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Synthesis of a new hypervalent iodine compound, [2-(hydroxydimethylsilyl)phenyl](phenyl)iodonium triflate as a convenient approach to benzyne

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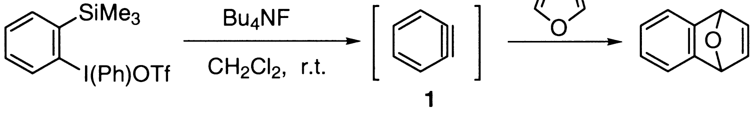
Abstract

A new benzyne precursor, [2-(hydroxydimethylsilyl)phenyl](phenyl)iodonium triflate, is prepared from 1,2-dibromobenzene in good yield. This procedure avoids the use of carcinogenic HMPA and the severe reaction conditions. The reaction of the benzyne precursor with Bu_4NF in the presence of a trapping agent under very mild conditions efficiently generates benzyne and gives the benzyne adduct in high yield. © 2000 Elsevier Science Ltd. All rights reserved.

Benzyne (**1**) is an important reactive intermediate which has been widely used in organic syntheses, mechanistic studies, and the synthesis of functional materials.[1] Although many benzyne precursors have been reported so far, there are only a few examples[2,3] of stable precursors that can be used under very mild reaction conditions that meet the requirements of ambient temperature and neutral conditions.

Very recently we have reported a trimethylsilyl-substituted phenyliodonium salt as a stable benzyne precursor that generates benzyne quantitatively in the reaction with Bu_4NF under mild conditions (room temperature and neutral condition), as shown in Scheme 1.[3] This benzyne precursor is very convenient because it is a stable crystalline compound and easy to handle.



Scheme 1.

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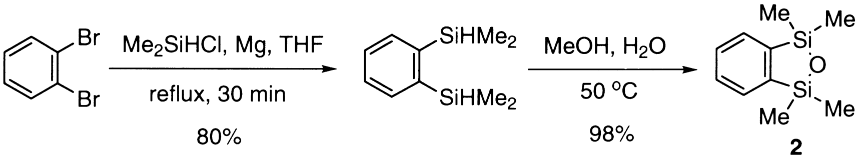
The synthesis of the benzyne precursor consists of two reaction steps: (1) 1,2-bis-trimethylsilylation of 1,2-dichlorobenzene with chlorotrimethylsilane and Mg by use of HMPA as the solvent; and (2) phenyliodination of the prepared 1,2-bis(trimethylsilyl)benzene with a $PhI(OAc)_2/TfOH$ reagent system.

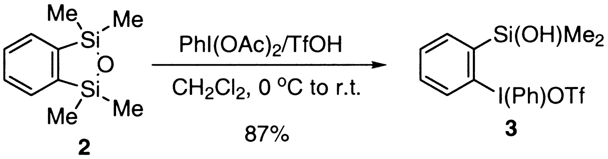
However, the synthesis of 1,2-bis(trimethylsilyl)benzene suffers the following disadvantages: (1) the use of carcinogenic HMPA as the solvent is necessary; and (2) the reaction requires severe conditions (high temperature and long reaction time). We have developed a new stable hypervalent iodine–benzyne precursor that can be prepared without the use of a high temperature and HMPA solvent.[4]

The new approach was undertaken with the bisdimethylsilylation of 1,2-dibromobenzene to avoid the use of HMPA. 1,2-Bis(dimethylsilyl)benzene was prepared by the reaction of 1,2-dibromobenzene with chlorodimethylsilane and Mg in THF according to the literature (Scheme 2).[5] The hydrolysis of 1,2-bis(dimethylsilyl)benzene with MeOH and H_2O in the presence of NaOMe gave 1,3-dihydro-1,1,3,3-tetramethyl-2,1,3-benzoxadisilole (**2**)[5] in a high yield.



Scheme 2.

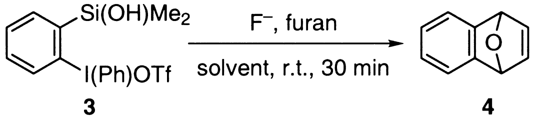
Phenyliodination of benzoxadisilole **2** was conducted with a hypervalent iodine reagent system, $PhI(OAc)_2/TfOH$.[6] Treatment of benzoxadisilole **2** with $PhI(OAc)_2/TfOH$ gave [2-(hydroxydimethylsilyl)phenyl](phenyl)iodonium triflate (**3**)[7] as crystals in 87% yield (Eq. (1)). This 2-(hydroxydimethylsilyl)phenyliodonium triflate **3** was quite stable at room temperature up to melting point, not sensitive to air and moisture, and not hygroscopic.



(1)

The generation and trapping reaction of benzyne **1** could be conducted by simply mixing the precursor **3** with a fluoride source in the presence of trapping agents (Eq. (2)). The trapping reaction of benzyne **1** with furan was carried out under various conditions. The benzyne adduct, 1,4-dihydro-1,4-epoxynaphthalene (**4**),[8] was obtained in good to high yields. The results are given in Table 1.

Table 1 shows that 2-(hydroxydimethylsilyl)phenyliodonium triflate **3** behaves well as the benzyne precursor. The best result (98% yield of benzyne adduct **4**) was obtained when the reaction was carried out by the use of Bu_4NF as the fluoride source, CH_2Cl_2 as the solvent, and 5 equiv. of furan. This result is the same as the previous one by the trimethylsilyl-substituted phenyliodonium salt.[3] Cesium fluoride also acts as a good desilylating agent and gives the benzyne adduct **4** in 85% yield.



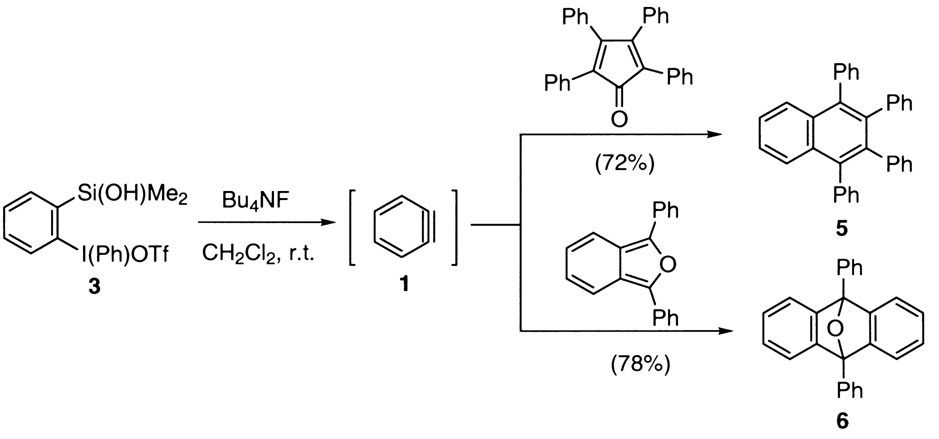
(2)

Table 1
Generation of benzyne **1** and trapping with furan[a]

Entry	Fluoride source (mmol)	Furan (mmol)	Solvent	Yield of **4** (%)[b]
1	Bu_4NF (1.2)	5	CH_2Cl_2	98
2	Bu_4NF (1.2)	2	CH_2Cl_2	90
3	Bu_4NF (1.2)	5	MeCN	62
4	CsF (2.0)	5	MeCN	85
5	KF (2.0)[c]	5	CH_2Cl_2[d]	64

[a] Reaction was conducted by using **1** (1.0 mmol) and a fluoride in a solvent (5 mL) in the presence of furan at r.t. for 30 min.
[b] Isolated yield by column chromatography.
[c] 18-Crown-6 (2.0 mmol) was also added.
[d] 10 mL was used.

Similar reactions of 2-(hydroxydimethylsilyl)phenyliodonium triflate **3** with Bu_4NF in the presence of other trapping agents were conducted (Scheme 3). In the presence of tetraphenylcyclopentadienone, the benzyne adduct, 1,2,3,4-tetraphenylnaphthalene (**5**),[9] was obtained in 72% yield when the benzyne precursor **3** was reacted with Bu_4NF in CH_2Cl_2. The benzyne **1** generated similarly from the precursor **3** was trapped with 1,3-diphenylisobenzofuran to give 9,10-dihydro-9,10-*o*-benzenoanthracene (**6**)[10] in 78% yield.



Scheme 3.

The above experiments illustrate that 2-(hydroxydimethylsilyl)phenyliodonium triflate **3** generates benzyne **1** with a high efficiency under mild conditions. In addition, the present benzyne precursor **3** has a preferable procedure of the synthesis compared with the previously reported 2-(trimethylsilyl)phenyliodonium triflate.[3]

In conclusion, we have developed a new approach to an excellent benzyne precursor. A new benzyne precursor, 2-(hydroxydimethylsilyl)phenyliodonium triflate **3**, is readily prepared via the bisdimethylsilylation of 1,2-dibromobenzene followed by the hydrolysis to benzoxadisilole **2** and the phenyliodination. This procedure avoids the use of carcinogenic HMPA and the severe reaction conditions required in the synthesis of [2-(trimethylsilyl)phenyl](phenyl)iodonium triflate. The new benzyne precursor **3** gives benzyne adducts in high yields in the reaction with Bu_4NF in the presence of trapping agents under very mild conditions.

Acknowledgements

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4. A referee suggested the preparation of 1,2-bis(trimethylsilyl)benzene from 1,2-dibromobenzene in THF. However, this method did not give the desirable yield of 1,2-bis(trimethylsilyl)benzene but resulted in the formation of many by-products that caused the difficulty in the purification. The reaction of 1,2-dibromobenzene, chlorodimethylsilane, and Mg in THF gave a high yield of 1,2-bis(dimethylsilyl)benzene. Although [2-(dimethylsilyl)phenyl](phenyl)iodonium triflate could be prepared from 1,2-bis(dimethylsilyl)benzene and $PhI(OAc)_2/TfOH$ reagent, the 2-(dimethylsilyl)phenyliodonium salt was found to be lacking in sufficient stability.
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7. For **3**: mp 119–122°C ($CHCl_3$–ether); ^1H NMR ($CDCl_3$) δ 0.59 (s, 6H), 2.02 (s, 1H), 7.38–7.69 (m, 6H), 7.83 (d, $J=7.8$ Hz, 2H), 7.94 (d, $J=7.8$ Hz, 1H); ^{13}C NMR (CD_3OD) δ 2.32, 114.91, 121.67 (q, $J=319$ Hz), 122.02, 133.20, 133.32, 133.49, 135.00, 135.18, 139.44, 139.80, 145.09; IR (KBr) 3520 cm^{-1} (OH). Anal. calcd for $C_{15}H_{16}F_3IO_3SSi$: C, 35.73; H, 3.20. Found: C, 35.97; H, 3.11.
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