Synthesis and Reactions of a Hypervalent Iodine-Benzyne Precursor Possessing an Ester Group

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Abstract: The Diels-Alder reaction of methyl 2-pyrone-5-carboxylate and bis(trimethylsilyl)acetylene gave methyl 3,4-bis(trimethylsilyl)-benzoate which was transformed into [5-(methoxycarbonyl)-2-(trimethylsilyl)phenyl](phenyl)iodonium triflate by the reaction with a hypervalent iodine reagent $PhI(OAc)_2/TfOH$. The generation and trapping reactions of 4-(methoxycarbonyl)-1,2-didehydrobenzene were successfully conducted by the reaction of the iodonium triflate with Bu_4NF.

Key words: hypervalent iodine compound, benzyne, Diels-Alder reaction, methyl 2-pyrone-5-carboxylate, bis(trimethylsilyl)acetylene

Hypervalent iodine compounds are very useful reagents in organic synthesis since their reactions occur efficiently under mild conditions.[1] Recently we have found that phenyl[2-(trimethylsilyl)phenyl]iodonium triflate reacts with Bu_4NF to generate benzyne under very mild conditions.[2] The benzyne generated by this method is efficiently trapped with dienes in high yield. Synthesis of the benzyne precursor is readily performed by using 1,2-bis(trimethylsilyl)benzene and a hypervalent iodine reagent $PhI(OAc)_2/TfOH$. However, the preparation of 1,2-bis(trimethylsilyl)benzene[3] requires a high temperature and a long reaction time, in addition to the use of HMPA that is a toxic solvent. Furthermore, the procedure suffers the disadvantage that this method cannot be applied to the substrate having functional groups that are sensitive to bases or reagents. To remove the disadvantage, we have studied the new procedure for the synthesis of hypervalent iodine-benzyne precursor possessing an ester group.

The previous method[3] using haloarenes and Me_3SiCl/Mg reagent system is not applicable to the substrate having methoxycarbonyl group since the methoxycarbonyl group reacts with the Grignard reagent. We have adopted the Diels-Alder cycloaddition of 2-pyrone and bis(trimethylsilyl)acetylene.[4] This method involves the reaction conditions at 150 °C for 4.5 days in bromobenzene. In the reaction conditions described in the literature (Table 1, entries 1 and 2), however, satisfactory results were not obtained. Then, the mixture of methyl 2-pyrone-5-carboxylate (**1**) and bis(trimethylsilyl)acetylene (**2**) were placed in a sealed stainless steel tube and heated. Heating at 200 °C for more than 12 hr gave methyl 3,4-bis(trimethylsilyl)benzoate (**3**) in almost quantitative yield (Table 1, entries 5 and 6). In addition, **3** was obtained in 80% yield on a larger scale: **1** (8 mmol) and **2** (16 mmol) at 200 °C for 48 h.

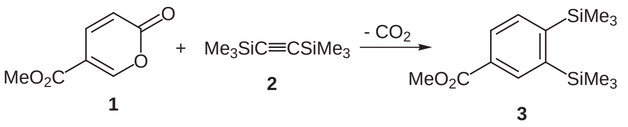
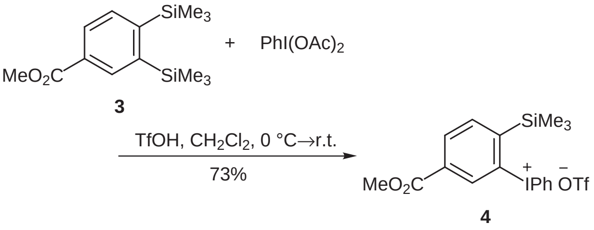


Table 1 Synthesis of Methyl 3,4-Bis(trimethylsilyl)benzoate **3**

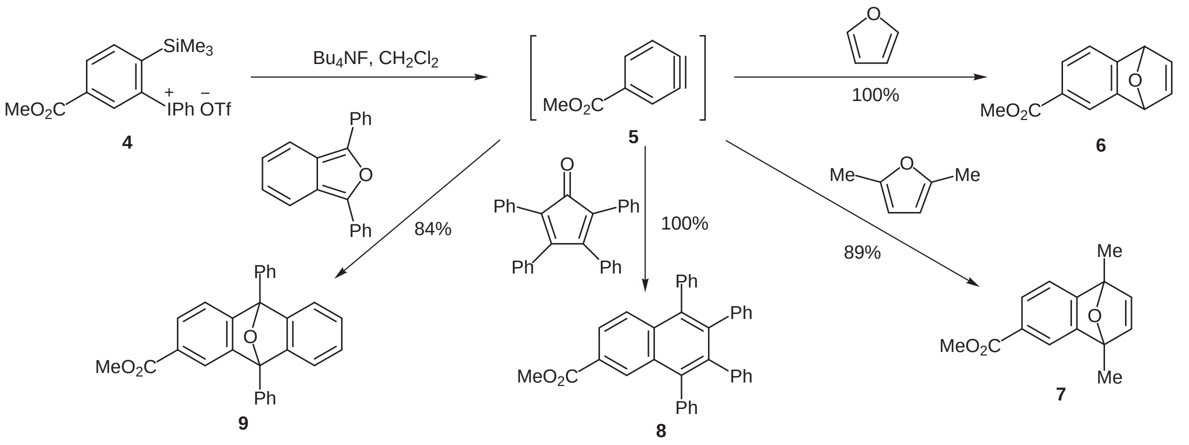
Entry	Conditions[a]	Time (h)	Yield of **3** (%)
1	PhCl, reflux	24	27
2	PhBr, reflux	44	36
3	In a sealed tube, 170 °C	12	19
4	In a sealed tube, 200 °C	9	53
5	In a sealed tube, 200 °C	12	93
6	In a sealed tube, 200 °C	24	98

[a] **1** (1 mmol) and **2** (2 mmol). In entries 1 and 2, a halobenzene (10 ml) was used.

When methyl 3,4-bis(trimethylsilyl)benzoate **3** was reacted with a hypervalent iodine reagent $PhI(OAc)_2/TfOH$[5] in CH_2Cl_2, [5-(methoxycarbonyl)-2-(trimethylsilyl)phenyl](phenyl)iodonium triflate (**4**) was obtained in 73% yield.[6] The iodonium triflate **4** is a stable crystalline compound and melts at 143-144 °C. The phenyliodination of **3** occurs selectively at the meta position to the ester group. No other products were detected.



The generation and reaction of 4-(methoxycarbonyl)-1,2-didehydrobenzene (**5**) could be conducted by simply adding Bu_4NF to the solution of the [5-(methoxycarbonyl)-2-(trimethylsilyl)phenyl]iodonium triflate **4** in the presence of trapping agents (Scheme).[7] Treatment of [5-(methoxycarbonyl)-2-(trimethylsilyl)phenyl]iodonium triflate **4** with Bu_4NF in the presence of furan and 2,5-dimethyl-



Scheme

furan gave the corresponding adducts, methyl 1,4-dihydro-1,4-epoxy-6-naphthalenecarboxylate (**6**) and methyl 1,4-dihydro-1,4-epoxy-1,4-dimethyl-6-naphthalenecarboxylate (**7**), respectively, in 100 and 89% yields. Similar reaction of iodonium triflate **4** with Bu_4NF in the presence of tetraphenylcyclopentadienone afforded methyl 1,2,3,4-tetraphenyl-6-naphthalenecarboxylate (**8**) in 100% yield. Trapping reaction of the benzyne **5** with 1,3-diphenylisobenzofuran was also successfully carried out to give methyl 9,10-diphenyl-9,10-epoxy-2-anthracenecarboxylate (**9**) in 84% yield.

The hypervalent iodine precursor, [5-(methoxycarbonyl)-2-(trimethylsilyl)phenyl]iodonium triflate **4**, efficiently generates 4-(methoxycarbonyl)-1,2-didehydrobenzene **5** in situ with action of Bu_4NF. The ester group is not damaged by this treatment at all. The 4-(methoxycarbonyl)-1,2-didehydrobenzene **5** can be trapped effectively to give the adducts in high yields. The present result indicates that this alternate synthesis of [5-(methoxycarbonyl)-2-(trimethylsilyl)phenyl]iodonium triflate **4** is very excellent and convenient for the procedure of hypervalent iodine-benzyne precursors because of the high yields of the adducts and no damage of the sensitive ester group.

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(6) A typical procedure is as follows. To a suspension of $PhI(OAc)_2$ (1 mmol) in CH_2Cl_2 (5 ml) was added TfOH (2 mmol) dropwise at 0 °C, and the mixture was stirred for 30 min at room temperature. Methyl 3,4-bis(trimethylsilyl)-benzoate **3** (1 mmol) was added at 0 °C, and the mixture was stirred for 24 h at room temperature. 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 [5-(methoxycarbonyl)-2-(trimethylsilyl)phenyl]-(phenyl)iodonium triflate **4** (409 mg, 73%): mp 143-144 °C; ^1H NMR ($CDCl_3$) δ 0.46 (s, Me, 9 H), 3.96 (s, OMe, 3 H), 7.44-7.50 (m, ArH, 2 H), 7.56-7.59 (m, 2 H, ArH), 7.79-7.82 (m, ArH, 3 H), 8.25-8.28 (m, ArH, 2 H), 8.65 (s, ArH, 1 H); ^{13}C NMR ($CDCl_3$) δ -0.06, 52.786, 113.955, 121.513, 131.996, 132.235, 132.326, 133.183, 134.155, 138.219, 139.389, 152.617, 164.295.

(7) The representative trapping experiment is as follows. To a solution of **4** (0.2 mmol) and furan (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, and the mixture was stirred for 30 min. Water was added to the mixture, and the product was extracted with CH_2Cl_2. After evaporation of the solvent, the product was purified by column chromatography on silica gel (hexane/CH_2Cl_2) to yield crystals of the adduct **6** (100%): mp 97-98 °C; ^1H NMR ($CDCl_3$) δ 3.79 (s, OMe, 3 H), 5.66 (bs, CH, 2 H), 6.90-6.95 (m, 2 H, = CH), 7.20 (d, J = 7.4 Hz, ArH, 1 H), 7.67 (d, J = 7.4 Hz, ArH, 1 H), 7.78 (s, ArH, 1 H); ^{13}C NMR ($CDCl_3$) δ 51.95, 81.98, 82.00, 119.79, 120.54, 127.08, 127.94, 142.26, 143.22, 149.44, 154.33, 166.77.

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