(Phenyl)[*o*-(Trimethylsilyl)phenyl]iodonium Triflate. A New and Efficient Precursor of Benzyne

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(Phenyl)[*o*-(trimethylsilyl)phenyl]iodonium triflate readily prepared from *o*-bis(trimethylsilyl)benzene and the hypervalent iodine(III) reagent [PhI(OAc)$_2$·2TfOH] shows excellent formation of benzyne under mild and neutral conditions and efficiently provides adducts with typical trapping agents, *e.g.* furan, anthracene, diphenylisobenzofuran and tetraphenylcyclopentadienone.

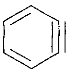
Benzyne **1** is an important reactive intermediate and many studies on its generation and reactions have been undertaken.[1] Many methods of generating benzyne from a variety of precursors[1] such as *o*-halogenophenyl anions **2**, benzenediazonium-2-carboxylate **3**, diphenyliodonium-2-carboxylate **4** and *ortho*-fused benzene derivatives, *e.g.* 1-aminobenzotriazole and benzothiadiazole-1,1-dioxide, have been reported. Recently, *o*-trimethylsilylphenyl triflate **5** was reported to generate benzyne under mild conditions.[2]

To have synthetic and mechanistic use, the benzyne precursors should fulfill the following requirements: (*a*) practical facility in their synthesis; (*b*) formation of only one aryne for a given precursor; (*c*) relative stability and safe ease of handling and (*d*) the absence of a requirement to use a strong base or high temperature in the generation of benzyne.

Recently organoiodine(III) compounds have received considerable attention in synthetic application. Specifically, the high nucleofugacity of the phenyliodonio group is effective for nucleophilic substitution of aryl, alkenyl, alkynyl and perfluoroalkyl-iodonium salts.[3] Recently Okuyama and Ochiai reported that cyclohexenyl(phenyl)iodonium tetrafluoroborate solvolyses much faster than cyclohexenyl triflate.[4] Accordingly, diaryliodonium salts are good candidates as benzyne precursors because of the high nucleofugacity of the phenyliodonio group. Diphenyliodonium-2-carboxylate **4** is a widely used benzyne precursor,[5] but despite containing the good leaving phenyliodonio group, decomposition to generate benzyne requires a high temperature (> 180 °C). Thus, we investigated (phenyl)[*o*-(trimethylsilyl)phenyl] iodonium salts as candidates for generation of benzyne, expecting them to satisfy the requirements (*a*)–(*d*).

The new precursor, (phenyl)[*o*-(trimethylsilyl)phenyl] iodonium triflate **6**, was readily prepared in 88% yield by treatment of *o*-bis(trimethylsilyl)benzene[6] with iodobenzene diacetate [PhI(OAc)$_2$] activated with trifluoromethanesulfonic acid (TfOH)[7] in CH$_2$Cl$_2$ (Scheme 1). The crystalline product **6** is quite stable (mp 132–134 °C) and can be stored for extended periods.

Reaction of **6** with NBu$_4$F was conducted in the presence of furan at room temperature. Addition of NBu$_4$F (1.2 mmol) in THF to a CH$_2$Cl$_2$ solution of **6** (1.0 mmol) in the presence of furan (5.0 mmol) led to an exothermic reaction and after stirring for 10 min the reaction mixture could be worked up and purified by column chromatography (alumina), to give 1,4-dihydronaphthalene-1,4-*endo*-oxide **7**[8] in quantitative yield (Scheme 2). This indicates that benzyne is generated and effectively trapped by furan.



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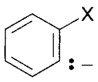

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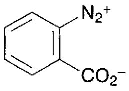

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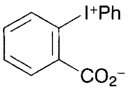

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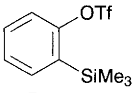

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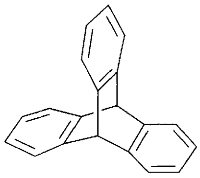
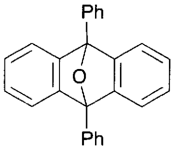
The same reaction (room temperature, 180 min) was observed when KF (3.0 mmol) and 18-crown-6 (0.6 mmol) were used instead of NBu$_4$F. The adduct **7** was obtained in 88% yield but extended reaction times were required.

Diphenyliodonium-2-carboxylate,[5] in spite of the high nucleofugacity of the phenyliodonio group, shows only low reactivity in benzyne formation. The present study indicates that the high reactivity of the benzyne precursor **6** is achieved by replacement of the strongly bound carboxy group with the more weakly bound trimethylsilyl group which is readily cleaved by fluoride anion. Taking into account the observation by Okuyama and Ochiai[4] that the phenyliodonio group exhibits a much higher nucleofugacity than triflate in solvolytic reactions of vinyl derivatives, [*o*-(trimethylsilyl)phenyl] (phenyl)iodonium triflate **6** is the best precursor for benzyne formation.

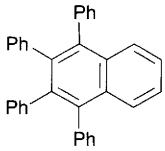
Trapping of benzyne with other reagents such as anthracene, 1,3-diphenylisobenzofuran, and 2,3,4,5-tetraphenylcyclopentadienone was conducted in the same manner. Tripticene, 9,10-epoxy-9,10-diphenyl-9,10-dihydroanthracene and 1,2,3,4-tetraphenylnaphthalene were obtained in 86, 100, and 100% yields, respectively.



(86%)



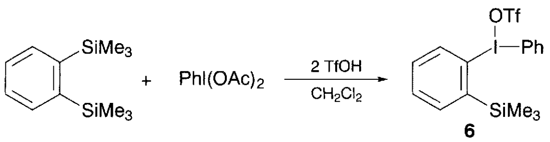
(100%)



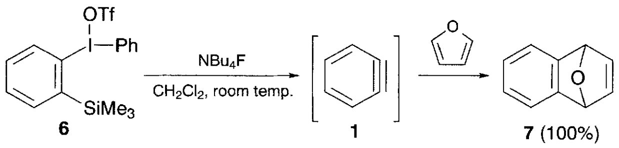
(100%)

In order to illustrate the generality of this method for benzyne generation and the clean formation of benzyne from the given precursor, substituted *o*-(trimethylsilyl)phenyliodonium triflates were investigated. [2-Methyl-6-(trimethylsilyl)phenyl]- and [4-methyl-6-(trimethylsilyl)phenyl]-(phenyl) iodonium triflates were prepared by similar treatments of 1-methyl-2,3-bis(trimethylsilyl) benzene and 4-methyl-1,2-bis(trimethylsilyl)benzene in 48 and 58% yields, respectively. Reactions of these two reagents with NBu$_4$F in the presence of furan gave 5-methyl- and 6-methyl-1,4-dihydronaphthalene-1,4-*endo*-oxides, respectively, in quantitative yields.

Compared with previous results,[1] the present preliminary work provides the best results, in addition to the use of mild and neutral conditions.



Scheme 1



Scheme 2

In summary, our iodine reagent, (phenyl)[o-(trimethylsilyl) phenyl]iodonium triflate, is an excellent precursor of benzyne and can be applied in a wide range of synthetic and mechanistic studies. Further studies on such applications under mild and neutral conditions are now in progress.

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