

**(Phenyl)[3-(Trimethylsilyl)-2-naphthyl]iodonium Triflate as a New Precursor of 2,3-Didehydronaphthalene**

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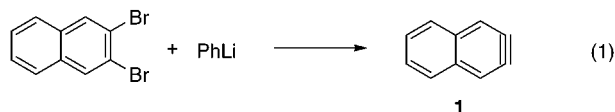
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**Introduction**

2,3-Didehydronaphthalene (**1**) is a useful intermediate available for construction of polycyclic aromatic hydrocarbons. There has been reported the generation of 2,3-didehydronaphthalene (**1**) in different reactions involving several precursors such as 3-amino-2-naphthoic acid,<sup>1</sup> 1-amino-1*H*-naphtho[2,3-*d*]triazole,<sup>2</sup> and mono- and dihalonaphthalenes.<sup>3</sup> The reported generation of **1** either involves a lengthy procedure for the precursor synthesis and/or gives the Diels–Alder adduct in poor yield.

LeHoullier and Gribble<sup>4</sup> reported a convenient generation of **1** using 2,3-dibromonaphthalene and phenyllithium (eq 1). This method is practically useful for the



generation of **1** and seems to have wide application to synthesis of polycyclic aromatic hydrocarbons. However, a strong base such as phenyllithium is essential for the generation of 2,3-didehydronaphthalene in this procedure.

On the other hand, hypervalent iodine compounds have been recognized as useful reagents in organic synthesis.<sup>5</sup> Recently, we have found that a hypervalent iodine compound, (phenyl)[*o*-(trimethylsilyl)phenyl]iodonium tri-

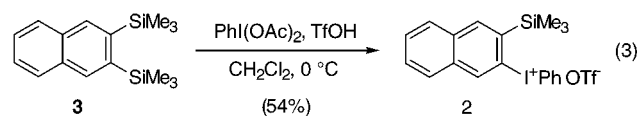
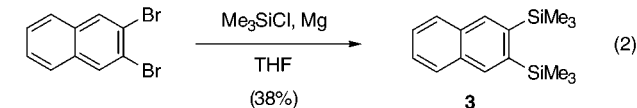
flate, is an excellent precursor of benzyne.<sup>6</sup> This benzyne precursor generates benzyne under very mild conditions (room temperature and neutral conditions). The generated benzyne can be efficiently trapped with furan to give 1,4-dihydro-1,4-epoxynaphthalene quantitatively (Scheme 1).

Hypervalent iodine precursors have been also applied to the generation of 2,3-didehydronaphthalene (**1**).<sup>7</sup> The reaction of a 2-naphthyl aryliodonium-3-carboxylate in the presence of tetraphenylcyclopentadienone gives the adduct, 1,2,3,4-tetraphenylanthracene, in 55% yield (Scheme 2).

However, the reaction using the 2-naphthyl aryliodonium-3-carboxylate requires temperatures of about 200 °C or higher and the yield of the adduct is not high. Thus, we examined the preparation and reaction of a highly efficient hypervalent iodine precursor of **1**. In this paper, we report the hypervalent iodine precursor (phenyl)[3-(trimethylsilyl)-2-naphthyl]iodonium triflate (**2**) as a new 2,3-didehydronaphthalene precursor.

**Results and Discussion**

The hypervalent iodine precursor (phenyl)[3-(trimethylsilyl)-2-naphthyl]iodonium triflate (**2**), was prepared in two steps from 2,3-dibromonaphthalene (eqs 1 and 2). 2,3-



Bis(trimethylsilyl)naphthalene was prepared by bis(trimethylsilyl)ation of 2,3-dibromonaphthalene with chlorotrimethylsilane and Mg in a procedure similar to that for preparing 1,2-bis(trimethylsilyl)benzene from 1,2-dibromobenzene.<sup>8</sup> Phenyliodination of 2,3-bis(trimethylsilyl)naphthalene (**3**) was conducted with a hypervalent iodine reagent system, PhI(OAc)<sub>2</sub>/TfOH.<sup>9</sup> Treatment of **3** with PhI(OAc)<sub>2</sub> activated with TfOH gave **2** as stable crystals.

The generation and reaction of 2,3-didehydronaphthalene (**1**) could be conducted by simply adding Bu<sub>4</sub>NF to the solution of the precursor **2** in the presence of trapping reagents (Scheme 3). Treatment of [3-(trimethylsilyl)-2-naphthyl]iodonium triflate (**2**) with Bu<sub>4</sub>NF in the presence of furan (5 equiv) gave 1,4-dihydro-1,4-epoxyanthracene (**4a**) in 82% yield. Similar reactions of **2** with Bu<sub>4</sub>NF in the presence of 2-acetylfuran or 2,5-dimethylfuran (5 equiv) gave the corresponding adducts, 1,4-dihydro-1,4-epoxyanthracenes (**4b,c**), respectively, in 89

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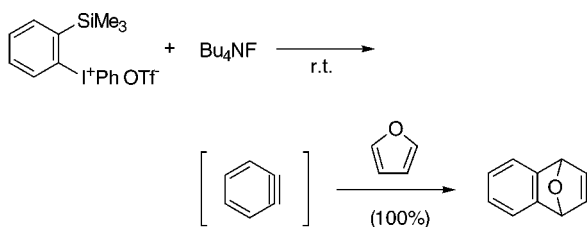
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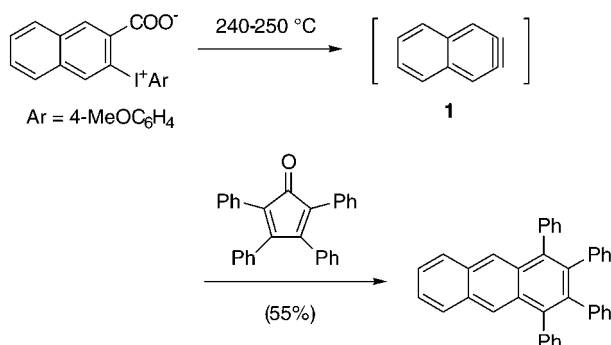
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## Scheme 1



## Scheme 2



and 92% yields. Tetraphenylcyclopentadienone is also a representative trapping agent of arynes.<sup>10</sup> Treatment of **2** with  $\text{Bu}_4\text{NF}$  in the presence of tetraphenylcyclopentadienone (2 equiv) afforded 1,2,3,4-tetraphenylanthracene (**5**) in 90% yield.

The hypervalent iodine precursor **2** has the following advantages in the generation and reactions of **1**. The trapping reactions of **1** with furan reported previously were conducted by use of a large excess of furan (about 77 times the molar quantity of furan<sup>4</sup> or as the solvent<sup>2</sup>). The present reaction using **2** does not require a large excess of furan. The trapping reactions with tetraphenylcyclopentadienone using 2-naphthyl arylidonium-3-carboxylate<sup>7</sup> and 1-aminonaphtho[2,3-*d*]triazole<sup>2</sup> gave 1,2,3,4-tetraphenylanthracene in 55% yield, respectively. The present reaction gives a higher yield than the previously reported ones.

The above experiments illustrate that **1** is generated efficiently from **2** under very mild conditions and can be trapped with cyclic dienes to give the corresponding adducts. Since the yields of the adducts are always high, **2** can be used synthetically as an excellent precursor of **1**.

Furthermore, we examined the 1,3-dipolar cycloaddition of **1** from **2** (Scheme 3). A similar treatment of **2** with  $\text{Bu}_4\text{NF}$  in the presence of *p*-tolyl azide or *p*-methoxyphenyl azide (5 equiv) gave the corresponding 1-arylnaphtho[2,3-*e*]triazoles (**6a,b**) in 62 and 72% yields, respectively. This result indicates that **2** is also suitable for the 1,3-dipolar cycloaddition using **1**.

In summary, we have demonstrated that (phenyl)[3-(trimethylsilyl)-2-naphthyl]iodonium triflate (**2**) is readily prepared by the reaction of 2,3-bis(trimethylsilyl)naphthalene with a  $\text{PhI}(\text{OAc})_2/\text{TfOH}$  reagent system and acts as a highly efficient 2,3-didehydronaphthalene precursor.

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Compared with previous precursors,<sup>1–4,7</sup> the present hypervalent iodine reagent **2** provides the best results, in addition to the use of mild and neutral conditions.

## Experimental Section

**General Methods.** Melting points are uncorrected. <sup>1</sup>H NMR spectra were obtained at 250 or 300 MHz. <sup>13</sup>C NMR spectra were recorded at 63 or 75 MHz. Elemental analyses were performed by the Service Center of the Elementary Analysis of Organic Compounds, Faculty of Science, Kyushu University. 2,3-Dibromonaphthalene was prepared by the reported procedures.<sup>4,11</sup>

**2,3-Bis(trimethylsilyl)naphthalene.** To a mixture of Mg (90 mmol), chlorotrimethylsilane (80 mmol), and THF (10 mL) was added a solution of 2,3-dibromonaphthalene (20 mmol) in THF (50 mL), and the mixture was heated at 80 °C for 24 h. After removal of THF in vacuo at room temperature, hexane was added to the residue and the whole contents were poured onto ice and water. The precipitates and unreacted Mg were filtered off, and the product was extracted with hexane. The hexane extract was washed with water and brine and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After evaporation of the solvent, the residue was separated by a bulb–bulb distillation. After removing volatile materials at 100 °C (oven temperature)/0.5 mmHg, the product was collected at 150 °C (0.5 mmHg) to give 2.08 g (38% yield) of 2,3-bis(trimethylsilyl)naphthalene: <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  0.44 (s, 18 H), 7.46–7.49 (m, 2 H), 7.77–7.80 (m, 2 H), 8.14 (s, 2 H); <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  2.0, 126.5, 127.7, 132.3, 135.6, 142.0. Anal. Calcd for  $\text{C}_{16}\text{H}_{24}\text{Si}_2$ : C, 70.51; H, 8.88. Found: C, 70.30; H, 8.71.

**(Phenyl)[3-(trimethylsilyl)-2-naphthyl]iodonium Triflate (**2**).** To a suspension of  $\text{PhI}(\text{OAc})_2$  (0.5 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL) was added TfOH (1 mmol) dropwise at 0 °C, and the mixture was stirred for 30 min at that temperature. 2,3-Bis(trimethylsilyl)naphthalene (0.5 mmol) was added at 0 °C, and the reaction mixture was stirred for 30 min. After evaporation of the solvent, the residue was crystallized by adding ether. The crystals were collected, washed with ether, and dried in vacuo to give **2** (149 mg, 54%): mp 182–184 °C ( $\text{CH}_2\text{Cl}_2$ –ether); <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  0.46 (s, 9 H), 7.44–7.93 (m, 9 H), 8.16 (s, 1 H), 8.69 (s, 1 H). <sup>13</sup>C NMR ( $\text{CDCl}_3 + \text{DMSO}-d_6$ )  $\delta$  -0.2, 114.1, 117.9, 127.4, 127.8, 128.2, 129.1, 131.0, 131.3, 132.1, 133.0, 134.3, 138.9, 139.6, 140.0. Anal. Calcd for  $\text{C}_{20}\text{H}_{20}\text{F}_3\text{IO}_3\text{SSi}$ : C, 43.48; H, 3.65. Found: C, 43.32; H, 3.74.

The similar reaction using  $\text{PhI}(\text{OAc})_2$  (4.0 mmol), TfOH (8.0 mmol),  $\text{CH}_2\text{Cl}_2$  (10 mL), and 2,3-bis(trimethylsilyl)naphthalene (4.0 mmol) gave 1.03 g (47%) of **2**.

**Reaction of [3-(Trimethylsilyl)-2-naphthyl]iodonium Triflate **2** with  $\text{Bu}_4\text{NF}$  in the Presence of Furans.** To a solution of **2** (0.2 mmol) and a furan (1.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL) was added a THF solution of  $\text{Bu}_4\text{NF}$  (1 M, 0.25 mL) at 0 °C, and the mixture was stirred for 30 min. Water was added to the mixture, and the product was extracted with  $\text{CH}_2\text{Cl}_2$ . After evaporation of the solvent, the product was purified by column chromatography on silica gel (hexane/ $\text{CH}_2\text{Cl}_2$ ) to yield crystals of the adduct, 1,4-dihydro-1,4-epoxyanthracenes (**4**).

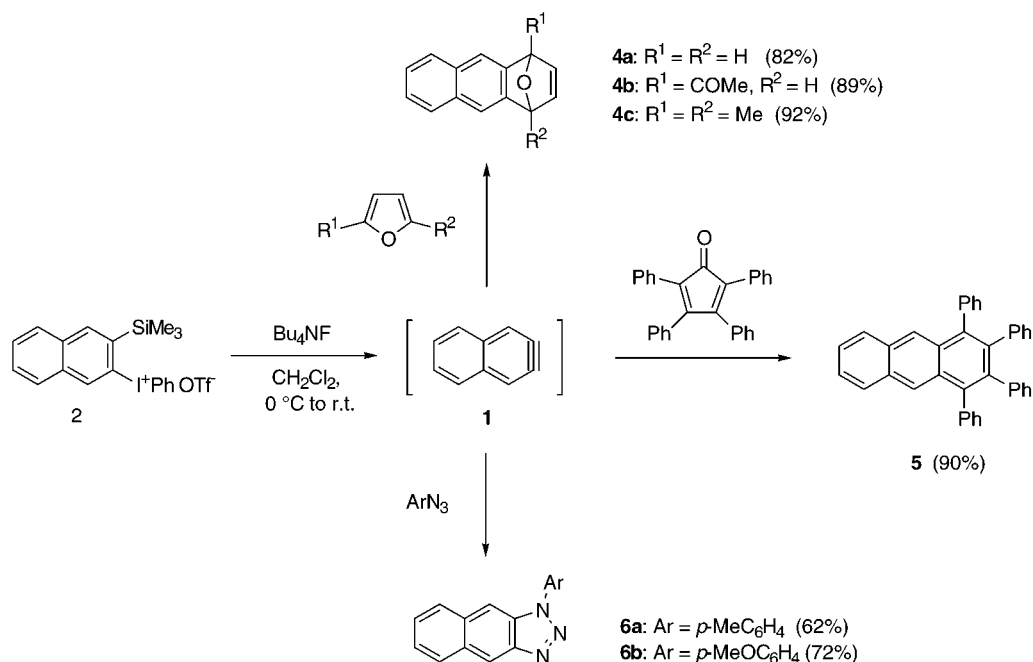
**1,4-Dihydro-1,4-epoxyanthracene (4a):** 31.9 mg (82%); mp 163–164 °C (hexane) (lit.<sup>2</sup> mp 164–165 °C); <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  5.80 (s, 2 H), 6.96 (s, 2 H), 7.41–7.44 (m, 2 H), 7.58 (s, 2 H), 7.69–7.72 (m, 2 H); <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  81.8, 118.6, 126.1, 128.1, 131.9, 141.7, 144.1.

**1-Acetyl-1,4-dihydro-1,4-epoxyanthracene (4b):** 42.1 mg (89%); mp 140–143 °C (hexane); <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  2.44 (s, 3 H), 5.88 (s, 1 H), 6.96–7.02 (m, 2 H), 7.43–7.70 (m, 6 H); <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  26.9, 81.8, 95.1, 118.2, 119.1, 126.47, 126.55, 128.0, 128.4, 131.6, 131.7, 141.0, 142.0, 142.5, 143.0, 205.0. Anal. Calcd for  $\text{C}_{16}\text{H}_{12}\text{O}_2$ : C, 81.31; H, 5.12. Found: C, 81.13; H, 5.24.

**1,4-Dimethyl-1,4-dihydro-1,4-epoxyanthracene (4c):** 40.9 mg (92%); mp 104–106 °C (hexane); <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  1.97 (s, 6 H), 6.72 (s, 2 H), 7.40–7.44 (m, 4 H), 7.70–7.73 (m, 2 H); <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  15.3, 88.0, 116.7, 126.0, 128.0, 131.7, 145.4.

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Scheme 3



148.6. Anal. Calcd for  $C_{16}H_{14}O$ : C, 86.45; H, 6.35. Found: C, 86.34; H, 6.53.

The similar trapping reaction with 2,5-dimethylfuran on a larger scale (0.5 mmol of **2**) gave **4c** in 93% yield (103 mg).

**Reaction of [3-(Trimethylsilyl)-2-naphthyl]iodonium Triflate (2) with  $Bu_4NF$  in the Presence of Tetraphenylcyclopentadienone.** To a solution of **2** (0.2 mmol) and an aryl azide (0.4 mmol) in  $CH_2Cl_2$  (3 mL) was added a THF solution of  $Bu_4NF$  (1 M, 0.25 mL) at 0 °C. After the mixture was stirred for 30 min at 0 °C, water was added and the product was extracted with  $CH_2Cl_2$ . After evaporation of the solvent, the product was separated by column chromatography on silica gel (hexane/ $CH_2Cl_2$ ) to give 1,2,3,4-tetraphenylanthracene (**5**) in 90% yield (86.9 mg): mp 290–293 °C (EtOH–toluene) (lit.<sup>2,7</sup> mp 293–294 °C);  $^1H$  NMR ( $CDCl_3$ )  $\delta$  6.8 (s, 10 H), 7.30–7.39 (m, 12 H), 7.80–7.83 (m, 2 H), 8.19 (s, 2 H).

**Reaction of 2 with  $Bu_4NF$  in the Presence of Aryl Azides.** To a solution of **2** (0.2 mmol) and an aryl azide (1.0 mmol) in  $CH_2Cl_2$  (2 mL) was added a THF solution of  $Bu_4NF$  (1 M, 0.25 mL) at 0 °C. After the mixture was stirred for 30 min at 0 °C, water was added and the product was extracted with  $CH_2Cl_2$ . After evaporation of the solvent, the product was separated by column chromatography on silica gel (hexane/ $CH_2Cl_2$ ) to give crystals of the adduct, naphthotriazole **6**.

**1-(4-Methylphenyl)naphtho[2,3-*d*][1,2,3]triazole (6a):** 32.2 mg (62%); mp 155–157 °C (hexane);  $^1H$  NMR ( $CDCl_3$ )  $\delta$  2.51 (s, 3 H), 7.44–8.11 (m, 8 H), 8.18 (s, 1 H), 8.70 (s, 1 H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  21.2, 106.2, 118.3, 122.6, 124.9, 126.8, 128.1, 129.4, 130.4, 130.7, 130.9, 133.4, 134.9, 138.4, 145.7. Anal. Calcd for  $C_{17}H_{13}N_3$ : C, 78.74; H, 5.05; N, 16.20. Found: C, 78.54; H, 5.08; N, 16.12.

**1-(4-Methoxyphenyl)naphtho[2,3-*d*][1,2,3]triazole (6b):** 39.6 mg (72%); mp 173–175 °C (hexane);  $^1H$  NMR ( $CDCl_3$ )  $\delta$  3.83 (s, 3 H), 7.07 (d,  $J = 9$  Hz, 2 H), 7.35–7.43 (m, 2 H), 7.68 (d,  $J = 9$  Hz, 2 H), 7.84–8.03 (m, 3 H), 8.60 (s, 1 H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  55.7, 106.0, 115.0, 118.2, 124.4, 124.9, 126.8, 128.0, 129.4, 130.4, 130.7, 131.2, 133.3, 145.5, 159.6. Anal. Calcd for  $C_{17}H_{13}N_3O$ : C, 74.17; H, 4.76; N, 15.26. Found: C, 74.07; H, 4.83; N, 15.21.

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