Exploratory Study of Photocyclization Reactions of *N*-(Trimethylsilylmethylthioalkyl)phthalimides

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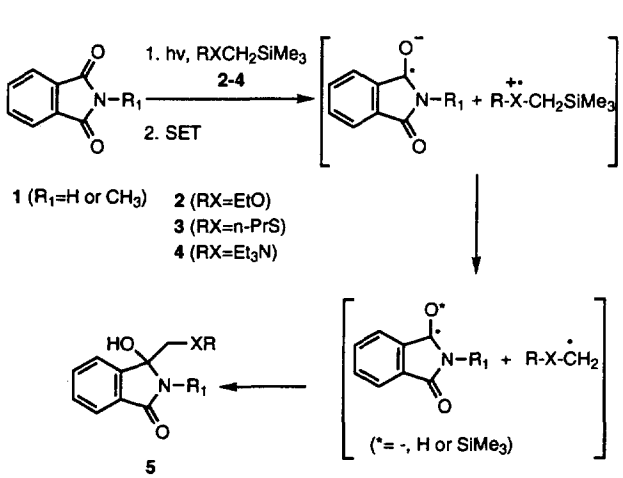
Received September 13, 1993

Studies have been conducted to explore single electron transfer (SET) induced photocyclization reactions of *N*-(trimethylsilylmethylthioalkyl)phthalimides (alkyl=ethyl, *n*-propyl, *n*-butyl, *n*-pentyl, and *n*-hexyl). Photocyclizations occur in methanol in modest to high yields to produce cyclized products in which phthalimide carbonyl carbon is bonded to the carbon of side chain in place of the trimethylsilyl group. Mechanism for these photocyclizations involving intramolecular SET from sulfur in the α-silylmethylthioalkyl groups to the singlet excited state phthalimide moieties followed by desilylation of the intermediate α-silylmethylthio cation radicals and cyclization by radical coupling is proposed. In contrast, photoreactions of *N*-(trimethylsilylmethylthioalkyl)phthalimides in acetone follow different reaction routes to produce another cyclized products in which carbon-carbon bond formation takes place between the phthalimide carbonyl carbon and the carbon α to silicon and sulfur atoms *via* triplet carbonyl hydrogen abstraction pathway. The normal singlet SET pathway dominates this triplet process for photoreactions of these substances in methanol while the triplet process dominates the singlet SET pathway for those in acetone. The efficient and regioselective cyclization reactions observed for photolyses in methanol represent synthetically useful processes for construction of medium and large ring heterocyclic compounds.

Introduction

There have been recently a number of reports for photochemical cyclizations of N-substituted phthalimides leading new heterocycles with either nitrogen and oxygen, nitrogen and sulfur, or nitrogen and nitrogen in the newly formed rings.[1] However the photochemical cyclization reactions utilized a mechanistic route which follows intramolecular hydrogen abstraction by excited carbonyl or single electron transfer(SET)-deprotonation and suffered from both low regioselectivities in the generation of intermediate carbon radicals and low product yields.

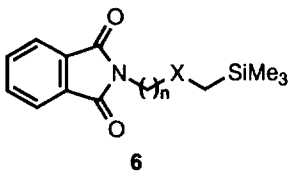
Our studies in the area of SET photochemistry using α-silyl electron donors led to the observation that photoinduced sequential SET-desilylation pathways have the potential of serving as efficient and highly regioselective methods for carbon centered radical generation.[2] Further studies of photoinduced SET reactions between phthalimides **1** and *n*-electron donors **2-4** revealed that photoaddition reactions occur to yield photoadduct **5** *via* SET-desilylation mechanistic pathway exclusively[3] (Scheme 1).



Scheme 1.

Based on our previous investigations of SET photochemistry using α-silyl-*n*-electron donors[1,3], we felt that photocyclizations of the silicon substituted phthalimides **6** could be highly efficient and regioselective and, as a result, might be useful for construction of medium and large ring heterocyclic compounds such as **7**.

In previous investigations, we have explored photocyclization reactions of *N*-(trimethylsilylmethoxyalkyl)phthalimides **6** (X=O)[4] to test the porposal and have observed that the photoinduced SET photocyclization reactions occur in high yields to produce cyclized product **7**.



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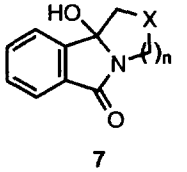

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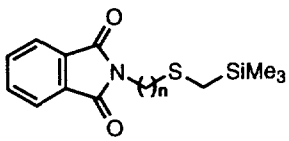
We now report preparative aspects of photocyclization reactions of *N*-(trimethylsilylmethylthioalkyl)phthalimides **6a-e**.

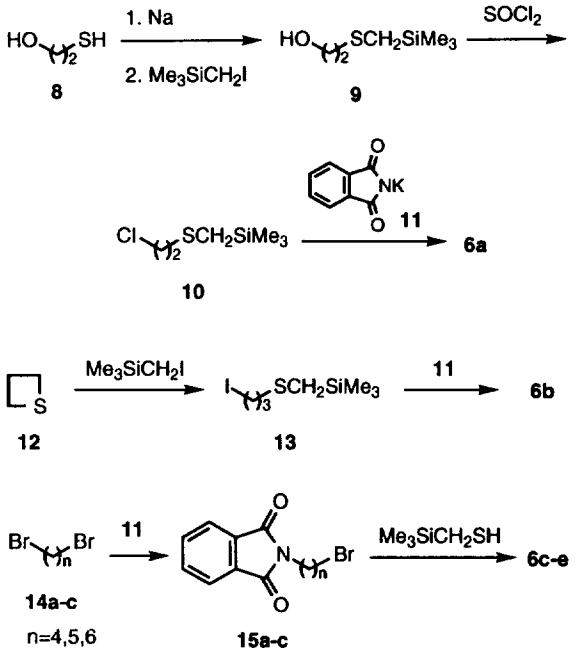


6a (n=2), **6b** (n=3)
6c (n=4), **6d** (n=5)
6e (n=6)

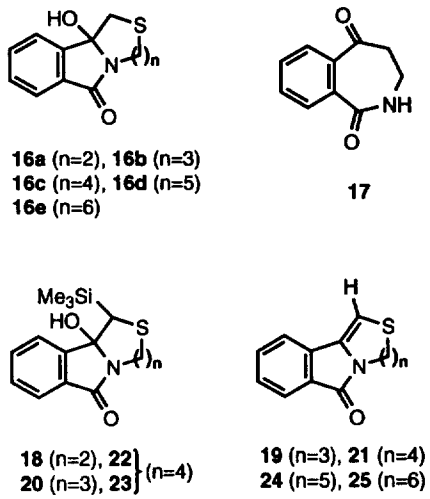
Table 1. Photochemical Reactions of *N*-(Trimethylsilylmethylthioalkyl)phthalimides

Phthalimide	Concentration (mM)	Solvent	Reaction time (h)	% Conversion	Products (Yields)[a]
6a	8.9	methanol	9	30	**16a**(50%), **17**(6%)
6a	3.4	acetone	2	50	**18**(60%)
6b	16.3	methanol	9	30	**16b**(45%), **19**(14%)
6b	8.6	acetone	2.5	58	**16b**(13%), **19**(7%), **20**(52%)
6c	10.1	methanol	9	37	**16c**(76%), **21**(12%)
6c	8.6	acetone	3.5	87	**16c**(36%), **21**(5%), **22**(23%), **23**(19%)
6d	4.5	methanol	8	30	**16d**(88%), **24**(<5%)
6e	5.0	methanol	9	96	**25**(62%)

[a]Yields are based on consumed phthalimides **6a-e**.



Scheme 2.



Results

Preparation of *N*-(Trimethylsilylmethylthioalkyl)phthalimides. For the photochemical studies five *N*-(trimethylsilylmethylthioalkyl)phthalimide derivatives, **6a-e** were selected and prepared in modest to good yields starting with 2-mercaptoethanol **8**, trimethylenesulfide **12** or dibromoalkanes **14a-e** by use of the reaction sequences outlined in Scheme 2 (see Experimental Section).

Photocyclizations of *N*-(Trimethylsilylmethylthioalkyl)phthalimides. Photocyclization reactions of *N*-(trimethylsilylmethylthioalkyl)phthalimides **6a-e** were explored. Preparative photocyclization reactions were performed by irradiation of methanol or acetone solutions of phthalimides (3.4-16.3 mM) by using Pyrex filtered-light (λ>290 nm) and products were separated by silica gel chromatography (see Experimental Section). Product distributions and yields along with reaction conditions employed are given in Table 1.

Irradiations of *N*-(trimethylsilylmethylthioalkyl)phthalimides **6a-d** in methanol lead to modest to high yielding production of the cyclized products **16a-d** as the major products. However photoreactions of **6a-c** in acetone occur much more rapidly than in methanol and produce the silicon-containing cyclized products **18, 20,** and **22** and **23** as the exclusive or the major products. Except in the case of *N*-(trimethylsilylmethylthioethyl)phthalimide **6a**, irradiations of phthalimides **6b-e** which contain longer alkyl units (n=3, 4, 5, 6) in methanol lead to production of enthiol ethers **19, 21, 24,** and **25** along with the major cyclized products **16b-d**. The yields of enthiol ethers increase as ring size of the cyclized products increase and the enthiol ether **25** become the exclusive product in photoreaction of **6e** (n=6) in methanol. The internal enthiol ethers are believed to be formed by dehydration of **16b-e**. In photoreaction of **6a** in methanol, the minor product **17** is also observed.

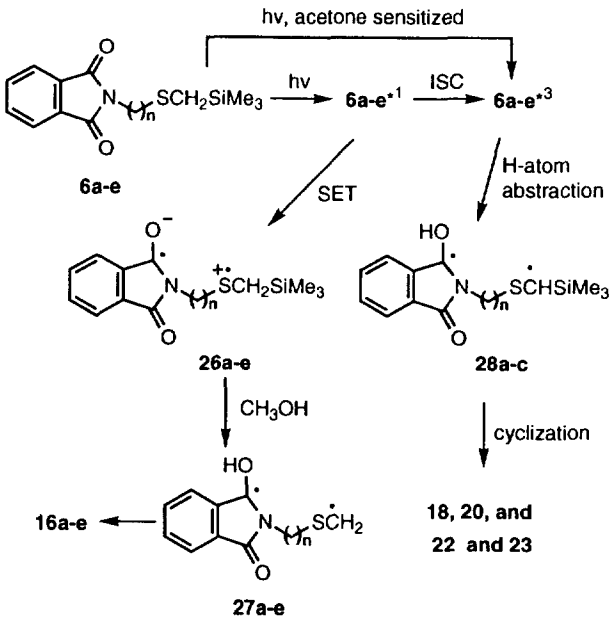
Structural assignments to the photoproducts were made on the basis of spectroscopic data (see Experimental Section). IR spectra of major cyclized products **16a-d** show characteristic absorption bands for the hydroxy group at 3050-3600 cm^{-1} and imide carbonyl group at 1670-1680 cm^{-1}. Their ^{13}C-NMR spectra clearly show resonances which correspond to quaternary carbon C-3 at 82.9-93.6 ppm and methylene carbon α to sulfur atom at 37.9-44.1 ppm. Further their ^{1}H-NMR spectra characteristically show a pair of doublet (J=14-15 Hz) in the region of 2.72-3.44 ppm for two diastereomeric methylene hydrogens α to sulfur atom. Along with disappearance of resonances for trimethylsilyl group in the ^{1}H-NMR and ^{13}C-NMR spectra of 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 sulfur formerly occupied by the silicon substituents. In contrast, ^{13}C-NMR spectra of **19, 21, 24,** and **25** have resonances at 95.1-104.2 ppm and 127.6-128.3 ppm for the corresponding olefinic carbons instead of resonances at *ca.* 82-94 ppm for quaternary carbon (C-3) and at *ca.* 37-44 ppm for methylene carbon α to sulfur which are observed in the spectra of **16a-d**. Their ^{1}H-NMR spectra also contain singlet peaks for their olefinic hydrogens at 6.20-6.34 ppm. The ^{1}H-NMR and ^{13}C-NMR of cyclized products **18, 20, 22,** and **23** contain characteristic resonance at −2.2-0.3 ppm for the trimethylsilyl groups, 43.6-54.3 ppm for the methine carbons with α-silyl substituent and 87.2-96.2 ppm for the quaternary carbon C-3. Their ^{1}H-NMR spectra also show resonances at −0.26-0.24 ppm for the trimethylsilyl groups and singlet peaks at 2.27-3.84 ppm for the methine hydrogens of carbons with α-silyl substituent. These observations indicate that photocyclizations have taken place between the phthalimide carbonyl and TMS substituted carbons. In addition to data described above, all of the other spectroscopic properites (^{1}H-NMR, ^{13}C-NMR, IR, and high resolution mass spectra) are in complete accord with the structures assigned.

Oxygen Quenching of Photoreaction of *N*-(Trimethylsilylmethylthioethyl)phthalimide. As described above, noticeable changes occur in the product distributions and reaction rates when acetone is used as solvent instead of methanol for photoreactions of phthalimides **6a-c**. Compared with photoreactions of **6a-c** in methanol, silicon-containing products **18, 20** and **22** and **23** become the major products instead of **16a-c** and reaction rate become much faster when irradiations are performed on solutions of **6a-c** in acetone. These observations suggest that excited states of phthalimides responsible for formation of products **18, 20,** and **22** and **23** are triplets formed by energy transfer from triplet acetone while those for cyclized products **16a-c** are singlets arising by direct excitation. In order to obtain further information about the reactive excited states, oxygen quenching experiment was performed on photoreaction of **6a**. Oxygen was found not to affect the efficiency of formation of **16a** while oxygen results in quenching of the formation of **17** in methanol and almost complete quenching of the production of **18** in acetone. These results support the proposal made above about the phthalimide excited states responsible for formation of products **18, 20,** and **22** and **23**.

Discussion

The observations presented above show that *N*-(trimethylsilylmethylthioalkyl)phthalimides undergo photocyclizations in methanol with high degree of chemoselectivity and regioselectivity to generate heterocycles with nitrogen and sulfur in the newly formed ring of various sizes (six to ten-membered) in which the phthalimide carbonyl carbon is bonded to the α-sulfur carbon in place of the trimethylsilyl group. Except in the case of *N*-(trimethylsilylmethylthioethyl)phthalimide **6a**, the initially formed photocyclization products **16b-e** undergo water elimination to yield olefinic products **19, 21, 24,** and **25** in secondary ground state reactions[3] and efficiency of the elimination increases as ring size of the cyclized products **16b-e** increases.



Scheme 3.

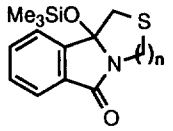
Results obtained in this study and those made in our earlier investigations of intermolecular photoinduced SET reactions of phthalimides **1** with α-silyl-*n*-electron donors **2-4** in methanol or acetonitrile[3] and intramolecular photoinduced SET reactions of *N*-(trimethylsilylmethoxyalkyl)phthalimides **6** (X=O)[4] suggest that photocyclizations leading **16a-d, 19, 21, 24,** and **25** follow the excited singlet state SET mechanisms (Scheme 3).

Accordingly, intramolecular SET in singlet excited phthalimides **6a-e**^{*1} results in generation of radical ion intermediates **26a-e** which undergo exclusive desilylation leading to biradicals **27a-e**. Unlike the case of cyclohexenone-α-silylamine systems probed previously[5], proton transfer between the two ion radical centers of **26a-e** is not favorable due to low basicity of the phthalimide radical anion[6]. Instead, preferential desilylation either with solvent, methanol as a nucleophile or liberating a short-lived silenium ion dominates in the phthalimide systems[7]. Biradicals **27a-e** undergo cyclization to produce cyclized products **16a-e**. The generation of benzazepinone lactam **17** in photoreaction of *N*-(trimethylsilylmethylthioethyl)phthalimide (**6a**) has a precedent in photocyclizations of *N*-butylphthalimide[8] and *N*-(trimethylsilylmethoxybutyl)phthalimide **6a** (X=O, n=4)[4] and is believed to occur *via* triplet two-fold Norrish type II reactions (*i.e.*, sequential Type II cyclization and Type II elimination pathways).

Further observations made in studies of the photoreactions of *N*-(trimethylsilylmethylthioalkyl)phthalimides **6a-c** in acetone and in oxygen quenching experiment on photoreaction of **6a** suggest that phthalimide singlet excited states follow SET-desilylation pathway to produce cyclized products **16a-e** whereas triplet reactions involve hydrogen atom abstraction route to form products **18, 20,** and **22** and **23** (Scheme 3).

In theory, the triplet excited state of phthalimides **6a-c** can be generated by acetone sensitization or *via* intersystem crossing from initially populated singlet excited state phthalimides. The carbonyl triplet excited state of the phthalimides can undergo hydrogen atom abstraction to produce biradicals

28a-c leading to the production of **18**, **20**, and **22** and **23**. However trimethylsilyl group abstractions by triplet excited carbonyl leading to cyclized products **29** are not observed to occur in photoreactions of *N*-(trimethylsilylmethylthioalkyl)-phthalimides unlike the case of *N*-(trimethylsilylmethoxyethyl)phthalimide (**30**) in which trimethylsilyl group abstraction predominates over hydrogen atom atom abstraction[4,9].



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The silicon-containing cyclized products **18** and **20** are isolated as a single diastereomer from **6a** and **6b** respectively while a pair of diastereomeric products **22** and **23** are obtained from photoreaction of **6c**. The observation indicates that the cyclized products **18** and **20** are the only stable isomers for smaller rings (six to seven-membered) while two diastereomeric products **22** and **23** are allowed to be formed for the larger eight-membered ring of diminished strain. As described above, irradiations of *N*-(trimethylsilylmethylthioalkyl)phthalimides **6a-e** in methanol lead to high yielding production of the cyclized products **16a-d**, **19**, **21**, **24** and **25** *via* singlet SET-desilylation pathway. Further the only product which is believed to be generated through triplet excited state is benzazepinone lactam **17** (6%) among photoproducts obtained photoreactions of **6a-e**. These observations suggest that intersystem crossing from initially populated singlet excited state of phthalimides is not efficient enough to complete with the intramolecular singlet SET process. However the photoreactions of *N*-(trimethylsilylmethylthioalkyl)-phthalimides in acetone appear to be *ca.* 4 times faster than those in methanol judging from irradiation times and phthalimides conversions (Table 1). The observation indicates that triplet hydrogen abstraction is much more efficient than singlet intramolecular SET in photoreactions of *N*-(trimethylsilylmethylthioalkyl)phthalimides and is in contrast to that made in study of *N*-(trimethylsilylmethoxyalkyl)phthalimide **6** (X=O)[4] which showed that photoreactions in methanol are faster than those in acetone. Comparison of the approximate efficiencies of photoreactions of *N*-(trimethylsilylmethoxyalkyl)phthalimides **6** (X=O) previously probed[4] with those of *N*-(trimethylsilylmethylthioalkyl)phthalimides **6a-e** reveals that intramolecular SET in *N*-(trimethylsilylmethylthioalkyl)-phthalimides **6a-e** is *ca.* 5-10 times less efficient than that in *N*-(trimethylsilylmethoxyalkyl)phthalimides **6** (X=O). Considering the fact that alkyl thioethers have lower oxidation potentials[3] and thus, are better electron donor than alkyl ethers, less reactivity of the alkyl thioether analogs **6a-e** towards SET than the alkyl ether analogs **6** (X=O) seems to be strange. However the observations are consistent with those made in the study of photocyclization reaction of tertiary amine analog *N*-(N-methyl-N-trimethylsilylmethylaminoethyl)-phthalimide (**31**)[9] in which (1) photoreaction of **31** in methanol is about 8 times slower than that of alkyl ether analog **30** in methanol (2) photoreation of **31** in methanol is more sluggish than that in acetone. The results suggest that α-silylamine or α-silylthioether group acts as an efficient electron transfer quencher[1c,10] of the phthalimide singlet excited state and the efficient intramolecular electron transfer quenchings cause photoreactions of **16a-e** and tertiary amine analog **31** to become sluggish. Hydrogen abstractions leading to the production of products **18**, **20** and **22** and **23** are believed to follow eight to ten-membered transition states rather than the typically more favorable six-membered transition state perhaps owing to α-heteroatom[11] and α-silyl group[4,12] effect on weakening the C-H bonds.

Summary

This study demonstrates that photoreactions of *N*-(trimethylsilylmethylthioalkyl)phthalimides lead to modest to high yielding production of cyclized products with high degree of chemoselectivity and regioselectivity. Thus the reactions appear to hold synthetic potential for the construction of medium and large ring heterocyclic compounds. We are continuing to explore the photocyclization reactions of phthalimides with α-silylamidoalkyl-, α-carboxymethoxyalkyl- and α-carboxymethylthioalkyl chains in efforts to develop new methods for heterocycle synthesis.

Experimental Section

General Procedures. ^{1}H-NMR and ^{13}C-NMR spectra were recorded by using 200 MHz and 400 MHz spectrometer using tetramethylsilane as 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. Preparative photolyses were conducted with an apparatus consisting of 450 W Hanovia medium mercury vapor lamp surrounded by a pyrex filter in a quartz immersion well under inert atmospheres. Low resolution mass spectral analyses were performed at 70 eV on Hitachi RMU-6 mass spectrometer. High resolution mass spectral analyses were performed at 70 eV on Hitachi VG-7070 mass spectrometer. Preparative TLC was performed on 20×20 cm plate coated with E-Merck silica gel PF_{254}.

Preparation of 2-(Trimethylsilylmethylthio)ethyl alcohol (9). To 2-mercaptoethanol (**8**, 15 m*l*, 214 mmol) was added Na metal (1.2 g, 51 mmol) portionwise over a 30 min period with stirring. To this solution was added trimethylsilylmethyl iodide (11 g, 51 mmol) dropwise and the resulting mixture was heated for 14 h at 80°. The mixture was cooled to room temperature and extracted with n-pentane. The pentane solution was washed with water, dried with magnesium sulfate and concentrated in vacuo to afford a residue. Molecular distillation (1.5 torr, 90°) of the residue gave 7.5 g (90%) of alcohol **9**. Spectral data for **9**: ^{1}H-NMR ($CDCl_3$) 0.07 (s, 9H, $Si(CH_3)_3$), 1.73 (s, 2H, $SC\underline{H}_2Si(CH_3)_3$), 2.23 (s, 1H, OH), 2.68 (t, 2H, J=5.9 Hz, $HOCH_2C\underline{H}_2S$), 3.70 (t, 2H, J=5.9 Hz, $HOC\underline{H}_2CH_2S$); ^{13}C-NMR ($CDCl_3$) −1.8 ($Si(CH_3)_3$), 17.4 ($S\underline{C}H_2Si(CH_3)_3$), 39.1 ($HOCH_2\underline{C}H_2S$), 59.1 ($HO\underline{C}H_2$-$CH_2S$); IR (KBr) 3050-3600 (OH stretching), 1200, 1050 and 850 cm^{-1}; mass spec. (EI), m/z (rel. intensity) 164 (M^+, 3) 149 (15), 147 (M^+-OH, 3), 133 (7), 119 (7), 103 (13), 73 (100); high resolution mass spec., m/z 164.0693($C_6H_{16}OSSi$ requires 164.0692).

Preparation of 2-(Trimethylsilylmethylthio)ethyl chloride (10). To a stirred solution of 7.0 g (42.6 mmol) of

removal of methanol under reduced pressure, remained residue was subjected to preparative TLC ($CHCl_3$: ethyl acetate=3 : 1), to yield 103 mg (45%) of **16b**[13], 30 mg (14%) of **19**. Spectral data for **16b**: mp. 162-163°; ^{1}H-NMR ($CDCl_3$) 1.84-2.05 (m, 2H, $SCH_2\underline{CH_2}CH_2N$), 2.58-2.65 (m, 2H, $SCH_2CH_2\underline{CH_2}N$), 3.04 (d, 1H, J=15 Hz, $SC\underline{H_2}C(OH)$), 3.17-3.33 (m, 1H, $SCH_2CH_2\underline{CH_2}N$), 3.44 (d, 1H, J=15 Hz, $SC\underline{H_2}C(OH)$), 3.84-3.95 (m, 1H, $SCH_2CH_2\underline{CH_2}N$), 7.39-7.66 (m, 4H, aromatic); ^{13}C-NMR ($CDCl_3$) 30.0 (S $\underline{CH_2}CH_2CH_2N$), 35.6 ($S\underline{CH_2}CH_2CH_2N$), 39.5 ($SCH_2\underline{CH_2}CH_2N$), 44.1 ($S\underline{CH_2}C(OH)$), 93.6 (quaternary C-3), 123.1 (CH, aromatic), 123.5 (CH, aromatic), 130.6 (CH, aromatic), 133.2 (C, aromatic), 133.7 (CH, aromatic), 148.5 (C, aromatic), 170.2 (C=O); IR (KBr) 3050-3500 (OH stretching), 1672 (C=O stretching), 1418 and 1069 cm^{-1}; mass spec., m/z (rel. intensity) 235 (M^+, 21), 217 (M^+-H_2O, 14) 188 (100), 169 (23), 161 (51), 160 (47); high resolution mass spec., m/z 235.0663 ($C_{12}H_{13}NO_2S$ requires 235.0667). Spectral data for **19**: ^{1}H-NMR ($CDCl_3$) 2.20 (quintet, 2H, J=6 Hz, $SCH_2\underline{CH_2}CH_2N$), 3.19 (t, 2H, J=6 Hz, $SCH_2CH_2\underline{CH_2}N$), 4.24 (t, 2H, J=6 Hz, $SCH_2CH_2\underline{CH_2}N$), 6.31 (s, 1H, alkenic), 7.37-7.80 (m, 4H, aromatic); ^{13}C-NMR ($CDCl_3$) 28.5 ($SCH_2\underline{CH_2}CH_2N$), 35.4 ($S\underline{CH_2}CH_2CH_2N$), 40.9 ($SCH_2CH_2\underline{CH_2}N$), 104.2 (C, alkenic), 118.8, 123.1, 128.3 and 131.6 (CH, aromatic), 127.6 (C, alkenic), 135.5 and 137.0 (C, aromatic), 167.8 (C=O); IR (KBr) 2939, 1713 (C=O stretching), 1394 and 846 cm^{-1}; mass spec., m/z (rel. intensity) 217 (M^+, 100), 204 (37), 188 (17); high resolution mass spec., m/z 217.0563 ($C_{12}H_{11}NOS$ requires 217.0561).

Irradiation of *N*-(Trimethylsilylmethylthiopropyl)-phthalimide (6b) in Acetone. *N*-(Trimethylsilylmethylthiopropyl)phthalimide (**6b**, 530 mg, 1.73 mmol) was dissolved in 200 m*l* of acetone and irradiated through pyrex filter under N_2 purging for 2 h, resulting *ca.* 58% conversion. After removal of acetone under reduced pressure, remained residue was subjected to preparative TLC ($CHCl_3$: ethyl acetate=3 : 1), to yield 15 mg (7%) of **19**, 167 mg (52%) of **20**, and 31 mg (13%) of **16b**. Spectral data for **20**: ^{1}H-NMR ($CDCl_3$) 0.24 (s, 9H, $Si(CH_3)_3$), 1.67-1.82 (m, 1H, $SCH_2\underline{CH_2}CH_2N$), 1.82-2.10 (m, 1H, $SCH_2CH_2\underline{CH_2}N$), 2.29 (s, 1H, $SC\underline{H}(Si(CH_3)_3)$, 2.28-2.47 (m, 1H, $SCH_2CH_2\underline{CH_2}N$), 2.56-2.71 (m, 1H, $SCH_2C\underline{H_2}CH_2N$), 2.92-3.19 (m, 2H, $SC\underline{H_2}CH_2CH_2N$ and $SCH_2CH_2C\underline{H_2}N$), 4.68 (s, 1H, OH), 7.34-7.64 (m, 4H, aromatic); ^{13}C-NMR ($CDCl_3$) −0.5 ($Si(CH_3)_3$), 27.6 ($SCH_2\underline{CH_2}CH_2N$), 36.7 ($S\underline{CH_2}CH_2CH_2N$), 37.9 ($SCH_2CH_2\underline{CH_2}N$), 44.0 ($S\underline{CH}(SiCH_3)_3$)), 96.2 (quaternary, C-3), 122.7, 123.6, 129.2 and 131.4 (CH, aromatic), 132.0 and 145.7 (C, aromatic), 168.3 (C=O); IR (KBr) 3100-3500 (OH stretching), 1678 (C=O stretching), 1414, 1064 and 848 cm^{-1}; mass spec., m/z (rel. intensity) 307 (M^+, 16), 292 (34), 289 (M^+-H_2O, 26), 262 (15), 261 (65), 260 (63), 246 (36), 233 (42), 232 (100), 188 (29), 187 (28); high resolution mass spec., m/z 307.1060 ($C_{15}H_{21}NO_2SSi$ requires 307.1062).

Preparations of *N*-(Bromoalkyl)phthalimides (15a-c)[14]. Solutions of dibromoalkanes (**14a**, 7.0 g, 32.4 mmol; **14b**, 7.5 g, 32.6 mmol; **14c**, 7.9 g, 32.4 mmol) and potassium phthalimide (**11**, 6 g, 32.4 mmol) in DMF (60 m*l*) were heated for 5 h at 80°. After removal of DMF under reduced pressure, the residue dissolved in CH_2Cl_2 and the solution filtered. The filtrate concentrated under reduced pressure and the residue was subjected to column chromatography (CH_2Cl_2) to give N-(bromoalkyl)phthalimide (**15a**, 7.5 g, 82%; **15b**, 7.3 g 76%; **15c**, 7.3 g, 73%). **15a**; mp. 79-82° (78-79°[14a], 80°[14b]), **15b**; mp. 62-64° (57-59°[14a], 61°[14c]), **15c**; mp. 55-57° (52-54°[14a], 58°[14c]).

Preparations of *N*-(Trimethylsilylmethylthioalkyl)phthalimides (6c-e). To (trimethylsilyl)methanethiol[15] (1 g, 8.3 mmol) was added sodium hydride (0.2 g, 8.3 mmol) with stirring in a ice bath until all thiol precipitates. Then solution of N-(bromoalkyl)phthalimide (**15a**, 2.4 g, 8.3 mmol; **15b**, 2.5 g, 8.3 mmol, **15c**, 2.6 g, 8.3 mmol) in 20 m*l* of DMF was added and mixture was heated for 5 h. After removal of DMF under reduced pressure, the residue was dissolved in CH_2Cl_2 and solution was filtered. The resiude was subjected to column chromatography (CH_2Cl_2) to yield N-(trimethylsilylthioalkyl)phthalimide (**6c**, 1.8 g, 67%; **6d**, 1.7 g, 61%; **6e**, 1.9 g, 66%). Spectral data for **6c**: ^{1}H-NMR ($CDCl_3$) 0.02 (s, 9H, $Si(CH_3)_3$), 1.45-1.82 (m, 4H, $NCH_2(C\underline{H_2})_2CH_2S$), 1.69 (s, 2H, $SC\underline{H_2}Si(CH_3)_3$), 2.48 (t, 2H, J=6.5 Hz, $SC\underline{H_2}(CH_2)_2N$), 3.65 (t, 2H, J=6.5 Hz, $NC\underline{H_2}(CH_2)_2CH_2S$), 7.62-7.81 (m, 4H, aromatic); ^{13}C-NMR ($CDCl_3$) −1.8 ($Si(CH_3)_3$), 18.3 ($S\underline{CH_2}Si(CH_3)_3$), 26.2 ($SCH_2\underline{CH_2}CH_2CH_2N$), 27.6 ($SCH_2CH_2\underline{CH_2}$-$CH_2N$), 35.5 ($S\underline{CH_2}(CH_2)_2CH_2N$), 37.5 ($SCH_2(CH_2)_2\underline{CH_2}N$), 123.1 and 133.8 (CH, aromatic), 132.1 (C, aromatic), 168.2 (C=O); IR (KBr) 2950, 1780 and 1700 (C=O stretching) 1400 and 850 cm^{-1}; mass spec., m/z (rel. intensity) 321 (M^+, 25), 306 (M^+-CH_3, 28), 274 (45), 260 (4), 246 (20), 160 (40), 130 (12), 120 (44), 105 (25), 73 (100); high resolution mass spec., m/z 321.1223 ($C_{16}H_{23}NO_2SSi$ requires 321.1219). Spectral data for **6d**: ^{1}H-NMR ($CDCl_3$) 0.04 (s, 9H, $Si(CH_3)_3$), 1.38-1.52 (m, 2H, NCH_2 $CH_2\underline{CH_2}CH_2CH_2S$), 1.52-1.79 (m, 4H, $NCH_2\underline{CH_2}CH_2\underline{CH_2}CH_2S$), 1.71 (s, 2H, $SC\underline{H_2}Si(CH_3)_3$), 2.46 (t, 2H, J=7.2 Hz, $SC\underline{H_2}(CH_2)_3$ CH_2N), 3.65 (t, 2H, J=7.2 Hz, $SCH_2(CH_2)_3C\underline{H_2}N$), 7.64-7.82 (m, 4H, aromatic); ^{13}C-NMR ($CDCl_3$) −1.8 ($Si(CH_3)_3$), 18.3 ($S\underline{CH_2}Si(CH_3)_3$), 26.0 ($NCH_2CH_2\underline{CH_2}CH_2CH_2S$), 28.2 ($NCH_2CH_2$-$CH_2\underline{CH_2}CH_2S$), 28.4 ($NCH_2\underline{CH_2}CH_2CH_2CH_2S$), 35.9 ($NCH_2$ $(CH_2)_3\underline{CH_2}S$), 37.8 ($N\underline{CH_2}(CH_2)_3CH_2S$), 123.1 and 133.8 (CH, aromatic), 132.1 (C, aromatic), 168.3 (C=O); mass spec., m/z (rel. intensity) 335 (M^+, 10), 321 (M^+-CH_3, 6), 320 (24), 288 (37), 260 (6), 246 (8), 232 (12), 175 (10), 161 (23), 160 (100); high resolution mass spec. m/z 335.1363 ($C_{17}H_{25}NO_2SSi$ requires 335.1375). Spectral data for **6e**: ^{1}H-NMR ($CDCl_3$) 0.02 (s, 9H, $Si(CH_3)_3$), 1.23-1.70 (m, 8H, $SCH_2(C\underline{H_2})_4CH_2N$), 2.42 (t, 2H, J=7 Hz, $SC\underline{H_2}(CH_2)_4CH_2N$), 3.65 (t, 2H, J=7.5 Hz, $SCH_2(CH_2)_4C\underline{H_2}N$), 7.61-7.80 (m, 4H, aromatic); ^{13}C-NMR ($CDCl_3$) −1.8 ($Si(CH_3)_3$), 18.3 ($S\underline{CH_2}Si(CH_3)_3$), 26.4, 28.2, 28.4 and 28.8 ($SCH_2(\underline{CH_2})_4CH_2N$), 36.0 ($S\underline{CH_2}(CH_2)_4CH_2N$), 37.9 ($SCH_2(CH_2)_4\underline{CH_2}N$), 123.0 and 133.7 (CH, aromatic), 132.1 (C, aromatic), 168.3 (C=O); IR (KBr) 2950, 1780 and 1700 (C=O stretching), 1400 and 850 cm^{-1}; mass spec., m/z (rel. intensity) 349 (M^+, 28), 334 (M^+-CH_3, 30), 302 (40), 160 (43), 120 (36), 105 (22), 73 (100); high resolution mass spec., m/z 349.1528 ($C_{18}H_{27}NO_2SSi$ requires 349.1532).

Irradiation of *N*-(Trimethylsilylmethylthiobutyl)phthalimide (6c) in Methanol. *N*-(Trimethylsilylmethylthiobutyl)phthalimide (**6c**, 650 mg, 2.0 mmol) was dissolved in 200 m*l* of methanol and irradiated through pyrex filter under N_2 purging for 9 h, resulting *ca.* 37% conversion. After removal of methanol under reduced pressure, remained residue was subjected to column chromatography ($CHCl_3$: ethyl acetate=3 : 1), to yield 140 mg (76%) of **16c** and 21 mg (12%) of **21**. Spectral data for **16c**: mp. 118-121°; ^{1}H-NMR ($CDCl_3$) 1.49-1.68 (m, 2H, $SCH_2C\underline{H_2}CH_2CH_2N$), 1.71-1.85 (m, 1H, SCH_2 $CH_2C\underline{H_2}CH_2N$), 1.85-1.99 (m, 1H, $SCH_2CH_2C\underline{H_2}CH_2N$), 2.38-2.

2-(trimethylsilylmethylthio)ethyl alcohol (**9**) in 30 m*l* of chloroform at 50° is added 4 m*l* (54.8 mmol) of thionyl chloride. After 5 h the mixture was concentrated under reduced pressure to afford a residue. Molecular distillation (1.6 torr, 95°) of the residue gave 7.71 g (99%) of ethyl chloride **10**. Spectral data for **10**: ^{1}H-NMR ($CDCl_3$) 0.08 (s, 9H, $Si(CH_3)_3$), 1.82 (s, 2H, $SCH_2Si(CH_3)_3$), 2.83 (t, 2H, J=8.0 Hz, $ClCH_2CH_2S$), 3.63 (t, 3H, J=8.0 Hz, $ClCH_2CH_2S$); ^{13}C-NMR ($CDCl_3$) −1.8 ($Si(CH)_3)_3$), 18.7 ($CH_2Si(CH_3)_3$), 38.1 ($ClCH_2CH_2S$), 42.6 ($ClCH_2CH_2S$); mass spec. (EI), m/z (rel. intensity) 184 (M^+ + 2, 1), 182 (M^+, 3), 146 (20), 119 (9), 71 (100); high resolution mass spec. (EI), m/z 182.0338 ($C_6H_{15}ClSSi$ requires 182.0354).

Preparation of *N*-(Trimethylsilylmethylthioethyl)phthalimide (6a). Solution of 2-(trimethylsilylmethylthio) ethyl chloride (**10**, 3 g, 16 mmol) and potassium phthalimide (**11**, 4 g, 22 mmol) in 20 m*l* of DMF were heated for 4 h at 80°. After removal of DMF under reduced pressure, the residue was dissolved in ether and solution was filtered. The filtrate was concentrated under reduced pressure and the residue was subjected to column chromatography ($CHCl_3$) to yield 3.3 g (70%) of N-alkyl phthalimide **6a**. Spectral data for **6a**: mp. 63-65°; ^{1}H-NMR ($CDCl_3$) 0.04 (s, 9H, $Si(CH_3)_3$), 1.86 (s, 2H, $SCH_2Si(CH_3)_3$), 2.76 (t, 2H, J=7.0 Hz, NCH_2CH_2S), 3.88 (t, 2H, J=7.0 Hz, NCH_2CH_2S), 7.65-7.70 (m, 2H, aromatic), 7.78-7.83 (m, 2H, aromatic); ^{13}C-NMR ($CDCl_3$) −1.8 ($Si(CH_3)_3$), 17.7 ($S\text{-}CH_2Si(CH_3)_3$), 33.8 (NCH_2CH_2S), 36.2 (NCH_2CH_2S), 123.2 (CH, aromatic), 132.1 (C, aromatic), 133.9 (CH, aromatic), 168.1 (C=O); IR (KBr) 2956, 2920, 1770 and 1720 (C=O stretching), 1500, 1080 and 840 cm^{-1}; mass spec., m/z (rel. intensity) 293 (M^+, 14), 278 (16), 247 (46), 246 (57), 218 (17), 204 (12), 174 (11), 160 (13), 131 (20), 130 (25), 73 (100); high resolution mass spec. m/z 293.0883 ($C_{14}H_{19}NO_2SSi$ requires 293.0907).

Preparation of 3-(Trimethylsilylmethylthio)propyl iodide (13). Solution of trimethylsilylmethyl iodide (7 m*l*, 47.2 mmol) and trimethylenesulfide (**12**, 3.5 g, 47.2 mmol) in 30 ml of acetonitrile was heated for 14 h at 60°. After removal of acetonitrile under reduced pressure, the residue was subjected to column chromatography (hexane) to yield 7 g (51%) of product **13**. Spectral data for **13**: mp. 42-47°; ^{1}H-NMR ($CDCl_3$) 0.05 (s, 9H, $Si(CH_3)_3$), 1.72 (s, 2H, $SCH_2Si(CH_3)_3$), 2.04 (quintet, 2H, J=6.9 Hz, $ICH_2CH_2CH_2S$), 2.55 (t, 2H, J=6.9 Hz, $ICH_2CH_2CH_2S$), 3.23 (t, 2H, J=6.9 Hz, $ICH_2CH_2CH_2S$); ^{13}C-NMR ($CDCl_3$) −1.8 ($Si(CH_3)_3$), 5.1 ($SCH_2Si(CH_3)_3$), 18.2 ($ICH_2CH_2CH_2S$), 32.3 ($ICH_2CH_2CH_2S$), 36.4 ($ICH_2CH_2CH_2S$); IR (KBr) 2950, 1250, 850 cm^{-1}; mass spec. (EI) m/z (rel. intensity) 288 (M^+, 14), 272 (9), 199 (10), 193 (29), 161 (34), 133 (8), 119 (10), 73 (100); high resolution mass spec., m/z 287.9865 ($C_7H_{17}ISSi$ requires 287.9866).

Preparation of *N*-(Trimethylsilylmethylthiopropyl)phthalimide (6b). Solution of 3-(trimethylsilylmethylthio) propyl iodide (**13**, 4 g, 13.6 mmol) and potassium phthalimide (**11**, 3.3 g, 17.7 mmol) in 30 m*l* of DMF was heated for 30 min at 80°. After removal of DMF under reduced pressure, the residue was dissolved in chloroform and solution was filtered. The filtrate was concentrated under reduced pressure and the residue was subjected to column chromatography (CH_2Cl_2) to yield 4 g (96%) of product **6b**. Spectral data for **6b**: mp. 42-47°; ^{1}H-NMR ($CDCl_3$) 0.04 (s, 9H, $Si(CH_3)_3$), 1.74 (s, 2H, $SCH_2Si(CH_3)_3$), 1.95 (quintet, 2H, J=7.2 Hz, $NCH_2CH_2CH_2S$), 2.53 (t, 2H, J=7.2 Hz, $NCH_2CH_2CH_2S$), 3.76 (t, 2H, J=7.2 Hz, $NCH_2CH_2CH_2S$), 7.63-7.73 (m, 2H, aromatic), 7.77-7.84 (m, 2H, aromatic); ^{13}C-NMR ($CDCl_3$), −1.8 ($Si(CH_3)_3$), 18.2 ($SCH_2Si(CH_3)_3$), 27.7 ($NCH_2CH_2CH_2S$), 33.3 ($NCH_2CH_2CH_2S$), 37.2 ($NCH_2CH_2CH_2S$), 123.2 (CH, aromatic), 132.1 (C, aromatic), 133.9 (CH, aromatic), 168.3 (C=O); IR (KBr) 2950, 1770 and 1720 (C=O stretching), 1400, 850 and 720 cm^{-1}; mass spec., m/z (rel. intensity) 307 (M^+, 60), 292 (M^+-CH_3, 70), 261 (74), 246 (29), 232 (100); high resolution mass spec., m/z 307.1058 ($C_{15}H_{21}NO_2SSi$ requires 307.1062).

Irradiation of *N*-(Trimethylsilylmethylthioethyl)phthalimide (6a) in Methanol. *N*-(Trimethylsilylmethylthioethyl)phthalimide (**6a**, 520 mg, 1.77 mmol) was dissolved in 200 m*l* of methanol and irradiated through pyrex filter under N_2 purging for 9 h, resulting *ca.* 30% conversion. After removal of methanol under reduced pressure, remained residue was subjected to preparative TLC ($CHCl_3$; ethyl acetate=3 : 1) to yield 59 mg (50%) of **16a** and 7 mg (6%) of **17**. Spectral data for **16a**: mp. 155-156°; ^{1}H-NMR ($CDCl_3$) 2.50-2.57 (m, 1H, NCH_2CH_2S), 2.59-2.68 (m, 1H, NCH_2CH_2S), 2.72 (d, 1H, J=14 Hz, $C(OH)CH_2S$), 3.12 (d, 1H, J=14 Hz, $C(OH)CH_2S$), 3.29-3.37 (m, 1H, NCH_2CH_2S), 4.43-4.49 (m, 1H, NCH_2CH_2S), 4.46 (br. s, 1H, OH), 7.47-7.51 (m, 1H, aromatic), 7.54-7.60 (m, 2H, aromatic), 7.74-7.76 (m, 1H, aromatic); ^{13}C-NMR ($CDCl_3$) 27.5 (SCH_2CH_2N), 37.5 (SCH_2CH_2N), 38.9 ($SCH_2C(OH)$) 82.9 (quaternary C-3), 121.6 (CH, aromatic), 123.8 (CH, aromatic), 130.1 (CH, aromatic), 131.1 (C, aromatic), 132.3 (CH, aromatic), 145.8 (C, aromatic), 164.9 (C=O); IR (KBr) 3050-3500 (br. OH stretching), 1674 (C=O stretching), 1470 and 1417 cm^{-1}; mass spec. (EI), m/z (rel. intensity) 221 (M^+, 12), 204 (M^+-OH, 2), 203 (M^+-H_2O, 3), 160 (13), 146 (7), 130 (8), 105 (7), 77 (10), 76 (9), 75 (7), 74 (100); high resolution mass spec., m/z 221.0499 ($C_{11}H_{11}NO_2S$ requires 221.05105).

Irradiation of *N*-(Trimethylsilylmethylthioethyl)phthalimide (6a) in Acetone. *N*-(Trimethylsilylmethylthioethy)phthalimide (**6a**, 200 mg, 0.68 mmol) was dissolved in 200 m*l* of acetone and irradiated through pyrex filter under N_2 purging for 2 h, resulting *ca.* 50% conversion. After removal of acetone under reduced pressure, remained residue was subjected to preparative TLC ($CHCl_3$: ethyl acetate=3 : 1), to yield 63 mg (60%) of **18**. Spectral data for **18**: mp. 128-129°; ^{1}H-NMR ($CDCl_3$) 0.20 (s, 9H, $Si(CH_3)_3$), 2.37 (s, 1H, $CHSi(CH_3)_3$), 2.51-2.56 (m, 1H, NCH_2CH_2S), 2.63-2.71 (m, 1H, SCH_2CH_2N), 3.32-3.40 (m, 1H, SCH_2CH_2N), 4.51-4.56 (m, 1H, SCH_2CH_2N), 4.62 (s, OH), 7.46-7.55 (m, 2H, aromatic), 7.65-7.67 (m, 1H, aromatic), 7.77-7.80 (m, 1H, aromatic); ^{13}C-NMR ($CDCl_3$) 0.3 ($Si(CH_3)_3$), 29.1 (SCH_2CH_2N), 37.6 (SCH_2CH_2N), 43.6 ($CHSi(CH_3)_3$), 87.2 (quaternary C-3), 123.7 (CH, aromatic), 124.1 (CH, aromatic), 129.9 (CH, aromatic), 130.9 (CH, aromatic), 132.1 (C, aromatic), 145.7 (C, aromatic), 164.0 (C=O); IR (KBr) 3050-3500 (br. OH stretching), 1678 (C=O stretching), 1469, 1415 and 1250 cm^{-1}; mass spec. (EI), m/z (rel. intensity) 293 (M^+, 16), 278 (M^+-CH_3, 16), 275 (M^+-H_2O, 14), 248 (16), 247 (72), 246 (100), 218 (23), 204 (20), 203 (61), 190 (16), 188 (31), 160 (24); high resolution mass spec. (EI), m/z 293.0906 ($C_{14}H_{19}NO_2SSi$ requires 293.0906).

Irradiation of *N*-(Trimethylsilylmethylthiopropyl)phthalimide (6b) in Methanol. *N*-(Trimethylsilylmethylthiopropyl)phthalimide (**6b**, 1 g, 3.26 mmol) was dissolved in 200 m*l* of methanol and irradiated through pyrex filter under N_2 purging for 9 h, resulting *ca.* 30% conversion. After

52 (m, 2H, $SCH_2(CH_2)_2CH_2N$), 2.96 (d, 1H, J=15 Hz, SCH_2C(OH)), 3.24 (d, 1H, J=15 Hz, SCH_2C(OH)), 3.30-3.52 (m, 2H, $SCH_2(CH_2)_2CH_2N$); 7.29-7.50 (m, 4H, aromatic); ^{13}C-NMR ($CDCl_3$) 25.5 ($SCH_2CH_2CH_2CH_2N$), 26.4 ($SCH_2CH_2CH_2CH_2N$), 32.2 ($SCH_2(CH_2)_2CH_2N$), 37.2 ($SCH_2(CH_2)_2CH_2N$), 38.5 (SCH_2C(OH)), 88.8 (quaternary C-3), 121.5, 122.8, 129.4 and 132.2 (CH, aromatic), 131.1 and 146.7 (C, aromatic), 168.2 (C=O); IR (KBr) 3100-3600 (OH stretching), 1690 (C=O stretching), 1400, 1100, 1050 and 750 cm^{-1}; mass spec., m/z (rel. intensity) 249 (M^+, 3), 232 (M^+-OH, 7), 231 (M^+-H_2O, 43), 216 (3), 202 (64), 198 (16), 188 (14), 161 (13), 160 (100); high resolution mass spec., m/z 249.0834 ($C_{13}H_{15}NO_2S$, requires 249.0824). Spectral data for **21**: ^{1}H-NMR ($CDCl_3$) 1.78 (quintet, 2H, J=6 Hz, $SCH_2CH_2CH_2CH_2N$), 1.97 (quintet, 2H, J=6 Hz, $SCH_2CH_2CH_2CH_2N$), 2.93 (t, 2H, J=6 Hz, $SCH_2(CH_2)_2CH_2N$), 4.62 (t, 2H, J=6 Hz, $SCH_2(CH_2)CH_2N$), 6.20 (s, 1H, alkenic), 7.42-7.59 (m, 4H, aromatic); ^{13}C-NMR($CDCl_3$) 22.8 ($SCH_2CH_2CH_2CH_2N$), 29.8 ($SCH_2CH_2CH_2CH_2N$), 36.0 ($SCH_2(CH_2)_2CH_2N$), 38.5 ($SCH_2(CH_2)_2CH_2N$), 95.1 (CH, alkenic), 119.2, 123.0, 129.2, 131.8 (CH, aromatic), 128.1 (C, alkenic), 136.1 and 144.4 (C, aromatic), 167.6 (C=O); mass spec., m/z (rel. intensity) 231 (100), 218 (5), 198 (47), 188 (41); high resolution mass spec., m/z 231.0700 ($C_{13}H_{13}NOS$ requires 231.0718).

Irradiation of *N*-(Trimethylsilylmethylthiobutyl)phthalimide (6c) in Acetone. *N*-(Trimethylsilylmethylthiobutyl)phthalimide (**6c**, 550 mg, 1.7 mmol) was dissolved in 200 m*l* of acetone and irradiated through pyrex filter under N_2 purging for 3.5 h, resulting *ca.* 87% conversion. After removal of acetone under reduced pressure, remained residue was subjected to column chromatography ($CHCl_3$: ethyl acetate=3 : 1), to yield 17 mg (5%) of **21**, 134 mg (36%) of **16c** and 115 mg (23%) of **22** and 95 mg (19%) of **23**. Spectral data for **22**: ^{1}H-NMR ($CDCl_3$) −0.26 (s, 9H, $Si(CH_3)_3$), 1.43-1.50 (m, 1H, $SCH_2CH_2CH_2CH_2N$), 1.55-1.68 (m, 1H, $SCH_2(CH_2)_2CH_2N$), 1.91-1.98 (m, 1H, $SCH_2CH_2CH_2CH_2N$), 1.76-2.23 (m, 2H, $SCH_2CH_2CH_2CH_2N$), 2.47-2.56 (m, 1H, $SCH_2(CH_2)_2CH_2N$), 2.89-2.97 (m, 1H, $SCH_2(CH_2)_2CH_2N$), 3.28 (s, 1H, $SCHSi(CH_3)_3$), 3.78-3.82 (m, 1H, $NCH_2(CH_2)_2CH_2S$), 4.87 (s, 1H, OH), 7.16-7.51 (m, 4H, aromatic); ^{13}C-NMR ($CDCl_3$) -2.2 ($Si(CH_3)_3$), 19.7 ($SCH_2CH_2CH_2CH_2N$), 26.0 ($SCH_2CH_2CH_2CH_2N$), 35.6 ($SCH_2(CH_2)_2CH_2N$), 36.9 ($SCH_2(CH_2)_2CH_2N$), 52.5 ($SCH(Si(CH_3)_3$), 89.4 (quaternary C-3), 121.8, 122.7, 129.1 and 130.8 (CH, aromatic), 131.9 and 146.6 (C, aromatic), 166.0 (C=O); IR (KBr) 3400-3100 (OH stretching), 2950, 1680 (C=O stretching), 1410 and 860 cm^{-1}; mass spec. m/z (rel. intensity) 321 (M^+, 18), 320 (M^+-1, 14), 303 (M^+-H_2O, 100), 288 (9), 274 (48), 260 (6), 246 (24); high resolution mass spec., m/z 321.1225 ($C_{16}H_{23}NO_2SSi$ requires 321.1219). Spectral data for **23**: ^{1}H-NMR ($CDCl_3$) 0.09 (s, 9H, $Si(CH_3)_3$), 1.20-1.44 (m, 2H, $SCH_2CH_2CH_2CH_2N$), 1.77-1.83 (m, 1H, $SCH_2CH_2CH_2CH_2N$), 2.02-2.10 (m, 1H, $SCH_2CH_2CH_2CH_2N$), 2.12-2.22 (m, 1H, $SCH_2(CH_2)_2CH_2N$), 2.26-2.32 (m, 1H, $SCH_2(CH_2)_2CH_2N$), 2.88-2.97 (m, 1H, $SCH_2(CH_2)_2CH_2N$), 3.84 (s, 1H, $CHSi(CH_3)_3$), 3.91-3.97 (m, 1H, $SCH_2(CH_2)_2CH_2N$), 7.34-7.52 (m, 3H, aromatic), 8.17-8.20 (m, 1H, aromatic); ^{13}C-NMR ($CDCl_3$) −1.7 ($Si(CH_3)_3$), 26.4 ($SCH_2CH_2CH_2CH_2N$), 28.1 ($SCH_2CH_2CH_2CH_2N$), 29.7 ($SCH_2(CH_2)_2CH_2N$), 35.4 ($SCH_2(CH_2)_2CH_2N$), 54.3 ($CH(Si(CH_3)_3$), 88.4 (quaternary C-3), 123.1, 124.7, 129.5 and 131.6 (CH, aromatic), 130.7 and 147.0 (C, aromatic), 165.0 (C=O); IR (KBr) 3450-3150 (OH stretching), 2900, 1660 (C=O stretching), 1410 and 850 cm^{-1}; mass spec., m/z (rel. intensity) 321 (M^+, 33), 303 (M^+-H_2O, 38), 288 (8), 274 (100), 260 (22), 246 (61); high resolution mass spec., m/z 321.1239 ($C_{16}H_{23}NO_2SSi$ requires 321.1219).

Irradiation of *N*-(Trimethylsilylmethylthiopentyl)phthalimide (6d) in Methanol. *N*-(Trimethylsilylmethylthiopentyl)phthalimide (**6d**, 300 mg, 0.9 mmol) was dissolved in 200 m*l* of methanol and irradiated through pyrex filter under N_2 purging for 8 h, resulting *ca.* 30% conversion. After removal of methanol under reduced pressure, remained residue was subjected to column chromatography (CH_3Cl : ethyl acetate=3 : 1), to yield 58 mg (88%) of **16d** and 3 mg (<5%) of **24**. Spectral data for **16d**: mp. 142-145°; ^{1}H-NMR ($CDCl_3$) 1.40-1.52 (m, 2H, $SCH_2CH_2CH_2CH_2CH_2N$), 1.52-1.78 (m, 2H, $SCH_2CH_2(CH_2)_2CH_2N$), 1.79-1.86 (m, 1H, $SCH_2(CH_2)_2CH_2CH_2N$), 1.96-2.09 (m, 1H, $SCH_2(CH_2)_2CH_2CH_2N$), 2.23-2.33 (m, 1H, $SCH_2(CH_2)_3CH_2N$), 2.44-2.52 (m, 1H, $SCH_2(CH_2)_3CH_2N$), 3.17 (d, 1H, J=15.2 Hz, SCH_2C(OH)), 3.23 (d, 1H, J=15.2 Hz, SCH_2C(OH)), 3.25-3.39 (m, 2H, $SCH_2(CH_2)_3CH_2N$), 7.27-7.50 (m, 4H, aromatic); ^{13}C-NMR ($CDCl_3$) 21.4 ($SCH_2CH_2CH_2CH_2CH_2N$), 24.7 ($SCH_2CH_2(CH_2)_2CH_2N$), 26.0 ($SCH_2(CH_2)_2CH_2CH_2N$), 31.2 ($SCH_2(CH_2)_3CH_2N$), 36.7 ($SCH_2(CH_2)_3CH_2N$), 37.9 (SCH_2C(OH)), 91.0 (quaternary C-3), 121.5, 122.6, 129.4 and 132.2 (CH, aromatic), 131.9 and 146.4 (C, aromatic), 169.3 (C=O); IR (KBr) 3500-3050 (OH stretching), 1680 (C=O stretching), 1400, 1050, 750 cm^{-1}; mass spec., m/z (rel. intensity) 263 (M^+, 5), 246 (M^+-OH, 6), 245 (M^+-H_2O, 22), 217 (10), 216 (67), 188 (23), 184 (54), 174 (16), 160 (100); high resolution mass spec., m/z 263.0992 ($C_{14}H_{17}NO_2S$ requires 263.0980). Spectral data for **24**: ^{1}H-NMR ($CDCl_3$) 1.52-1.68 (m, 2H, $SCH_2CH_2CH_2CH_2CH_2N$), 1.68-1.90 (m, 4H, $SCH_2CH_2CH_2CH_2CH_2N$), 2.67 (t, 2H, J=6 Hz, $SCH_2(CH_2)_3CH_2N$), 4.77 (br. s, 2H, $SCH_2(CH_2)_3CH_2N$), 6.34 (s, 1H, alkenic H), 7.45-7.82 (m, 4H, aromatic); ^{13}C-NMR ($CDCl_3$) 23.8 ($SCH_2CH_2CH_2CH_2CH_2N$), 29.9 ($SCH_2CH_2(CH_2)_2CH_2N$), 30.6 ($SCH_2(CH_2)_2CH_2CH_2N$), 38.3 ($SCH_2(CH_2)_3CH_2N$), 40.3 ($SCH_2(CH_2)_3CH_2N$), 96.1 (CH, alkenic), 119.4, 122.9, 129.6 and 131.9 (CH, aromatic), 128.3 (C, alkenic), 137.1 and 145.5 (C, aromatic), 168.4 (C=O); IR (KBr) 2950, 1710 (C=O stretching), 1600, 750 cm^{-1}; mass spec., m/z (rel. intensity) 245(M^+, 100), 216(3), 183(13); high resolution mass spec., m/z 245.0891 ($C_{14}H_{15}NOS$ requires 245.0874).

Irradiation of *N*-(Trimethylsilylmethylthiohexyl)phthalimide (6e) in Methanol. *N*-(Trimethylsilylmethylthiohexyl)phthalimide (**6e**, 350 mg, 1.0 mmol) was dissolved in 200 m*l* of methanol and irradiated through pyrex filter under N_2 purging for 9 h, resulting *ca.* 96% convesion. After removal of methanol under reduced pressure, remained residue was subjected to column chromatography (CH_3Cl : ethyl acetate=3 : 1), to yield 155 mg (62%) of **25**. Spectral data for **25**: ^{1}H-NMR ($CDCl_3$) 1.20-1.95 (m, 8H, $SCH_2(CH_2)_4CH_2N$), 2.87 (br. s. 2H, $SCH_2(CH_2)_4CH_2N$), 4.17 (br. s. 1H, $SCH_2(CH_2)_4CH_2N$), 5.21 (br. s, 1H, $SCH_2(CH_2)_4CH_2N$), 6.30 (s, 1H, alkenic), 7.43-7.80 (m, 4H, aromatic); ^{13}C-NMR ($CDCl_3$) 22.9 and 23.2 ($SCH_2CH_2(CH_2)_2CH_2CH_2N$), 25.3 ($SCH_2CH_2(CH_2)_2CH_2CH_2N$), 27.6 ($SCH_2(CH_2)_3CH_2CH_2N$), 37.7 ($SCH_2(CH_2)_4CH_2N$), 38.8 ($SCH_2(CH_2)_4CH_2N$), 98.1 (CH, alkenic), 119.4, 123.0, 129.4 and 131.8 (CH, aromatic), 128.0 (C, alkenic), 137.6 and 143.0 (C, aromatic), 168.8 (C=O); IR (KBr) 2950, 1700 (C=O stretching), 1600, 750 cm^{-1}; mass spec., m/z (rel. intensity) 259 (M^+, 37), 226 (6), 199 (21), 198 (100), 188 (25); high resolution mass spec., m/z 259.1017 ($C_{15}H_{17}NOS$ requires 259.1031).

Acknowledgement. The present studies were supported by the Professor Training Program of Ministry of Education, Korea, 1991 and grant from the Korea Science and Engineering Foundation (CBM of POSTECH).

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The Effect of Alkali Metal Ions on Nucleophilic Substitution Reactions of Aryl Substituted Benzenesulfonates

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Received October 5, 1993

Rate constants have been measured spectrophotometrically for the nucleophilic substitution reactions of aryl substituted benzenesulfonates **(3)** with alkali metal ethoxides (EtO^-M^+) and butane-2,3-dione monoximates (Ox^-M^+) in ethanol at 25℃. The reactivity of the alkali metal ethoxides decreases in the order $EtO^-K^+ > EtO^- > EtO\ Li^+$, indicating that K^+ ion behaves as a catalyst and Li^+ ion acts as an inhibitor for all the substrates studied. For the corresponding reactions of **3** with Ox^-M^+, Li^+ ion also exhibits inhibitory effect for all the substrates, while, K^+ ion shows catalytic or inhibitory effects depending on the nature of substituents on the acyl and phenyl moieties. A study of substituent effect on rate has revealed that both EtO^- and Ox^- systems have the same reaction mechanism. The different behavior shown by K^+ ion for the reaction of **3** with EtO^- and Ox^- would be attributed to a difference in charge polarization of S=O bond in the transition state between the two systems and/or a change in conformation of Ox^-K^+.

Introduction

Studies of metal ion effect on organic reactions have attracted a great deal of attention due to the important role of metal ions in biological processes[1-3]. However, the studies have mostly been confined to multivalent metal ions which could exert catalytic effect by acting as Lewis acids[4]. Investigation of the effect of alkali metal ions on organic reactions has been initiated only recently[5].

In recent studies alkali metal ions in various organic reactions have been demonstrated to exhibit catalytic or inhibitory effects depending on the type of substrates (phosphinic, carboxylic, or sulfonic esters) and nucleophiles, and on the size of alkali metal ions. Buncel and his coworkers have reported that alkali metal ions exhibit significant catalytic effect in the reaction of a phosphinic ester **(1)** with alkali metal ethoxides (EtO^-M^+) in ethanol[5-7]. On the contrary, we have found that alkali metal ions show significant inhibitory effect