A New and Efficient Hypervalent Iodine−Benzyne Precursor, (Phenyl)[o-(trimethylsilyl)phenyl]iodonium Triflate: Generation, Trapping Reaction, and Nature of Benzyne

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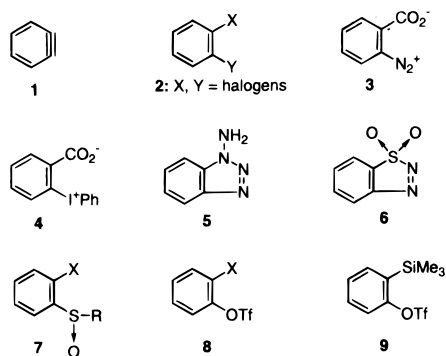
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Abstract: A new and efficient hypervalent iodine−benzyne precursor, (phenyl)[2-(trimethylsilyl)phenyl]-iodonium triflate (**10**), is reported. The hypervalent iodine−benzyne precursor **10** is readily prepared by reaction of 1,2-bis(trimethylsilyl)benzene with a PhI(OAc)$_2$/TfOH reagent system. Treatment of **10** with Bu$_4$NF in CH$_2$Cl$_2$ at room temperature gives high yields of the benzyne adducts in the presence of a trapping agent such as furan, 2-methylfuran, anthracene, tetraphenylcyclopentadienone, or 1,3-diphenylisobenzofuran. Especially, the result of the reaction in the presence of furan indicates a quantitative generation of benzyne and its efficient capture by the furan. Similarly, methylbenzynes (**22** and **27**) are efficiently generated from the corresponding methyl-substituted (trimethylsilyl)phenyliodonium triflates (**12** and **13**). The preparation of the hypervalent iodine−benzyne precursors, the generation of benzynes, the trapping reactions, and the nature are described in detail together with the advantages of the present reagents over the previously reported benzyne precursors.

Benzyne (**1**) is an important reactive intermediate and has been used in organic synthesis, mechanistic studies, and synthesis of functional materials.[1] Recently, there has been considerable progress in the application of benzyne chemistry to natural product synthesis. The intramolecular and intermolecular cycloaddition reactions using the benzyne intermediate construct the fundamental skeletons of the natural products.[1c] Taking into consideration the advances made in these fields, methodology is desired for benzyne precursors to generate benzyne with high efficiency and under very mild conditions.

Representative benzyne precursors reported previously[1] are *o*-dihalobenzene derivatives (**2**), benzenediazonium-2-carboxylate (**3**), diphenyliodonium-2-carboxylate (**4**), and *ortho*-fused benzene derivatives such as 1-aminobenzotriazole (**5**) and benzothiadiazole *S,S*-dioxide (**6**). Recently, *o*-halophenylsulfoxides (**7**), *o*-halophenyl tosylates and triflates (**8**), and *o*-trimethylsilylphenyl triflate (**9**) have been reviewed.[1c] Especially, it is noted that the *o*-trimethylsilylphenyl triflate **9** generates benzyne under mild reaction conditions.[2]

Although many benzyne precursors have been reported as above, there are few precursors that generate benzyne quanti-

tatively under very mild conditions (at an ambient temperature and under neutral conditions). If such excellent benzyne precursors become available, they will be valuable reagents for the synthesis of natural products and in trapping experiments of unstable intermediates. Such excellent precursors should meet the following requirements. (1) The benzyne precursor is prepared readily from easily available chemicals. (2) Only one benzyne among the possible isomers is generated from the given precursor. (3) The benzyne precursor is stable enough to be handled without any special precaution. It is preferred that the benzyne precursor is a crystalline compound since the handling becomes much easier. (4) In the generation of benzyne, no strong bases are required. Such precursors requiring a base cannot be used in the reaction of substances unstable toward bases. (5) The benzyne precursors do not require high temperature for generation of benzyne. If the benzyne precursors need high temperature for generation of benzyne, they cannot be used in the reaction of thermally unstable substances.
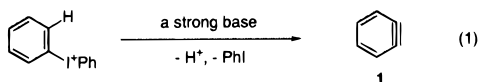
On the other hand, hypervalent iodine compounds have recently received much attention in organic synthesis and considerable progress has been made in such fields.[3] The most significant advantage of the use of hypervalent iodine compounds in organic synthesis is the high nucleofugality of the hypervalent iodine groups. For example, in the solvolysis of 1-iodonorbornane, the reactivity is greatly enhanced by adding bromine.[4] This high reactivity is understood when viewed from the fact that (dibromoiodo)norbornane is formed as the intermediate. The leaving ability of the hypervalent dibromoiodanyl

(1) (a) Hoffmann, R. W. *Dehydrobenzene and Cycloalkynes*; Academic Press: New York, 1967. (b) Gilchrist, T. L. In *The Chemistry of Functional Groups,* Supplement C; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1983, Chapter 11. (c) Hart, H. In *The Chemistry of Triple-Bonded Functional Groups,* Supplement C2; Patai, S., Ed.; Wiley: Chichester, 1994; Chapter 18.

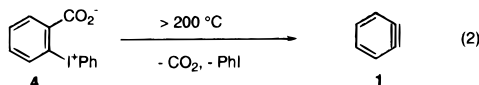(2) Himeshima, Y.; Sonoda, T.; Kobayashi, H. *Chem. Lett.* **1983**, 1211−1214.

group is much superior to that of the iodo group and plays an important role in the solvolysis. Also, the high reactivity of hypervalent iodine compounds has been observed in solvolysis of cyclohexenyl derivatives. The phenyliodanyl group is about 10^6 more reactive than the trifluoromethylsulfonyloxy group (OTf).[5] This result suggests that the nucleofugality is enhanced by 10^{10}–10^{12} times when the iodine group is replaced by a hypervalent iodine group.[6] It is, therefore, expected that the reaction conditions generating benzyne become very mild by using of hypervalent iodine compounds as the benzyne precursor.

It has been reported that benzyne is formed by the reaction of diphenyliodonium salts with a base (eq 1).[7] In this reaction,

$$\text{(eq 1)}$$

however, a strong base is necessary to abstract the *ortho* proton and two types of benzyne isomers can be generated by the possible abstraction of two *ortho* protons when the precursor has a substituent. The attack of a strong base upon the positive iodine retards the generation of benzyne.

Diphenyliodonium-2-carboxylate **4** is a well-known benzyne precursor containing hypervalent iodine and is used widely in organic synthesis (eq 2).[8] However, high temperature (>200

$$\text{(eq 2)}$$

°C) is required to generate benzyne efficiently. This means that decarboxylation is a key step in the reaction of **4** because the phenyliodanyl group has high leaving ability.

The trimethylsilyl group is a significant functional group in organic synthesis. In particular, it is useful as a protecting group and can be removed easily by using a fluoride ion.[2,9] By applying the high affinity of the fluoride ion toward silyl groups, a trimethylsilyl group can be utilized instead of a carboxylate group of diphenyliodonium-2-carboxylate **4**. Thus, we have prepared *o*-trimethylsilylphenyliodonium salt as an excellent

benzyne precursor conforming to all of the requirements described above. In this paper, we describe the preparation and reaction of (phenyl)[2-(trimethylsilyl)phenyl]iodonium triflate (**10**), and the related species,[10] as a new type of benzyne precursor and discuss the generation and nature of benzyne.

Results and Discussion

Preparation of (Phenyl)[2-(trimethylsilyl)phenyl]iodonium Triflate (10). Phenyliodination of arylsilanes and -stannanes has been successfully conducted by using hypervalent iodine reagents, Koser's reagent[11] PhI(OH)OTs, and Stang's reagent[12] PhI(CN)OTf. In this study, we used our hypervalent iodine reagent readily prepared from (diacetoxyiodo)benzene [PhI(OAc)$_2$] and trifluoromethanesulfonic acid (TfOH).[13] First, we prepared bis(trimethylsilyl)benzene from dichlorobenzene according to the literature method.[14] When 1,2-dichlorobenzene was reacted with chlorotrimethylsilane in the presence of Mg in HMPA at 100 °C for 2 d, 1,2-bis(trimethylsilyl)benzene was obtained in 74% yield (eq 3).

$$\text{(eq 3)}$$

Then, 1,2-bis(trimethylsilyl)benzene was treated with PhI(OAc)$_2$ activated with a double molar quantity of TfOH, and (phenyl)[2-(trimethylsilyl)phenyl]iodonium triflate (**10**) was obtained in 86% yield as colorless crystals (eq 4). This

$$\text{(eq 4)}$$

[2-(trimethylsilyl)phenyl]iodonium triflate **10** is quite stable at room temperature up to the melting point (decomposition), is not sensitive to air and moisture, and is not hygroscopic. Accordingly, this iodonium salt **10** is very easy to handle. The iodonium salt **10** is soluble in polar organic solvents such as CH$_2$Cl$_2$, MeCN, DMSO, DMF, and alcohols, but not as soluble or insoluble in less polar solvents such as ether, THF, benzene, and hexane. Unlike in arylstannanes,[12] bisphenyliodination leading to *o*-phenylenebisiodonium ditriflate (**11**) did not take place at all.

$$\textbf{11}$$

Preparation of [4-Methyl-2-(trimethylsilyl)phenyl](phenyl)iodonium Triflate (12) and [2-Methyl-6-(trimethylsilyl)phenyl](phenyl)iodonium Triflate (13). In a method similar to the preparation of 1,2-bis(trimethylsilyl)benzene, 3,4-bis-

(3) For recent reviews and books, see: Koser, G. F. In *The Chemistry of Functional Groups,* Supplement D; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1983; Chapters 18 and 25. Varvoglis, A. *Synthesis* **1984**, 709–726. Moriarty, R. M.; Prakash, O. *Acc. Chem. Res.* **1986**, *19*, 244–250. Merkushev, E. B. *Russ. Chem. Rev. (Eng. Transl.)* **1987**, *56*, 826–845. Ochiai, M. *Rev. Heteroat. Chem.* **1989**, *2*, 92–111. Moriarty, R. M.; Vaid, R. K. *Synthesis* **1990**, 431–447. Moriarty, R. M.; Vaid, R. K.; Koser, G. F. *Synlett* **1990**, 365–383. Varvoglis, A. *The Organic Chemistry of Polycoordinated Iodine*; VCH Publishers: New York, 1992. Kita, Y.; Tohma, H.; Yakura, Y. *Trends Org. Chem.* **1992**, *3*, 113–128. Prakash, O.; Saini, N.; Sharma, P. K. *Synlett* **1994**, 221–227. Kitamura, T. *Yuki Gosei Kagaku Kyokai Shi* **1995**, *53*, 893–905. Koser, G. F. In *Supplement D2: The Chemistry of Halides, Pseudo-Halides and Azides*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1995; Chapter 21. Stang, P. J.; Zhdankin, V. V. *Chem. Rev.* **1996**, *96*, 1123–1178. Varvoglis, A. *Hypervalent Iodine in Organic Synthesis*; Academic Press: San Diego, 1997. Kitamura, T.; Fujiwara, Y. *Org. Prep. Proced. Int.* **1997**, *29*, 409–458. Togo, H.; Hoshina, Y.; Nogami, G.; Yokoyama, M. *Yuki Gosei Kagaku Kyokai Shi* **1997**, *55*, 90–98.
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(5) Okuyama, T.; Takino, T.; Sueda, T.; Ochiai, M. *J. Am. Chem. Soc.* **1995**, *117*, 3360–3367.
(6) Kitamura, T.; Taniguchi, H.; Tsuno, Y. In *Dicoordinated Cations*; Rappoport, Z., Stang, P. J., Eds.; John Wiley & Sons: Chichester, 1997; Chapter 7.
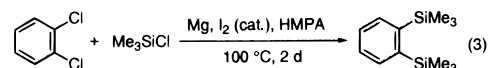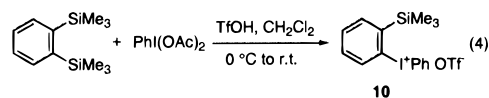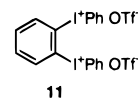(7) Akiyama, T.; Iwasaki, Y.; Kawanishi, M. *Chem. Lett.* **1974**, 229–230. Cadogan, J. I. G.; Rowley, A. G.; Sharp, J. T.; Sledzinski, B.; Wilson, N. H. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1072–1074.
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(9) For a fluoride ion-induced desilylation, see: Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; John Wiley & Sons: New York, 1991. Cunico, R. F.; Dexheimer, E. M. *J. Am. Chem. Soc.* **1972**, *94*, 2868–2869. Cunico, R. F.; Dexheimer, E. M. *J. Organomet. Chem.* **1973**, *59*, 153–160. Atanes, N. A.; Escudero, S.; Pérez, D.; Guitiá, E.; Castedo, L. *Tetrahedron Lett.* **1998**, *39*, 3039–3040.
(10) For a preliminary report, see: Kitamura, T.; Yamane, M. *J. Chem. Soc., Chem. Commun.* **1995**, 983–984.
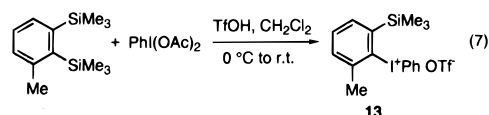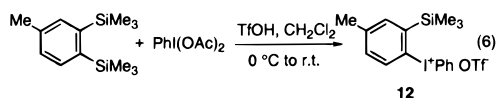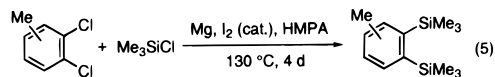(11) Neiland, O.; Karele, B. *J. Org. Chem. USSR (Engl. Transl.)* **1970**, *6*, 889. Koser, G. F.; Wettach, R. H. *J. Org. Chem.* **1977**, *42*, 1476–1478. Koser, G. F.; Wettach, R. H.; Smith, C. S. *J. Org. Chem.* **1980**, *45*, 1544–1546.
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(13) Kitamura, T.; Matsuyuki, J.; Taniguchi, H. *Synthesis*, **1994**, 147–148.
(14) Bourgeois, P.; Calas, R. *J. Organomet. Chem.* **1975**, *84*, 165–175.

(trimethylsilyl)toluene and 2,3-bis(trimethylsilyl)toluene were prepared from the corresponding dichlorotoluenes, respectively. These preparations required higher reaction temperature (130 °C) and longer reaction time (4 d) than the preparation of 1,2-bis(trimethylsilyl)benzene (eq 5). When 3,4-bis(trimethylsilyl)toluene was treated with PhI(OAc)$_2$ activated with TfOH, [4-methyl-2-(trimethylsilyl)phenyl]iodonium triflate (**12**) was obtained in 72% yield (eq 6). A similar reaction of 2,3-bis-(trimethylsilyl)toluene with PhI(OAc)$_2$ activated with TfOH gave [2-methyl-6-(trimethylsilyl)phenyl]iodonium triflate (**13**) in 78% yield (eq 7).

In these reactions, phenyliodination by the hypervalent iodine reagent took place regioselectivity at the trimethylsily group *para* or *ortho* to the methyl group between the two possible positions. No other isomers **14** and **15** derived from the phenyliodination of the trimethylsilyl group *meta* to the methyl group were formed. Even if the isomers **14** and **15** were formed,

the isomers **12** and **13** can be easily distinguished from the isomers **14** and **15**, respectively, on the basis of ¹H NMR. Phenyliodonium salts have characteristic *ortho* protons which show a considerable downfield shift by the iodine atom and appear around 8 ppm. The iodonium triflate **12** has one *ortho* proton which splits to a doublet, but the iodonium triflate **14** has one *ortho* proton which shows a singlet (exactly a doublet by the *meta* coupling in a higher-resolution NMR). Therefore, the iodonium triflate **12** is readily distinguishable from the iodonium triflate **14**. Similarly, the iodonium triflate **13** has no *ortho* protons and is distinct from the iodonium triflate **15** which bears one *ortho* proton.
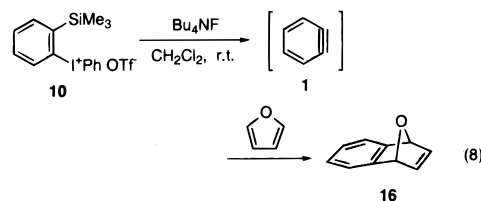
Generation of Benzyne 1 from (Phenyl)[2-(trimethylsilyl)phenyl]iodonium Triflate (10). As the silicon–fluorine bond is the strongest of silicon bonds,[15] a fluoride ion is a suitable reagent to remove the trimethylsilyl group from (trimethylsilylphenyl)iodonium salts. Tetrabutylammonium fluoride is a well-known reagent as a desilylating agent.[2,9] This fluoride is soluble in most organic solvents so that the reaction can be conducted in homogeneous solution. We first used furan as a trapping agent of benzyne. A THF solution of Bu$_4$NF was added to a solution of [2-(trimethylsilyl)phenyl]iodonium triflate **10** in CH$_2$Cl$_2$ in the presence of furan. After the reaction for 30 min, the benzyne adduct with furan, 1,4-epoxy-1,4-dihydronaph-

(15) Eaborn, C. *Organosilicon Compounds*, Butterworths: London, 1960. Armitage, D. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 2, Chapter 9.1.

Table 1. Trapping Reaction of Benzyne **1** Derived from Iodonium Triflate **10**

Diene	Adduct	Yield (%)	
		This Work[a]	Reported[b]
(2-Me furan) **16**	**17**	100	80[c]
(anthracene)	**18**	86	75[d]
(tetraphenylcyclopentadienone)	**19**	100	95[e]
(1,3-diphenylisobenzofuran)	**20**	100	85[f]

[a] Conditions: **10** (1 mmol), a diene (5 mmol), Bu$_4$NF (1.2 mmol) in THF, CH$_2$Cl$_2$ (20 mL), room temperature, 30 min. [b] Selected the best result from the previously reported results. [c] Reference 16. [d] References 16 and 17. [e] Reference 18. [f] Reference 19.

thalene (**16**), was obtained quantitatively (eq 8). This reaction was completed in 10 min. This result indicates that benzyne **1**
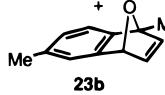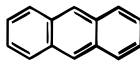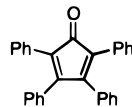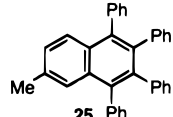

generates immediately and reacts with furan effectively. When KF was used as the desilylating agent together with 18-crown-6, the benzyne adduct **16** was obtained in 88% yield. This result indicates that other fluoride reagents also work well in this reaction.

Trapping Reactions of Benzyne 1 Generated from [2-(Trimethylsilyl)phenyl]iodonium Triflate (10). Other trapping reactions of benzyne using [2-(trimethylsilyl)phenyl]iodonium triflate **10** were examined. The trapping reactions of benzyne **1** were conducted by adding Bu$_4$NF to a mixture of iodonium triflate **10** and an appropriate diene in CH$_2$Cl$_2$. The results are given in Table 1. The benzyne **1** derived from iodonium triflate **10** reacts well with 2-methylfuran, anthracene, tetraphenylcyclopentadienone, and 1,3-diphenylisobenzofuran to give the corresponding cycloadducts in high yields. Each reaction in this study gives better results in comparison with the yields reported in previous works using a different benzyne precursor. Therefore, [2-(trimethylsilyl)phenyl]iodonium triflate **10** acts as an excellent benzyne precursor and can be used as a widely applicable reagent.

Generation and Reaction of Methylbenzynes Derived from Methyl-Substituted [2-(Trimethylsilyl)phenyl]iodonium Triflates (12) and (13). In the generation of benzyne, there is a case that two kinds of benzynes are formed when a benzyne precursor has substituents. In such a case, the regioselectivity
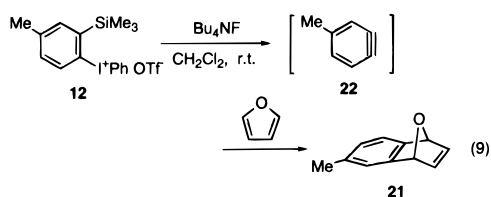
Table 2. Trapping Reaction of 4-Methylbenzyne **22** Derived from Iodonium Triflate **12**[a]

Diene	Adduct	Yield (%)
	23a + **23b**	97[b]
	24	62
	25	88

[a] Conditions: **12** (1 mmol), a diene (5 mmol), Bu$_4$NF (1.2 mmol) in THF, CH$_2$Cl$_2$ (20 mL), room temperature, 30 min. [b] A 1:1 mixture of the regioisomers **23a** and **23b**.
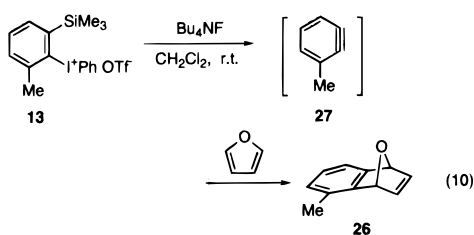
of the reaction becomes important. When [4-methyl-2-(trimethylsilyl)phenyl]iodonium triflate (**12**) was treated with Bu$_4$NF in CH$_2$Cl$_2$ in the presence of furan, 1,4-epoxy-1,4-dihydro-6-methylnaphthalene (**21**) was obtained quantitatively (eq 9). This

result indicates that 4-methylbenzyne (**22**) is generated quantitatively and regioselectively and is trapped with furan efficiently.
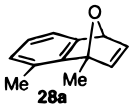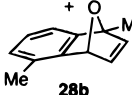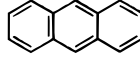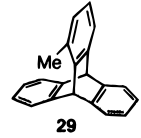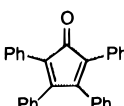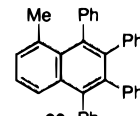
Other dienes such as 2-methylfuran, anthracene, and tetraphenylcyclopentadienone worked well as the trapping agent of 4-methylbenzyne **22**. The results are given in Table 2. In the case of the reaction with 2-methylfuran, there exist two regioisomers of the 4-methylbenzyne adducts in the ratio of 1:1.

In the case of [6-methyl-2-(trimethylsilyl)phenyl]iodonium triflate (**13**), the treatment with Bu$_4$NF in the presence of furan gave 1,4-epoxy-1,4-dihydro-5-methylnaphthalene (**26**) in a quantitative yield (eq 10). Again, the efficient generation of

3-methylbenzyne (**27**) is indicated. Similarly, the reactions with 2-methylfuran, anthracene, and tetraphenylcyclopentadienone afforded the corresponding 3-methylbenzyne adducts in high yields, as shown in Table 3. In this case, the reaction with

Table 3. Trapping Reaction of 3-Methylbenzyne **27** Derived from Iodonium Triflate **13**[a]
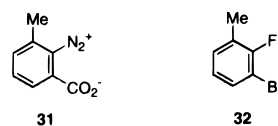
Diene	Adduct	Yield (%)
	28a + **28b**	100[b]
	29	76
	30	100

[a] Conditions: **13** (1 mmol), a diene (5 mmol), Bu$_4$NF (1.2 mmol) in THF, CH$_2$Cl$_2$ (20 mL), room temperature, 30 min. [b] A 33:67 mixture of the regioisomers **28a** and **28b**.

2-methylfuran led to a mixture of the regioisomers in the ratio of 33:67. Again, this hypervalent iodine−benzyne precursor afforded only one methylbenzyne.

When the results obtained here are compared with the reported data available in the literature [**21** (54%),[20] **24** (50%),[16] and **29** (58%)[21]], better results are obtained by using the hypervalent iodine−benzyne precursors **12** and **13**.

Regioselectivity in the Reaction with 2-Substituted Furans and Comparison with Other Benzyne Precursors. The reaction of 3-methylbenzyne **27** generated from [6-methyl-2-(trimethylsilyl)phenyl]iodonium triflate **13** leads to the formation of the regioisomers of the benzyne adducts with 2-methylfuran. The regioselectivity in the reaction of 3-methylbenzyne **27** seems to be attributable to the nature of the benzyne precursors. Thus, we conducted the reaction of [6-methyl-2-(trimethylsilyl)phenyl]iodonium triflate **13** with 2-*tert*-butylfuran and compared the results with those reported for other methylbenzyne precursors such as toluenediazonium-2-carboxylates (**31**) and bromofluorotoluene (**32**).[22]

Similarly, the reaction of iodonium triflate **13** with Bu$_4$NF in the presence of 2-*tert*-butylfuran provided a mixture of the corresponding regioisomers of the adducts. A comparison of the results obtained by methylbenzyne precursors **13**, **31**, and **32** is given in Table 4.

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Table 4. Regioselectivity in the Reaction of 3-Methylbenzyne **27** with 2-Substituted Furans

3-Methylbenzyne Precursor	2-Substituted Furan R	Yield and Ratio of Adducts		
		Yield (%)	Me R (ratio)	Me (R) (ratio)
13	Me	100	33	67	this work
	tert-Bu	72	30	70	this work
31	Me	50	42	58	a
	tert-Bu	51	34	66	a
32	Me	74	42	58	a
	tert-Bu	73	36	64	a

a Reference 22.

Table 4 shows that the ratio of the 3-methylbenzyne adducts in the reaction of the precursors **13**, **31**, and **32** is almost the same. It is, therefore, indicated that the steric effects on the regioselectivity in the reactions are similar. Also, this means that the nature of benzyne generated from the hypervalent iodine−benzyne precursors is similar to that of other benzyne precursors such as benzenediazonium-2-carboxylate and 1,2-dihalobenzenes.

Conclusions

A new and efficient benzyne precursor, (phenyl)[2-(trimethylsilyl)phenyl]iodonium triflate **10** has been constructed by a combination of hypervalent iodine and trimethylsilyl groups. The high efficiency of the benzyne formation is attributable both to the high leaving ability of the hypervalent iodine group and to the facile cleavage of the trimethylsilyl group by a fluoride ion. As a result, benzyne is efficiently generated under very mild conditions that are applicable for thermally unstable and/or base-sensitive substrates. The advantages of the use of our hypervalent iodine−benzyne precursors are as follows. (1) The hypervalent iodine−benzyne precursors are stable crystalline compounds up to the melting points, usually to 130 °C. (2) The hypervalent iodine−benzyne precursors are not hygroscopic, are stable to air, and can be handled without any special precaution. (3) The generation of benzyne can be conducted under neutral conditions and at room temperature. (4) An extremely high efficiency of benzyne formation is observed by using Bu₄NF as the desilylating agent. (5) Only one isomer of the possible benzynes is generated from the present precursor, and it does not isomerize under the present conditions when the precursor bears a substituent.

The present benzyne precursor **10** provides much better results than a similar precursor, 2-(trimethylsilyl)phenyl triflate **(9)**, which also generates benzyne under mild conditions (room temperature and neutral). Our benzyne precursor **10** gives the adduct, 1,4-epoxy-1,4-dihydronaphthalene, quantitatively in the reaction with furan, while the reaction of the benzyne precursor **9** under the same conditions leads to a lower yield of the adduct and also needs prolonged reaction time.[2]

The reaction of thiobenzophenones with benzyne shows the superiority of the present iodine precursor **10** over benzenediazonium-2-carboxylate which is widely used.[23] The reaction of the hypervalent iodine precursor **10** with thiobenzophenones affords the [4 + 2] cycloadducts derived from benzyne and thiophenzophenones under mild conditions. However, the reaction with benzenediazonium-2-carboxylate gives no benzyne adducts,

but benzoxathinones which are presumably derived from the reaction of the 2-carboxyphenyl cation and the cyclization.

[2-(Trimethylsilyl)phenyl]iodonium triflates **10**, **12**, and **13** provide a new class of benzyne precursors of high utility. We believe that this type of hypervalent iodine−benzyne precursor will have broad use in mechanistic and synthetic studies.[24]

Experimental Section

General. Melting points were determined with a Yanaco melting point apparatus and are uncorrected. NMR spectra were taken with JEOL JNM-AL 300 or Bruker AC-250. Elemental analyses were performed by the Service Center of the Elementary Analysis of Organic Compounds, Faculty of Science, Kyushu University.

Preparation of 1,2-Bis(trimethylsilyl)benzene.[14] To a mixture of Mg (9.72 g, 400 mmol), HMPA (80 mL), a catalytic amount of I₂, and 1,2-dichlorobenzene (11.3 mL, 100 mmol) was added chlorotrimethylsilane (51 mL, 400 mL) dropwise at 70 °C. The mixture was stirred for additional 30 min and then heated at 100 °C for 48 h. After cooling, the reaction mixture was poured onto ice and NaHCO₃. The precipitates and Mg were filtered off, and the filtrate was extracted with ether. The ethereal extracts were washed with water and brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. Distillation at 128−133 °C/20 mmHg gave 1,2-bis(trimethylsilyl)benzene, 16.40 g (74%). ¹H NMR (CDCl₃) δ 0.36 (s, Me, 18 H), 7.28−7.34 (m, ArH, 2 H), 7.64−7.68 (m, ArH, 2 H); ¹³C NMR (CDCl₃) δ 2.0, 127.8, 135.2, 146.0.

Preparation of 3,4-Bis(trimethylsilyl)toluene. To a mixture of Mg (9.72 g, 400 mmol), HMPA (80 mL), a catalytic amount of I₂, and 3,4-dichlorotoluene (12.9 mL, 100 mmol) was added chlorotrimethylsilane (51 mL, 400 mL) dropwise at 80 °C. The mixture was stirred for an additional 30 min and then heated at 130 °C for 4 days. After workup similar to that above, distillation at 106−112 °C/5 mmHg gave 3,4-bis(trimethylsilyl)toluene,[25] 14.66 g (62%). ¹H NMR (CDCl₃) δ 0.35 (s, Me, 18 H), 2.33 (s, Me, 3 H), 7.15−7.64 (m, ArH, 3 H).

Preparation of 2,3-Bis(trimethylsilyl)toluene. To a mixture of Mg (9.72 g, 400 mmol), HMPA (80 mL), a catalytic amount of I₂, and 2,3-dichlorotoluene (13.1 mL, 100 mmol) was added chlorotrimethylsilane (51 mL, 400 mL) dropwise at 70 °C. The mixture was stirred for additional 30 min, and then heated at 130 °C for 4 days. After workup similar to that above, distillation at 92−115 °C/5 mmHg gave 2,3-bis(trimethylsilyl)toluene,[25] 8.05 g (34%). ¹H NMR (CDCl₃) δ 0.37 (s, Me, 9 H), 0.40 (s, Me, 9 H), 2.47 (s, Me, 3 H), 7.08−7.31 (m, ArH, 3 H).

Preparation of (Phenyl)[2-(trimethylsilyl)phenyl]iodonium Triflate (10). To a suspension of PhI(OAc)₂ (9.66 g, 30 mmol) in CH₂Cl₂ (60 mL) was added TfOH (5.1 mL, 58 mmol) dropwise at 0 °C, and the mixture was stirred for 2 h. A solution of 1,2-bis(trimethylsilyl)-benzene (6.67 g, 30 mmol) in CH₂Cl₂ (10 mL) was added at 0 °C and the reaction mixture was stirred at room temperature for 2 h. Evaporation of the solvent gave crystals, which were triturated in ether and collected by filtration to give 13.0 g (86%) of (phenyl)[2-(trimethylsilyl)phenyl]iodonium triflate (**10**): mp 140−142 °C (ether−MeOH); ¹H NMR (CDCl₃) δ 0.42 (s, Me, 9 H), 7.26−8.13 (m, ArH, 9 H); ¹³C NMR (CDCl₃) δ 0.1, 114.0, 121.2, 132.2, 133.2, 133.4, 138.5, 139.1, 147.3. Anal. Calcd for C₁₆H₁₈F₃IO₃SSi: C, 38.25; H, 3.61. Found: C, 38.21; H, 3.61.

Preparation of [4-Methyl-2-(trimethylsilyl)phenyl](phenyl)-iodonium Triflate (12). Reaction of 3,4-bis(trimethylsilyl)toluene with a hypervalent iodine reagent system, PhI(OAc)₂/TfOH, similar to that described above gave 11.1 g (72%) of [4-methyl-2-(trimethylsilyl)-

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phenyl](phenyl)iodonium triflate (**12**): mp 128−132 °C (ether−MeOH); ^{1}H NMR (CDCl$_3$) δ 0.39 (s, Me, 9 H), 2.43 (s, Me, 3 H), 7.25−8.03 (m, ArH, 8 H). Anal. Calcd for C$_{17}$H$_{20}$F$_3$IO$_3$SSi: C, 39.54; H, 3.90. Found: C, 39.37; H, 3.90.

Preparation of [2-Methyl-6-(trimethylsilyl)phenyl](phenyl)-iodonium Triflate (13). Similar reaction of 2,3-bis(trimethylsilyl)-toluene with a hypervalent iodine reagent system, PhI(OAc)$_2$/TfOH, as described above gave 12.0 g (78%) of [2-methyl-6-(trimethylsilyl)-phenyl](phenyl)iodonium triflate (**13**): mp 142−144 °C (ether−MeOH); ^{1}H NMR (CDCl$_3$) δ 0.42 (s, Me, 9 H), 2.58 (s, Me, 3 H), 7.26−8.13 (m, ArH, 8 H). Anal. Calcd for C$_{17}$H$_{20}$F$_3$IO$_3$SSi: C, 39.54; H, 3.90. Found: C, 39.44; H, 3.93.

Reaction of (Phenyl)[2-(trimethylsilyl)phenyl]iodonium Triflate 10 with Bu$_4$NF in the Presence of Furan. To a solution of (phenyl)-[2-(trimethylsilyl)phenyl]iodonium triflate **10** (0.502 g, 1.0 mmol) and furan (0.340 g, 5.0 mmol) in CH$_2$Cl$_2$ (3 mL) was added dropwise a THF solution of Bu$_4$NF (1.0 M, 1.2 mL) at 0 °C, and the reaction mixture was stirred at room temperature for 30 min. Then, water was added and the resulting mixture was extracted with CH$_2$Cl$_2$. The organic extracts were dried over anhydrous Na$_2$SO$_4$ and concentrated. The residue was purified by column chromatography on silica gel using CH$_2$Cl$_2$ as the eluent. Evaporation of the solvent gave colorless crystals of 1,4-dihydro-1,4-epoxynaphthalene (**16**):[26] 0.144 g (100%); mp 51−55 °C; ^{1}H NMR (CDCl$_3$) δ 5.69 (s, CH 2 H), 6.94−6.96 (m, ArH, 2 H), 7.00 (s, =CH), 7.22−7.24 (m, ArH, 2 H); ^{13}C NMR (CDCl$_3$) δ: 82.2, 120.2, 124.9, 142.9, 148.9.

Reaction of 10 with KF/18-Crown-6 in the Presence of Furan. To a suspension of KF (3.0 mmol) and 18-Crown-6 (0.6 mmol) in CH$_2$Cl$_2$ (3 mL) was added furan (5.0 mmol) and **10** (0.502 g, 1.0 mmol) at room temperature. After stirring for 3 h, water was added, and the resulting mixture was extracted with CH$_2$Cl$_2$. The organic extracts were dried over anhydrous Na$_2$SO$_4$ and concentrated. The residue was purified by column chromatography on silica gel using CH$_2$Cl$_2$ as the eluent. Evaporation of the solvent gave 0.127 g (88%) of **16**.

Trapping Reaction of Benzyne Generated from 10 with Cyclic Dienes. To a solution of (phenyl)[2-(trimethylsilyl)phenyl]iodonium triflate **10** (0.502 g, 1.0 mmol) and a cyclic diene (5.0 mmol) in CH$_2$-Cl$_2$ (3−7 mL) was added dropwise a THF solution of Bu$_4$NF (1.0 M, 1.2 mL) at 0 °C, and the reaction mixture was stirred at room temperature for 30 min. Water was then added, and the resulting mixture was extracted with CH$_2$Cl$_2$. The organic extracts were dried over anhydrous Na$_2$SO$_4$ and concentrated. The residue was purified by column chromatography on silica gel. The reaction with 2-methylfuran, anthracene, tetraphenylcyclopentadienone, and 1,3-diphenylisobenzo-furan gave the following products.

1-Methyl-1,4-dihydro-1,4-epoxynaphthalene (17):[20] 0.158 g (100%); oil; ^{1}H NMR (CDCl$_3$) δ 1.90 (s, Me, 3 H), 5.60 (s, CH, 1 H), 6.74−7.21 (m, =CH and ArH, 6 H); ^{13}C NMR (CDCl$_3$) δ 15.1, 81.7, 89.3, 118.7, 119.8, 124.6, 124.9, 144.3, 145.5, 150.5, 151.3.

9,10-Dihydro-9,10-o-benzenoanthracene (18):[27] 0.218 g (86%); mp 253−256 °C; ^{1}H NMR (CDCl$_3$) δ 5.41 (s, CH, 2 H), 6.94−7.00 (m, ArH, 6H), 7.34−7.40 (m, ArH, 6 H); ^{13}C NMR (CDCl$_3$) δ 54.1, 123.6, 125.1, 145.2.

1,2,3,4-Tetraphenylnaphthalene (19):[28] 0.432 g (100%); mp 205−206 °C; ^{1}H NMR (CDCl$_3$) δ 6.80−6.89 (m, ArH, 10 H), 7.15−7.27 (m, ArH, 10 H), 7.37−7.40 (m, ArH, 2 H), 7.61−7.66 (m, ArH, 2 H); ^{13}C NMR (CDCl$_3$) δ 125.3, 125.8, 126.4, 126.5, 127.0, 127.5, 131.3 (2 carbons), 132.0, 138.4, 138.9, 139.6, 140.5.

9,10-Diphenyl-9,10-dihydro-9,10-epoxyanthracene (20):[19] 0.346 g (100%); mp 187−188 °C; ^{1}H NMR (CDCl$_3$) δ 6.99−7.04 (m, ArH, 4 H), 7.32−7.68 (m, ArH, 10 H), 7.92−7.95 (m, ArH, 4 H); ^{13}C NMR (CDCl$_3$) δ 90.5, 120.3, 125.6, 126.7, 128.2, 128.7, 135.1, 150.4

Trapping Reaction of 4-Methylbenzyne 22 Generated from 12 with Cyclic Dienes. To a solution of (phenyl)[4-methyl-2-(trimethyl-silyl)phenyl]iodonium triflate **12** (0.516 g, 1.0 mmol) and a cyclic diene (5.0 mmol) in CH$_2$Cl$_2$ (3−7 mL) was added dropwise a THF solution of Bu$_4$NF (1.0 M, 1.2 mL) at 0 °C, and the reaction mixture was stirred

at room temperature for 30 min. Water was then added, and the resulting mixture was extracted with CH$_2$Cl$_2$. The organic extracts were dried over anhydrous Na$_2$SO$_4$ and concentrated. The residue was purified by column chromatography on silica gel. The reaction with furan, 2-methylfuran, anthracene, and tetraphenylcyclopentadienone gave the following products.

1,4-Dihydro-1,4-epoxy-6-methylnaphthalene (21):[20] 0.158 g (100%); oil; ^{1}H NMR (CDCl$_3$) δ 2.25 (s, Me, 3 H), 5.61 (s, CH, 1 H), 5.63 (s, CH, 1 H), 6.70−7.08 (m, =CH and ArH, 5 H); ^{13}C NMR (CDCl$_3$) δ 21.1, 82.1, 82.2, 119.8, 121.5, 125.3, 134.7, 142.8, 143.2, 146.0, 149.2.

1,4-Dihydro-1,6-dimethyl-1,4-epoxynaphthalene and 1,4-dihydro-1,7-dimethyl-1,4-epoxynaphthalene (23): 0.167 g (97%); a 1:1 mixture; oil; ^{1}H NMR (CDCl$_3$) δ 1.89 (s, Me x 2), 2.25 (s, Me), 2.27 (s, Me), 5.54−5.56 (m, CH), 6.69−7.06 (m, =CH and ArH). These isomers could not be separated purely.

9,10-Dihydro-2-methyl-9,10-o-benzenoanthracene (24):[16] 0.166 g (62%); mp 205−206 °C; ^{1}H NMR (CDCl$_3$) δ 2.24 (s, Me, 3 H), 5.36 (s, CH, 1 H), 5.37 (s, CH, 1 H), 6.93−7.40 (m, ArH, 11 H); ^{13}C NMR (CDCl$_3$) δ 21.1, 53.7, 54.1, 123.3, 123.47, 123.51, 124.6, 125.0, 125.1, 125.4, 134.7, 142.5, 145.3, 145.4, 145.5.

6-Methyl-1,2,3,4-tetraphenylnaphthalene (25): 0.351 g (88%); mp 217.5−220.5 °C; ^{1}H NMR (CDCl$_3$) δ 2.37 (s, Me, 3 H), 6.75−7.56 (m, ArH, 23 H); ^{13}C NMR (CDCl$_3$) δ 22.2, 125.9, 126.2, 126.6, 127.0, 127.5, 127.9, 130.5, 131.4, 131.7, 132.3, 135.8, 138.0, 138.2, 138.4, 139.1, 139.9, 140.8, 140.9. Anal. Calcd for C$_{35}$H$_{26}$: C, 94.13; H, 5.87. Found: C, 93.94; H, 5.88.

Trapping Reaction of 3-Methylbenzyne 27 Generated from 13 with Cyclic Dienes. To a solution of (phenyl)[2-methyl-6-(trimethyl-silyl)phenyl]iodonium triflate **13** (0.516 g, 1.0 mmol) and a cyclic diene (5.0 mmol) in CH$_2$Cl$_2$ (3−7 mL) was added dropwise a THF solution of Bu$_4$NF (1.0 M, 1.2 mL) at 0 °C, and the reaction mixture was stirred at room temperature for 30 min. Water was then added and the resulting mixture was extracted with CH$_2$Cl$_2$. The organic extracts were dried over anhydrous Na$_2$SO$_4$ and concentrated. The residue was purified by column chromatography on silica gel. The reaction with furan, 2-*tert*-butylfuran, 2-methylfuran, anthracene, and tetraphenylcyclopentadi-enone gave the following products. The regioisomers obtained in the reaction with 2-*tert*-butylfuran or 2-methylfuran were determined by the observation of NOE between the substituents.

1,4-Dihydro-1,4-epoxy-5-methylnaphthalene (26): 0.158 g (100%); oil; ^{1}H NMR (CDCl$_3$) δ 2.27 (s, Me, 3 H), 5.65 (s, CH, 1 H), 5.76 (s, CH, 1 H), 6.72−7.06 (m, =CH and ArH, 5 H); ^{13}C NMR (CDCl$_3$) δ 18.0, 80.7, 82.4, 117.7, 124.9, 126.6, 129.8, 142.6, 143.1, 147.3, 148.6. Anal. Calcd for C$_{11}$H$_{10}$O: C, 83.52; H, 6.37. Found: C, 83.38; H, 6.30.

1,4-Dihydro-1,5-dimethyl-1,4-epoxynaphthalene and 1,4-dihydro-1,8-dimethyl-1,4-epoxynaphthalene (28):[22] 0.172 g (100%); a 33:67 mixture; oil; ^{1}H NMR (CDCl$_3$) δ 1.89 (s, Me), 2.01 (s, Me), 2.27 (s, Me), 2.34 (s, Me), 5.54 (d, J = 1.8 Hz, CH), 5.70 (d, J = 1.8 Hz, CH), 6.69−7.02 (m, =CH and ArH). These isomers could not be separated purely.

1-*tert*-Butyl-1,4-Dihydro-1,4-epoxy-5-methylnaphthalene and 1-*tert*-butyl-1,4-dihydro-1,4-epoxy-8-methylnaphthalene:[22] 0.154 g (72%); a 30:71 mixture; oil; ^{1}H NMR (CDCl3) δ 1.20 (s, t-Bu), 1.24 (s, t-Bu), 2.22 (s, Me), 2.40 (s, Me), 5.50 (s, CH), 5.67 (s, CH), 6.69−7.18 (m, =CH and ArH). These isomers could not be separated purely.

9,10-Dihydro-1-methyl-9,10-o-benzenoanthracene (29):[21] 0.204 g (76%); mp 189−190 °C; ^{1}H NMR (CDCl$_3$) δ 2.50 (s, Me, 3 H), 5.39 (s, CH, 1 H); ^{13}C NMR (CDCl$_3$) δ 18.5, 50.3, 54.4, 121.4, 123.6, 124.8, 125.0, 125.1, 126.7, 131.8, 143.4, 145.1, 145.2, 145.6. Anal. Calcd for C$_{21}$H$_{16}$: C, 93.99; H, 6.01. Found: C, 93.95; H, 5.96.

5-Methyl-1,2,3,4-tetraphenylnaphthalene (30): 0.398 g (100%); mp 232.5−234 °C; ^{1}H NMR (CDCl$_3$) δ 1.86 (s, Me, 3 H), 6.63−7.46 (m, ArH, 23 H). Anal. Calcd for C$_{35}$H$_{26}$: C, 94.13; H, 5.87. Found: C, 94.01; H, 5.86.

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