Simple and Practical Method for Preparation of [(Diacetoxy)iodo]arenes with Iodoarenes and *m*-Chloroperoxybenzoic Acid

Masataka Iinuma, Katsuhiko Moriyama, Hideo Togo*

Graduate School of Science, Chiba University, Yayoi-cho 1-33, Inage-ku, Chiba 263-8522, Japan Fax +81(43)2902792; E-mail: togo@faculty.chiba-u.jp

Received: 23.08.2012; Accepted after revision: 11.09.2012

Abstract: Various [(diacetoxy)iodo]arenes bearing 4-methylphenyl, phenyl, 4-nitrophenyl, 3-nitrophenyl, 4-cyanophenyl, 4-bromophenyl, 4-methoxycarbonyphenyl, 3,5-bis(trifluoromethyl)phenyl, and 4-(N,N,N-trimethylammonium)methylphenyl groups were efficiently prepared by the treatment of iodoarenes with *m*-chloroperoxybenzoic acid in acetic acid. The great advantage of the present method is the easy preparation and isolation of [(diacetoxy)iodo]arenes bearing electron-withdrawing groups, such as 4-nitro, 4-cyano, 4-methoxycarbonyl, and 3,5-bis(trifluoromethyl) groups, on the aromatic ring.

Key words: [(diacetoxy)iodo]arene, *m*-chloroperoxybenzoic acid, iodoarene, oxidation, acetic acid, electron-deficient aromatic ring

Hypervalent iodine reagents have received considerable attention for use in organic synthesis due to their nonmetallic and less toxic nature, making them environmentally benign as well as their excellent oxidation ability with high chemoselectivity.¹ Especially [(diacetoxy)iodo]benzene (DIB) is one of the most typical and well-used hypervalent iodine reagents and can be used for various oxidative reactions.² As typical and practical methods for the preparation of [(diacetoxy)iodo]arenes, they are generally prepared by the reaction of iodoarenes with peracetic acid,^{2a} which is generated from the reaction of acetic anhydride and hydrogen peroxide, and with sodium peroxoborate tetrahydrate (NaBO₃·4H₂O),^{3a} as less toxic and direct methods. Another method for the preparation of [(diacetoxy)iodo]arenes involves the two-step conversion of iodoarenes with CrO₃ in a mixture of sulfuric acid and acetic anhydride, followed by the treatment with ammonium acetate.^{3b} This method has a strong oxidation ability furnishing [(diacetoxy)iodo]arenes bearing electron-withdrawing groups, such as 4-nitro and 4-cyano groups, in good yields. However, it requires two steps and CrO₃ is highly toxic. Recently, the preparation of [(diacetoxy)iodo]arenes from the reaction of iodoarenes with potassium peroxodisulfate $(K_2S_2O_8)$ in a mixture of sulfuric acid and acetic acid was reported as another less toxic method.^{3c} However, the preparation of [(diacetoxy)iodo]arenes bearing electron-deficient aromatic groups, such as 4-nitro[(diacetoxy)iodo]benzene, 4-cyano[(diacetoxy)iodo]-4-methoxycarbonyl[(diacetoxy)iodo]benzene, benzene, and 3,5-bis(trifluoromethyl)-1-[(diacetoxy)iodo]benzene, with peracetic acid,^{2a} sodium peroxoborate in acetic

SYNLETT 2012, 23, 2663–2666 Advanced online publication: 09.10.2012

DOI: 10.1055/s-0032-1317345; Art ID: ST-2012-U0705-L

© Georg Thieme Verlag Stuttgart · New York

acid,^{3a} or potassium peroxodisulfate^{3c} is very difficult and generally, the yields of [(diacetoxy)iodo]arenes bearing those electron-withdrawing groups are extremely low even if the reactions are carried out under heating conditions for a long reaction time. Recently, the preparation of [bis(trifluoroacetoxy)iodo]arenes bearing electron-withdrawing groups, such as 4-nitro, 3-nitro, and 4-trifluoro-methyl groups on the aromatic ring, with iodoarenes and Oxone[®] in trifluoroacetic acid was reported.⁴

On the other hand, recently, in situ formation of hypervalent iodines from the reaction of iodobenzene and m-chloroperoxybenzoic acid (MCPBA) for use in organic synthesis has become very popular.⁵ We previously reported the direct preparation of [(hydroxy)(tosyloxy)iodolarenes from the reaction of iodoarene and PTSA·H₂O with MCPBA,^{6a} the α-tosyloxylation of ketones with iodobenzene, PTSA·H₂O, and MCPBA,^{6b-d} the preparation of oxazoles from ketones with nitriles, iodobenzene, MCPBA, and TfOH,6e,f and the formation of benzosultams from 2-arylethanesulfonamides, iodobenzene, and MCPBA.^{6g,h} During this study, we found that [(diacetoxy)iodo]arenes can be isolated by the reaction of iodoarenes with MCPBA in acetic acid, and the products can be obtained by simple precipitation and subsequent filtration, after chloroform extraction of the reaction mixture. The great advantage of the present method is that [(diacetoxy)iodo]arenes bearing electron-withdrawing groups on the aromatic ring, such as 4-nitro, 3-nitro, 4-cyano, 4-methoxycarbonyl, 3,5-bis(trifluoromethyl), and 4-(N,N,N-trimethylammonium) methyl group, can be prepared in good yields by the simple experimental procedure. It is well known that MCPBA is a stronger oxidant than peracetic acid, because the 3-chlorophenyl group is an electron-withdrawing group connected to the peracid group in MCPBA.

Thus, to a solution of 4-iodonitrobenzene (1c) in acetic acid was added MCPBA, and the mixture was stirred at 55 °C for 48 hours. After the reaction, water was added to the mixture, and 4-nitro[(diacetoxy)iodo]benzene (2c) was extracted with chloroform. After being dried over Na₂SO₄, filtration, and removal of the solvent, diethyl ether and hexane were added to the residue to provide 4nitro[(diacetoxy)iodo]benzene (2c) in 81% yield as a pure isolated product.⁷ 4-Nitro[(diacetoxy)iodo]benzene could not be obtained by the peracetic acid method and the peroxoborate tetrahydrate method, respectively, in our study, due to the lower oxidation ability of those oxidants compared to MCPBA. The reaction progress was easily

monitored by TLC. When 4-iodotoluene (1a) and iodobenzene (1b), which are much more reactive than 4-iodonitrobenzene (1c), were used, each mixture of 4iodotoluene or iodobenzene with MCPBA in acetic acid was stirred at room temperature to provide 4-[(diacetoxy)iodo]toluene (2a) in 71% yield or [(diacetoxy)iodo]benzene (2b) in 83% yield, as a pure isolated product (Table 1, entries 1-3). Other [(diacetoxy)iodo]arenes could be obtained in good yields by the same procedure (Table 1, entries 4–9). Thus, using this method, both [(diacetoxy)iodo]arenes bearing an electron-deficient aromatic group, such as 4-nitrophenyl, 3-nitrophenyl, 4cyanophenyl, 4-methoxycarbonylphenyl, 3,5-bis(trifluoromethyl)phenyl, and 4-(*N*,*N*,*N*-trimethylammonium)methylphenyl, and [(diacetoxy)iodo]benzene bearing an electron-rich aromatic group, such as 4-methylphenyl, could be obtained in good yields by the same procedure, although the reaction temperature and the reaction time would depend on the reactivity of the substrates.

 Table 1
 Preparation of [(Diacetoxy)iodo]arenes with Iodoarenes and MCPBA

Ar—I	AcOH temp time	→ Ar-	−l(OAc)₂		
1	, toor i, tomp, time		2		
Entry	Ar	Temp (°C)	Time (h)	Product 2	Yield (%) ^a
1	Me	r.t.	24	2a	71
2		r.t.	15	2b	83
3	O ₂ N	55	48	2c	81
4	$\frac{1c}{O_2N}$	55	24	2d	78
5	NC Le	55	9	2e	80
6	Br If	r.t.	24	2f	76

 Table 1
 Preparation of [(Diacetoxy)iodo]arenes with Iodoarenes and MCPBA (continued)

A.c. 1	MCPBA (1.1 equiv)	- Ar-	—I(OAc)a		
1	AcOH, temp, time	- 1	2		
Entry	Ar	Temp (°C)	Time (h)	Product 2	Yield (%) ^a



^a Isolated yield.

QAc

^b Product was compound 2j.

2

1-Acetoxy-1,2-benziodoxole-3(1H)-one, a cyclic trivalent iodine, could also be obtained from 2-iodobenzoic acid with MCPBA in good yield (Table 1, entry 10). When the present reaction was carried out with 20 mmol of 4-iodonitrobenzene with MCPBA at 55 °C, 4-nitro[(diacetoxy)iodo]benzene was obtained in over 80% yield. Thus, the scale-up preparation of these [(diacetoxy)-iodo]arenes can be carried out easily.

The chemistry of 4-nitro[(diacetoxy)iodo]benzene (**2c**), which may has a stronger oxidation ability than DIB (**2b**), has not been studied well. Recently, the oxidative deamination of (*N*,*N*-diisopropylamino)methylarenes with DIB at 60 °C to produce aromatic aldehydes was reported.⁸ Thus, we compared the reactivity of 4-nitro[(diacetoxy)iodo]benzene (**2c**) and DIB (**2b**) for the oxidative deamination of (*N*,*N*-diisopropylamino)methylarenes to produce aromatic aldehydes at room temperature, as shown in Table 2. The results indicate that 4-nitro[(diacetoxy)iodo]benzene (**2c**) is a more effective reagent than DIB (**2b**) for the oxidative deamination of (*N*,*N*-diisopropylamino) for the oxidative deamination of (**2c**) is a more effective reagent than DIB (**2b**) for the oxidative deamination of (*N*,*N*-diisopropylamino) for the oxidative deamination of (*N*,*N*-diacetoxy) here a more effective reagent than DIB (**2b**) for the oxidative deamination of (*N*,*N*-diacetoxy) here a more effective reagent than DIB (**2b**) for the oxidative deamination of (*N*,*N*-diacetoxy) here a more effective reagent than DIB (**2b**) for the oxidative deamination of (*N*,*N*-diacetoxy) here a more effective reagent than DIB (**2b**) for the oxidative deamination of (*N*,*N*-diacetoxy) here a more effective reagent than DIB (**2b**) for the oxidative deamination of (*N*,*N*-diacetoxy) here a more effective reagent than DIB (**2b**) for the oxidative deamination of (*N*,*N*-diacetoxy) here a more effective reagent than DIB (**2b**) for the oxidative deamination of (*N*,*N*-diacetoxy) here a more effective reagent than DIB (**2b**) for the oxidative deamination of (*N*,*N*-diacetoxy) here a more effective reagent than DIB (**2b**) for the oxidative deamination of (*N*,*N*-diacetoxy) here a more effective reagent than DIB (**2b**) for the oxidative deamination of (*N*,*N*-diacetoxy) here a more effective reagent than DIB (**2b**) for the oxidative deamination of (*N*,*N*-diacetoxy) here a more effective reagent than DIB (**2b**) for the oxidative deami

Ar N	oxidant (1.4 equiv NaHCO ₃ (1.2 equiv CHCl ₃ , r.t., 2 h	r), iv) → Ar ∕o	
Entry	Ar	Oxidant	Yield (%) ^a
1		2b	48
2		2c	95
3	Me	2b	45
4		2c	91
5	O ₂ N	2b	51
6		2c	92

^a Isolated yield.

propylamino)methylarenes to give the corresponding aromatic aldehydes in good yields, while DIB (2b) is not effective at room temperature. Thus, 4-nitro[(diacetoxy)iodo]benzene (2c) has a stronger oxidation ability than DIB (2b). We believe the wide synthetic utility of 4-nitro[(diacetoxy)iodo]benzene (2c) compared to DIB (2b) will open doors to a new route in organic synthesis.

In conclusion, various [(diacetoxy)iodo]arenes bearing 4-methylphenyl, phenyl, 4-nitrophenyl, 3-nitrophenyl, 4-cyanophenyl, 4-bromophenyl, 4-methoxycarbonylphenyl, 3,5-bis(trifluoromethyl)phenyl, and 4-(N,N,N-trimethylammonium)methylphenyl groups were efficiently prepared by the treatment of iodoarenes with MCPBA in acetic acid. The scale-up preparation of [(diacetoxy)iodo]arenes is easily accomplished. The great advantage of the present method is the easy preparation and isolation of [(diacetoxy)iodo]arenes bearing electron-withdrawing groups, such as 4-nitro, 3-nitro, 4-cyano, 4-methoxycarbonyl, and 4-(N,N,N-trimethylammonium)methyl groups.

Acknowledgement

Financial support in the form of a Grant-in-Aid for Scientific Research (No. 20550033) from the Ministry of Education, Culture, Sports, Science, and Technology in Japan and the Iodine Research Project in Chiba University is gratefully acknowledged.

References and Notes

(1) Recent reviews: (a) Togo, H.; Katohgi, M. Synlett 2001, 565. (b) Zhdankin, V. V.; Stang, P. J. Chem Rev. 2002, 102, 2523. (c) Stang, P. J. J. Org. Chem. 2003, 68, 2997. (d) Tohma, H.; Kita, Y. Adv. Synth. Catal. 2004, 346. (e) Moriarty, R. M. J. Org. Chem. 2005, 70, 2895. (f) Wirth, T. Angew. Chem. Int. Ed. 2005, 44, 3656. (g) Richardson, R. D.; Wirth, T. Angew. Chem. Int. Ed. 2006, 45, 4402. (h) Ochiai, M. Chem. Rev. 2007, 7, 12. (i) Zhdankin, V. V.; Stang, P. J. Chem. Rev. 2008, 108, 5299. (j) Merritt, E. A.; Olofsson, B. Angew. Chem. Int. Ed. 2009, 48, 9052. (k) Ochiai, M.; Miyamoto, K. Eur. J. Org. Chem. 2008, 4229. (1) Dohi, T.; Kita, Y. Chem.

Commun. 2009, 2073. (m) Uyanik, M.; Ishihara, K. Chem.

1 (2)

(3)

(4)

(5)

5 (7)

(6)

<i>Commun.</i> 2009 , 2086. (n) Pouységu, L.; Deffieux, D.;
Quideau, S. <i>Tetrahedron</i> 2010 , <i>66</i> , 2235. (o) Zhdankin, V.
V. J. Org. Chem. 2011, 76, 1185. (p) Merritt, E. A.;
Olofsson, B. Synthesis 2011, 517. (q) Hypervalent Iodine
Chemistry, In Topics in Current Chemistry; Vol. 224; Wirth,
T., Ed.; Springer: Berlin, 2003.
(a) Varvoglis, A. Hypervalent Iodine in Organic Synthesis;
Academic Press: San Diego, 1997. Reviews:
(b) Kirschning, A. J. Prakt. Chem. 2000, 342, 731.
(c) Kirschning, A. J. Prakt. Chem. 1998, 340, 184.
(d) Varvoglis, A. Chem. Soc. Rev. 1981. 10, 377. Recent
reports: (e) Zhao, Y.; Yim, W.; Tan, C. K.; Yeung, Y. Org.
<i>Lett.</i> 2011 . <i>13</i> . 4308. (f) Ye. Y.: Wang. H.: Fan. R. Svnlett
2011 923 (g) Fujita M · Wakita M · Sugimura T Chem
Commun 2011 47 3983
(a) McKillon A · Kemp D Tetrahedron 1989 45 3299
(b) Kazmierczak P · Skulski I Synthesis 1998 1721
(c) Hossain M D: Kitamura T Sunthasis 2005 1032
Zagulyaawa A A : Yusubay M S : Zhdankin V V L Org
<i>Cham</i> 2010 75 2110
(a) Dahi T.: Maruyama A.: Vashimura M.: Marimata K.:
(a) Doni, I.; Maruyama, A.; Yosnimura, M.; Morimoto, K.; Tahwa H.; Kita N. A
Iohma, H.; Kita, Y. Angew. Chem. Int. Ed. 2005, 44, 6193.
(b) Ochiai, M.; Takeuchi, Y.; Katayama, T.; Sueda, T.;
Miyamoto, K. J. Am. Chem. Soc. 2005, 127, 12244.
(c) Dohi, T.; Maruyama, A.; Minamitsuji, Y.; Takenaga, N.;
Kita, Y. <i>Chem. Commun.</i> 2007 , 1224. (d) Merritt, E. A.;
Carneiro, V. M. T.; Silva, L. F.; Olofsson, B. J. Org. Chem.
2010 , <i>75</i> , 7461. (e) Dohi, T.; Nakae, T.; Ishikado, Y.; Kato,
D.; Kita, Y. Org. Biomol. Chem. 2011, 9, 6899. (f) Zhong,
W.; Liu, S.; Yang, J.; Meng, X.; Li, Z. Org. Lett. 2012, 14,
2224
3336.
(a) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2005 , 2486.
 (a) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2005, 2486. (b) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2006, 798.
 (a) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2005, 2486. (b) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2006, 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H.
 (a) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2005, 2486. (b) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2006, 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. <i>Tetrahedron</i> 2007, <i>63</i>, 4680. (d) Akiike, J.; Yamamoto, Y.;
 (a) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2005, 2486. (b) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2006, 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. <i>Tetrahedron</i> 2007, <i>63</i>, 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. <i>Synlett</i> 2007, 2168. (e) Kawano, Y.; Togo, H.
 (a) Yamamoto, Y.; Togo, H. Synlett 2005, 2486. (b) Yamamoto, Y.; Togo, H. Synlett 2006, 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. Tetrahedron 2007, 63, 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. Synlett 2007, 2168. (e) Kawano, Y.; Togo, H. Synlett 2008, 217. (f) Kawano, Y.; Togo, H. Tetrahedron
 (a) Yamamoto, Y.; Togo, H. Synlett 2005, 2486. (b) Yamamoto, Y.; Togo, H. Synlett 2006, 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. Tetrahedron 2007, 63, 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. Synlett 2007, 2168. (e) Kawano, Y.; Togo, H. Synlett 2008, 217. (f) Kawano, Y.; Togo, H. Tetrahedron 2009, 65, 6251. (g) Moroda, A.; Togo, H. Synthesis 2008,
 (a) Yamamoto, Y.; Togo, H. Synlett 2005, 2486. (b) Yamamoto, Y.; Togo, H. Synlett 2006, 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. Tetrahedron 2007, 63, 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. Synlett 2007, 2168. (e) Kawano, Y.; Togo, H. Synlett 2008, 217. (f) Kawano, Y.; Togo, H. Tetrahedron 2009, 65, 6251. (g) Moroda, A.; Togo, H. Synthesis 2008, 1257. (h) Ishiwata, Y.; Togo, H. Tetrahedron Lett. 2009, 50,
 (a) Yamamoto, Y.; Togo, H. Synlett 2005, 2486. (b) Yamamoto, Y.; Togo, H. Synlett 2006, 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. Tetrahedron 2007, 63, 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. Synlett 2007, 2168. (e) Kawano, Y.; Togo, H. Synlett 2008, 217. (f) Kawano, Y.; Togo, H. Tetrahedron 2009, 65, 6251. (g) Moroda, A.; Togo, H. Synthesis 2008, 1257. (h) Ishiwata, Y.; Togo, H. Tetrahedron Lett. 2009, 50, 5354.
 (a) Yamamoto, Y.; Togo, H. Synlett 2005, 2486. (b) Yamamoto, Y.; Togo, H. Synlett 2006, 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. Tetrahedron 2007, 63, 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. Synlett 2007, 2168. (e) Kawano, Y.; Togo, H. Synlett 2008, 217. (f) Kawano, Y.; Togo, H. Tetrahedron 2009, 65, 6251. (g) Moroda, A.; Togo, H. Synthesis 2008, 1257. (h) Ishiwata, Y.; Togo, H. Tetrahedron Lett. 2009, 50, 5354. Preparation of I(Diacetoxy)iodolbenzene (2b: Non-
 (a) Yamamoto, Y.; Togo, H. Synlett 2005, 2486. (b) Yamamoto, Y.; Togo, H. Synlett 2006, 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. Tetrahedron 2007, 63, 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. Synlett 2007, 2168. (e) Kawano, Y.; Togo, H. Synlett 2008, 217. (f) Kawano, Y.; Togo, H. Tetrahedron 2009, 65, 6251. (g) Moroda, A.; Togo, H. Synthesis 2008, 1257. (h) Ishiwata, Y.; Togo, H. Tetrahedron Lett. 2009, 50, 5354. Preparation of [(Diacetoxy)iodo]benzene (2b; Non- Electron-Deficient Iodoarene)
 (a) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2005, 2486. (b) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2006, 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. <i>Tetrahedron</i> 2007, 63, 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. <i>Synlett</i> 2007, 2168. (e) Kawano, Y.; Togo, H. <i>Synlett</i> 2008, 217. (f) Kawano, Y.; Togo, H. <i>Tetrahedron</i> 2009, 65, 6251. (g) Moroda, A.; Togo, H. <i>Synthesis</i> 2008, 1257. (h) Ishiwata, Y.; Togo, H. <i>Tetrahedron Lett.</i> 2009, 50, 5354. Preparation of [(Diacetoxy)iodo]benzene (2b; Non-Electron-Deficient Iodoarene) To a solution of 4-jodobenzene (0.61g, 3 mmol) in AcOH (3)
 (a) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2005, 2486. (b) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2006, 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. <i>Tetrahedron</i> 2007, 63, 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. <i>Synlett</i> 2008, 217. (f) Kawano, Y.; Togo, H. <i>Tetrahedron</i> 2009, 65, 6251. (g) Moroda, A.; Togo, H. <i>Synthesis</i> 2008, 1257. (h) Ishiwata, Y.; Togo, H. <i>Tetrahedron Lett.</i> 2009, 50, 5354. Preparation of [(Diacetoxy)iodo]benzene (2b; Non-Electron-Deficient Iodoarene) To a solution of 4-iodobenzene (0.61g, 3 mmol) in AcOH (3 ml) was added MCPBA (ca 65% 0.88 g 3.3 mmol). The
 (a) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2005, 2486. (b) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2006, 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. <i>Tetrahedron</i> 2007, 63, 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. <i>Synlett</i> 2008, 217. (f) Kawano, Y.; Togo, H. <i>Tetrahedron</i> 2009, 65, 6251. (g) Moroda, A.; Togo, H. <i>Synthesis</i> 2008, 1257. (h) Ishiwata, Y.; Togo, H. <i>Tetrahedron Lett.</i> 2009, 50, 5354. Preparation of [(Diacetoxy)iodo]benzene (2b; Non-Electron-Deficient Iodoarene) To a solution of 4-iodobenzene (0.61g, 3 mmol) in AcOH (3 mL) was added MCPBA (ca. 65%, 0.88 g, 3.3 mmol). The mixture was stirred at rt for 2 h. Then H.O (30 mL) was
 (a) Yamamoto, Y.; Togo, H. Synlett 2005, 2486. (b) Yamamoto, Y.; Togo, H. Synlett 2006, 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. Tetrahedron 2007, 63, 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. Synlett 2007, 2168. (e) Kawano, Y.; Togo, H. Synlett 2008, 217. (f) Kawano, Y.; Togo, H. Tetrahedron 2009, 65, 6251. (g) Moroda, A.; Togo, H. Synthesis 2008, 1257. (h) Ishiwata, Y.; Togo, H. Tetrahedron Lett. 2009, 50, 5354. Preparation of [(Diacetoxy)iodo]benzene (2b; Non- Electron-Deficient Iodoarene) To a solution of 4-iodobenzene (0.61g, 3 mmol) in AcOH (3 mL) was added MCPBA (ca. 65%, 0.88 g, 3.3 mmol). The mixture was stirred at r.t. for 2 h. Then, H₂O (30 mL) was added to the reaction mixture and then it was astrapted with
 (a) Yamamoto, Y.; Togo, H. Synlett 2005, 2486. (b) Yamamoto, Y.; Togo, H. Synlett 2006, 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. Tetrahedron 2007, 63, 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. Synlett 2007, 2168. (e) Kawano, Y.; Togo, H. Synlett 2008, 217. (f) Kawano, Y.; Togo, H. Tetrahedron 2009, 65, 6251. (g) Moroda, A.; Togo, H. Synthesis 2008, 1257. (h) Ishiwata, Y.; Togo, H. Tetrahedron Lett. 2009, 50, 5354. Preparation of [(Diacetoxy)iodo]benzene (2b; Non- Electron-Deficient Iodoarene) To a solution of 4-iodobenzene (0.61g, 3 mmol) in AcOH (3 mL) was added MCPBA (ca. 65%, 0.88 g, 3.3 mmol). The mixture was stirred at r.t. for 2 h. Then, H₂O (30 mL) was added to the reaction mixture and then it was extracted with CHCl. (3 × 20 mL). After baing dried over Na SO.
(a) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2005 , 2486. (b) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2006 , 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. <i>Tetrahedron</i> 2007 , 63, 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. <i>Synlett</i> 2007 , 2168. (e) Kawano, Y.; Togo, H. <i>Synlett</i> 2008 , 217. (f) Kawano, Y.; Togo, H. <i>Tetrahedron</i> 2009 , 65, 6251. (g) Moroda, A.; Togo, H. <i>Synthesis</i> 2008 , 1257. (h) Ishiwata, Y.; Togo, H. <i>Tetrahedron Lett.</i> 2009 , 50, 5354. Preparation of [(Diacetoxy)iodo]benzene (2b; Non- Electron-Deficient Iodoarene) To a solution of 4-iodobenzene (0.61g, 3 mmol) in AcOH (3 mL) was added MCPBA (ca. 65%, 0.88 g, 3.3 mmol). The mixture was stirred at r.t. for 2 h. Then, H ₂ O (30 mL) was added to the reaction mixture and then it was extracted with CHCl ₃ (3 × 20 mL). After being dried over Na ₂ SO ₄ , filteration and remained of the solvent (asciducane 2 mL)
(a) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2005 , 2486. (b) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2006 , 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. <i>Tetrahedron</i> 2007 , <i>63</i> , 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. <i>Synlett</i> 2007 , 2168. (e) Kawano, Y.; Togo, H. <i>Synlett</i> 2008 , 217. (f) Kawano, Y.; Togo, H. <i>Tetrahedron</i> 2009 , <i>65</i> , 6251. (g) Moroda, A.; Togo, H. <i>Synthesis</i> 2008 , 1257. (h) Ishiwata, Y.; Togo, H. <i>Tetrahedron Lett.</i> 2009 , <i>50</i> , 5354. Preparation of [(Diacetoxy)iodo]benzene (2b; Non- Electron-Deficient Iodoarene) To a solution of 4-iodobenzene (0.61g, 3 mmol) in AcOH (3 mL) was added MCPBA (ca. 65%, 0.88 g, 3.3 mmol). The mixture was stirred at r.t. for 2 h. Then, H ₂ O (30 mL) was added to the reaction mixture and then it was extracted with CHCl ₃ (3 × 20 mL). After being dried over Na ₂ SO ₄ , filteration, and removal of the solvent (residue ca. 3 mL), Et O (20 mL) was diverse of (20 mL) was and,
 (a) Yamamoto, Y.; Togo, H. Synlett 2005, 2486. (b) Yamamoto, Y.; Togo, H. Synlett 2006, 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. Tetrahedron 2007, 63, 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. Synlett 2007, 2168. (e) Kawano, Y.; Togo, H. Synlett 2008, 217. (f) Kawano, Y.; Togo, H. Tetrahedron 2009, 65, 6251. (g) Moroda, A.; Togo, H. Synthesis 2008, 1257. (h) Ishiwata, Y.; Togo, H. Tetrahedron Lett. 2009, 50, 5354. Preparation of [(Diacetoxy)iodo]benzene (2b; Non- Electron-Deficient Iodoarene) To a solution of 4-iodobenzene (0.61g, 3 mmol) in AcOH (3 mL) was added MCPBA (ca. 65%, 0.88 g, 3.3 mmol). The mixture was stirred at r.t. for 2 h. Then, H₂O (30 mL) was added to the reaction mixture and then it was extracted with CHCl₃ (3 × 20 mL). After being dried over Na₂SO₄, filteration, and removal of the solvent (residue ca. 3 mL), Et₂O (20 mL) and hexane (20 mL) were added to the residue,
(a) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2005 , 2486. (b) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2006 , 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. <i>Tetrahedron</i> 2007 , 63, 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. <i>Synlett</i> 2007 , 2168. (e) Kawano, Y.; Togo, H. <i>Synlett</i> 2008 , 217. (f) Kawano, Y.; Togo, H. <i>Tetrahedron</i> 2009 , 65, 6251. (g) Moroda, A.; Togo, H. <i>Synthesis</i> 2008 , 1257. (h) Ishiwata, Y.; Togo, H. <i>Tetrahedron Lett.</i> 2009 , 50, 5354. Preparation of [(Diacetoxy)iodo]benzene (2b; Non- Electron-Deficient Iodoarene) To a solution of 4-iodobenzene (0.61g, 3 mmol) in AcOH (3 mL) was added MCPBA (ca. 65%, 0.88 g, 3.3 mmol). The mixture was stirred at r.t. for 2 h. Then, H ₂ O (30 mL) was added to the reaction mixture and then it was extracted with CHCl ₃ (3 × 20 mL). After being dried over Na ₂ SO ₄ , filteration, and removal of the solvent (residue ca. 3 mL), Et ₂ O (20 mL) and hexane (20 mL) were added to the residue, and the mixture was cooled to 0 °C to induce precipitation
(a) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2005 , 2486. (b) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2006 , 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. <i>Tetrahedron</i> 2007 , <i>63</i> , 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. <i>Synlett</i> 2007 , 2168. (e) Kawano, Y.; Togo, H. <i>Synlett</i> 2008 , 217. (f) Kawano, Y.; Togo, H. <i>Tetrahedron</i> 2009 , <i>65</i> , 6251. (g) Moroda, A.; Togo, H. <i>Synthesis</i> 2008 , 1257. (h) Ishiwata, Y.; Togo, H. <i>Tetrahedron Lett.</i> 2009 , <i>50</i> , 5354. Preparation of [(Diacetoxy)iodo]benzene (2b; Non- Electron-Deficient Iodoarene) To a solution of 4-iodobenzene (0.61g, 3 mmol) in AcOH (3 mL) was added MCPBA (ca. 65%, 0.88 g, 3.3 mmol). The mixture was stirred at r.t. for 2 h. Then, H ₂ O (30 mL) was added to the reaction mixture and then it was extracted with CHCl ₃ (3 × 20 mL). After being dried over Na ₂ SO ₄ , filteration, and removal of the solvent (residue ca. 3 mL), Et ₂ O (20 mL) and hexane (20 mL) were added to the residue, and the mixture was cooled to 0 °C to induce precipitation (method A). After filtration, the solids were washed with a
 (a) Yamamoto, Y.; Togo, H. Synlett 2005, 2486. (b) Yamamoto, Y.; Togo, H. Synlett 2006, 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. Tetrahedron 2007, 63, 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. Synlett 2007, 2168. (e) Kawano, Y.; Togo, H. Synlett 2008, 217. (f) Kawano, Y.; Togo, H. Tetrahedron 2009, 65, 6251. (g) Moroda, A.; Togo, H. Synthesis 2008, 1257. (h) Ishiwata, Y.; Togo, H. Tetrahedron Lett. 2009, 50, 5354. Preparation of [(Diacetoxy)iodo]benzene (2b; Non- Electron-Deficient Iodoarene) To a solution of 4-iodobenzene (0.61g, 3 mmol) in AcOH (3 mL) was added MCPBA (ca. 65%, 0.88 g, 3.3 mmol). The mixture was stirred at r.t. for 2 h. Then, H₂O (30 mL) was added to the reaction mixture and then it was extracted with CHCl₃ (3 × 20 mL). After being dried over Na₂SO₄, filteration, and removal of the solvent (residue ca. 3 mL), Et₂O (20 mL) and hexane (20 mL) were added to the residue, and the mixture was cooled to 0 °C to induce precipitation (method A). After filtration, the solids were washed with a mixture of Et₂O and hexane to provide
(a) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2005 , 2486. (b) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2006 , 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. <i>Tetrahedron</i> 2007 , <i>63</i> , 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. <i>Synlett</i> 2007 , 2168. (e) Kawano, Y.; Togo, H. <i>Synlett</i> 2008 , 217. (f) Kawano, Y.; Togo, H. <i>Tetrahedron</i> 2009 , <i>65</i> , 6251. (g) Moroda, A.; Togo, H. <i>Synthesis</i> 2008 , 1257. (h) Ishiwata, Y.; Togo, H. <i>Tetrahedron Lett.</i> 2009 , <i>50</i> , 5354. Preparation of [(Diacetoxy)iodo]benzene (2b; Non- Electron-Deficient Iodoarene) To a solution of 4-iodobenzene (0.61g, 3 mmol) in AcOH (3 mL) was added MCPBA (ca. 65%, 0.88 g, 3.3 mmol). The mixture was stirred at r.t. for 2 h. Then, H ₂ O (30 mL) was added to the reaction mixture and then it was extracted with CHCl ₃ (3 × 20 mL). After being dried over Na ₂ SO ₄ , filteration, and removal of the solvent (residue ca. 3 mL), Et ₂ O (20 mL) and hexane (20 mL) were added to the residue, and the mixture was cooled to 0 °C to induce precipitation (method A). After filtration, the solids were washed with a mixture of Et ₂ O and hexane to provide [(diacetoxy)iodo]benzene in 83% yield.
(a) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2005 , 2486. (b) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2006 , 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. <i>Tetrahedron</i> 2007 , <i>63</i> , 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. <i>Synlett</i> 2007 , 2168. (e) Kawano, Y.; Togo, H. <i>Synlett</i> 2008 , 217. (f) Kawano, Y.; Togo, H. <i>Tetrahedron</i> 2009 , <i>65</i> , 6251. (g) Moroda, A.; Togo, H. <i>Synthesis</i> 2008 , 1257. (h) Ishiwata, Y.; Togo, H. <i>Tetrahedron Lett.</i> 2009 , <i>50</i> , 5354. Preparation of [(Diacetoxy)iodo]benzene (2b; Non- Electron-Deficient Iodoarene) To a solution of 4-iodobenzene (0.61g, 3 mmol) in AcOH (3 mL) was added MCPBA (ca. 65%, 0.88 g, 3.3 mmol). The mixture was stirred at r.t. for 2 h. Then, H ₂ O (30 mL) was added to the reaction mixture and then it was extracted with CHCl ₃ (3 × 20 mL). After being dried over Na ₂ SO ₄ , filteration, and removal of the solvent (residue ca. 3 mL), Et ₂ O (20 mL) and hexane (20 mL) were added to the residue, and the mixture was cooled to 0 °C to induce precipitation (method A). After filtration, the solids were washed with a mixture of Et ₂ O and hexane to provide [(diacetoxy)iodo]benzene in 83% yield. Preparation of 4-Nitro](diacetoxy)iodo]benzene (2c;
 (a) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2005, 2486. (b) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2006, 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. <i>Tetrahedron</i> 2007, 63, 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. <i>Synlett</i> 2008, 217. (f) Kawano, Y.; Togo, H. <i>Tetrahedron</i> 2009, 65, 6251. (g) Moroda, A.; Togo, H. <i>Synthesis</i> 2008, 1257. (h) Ishiwata, Y.; Togo, H. <i>Tetrahedron Lett.</i> 2009, 50, 5354. Preparation of [(Diacetoxy)iodo]benzene (2b; Non-Electron-Deficient Iodoarene) To a solution of 4-iodobenzene (0.61g, 3 mmol) in AcOH (3 mL) was added MCPBA (ca. 65%, 0.88 g, 3.3 mmol). The mixture was stirred at r.t. for 2 h. Then, H₂O (30 mL) was added to the reaction mixture and then it was extracted with CHCl₃ (3 × 20 mL). After being dried over Na₂SO₄, filteration, and removal of the solvent (residue ca. 3 mL), Et₂O (20 mL) and hexane (20 mL) were added to the residue, and the mixture was cooled to 0 °C to induce precipitation (method A). After filtration, the solids were washed with a mixture of Et₂O and hexane to provide [(diacetoxy)iodo]benzene (2c; Electron-Deficient Iodoarene)
(a) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2005 , 2486. (b) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2006 , 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. <i>Tetrahedron</i> 2007 , <i>63</i> , 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. <i>Synlett</i> 2007 , 2168. (e) Kawano, Y.; Togo, H. <i>Synlett</i> 2008 , 217. (f) Kawano, Y.; Togo, H. <i>Tetrahedron</i> 2009 , <i>65</i> , 6251. (g) Moroda, A.; Togo, H. <i>Synthesis</i> 2008 , 1257. (h) Ishiwata, Y.; Togo, H. <i>Tetrahedron Lett.</i> 2009 , <i>50</i> , 5354. Preparation of [(Diacetoxy)iodo]benzene (2b; Non- Electron-Deficient Iodoarene) To a solution of 4-iodobenzene (0.61g, 3 mmol) in AcOH (3 mL) was added MCPBA (ca. 65%, 0.88 g, 3.3 mmol). The mixture was stirred at r.t. for 2 h. Then, H ₂ O (30 mL) was added to the reaction mixture and then it was extracted with CHCl ₃ (3 × 20 mL). After being dried over Na ₂ SO ₄ , filteration, and removal of the solvent (residue ca. 3 mL), Et ₂ O (20 mL) and hexane (20 mL) were added to the residue, and the mixture was cooled to 0 °C to induce precipitation (method A). After filtration, the solids were washed with a mixture of Et ₂ O and hexane to provide [(diacetoxy)iodo]benzene in 83% yield. Preparation of 4-Nitro](diacetoxy)iodo]benzene (2c; Electron-Deficient Iodoarene) To a solution of 4-iodonitrobenzene (0.75g, 3 mmol) in
(a) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2005 , 2486. (b) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2006 , 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. <i>Tetrahedron</i> 2007 , <i>63</i> , 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. <i>Synlett</i> 2007 , 2168. (e) Kawano, Y.; Togo, H. <i>Synlett</i> 2008 , 217. (f) Kawano, Y.; Togo, H. <i>Tetrahedron</i> 2009 , <i>65</i> , 6251. (g) Moroda, A.; Togo, H. <i>Synthesis</i> 2008 , 1257. (h) Ishiwata, Y.; Togo, H. <i>Tetrahedron Lett.</i> 2009 , <i>50</i> , 5354. Preparation of [(Diacetoxy)iodo]benzene (2b; Non- Electron-Deficient Iodoarene) To a solution of 4-iodobenzene (0.61g, 3 mmol) in AcOH (3 mL) was added MCPBA (ca. 65%, 0.88 g, 3.3 mmol). The mixture was stirred at r.t. for 2 h. Then, H ₂ O (30 mL) was added to the reaction mixture and then it was extracted with CHCl ₃ (3 × 20 mL). After being dried over Na ₂ SO ₄ , filteration, and removal of the solvent (residue ca. 3 mL), Et ₂ O (20 mL) and hexane (20 mL) were added to the residue, and the mixture was cooled to 0 °C to induce precipitation (method A). After filtration, the solids were washed with a mixture of Et ₂ O and hexane to provide [(diacetoxy)iodo]benzene in 83% yield. Preparation of 4-Nitro](diacetoxy)iodo]benzene (2c; Electron-Deficient Iodoarene) To a solution of 4-iodonitrobenzene (0.75g, 3 mmol) in AcOH (20 mL) was added MCPBA (ca. 65%, 0.88 g, 3.3
(a) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2005 , 2486. (b) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2006 , 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. <i>Tetrahedron</i> 2007 , <i>63</i> , 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. <i>Synlett</i> 2007 , 2168. (e) Kawano, Y.; Togo, H. <i>Synlett</i> 2008 , 217. (f) Kawano, Y.; Togo, H. <i>Tetrahedron</i> 2009 , <i>65</i> , 6251. (g) Moroda, A.; Togo, H. <i>Synthesis</i> 2008 , 1257. (h) Ishiwata, Y.; Togo, H. <i>Tetrahedron Lett.</i> 2009 , <i>50</i> , 5354. Preparation of [(Diacetoxy)iodo]benzene (2b; Non- Electron-Deficient Iodoarene) To a solution of 4-iodobenzene (0.61g, 3 mmol) in AcOH (3 mL) was added MCPBA (ca. 65%, 0.88 g, 3.3 mmol). The mixture was stirred at r.t. for 2 h. Then, H ₂ O (30 mL) was added to the reaction mixture and then it was extracted with CHCl ₃ (3 × 20 mL). After being dried over Na ₂ SO ₄ , filteration, and removal of the solvent (residue ca. 3 mL), Et ₂ O (20 mL) and hexane (20 mL) were added to the residue, and the mixture was cooled to 0 °C to induce precipitation (method A). After filtration, the solids were washed with a mixture of Et ₂ O and hexane to provide [(diacetoxy)iodo]benzene in 83% yield. Preparation of 4-Nitro](diacetoxy)iodo]benzene (2c; Electron-Deficient Iodoarene) To a solution of 4-iodonitrobenzene (0.75g, 3 mmol) in AcOH (20 mL) was added MCPBA (ca. 65%, 0.88 g, 3.3 mmol). The mixture was stirred for 48 h at 55 °C. Then, H ₂ O
(a) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2005 , 2486. (b) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2006 , 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. <i>Tetrahedron</i> 2007 , <i>63</i> , 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. <i>Synlett</i> 2007 , 2168. (e) Kawano, Y.; Togo, H. <i>Synlett</i> 2008 , 217. (f) Kawano, Y.; Togo, H. <i>Tetrahedron</i> 2009 , <i>65</i> , 6251. (g) Moroda, A.; Togo, H. <i>Synthesis</i> 2008 , 1257. (h) Ishiwata, Y.; Togo, H. <i>Tetrahedron Lett.</i> 2009 , <i>50</i> , 5354. Preparation of [(Diacetoxy)iodo]benzene (2b; Non- Electron-Deficient Iodoarene) To a solution of 4-iodobenzene (0.61g, 3 mmol) in AcOH (3 mL) was added MCPBA (ca. 65%, 0.88 g, 3.3 mmol). The mixture was stirred at r.t. for 2 h. Then, H ₂ O (30 mL) was added to the reaction mixture and then it was extracted with CHCl ₃ (3 × 20 mL). After being dried over Na ₂ SO ₄ , filteration, and removal of the solvent (residue ca. 3 mL), Et ₂ O (20 mL) and hexane (20 mL) were added to the residue, and the mixture was cooled to 0 °C to induce precipitation (method A). After filtration, the solids were washed with a mixture of Et ₂ O and hexane to provide [(diacetoxy)iodo]benzene in 83% yield. Preparation of 4-Nitro](diacetoxy)iodo]benzene (2c; Electron-Deficient Iodoarene) To a solution of 4-iodonitrobenzene (0.75g, 3 mmol) in AcOH (20 mL) was added MCPBA (ca. 65%, 0.88 g, 3.3 mmol). The mixture was stirred for 48 h at 55 °C. Then, H ₂ O (30 mL) was added to the reaction mixture and then it was
(a) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2005 , 2486. (b) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2006 , 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. <i>Tetrahedron</i> 2007 , <i>63</i> , 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. <i>Synlett</i> 2007 , 2168. (e) Kawano, Y.; Togo, H. <i>Synlett</i> 2008 , 217. (f) Kawano, Y.; Togo, H. <i>Tetrahedron</i> 2009 , <i>65</i> , 6251. (g) Moroda, A.; Togo, H. <i>Synthesis</i> 2008 , 1257. (h) Ishiwata, Y.; Togo, H. <i>Tetrahedron Lett.</i> 2009 , <i>50</i> , 5354. Preparation of [(Diacetoxy)iodo]benzene (2b; Non- Electron-Deficient Iodoarene) To a solution of 4-iodobenzene (0.61g, 3 mmol) in AcOH (3 mL) was added MCPBA (ca. 65%, 0.88 g, 3.3 mmol). The mixture was stirred at r.t. for 2 h. Then, H ₂ O (30 mL) was added to the reaction mixture and then it was extracted with CHCl ₃ (3 × 20 mL). After being dried over Na ₂ SO ₄ , filteration, and removal of the solvent (residue ca. 3 mL), Et ₂ O (20 mL) and hexane (20 mL) were added to the residue, and the mixture was cooled to 0 °C to induce precipitation (method A). After filtration, the solids were washed with a mixture of Et ₂ O and hexane to provide [(diacetoxy)iodo]benzene in 83% yield. Preparation of 4-Nitro](diacetoxy)iodo]benzene (2c; Electron-Deficient Iodoarene) To a solution of 4-iodonitrobenzene (0.75g, 3 mmol) in AcOH (20 mL) was added MCPBA (ca. 65%, 0.88 g, 3.3 mmol). The mixture was stirred for 48 h at 55 °C. Then, H ₂ O (30 mL) was added to the reaction mixture and then it was extracted with CHCl ₃ (3 × 20 mL). After being dried over
(a) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2005 , 2486. (b) Yamamoto, Y.; Togo, H. <i>Synlett</i> 2006 , 798. (c) Yamamoto, Y.; Kawano, Y.; Toy, P. H.; Togo, H. <i>Tetrahedron</i> 2007 , <i>63</i> , 4680. (d) Akiike, J.; Yamamoto, Y.; Togo, H. <i>Synlett</i> 2007 , 2168. (e) Kawano, Y.; Togo, H. <i>Synlett</i> 2008 , 217. (f) Kawano, Y.; Togo, H. <i>Tetrahedron</i> 2009 , <i>65</i> , 6251. (g) Moroda, A.; Togo, H. <i>Synthesis</i> 2008 , 1257. (h) Ishiwata, Y.; Togo, H. <i>Tetrahedron Lett.</i> 2009 , <i>50</i> , 5354. Preparation of [(Diacetoxy)iodo]benzene (2b; Non- Electron-Deficient Iodoarene) To a solution of 4-iodobenzene (0.61g, 3 mmol) in AcOH (3 mL) was added MCPBA (ca. 65%, 0.88 g, 3.3 mmol). The mixture was stirred at r.t. for 2 h. Then, H ₂ O (30 mL) was added to the reaction mixture and then it was extracted with CHCl ₃ (3 × 20 mL). After being dried over Na ₂ SO ₄ , filteration, and removal of the solvent (residue ca. 3 mL), Et ₂ O (20 mL) and hexane (20 mL) were added to the residue, and the mixture was cooled to 0 °C to induce precipitation (method A). After filtration, the solids were washed with a mixture of Et ₂ O and hexane to provide [(diacetoxy)iodo]benzene in 83% yield. Preparation of 4-Nitro](diacetoxy)iodo]benzene (2c; Electron-Deficient Iodoarene) To a solution of 4-iodonitobenzene (0.75g, 3 mmol) in AcOH (20 mL) was added MCPBA (ca. 65%, 0.88 g, 3.3 mmol). The mixture was stirred for 48 h at 55 °C. Then, H ₂ O (30 mL) was added to the reaction mixture and then it was extracted with CHCl ₃ (3 × 20 mL). After being dried over Na ₂ SO ₄ , filteration, and removal of the solvent (residue ca. 3

mL), Et₂O (20 mL) and hexane (20 mL) were added to the residue, and the mixture was cooled to -78 °C to induce precipitation (method B). After filtration, the solids were washed with a mixture of Et₂O and hexane to provide 4-nitro[(diacetoxy)iodo]benzene in 81% yield.

Conditions for the Precipitation of (Diacetoxyiodo)arenes Method A

Et₂O (20 mL) and hexane (20 mL) were added to the residue, and the mixture was cooled at 0 °C for (diacetoxyiodo)benzene, 4-cyano(diacetoxyiodo)benzene, and 1acetoxy-1,2-benziodoxole-3(1H)-one.

Method B

Et₂O (20 mL) and hexane (20 mL) were added to the residue, and the mixture was cooled at -78 °C for 4-nitro[(diacetoxy)iodo]benzene and 3-nitro[(diacetoxy)iodo]benzene. Method C

Et₂O (20 mL) and hexane (40 mL) were added to the residue, and the mixture was cooled at -78 °C for 4-bromo[(diacetoxy)iodo]benzene, 4-methoxycarbonyl[(diacetoxy)iodo]benzene, (diacetoxy)iodotoluene, and 3,5bis(trifluoromethyl)-1-[(diacetoxy)iodo]benzene.

Method D

Et₂O (30 mL) was added to the residue for 4-[(diacetoxy)iodo]benzyl-N,N,N-trimethylammonium tosylate.

(Diacetoxyiodo)toluene

Mp 102–103 °C (lit.^{3c} mp 106–108 °C). IR (KBr): 663, 1267, 1410, 1567, 1649 cm⁻¹. ¹H NMR (500 MHz, CDCl₃ TMS): $\delta = 2.00 (s, 6 H), 2.45 (s, 3 H), 7.30 (d, 2 H, J = 8.3 Hz), 7.97$ (d, 2 H, J = 8.3 Hz). ¹³C NMR (125 MHz, CDCl₃, TMS): δ = 20.27, 21.43, 118.27, 131.65, 134.88, 142.57, 176.26.

(Diacetoxyiodo)benzene

Mp 156-158 °C (lit.9 mp 161-162 °C). IR (KBr): 666, 743, 1271, 1644 cm⁻¹. ¹H NMR (500 MHz,CDCl₃, TMS): δ = 2.01 (s, 6 H), 7.49 (d, 2 H, J = 7.3 Hz), 7.60 (t, 1 H J = 7.4 Hz), 8.10 (d, 2 H, J = 7.5 Hz). ¹³C NMR (125 MHz, CDCl₃, TMS): δ = 20.32, 121.57, 130.92, 131.69, 134.90, 176.37.

4-Nitro(diacetoxyiodo)benzene

Mp 103-104 °C (lit.3c mp 104-105 °C). IR (KBr): 673, 734, 849, 1274, 1348, 1414, 1515, 1570, 1644 cm⁻¹. ¹H NMR $(500 \text{ MHz}, \text{CDCl}_3, \text{TMS}): \delta = 2.03 \text{ (s, 6 H)}, 8.28 \text{ (d, 2 H)}$ J = 9.1 Hz), 8.32 (d, 2 H, J = 9.3 Hz). ¹³C NMR (125 MHz, CDCl₃, TMS): δ = 20.27, 125.59, 126.72, 136.03, 149.40, 176.66.

3-Nitro(diacetoxyiodo)benzene

Mp 144–146 °C (lit.^{3b} mp 148–150 °C). IR (KBr): 714, 815, 1346, 1569, 1647 cm⁻¹. ¹H NMR (500 MHz, CDCl₃, TMS): $\delta = 2.04$ (s, 6 H), 7.73 (t, 1 H, J = 8.2 Hz), 8.40 (d, 1 H, J = 9.7 Hz), 8.45 (d, 1 H, J = 9.3 Hz), 8.95 (s, 1 H). ¹³C NMR $(125 \text{ MHz}, \text{CDCl}_3, \text{TMS}): \delta = 20.28, 120.60, 126.31,$ 130.07, 131.50, 140.37, 148.65, 176.78.

4-Cyano(diacetoxyiodo)benzene

Mp 168–170 °C (lit.^{3b} mp 172–173 °C). IR (KBr): 673, 821, 1009, 1270, 1650, 2227 cm⁻¹. ¹H NMR (500 MHz, CDCl₃, TMS): $\delta = 2.03$ (s, 6 H), 7.78 (d, 2 H, J = 8.9 Hz), 8.20 (d, 2 H, J = 8.6 Hz). ¹³C NMR (125 MHz, CDCl₃, TMS): $\delta = 20.26, 115.65, 117.05, 125.20, 134.01, 135.54, 176.61.$

4-Bromo(diacetoxyiodo)benzene

Mp 116–118 °C (lit. 3b mp 120–122 °C). IR (KBr): 669, 746, 804, 1380, 1411, 1644 cm⁻¹. ¹H NMR (500 MHz, CDCl₃, TMS): $\delta = 2.01$ (s, 6 H), 7.62 (d, 2 H, J = 8.6 Hz), 7.95 (d, 2 H, J = 8.6 Hz). ¹³C NMR (125 MHz, CDCl₃, TMS): $\delta = 20.31, 119.58, 126.80, 134.15, 136.41, 176.50.$ 4-Bromo(diacetoxyiodo)benzene Mp 116–118 °C (lit.^{3b} mp 120–122 °C). IR (KBr): 669, 746, 804, 1380, 1411, 1644 cm⁻¹. ¹H NMR (500 MHz, CDCl₃, TMS): $\delta = 2.01$ (s, 6 H), 7.62 (d, 2 H, J = 8.6 Hz), 7.95 (d, 2 H, J = 8.6 Hz). ¹³C NMR (125 MHz, CDCl₃, TMS): $\delta = 20.31, 119.58, 126.80, 134.15, 136.41, 176.50.$ 4-Methoxycarbonyl(diacetoxyiodo)benzene Mp 127-130 °C. IR (KBr): 670, 755, 826, 1284, 1410, 1566, 1642, 1716 cm⁻¹. ¹H NMR (500 MHz, CDCl₃, TMS): $\delta = 2.02 (s, 6 H), 3.97 (s, 3 H), 8.13 (d, 2 H, J = 8.9 Hz), 8.17$ (d, 2 H, J = 8.6 Hz). ¹³C NMR (125 MHz, CDCl₃, TMS):

δ = 20.25, 52.65, 125.67, 131.74, 133.00, 134.84, 165.45 176.45. ESI-HRMS: $m/z [M + Na]^+$ calcd for $C_{12}H_{13}O_6INa$: 402.9649; found: 402.9639.

3,5-Bis(trifluoromethyl)-1-(diacetoxyiodo)benzene Mp 102–104 °C (lit. ^{3c} mp 108–110 °C). IR (KBr): 670, 1131, 1185, 1278, 1349, 1369, 1649 cm⁻¹. ¹H NMR (125 MHz, $CDCl_3$, TMS): $\delta = 2.05$ (s, 6 H), 8.09 (s, 1 H), 8.51(s, 2 H). ¹³C NMR (500 MHz, CDCl₃, TMS): $\delta = 20.24$, 129.03, 123.21, 125.49, 133.73 (q, J = 34.4 Hz), 134.95, 176.97. ¹⁹F NMR (500 MHz, CDCl₃, TMS): $\delta = -62.72$ (CF₃). 4-[(Diacetoxy)iodo]benzyltrimethylammonium Tosylate Oil. IR (neat): 566, 684, 1009, 1034, 1123, 1186, 1267, 1482, 1646 cm⁻¹. ¹H NMR (500 MHz, DMSO- d_6): $\delta = 1.90$ (s, 6 H), 2.28 (s, 3 H), 3.04 (s, 9 H), 4.60 (s, 2 H), 7.12 (d, 2 H, J = 7.8 Hz), 7.50 (d, 2 H, J = 7.7 Hz), 7.73 (d, 2 H J = 8.0Hz), 8.07 (d, 2 H, J = 8.0 Hz). ¹³C NMR (125 MHz, DMSO d_6): $\delta = 20.82, 21.11, 51.94, 67.05, 97.85, 125.52, 127.17,$ 128.16, 133.31, 134.86, 137.81, 145.59, 172.08. ESI-HRMS (+): m/z calcd for C₁₄H₂₁O₄NI: 394.0510; found: 394.0497. ESI-HRMS (anion): m/z calcd for C₇H₇O₃S: 171.0110; found: 171.0113.

1-Acetoxy-1,2-benziodoxole-3-(1H)-one

Mp 168–170 °C (lit.¹⁰ mp 164–168 °C). IR (KBr): 743, 1563, 1613 cm⁻¹. ¹H NMR (500 MHz, DMSO- d_6): $\delta = 1.90$ (s, 3 H), 7.70 (t, 1 H, J = 7.2 Hz), 7.84 (d, 1 H, J = 8.0 Hz), 7.96 (t, 1 H, J = 7.6 Hz), 8.01 (d, 1 H, J = 7.5 Hz). ¹³C NMR(500 MHz, DMSO- d_6): $\delta = 21.08, 120.45, 126.31,$ 130.40, 131.13, 131.52, 134.52, 167.77, 172.07.

- (8) Desjardins, S.; Jacquemot, G.; Canesi, S. Synlett 2012, 23, 1497.
- (9) Leffler, J. E.; Story, L. J. J. Am. Chem. Soc. 1967, 89, 2333.
- (10) Eisenberger, P.; Gischig, S.; Togni, A. Chem.-Eur. J. 2006, 12, 2579.

Copyright of Synlett is the property of Georg Thieme Verlag Stuttgart and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.