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A Novel Hypervalent Iodine Reagent Prepared from *o*-Iodosylbenzoic Acid and Trifluoromethanesulfonic Acid. Preparation and Reactions of Alkynyl(*o*-Carboxyphenyl)iodonium Triflates

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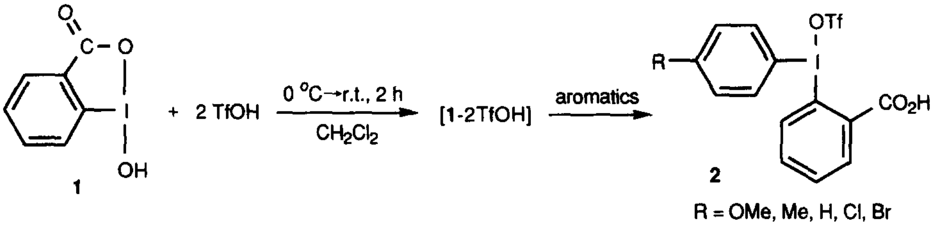
Abstract: A hypervalent iodine reagent prepared from *o*-iodosylbenzoic acid and trifluoromethanesulfonic acid (TfOH) (1:2) showed a high reactivity toward aromatic substrates, giving aryl(*o*-carboxyphenyl)iodonium triflates in good to high yields. Treatment of the iodine reagent with 1-trimethylsilylalkynes afforded alkynyliodonium triflates bearing carboxy group in high yields. The alkynyliodonium triflates indicated a high efficiency as a Michael acceptor to nucleophiles and the *o*-carboxyphenyliodonio group behaved as a good leaving group.

Recently hypervalent iodine(III) chemistry has been progressed remarkably in the field of organic synthesis.[2,3] Diaryliodonium salts are used in arylation of nucleophilic substrates[2,3c,d] and utilized as photoinitiators of polymerization and in imaging process of photoresists.[4] Especially, alkynyliodonium salts are synthetically useful reagents since they undergo nucleophilic reaction,[3f,h,k,5] the Diels-Alder reaction,[6] and the coupling reaction with organocopper reagents.[7]

We have prepared reactive hypervalent iodine reagents from iodosylbenzene (PhIO) and trifluoromethanesulfonic acid (TfOH).[8,9] Among the reagents, the hypervalent iodine reagent prepared from a 1:2 molar ratio of PhIO and TfOH possesses a (*p*-phenylene)bisiodine(III) structure.[9] In the course of an investigation on reactive hypervalent iodine reagents, we found a novel hypervalent iodine(III) reagent from a 1:2 molar ratio of *o*-iodosylbenzoic acid (**1**) and TfOH and applied to preparation of alkynyl(*o*-carboxyphenyl)iodonium triflates. Here we report that the hypervalent iodine(III) reagent [**1**-2TfOH] shows a high reactivity toward aromatic substrates and the alkynyl(*o*-carboxyphenyl)iodonium triflates prepared by the reaction with 1-trimethylsilylalkynes act as a good Michael acceptor to nucleophiles.



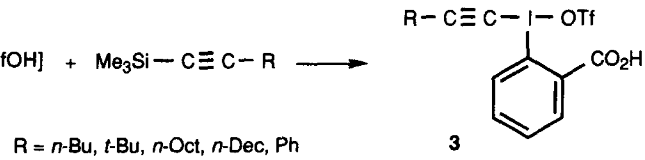
When **1** was treated with an equimolar amount of TfOH in CH_2Cl_2 and then reacted with anisole, no diaryliodonium salts were formed. However, the similar treatment of **1** with double the molar amount of TfOH followed by the reaction with anisole provided (2-carboxyphenyl)(4-methoxyphenyl)iodonium triflate (**2a**) in 93% yield. The reagent [**1**-2TfOH] was not stable enough to isolate and used in situ for the reaction. Similarly the reactions with other aromatic substrates gave the corresponding diaryliodonium triflates **2** in good to high yields. The results are given in Table 1. The favorable formation of **2** in the reaction with halogenobenzenes indicates a high reactivity of the present iodine reagent [**1**-2TfOH].

Table 1. Reaction of the iodine reagent [**1**-2TfOH] with aromatic substrates.[a]

aromatic substrate	product	isolated yield (%)	mp (^oC)
anisole	**2a**: R = OMe	93	195-206
toluene	**2b**: R = Me	94	193-194
benzene	**2c**: R = H	65	198-220
chlorobenzene	**2d**: R = Cl	85[b]	218-220
bromobenzene	**2e**: R = Br	50[b]	220-226

[a] Reaction was carried out at room temperature. [b] Reflux in CH_2Cl_2.

The high reactivity of the iodine reagent [**1**-2TfOH] was applied to preparation of alkynyliodonium triflates bearing carboxy group at the *ortho* position of phenyl ring. The iodine reagent [**1**-2TfOH] was prepared in the same manner as above and reacted with 1-trimethylsilylalkynes. High yields of alkynyl(*o*-carboxyphenyl)iodonium triflates (**3**) were achieved by this method. The results are given in Table 2. The alkynyl(*o*-carboxyphenyl)iodonium triflates **3** are not cyclic iodoxolone structures (**4**) but acyclic structures. Cyclic aryliodinanes are generally more stable than the acyclic analog.[2,3c] In fact, alkynyliodoxolones **4** have been prepared by Ochiai et al.[10] Accordingly, the present result may be attributed to the structure of the iodine reagent [**1**-2TfOH] may possess an open structure.



R = *n*-Bu, *t*-Bu, *n*-Oct, *n*-Dec, Ph

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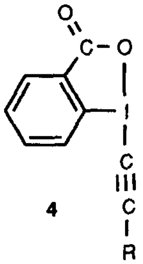

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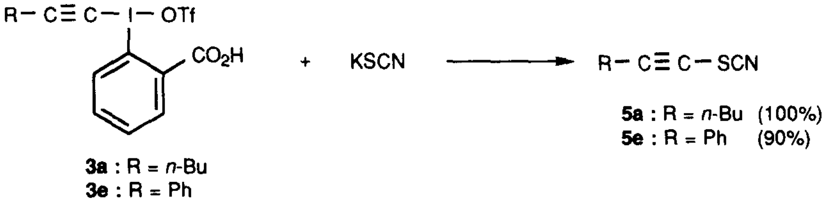
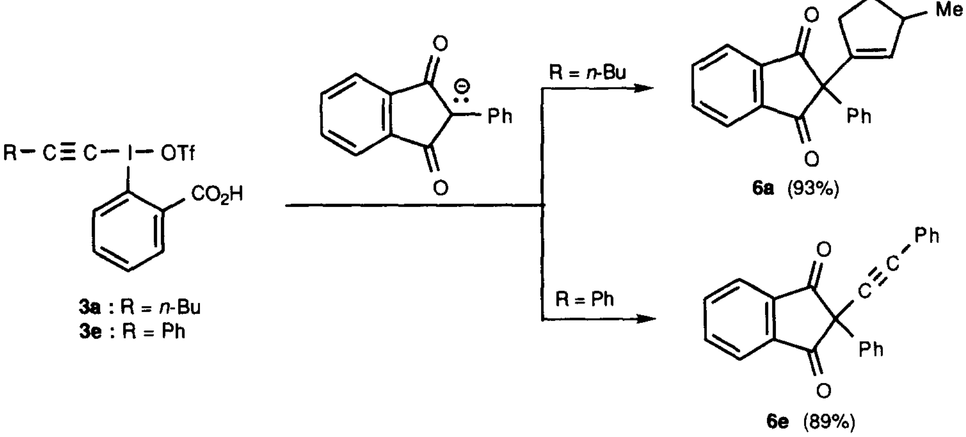
Table 2. Reaction of the iodine reagent [**1**-2TfOH] with 1-trimethylsilylalkynes.

silylalkynes	product	isolated yield (%)	mp (^oC)
R = *n*-Bu	**3a**: R = *n*-Bu	98	126-128
R = *t*-Bu	**3b**: R = *t*-Bu	67	146-149
R = *n*-Oct	**3c**: R = *n*-Oct	89	132-135
R = *n*-Dec	**3d**: R = *n*-Dec	75	136-140
R = Ph	**3e**: R = Ph	97	112-120

Reaction of alkynyliodoxolones **4** has not been investigated yet. Preliminarily the reactions with typical nucleophiles such as thiocyanate anion and an enolate anion of 2-phenylindan-1,3-dione were examined in the cases of 1-hexynyl- and phenylethynyl(*o*-carboxyphenyl)iodonium triflates **3a** and **3e**. The reaction of **3a** and

3e with potassium thiocyanate gave alkynyl thiocyanates **5a** and **5e**[5l,n] in 100 and 90% yields, respectively. On the other hand, in the reaction with the enolate anion of 2-phenylindan-1,3-dione, phenylethynyl-substituted iodonium triflate **3e** provided phenylethynyl derivative **6e**[5c] (89%), while 1-hexynyl-substituted one **3a** afforded pentenyl derivative **6a**[5c] (93%).





The reactions described above are explained by the previous proposed mechanism,[3f,h,k,5] that is, the Michael addition of the nucleophile at the β carbon of the triple bond followed by formation of alkylidenecarbenes by elimination of *o*-iodobenzoic acid and reaction of the resulting alkylidenecarbenes, 1,2-rearrangement or 1,5-C-H insertion. High yields of the products **5** and **6** imply that the present substrates **3** can be applied to organic reactions, i.e., generation of alkylidenecarbenes, preparation of alkynyl or cyclopentenyl derivatives, and other purposes.[3f,h,k]

The leaving moiety of alkynyl(*o*-carboxyphenyl)iodonium triflates **3** was easily separated from the products just only by extraction with saturated $NaHCO_3$ and isolated as *o*-iodobenzoic acid. Accordingly, the product was obtained in almost pure form by extraction owing to the high yield.

In summary, *o*-iodosylbenzoic acid (**1**) requires double the molar amount of TfOH to generate reactive reagent [**1**-2TfOH] in contrast with the result by Ochiai et al.[10] The iodine reagent [**1**-2TfOH] shows a high electrophilic character and can be utilized to prepare various substituted *o*-carboxyphenyliodonium salts. Alkynyl(*o*-carboxyphenyl)iodonium triflates **3** indicate a potent wide application to organic reactions.

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