

Single Electron Transfer Induced Photoaddition Reactions of Silyl Enol Ether to *N*-Methylphthalimide

Sun Wha Oh,[†] Jin Young Kim, Dae Won Cho, Jung Hei Choi, and Ung Chan Yoon*

Department of Chemistry, Pusan National University, Busan 609-735, Korea. *E-mail: ucyyoon@pusan.ac.kr

[†]Basic Science Research Institute, Pukyong National University, Busan 608-737, Korea

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Photochemical reactions of *N*-methylphthalimide with silyl enol ethers have been explored. Irradiations of phthalimide (**1**) and cyclic silyl enol ethers (**5a-b**) are observed to promote formation of photoreduced phthalimides and photoaddition products by sequential SET-desilylation pathways. The photoreaction of phthalimide (**1**) and acyclic silyl enol ethers (**5c-d**) leads to produce oxetanes which arise by competitive single electron transfer (SET) and classical 2+2 photocycloaddition (Paterno-Büchi reaction) pathways.

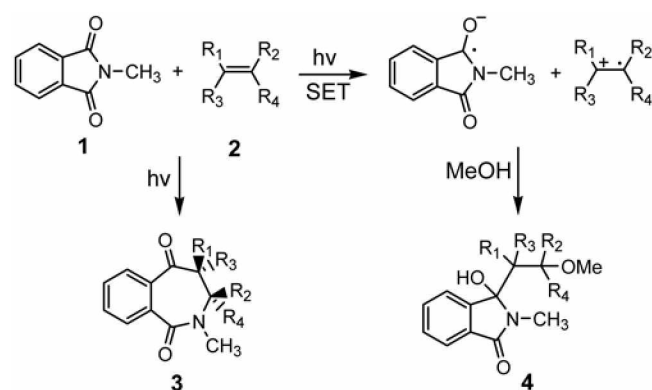
Key Words : *N*-Methylphthalimide, Silyl enol ethers, Single electron transfer, Oxetane, Photocycloaddition

Introduction

Our recent studies of single electron transfer (SET) photochemistry using α -silyl electron donors have shown that photoinduced sequential SET-desilylation serves as an efficient and highly regioselective pathway leading to carbon-centered radical generation and eventually, to carbon-carbon bond formation.¹⁻⁴ Numerous examples of SET-promoted excited states processes in which intermediate cation radical desilylation serves as the driving force are found in the photochemistry of phthalimides.^{5,6}

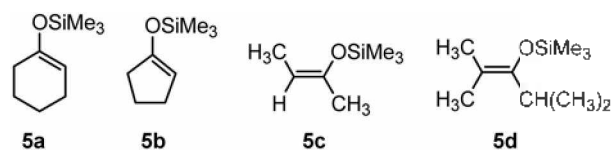
Mazzocchi *et al.* reported that the photochemistry of *N*-methylphthalimide (**1**) in presence of alkenes is characterized by the two competing processes⁷: In one of these reactions the alkene adds to the C(O)-N bond of *N*-methylphthalimide that ultimately leads to a ring expanded benzazepinedione (**3**).⁸ A competing electron transfer process results in the formation of a radical cation-radical anion pair which can be efficiently trapped in alcohol solvents such as **4** (Scheme 1).^{9,10} The study on the SET photochemistry of the easily oxidized trimethylsilyl enol ether have shown that photoinduced SET occurs from a simple trimethylsilyl enol ether to generate an intermediate cation radical, which is converted into the precursor aldehyde or ketone.¹¹⁻¹³

In this research, the SET-induced photochemical reaction



Scheme 1

of silyl enol ether (**5a-d**) with *N*-methylphthalimide (**1**) was investigated. The results of this efforts, reported below, show that *N*-methylphthalimide with cyclic silyl enol ether as an electron donor undergoes photoaddition reaction exclusively *via* SET-desilylation pathways. On the other hand, *N*-methylphthalimide with acyclic silyl enol ether participates in two competing excited state reaction pathways involving SET-induced and classical oxetane formation.



Experimental

General Procedure. The Chemical shifts of resonances in the ¹H- and ¹³C-NMR (200 and 300 MHz) spectra were recorded on CDCl₃ solutions are reported in parts per million relative to Me₄Si as an internal standard. For compounds containing Me₃Si groups, CHCl₃ was used as an internal standard. IR spectral bands are reported in cm⁻¹. Preparative photochemical reactions were conducted with an apparatus consisting of a 450W Hanovia medium pressure mercury vapor lamp surrounded by a Pyrex 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 irradiations. The photolysates were concentrated under reduced pressure giving residues which were subjected to preparative TLC on 20 × 20 cm silica gel coated plates. Low and high resolution (HRMS) mass spectra were obtained by use of electron impact ionization unless otherwise noted. All starting materials used in the photoreactions derived from commercial sources. All new compounds described are isolated as oils in > 90% purity (by NMR analysis) unless noted otherwise.

Irradiation of *N*-Methylphthalimide (1**) and 1-(Trimethylsilyloxy)cyclohexene (**5a**).** Methanol. A solution of

N-methylphthalimide (**1**) (500 mg, 3.10 mmol) and 1-(trimethylsilyloxy)cyclohexene (**5a**) (5.28 g, 31.0 mmol) in 100 mL of methanol was irradiated for 12 h (ca. 50% conversion of **1**). Work-up and chromatographic (1:1, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 52 mg (21%) of **8** and 84 mg (17%) of **9**.

Acetonitrile. A solution of *N*-methylphthalimide (**1**) (500 mg, 3.10 mmol) and 1-(trimethylsilyloxy)cyclohexene (**5a**) (5.28 g, 31.0 mmol) in 100 mL of acetonitrile was irradiated for 12 h (ca. 60% conversion of **1**). Work-up and chromatographic (1:1, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 37 mg (12%) of **8**, 97 mg (16%) **9**, 63 mg (13%) of diastereomeric photoadducts **6a** and 15 mg (3%) of **7a**.

6a: (1:1.4 mixture of two diastereomers based on $^1\text{H-NMR}$ integration): $^1\text{H-NMR}$ of diastereomer A 1.76-2.00 (m, 6H, $\text{COCH}_2(\text{CH}_2)_3$), 2.22-2.25 (m, 2H, $\text{COCH}_2(\text{CH}_2)_3$), 2.55 (s, 3H, CH_3), 3.25-3.30 (m, 1H, CH), 4.60 (s, 1H, OH), 7.37-7.44 (m, 3H, aromatic), 7.85-7.88 (m, 1H, aromatic), diastereomer B 1.76-2.00 (m, 6H, $\text{COCH}_2(\text{CH}_2)_3$), 2.22-2.25 (m, 2H, $\text{COCH}_2(\text{CH}_2)_3$), 2.65 (s, 3H, CH_3), 3.25-3.30 (m, 1H, CH), 4.70 (s, 1H, OH), 7.37-7.44 (m, 3H, aromatic), 7.85-7.88 (m, 1H, aromatic); $^{13}\text{C-NMR}$ of diastereomer A 23.6 (CH_3), 24.9, 25.1, 40.8 and 42.6 (CH_2), 44.1 (CH), 91.5 (COH), 123.2, 123.3, 129.7 and 131.7 (CH, aromatic), 132.0 and 145.0 (C, aromatic), 167.0 (imide C=O), 210.4 (C=O), diastereomer B 23.0 (CH_3), 24.3, 25.9, 41.0, and 42.1 (CH_2), 43.9 (CH), 91.6 (COH), 122.8, 123.2, 129.7 and 131.5 (CH, aromatic), 131.9 and 144.5 (C, aromatic), 167.3 (imide C=O), 209.6 (C=O); IR (KBr) 3000-3550 (br. OH stretching), 1710 and 1680 cm^{-1} (C=O stretching).

7a: mp 113-116 $^\circ\text{C}$; $^1\text{H-NMR}$ 1.61-1.81 (m, 4H, $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{CO}_2\text{H}$), 2.43 (t, 2H, $J = 7.0$ Hz, $\text{CH}_2\text{CO}_2\text{H}$), 2.66 (q, 2H, $J = 7.3$ Hz, =CCH₂), 3.52 (s, 3H, CH_3), 5.60 (t, 1H, $J = 7.8$ Hz, =CH), 7.42-7.83 (m, 4H, aromatic), 10.5 (s, 1H, COOH); $^{13}\text{C-NMR}$ 24.4, 26.2, 29.4 (CH_2), 30.1 (CH_3), 33.9 ($\text{CH}_2\text{CO}_2\text{H}$), 108.6 (=CH), 118.8, 123.1, 128.5 and 131.7 (CH, aromatic), 134.0 and 137.7 (C, aromatic), 135.7 ($\text{C}=\text{CH}$), 168.3 (imide C=O), 178.9 (COOH); IR (KBr) 3200-3600 (br. OH stretching), 1720 and 1650 cm^{-1} (C=O stretching).

Acetone. A solution of *N*-methylphthalimide (**1**) (500 mg, 3.10 mmol) and 1-(trimethylsilyloxy)cyclohexene (**5a**) (5.28 g, 31.0 mmol) in 100 mL of acetone was irradiated for 12 h (ca. 66% conversion of **1**). Work-up and chromatographic (1:1, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 22 mg (7%) of **8**, 62 mg (9%) **9**, 87 mg (17%) **6a** and 15 mg (3%) of **7a**.

Benzene. A solution of *N*-methylphthalimide (**1**) (500 mg, 3.10 mmol) and 1-(trimethylsilyloxy)cyclohexene (**5a**) (5.28 g, 31.0 mmol) in 100 mL of benzene was irradiated for 12 h (ca. 10% conversion of **1**). Work-up and chromatographic (1:1, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 8 mg (16%) of **8**, 10 mg (12%) **6a** and 15 mg (19%) of **7a**.

Irradiation of *N*-Methylphthalimide (1**) and 1-(Trimethylsilyloxy)cyclopentene (**5b**)**, *Methanol*. A solution of *N*-methylphthalimide (**1**) (500 mg, 3.10 mmol) and 1-

(trimethylsilyloxy)cyclopentene (**5b**) (4.85 g, 31.0 mmol) in 100 mL of methanol was irradiated for 12 h (ca. 50% conversion of **1**). Work-up and chromatographic (1:1, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 70 mg (27%) of **8** and 139 mg (27%) **9**.

Acetonitrile. A solution of *N*-methylphthalimide (**1**) (500 mg, 3.10 mmol) and 1-(trimethylsilyloxy)cyclopentene (**5b**) (4.85 g, 31.0 mmol) in 100 mL of acetonitrile was irradiated for 12 h (ca. 35% conversion of **1**). Work-up and chromatographic (1:1, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 23 mg (13%) of **8**, 56 mg (16%) **9**, 43 mg (16%) of diastereomeric photoadducts **6b** and 5 mg (2%) of **7b**.

6b: (1:1.2 mixture of two diastereomers based on $^1\text{H-NMR}$ integration.) $^1\text{H-NMR}$ of diastereomer A 1.98-2.06 (m, 6H, $(\text{CH}_2)_3$), 2.63 (s, 3H, CH_3), 3.14-3.20 (m, 1H, CH), 4.90 (s, 1H, OH), 7.37-7.44 (m, 3H, aromatic), 7.85-7.88 (m, 1H, aromatic), diastereomer B 1.98-2.06 (m, 6H, $(\text{CH}_2)_3$), 2.59 (s, 3H, CH_3), 3.14-3.20 (m, 1H, CH), 4.90 (s, 1H, OH), 7.37-7.44 (m, 3H, aromatic), 7.85-7.88 (m, 1H, aromatic); $^{13}\text{C-NMR}$ of diastereomer A 23.6 (CH_3), 23.9, 37.3 and 40.1 (CH_2), 43.1 (CH), 91.3 (COH), 123.1, 123.2, 129.7 and 131.3 (CH, aromatic), 131.9 and 144.8 (C aromatic), 167.0 (C=O imide), 216.5 (C=O), diastereomer B 23.3 (CH_3), 23.5, 38.6 and 39.5 (CH_2), 42.3 (CH), 91.2 (COH), 123.0, 123.1, 129.7 and 131.6 (CH, aromatic), 131.9 and 144.6 (C aromatic), 166.8 (C=O imide), 217.8 (C=O); IR (KBr) 3050-3500 (br. OH stretching), 1740 and 1680 cm^{-1} (C=O stretching).

7b: mp 134-136 $^\circ\text{C}$; $^1\text{H-NMR}$ (CD_3OD) 1.89 (q, 2H, $J = 7.3$ Hz, $\text{CH}_2\text{-CH}_2\text{CO}_2\text{H}$), 2.44 (t, 2H, $J = 7.2$ Hz, $\text{CH}_2\text{CO}_2\text{H}$), 2.72 (q, 2H, $J = 7.2$ Hz, $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{CO}_2\text{H}$), 3.53 (s, 3H, CH_3), 5.85 (t, 1H, $J = 8.1$ Hz, =CH), 7.47-7.80 (m, 4H, aromatic); $^{13}\text{C-NMR}$ (CD_3OD) 22.1 ($\text{CH}_2\text{-CH}_2\text{CO}_2\text{H}$), 27.1 ($\text{CH}_2\text{-CH}_2\text{-CH}_2\text{CO}_2\text{H}$), 29.8 (CH_3), 34.5 ($\text{CH}_2\text{CO}_2\text{H}$), 111.1 (=CH), 120.6, 123.7, 129.2 and 129.9 (CH, aromatic), 133.5 and 139.4 (C, aromatic), 136.6 ($\text{C}=\text{CH}$), 170.2 (imide C=O), 177.4 (COOH); IR (KBr) 3100-3550 (br. OH stretching), 1730 and 1650 cm^{-1} (C=O stretching).

Acetone. A solution of *N*-methylphthalimide (**1**) (500 mg, 3.10 mmol) and 1-(trimethylsilyloxy)cyclopentene (**5b**) (4.85 g, 31.0 mmol) in 100 mL of acetone was irradiated for 12 h (ca. 40% conversion of **1**). Work-up and chromatographic (1:1, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 20 mg (10%) of **8**, 32 mg (8%) **9**, 55 mg (18%) of diastereomeric photoadducts **6b** and 6 mg (2%) of **7b**.

Benzene. A solution of *N*-methylphthalimide (**1**) (500 mg, 3.10 mmol) and 1-(trimethylsilyloxy)cyclopentene (**5b**) (4.85 g, 31.0 mmol) in 100 mL of benzene was irradiated for 12 h (ca. 12% conversion of **1**). Work-up and chromatographic (1:1, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 8 mg (13%) of **8**, 10 mg (11%) of diastereomeric photoadducts **6b** and 15 mg (16%) of **7b**.

Irradiation of *N*-Methylphthalimide (1**) and 2-(Trimethylsilyloxy)-2-butene (**5c**)**, *Acetone*. A solution of *N*-methylphthalimide (**1**) (500 mg, 3.10 mmol) and 1-(trimethylsilyloxy)-2-butene (**5c**) (4.48 g, 31.0 mmol) in 100

mL of acetone was irradiated for 6 h (54% conversion of 1). Work-up and chromatographic (1:1, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 63 mg (16%) of **13**, 25 mg (9%) of **7c**, 87 mg (17%) of **14** and 150 mg (29%) of **15**.

13: (1:4 mixture of two diastereomers based on $^1\text{H-NMR}$ integration.) $^1\text{H-NMR}$ of diastereomer A 0.62 (d, 3H, $J = 7.2$ Hz, CHCH_3), 2.45 (s, 3H, COCH_3), 2.83 (s, 3H, N- CH_3), 3.29 (q, 1H, $J = 7.0$ Hz, CHCH_3), 4.61 (s, 1H, OH), 7.38-7.57 (m, 4H, aromatic), diastereomer B 0.90 (d, 3H, $J = 7.2$ Hz, CHCH_3), 2.25 (s, 3H, COCH_3), 2.74 (s, 3H, N- CH_3), 3.29 (q, 1H, $J = 7.0$ Hz, CHCH_3), 5.15 (s, 1H, OH), 7.37-7.59 (m, 4H, aromatic). $^{13}\text{C-NMR}$ of diastereomer A 11.6 (CHCH_3), 23.1 (COCH_3), 32.6 (N- CH_3), 49.4 (CHCH_3), 91.4 (COH), 122.6, 123.6, 129.5 and 131.8 (CH, aromatic), 131.2 and 144.0 (C, aromatic), 167.3 (C=O, imide), 210.2 (C=O, ketone), diastereomer B 11.5 (CHCH_3), 24.7 (COCH_3), 31.2 (N- CH_3), 52.0 (CHCH_3), 91.4 (COH), 121.8, 122.9, 129.6 and 132.2 (CH, aromatic), 130.9 and 146.2 (C, aromatic), 167.6 (C=O, imide), 210.1 (C=O, ketone); IR (KBr) 3200-3600 (br. OH stretching), 1700 and 1680 cm^{-1} (C=O stretching); CIMS, m/z (rel. intensity) 234 ($\text{M}^+ + 1$, 4), 216 ($\text{M}^+ - \text{OH}$, 6), 161 (60), 133 (36), 117 (29), 104 (33), 76 (40), 72 (100); HRMS, m/z 234.1131 ($\text{C}_{13}\text{H}_{16}\text{NO}_3$ requires 234.1130).

7c: $^1\text{H-NMR}$ 2.21 (d, 3H, $J = 5.1$ Hz, CHCH_3), 3.23 (s, 3H, N- CH_3), 5.50 (q, 1H, $J = 5.0$ Hz, CHCH_3), 7.24-7.66 (m, 4H, aromatic). $^{13}\text{C-NMR}$ 12.9 (CHCH_3), 25.7 (N- CH_3), 105.6 (CHCH_3), 136.9 ($\text{C}=\text{CHCH}_3$), 123.1, 123.2, 128.4 and 131.5 (CH, aromatic), 130.7 and 135.4 (C, aromatic), 166.2 (C=O); IR (KBr) 1680 cm^{-1} (C=O stretching); EIMS, m/z (rel. intensity) 173 (M^+ , 100), 158 ($\text{M}^+ - \text{CH}_3$, 38), 144 (34), 130 (23), 117 (53), 89 (14), 76 (48); HRMS, m/z 173.0833 ($\text{C}_{11}\text{H}_{11}\text{NO}$ requires 173.0841).

14: (1:1 mixture of two diastereomers based on $^1\text{H-NMR}$ integration.) $^1\text{H-NMR}$ of diastereomer A 0.30 (s, 9H, SiMe_3), 0.94 (d, 3H, $J = 7.4$ Hz, CHCH_3), 1.79 (s, 3H, CH_3), 3.16 (s, 3H, N- CH_3), 3.33 (q, 1H, $J = 7.4$ Hz, CHCH_3), 7.27-7.89 (m, 4H, aromatic), diastereomer B 0.30 (s, 9H, SiMe_3), 1.19 (d, 3H, $J = 8.0$ Hz, CHCH_3), 1.72 (s, 3H, CH_3), 3.22 (s, 3H, N- CH_3), 3.45 (q, 1H, $J = 8.0$ Hz, CHCH_3), 7.42-7.89 (m, 4H, aromatic).

15: (1:1.6 mixture of two diastereomers based on $^1\text{H-NMR}$ integration.) $^1\text{H-NMR}$ of diastereomer A 0.08 (s, 9H, SiMe_3), 1.43 (s, 3H, CH_3), 1.46 (d, 3H, $J = 6.2$ Hz, CHCH_3), 3.27 (s, 3H, N- CH_3), 4.77 (q, 1H, $J = 6.4$ Hz, CHCH_3), 7.44-7.77 (m, 4H, aromatic), diastereomer B -0.18 (s, 9H, SiMe_3), 1.44 (d, 3H, $J = 6.4$ Hz, CHCH_3), 1.52 (s, 3H, CH_3), 3.16 (s, 3H, N- CH_3), 4.88 (q, 1H, $J = 6.4$ Hz, CHCH_3), 7.47-7.84 (m, 4H, aromatic); $^{13}\text{C-NMR}$ of diastereomer A 0.1 (SiMe_3), 16.1 (CHCH_3), 25.3 (CH_3), 27.6 (N- CH_3), 83.2 (CHCH_3), 86.1 ($\text{C}(\text{OSiMe}_3)\text{CH}_3$), 102.2 (COCHCH_3), 123.2, 124.1, 129.7 and 131.4 (CH, aromatic), 134.0 and 143.7 (C, aromatic), 167.9 (C=O), diastereomer B 1.6 (SiMe_3), 16.5 (CHCH_3), 19.1 (CH_3), 27.3 (N- CH_3), 83.7 (CHCH_3), 84.7 ($\text{C}(\text{OSiMe}_3)\text{CH}_3$), 102.2 (COCHCH_3), 122.7, 126.4, 129.7 and 131.3 (CH, aromatic), 134.0 and 143.3 (C, aromatic), 169.2 (C=O).

Irradiation of *N*-Methylphthalimide (1) and 2,4-Di-

methyl-3-(Trimethylsilyloxy)-2-pentene (5d). Acetonitrile. A solution of *N*-methylphthalimide (**1**) (500 mg, 3.10 mmol) and 2,4-dimethyl-3-(trimethylsilyloxy)-2-pentene (**5d**) (5.78 g, 31.0 mmol) in 100 mL of acetonitrile was irradiated for 11 h (67% conversion of 1). Work-up and chromatographic (1:1, ethyl acetate : *n*-hexane, v/v) separation (see General) gave 58 mg (9%) of **16**, 326 mg (32%) of **17**, 58 mg (7%) of **18**, 67 mg (18%) of **19** and 60 mg (14%) of **7d**.

16: mp 80-84 $^\circ\text{C}$; $^1\text{H-NMR}$ 1.08 (s, 3H, $\text{C}(\text{CH}_3)_2$), 1.14 (d, 3H, $J = 6.7$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.17 (d, 3H, $J = 6.6$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.37 (s, 3H, $\text{C}(\text{CH}_3)_2$), 2.91 (s, 3H, N- CH_3), 3.08 (s, 1H, OH), 3.18 (septet, 1H, $J = 6.7$ Hz, $\text{CH}(\text{CH}_3)_2$), 7.46-7.80 (m, 4H, aromatic); $^{13}\text{C-NMR}$ 20.1 and 20.3 ($\text{C}(\text{CH}_3)_2$), 20.4 and 22.6 ($\text{CH}(\text{CH}_3)_2$), 26.5 (N- CH_3), 36.6 ($\text{CH}(\text{CH}_3)_2$), 52.6 ($\text{C}(\text{CH}_3)_2$), 95.1 (COH), 123.3, 123.6, 129.7 and 131.7 (CH, aromatic), 134.0 and 145.4 (C, aromatic), 168.1 (C=O, imide), 224.5 (C=O, ketone); IR (KBr) 3150-3600 (br. OH stretching), 1720 and 1690 cm^{-1} (C=O stretching).

17: mp 103-106 $^\circ\text{C}$; $^1\text{H-NMR}$ 0.36 (s, 9H, SiMe_3), 0.90 (d, 3H, $J = 6.7$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.09 (s, 3H, $\text{C}(\text{CH}_3)_2$), 1.11 (d, 3H, $J = 5.6$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.32 (s, 3H, $\text{C}(\text{CH}_3)_2$), 2.65 (septet, 1H, $J = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 3.21 (s, 3H, N- CH_3), 7.46-7.79 (m, 4H, aromatic); $^{13}\text{C-NMR}$ 3.2 (SiMe_3), 15.3 and 17.9 ($\text{C}(\text{CH}_3)_2$), 21.4 and 24.2 ($\text{CH}(\text{CH}_3)_2$), 28.5 (N- CH_3), 34.3 ($\text{CH}(\text{CH}_3)_2$), 53.8 ($\text{C}(\text{CH}_3)_2$), 99.0 ($\text{C}(\text{N-CH}_3)$), 110.8 ($\text{C}(\text{OSiMe}_3)$), 123.4, 125.6, 129.9 and 131.2 (CH, aromatic), 134.3 and 144.7 (C, aromatic), 169.0 (C=O); IR (KBr) 1720 cm^{-1} (C=O stretching); CIMS, m/z (rel. intensity) 348 ($\text{M}^+ + 1$, 1), 304 (2), 236 (3), 186 (100), 171 (31), 143 (14), 75 (31); HRMS, m/z 348.1989 ($\text{C}_{19}\text{H}_{30}\text{NO}_3\text{Si}$ requires 348.1995).

18: $^1\text{H-NMR}$ -0.16 (s, 9H, SiMe_3), 0.99 (s, 3H, $\text{C}(\text{CH}_3)_2$), 1.08 (d, 3H, $J = 6.7$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.11 (d, 3H, $J = 6.6$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.33 (s, 3H, $\text{C}(\text{CH}_3)_2$), 2.90 (s, 3H, N- CH_3), 3.37 (septet, 1H, $J = 6.6$ Hz, $\text{CH}(\text{CH}_3)_2$), 7.47-7.50 (m, 4H, aromatic).

7d: $^1\text{H-NMR}$ 2.30 (s, 3H, $\text{C}(\text{CH}_3)_2$), 2.32 (s, 3H, $\text{C}(\text{CH}_3)_2$), 3.54 (s, 3H, N- CH_3), 7.42-7.90 (m, 4H, aromatic); $^{13}\text{C-NMR}$ 16.1 and 16.4 ($\text{C}(\text{CH}_3)_2$), 27.5 (N- CH_3), 105.3 ($\text{C}(\text{CH}_3)_2$), 129.0 ($\text{C}=\text{C}(\text{CH}_3)_2$), 126.3, 126.2, 126.8 and 131.8 (CH, aromatic), 131.2 and 133.7 (C, aromatic), 162.8 (C=O); IR (KBr) 1690 cm^{-1} (C=O stretching).

Results and Discussion

For the photochemical studies, *N*-methylphthalimide (**1**) as an electron acceptor and four silyl enol ethers (**5a-d**) as an electron donor were used. 1-(Trimethylsilyloxy)-2-butene (**5c**) and 2,4-dimethyl-3-(trimethylsilyloxy)-2-pentene (**5d**) were prepared with 2-butanone and 2,4-dimethyl-3-pentanone by use of the general reaction sequence outlined in literature and confirmed by NMR and MS.^{11,14}

The photochemical reactions were performed by irradiation of CH_3CN , CH_3OH , acetone or benzene solution of *N*-methylphthalimide **1** (31.0 mM) and silyl enol ethers **5a-d** (310 mM) using Pyrex filtered-light ($\lambda > 290$ nm) for time periods resulting in 10-67% conversion of the *N*-methylphthalimide. Products separation in each case was performed

Table 1. Photoreactions of *N*-methylphthalimide **1** and silyl enol ethers **5a-c**^a

Entry	Reactant	Solvent	Reaction time (h)	Conversion (%)	Products (% yield) ^b
1	1+5a	CH ₃ OH	12	50	8 (21), 9 (17)
2	1+5a	CH ₃ CN	12	60	6a (13), 7a (3), 8 (12), 9 (16)
3	1+5a	Acetone	12	66	6a (17), 7a (3), 8 (7), 9 (9)
4	1+5a	Benzene	12	10	6a (12), 7a (19), 8 (16)
5	1+5b	CH ₃ OH	12	50	8 (27), 9 (27)
6	1+5b	CH ₃ CN	12	35	6b (16), 7b (2), 8 (13), 9 (16)
7	1+5b	CH ₃ CN-15% <i>H</i> ₂ O	12	20	6b (7), 8 (38), 9 (40)
8	1+5b	Acetone	12	40	6b (18), 7b (2), 8 (10), 9 (8)
9	1+5b	Benzene	12	12	6b (11), 7b (16), 8 (13)
10	1+5c	Acetone	6	54	13 (16), 7c (9), 14 (17), 15 (29)
11	1+5d	CH ₃ CN	11	67	16 (9), 17 (32), 18 (7), 19 (18), 7d (14)

^aConcentrations of reactants, [phthalimide]:[silyl enol ether] are 31/310 (mM). ^bYields are based on consumed phthalimide.

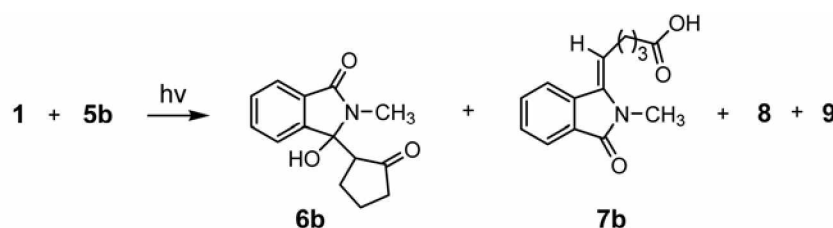
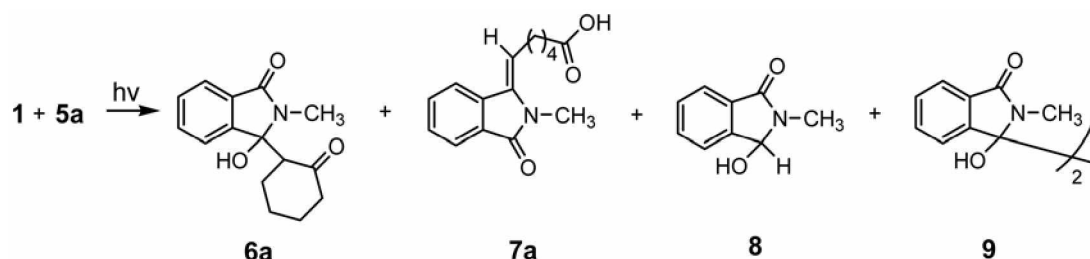
by silica gel chromatography. Irradiation times, solvents, products and yields for these processes are recorded in Table 1.

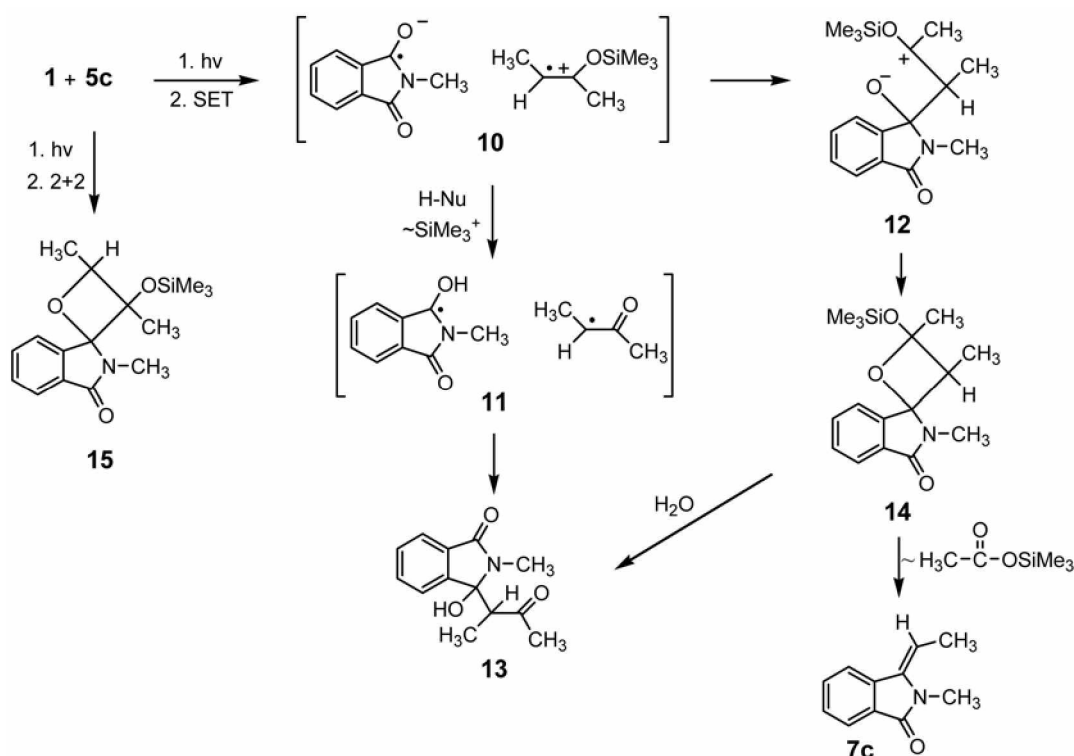
Irradiation of *N*-methylphthalimide (**1**) and 1-(trimethylsilyloxy)cyclohexene (**5a**) in CH₃CN or acetone leads to production of a complex mixture of products including the photoaddition product **6a**, **7a** by opening of **6a**, reduced phthalimide **8** and dimer **9** (Scheme 2). On the other hands, irradiation of *N*-methylphthalimide (**1**) and silyl enol ether (**5a**) in methanol leads to the production of photoreduction products **8** and **9** exclusively. Structural assignments to the photoproducts were made on the basis of spectroscopic data. The photoaddition product **6a** is formed by sequential SET-desilylation pathways and exists as diastereomers in ca. 1 to 1.4 ratios according to ¹H-NMR and ¹³C-NMR spectra data. IR spectra of photoaddition products **6a** and **7a** show characteristic absorption bands for hydroxyl group at 3000-3600 cm⁻¹ and carbonyl group at 1650-1710 cm⁻¹. The ¹³C-NMR spectra of **6a** and **7a** contain resonances which correspond to C-3 quaternary carbon at 91.5-91.6 ppm and olefinic carbons at 108.6 and 135.7 ppm. Their ¹H-NMR spectra also

show singlet peaks at 2.55-3.52 ppm for methyl groups. In order to obtain further information about the reactive excited states of **1** and **5a**, oxygen quenching experiment was investigated. The oxygen results in complete quenching of all photoproducts in the photoreaction of **1** and **5a** in CH₃CN. This result shows that photochemical reaction appears to occur by SET of triplet excited state.

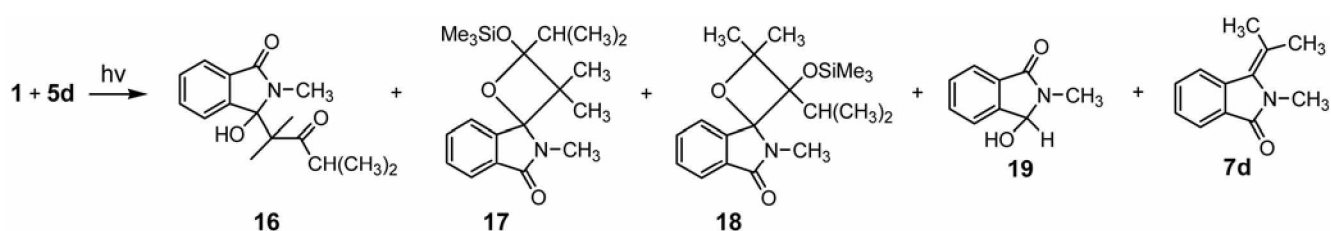
As shown in Table 1, photochemical reaction of *N*-methylphthalimide (**1**) and 1-(trimethylsilyloxy)cyclopentene (**5b**) is similar to that of silyl enol ether **5a** (Scheme 3). When **1** and **5b** were irradiated in mixing solvent (CH₃CN-15%*H*₂O), the yields of photoreduction products **8** and **9** were increased by ca. 3 times while photoaddition product **6b** was reduced by comparison with photolysis in CH₃CN. This indicates that photoreaction of **1** and **5b** in aqueous solvent system appears to occur electron-transfer-mediated process but it is difficult to form photoaddition product by sequential SET-desilylation pathways.

Irradiation of *N*-methylphthalimide (**1**) and 1-(trimethylsilyloxy)-2-butene (**5c**) in acetone was investigated. The result shows that **1** and **5c** participates in two competing





Scheme 4



Scheme 5

excited state reaction pathways involving SET-induced and classical oxetane formation. As shown in Scheme 4, the SET-process results in production of the ion radical pair 10 which can partition to the β -hydroxyketone 13 or oxetane 14 adducts by respective desilylation or zwitterion forming C-C bonding pathways. Owing to the lability of oxetane 14, it undergoes rapid hydrolytic conversion to the β -hydroxyketone 13. The ethylidenyl product 7c was observed by the bond cleavage of oxetane 14. In competition with these routes, direct cycloaddition of the silyl enol ether (5c) with the triplet phthalimide occurs to generate classical Paterno-Büchi products, oxetane 15 by 2+2 photocycloaddition.¹⁵

The photochemical reaction of *N*-methylphthalimide (1) and 2,4-dimethyl-3-(trimethylsilyloxy)-2-pentene (5d) in acetonitrile shows similar results that of 5c (Scheme 5). Irradiation of 1 and 5d in CH_3CN leads to production of reduced phthalimide 19, β -hydroxyketone 16, ethylidenyl product 7d and two oxetanes 17, 18. As depicted in Scheme 4 above, the SET-process results in production of hydroxyketone 16 and oxetane 17 adducts by respective desilylation

and zwitterion forming C-C bonding pathways. The oxetane 18 is classical Paterno-Büchi product, formed by 2+2 photocycloaddition. It is interesting that the oxetane product 17, which contains labile function, is observed to undergo rapid hydrolysis to form the Aldol type β -hydroxyketone 16.

In Scheme 5, the ratio of photoproducts by SET pathway is increased and 2+2 photocycloaddition product is decreased as compared with irradiation of 1 and 5c. The relative efficiencies of the SET and classical cycloaddition reactions should be governed by the nature of the silyl enol ether donor which, in turn, is a function of the degree of methyl substitution on the vinyl moiety. Thus, the predominant production of oxetane 17 (from SET route) *versus* oxetane 18 (from Paterno-Büchi route) clearly reflects the control offered by this property. The same trend was observed for the photoreaction of silyl ketene acetals as electron donors in the previous research.¹⁶

Finally, the photoaddition of *N*-methylphthalimide with silyl enol ether in most cases serve as procedure to prepare β -hydroxyketone products either by *in situ* or subsequent

acid-catalyzed hydrolysis of the initially formed oxetanes. The results of this study demonstrate that irradiations of *N*-methylphthalimide and silyl enol ethers serve as efficient procedures to prepare Aldol type β -hydroxyketone products by SET-desilylation pathways.

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