl amine **11** and (N-trimethylsilylmethyl)benzamide **12** (Scheme 4). As the reaction time increased, the conversion of N-mesyl-N-phenacyl amine **10** to phenacyl amine **11** was observed. Structural assignments of the photoproducts were made on the basis of spectroscopic data (see Materials and Methods Section).

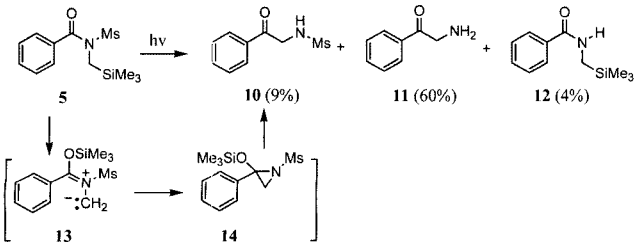
In the previous investigation [4], the mono- and diaryl substituted silylmethyl imides were participated in the general excited state C to O silyl-migration reaction. However, unlike



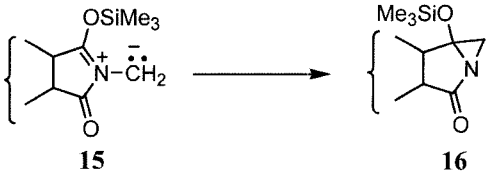
Scheme 2.



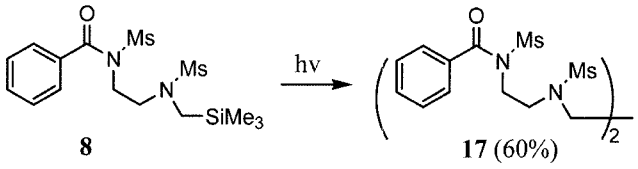
Scheme 3.



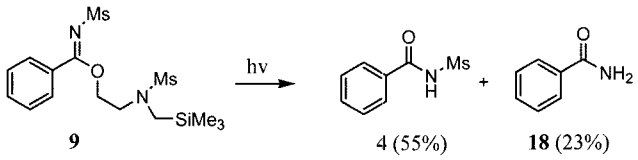
Scheme 4.



Scheme 5.



Scheme 6.



Scheme 7.

the azomethine ylide intermediate derived from phthalimide and maleimide counterparts, the produced in photoreaction of **5** undergoes rapid 4π-electrocyclization to form aziridine intermediate **14**. It is observed the formation of phenacyl amine **10** by the opening of aiziridine [5,6] ring. It was reported that cyclic azomethine ylide have not occurred electrocyclization in the photoreaction of phthalimide and maleimide systems [6]. The reason why the cyclic azomethine ylides **15** do not electrocyclize rapidly may be due to ring strain developing in the bicyclic aziridines **16** which would be formed in this route (Scheme 5).

Irradiation of N-sulfonylbenzamide **8** in 35% H_2O-CH_3CN leads to exclusive formation of dimmer **17** (Scheme 6). In comparison with phthalimide and maleimide systems, the photocyclized propdct is not formed by sequential SET-desilylation pathways [7,8]. It is indicated that inefficient SET-silyl tranfer is due to the strong electron-withdrawing effect of N-sulfonyl group.

Irradiation of N-sulfonylbenzimidate **9** in CH_3CN leads to production of N-mesylbenzamide **4** and benzamide **18** (Scheme 7). The conversion of N-sulfonylbenzimidate **9** to N-sulfonylbenzamide **8** has not been observed. The photoreaction of N-sulfonylbenzimidate **9** in CH_3CN appears to occur by homolysis of C-O bond and hydrogen abstraction pathways.

The results of this research demonstrate that photoreactions of N-trimethylsilylmethyl substituted acyclic N-sulfonyl-benzamides have uncovered synthetically useful chemistry. It is expected that dipolarophile trapping of this new azomethine ylide can be useful for the synthesis of functionalized nitrogen heterocycles.

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