



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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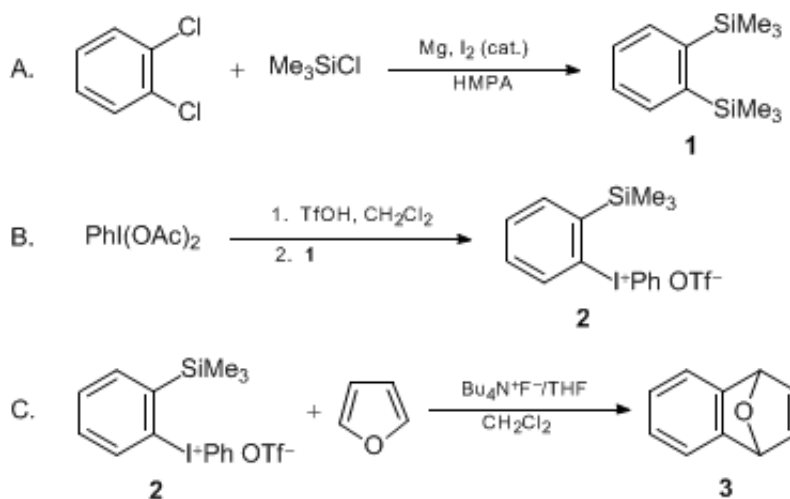
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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

**(PHENYL)[2-(TRIMETHYLSILYL)PHENYL]IODONIUM TRIFLATE.
AN EFFICIENT AND MILD BENZYNE PRECURSOR**

[Iodonium, phenyl-, 2-(trimethylsilyl)phenyl-, salt with trifluoromethane-sulfonic acid]



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Discussion Addendum *Org. Synth.* **2012**, *89*, 98

1. Procedure

A. *1,2-Bis(trimethylsilyl)benzene* (**1**). A dry, 500-mL, three-necked, round-bottomed flask is equipped with a large Teflon-covered magnetic stir bar, 100-mL pressure-equalizing addition funnel, Dimroth condenser (Note 1) fitted with a drying tube, and a glass stopper. The flask is charged with 9.72 g (0.400 mol) of magnesium turnings (Note 2), 70 mL of hexamethylphosphoramide (HMPA) (Note 3), 11.25 mL (0.100 mol) of 1,2-dichlorobenzene (Note 4), and 0.254 g (1.00 mmol) of iodine (I_2) (Note 5). The addition funnel is charged with 51.0 mL (0.400 mol) of freshly distilled chlorotrimethylsilane (Note 6). The flask is immersed in an oil bath at 70°C , stirring is initiated, and chlorotrimethylsilane is added slowly, dropwise with vigorous stirring. After completion of the addition, the oil bath is heated to 100°C and the reaction mixture is stirred at this temperature for 2 days. During this time, the reaction mixture becomes viscous and finally separates into two phases. The reaction mixture is cooled to ca. 40°C (Note 7) and poured into a 1-L beaker containing saturated sodium bicarbonate (NaHCO_3) solution (200 mL), diethyl ether (100 mL), and ice (ca. 100 g). Solids and unreacted magnesium metal are separated by suction filtration, the filtrate is transferred to a separatory funnel, and the aqueous phase is extracted with three 150-mL portions of ether. The combined ethereal extracts are washed with water (500 mL) and saturated sodium chloride (500 mL), dried over anhydrous sodium sulfate, and filtered. The solvent is evaporated under reduced pressure and the residue is distilled from a 100-mL, round-bottomed flask with a magnetic stir bar through a 20-cm Vigreux column at reduced pressure. The fraction boiling at $128\text{--}133^\circ\text{C}$ (20 mm) is collected to afford 16.5–16.7 g (74–75%) of 1,2-bis(trimethylsilyl)benzene (**1**) (Note 8) as a colorless liquid.

B. *(Phenyl)[2-(trimethylsilyl)phenyl]iodonium triflate* (**2**). A 100-mL round-bottomed flask equipped with an argon inlet adapter and a magnetic stir bar is charged with 12.9 g (40.0 mmol) of finely ground diacetoxyiodobenzene (Note 9) and 70 mL of dichloromethane (Note 10). The suspension is cooled at 0°C with an ice bath and 6.9 mL (78 mmol) of trifluoromethanesulfonic acid (Note 11) is added in one portion by syringe. The resulting clear yellow solution is stirred at room temperature for 2 hr and a solution of 8.9 mL (40.0 mmol) of 1,2-bis(trimethylsilyl)benzene in 10 mL of dichloromethane is added dropwise by syringe. The resulting mixture is stirred at room temperature for 12 hr, and the solvent is

removed by rotary evaporation under reduced pressure to afford the product as colorless crystals. (When an oily residue is obtained, it can be crystallized by triturating with [diethyl ether](#).) The crystals are collected by filtration and washed with 40 mL of [diethyl ether](#) to afford 14.7-15.7 g (73-78%) of [\(phenyl\)\[2-\(trimethylsilyl\)phenyl\]iodonium triflate \(2\)](#) as colorless needles, mp 142-143°C (Notes [12](#), [13](#)).

C. Generation of benzyne and trapping with furan. A 50-mL round-bottomed flask fitted with a pressure-equalizing addition funnel equipped with an argon inlet adapter and a magnetic stir bar is charged with 1.51 g (3.00 mmol) of [\(phenyl\)\[2-\(trimethylsilyl\)phenyl\]iodonium triflate \(2\)](#), 10 mL of [dichloromethane](#), and 1.10 mL (15.1 mmol) of [furan](#) (Note [14](#)). The addition funnel is charged with 3.6 mL (3.6 mmol) of 1.0 M [tetrabutylammonium fluoride](#) ($\text{Bu}_4\text{N}^+\text{F}^-$) in [tetrahydrofuran](#) (THF) (Note [15](#)). The flask is placed in an ice bath and the [tetrabutylammonium fluoride](#) solution is added dropwise over ca. 5 min. The reaction mixture is stirred at room temperature for 30 min, and water (20 mL) is added. The aqueous phase is separated and extracted with three 10-mL portions of [dichloromethane](#). The combined organic extracts are washed with 15 mL of water, dried over anhydrous [sodium sulfate](#), and filtered. The solvent is evaporated by rotary evaporation under reduced pressure, and the residual oil is purified by column chromatography through 60 g of silica gel packed in a 4-cm diameter column (elution with [dichloromethane](#)) to give 0.415-0.418 g (96-97%) of [1,4-dihydronaphthalene 1,4-oxide \(3\)](#) as colorless crystals, mp 52-55°C (Notes [16](#), [17](#)).

2. Notes

1. A highly efficient reflux condenser is required to avoid the loss of [chlorotrimethylsilane](#) by evaporation during the reaction.
2. [Magnesium turnings](#) were purchased from Nacalai Tesque, Inc. or Fisher Scientific Company.
3. HMPA, [hexamethylphosphoramide](#), is toxic and a cancer-suspect agent. It was purchased from Tokyo Kasei Kogyo Co. or Aldrich Chemical Company, Inc. and distilled from [calcium hydride](#) under reduced pressure before use. When [dimethylpropyleneurea](#) (DMPU) was used in place of HMPA, none of the desired [bis\(trimethylsilyl\)benzene](#) was obtained.
4. [1,2-Dichlorobenzene](#) was purchased by the submitters from Tokyo Kasei Kogyo Co. and distilled under reduced pressure. The checkers used 99% anhydrous [1,2-dichlorobenzene](#) from Aldrich Chemical Company, Inc., without further purification.
5. [Iodine](#) was purchased from Tokyo Kasei Kogyo Co. or Aldrich Chemical Company, Inc., and used as received.
6. The submitters purchased [chlorotrimethylsilane](#) from Shin-Etsu Chemicals and distilled it prior to use. The checkers used 99+% [chlorotrimethylsilane](#) from Aldrich Chemical Company, Inc., without further purification.
7. If cooled to room temperature, the lower layer solidifies.
8. [Bis\(trimethylsilyl\)benzene \(1\)](#) has the following spectral properties: ^1H NMR (300 MHz, CDCl_3) δ : 0.36 (s, 18 H), 7.28-7.34 (m, 2 H), 7.64-7.68 (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ : 2.0, 127.8, 135.2, 146.0.
9. [\(Diacetoxyiodo\)benzene](#) was purchased from Aldrich Chemical Company, Inc., and was used as received.
10. [Dichloromethane](#) was distilled from [phosphorus pentoxide](#) (P_2O_5) or [calcium hydride](#) prior to use.
11. [Trifluoromethanesulfonic acid](#) from Central Glass Co. or Aldrich Chemical Company, Inc., was employed.
12. Product **2** has the following spectral properties: ^1H NMR (400 MHz, CDCl_3) δ : 0.42 (s, 9 H), 7.26-8.13 (m, 9 H); ^{13}C NMR (100 MHz, CDCl_3) δ : 0.1, 114.0, 121.2, 132.2, 133.2, 133.4, 138.5, 139.1, 147.3.
13. The submitters obtained **2** in 86% yield.
14. [Furan](#) was purchased from Tokyo Kasei Kogyo Co. or Aldrich Chemical Company, Inc., and distilled prior to use.
15. 1.0 M [Tetrabutylammonium fluoride](#) in THF was obtained from Aldrich Chemical Company, Inc.
16. If the product is obtained as an oil, it is cooled in a -78°C bath to induce crystallization.

17. Product **3** has the following spectral properties: ^1H NMR (400 MHz, CDCl_3) δ : 5.69 (s, 2 H), 6.94-6.96 (m, 2 H), 7.00 (s, 2 H), 7.22-7.24 (m, 2 H) ; ^{13}C NMR (100 MHz, CDCl_3) δ : 82.2, 120.2, 124.9, 142.9, 148.9 .

Waste Disposal Information

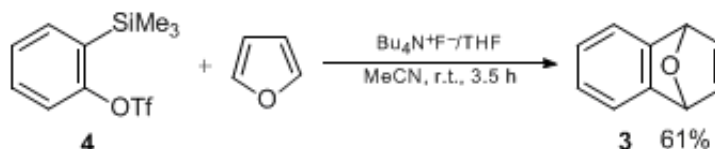
All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

3. Discussion

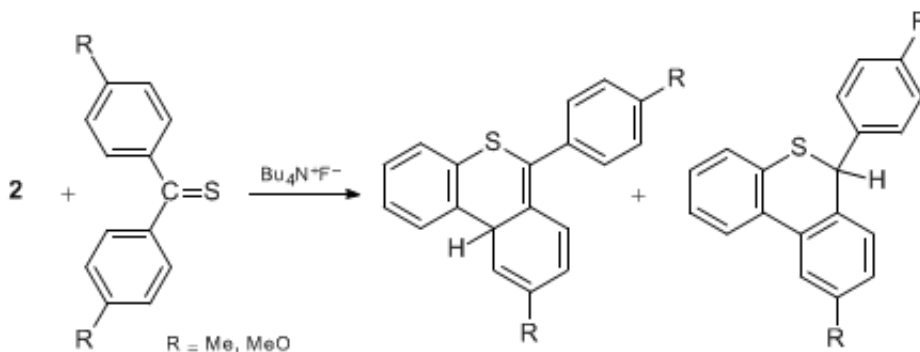
Benzynes are one of a group of reactive intermediates widely applicable to organic synthesis.^{2 3 4 5} The title hypervalent iodine-benzynes precursor, (phenyl)[2-(trimethylsilyl)phenyl]iodonium triflate **2**,⁶ is prepared by only two steps from commercially available reagents. Products **1** and **2** are stable and easily purified. The hypervalent iodine-benzynes precursor **2** is obtained as a stable solid and handled without any precautions. More importantly, benzynes are generated by using tetrabutylammonium fluoride under mild and neutral conditions. Therefore, compound **2** is useful for reactions of substrates that cannot be conducted at high temperatures or under basic conditions.

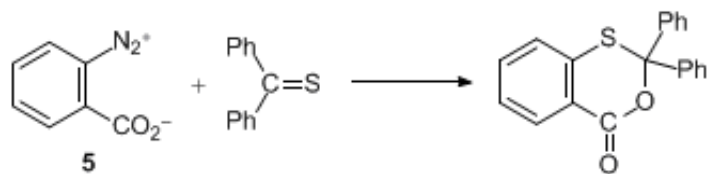
The advantages of the use of this hypervalent iodine-benzynes precursor **2** are as follows: (1) The benzynes precursor **2** is a stable crystalline compound up to its melting point, usually to 130°C. (2) The benzynes precursor **2** is not hygroscopic and is stable to air; it can be handled without any special precautions. (3) The generation of benzynes can be conducted under neutral conditions and at room temperature.

The high efficiency of the present benzynes precursor **2** is demonstrated by comparison with a similar precursor, 2-(trimethylsilyl)phenyl triflate (**4**), which generates benzynes under mild conditions (room temperature and neutral).⁷ Benzynes precursor **2** gives the adduct, 1,4-epoxy-1,4-dihydronaphthalene **3**, quantitatively in the reaction with furan, while the reaction of benzynes precursor **4** under the same conditions leads to a lower yield of adduct **3** and needs longer reaction time.



The reaction of thiobenzophenones with benzynes shows the superiority of the present iodine precursor **2** over benzenediazonium-2-carboxylate (**5**), which is widely used.⁸ The reaction of the hypervalent iodine precursor **2** with thiobenzophenones affords [4+2] cycloadducts from benzynes and thiobenzophenones under mild conditions. However, the reaction with benzenediazonium-2-carboxylate **5** gives no benzynes adducts, but benzoxathianones, which are presumably derived from the reaction of 2-carboxyphenyl cation and cyclization.





References and Notes

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Appendix

Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

(Phenyl) [2-(trimethylsilyl)phenyl]iodonium triflate:

Iodonium, phenyl-, 2-(trimethylsilyl)phenyl-, salt with trifluoromethanesulfonic acid (1:1) (13); (164594-13-2)

1,2-Bis(trimethylsilyl)benzene:

Silane, o-phenylenebis(trimethyl- (8);

Silane, 1,2-phenylenebis(trimethyl- (9); (17151-09-6)

Magnesium (8,9); (7439-95-4)

Hexamethylphosphoramide: HIGHLY TOXIC: CANCER SUSPECT AGENT:

Phosphoric triamide, hexamethyl- (8,9) (680-31-9)

1,2-Dichlorobenzene;

Benzene, o-dichloro- (8);

Benzene, 1,2-dichloro- (9); (95-50-1)

Iodine (8,9); (7553-56-2)

Chlorotrimethylsilane:

Silane, chlorotrimethyl- (8,9); (75-77-4)

(Diacetoxyiodo)benzene: Aldrich:

Iodobenzene diacetate:

Benzene, (diacetoxyiodo)- (8);

Iodine, bis(aceto-O)phenyl- (9); (3240-34-4)

Trifluoromethanesulfonic acid: HIGHLY CORROSIVE:
Methanesulfonic acid, trifluoro- (8,9); (1493-13-6)

Furan (8,9); (110-00-9)

Tetrabutylammonium fluoride:
Ammonium, tetrabutyl-, fluoride (8);
1-Butanaminium, N,N,N-tributyl-, fluoride (9); (429-41-4)

1,4-Dihydronaphthalene 1,4-oxide:
1,4-Epoxy-1,4-dihydronaphthalene:
1,4-Epoxynaphthalene, 1,4-dihydro- (8,9); (573-57-9)