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Reaction of Arenes with Iodine in the Presence of Potassium Peroxodisulfate in Trifluoroacetic Acid. Direct and Simple Synthesis of Diaryliodonium Triflates

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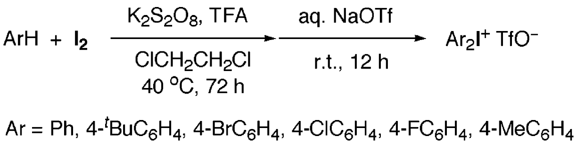

$$\mathrm{ArH} + \mathbf{I_2} \xrightarrow[\substack{\mathrm{ClCH_2CH_2Cl} \\ 40\ ^\circ\mathrm{C},\ 72\ \mathrm{h}}]{\mathrm{K_2S_2O_8,\ TFA}} \xrightarrow[\mathrm{r.t.,\ 12\ h}]{\mathrm{aq.\ NaOTf}} \mathrm{Ar_2I^+\ TfO^-}$$

$\mathrm{Ar} = \mathrm{Ph}, 4\text{-}{}^t\mathrm{BuC_6H_4}, 4\text{-}\mathrm{BrC_6H_4}, 4\text{-}\mathrm{ClC_6H_4}, 4\text{-}\mathrm{FC_6H_4}, 4\text{-}\mathrm{MeC_6H_4}$

Diaryliodonium triflates have been directly prepared by reaction of arenes with elemental iodine in good yields by using $K_2S_2O_8$ and TFA, followed by treatment with NaOTf. This procedure avoids the use of high temperature and severe reaction conditions.

Hypervalent iodine reagents have attracted increasing interest as useful oxidants in organic synthesis due to their low toxicity, ready availability, easy handling, high efficiency, stability to air and moisture, and as an environment-friendly alternative to heavy metal reagents such as lead(IV), thallium(III), and mercury(II). Recently, extensive studies on hypervalent iodine compounds such as (diacetoxyiodo)arenes, [bis(trifluoroacetoxy)-iodo]arenes, [hydroxy(tosyloxy)iodo]arenes, and diaryliodonium salts have been carried out, and their application for organic synthesis has been reviewed.[1] Especially, symmetric and unsymmetric diaryliodonium salts represent an important class of aromatic iodine(III) derivatives. They are used in organic synthesis mostly as arylating reagents for a variety of organic and inorganic nucleophiles[2] and have been applied to the photochemical polymerization process as a photoacid generator[3] and to chemical amplification in imaging systems.[4] In addition, some of the diaryliodonium salts have also shown biological activity.[5] Diaryliodonium salts are generally solid compounds, mostly stable toward heat, oxygen, and humidity; they are mildly light-sensitive and should be stored in the dark, without refrigeration. Many methods have been described for the preparation of symmetric and unsymmetric diaryliodonium salts,[6] but very few of these involve the synthesis of diaryliodonium triflate salts that can be used as a strong acid generator.[3] The methods used so far are generally as follows: (a) One-pot preparation of diaryliodonium triflates through the in situ preparation of a reactive hypervalent iodine(III) reagent from iodosylbenzene and triflic acid and its reaction with aromatic substrates; [7] (b) A convenient synthesis of diaryliodonium triflates via the reaction of (diacetoxyiodo)benzene and triflic acid with aromatic substrates;[8] (c) A direct synthesis of diaryliodonium triflates by the reaction of iodosyl triflate with the trimethylsilyl derivatives of aromatic compounds;[9](d) Synthesis of unsymmetrical diaryliodonium triflates by the treatment of β-(trifyloxy)vinyl iodonium triflates with aryl lithium reagents;[10](e) A generalized synthesis of unsymmetrical functionalized diaryliodonium triflates through the direct reaction of (diacetoxyiodo)-arenes with arenes in a triflic acid or trifluoroacetic acid medium;[11](f) Diaryliodonium triflates were prepared by the reaction of xenon difluoride, triflic acid, iodoarenes, and aromatic compounds.[12]

However, the above methods mostly involve iodoarenes, iodosylarenes, and (diacetoxyiodo)arenes. Considering the useful properties of salts and other derivatives of triflic acid,[13] the development of a simple and efficient procedure for the preparation of diaryliodonium triflates is a desirable goal. The most ideal procedure for diphenyliodonium triflate should involve a straightforward synthesis from benzene and iodine. This procedure gives a direct and efficient method that does

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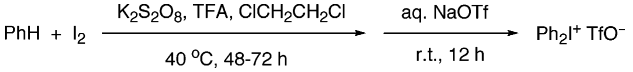
SCHEME 1



$$PhH + I_2 \xrightarrow[40\ ^{\circ}C,\ 48\text{-}72\ h]{K_2S_2O_8,\ TFA,\ ClCH_2CH_2Cl} \xrightarrow[r.t.,\ 12\ h]{aq.\ NaOTf} Ph_2I^+\ TfO^-$$

TABLE 1. Optimization for Preparation of Diphenyliodonium Triflate[a]

entry	benzene (mmol)	I_2 (mmol)	$K_2S_2O_8$ (mmol)	TFA (mL)	$ClCH_2CH_2Cl$ (mL)	time (h)	yield (%)
1	4	0.5	4	9	5	48	48
2	10	0.5	4	9	5	72	58
3	10	0.5	5	9	5	72	66
4	10	0.5	6	9	5	72	64
5	20	0.5	5	9	5	72	45
6	10	0.5	5	10	5	72	71
7	100	5	50	100	50	72	69

[a] The reaction of benzene with iodine was carried out in TFA and 1,2-dichloroethane in the presence of $K_2S_2O_8$ at 40 °C. Then, the reaction mixture was treated with NaOTf solution at room temperature for 12 h.

not contain the step via iodobenzene or the related synthesis. However, to the best of our knowledge, there are no methods for preparing diphenyliodonium triflate directly from benzene and iodine.

Recently, we have reported easy preparation of [bis(trifluoroacetoxy)iodo]arenes, $ArI(OCOCF_3)_2$, from respective iodoarenes in trifluoroacetic acid (TFA), using commercial potassium peroxodisulfate, $K_2S_2O_8$, as the oxidant.[14] $ArI(OCOCF_3)_2$ is a relatively reactive reagent and can undergo arylation reaction to give diaryliodoniun salts. We also found that diaryliodonium salts were formed by the reaction of iodoarenes with aromatic substrates in the presence of $K_2S_2O_8$ in TFA.[15] During the course of our systematic studies on effective and easy preparation of hypervalent iodine compounds, we examined a simpler and more convenient method for preparing $ArI(OCOCF_3)_2$. This simple and convenient system consisted of arenes and molecular iodine. We expected that diaryliodonium salts would be formed when iodoarenes were produced in situ in the reaction of arenes with iodine. Thus, we conducted the reaction of arenes with molecular iodine in the presence of $K_2S_2O_8$ in TFA, followed by treatment with NaOTf. Herein, we wish to report a direct, easy method for the preparation of diphenyliodonium triflate from benzene. Also, we describe an application to *tert*-butylbenzene, toluene, and less reactive halobenzenes.

A simple, easy, and efficient method for the direct preparation of diphenyliodonium triflate, $Ph_2I^+OTf^-$, from benzene and iodine was examined. At first, the reaction of benzene with elemental iodine was conducted in TFA in the presence of commercial $K_2S_2O_8$ as the oxidant at 40 °C, where diphenyliodonium trifluoroacetate $[Ph_2I^+(OCOCF_3)^-]$ was formed. $K_2S_2O_8$ is used as a strong oxidizing agent in many applications. It has the particular advantages of being almost nonhygroscopic, having particularly good storage stability and being easy and safe to handle. 1,2-Dichloroethane was added for dissolving iodine completely. Next, $Ph_2I^+(OCOCF_3)^-$ was treated with aqueous sodium triflate (NaOTf) solution at room temperature to provide the corresponding diphenyliodonium triflate. The outline is shown in Scheme 1.

Table 1 summarizes the results obtained by optimization of the preparation of diphenyliodonium triflate. The reaction of benzene (4 mmol) with iodine (0.5 mmol) was carried out in the presence of $K_2S_2O_8$ (4 mmol) in TFA and 1,2-dichloroethane at room temperature for 48 h. After treatment with aqueous NaOTf, diphenyliodonium triflate was obtained in 48% yield (entry 1). Use of 10 mmol of benzene gave diphenyliodonium triflate in 58% yield (entry 2). Use of 5 mmol of $K_2S_2O_8$ led to better yield, 66%, but further improvement was observed in the case of 6 mmol of $K_2S_2O_8$ (entries 3 and 4). Increase of benzene from 10 to 20 mmol decreased the yield, 45% (entry 5). The best result, 71% yield, was obtained by using benzene (10 mmol), iodine (0.5 mmol), $K_2S_2O_8$ (5 mmol), TFA (10 mL), and 1,2-dichloroethane (5 mL) (entry 6). The direct conversion of benzene to diphenyliodonium triflate can be easily scaled up and has the advantages of $K_2S_2O_8$ outlined above, together with the complete absence of effluent or byproduct problems. When the reaction of benzene (100 mmol) with iodine (5 mmol) was conducted in the presence of $K_2S_2O_8$ (50 mmol) in TFA (100 mL) and 1,2-dichloroethane (50 mL) under the same conditions, diphenyliodonium triflate was obtained in 69% yield (entry 7). No large decrease of the yield was observed even in the case of the 10-fold scale experiment.

As described above, the reaction of benzene with iodine in the presence of $K_2S_2O_8$ initially affords diphenyliodonium trifluoroacetate, which is subject to exchange acetate with triflate to give diphenyliodonium triflate. To confirm the formation of diphenyliodonium trifluoroacetate, we examined the isolation of diphenyliodonium trifluoroacetate. We worked up the reaction mixture without the treatment with aqueous NaOTf solution. After completion of the reaction according to entry 6 in Table 1, the reaction mixture was quenched with water and the product was extracted with CH_2Cl_2. Evaporation of the solvent gave diphenyliodonium trifluoroacetate in 81% yield, as shown in

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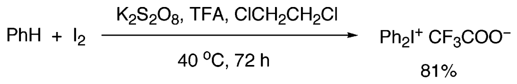
SCHEME 2



SCHEME 3

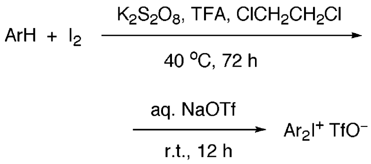
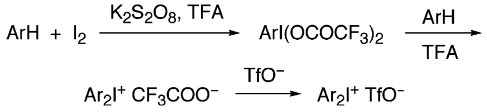


TABLE 2. **Preparation of Diaryliodonium Triflates from Arenes**[a]

entry	arene	product	yield (%)
1	chlorobenzene	$(4\text{-ClC}_6H_4)_2I^+TfO^-$	57
2	bromobenzene	$(4\text{-BrC}_6H_4)_2I^+TfO^-$	54
3	fluorobenzene	$(4\text{-FC}_6H_4)_2I^+TfO^-$	60
4	iodobenzene	$(4\text{-IC}_6H_4)(Ph)I^+TfO^-$	69
5	*tert*-butylbenzene	$(4\text{-}\textit{tert}\text{-BuC}_6H_4)_2I^+TfO^-$	55
6	toluene	$(4\text{-MeC}_6H_4)_2I^+TfO^-$	11

[a] The reaction of an arene (10 mmol) was carried out in TFA (10 mL), 1,2-dichloroethane (5 mL), and iodine (0.5 mmol) in the presence of $K_2S_2O_8$ (5 mmol) at 40 °C for 72 h. Then, the reaction mixture was treated with NaOTf solution (10 mL) at room temperature for 12 h.

SCHEME 4



Scheme 2. This result indicates that diphenyliodonium trifluoroacetate is formed at the first step, and then it is converted to diphenyliodonium triflate by anion exchange.

The presence of $K_2S_2O_8$ was indispensable for this reaction because without its addition the oxidation reactions did not proceed and the starting materials were recovered unchanged. In order to explore the scope of this reaction, we applied it to other aromatic substrates. The outline is shown in Scheme 3. The results are given in Table 2. Interestingly, arenes bearing weakly deactivated groups such as chloro, bromo, and fluoro groups gave diaryliodonium triflates in good yields. However, a similar reaction of iodobenzene did not give bis(4-iodophenyl)iodonium triflate but afforded (4-iodophenyl)(phenyl)iodonium triflate in 69% yield. In the reaction of iodobenzene, it is considered that the iodo group of iodobenzene is oxidized to form [bis(trifluoroacetoxy)iodo]benzene, which reacts with iodobenzene to yield the (4-iodophenyl)(phenyl)iodonium salt. *tert*-Butylbenzene also gave bis(4-*tert*-butylphenyl)iodonium triflate in good yield, but toluene afforded bis(4-methylphenyl)iodonium triflate only in 11% yield. This method was not applicable for electron-rich arenes such as anisole, mesitylene, and *p*-xylene. For example, in the case of anisole, the reaction mixture was quickly oxidized to indicate black color, but no diaryliodonium salts were obtained. This method was not effective for arenes with strong electron-withdrawing groups such as trifluoromethyl and nitro groups due to their decreased reactivity.

From the above results, it is considered that the reaction proceeds with three major fundamental steps: bis(trifluoroacetoxy)iodination, arylation, and anion exchange. The key step is the first bis(trifluoroacetoxy)iodination. The in situ formation of [bis(trifluoroacetoxy)iodo]arenes is a novel direct reaction from arenes and iodine promoted by $K_2S_2O_8$. Although a similar Selectfluor-promoted preparation of difluoroiodoarenes or (diacetoxyiodo)arenes has been reported,[16] there are no reports on the synthesis of [bis(trifluoroacetoxy)iodo]arenes. According to the literature,[16,17] the Selectfluor-promoted reaction seems to be applicable only for electron-rich aromatics. The mechanism on the formation of [bis(trifluoroacetoxy)iodo]arenes is not clear, but it is considered that the mechanism involves the oxidation of iodoarenes by $K_2S_2O_8$ because iodoarenes are efficiently oxidized by $K_2S_2O_8$ in TFA to give [bis(trifluoroacetoxy)iodo]arenes.[14] Once [bis(trifluoroacetoxy)iodo]arenes are formed, they immediately react with arenes to yield diaryliodonium trifluoroacetates.[15] Finally, exchange of anions in the diaryliodonium salts is well recognized and occurs easily.The present method described above covers relatively electron-rich to weakly deactivated aromatic substrates. This method involves fundamental starting materials (simple arenes and elemental iodine, and commercial $K_2S_2O_8$). The simple and convenient procedure for diaryliodonium triflates has a significant advantage over the previous reported ones.

In conclusion, we have demonstrated a novel, simple, and direct method for the preparation of diaryliodonium triflates. The new method gives diaryliodonium triflates in good yields by the reaction of arenes with elemental iodine, $K_2S_2O_8$, TFA, and 1,2-dichloroethane at 40 °C, followed by treatment with NaOTf. Since the present procedure can be scaled up easily, it is expected that this procedure will be used widely for many purposes.

Experimental Section

Optimized Procedure for Preparing Diaryliodonium Triflates from Arenes. A solution of the appropriate arene (10 mmol) in a mixture of molecular iodine (0.5 mmol), TFA (10 mL), and 1,2-dichloroethane (5 mL) was heated with stirring to 40 °C. After dissolving iodine, $K_2S_2O_8$ (5 mmol) was added. The reaction mixture was stirred at that temperature for 72 h. After completion of the reaction, water (20 mL) was added. The resulting precipitates were collected by filtration under reduced pressure, washed with CH_2Cl_2 (10 mL), and discarded. The crude product was obtained by extraction of the filtrate with CH_2Cl_2 (3 × 10 mL), followed by drying (anhydrous Na_2SO_4), filtration, and removal of the solvent by evaporation. The crude product was treated with aqueous NaOTf (ca. 1 M, 10 mL) solution at room temperature for 12 h. The precipitates were collected by filtration under reduced pressure, washed with H_2O (10 mL), and dried in vacuo. Another crop was obtained by extraction of the filtrate with dichloromethane (3 × 10 mL), followed by drying (anhydrous Na_2SO_4), filtration, and removal of the solvent by evaporation. The combined crude product was recrystallized from CH_2Cl_2/hexane.

Large-scale synthesis was conducted for diphenyliodonium triflate in a similar manner. A solution of benzene (7.9 g, 100 mmol) in a mixture of TFA (100 mL), 1,2-dichloroethane (50 mL), and I_2 (1.28 g, 5 mmol) was heated with stirring to 40 °C. After dissolving iodine, $K_2S_2O_8$ (50 mmol) was added, and the stirring was continued for 72 h, followed by treatment with NaOTf (ca. 1 M, 100 mL). Workup of the reaction mixture gave pure product (2.97 g, 69%).

Supporting Information Available: Characterization data for iodonium salts obtained. This material is available free of charge via the Internet at http://pubs.acs.org.

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