

Photoaddition Reactions of *N*-Methylthiophthalimide with α -Silyl-*n*-electron Donors via Single Electron Transfer-Desilylation and Hydrogen Atom Abstraction Pathways[†]

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Studies have been conducted to explore photoaddition reactions of *N*-methylthiophthalimide with α -silyl-*n*-electron donors $\text{Et}_2\text{NCH}_2\text{SiMe}_3$, $n\text{-PrSCH}_2\text{SiMe}_3$ and $\text{EtOCH}_2\text{SiMe}_3$. Photoaddition of α -silyl amine $\text{Et}_2\text{NCH}_2\text{SiMe}_3$ to *N*-methylthiophthalimide occurs in CH_3CN and benzene to produce non-silicon containing adduct in which thiophthalimide thione carbon is bonded to α -carbon of α -silyl amine in place of the trimethylsilyl group. In contrast, photoaddition of $\text{EtOCH}_2\text{SiMe}_3$ to *N*-methylthiophthalimide generates two diastereomeric adducts in which thiophthalimide thione carbon is connected to α -carbon of α -silyl ether in place of α -hydrogen. Based on a consideration of the oxidation potentials of α -silyl-*n*-electron donors and the nature of photoadducts, mechanism for these photoadditions involving single electron transfer (SET) -desilylation and H atom abstraction pathways are proposed.

key words: photoaddition reaction, *N*-methylthiophthalimide, α -silyl-*n*-electron donors, single electron transfer, hydrogen atom abstraction

INTRODUCTION

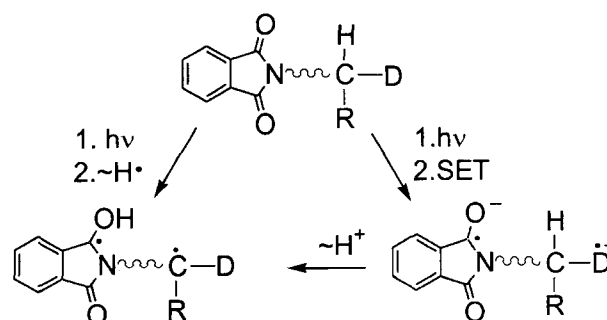
Phthalimides have been the subject of a number of in-depth photochemical [1] and photophysical [2] studies in recent years due to the developing application of the excited state chemistry of these substances. Exploratory investigations of preparative aspects of phthalimides photochemistry have uncovered the operation of two major excited-state reaction pathways. These include the sometimes indistinguishable processes initiated by inter- or intramolecular hydrogen atom abstraction and single electron transfer (SET) followed by deprotonation (Scheme 1).

A consideration of the highly efficient and selective nature of β -silyl cation desilylation process [3] and the reduced oxidation potentials [4,5] of α -silyl-*n*-electron donors promoted our recent studies in the area of SET photochemistry using α -silyl-*n*-electron donors. The studies have shown that SET from α -silyl-*n*-electron donors is efficient and photoinduced sequential SET-desilylation serves as an efficient and highly regioselective pathway for formation of heteroatom-stabilized, carbon-centered radical [6] (Scheme 2).

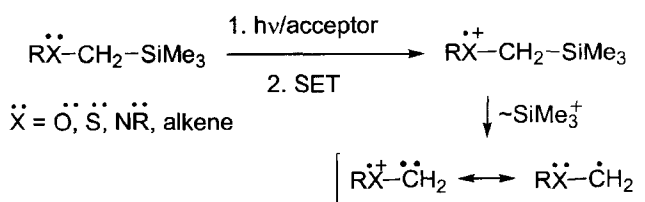
Phthalimides undergo smooth photoaddition reactions [7]

with α -silyl-*n*-electron donors to generate 3-substituted products via mechanistic routes which involve sequential SET-desilylation (Scheme 3).

Similarly phthalimides tethered with α -silyl-ether [8], -thioether [9], -*N*-acetylamido group [10] or -*N*-mesylamido group [10] undergo efficient and high yielding photocyclization reactions to provide medium and large ring heterocycles.



Scheme 1.



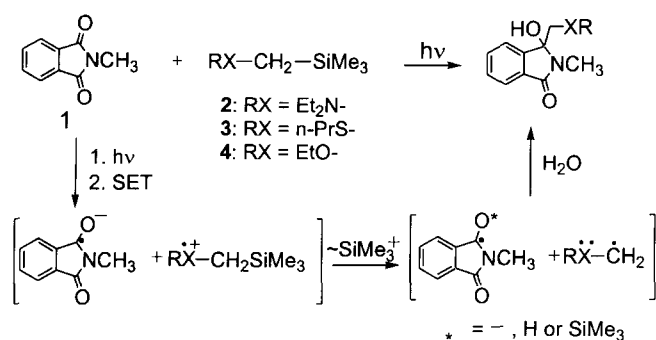
Scheme 2.

[†] The authors dedicate this paper to Professor Sang Chul Shim commemorating his retirement who has been a great organic photochemist and one of driving forces behind the creation of the Korean Society of Photoscience.

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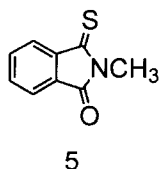
Scheme 3.

Further photochemistry of phthalimides containing *N*-linked ω -trimethylsilylmethyl-substituted polyether, polythioether and polysulfonamide allows efficient and highly regioselective production of the corresponding macrocyclic polyether, polythioether and polysulfonamide products [11]. The methodology utilizing photoinduced sequential SET-desilylation pathways was expanded to include arenecarbonitriles [6c], cyclohexenones [6d,e] and quinonedione [6f].

Although there are a number of reported photochemistry of cyclic imides, number of reports for photochemistry of cyclic thioimides is much less comparing with that involving cyclic imides. However, there are some reports of photochemistry of thioimides including thiophthalimides [12] and thiosuccinimides [13]. Thiophthalimides show different excited state reactivity from phthalimides and undergo inter- and intra-molecular Paterno-Buchi type photocycloaddition reactions with alkenes [12a,b,e, 13a,c,e] and alkynes [12c]. Inter- and intra-molecular hydrogen abstractions are not generally efficient in the photochemistry of thioimide [14] in contrast with that of imide analogs.

In a continuation of our effort to develop new single electron transfer induced photochemical reaction, we have investigated the photochemical reactions of *N*-methylthiophthalimide (**5**) with α -silyl-*n*-electron donors (**2**–**4**).

We now report new photochemical reactivity of **5** observed in the investigation. *N*-Methylthiophthalimide (**5**) undergoes photoaddition reactions with α -silyl-*n*-electron donors through SET-desilylation and hydrogen atom abstraction pathways depending upon their oxidation potentials.



MATERIALS AND METHODS

General procedures

¹H nuclear magnetic resonance (NMR) and ¹³C-NMR spectra

were recorded using 200 MHz and 300 MHz spectrometers and chemical shifts are reported in parts per million downfield from tetramethylsilane employed as an internal standard; abbreviations used are s (singlet), d (doublet), t (triplet) and m (multiplet). Preparative photolyses were conducted with an apparatus consisting of a 450 W medium pressure mercury lamp surrounded by a uranium filter in a quartz immersion well under an inert atmosphere. Low- and high-resolution mass spectral analyses were performed by 70 eV on mass spectrometer. α -Silyl-*n*-electron donors **2**–**4** were prepared with reported method [7].

Preparation of *N*-methylthiophthalimide (**5**)

N-Methylthiophthalimide (**5**) was prepared from *N*-methylphthalimide using reported method with Lawesson's reagent [12b].

5: ¹H-NMR (CDCl₃) δ 3.18 (s, 3H, CH₃), 7.69–7.73 (m, 2H, aromatic), 7.83–7.87 (m, 2H, aromatic); ¹³C-NMR (CDCl₃) δ 27.5 (CH₃), 122.7, 123.6, 133.0 and 134.0 (CH aromatic), 127.4 and 137.1 (C aromatic), 169.7 (C=O), 197.3 (C=S); IR(KBr), 1740 (C=O), 1080 (C=S); MS(EI), *m/z* (rel. intensity) 177 (M⁺, 100), 149 (11), 121 (17), 117 (35). HRMS(EI), *m/z* 177.0251 (C₉H₇NOS requires 177.0248).

Irradiation of *N*-methylthiophthalimide(**5**) and trimethylsilylmethyldiethyl amine (**2**) in CH₃CN

A solution of **4** (300 mg, 1.69 mmol) and **3** (1.90 g, 11.8 mmol) in 150 mL of CH₃CN was irradiated under Ar for 30 min (*ca.* conversion of 62%). Concentration of the photolyzate gave a residue which was subjected to column chromatography (silica, ethyl acetate : hexane=1:10, v/v) yielding 14 mg (7%) of **1** and 227 mg (82%) of **6**.

6: ¹H-NMR (CDCl₃) δ 0.84 (t, 6H, *J*=7.2 Hz, N(CH₂CH₃)₂), 2.32–2.44 (m, 4H, N(CH₂CH₃)₂), 3.16 (s, 3H, NCH₃), 3.63 (s, 2H, CH₂NEt₂), 5.49 (s, 1H, SH), 7.44–7.82 (m, 4H, aromatic); ¹³C-NMR (CDCl₃) δ 12.9 (N(CH₂CH₃)₂), 26.8 (NCH₃), 46.5 (N(CH₂CH₃)₂), 54.5 (CH₂NEt₂), 64.8 (HS-C), 123.2, 123.4, 128.8 and 131.9 (CH aromatic), 132.1 and 143.6 ((C aromatic), 167.4 (C=O); IR(KBr) 2340 (SH), 1700 (C=O).

Irradiation of *N*-methylthiophthalimide (**5**) and trimethylsilylmethyl ethyl Ether (**4**) in CH₃CN

A solution of **5** (300 mg, 1.69 mmol) and **4** (1.50 g, 11.8 mmol) in 150 mL of CH₃CN was irradiated under Ar for 2 h (*ca.* conversion of 85%). Concentration of the photolyzate gave a residue which was subjected to column chromatography (silica, ethyl acetate : hexane=1:10, v/v) yielding 50 mg (8%) of **1**, 120 mg (25%) of **7a** and 120 mg (25%) of **7b**.

7a: ¹H-NMR (CDCl₃) δ 0.05 (s, 9H, TMS), 1.08 (t, 3H, *J*=7.0Hz, OCH₂CH₃), 3.19 (s, 3H, NCH₃), 3.38 (q, 2H, *J*=7.0Hz, OCH₂CH₃), 3.77 (s, 1H, TMSCH), 5.54 (s, 1H, SH), 7.44–7.85 (m, 4H, aromatic); ¹³C-NMR (CDCl₃) -3.0 (TMS), 15.0 (OCH₂CH₃),

27.1 (NCH₃), 65.6 (OCH₂CH₃), 67.0 (HS-C), 74.5 (TMS-C), 123.2, 123.7, 128.9 and 131.6 (CH aromatic), 12.85 and 142.6 (C aromatic), 167.2 (C=O); IR(KBr) 2360(S-H), 1720 (C=O); MS (EI), *m/z* (rel. intensity) 293 (M+, 1), 279 (24), 218 (8), 167 (37), 148 (100), 71 (27); HRMS (EI), *m/z* 293.1258 (C₁₅H₂₃NOSSi requires 293.1270).

7b: ¹H-NMR (CDCl₃) δ 0.09 (s, 9H, TMS), 0.69 (t, 3H, *J*=7.0Hz, OCH₂CH₃), 2.91 (q, 2H, *J*=7.0Hz, OCH₂CH₃), 3.11 (s, 3H, NCH₃), 4.00 (s, 1H, TMSCH), 5.45 (s, 1H, SH), 7.40-7.85 (m, 4H, aromatic); ¹³C-NMR (CDCl₃) δ -2.7 (TMS), 14.8 (OCH₂CH₃), 27.0 (NCH₃), 64.8 (OCH₂CH₃), 66.1 (HS-C), 74.5 (TMS-C), 123.2, 123.7, 128.9 and 131.6 (CH aromatic), 12.85 and 142.6 (C aromatic), 168.1 (C=O); IR(KBr) 2360 (S-H), 1720 (C=O); MS (EI), *m/z* (rel. intensity) 293 (M+, 1), 279 (24), 218 (8), 167 (37), 148 (100), 71 (27); HRMS (EI), *m/z* 293.1258 (C₁₅H₂₃NOSSi requires 293.1270).

Irradiation of *N*-methylthiophthalimide (5) and trimethylsilylmethyl propylthio ether (3) in CH₃CN

A solution of **5** (300 mg, 1.69 mmol) and **3** (1.50 g, 11.8 mmol) in 150 mL of CH₃CN was irradiated under Ar for 9 h (ca. conversion of 20%). Concentration of the photolyzate gave a residue which was subjected to column chromatography (silica, ethyl acetate : hexane=1:10, v/v) yielding 44 mg (80%) of **1**.

RESULTS AND DISCUSSION

Photoaddition Reactions of *N*-Methylthiophthalimide with α -Silyl-*n*-electron Donors

Photoaddition reaction of *N*-methylthiophthalimides (**5**) with α -silyl-*n*-electron donors **2**–**4** were explored. Preparative photoaddition reactions were performed by irradiation of CH₃CN and benzene solutions of thiophthalimide (11 mM) in the presence of α -silyl-*n*-electron donors **2**–**4** (79 mM) by using uranium filtered-light ($\lambda > 330$ nm) and products **6**, **7a**–**b** were separated by silica gel chromatography. Products and yields along with reaction conditions employed were given in Table 1.

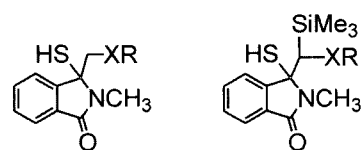
Irradiation of *N*-methylthiophthalimide (**5**) in the presence of α -silyl amine **2** in the CH₃CN leads to rapid and high

Table 1. Photochemical Reactions of *N*-Methylthiophthalimide (**5**) with α -Silyl-*n*-electron Donors **2**–**4**

| Reactant | Solvent ^a | Reaction Time (h) | Conversion (%) | Products ^b (% yield) |
|------------|----------------------|-------------------|----------------|---|
| 5+2 | CH ₃ CN | 0.5 | 62 | 6 (82), 1 (7) |
| 5+2 | benzene | 2 | 70 | 6 (45), 1 (30) |
| 5+3 | CH ₃ CN | 9 | 20 | 1 (80) |
| 5+3 | benzene | 6 | 20 | 1 (80) |
| 5+4 | CH ₃ CN | 2 | 85 | 7a (25), 7b (25), 1 (8) |
| 5+4 | benzene | 2 | 90 | 7a (30), 7b (30), 1 (10) |

^a Photochemical reactions of **5** in the benzene with **2**–**4** were performed under similar conditions to those in CH₃CN

^b Products yield were based on consumed reactant **5**.



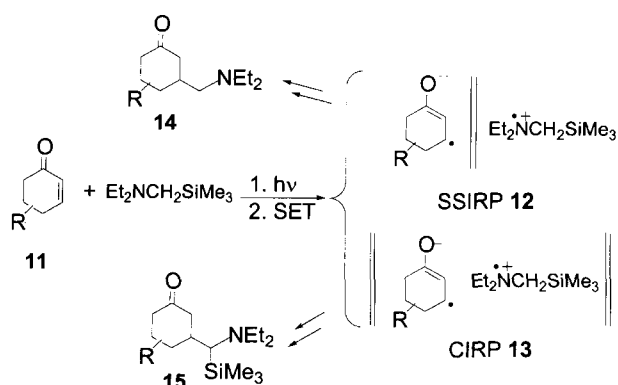
6: RX = Et₂N-
8: RX = *n*-PrS-
9: RX = EtO-
7: RX = EtO-
10: RX = *n*-PrS-
11: RX = Et₂N-

yielding production of non-silicon containing photoadduct **6** (82%) along with a small amount of oxidized product, *N*-methylphthalimide (**1**) (7%). Photoreaction of **5** with **2** in benzene also produces photoadduct **6** as a major product with oxidized product, *N*-methylphthalimide (**1**). However the photoreaction in benzene proceeds in a slower rate than in CH₃CN as shown with reaction time in Table 1. In the photoreactions of *N*-methylthiophthalimide (**5**) with α -silyl ether **4** in both CH₃CN and benzene, silicon-containing diastereomeric photoadducts **7** are generated in a ca. 1:1 ratio. In contrast to the production of photoadduct **6** or **7** from photoreaction of **5** with α -silyl amine **2** or α -silyl ether **4**, irradiations of **5** in the presence of α -silyl thioether **3** in CH₃CN and benzene provide no photoadduct like **8** or **10** but only oxidized product, *N*-methylphthalimide (**1**) as only observable product upon prolonged irradiation.

Structural assignments to photoadducts **6** and **7** were made on the basis of characteristic spectroscopic data (see the Materials and Methods section). IR spectra of these photoadducts contain characteristic bands for sulfhydryl groups at 2340–2360 cm⁻¹ and their ¹H-NMR show singlet peaks corresponding to sulfhydryl hydrogen at 5.45–5.54 ppm. ¹H-NMR and ¹³C-NMR spectra of photoadduct **6** and **7** show resonances which correspond to the respective (diethylamino)methyl and ethoxy (trimethylsilyl)methyl groups. The photoadducts **7a** and **7b** show singlets for nine hydrogens at 0.05–0.09 ppm in their ¹H-NMR spectra and at -3.0–-2.7 ppm in their ¹³C-NMR corresponding to the trimethylsilyl groups. Further ¹³C-NMR of photoadducts **6** and **7** show resonances at 64.5–66.1 ppm for the carbon which has sulfhydryl group and amide nitrogen.

Mechanism for Photoadditions of *N*-Methylthiophthalimide with α -Silyl-*n*-electron Donors

Photoreaction of *N*-methylthiophthalimide (**5**) with α -silyl amine **2** in both CH₃CN and benzene results in production of the non-silicon containing adduct **6** as a sole addition product. This result is different from those found in our earlier studies of the photoadditions of α -silyl amines to conjugated cyclohexenones [6d,e]. In these cases, non-silicon containing adducts **14** predominate only in those photoadditions which occur in polar-protic solvents such as CH₃OH while silicon containing adducts **15** are found selectively or exclusively for reactions in less polar aprotic solvents like MeCN (Scheme 4). However the result that photoreaction of **5** with **2** produces the non-silicon containing

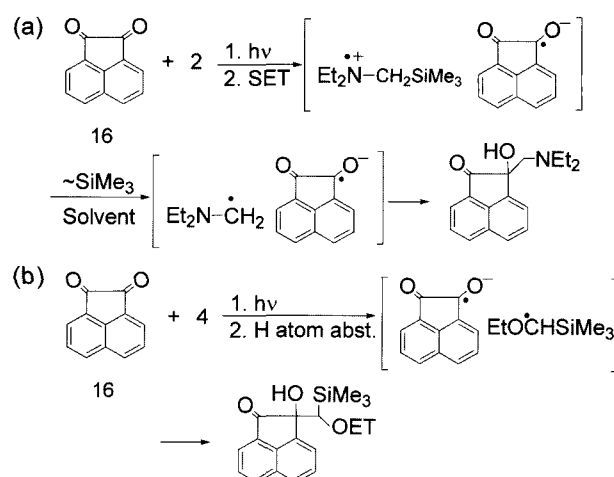


Scheme 4.

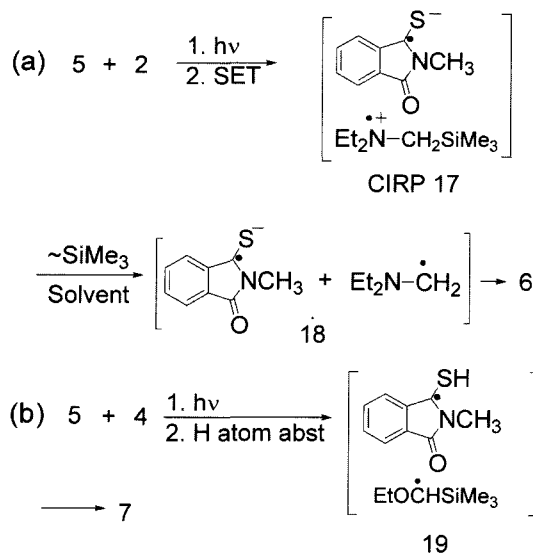
adduct **6** as only photoaddition product is similar to the result obtained in photoaddition reaction of acenaphthylenedione (**16**) with α -silyl amine **2**. In these studies, non-silicon containing photoadduct was observed to be generated as exclusive product in less polar aprotic solvent like CH_3CN [6f]. Studies of photoaddition reactions occurring between the α -silyl amine **2** and conjugated cyclohexenones **11** revealed that SET-desilylation and SET-deprotonation pathways are competitive and that this competition can be governed by reaction conditions, especially the photoreaction medium, which control the preference for formation of solvent separated ion radical pairs (SSIRP) **12** and contact ion radical pair (CIRP) **13** (Scheme 4) and/ or the basicity of the enone anion radical. Specifically, in aprotic media the intermediate CIRP **13** undergoes proton transfer of the acidic α -proton of the α -silyl amine radical cation to the oxy anion center in the cyclohexenone anion radical leading to trimethylsilyl-substituted adducts whereas in protic media the SSIRP **12** undergoes desilylation to generate non-silicon-containing adducts [6d,e].

Studies of photoaddition reaction of acenaphthylenedione (**16**) have demonstrated that acenaphthylenedione (**16**) undergoes photoaddition reactions with the α -silyl-*n*-electron donors **2**–**4** via two competing pathways involving triplet SET-desilylation (Scheme 5a) and triplet α -hydrogen atom abstraction (Scheme 5b) depending on the oxidation potential of the donor, and the SET-induced processes followed by **2** take place by exclusive desilylation of cation radical intermediates even in aprotic solvents, indicating that the acenaphthylenedione anion radical is nonbasic and this causes proton transfer from the corresponding cation radicals in the CIRP to be inefficient.

The observation that the silicon containing photoadducts **7a**–**b** are generated as sole addition products without formation of non-silicon containing adduct **9** in the photoreaction of *N*-methylthiophthalimide (**5**) with α -silyl ether **4** of high oxidation potential [6f] is similar to that from photoaddition reaction of acenaphthylenedione (**16**) with α -silyl ether **4** (Scheme 5b). Combining with results obtained in our previous studies on the photoaddition reaction of cyclohexenones and acenaphthylenedione, different nature of photoaddition products of *N*-



Scheme 5.



Scheme 6.

methylthiophthalimide (**5**) with α -silyl-*n*-electron donors **2**–**4** depending upon oxidation potentials; α -silyl amine **2** has lower oxidation potential than α -silyl ether **4** suggests that photoaddition reaction of **5** with **2** occurs via sequential SET-desilylation route (Scheme 6a) and that of **5** with **4** proceeds via α -hydrogen abstraction of α -silyl ether **4** by the excited thione (Scheme 6b).

Single electron transfer from α -silyl amine **2** to the excited *N*-methylthiophthalimide will generate contact ion radical pair **7** (CIRP **7**) in nonpolar, aprotic solvents like CH_3CN and benzene where α -deprotonation of α -silyl amine radical cation by thioanion is inefficient due to very low basicity of thioanion and α -desilylation of α -silyl amine radical cation by solvent occurs rapidly to generate the precursor of photoadduct **6**. On the other hand, the excited thione chromophore of **5** undergoes hydrogen abstraction with α -silyl ether **4** of high oxidation potential to yield the precursor of silicon containing photoadduct

7. The solvent effect observed in the photoreaction of **5** with **2** in benzene of lower polarity than CH₃CN that the photoreaction in benzene occurs in a slower rate than in CH₃CN is also consistent with our proposal for the reaction via SET-desilylation pathway.

In contrast to the photoaddition reaction of *N*-methylthiophthalimide (**5**) with α -silyl amine **2** and α -silyl ether **4**, photoreaction of **5** with α -silyl thioether **3** shows totally different that the irradiation leads to no photoaddition product and leads to oxidized product *N*-methylphthalimide (**1**) very inefficiently [15]. The result is also different from that of photoaddition reaction of acenaphthylenedione (**16**) with α -silyl thioether **3** where photoadducts are generated by two competing pathways of SET-desilylation and α -hydrogen atom abstraction. The reason why photoreaction of **5** with α -silyl thioether **3** does not yield any photoadduct like **8** and **10** is unclear. It seems likely that C⁺IRP **17** generated by SET between excited **5** and α -silyl thioether **3** or radical pair like **19** formed by α -hydrogen abstraction undergoes a rapid back SET or back hydrogen abstraction and thus lead to no photoadduct.

In summary we report SET-induced photoaddition reaction of *N*-methylthiophthalimide with α -silyl amine and hydrogen abstraction process between excited *N*-methylthiophthalimide with α -silyl ether.

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14. Norrish type II reactions of thioimides have been reported [12f, 13e].
15. The formation of *N*-methylphthalimide (**1**) in the photoreaction of *N*-methylthiophthalimide (**5**) in the presence of O₂ has been reported [12d] and inefficient generation of **1** in the photoreaction of **5** with α -silyl thioether **3** is believed to arise from the photoreaction of **5** with O₂ impurity present in the reaction solution under Ar purging.