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Direct and Convenient Synthesis of [Bis(trifluoroacetoxy)iodo]arenes from Iodoarenes

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An easy, safe, and effective method for preparing [bis(trifluoroacetoxy)iodo]arenes, $ArI(OCOCF_3)_2$, in high yields from some iodoarenes are reported, using a $K_2S_2O_8/CF_3COOH/CH_2Cl_2$ system. This procedure avoids the use of high temperature and severe reaction conditions.

Hypervalent iodine reagents have been widely used as green oxidants in organic synthesis due to their low toxicity, ready availability, easy handling, high efficiency, stability to air and moisture, and them being a safe 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, and [hydroxy(tosyloxy)iodo]arenes have been carried out and their use for organic synthesis has been reported.[1] Among them, [bis(trifluoroacetoxy)iodo]arenes, $ArI(OCOCF_3)_2$, are fundamental reagents, potent and often chemoselective oxidants, and widely used in modern organic synthesis. They are also used for facile transformations of alkynes, ketones, and sulfur compounds, phenolic oxidation, oxidation of nitrogen compounds, oxidative biaryl coupling, etc.[2] Several methods are available for the preparation of $ArI(OCOCF_3)_2$. The methods used so far are generally as follows:

(a) Reaction of arenes with tris(trifluoroacetoxy)iodine.[3]

(b) Oxidation of iodoarenes with $HNO_3/(CF_3CO)_2O$,[4] xenon bis(trifluoroacetate),[5] sodium percarbonate/$(CF_3CO)_2O/CH_2Cl_2$,[6] and trifluoroperoxyacetic acid.[7]

(c) Reaction of iodosylarenes with $Me_3Si(OCOCF_3)$.[8]

(d) Ligand exchange of (diacetoxyiodo)arenes by dissolving with heating in CF_3CO_2H.[9]

(e) Reaction of (dichloroiodo)arenes with $AgOCOCF_3$.[10]

The most general synthetic method of $ArI(OCOCF_3)_2$ for laboratory use is to dissolve (diacetoxyiodo)arenes in CF_3CO_2H with heating.[9] However, there is yet room for improvement in this method because contamination with (diacetoxyiodo)arenes decreases the yields. In the reaction of $I(OCOCF_3)_3$ with arenes,[3] the reactivity of the arenes decreases in the order: p-$Me_2C_6H_4$ > MePh > PhH > PhCl > $PhCF_3$. However, this reaction does not work in the case of nitrobenzene due to its lack of reactivity.

Direct oxidation of iodoarenes to $ArI(OCOCF_3)_2$ is considered as a convenient method. The oxidation of iodoarenes by concd HNO_3 and $(CF_3CO)_2O$ appears only for deactivated substrates.[4] However, this procedure is accompanied with a vigorous evolution of toxic nitrogen oxides. In the sodium percarbonate method,[6] it is not suitable for the preparation of $NO_2C_6H_4I(OCOCF_3)_2$ isomers, and m-$CF_3C_6H_4I(OCOCF_3)_2$ is obtained in only 40% yield. The oxidation of iodoarenes with trifluoroperoxyacetic acid seems to be the most suitable method,[7] but preparation of trifluoroperoxyacetic acid requires 80% H_2O_2, which is not available commercially. Here, we wish to report an alternative, direct method for the preparation of [bis(trifluoroacetoxy)iodo]arenes from iodoarenes.

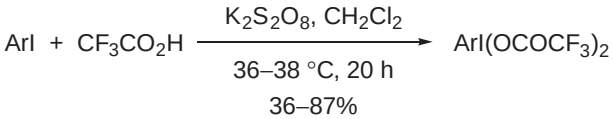
Recently, we have devised a simple, easy, and efficient method for the direct preparation of $ArI(OCOCF_3)_2$ from the respective iodoarenes in CF_3CO_2H, using commercial potassium peroxodisulfate, $K_2S_2O_8$, as the oxidant. For example, the reaction of iodobenzene in a mixed solvent of CF_3CO_2H and CH_2Cl_2 in the presence of $K_2S_2O_8$ at 36–38 °C for 20 h gave [bis(trifluoroacetoxy)iodo]benzene in 76% yield. The results are given in Table 1. $K_2S_2O_8$ is used as a strong oxidizing agent in many applications. It has the particular advantages of being almost non-hygroscopic, having a particular good storage stability, and being easy and safe to handle. The oxidation of iodoarenes to [bis(trifluoroacetoxy)iodo]arenes can be easily scaled up to give the advantages of $K_2S_2O_8$ outlined above, together with the complete absence of effluent or by-product problems. The essence of our novel method is described in Scheme 1.

The oxidative reactions shown in Scheme 1 were carried out at 36–38 °C in CF_3CO_2H. CH_2Cl_2 was added to dissolve iodoarenes completely. The presence of $K_2S_2O_8$ (in stoichiometric

Table 1. Preparation of [Bis(trifluoroacetoxy)iodo]arenes from Iodoarenes[a)]

Entry	Iodoarene	Yield/%
1	C_6H_5I	76
2	4-ClC_6H_4I	87
3	3-$CF_3C_6H_4I$	82
4	3-$NO_2C_6H_4I$[b)]	72
5	4-$NO_2C_6H_4I$[b)]	71
6	4-FC_6H_4I	71
7	4-BrC_6H_4I	75
8	3,5-$(CF_3)_2C_6H_3I$	36
9	4-ClC_6H_4I[c)]	81
10	4-ClC_6H_4I[c),d)]	79

a) The reaction of an iodoarene (1 mmol) was carried out at 20 h at 36–38 °C in the presence of $K_2S_2O_8$ (4 mmol) in CF_3CO_2H (9 mL) and CH_2Cl_2 (2 mL). b) CH_2Cl_2 (5 mL) was added. c) 1-Chloro-4-iodobenzene (5 mmol), $K_2S_2O_8$ (20 mmol), CF_3CO_2H (45 mL), and CH_2Cl_2 (10 mL) were added. d) CF_3CO_2H (30 mL) was used.



Ar = C_6H_5, 4-ClC_6H_4, 3-$CF_3C_6H_4$, 3-$NO_2C_6H_4$, 4-$NO_2C_6H_4$, 4-FC_6H_4, 4-BrC_6H_4, 3,5-$(CF_3)_2C_6H_3$

Scheme 1.

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quantities) in the reaction mixture was indispensable, because without its addition the oxidation reactions did not proceed. Iodoarenes bearing strong electron-withdrawing groups at the meta and para positions gave $ArI(OCOCF_3)_2$ in good yields, but the reaction of 1,3-bis(trifluoromethyl)-5-iodobenzene resulted in a low yield (36%) due to its lower reactivity. This method was not applicable for iodoarenes with strong electron-donating groups. For example, 4-iodotoluene and iodoanisoles were quickly oxidized in the reaction mixtures, but the reaction resulted in the decomposition to tarry products.

In conclusion, we have developed a new (or considerably improved) preparative procedure, which is easy and cheap. The new method gives [bis(trifluoroacetoxy)iodo]arenes in high yields by the reaction of iodoarenes with $K_2S_2O_8$ in CF_3CO_2H and CH_2Cl_2 at 36–38 °C. Because of its simplicity and convenience, we are sure that the present method will continue to attract significant research activity in the future.

Experimental

General. Melting points were determined with a Yanaco micro-melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-AL300 spectrometer and the chemical shifts were expressed in parts per million downfield from tetramethylsilane. Elemental analysis was conducted by the Service Center of the Elemental Analysis of Organic Compounds, Faculty of Science, Kyushu University.

Preparation of [Bis(trifluoroacetoxy)iodo]arenes from Iodoarenes. A solution of an appropriate iodoarene (1 mmol) in a mixture of CF_3CO_2H (9 mL) and CH_2Cl_2 (2 mL) was heated with stirring to 36–38 °C. Next, $K_2S_2O_8$ (4 mmol) was added portionwise over 10 min and the stirring was continued until TLC analysis indicated completion of the reaction. Reaction times needed 20 h. After completion of the reaction, water (10 mL) was added. The precipitated product was 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 dichloromethane (3 × 10 mL), followed by drying (anhydrous Na_2SO_4), filtration, and removal of the solvent by evaporation under reduced pressure. The crude product was washed with hexane (10 mL) and purified by recrystallization from CF_3CO_2H/hexane.

Large scale synthesis was conducted for 1-[bis(trifluoroacetoxy)iodo]-4-chlorobenzene in a similar manner. A solution of 1-chloro-4-iodobenzene (1.196 g, 5 mmol) in a mixture of CF_3COOH (45 mL) and CH_2Cl_2 (10 mL) was heated with stirring to 36–38 °C. Next, $K_2S_2O_8$ (20 mmol) was added portionwise over 20 min and the stirring was continued for 20 h. Workup of the reaction mixture gave the purified product (1.881 g, 81%). When CF_3CO_2H was decreased from 45 to 30 mL under the above conditions, the yield was slightly decreased (1.841 g, 79%).

[Bis(trifluoroacetoxy)iodo]benzene: 0.335 g (76%); mp 119–120 °C (lit.,[3] mp 120–121 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (t, J = 8 Hz, 1H, ArH), 7.74 (t, J = 8 Hz, 2H, ArH), 8.20 (d, J = 8 Hz, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.07 (q, J_{CF} = 41 Hz, *C*OCF$_3$), 135.14, 133.67, 132.02, 122.76, 112.84 (q, J_{CF} = 286 Hz, CO*C*F$_3$).

1-[Bis(trifluoroacetoxy)iodo]-4-chlorobenzene: 0.404 g (87%); mp 129–130 °C (lit.,[9b] mp 131–133 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, J = 9 Hz, 2H, ArH), 8.14 (d, J = 9 Hz, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.15 (q, J_{CF} = 41 Hz, *C*OCF$_3$), 140.84, 136.56, 132.38, 119.59, 112.82 (q, J_{CF} = 286 Hz, CO*C*F$_3$).

1-[Bis(trifluoroacetoxy)iodo]-3-(trifluoromethyl)benzene: 0.416 g (82%); mp 96–97 °C (lit.,[3] mp 99–100 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (t, J = 8 Hz, 1H, ArH), 8.0 (d, J = 8 Hz, 1H, ArH), 8.39 (d, J = 8 Hz, 1H, ArH), 8.44 (s, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.23 (q, J_{CF} = 41 Hz, *C*OCF$_3$), 138.12, 134.22 (q, J_{CF} = 34 Hz, *C*CF$_3$), 132.51, 131.82 (q, J_{CF} = 4 Hz, *C*CCF$_3$), 130.42 (q, J_{CF} = 4 Hz, *C*CCF$_3$), 122.30 (q, J_{CF} = 271 Hz, C*C*F$_3$), 121.79, 112.84 (q, J_{CF} = 286 Hz, CO*C*F$_3$).

1-[Bis(trifluoroacetoxy)iodo]-3-nitrobenzene: 0.347 g (72%); mp 143–144 °C (lit.,[4] mp 143 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (t, J = 8 Hz, 1H, ArH), 8.51 (d, J = 8 Hz, 1H, ArH), 8.55 (d, J = 8 Hz, 1H, ArH), 9.04 (s, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.17 (q, J_{CF} = 43 Hz, *C*OCF$_3$), 149.29, 141.02, 133.27, 130.77, 128.79, 121.42, 114.54 (q, J_{CF} = 282 Hz, CO*C*F$_3$).

1-[Bis(trifluoroacetoxy)iodo]-4-nitrobenzene: 0.341 g (71%); mp 158–159 °C (lit.,[4] mp 161 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41–8.49 (m, 4H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.03 (q, J_{CF} = 44 Hz, *C*OCF$_3$), 150.39, 136.31, 126.95, 126.83, 114.22 (q, J_{CF} = 284 Hz, CO*C*F$_3$).

1-[Bis(trifluoroacetoxy)iodo]-4-fluorobenzene: 0.319 g (71%); mp 94–96 °C (lit.,[6] mp 103–105 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (dd, J = 8, 9 Hz, 2H, ArH), 8.24 (dd, J = 5, 9 Hz, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.31 (d, J_{CF} = 259 Hz, *C*F), 161.17 (q, J_{CF} = 41 Hz, *C*OCF$_3$), 138.25 (q, J_{CF} = 9 Hz, *C*CCF), 119.76 (q, J_{CF} = 23 Hz, *C*CF), 116.38, 112.83 (q, J_{CF} = 286 Hz, CO*C*F$_3$).

1-[Bis(trifluoroacetoxy)iodo]-4-bromobenzene: 0.384 g (75%); mp 125–127 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, J = 9 Hz, 2H, ArH), 8.05 (d, J = 9 Hz, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.18 (q, J_{CF} = 41 Hz, *C*OCF$_3$), 136.53, 135.29, 129.23, 120.45, 112.82 (q, J_{CF} = 286 Hz, CO*C*F$_3$). Found: C, 23.48; H, 0.77%. Calcd for $C_{10}H_4BrF_6IO_4$: C, 23.60; H, 0.79%.

1-[Bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl)benzene: 0.205 g (36%); mp 121–123 °C (lit.,[7] mp 83 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (s, 1H, ArH), 8.75 (s, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.76 (q, J_{CF} = 38 Hz, *C*OCF$_3$), 134.81 (q, J_{CF} = 4 Hz, *C*CCF$_3$), 134.49 (q, J_{CF} = 34 Hz, *C*CF$_3$), 126.54 (q, J_{CF} = 4 Hz, *C*CCF$_3$) 123.57 (q, J_{CF} = 271 Hz, C*C*F$_3$), 123.29, 115.55 (q, J_{CF} = 287 Hz, CO*C*F$_3$).

References

1 Reviews on organohypervalent iodine compounds and their applications in organic synthesis: a) A. Varvoglis, *Chem. Soc. Rev.* **1981**, *10*, 377. b) E. B. Merkushev, *Russ. Chem. Rev. (Engl. Transl.)* **1987**, *56*, 826. c) M. Ochiai, *Rev. Heteroat. Chem.* **1989**, *2*, 92. d) R. M. Moriarty, R. K. Vaid, G. F. Koser, *Synlett* **1990**, 365. e) R. M. Moriarty, R. K. Vaid, *Synthesis* **1990**, 431. f) A. Varvoglis, *The Organic Chemistry of Polycoordinated Iodine*, VCH, Weinheim, **1992**. g) P. J. Stang, *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 274. h) O. Prakash, N. Sainai, P. K. Sharma, *Synlett* **1994**, 221. i) P. J. Stang, V. V. Zhdankin, *Chem. Rev.* **1996**, *96*, 1123. j) T. Umemoto, *Chem. Rev.* **1996**, *96*, 1757. k) Y. Kita, T. Takada, H. Toma, *Pure Appl. Chem.* **1996**, *68*, 627. l) A. Varvoglis, *Hypervalent Iodine in Organic Synthesis*, Academic Press, San Diego, **1997**. m) T. Kitamura, Y. Fujiwara, *Org. Prep. Proced. Int.* **1997**, *29*, 409. n) A. Varvoglis, *Tetrahedron* **1997**, *53*, 1179. o) T. Muraki, H. Togo, M. Yokoyama, *Rev. Heteroat. Chem.* **1997**, *17*, 213. p) H. Togo, Y. Hoshina, G. Nogami, M. Yokoyama, *Yuki Gosei Kagaku Kyokaishi* **1997**, *55*, 90. q) V. V. Zhdankin, *Rev. Heteroat. Chem.* **1997**, *17*, 133. r) A. Kirschning, *J. Prakt. Chem./Chem.-Ztg.* **1998**, *340*, 184.

s) R. M. Moriarty, O. Prakash, *Adv. Heterocycl. Chem.* **1998**, *69*, 1. t) A. Kirschning, *Eur. J. Org. Chem.* **1998**, 2267. u) V. V. Zhdankin, P. J. Stang, *Tetrahedron* **1998**, *54*, 10927. v) A. Varvoglis, S. Spyroudis, *Synlett* **1998**, 221. w) Y. Kita, M. Egi, T. Takada, H. Thoma, *Synthesis* **1999**, 885. x) T. Wirth, V. H. Hirt, *Synthesis* **1999**, 1271. y) V. V. Grushin, *Chem. Soc. Rev.* **2000**, *29*, 315. z) M. Ochiai, Y. Kitagawa, *Yuki Gosei Kagaku Kyokaishi* **2000**, *58*, 1048. aa) G. Pohnert, *J. Prakt. Chem.* **2000**, *342*, 731. bb) S. S. Chaudhari, *Synlett* **2000**, 278. cc) T. Wirth, *Angew. Chem., Int. Ed.* **2001**, *40*, 2812. dd) H. Togo, M. Katohgi, *Synlett* **2001**, 565. ee) V. V. Zhdankin, P. J. Stang, *Chem. Rev.* **2002**, *102*, 2523. ff) H. Togo, K. Sakuratani, *Synlett* **2002**, 1966. gg) *Hypervalent Iodine Chemistry: Modern Developments in Organic Synthesis*, ed. by T. Wirth, Springer-Verlag, Berlin, **2003**. hh) H. Thoma, Y. Kita, *Adv. Synth. Catal.* **2004**, *346*, 111. ii) H. Thoma, Y. Kita, *Yuki Gosei Kagaku Kyokaishi* **2004**, *62*, 116. jj) T. Wirth, *Angew. Chem., Int. Ed.* **2005**, *44*, 3656.

2 Applications of [bis(trifluoroacetoxy)iodo]arenes in organic synthesis: a) Y. Tamura, T. Yakura, H. Tohma, K. Kikuchi, Y. Kita, *Synthesis* **1989**, 126. b) Y. Kita, H. Tohma, K. Hatanaka, T. Takada, S. Fujita, S. Mitoh, H. Sakurai, S. Oka, *J. Am. Chem. Soc.* **1994**, *116*, 3684. c) T. Takada, M. Arisawa, M. Gyoten, R. Hamada, H. Tohma, Y. Kita, *J. Org. Chem.* **1998**, *63*, 7698. d) R. M. Moriarty, B. A. Berglund, R. Penmasta, *Tetrahedron Lett.* **1992**, *33*, 6065. e) Y. Tamura, T. Yakura, Y. Shirouchi, J. Haruta, *Chem. Pharm. Bull.* **1986**, *34*, 1061. f) G. Stork, K. Zhao, *Tetrahedron Lett.* **1989**, *30*, 287. g) R. Benhida, P. Blanchard, J. L. Fourrey, *Tetrahedron Lett.* **1998**, *39*, 6849. h) S. V. Ley, O. Schucht, A. W. Thomas, P. J. Murray, *J. Chem. Soc., Perkin Trans. 1* **1999**, 1251. i) Y. Kita, T. Yakura, H. Terashi, J. Haruta, Y. Tamura, *Chem. Pharm. Bull.* **1989**, *37*, 891. j) K. Kanematsu, S. Morita, S. Fukushima, E. Osawa, *J. Am. Chem. Soc.* **1981**, *103*, 5211. k) Y. Kita, H. Thoma, M. Inagaki, K. Hatanaka, *Heterocycles* **1992**, *33*, 503. l) B. D. Gates, P. Dalidowicz, A. Tebben, A. Wang, J. S. Swenton, *J. Org. Chem.* **1992**, *57*, 2135. m) G. M. Loudon, A. S. Radhakrishna, M. R. Almond, J. K. Blodgett, R. H. Boutin, *J. Org. Chem.* **1984**, *49*, 4272. n) Y. Kikugawa, M. Kawase, *Chem. Lett.* **1990**, 581. o) Y. Kita, T. Takada, S. Mihara, H. Tohma, *Synlett* **1995**, 211. p) E. B. Merkushev, N. D. Simakhina, G. M. Koveshnikova, *Synthesis* **1980**, 486. q) S. Spyroudis, A. Varvoglis, *J. Chem. Soc., Chem. Commun.* **1979**, 615. r) O. V. Sing, *Org. Prep. Proced. Int.* **1993**, *25*, 693.

3 I. I. Maletina, V. V. Orda, L. M. Yagupolskii, *J. Org. Chem. USSR (Engl. Transl.)* **1974**, *10*, 294.

4 L. M. Yagupolskii, I. I. Maletina, N. V. Kondratenko, V. V. Orda, *Synthesis* **1977**, 574.

5 T. M. Kasumov, V. K. Brel, Y. K. Grishin, N. S. Zefirov, P. J. Stang, *Tetrahedron* **1997**, *53*, 1145.

6 P. Kazmierczak, L. Skulski, *Molecules* **2002**, *7*, 810.

7 V. V. Zhdankin, M. C. Scheuller, P. J. Stang, *Tetrahedron Lett.* **1993**, *34*, 6853.

8 N. S. Zefirov, S. O. Safronov, A. A. Kaznacheev, V. V. Zhdankin, *J. Org. Chem. USSR (Engl. Transl.)* **1989**, *25*, 1807.

9 a) S. Spyroudis, A. Varvoglis, *Synthesis* **1975**, 445. b) J. D. White, G. Caravatti, T. B. Kline, E. Edstrom, K. C. Rice, A. Brossi, *Tetrahedron* **1983**, *39*, 2393.

10 N. W. Alcock, T. C. Waddington, *J. Chem. Soc.* **1963**, 4103.